

**COMPARISON OF COUPLING EFFECTIVENESS AMONG
AMINO-, CHLORO-, AND MERCAPTO SILANE IN
CHLOROPRENE RUBBER**

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COMPARISON OF COUPLING EFFECTIVENESS AMONG AMINO-, CHLORO-, AND MERCAPTO SILANE IN CHLOROPRENE RUBBER

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ABSTRACT

This research was divided into 2 parts. Part I, silica surface modification and characterization: the 3 types of silane coupling agent (SCA) were used to modify surfaces of precipitated silica (PSi) by silanization reaction. The characteristics of surface-modified PSi were determined by BET technique, particle size analysis, Sear number, Zeta potential, elementary analysis, DRIFT and ^{29}Si NMR spectroscopy. Also, a relative grafting ratio of silane onto surfaces of PSi prepared under different conditions was calculated. The 3 types of SCAs used in this work were: 3-aminopropyl triethoxysilane (APTES), 3-chloropropyl triethoxysilane (CPTES) and bis (3-triethoxysilylpropyl) tetrasulfide (TESPT) with various loadings up to 8 % by weight of PSi. Results revealed that the highest performance of grafting at a given SCA loading is found in TESPT-modified PSi. Part II was focused on the influence of PSi surface modification on properties of rubber compounds and vulcanizates. Polychloroprene rubber (CR) was mixed with unmodified and silane-modified PSi. Cure, viscoelastic, mechanical and dynamic properties of PSi filled CR were investigated. The Payne effect magnitude and bound rubber content were used to demonstrate the reinforcement behavior and the rubber-filler interaction of PSi filled CR, respectively. Moreover, the properties of rubber compounds as affected by different surface treatment techniques (i.e., in-situ and pre-modified techniques) were compared. Among APTES, CPTES and TESPT silanes, both APTES and TESPT were capable of reducing the filler network formation to a greater extent than the CPTES, leading to the superior compound processability especially when prepared by the in-situ technique. Mechanical properties of vulcanizates were investigated, and the results reveal that the type and loading of SCAs affect not only the compound processability, but also the vulcanizate mechanical properties. Moreover, the amino and mercapto groups of APTES and TESPT, respectively, significantly enhance the mechanical properties of CR vulcanizates more effectively than the chloro groups of CPTES. This might be ascribed to the combined effects of enhanced rubber-filler interaction, improved filler dispersion and state-of-mix as evidenced by Payne effect and SEM results.

KEY WORDS: POLYCHLOROPRENE RUBBER/
SILANE COUPLING AGENT/ SURFACE MODIFICATION/
PRECIPITATED SILICA/MECHANICAL PROPERTY

274 pages

การเปรียบเทียบประสิทธิภาพการเชื่อมประสานของอะมิโน คลอโร และเมอร์แคปโตไซเลนในยางคลอโรพรีน
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บทคัดย่อ

งานวิจัยนี้แบ่งการศึกษาก่อเป็น 2 ส่วน ดังนี้ ส่วนที่ 1 การปรับปรุงพื้นผิวของซิลิกาด้วยสารคู่ควบไซเลน 3 ชนิด อันได้แก่ อะมิโนไซเลน คลอโรไซเลน และเมอร์แคปโตไซเลน โดยการทำให้ไซลานในส้แซน (Silanization) จากนั้นทำการวิเคราะห์คุณสมบัติของซิลิกาที่ดัดแปรพื้นผิวเรียบร้อยแล้ว (SCA-modified PSi) โดยใช้เทคนิคการหาพื้นที่ผิวจำเพาะด้วย บีอีที (BET) การวัดขนาดของซิลิกาด้วยเครื่องวัดขนาด (Particle size analyzer) การไทเทรตหาปริมาณหมู่ไฮดรอกซิล (Sear number) การวัดค่าศักย์ไฟฟ้าบนพื้นผิว (Zeta potential) การวิเคราะห์หมู่ฟังก์ชันบนพื้นผิวที่เปลี่ยนไปด้วยเทคนิคอินฟราเรดสเปกโทรสโกปีแบบดิฟฟิวสรีเฟลคแทนซ์ (Diffuse reflectance infrared transform spectroscopy) และการวิเคราะห์โครงสร้างของสารคู่ควบไซเลนบนผิวของซิลิกาด้วยเทคนิคซิลิกอนเอนเอ็มอาร์ (^{29}Si -NMR spectroscopy) นอกจากนี้ทำการหาปริมาณอัตราส่วนสัมพัทธ์ (Relative grafting ratio) ของสารคู่ควบไซเลนบนผิวของซิลิกา (ในงานวิจัยนี้มีการใช้สารคู่ควบไซเลน 3 ชนิด ได้แก่ 3-อะมิโนโพรพิลไตรเอทอซซิลเลน (APTES) 3-คลอโรโพรพิลไตรเอทอซซิลเลน (CPTES) และ บิส (3-ไทรเอทอซซิล)ซิลิโพรพิล เตตระซัลไฟด์ (TESPT) โดยทำการแปรเปลี่ยนปริมาณของสารคู่ควบดังกล่าวจนสูงสุดที่ 8 เปอร์เซ็นต์โดยน้ำหนักของซิลิกา) ผลการศึกษาพบว่า สารคู่ควบชนิด TESPT มีประสิทธิภาพในการเกิดไซลานในส้แซนบนผิวของซิลิกาได้สูงที่สุด เมื่อเทียบปริมาณสารคู่ควบที่เท่ากัน ส่วนที่ 2 ศึกษาอิทธิพลของซิลิกาที่ดัดแปรพื้นผิวด้วยสารคู่ควบไซเลนที่มีต่อสมบัติของยางคอมพาวด์ (Rubber compounds) และยางวัลคาไนซ์ (Vulcanizates) โดยทำการผสมยางคลอโรพรีนกับซิลิกาที่ไม่ได้ดัดแปรพื้นผิว (Unmodified PSi) และซิลิกาที่ดัดแปรพื้นผิวด้วยสารคู่ควบไซเลน (SCA-modified PSi) และนำไปตรวจสอบพฤติกรรมการสุกตัว (Cure properties) สมบัติหยุ่นหนืด (Viscoelastic properties) สมบัติเชิงกล (Mechanical properties) และสมบัติเชิงพลวัต (Dynamic properties) โดยอธิบายพฤติกรรมการเสริมแรงของซิลิกาและอันตรกิริยาระหว่างยางกับซิลิกา ด้วยค่าปริมาณอันตรกิริยาระหว่างสารตัวเติมกับสารตัวเติม (Filler-filler interaction) และค่าปริมาณยางบาวด์ (Bound rubber content) ตามลำดับ นอกจากนี้ทำการเปรียบเทียบผลของเทคนิคการดัดแปรพื้นผิวของซิลิกาต่อสมบัติของยางคอมพาวด์ พบว่าระหว่างสารคู่ควบไซเลน 3 ชนิด อันได้แก่ APTES CPTES และ TESPT นั้น สารคู่ควบชนิด APTES และ TESPT สามารถลดแรงอันตรกิริยาระหว่างซิลิกากับซิลิกาได้มีประสิทธิภาพเหนือกว่าสารคู่ควบชนิด CPTES ส่งผลให้มีคุณภาพการผสมที่ดีกว่า ซึ่งสามารถเห็นได้ชัดในกรณีการดัดแปรพื้นผิวซิลิกาด้วยเทคนิคแบบใส่ลงผสมพร้อมกับยาง (in-situ technique) นอกจากนี้พบว่าชนิดและปริมาณของสารคู่ควบไซเลนไม่เพียงมีผลต่อกระบวนการผสมของยางคอมพาวด์เท่านั้น แต่ยังส่งผลต่อสมบัติเชิงกลของยางวัลคาไนซ์ด้วย โดยหมู่อะมิโนและหมู่เมอร์แคปโตของสารคู่ควบชนิด APTES และ TESPT สามารถปรับปรุงสมบัติเชิงกลของยางคลอโรพรีนได้เหนือกว่าหมู่คลอโรของสารคู่ควบชนิด CPTES ทั้งนี้เนื่องจากสารคู่ควบไซเลนทั้ง 2 ชนิดนี้สามารถเพิ่มอันตรกิริยาระหว่างยางกับซิลิกาและสามารถลดอันตรกิริยาระหว่างซิลิกากับซิลิกาได้มีประสิทธิภาพเหนือกว่า ส่งผลให้มีคุณภาพการผสมที่ดี ดังแสดงไว้ในผลของ Payne effect และกล้องจุลทรรศน์อิเล็กตรอนชนิดส่องกราด (Scanning electron microscope)

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LIST OF ABBREVIATIONS

CR	Chloroprene rubber
PSi	Precipitated silica
SCA	Silane coupling agent
BET	Brunauer emmett teller
DRIFT	Diffuse reflectance infrared transform spectroscopy
^{29}Si NMR	Silicon nuclear magnetic resonance spectroscopy
APTES	3-Amino-propyltriethoxysilane
CPTES	3-Chloro-propyltriethoxysilane
TESPT	Bis-(3-triethoxysilylpropyl) tetrasulfide
BRC	Bound rubber content
CB	Carbon black
ZnO	Zinc oxide
MgO	Magnesium oxide
TMTD	Tetramethyl thiuram disulfide
DOTG	N,N'-di-o-tolylguanidine
ETU	Ethylenethiourea
ZnCl ₂	Zinc chloride
CaCO ₃	Calcium carbonate
MgCl ₂	Magnesium chloride
CTAB	Cetyl trimethyl ammonium bromide
DBP	Dibutyl phthalate
OTR	Off-the-road
TEA	Triethanolamine
EM	Electron microscopy
XRD	X-Ray diffraction
UVP	Ultrasound vibration potential
ESA	Electrokinetic sonic amplitude

LIST OF ABBREVIATIONS (cont.)

PE	Polyethylene
KFM	Fluoroelastomer
EPDM	Ethylene propylene diene monomer
NR	Natural rubber
SBR	Styrene butadiene rubber
CSM	Chlorosulfonated polyethylene
ECO	Epichlorohydrin rubber
ACM	Polyacrylate
NBR	Acrylonitrile butadiene rubber
VOC	Volatile organic compound
SEM	Scanning electron microscope
MDR	Moving die rheometer
d(0.5)	Mean average agglomeration size
phr	Parts per hundred rubber
t_{s2}	Scorch time
t_{c99}	Optimum cure time
M_H	Maximum torque
M_L	Minimum torque
TS	Tensile strength
Eb	Elongation at break
$\tan\delta$	Damping factor/ Loss factor
PSD	Particle size distribution
C_B	Compression set (method B)
KSCN	Potassium thiocyanate

CHAPTER I

INTRODUCTION

The use of particulate fillers to achieve the desired reinforcement has widely been acknowledged by rubber industry. Generally, carbon black (CB) and precipitated silica (PSi) are most widely used as reinforcing filler. Between CB and PSi, the latter is typically used in light-colored products. Generally, the magnitude of PSi reinforcement is greatly influenced by its structure [1]. The surface chemistry of PSi is dramatically different from that of CB, due mainly to the presence of silanol groups. Thus, the interaction between PSi and rubber molecules is to be considered for maximizing the reinforcement efficiency [2]. Also, the surface energies of fillers are reported to play strong role on filler reinforcement. In the case of PSi, its surface energy is characterized by a low london dispersive component and a high polar component. The high polar component leads to the strong interactions among PSi clustering; in contrast, the low london dispersive component causes weak filler-rubber interaction, yielding the vulcanizates with low modulus and high elongation [1]. Thus, surface treatments are required to improve the reinforcement of the composites by increasing the london dispersive component of surface energy [3].

The interaction between PSi and rubber, and its influences on properties of rubber have been studied extensively for decades. Varieties of alkoxysilanes to modify PSi surfaces are used. The general formular of trialkoxysilanes is $\text{RSi}(\text{OX})_3$, where R is a functional group, and OX is a hydrolysable group giving a silanol group which can further condense with the free silanol groups on the PSi surfaces. The hydrolysis of alkoxy groups occurs rapidly under acidic conditions while the condensation reaction takes place slowly. Thus, the coupling agent could offer covalent or it bonds between PSi surfaces and rubber molecules [4]. Accordingly, a silane coupling agent (SCA) could function as a bridge between silica and polymer, thereby enhancing the interaction between these two. Many types of SCA, varying in chemistry and reactivity, are commercially available, for modifying the PSi surfaces [5]. The

presence of SCA on PSi surfaces could prevent or reduce the cluster formation of PSi aggregates by deactivating the free silanol groups. Additionally, some new functional groups, such as alkyl, amino, chloro, and mercapto, can be introduced [6]. Each type of SCA gives different properties of PSi filled vulcanizates [7]. It must be noted that vast published works focus mainly on the diene rubbers with either sulfur or peroxide curing system, but the number of work pointing at the rubber system with metal oxide curing system is still limited. Thus, the main aim of this work is to investigate the reinforcing efficiency of CR compounds and vulcanizates as modified with three SCAs under the metal oxide curing.

CHAPTER II

OBJECTIVES

The present research aims to investigate viscoelastic, mechanical and dynamics properties in precipitated silica (PSi) filled chloroprene rubber (CR) with different surface treatment techniques. The scope of this work consists of two main parts, as follows:

2.1 Surface modification and characterization of PSi

The main aim of this part is to modify surfaces of PSi by silanization method with amino-, chloro-, and mercapto alkoxysilanes. The influences of silane type and loading on surface modification efficiency will be investigated. Additionally, the influence of pH condition on silanization of APTES will be studied.

2.2 Effect of silane coupling agent (SCA) on properties CR compounds and vulcanizates

The main aim of this part is to investigate the effect of silane coupling agent (i.e., surface treatment technique, silane loading, silane type and pH condition) on viscoelastic, mechanical and dynamic properties of PSi filled CR compounds and vulcanizates. Two methods of surface treatment performed are: (i) in-situ and (ii) pre-modified methods by 3 silanes, i.e., 3-aminopropyl triethoxysilane (APTES), 3-chloropropyl triethoxysilane (CPTES) and bis-(3-triethoxysilyl)propyl tetrasulfide (TESPT or Si-69). Properties of CR compounds and vulcanizates are then investigated.

CHAPTER III

LITERATURE REVIEW

3.1 Polychloroprene (CR)

Polychloroprene or neoprene or chloroprene rubber (CR) is a diene based synthetic elastomer, which is produced by a polymerization of chloroprene monomer. The CR was invented by DuPont Company in 1930, and first marketed the compound in 1931 under the trade name DuPrene [5, 8]. Nowadays, the CR has been used as a raw material in numerous products, from wetsuits to protective gear. Neoprene demonstrates a compromise of properties, such as good resistances to aging, ozone, weather and good low-temperature flexibility [5, 8].

In principle, chemical structure of CR can be modified by copolymerizing the chloroprene with sulfur and/or 2,3-dichloro-1,3-butadiene to yield a family of materials with broad ranges of physical and chemical properties. The 5 monomeric repeating units can take up to 5 basic configurations as shown in Figure 3.1 [9].

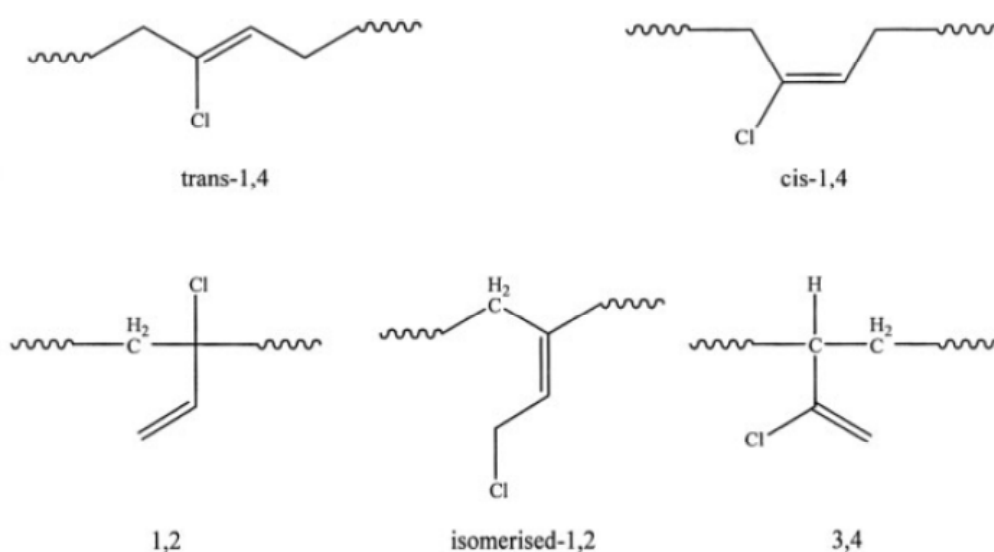


Figure 3.1 Isomeric structures typically found in CR.

3.1.1 Vulcanization of CR by the action of metal oxides

Chloro-butadiene or chloroprene rubbers (CR) are generally vulcanized by the action of metal oxides. Typical structure of CR is represented in Figure 3.2.

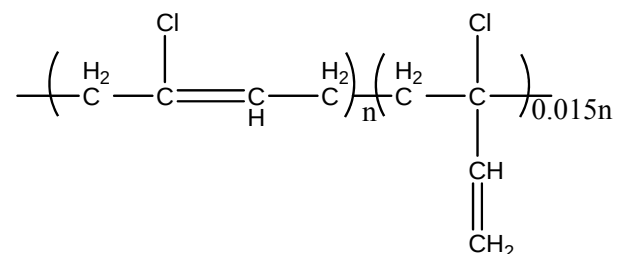


Figure 3.2 Typical structure of CR.

Crosslinking agent of CR is usually zinc oxide (ZnO), in conjunction with magnesium oxide (MgO) in order to gain a scorch resistance. The reaction is thought to involve the allylic chlorine atom which is the result of the small amount of 1,2-polymerization as illustrated in Figure 3.3 [10].

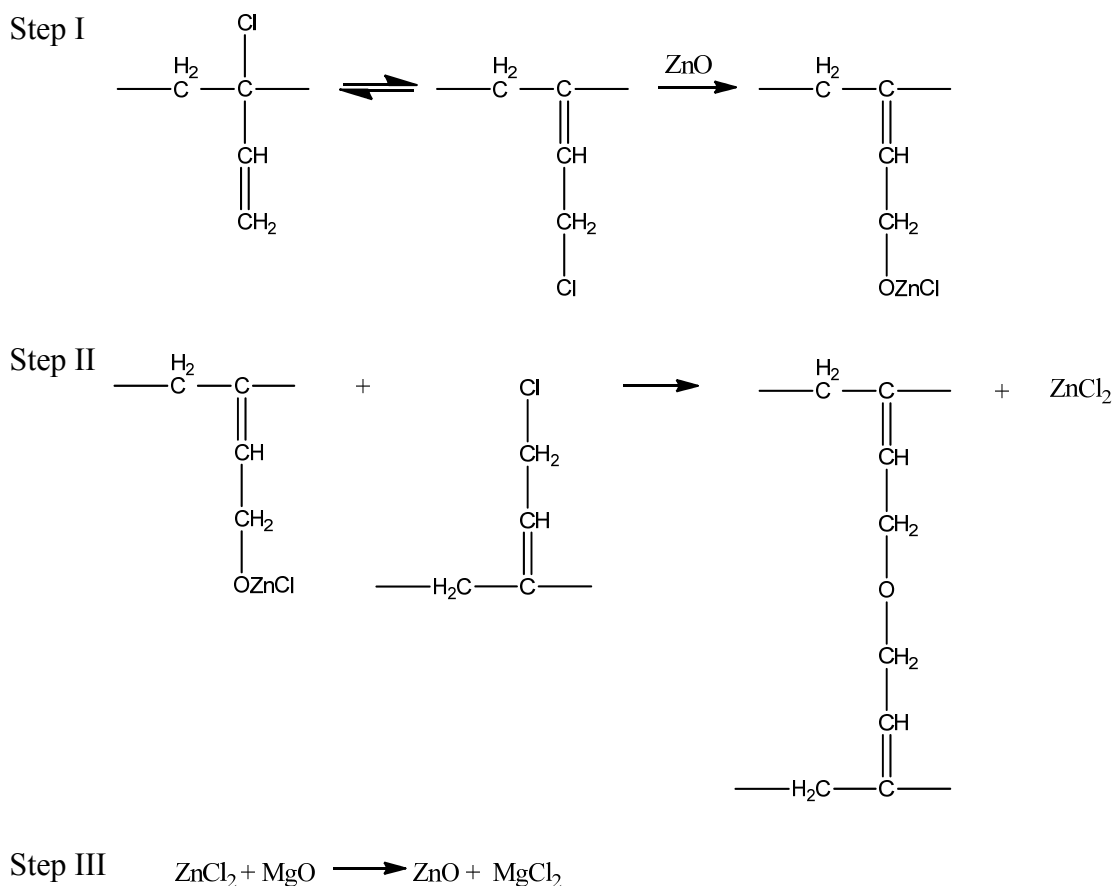


Figure 3.3 Crosslink reaction of CR by the actions of zinc oxide and magnesium oxide [10].

Most cure accelerators used in the accelerated-sulfur vulcanization of most high-diene rubbers are not functional in CR. The use of mixed curing system in which the metal oxide vulcanization is combined with accelerated-sulfur vulcanization is therefore introduced [5, 10-12]. Along with the metal oxides, tetramethyl thiuram disulfide (TMTD), N,N'-di-o-tolylguanidine (DOTG), and sulfur are used. This may be desirable for high resilience or for good dimensional stability of CR vulcanizates.

The accelerator, which has widely been used with metallic oxide cure is ethylenethiourea (ETU) or 2-mercaptoimidazoline. A mechanism for ETU acceleration of metal oxide curing is given in Figure 3.4 [13].

CR is curable upon heating [14], and the reaction is facilitated by the addition of ZnO or zinc chloride (ZnCl₂). Kuntz et al. [15] reported the involvement of

an allylic carbocation with the heating of 2,2,4,8,8-pentamethyl-4-nonene as a model, and proposed a mechanism in which two competing reactions are related: (i) the formation of a conjugated diene and (ii) the actual crosslinking. The dominant reaction of diene formation is thought to precede the crosslinking process due to a formation of zinc oxychloride or zinc chloride, acting as a catalyst for the crosslinking reaction. By contrast, Mallon et al. proposed the crosslinking reaction of CR with Zn based on two competing reactions involving the isomerized and unisomerized species of the 1,2-units, providing the sites for crosslinking the CR backbone. The crosslinking of unisomerized 1,2-units is rapid, and takes place first followed by the crosslinking of isomerized 1,2-units. It is proposed that the ZnCl_2 could catalyze the reaction of unisomerized 1,2-units while the ZnO promotes the allylic rearrangement of the 1,2-units. It is widely accepted that the allylic of 1,2-polymerized units in CR is an important step in the vulcanization of CR [16].

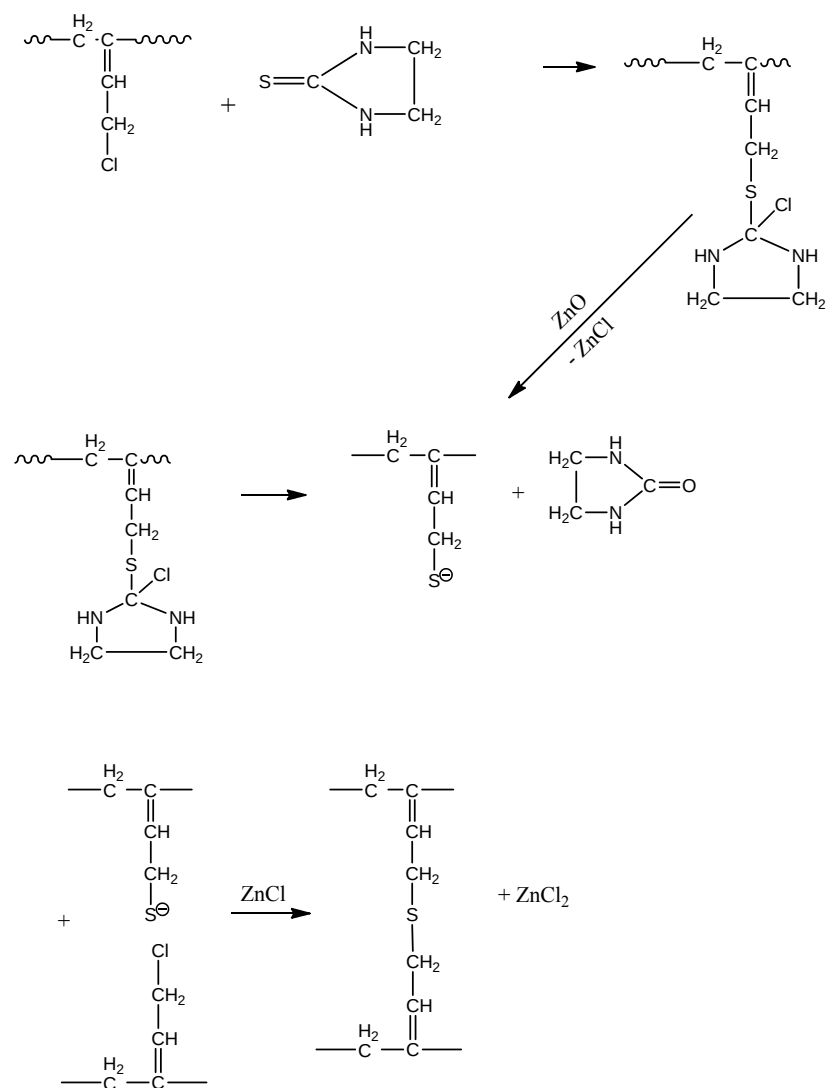


Figure 3.4 Mechanism of metal oxide crosslinking of CR as accelerated by ETU [13].

Example of CR compounding recipe for metal oxide curing is shown in Table 3.1.

Table 3.1 Example of vulcanization systems for CR ^a [17].

ZnO	5	5
MgO	4	4
Stearic acid	-	-
TMTM	-	1
DOTG	-	1
ETU	0.5	1
Sulfur	0.5	1
Cure condition ^b		
Temperature (°C)	153	153
Time (min)	15	15

^a Concentration in parts by weight per 100 parts of neoprene W

^b Conditions change depending on other aspects of the compositions

3.1.2 Application of CR

CR is not characterized by one excellent property, but its balance of properties is unique among synthetic elastomers. All types of CR have inherent characteristics, as follows [5]:

- Resistances to degradation from sunlight, ozone and weather
- Good performance when being in contact with oils and many chemicals
- Broad range of service temperature
- Outstanding physical toughness
- Resistance to flame

The balance of their properties causes the CR applicable in various applications, such as automotive, construction, footwear, specialty apparel, transportation, wires and cable industry [5, 18].

3.1.3 Families of CR

Dry rubber application of CR is available in 3 different families, namely, G-, W-, and T- types. Each type offers broad ranges of physical properties and processing conditions as illustrated in Table 3.2.

Table 3.2 Family characteristics of CR [5, 8, 11].

	G types	W types	T types
Raw polymers stability	Limited storage stability	Excellent storage stability	Excellent storage stability
	Peptizable to varying degrees	Non-peptizable	Least nerve
	No accelerators necessary	Accelerator required for giving high cure flexibility	Accelerator required for yielding high cure flexibility
	Fast curing, but safe processing		Best extrusion, calendaring performance
Vulcanizates	Best tear strength	Best compression set resistance	Properties similar to W types
	Best flex	Best heat aging	
	Best resilience		

CR “G” or Neoprene “G” Family

In the CR “G” family, the chloroprene monomer is copolymerized with sulfur to achieve high molecular weight. The sulfur presents in the polymer chains in cluster or a single atom between the chloroprene segments, as illustrated in Figure 3.5.

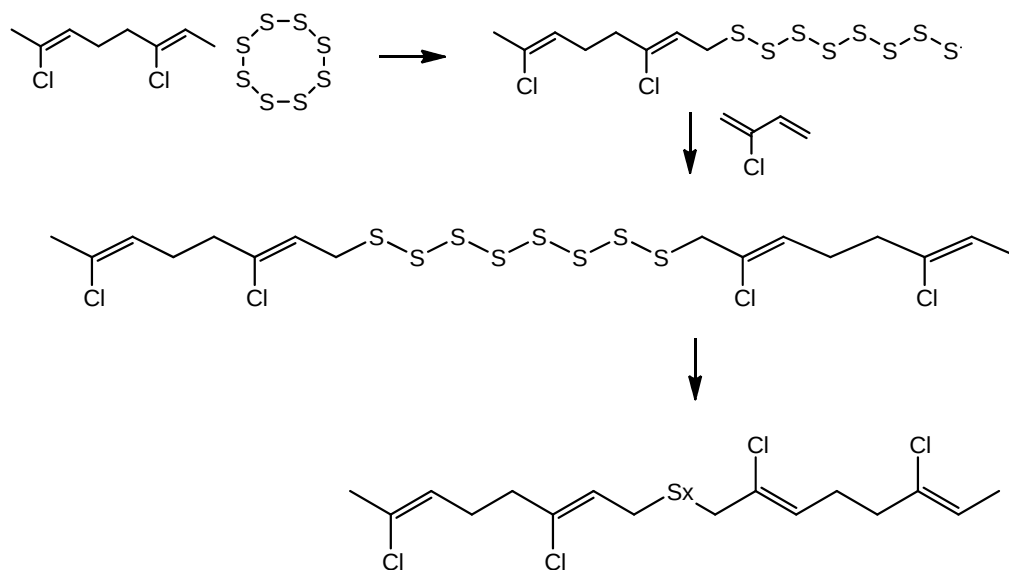


Figure 3.5 Polymerization of CR “G-type” (S_x is one or more sulfur atoms) [11].

Thereafter, the thiuram disulfides and dithiocarbamates are added to reduce the molecular weight to the desired level of Mooney viscosity. Thus, this family has different fundamental behavior from other families of CR. Typically, the G-type CR possesses much wider molecular weight distribution ranges than the W or T types CR to be mentioned later.

Neoprene “W” Family

The “W” family of CR is polymerized from the chloroprene homopolymers or copolymers of chloroprene and 2,3-dichloro-1,3-butadiene. They have none of elemental sulfur, thiuram disulfide, or other additives sulfur donor. The CR “W” also contains no staining stabilizer and has more uniform molecular weight distribution than the G types.

The W types are selected primarily in the products where high resistances to heat and compression set are required. Additionally, the W types are mastication resistant, i.e., its molecular weight is not significantly reduced under mechanical stress.

Neoprene “T” Family

Most chemical composition and performance characteristics of the “T” family are similar to those of the “W” types except that, the “T” types contain a highly

crosslinked CR gel acting as an internal processing aid. As a result, the T types generally exhibit superior processability to the W types.

3.2 Reinforcement of rubber with particulate fillers

By definition, the reinforcement refers to an enhancement in the end-of-use performance of the rubber compounds or vulcanizates, including increases in modulus and tensile properties, tear strength, and abrasion resistance [5, 19]. Commercial application of elastomers often needs reinforcing fillers to achieve the desirable level of reinforcement. Normally, the filler selection is dictated by the end application and economics of elastomer. According to view of rubber industry, fillers are divided into 3 main types: reinforcing, semi-reinforcing and non-reinforcing fillers. The nature of fillers such as particle size and shape, surface area, surface activity and filler matrix compatibility has profound effect on properties of rubber vulcanizates. It is recognized that the small filler particle size offers high reinforcing efficiency in rubber compounds and vulcanizates [20].

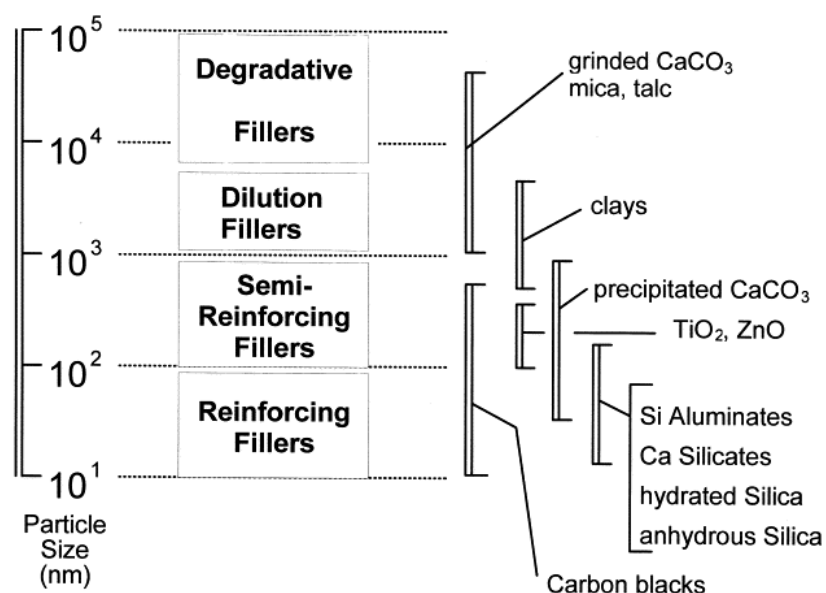


Figure 3.6 Classification of filler based on the average particle size [20].

The classification of filler based on the average particle size is illustrated in Figure 3.6. The fillers with particle size larger than 10^4 nm are defined as degradative fillers such as grinded calcium carbonate (CaCO_3), mica and talc, and mainly used for reducing the product cost. The fillers with particle size between 10^3 to 10^4 nm are widely used as diluents having no substantial effect on vulcanizate properties. The fillers with particle size range from 10^2 to 10^3 nm are called semi-reinforcing fillers. The ones with particle size in between 10 to 100 nm are called reinforcing filler capable of strongly improving the properties of rubber drastically. Among reinforcing fillers, the carbon black and silica are widely used in rubber industries.

3.2.1 Carbon black

Carbon black (CB) is prepared by incomplete combustion of hydrocarbons or by thermal cracking process. The CB is divided into furnace blacks, channel blacks, thermal blacks, lamp black and acetylene black, depending on their manufacturing methods. The furnace process is widely employed for producing most of CB used in rubber industry as reinforcing filler [21, 22].

CB is typically characterized based on its surface area, particle size and structure [5]. The iodine adsorption, nitrogen adsorption or cetyl trimethyl ammonium bromide (CTAB) adsorption is usually used to determine the surface area of CB. Structure refers to the bulkiness of the carbon black aggregate, i.e., a number of particles per aggregate (ASTM D3765/ISO 6810). Structure is measured by dibutyl phthalate (DBP) absorption technique (ASTM D-2414) method. Dispersion of CB in the elastomer also influences the magnitude of reinforcement. Typical characteristics of 4 different CB are given in Table 3.3 [23].

Table 3.3 Specifications of different carbon blacks [23].

Characteristics	Lamp black	Channel black	Furnace black	Thermal black
Average particle size (nm)	100 – 150	1 – 3	14 – 80	240 – 320
Surface area (N ₂)(m ² /g)	20 – 95	100 – 1125	27 – 145	7 – 11
Oil absorption (ml/g)	1.05 – 1.65	1.0 – 6.0	0.67 – 1.5	0.32 – 0.47
Volatile matter (%)	0.4 – 0.9	3.5 – 16.0	0.3 – 2.8	0.1 – 1.0
Ash (%)	0 – 0.16	0 – 0.1	0.1 – 1.0	0.2 – 0.5
Sulfur (ppm)	–	0 – 0.1	0.5 – 1.5	10
pH	3 – 7	3 – 6	5.0 – 9.5	7 – 9

In general, the CB possesses reactive organic groups on its surfaces providing the affinity to rubber matrix. Incorporation of CB with optimal loading into rubber gives enhanced modulus, improved fatigue and abrasion resistances [5, 23].

3.2.2 Non-black fillers

Non-black fillers include a range of inorganic materials with a variety of particle shapes and sizes. In the past, the non-black fillers used were mainly natural filler such as clay, whiting, barites, zinc oxide, zinc sulfide, blanc-fixe, mica, asbestos, kieselguhr, magnesium carbonate, iron oxide and litharge. These natural fillers are mainly employed in rubber for the purposes of reduced tack, increased hardness, improved durability and reduced cost [5, 24]. Synthetic silica is widely used in the rubber reinforcements for enhancing abrasion resistance as well as tensile and tear strengths. Table 3.4 represents a partial listing of many silica varieties used in rubber compounding.

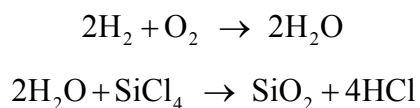
Table 3.4 Forms and properties of silica used in rubber compounding [24].

	Primary size, μm	Function in rubber
Natural (Crystalline):		
Ground quartz	1 – 10	Extending
Diatomite	1 – 5	Processing; extending
Neuberg silica	1 – 5	Extending
Synthetic (Amorphous):		
Fumed	0.005 – 0.02	Reinforcing
Precipitated	0.01 – 0.03	Reinforcing
Precipitated	0.04	Semi-reinforcing
Precipitated	0.08	Processing; color

However, there is a demand of non-black fillers with high magnitude of reinforcement in many rubber applications. Such fillers include hydrated silica and fumed silica as characterized by their fine particle size (very high specific surface area).

3.3 Manufacture of synthetic silica

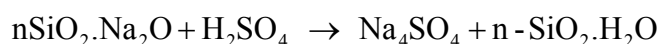
Silica produced by a thermal method is commonly called fumed silica. The original process was developed by Degussa Company in 1940, and the product is still marketed under the brand name Aerosil. This silica is prepared by flame hydrolysis of readily volatile silicon tetrachloride (SiCl_4). Silicon tetrachloride, hydrogen, and oxygen are burned in a cooled combustion chamber. The reactions taking place are shown below:



Typically, due to its relatively high cost, the fumed silica is only used in specific case where very high reinforcement is needed, particularly silicone rubber having poor mechanical strength [25].

Precipitated silica (PSi) is often used if highly reinforced non-black rubber compounds are required. A significant amount of PSi has replaced carbon black in many applications. Silica is used in off-the-road (OTR) tire treads for improving tear resistance, hence less chunking of treads and more resistance to cutting. In conventional tires, up to 20 or 25 parts of the CB loading may be replaced by silica to help lowering the rolling resistance, improving traction, and ensuring adhesion to the textile and steel cords used in carcass component [26].

The PSi is made by the action of acids on water glass [25]. The acid is usually sulfuric acid while the water glass is an alkaline solution of sodium silicate, normally having a mole ratio of 2.1 to 3.5. The reaction is as follows:



The hydrated precipitated silica ($n \cdot \text{SiO}_2 \cdot \text{H}_2\text{O}$) is filtered out and washed to remove the sodium sulfate. It is then dried and ground. Grinding reduces size of the PSi aggregates. A typical commercial specification of PSi is shown in Table 3.5 [27].

Table 3.5 Properties of precipitated silica [27].

Property	Range
Surface area (S_{BET}), Single point, m^2/g :	
Reinforcing	125 – 250
Semi-reinforcing	35 – 100
Free water, %loss @ 105°C	6 ± 3
Bound water, %(silanols)	3 ± 0.5
pH: Reinforcing	5 – 7
Semi-reinforcing	6 – 9
Particle size, μm (mean diameter)	10 – 100
Salt content, %	0.5 ± 2.5
Specific gravity in rubber (g/cm^3)	2 ± 0.05

For the use of PSi in the rubber, moisture content must carefully be controlled. Below 3% moisture content, a dispersion of PSi in rubber matrix is difficult. The PSi particles are porous as evidenced by the BET surface area values. Due to this porosity, the PSi could adsorb active compounding ingredients, particularly cure activator and accelerators, leading to a decrease in cure efficiency [23, 27].

3.4 Characterization of silica (Analytical properties)

Characterization of silica aims to determine the (surface) structure including size and shape of pores, absorption capacity, surface roughness, primary particle size with the development of siloxane bonds, and agglomerates formation via Van der Waals forces. Surface chemistry of silica is represented by the number of silanol groups and their arrangement, and the chemical composition of silica surfaces.

3.4.1 Characterization method of silica morphology

Specific surface area; The specific surface area of silica is generally determined by the Brunauer – Emmett – Teller (BET) adsorption method [28-30]. For a measurement, the sample is cooled down to the temperature of liquid nitrogen. At low temperature, nitrogen is adsorbed on the silica surfaces. The amount of adsorbed gas is a measure of surface area. When performed under defined conditions, the BET method yields perfectly reproducible results. The BET method provides the sum of the so-called outer geometrical surface and the inner surface, i.e., the surface within the porous silica structure.

CTAB surface area; The measurement of CTAB surface area is based on the adsorption of surface-active molecules from aqueous solutions of cetyltrimethylammonium bromide (CTAB) [31, 32]. The preferred adsorption site for these large CTAB molecules is the outer, geometrical surface, which correlates quite well with the surface area accessible to the rubber [31, 32]. Comparison with the BET surface, which is the sum of the outer and inner surfaces of a filler, the CTAB surface area is lower with a certain margin of error.

Sear number; The Sear number is a measure of the number of silanol groups on silica surfaces. The sear number is equivalent to the quantity of 0.1 N NaOH required to titrate a suspension of silica from pH 6 to pH 9. The acidic silanol groups on the silica surfaces react with NaOH. The sear number gives an indication of the number of reactive centers on the silica surfaces [33].

DBP number; The assessment of the liquid absorbing capacity of synthetic silicas and silicates may involve the absorption of dibutylphthalate (DBP) (ASTM D 2414). This measurement technique provides an indication of the total volume of liquid that can be absorbed by silica sample. The magnitude of the DBP number gives an initial indication of the inter-aggregate structure and dispersability of silica in rubber matrix. Owing to the toxicity of DBP oil, attempts are being made to replace the DBP with paraffin oil [34]. Considering the polarity of the silica, polar substances such as triethanolamine (TEA) can also be used to determine the inter-aggregate structure, analogous to the DBP measurement.

Microscopic method; The only method allowing direct insight into the dimensions of silica is electron microscopy (EM), which provides information on the size of primary particles and aggregates or agglomerates and, with certain limitation on the particle size distribution of an examined sample. EM surface images can be used to calculate particle size distributions, with the resulting values comparable to those from BET measurements [31, 32].

3.4.2 Characterization of silica surface chemistry

Chemical reactions of silanol groups, a variety of methods are reported to be suitable for determining silanol groups and their chemical reactivity on silica surfaces [25, 35-37]. Those methods are based on applying the experience gathered in small molecule and low molecular weight chemistry to surface chemistry. However, the flaw of this analogy is demonstrated [25]. On the surfaces of solids particularly in the interior of micro-pores, spatial inhibition, other equilibrium conditions, and other reaction possibilities may prevail [36, 38, 39]. Chemical reactions are nonetheless an important tool for characterizing the solid surfaces. The reaction generally yield reproducible characteristic values allowing different products to be compared.

NMR spectroscopy; With silicon nuclear magnetic resonance spectroscopy (^{29}Si -NMR) it is possible to monitor different surroundings of the silicon atom on the basis of the oxygen atoms and hydroxyl groups in the silica sample (Figure 3.7) [25, 40-42].

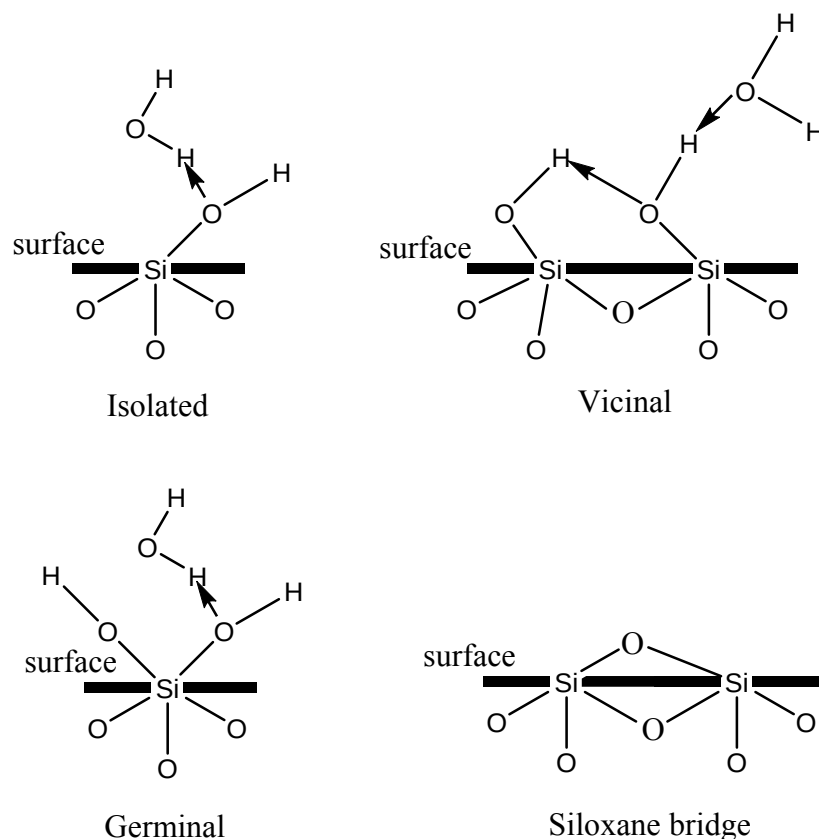


Figure 3.7 Surroundings of Si in silica: germinal, isolated, vicinal and siloxane bridge [25].

The ratios of the detected signal intensities correspond to the proportions of the various Si surroundings in the sample. With the solid NMR method, it is possible to distinguish among three main groups surrounding the silicon atom in silica:

1. Siloxane bridges (bulk) (chemical shift of approximately -110 ppm)
2. Isolated, terminal SiOH (chemical shift of approximately -100 ppm)
3. Germinal-SiOH (chemical shift of approximately -90 ppm)

The relative content of isolated or germinal silanol groups and siloxane bridges is quantifiable, and the different silanol groups show different reactivities. For

example, with respect to organosilanes as coupling agents germinal groups are considered to be the most reactive [25].

Infrared spectroscopy (IR); Infrared spectroscopy is another important method of differentiating among various silanol groups (barring germinal groups) [43]. An overview of the detectable groups is given in Table 3.6 [44-47].

Table 3.6 Infrared band assignments.

Frequency (cm ⁻¹)	Species
3,746	Free OH
3,742	germinal OH
3,730 – 3,720	hydrogen perturbed OH
3,650	Intra-globular OH
3,520	oxygen perturbed OH
3,400 – 3,500	molecular adsorbed H ₂ O
2,000 – 1,870	skeleton (overtone) vibrations
1,625	bending O-H (molecular water)
1,250 – 1,020	asymmetrical Si-O-Si stretching
970	Si-O-(H...H ₂ O) bending
870	bending O-H (silanol)
800	in-plane bending (geminol)
600	in-plane bending (geminol)

Variations of the IR technique contribute further refinement or elucidation of the chemical structure on silica surfaces. In the near infrared (NIR), for instance, the SiOH groups can be quantified by means of a combined oscillation band. With diffuse reflectance infrared fourier transform spectroscopy (DRIFT), an insight how the SiOH groups change as the degree of chemical modification increases is gained.

Thermo-analytical method; Thermal analysis is the term given to a group of methods that measure a physical properties of a substance (and/or its reaction products) as a function of temperature or time while subjecting the substance to a controlled temperature program [48]. With differential thermal analysis (DTA) it is

possible to monitor changes in enthalpy of a sample during the course of a temperature program. The DTA is often combined with thermogravimetry (TG), which records the weight loss of the sample as a function of the temperature. From the mass loss, information on resulting products and on the possible course of degradation reaction could be obtained [49]. In the case of silica, rational information is gained only by means of a combined DTA-TG measurement, because the thermal effects observed in DTA are generally negligible on their own [50]. It is also possible to calculate the surface characteristics in similar manner to the BET technique. This includes the ratio between the outer and inner surfaces, and the difference in silanol group as per the case of NMR.

Small angle scattering (SAS); This method is a well-known tool to characterize the structure of fine particles [51]. Because precipitated silica behaves in most cases as fractal scatterers, the scattering of these materials can be described with fractal structural concepts [51, 52]. In a typical scattering experiment, it is possible to estimate primary particle size and distribution, and aggregation size; all these parameters depend on the type of silica investigated. For precipitated silica samples, typical mass fractal dimension is 1.9 ± 0.2 dm [53, 54]. A huge advantage of the SAS method is the study capability of silica structure when dispersed in various matrix, for example, in rubber [55].

3.4.3 Chemical bulk analysis

X-Ray diffraction (XRD); Synthetic silica and silicates are amorphous solids. This is, unlike crystalline solids, they do not possess an infinite three-dimensional long-range order. Consequently, use of the classic X-ray diffraction method is not possible. Silicas, however, like glass, do have areas of short-range order that can be determined by appropriate evaluation of the diffuse X-ray diffraction bands. Silicas from a variety of manufacturing processes differ from one another in terms of their X-ray diffraction bands. When the sample is tempered, changes in the short-range order can be detected at temperature as low as 200°C using X-ray diffraction [56].

Electrokinetic measurements, Several electrokinetic methods lend themselves to the determination of surface activity of silicas. The majority are based

on measurement of the zeta (electrokinetic) potential. These include electrophoresis, flow potential, and electroacoustic measurements, such as measurement of the ultrasound vibration potential (UVP) or electrokinetic sonic amplitude (ESA). The correlation establishment for silicas partly modified with organosilanes has been reported [57]. The lower the SiOH concentration on the silica surfaces, the lower the hydrophilic nature of the silica, and thus the lower the surface activity leading to the higher the zeta potential in potassium chloride solution. This observation is accompanied by an upward shift in the isoelectric point (point of zero charge). Because the isoelectric point is a measure of the acidity of a surface, this signifies that the modified surface is of lower acidity than the unmodified surface. This finding is explained by the reaction of some SiOH with the organosilanes.

3.4.4 Characterization of the silica surfaces

The silica surfaces are composed of siloxane and silanol groups. The chemical characteristics of the silica surfaces are mainly determined by the amount of silanol groups, the degree of hydration, the amount of adsorbed water and the surface acidity. Three types of surface silanol hydroxyls have been identified by using ^{29}Si -NMR-experiments or infrared spectroscopy [25, 37] as shown in Figure 3.8.

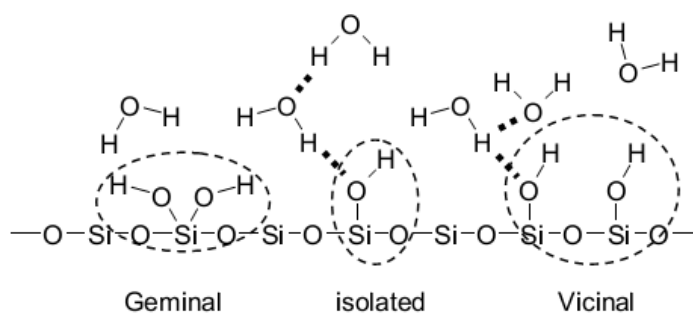


Figure 3.8 Types of hydroxyl groups on the silica surfaces [20].

Depending on the precipitation conditions, these 3 different types of hydroxyl groups can be formed. Adjacent silanols such as the geminal type of silanol groups are highly capable of absorbing water [20, 25].

3.4.5 Surface chemistry of silica

Filler-polymer interaction in rubber compounds strongly influences the magnitude of filler reinforcement. The silica surfaces are covered by a large number of silanol and siloxane groups, and can be characterized by the surface energy [47, 48]. The surface energy (γ_s) of a filler can be described by Equation 3.1, which is composed of dispersive and specific components [20]:

$$\gamma_s = \gamma_s^d + \gamma_s^{sp} \quad (3.1)$$

where γ_s^d is the dispersive component, indicating the tendency of adhesion to an organic matrix and γ_s^{sp} is the polar component, indicating the tendency of interaction with itself.

The specific component (γ_s^{sp}) of silica is relatively high compared to that of carbon black because of the large number of polar groups on the silica surfaces [58]. The dispersive component, responsible for the degree of wetting of fillers by polymers, depends on the difference of the solubility parameters of filler and polymer [59]. As shown in Table 3.7, silica shows relatively high solubility parameter value compared to the polymers, which means that these two materials are difficult to be mixed together.

Table 3.7 Solubility parameters of common compounding ingredients [60].

Materials	Hildebrand (solubility parameter)
FKM, Silicones	7.0 – 7.5
PE, EPM, EPDM	8.0
NR, BR, IIR	8.0 – 8.5
SBR, low molecular weight resins	8.5 – 9.0
CR, CSM, some NBR	9.0 – 9.5
Typical lubricants and processing aids	8.5 – 9.5
PVC, ECO, ACM, some NBR	9.5 – 10.0
Carbon black	12.0 – 15.0
Clay, Whiting, Talk	13.0 – 14.0
Silica (untreated)	14.0 – 18.0

3.4.6 Bound rubber model of silica-filled rubber

Bound rubber is defined as the rubber incapable of being extracted from an uncured filled rubber using good solvent for a rubber matrix, usually at room temperature. The bound rubber content (BRC) is known to be functions of rubber-filler interaction, filler surface area, molecular weight of the rubber, solvent used for the extraction, time and temperature for the extraction and filler loading in the composites [61, 62]. By definition, bound rubber of silica-filled rubber is mainly composed of 2 components: occluded rubber in the silica aggregates and crosslinked polymer due to polymer chain scission and re-coupling [61]. A simple model of silica/silane reinforcement based on the hydrodynamic-occlusion-interaction theory has been proposed as illustrated in Figure 3.9 [62].

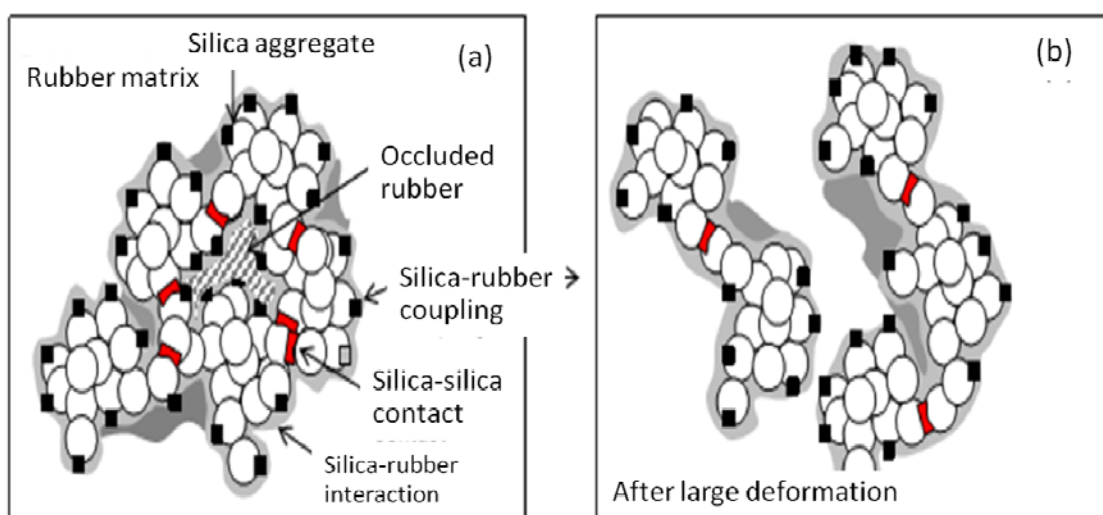


Figure 3.9 Simple model of silica/silane reinforcement: (a) No deformation and (b) After large deformation [62].

Due to the polarity difference between silica and polymer, the filler-filler networks can easily form, and therefore, part of the rubber matrix is occluded in this filler network. This means the occluded rubber is physically and chemically immobilized within the filler network. However, under large deformation, this filler network partially disrupts. Therefore, with increasing deformation of rubber, the immobilized rubber is reduced or released and then follows the matrix deformation.

With the presence of silane offering chemical bonds between rubber and silica surfaces, the occluded rubber and the rubber on the silica surfaces remain grossly immobilized, and therefore still contribute to the modulus even at high deformations. This chemically immobilized rubber is defined as “in-rubber structure” [62].

3.5 Surface modification of silica

Extensive works [63-69] have been carried out on structural developments in silica/rubber composites. The surface functional environment of silica particles is different from that of other fillers, due to the existence of silanol groups on its surfaces [31, 49, 70]. Thus, the primary discussion on the structural development in the silica/rubber systems is focused on the silica-rubber interaction. Numerous methods used to modify the surface properties of silica include thermal, chemical, direct fluorination and coupling agent treatments. For rubber industry, the surface treatment of silica by coupling agents is the most widely used technique, which will be reviewed subsequently

3.5.1 Silane coupling agent (SCA)

Typically, silane treatment of silica surfaces can improve processing, performance and durability of filler-modified products by:

- Improving adhesion or interaction between filler and the polymer
- Improving wet-out of the filler by the polymer
- Improving dispersion of the filler in the polymer
- Improving electrical properties
- Enhancing mechanical properties
- Reducing bulk viscosity of polymer compounds

General formula of silanes is usually either $R-(CH_2)_3Si(X)_3$ (Figure 3.10) or $R-(CH_2)_2Si(CH_3)(X)_2$. The X, as silicon functional group, is a hydrolyzable group selected to react with surface hydroxyl groups of the filler surfaces to create a stable bond, and is typically halogen or alkoxy. The silane coupling agents in commercial used are generally alkoxy-based, and bear one organic group attached to the silicon center. The organofunctional group, R, is tightly bound to the silicon via a short

carbon chain, and links with the polymer. This group has to ensure maximum compatibility with the polymer system. Bonding to the polymer takes place by either chemical reactions or physicochemical interaction such as hydrogen bonding, acid-base interaction, interpenetration of the polymer network (entanglement), or electrostatic attraction [71]. The group Y may be non-functional or functional (reactive); examples for the latter are vinyl, amino, methacryl, epoxy, mercapto, chloro, etc. For example, amino silanes may be used as adhesion promoters in many polymeric systems such as phenolic, melamine, epoxy, polyurethanes, polyesters and polyamides systems [72]. Glycidoxysilanes and methacrylatesilanes are widely used for the composites materials based on epoxy and acrylic resins, respectively. Vinyl- and methacryloxy-functional silanes are commonly used for polyolefins. The mercaptosilane and di-polysulfide silanes are most suitable for sulfur-crosslinked elastomers [72].

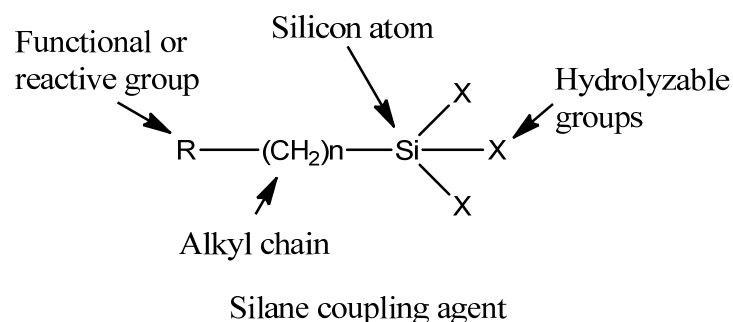


Figure 3.10 General structures of organosilanes [71].

3.5.2 Types of silanes

Waterborne silane systems

Organofunctional silanes can be applied to filler in many forms, such as aqueous or aqueous/alcohol solution and neat. The silane has to be water soluble, when the silane is added to aqueous filler slurry. Some silanes are water-soluble after being hydrolyzed, giving the formation of silanols (Si-OH). These Si-OH groups are extremely reactive for the development of covalent bond between filler surfaces and silane. In addition to fast hydrolysis, the reactivity of the silane is controlled by the availability of reactive hydroxyl units on the central silicon atom. Thus, the monomeric silanetriols are restricted for the activity of the silane, and these

monomeric units are stable for a period of a few hours to a few days in aqueous solutions [77].

The case of devising a stable waterborne silane system, the silane in silanol form is admirable since the silanol has higher solubility and reactivity than their alkoxysilane precursors. A series of waterborne silanes with different functionalities are commercially available. These silanes contain high concentrations of active silanol groups with stability in water for periods of up to a year, and therefore are considered to be free of volatile organic compounds (VOCs). They are notably useful in wet processes such as grinding and milling, where the VOCs are undesirable, and the filler can be in-situ treated in the aqueous process slurry.

Oligomeric silane systems

Formation of oligomeric silane structures occurs on the surfaces of the mineral filler by silane hydrolysis and condensation reactions. These silanes have low viscosity with high boiling and flash points, leading to a significantly reduced amount of alcohol [87]. Furthermore, with low VOCs evolution during application, the oligomers may supply additional benefits, such as superiority wettability in association with homogeneity of silane layer on filler surfaces. This results in smaller amounts of silane being needed to achieve the same final properties [71]. Different types of oligomers are available, ranging from homo-oligomers to various types of co-oligomers. The latter combine the benefits and properties of both silane monomers.

Silane hydrolysis

The action of alkoxysilanes initiates with hydrolysis reaction, depending on pH and type of organo- and silicon- functional groups. The silicon functional group has a major effect on hydrolysis rate. The order of reactivity is as follows: methoxy > ethoxy >> propoxy [71]. Normally, with excessive water, the reaction order of alkoxysilanes hydrolysis is found to be a pseudo-first order reaction. The next important parameter influencing the reaction rate is the pH of the silane hydrolysis medium. At high and very low pH values, the rate of hydrolysis is higher than that at neutral pH, at which silanes are most stable. For example, the reaction rate of monomeric trialkoxysilane in acetic acid solution increases by a factor of 10 when pH is changed from 4 to 3. This effect is even more marked on going from neutral to acidic condition (pH 3), for which the factor is about 25 to 50 depending on the

method of mixing. As an example, the hydrolysis of 3-methacryloxypropyl trimethoxysilane proceeds within a few minutes in a low pH environment as a result of the catalytic action of H^+ ions [71].

A strong dependence of reaction rate on pH is explained by the nucleophilic substitution reaction mechanism for the hydrolysis of alkoxysilane in acid media, where protons directly affect the rate-determining step of the reaction. The nature of the acid also affects the hydrolysis behavior. The effect of pH on the stability of the formed silanols is different from that on the stability of alkoxysilanes. Silanols are most stable at pH of approximately 3, and their reactivity is higher at the pH lower than 1.5 or higher than 4.5 (Figure 3.11). Silanols condense to form oligomers and, ultimately, two- and three-dimensional networks [4, 71].

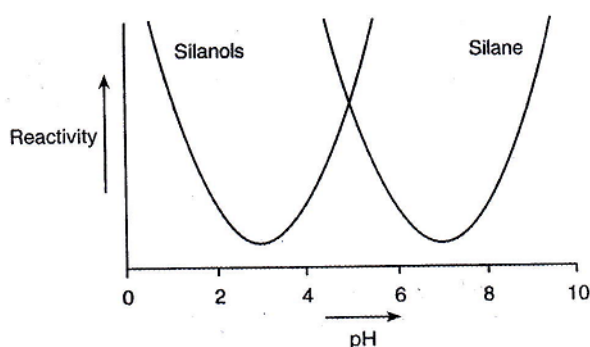


Figure 3.11 Effect of pH on reactivity of silanes and silanols [71].

When considering the silane hydrolysis and condensation reactions, different reactivities in different pH ranges could be expected. At very low pH, the silanes hydrolyze very quickly. The formed silanols are relatively stable and, over time, form coordinated networks. At neutral pH, the silanes hydrolyze very slowly to silanols, which are unstable and condense. Thus, in both cases (at low and neutral pH), there is still a slow reaction in the transition from silanes to Si-O-Si networks. At $pH > 8$, silanes become highly reactive once more, and form silanols very quickly. These silanols are very unstable and condense very quickly to give uncoordinated Si-O-Si networks. The build-up of Si-O-Si networks cannot be controlled, and the uniform coating of the filler surfaces becomes more difficult resulting in thicker uncoordinated layers.

The rate of hydrolysis is also influenced by the nature of the organic substituent on the trialkoxysilane. As the polarity of the organic substituent is diminished by increasing the length of the non-polar chain, as for example in long chain alkylsilanes, the hydrolysis rate decreases. This behavior can be explained in terms of the lower solubility of the non-polar silanes in the aqueous reaction system and the associated formation of micellar structures. By incorporating the polar moieties (functionalities other than alkyl), the susceptibility to hydrolysis is increased. However, it is not possible to determine whether the increased rate is directly linked to the functionality of the substituent, or is merely a consequence of improved solubility. The pH and/or the use of a catalyst also give a decisive effect on the hydrolysis behavior of trialkoxysilanes. With no exception, in all studied functional trialkoxysilanes, a complete hydrolysis of alkoxy substituents to the corresponding silanols takes place within a period ranging from a few minutes to a few hours, depending on nature of silane functional group. Reactivity towards the hydrolysis reaction increases with substituent in the following order: alkyl < vinyl $\cong$ methacryloxy < mercapto < epoxy < amino. In the case of 3-glycidyloxypropyltrimethoxysilane, as the reaction proceeds, not only hydrolysis of alkoxy groups, but also epoxy ring opening take place; increasing the rate of hydrolysis reaction.

3.5.3 Mechanism of silanization reaction

The silane chemistry is complicated because there are two reactive sites related: alkoxy groups and the organofunctional groups. The reaction between silane and silica, the so-called silanization, has been studied by many researchers [73-75].

The reaction mechanism of silanization is schematically summarized in Figures 3.12: (a) and (b). The primary step is the reaction of the first alkoxy group of the silane with silanol groups on the silica surfaces. Two possible mechanisms are reported as shown in Figure 3.12 (1) a direct reaction of the silanol groups on the silicon with the alkoxy group of silane, and (2) a hydrolysis of the alkoxy group to form a reactive silanol groups.

These reactions occur slowly on the silica surfaces in the presence of water [77]. The rate constant of hydrolysis increases with increasing temperature, and

additionally using a catalytic agent such as an acidic or alkaline medium. After the hydrolysis, the activated silane is capable of reacting with silanol groups on the silica. The rate constant of this reaction is relatively low compared to hydrolysis. This means that the hydrolysis reaction is the rate-determination step for the silanization reaction.

After the primary reaction, an intermolecular condensation between silanes on the silica surfaces, or the so-called secondary reaction takes place as shown in Figure 3.12.

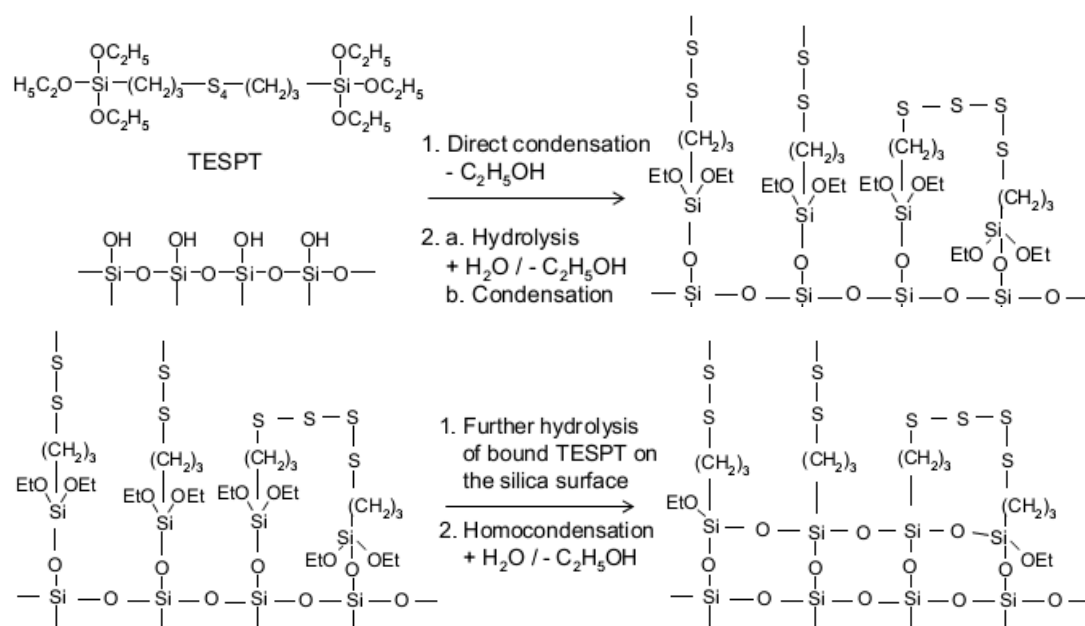


Figure 3.12 Reaction mechanism of silanization [76].

The reaction rate of the secondary reaction is rather slow compared to that of the primary reaction. The secondary reaction is also accelerated by water and temperature [78, 79]. A low degree of intermolecular condensation is required, if any, to achieve an optimal reinforcement magnitude.

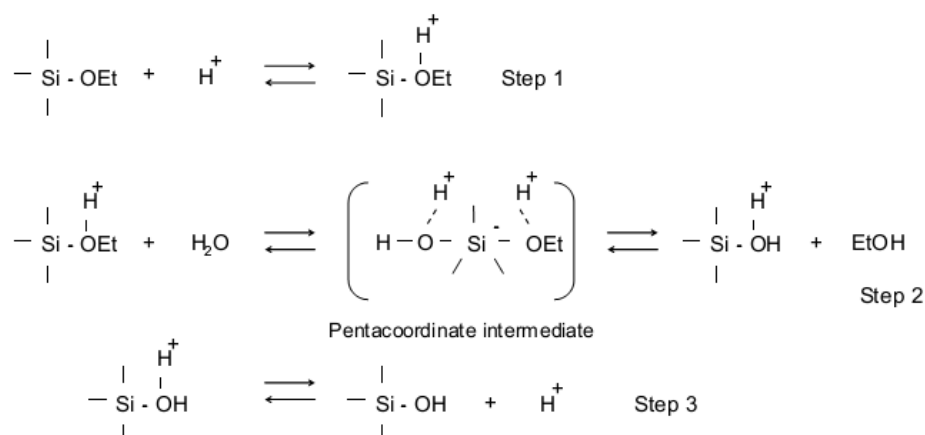
3.5.4 Silanization acceleration

The acceleration of silanization reaction depends on hydrolysis rate of the alkoxysilanes. With the presence of moisture on the silica surfaces as well as with the presence of an acid or alkaline catalyst, the hydrolysis reaction can be accelerated [80]. It is proposed that the promotion of silanization in the presence of acid- or

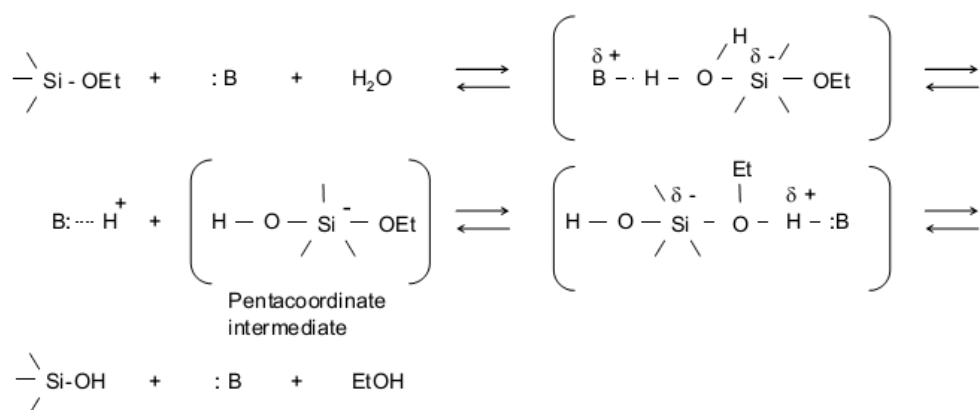
alkaline-catalysts is according to a bimolecular SN_2 type reaction as shown in Figure 3.13 [81].

3.5.5 Silane-rubber coupling reactions

Apart from the difficulty involved with mixing, silica being an acidic substance by virtue of acidic surface silanol groups could reduce efficiency of sulfur curing. Such cure retarding effect with differently of mixing could be overcome by the use of a silane coupling agent. Due to the enhanced degree of filler dispersion and polymer bonding, the formation of secondary filler structures (re-agglomeration) is then reduced [82]. A bifunctional organosilane coupling agent is generally characterized by two functions: one for the adhesion to the hydrophilic silica surface (the silane moiety) while the other for adhesion to hydrophobic polymer matrix. The formation of filler-rubber linkages via organosilanes has a major influence on the properties of rubber compounds [83]. By lowering the specific component of surface energy of silica, the level of adsorption of hydrocarbon rubber on the filler surfaces can be enhanced and subsequently filler-filler interactions are reduced. Coupling agents are used as a surface modification either by applying on the silica particle itself before the mixing (pre-treatment), or by admixing to the rubber compound (in-situ).



a) Acid catalyzed hydrolysis



b) Alkaline catalyzed hydrolysis

Figure 3.13 Hydrolysis mechanism of silane coupling agent: (a) acid catalyzed hydrolysis and (b) alkaline catalyzed hydrolysis [81].

The latter has been reported to be only 70 percent as the former. Also, the in-situ modification of silica with silane coupling agents requires a number of precautions regarding the mixing sequence and mixing temperature, as well as careful adjustment of mixing conditions for every silane-containing compound [26]. In silanized silicas, the silane already has undergone a chemical reaction with the silica, which renders the above precautions superfluous [82]. In addition, the already-reacted coupling agents improve the ease with which the silica may be mixed with the rubber matrix. The proposed reaction among silica, silane coupling agent and rubber matrix is illustrated in Figure 3.14.

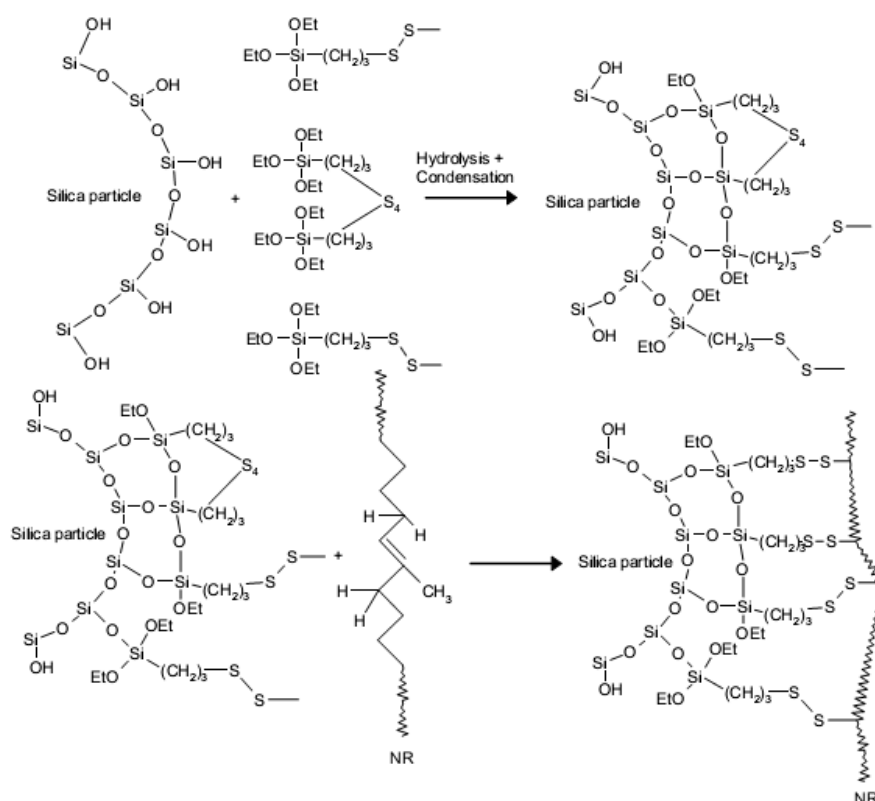


Figure 3.14 Modification reaction of silica with TESPT and formation of rubber to filler bonds [84].

Kilian [85] questioned the validity of the assumption that a chemical reaction between the silane coupling agent and the rubber matrix takes place. The coupling agents do react covalently with the silica surfaces, but upon the deformation, pronounced evidence of slippage of “anchored” rubber molecules along the silica surfaces is found. Thus, the coupling agents only seem to enhance the hydrophobicity of the silica surfaces. The reaction of the silane coupling agent with silica has been studied extensively by several authors. According to Hunsche et al., first a single bond with the silica surfaces is formed. This primary reaction is followed by a hydrolysis reaction, prior to condensation reactions between pairs of neighboring silane molecules already bound to the silica surfaces: the secondary reaction [73, 74]. Görl et al. [75, 86] studied the reaction between the coupling agent and the rubber matrix. The model results suggest that the reaction takes place via an intermediate asymmetric polysulfide, a reaction product of a rubber accelerator and the coupling agent. This

intermediate product is formed by the reaction of the coupling agent, already linked to the silica surfaces and a disulfide accelerator. In the subsequent reaction, the polysulfide is substituted into the allyl position of the rubber with release of the accelerator part. A covalent bond between rubber and filler is assumed to be formed by this reaction, resulting in a chemical link between rubber and filler.

3.6 Rubber reinforcement

Generally, most elastomers are not used in their pure form, because of their low mechanical properties. The use of fillers in rubber reinforcement fundamentally changes the properties of rubber. Figure 3.15 illustrates the influence of reinforcing fillers loading on various properties of rubber composites.

One of important factors offering high reinforcement magnitude is the interaction between the filler surfaces and polymer matrix. Such interaction can be strong, for example in the case of covalent bonds between functional groups on the filler surfaces and the polymer, or can be weak as in the case of physical attractive forces. When carbon black is mixed with a polymer, the level of physical interaction is high [89]. By contrast, the interaction between silica particles and the polymer is relatively weak. By the use of a coupling agent, a chemical bond (i.e., covalent bond) is formed between the filler and the polymer.

Apart from the polymer-filler interaction, the interaction between filler particles occurs, predominantly at the loading above a critical concentration threshold, (the percolation threshold). Such interaction is transient, leading to the filler-filler network formation and thus the alteration in properties of the material. This results for example in an over proportional increase in electrical conductivity of a carbon black filled compound. Figure 3.16 illustrates the strain-dependence of the shear modulus (or the so-called Payne effect) for carbon black and silica filled compounds [90]. The main contributions to the complex shear modulus are: (i) the hydrodynamic effect, (ii) the polymer network, (iii) the filler-polymer interaction and (iv) the filler-filler interaction.

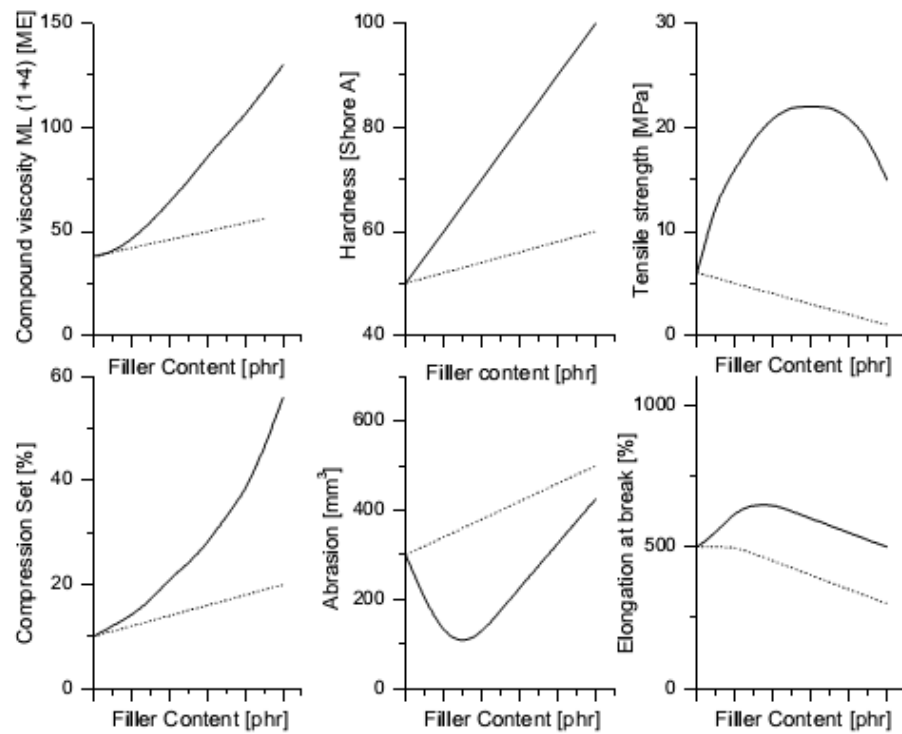


Figure 3.15 Influences of reinforcing fillers on the properties of an elastomer [88].

— active filler non active fillers

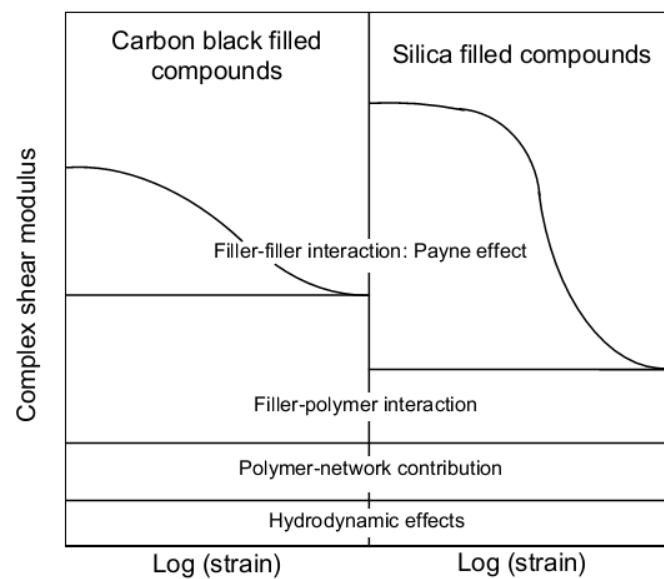


Figure 3.16 Effects contributing to the complex shear modulus [91].

3.6.1 Hydrodynamic effect

The addition of rigid filler to a viscous fluid increases the viscosity of the fluid or the so-called hydrodynamic effect. This effect is evidenced by the increase in modulus of the polymeric matrix as illustrated by the Einstein equation (Equation 3.2) [92].

$$\eta_f = \eta_0(1 + 2.5\phi) \quad (3.2)$$

where η_f is the viscosity of the fluid containing the rigid filler; η_0 is the viscosity of the pure fluid and ϕ is the volume fraction of the filler. Equation 3.2 is based on the following assumptions [92]:

- Perfect wettability of the spheres
- Uniform spherical particles
- No interaction between the particles

The last two assumptions are not often found in filler-polymer systems. The difference between Einstein's theory and practical experience was connected by the supplementary term as introduced by Guth and Gold [88]. The additional term in Guth and Gold equation is used to emphasize the influence of the filler concentration [93].

$$\eta_f = \eta_0(1 + 2.5\phi + 14.1\phi^2) \quad (3.3)$$

In the case of an elastic matrix, the viscosities of the material can be replaced by the shear modulus, as shown by Smallwood [94] (see Equation 3.4). It must be noted that the modulus calculated is not strain dependent.

$$G_f = G_0(1 + 2.5\phi + 14.1\phi^2) \quad (3.4)$$

3.6.2 Filler-polymer interaction

The filler-polymer interaction effects are determined by the special structure of the filler in the rubber matrix and its interaction with the polymer matrix. The occluded rubber contributes to this effect and the polymer chains are trapped in the voids of the filler agglomerates and aggregates, and therefore immobilized and shielded from the applied deformation. Occluded rubber increases the effective filler

loading, and thus the strain independent contribution to the modulus [95]. It has been experimentally established that the storage modulus drastically increases as the filler loading increases, resulting from filler-polymer interaction, so-called bound rubber. Several bound rubber models have been developed [96-99]. One of the models is the occluded rubber model proposed by Medalia and Kraus [96, 100]. In this model, rubber is partly trapped in the filler aggregates as shown in Figure 3.17, depending on filler aggregate or agglomerate geometry. This occluded rubber does not contribute to the deformation of the rubber matrix at lower strain.

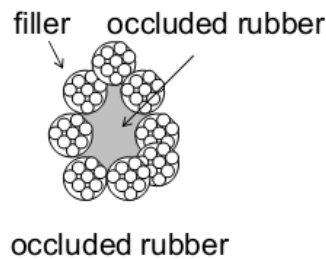


Figure 3.17 Bound rubber model; occluded rubber model [96, 100].

The filler-polymer interaction can be attributed to the physical interaction, for example Van der Waals forces, or chemical reaction as in the case of a silica-coupling agent system [95, 101-103].

3.6.3 Polymer network contribution

The polymer network formed during the vulcanization process is the third strain-independent contribution to the modulus. The modulus is proportional to the amount of elastically active network chains (ν) and the absolute temperature (T), with the proportionality constant being the Boltzmann constant (k_B) [104]

$$G_0 = \nu \cdot k_B T \quad (3.5)$$

3.6.4 Filler-filler interaction: Payne effect

The strain-dependent contribution to the modulus is caused by filler-filler interactions, i.e., the sigmoidal decrease of the storage modulus versus the double

strain amplitude in logarithmic scale from a limiting zero-amplitude value to a high amplitude plateau as a result of the disruption of filler transient network [105]. The Payne effect is largely reversible often strain removal is independent of polymer matrix but is rather dependent on filler type. Figure 3.16 shows a comparison of the Payne effect in the systems reinforced with carbon black and silica. The Payne-effect is considerably stronger for the silica filled system, as a consequence of the strong inter-aggregation via H-bond of silanol groups [103, 105].

CHAPTER IV

MATERIALS AND METHODS

4.1 Surfaces modification

4.1.1 Materials and methods

Precipitated silica (PSi, Tokusil 233) was manufactured by Tokuyama Siam Silica Co., Ltd. Silane coupling agents (SCAs), i.e., 3-aminopropyl triethoxysilane (APTES), 3-chloropropyl triethoxysilane (CPTES) and bis-(3-triethoxysilylpropyl) tetrasulfide (TESPT, or Si-69) were supplied by Evonic Co., Ltd. All chemicals were used as-received without further purification. Lists materials used in this work are summarized in Table 4.1.

Surfaces modification by different SCA type

Approximately 25 g of PSi was dispersed in 1:4 water:ethanol mixture under continuous stirring for 1 hour. 8% of silane (APTES, CPTES or TESPT) was added, and the mixture was refluxed at 80°C for 15 hours to allow the silanization reaction to take place on PSi surfaces. The modified PSi was then separated by centrifugation technique (30 min at 6,000 rpm), and washed 3 times with deionized water. Finally, the modified PSi was dried in an oven at 80°C for 15 hours.

Surfaces modification by different SCA loading

The amount of SCA added was varied from 0 – 8 %w of PSi. The step of silanization step does the similarity with different SCA type.

Surfaces modification by different pH condition

The amount of APTES added was kept at 1.5 gram (6 %w of PSi). Approximately 25 g of PSi was dispersed in 1:4 water:ethanol mixture under continuous stirring for 1 hour, and pH of dispersion was adjusted to 2, 6, and 12 by 1.0 M HCl and 0.1 M NaOH and then stirred for 2 hour. After that, 1.5 gram of APTES was added, and the mixture was refluxed at 80°C for 15 hours to allow the silanization reaction to take place on PSi surfaces. The modified PSi was then separated by

centrifugation technique (30 min at 6,000 rpm), and washed with deionized water until pH constant. Finally, the modified PSi was dried in an oven at 80°C for 15 hours.

4.1.2 Characterization of PSi surfaces modification

Specific surface area of PSi

The specific surface area of PSi estimated from the amount of nitrogen adsorbed according to ASTM D1993-03 (2008) using a multipoint Brunauer Emmett and Teller (BET) nitrogen adsorption apparatus. The samples were evacuated at 300°C for 2 h prior to commencing the test. The BET-specific surface area was calculated using adsorption data acquired at a relative pressure (P/P_0) range of 5×10^{-6} – 0.05.

Particle size of PSi

The particle size of unmodified and modified PSi was measured using the particle size analyzer at room temperature. The PSi pre-dispersed in distilled water was filled in the measuring unit, under a continuous stirring. The distilled water was used as a blank media. An average particle size at $d(0.5)$ of all samples as reported.

Identification of silica surfaces by FTIR and ^{29}Si NMR spectroscopy

FTIR spectra of the PSi were recorded on Bruker Equinox55 fourier transform infrared spectrophotometer by diffuse reflectance (DRIFT) mode with the scan range of $4,000\text{--}400\text{ cm}^{-1}$ with a resolution of 4 cm^{-1} over 64 scans. The concentration of sample in KBr was kept constant at 1% w/w. A background spectrum of KBr powder was subtracted from the acquired spectra in all cases. All data were processed with the standard OPUS software version 4.0.

The ^{29}Si solid state nuclear magnetic resonance, AVANCE 300 MHz Digital NMR Spectrometer (Bruker Biospin; DPX-300), was used for investigating a change in chemical structure of silane in bulk and at surface of PSi. The modified PSi was characterized at room temperature, and the spectra were recorded at frequency of 60 MHz and scanning rate of $4,000\text{ ns}^{-1}$. The samples were filled into 7 mm zirconia rotors and sealed with Kel-F caps. The spectra were acquired in the cross 3 polarization mode using contact times of 10 ms and high power dipolar decoupling to reduce line broadening. The pulse repetition times of 5 s with 10,000 - 30,000 scans were used to achieve sufficient signal to noise (S/N) ratio.

Determination of relative grafting ratio with the uses of FTIR

The samples (unmodified PSi and modified PSi) were mixed with potassium bromide (KBr) and potassium thiocyanate (KSCN) (0.1%w sample: 0.01%KSCN: 1% KBr). FTIR spectra of all samples were recorded on Bruker Equinox55 fourier transform infrared spectrophotometer by diffuse reflectance (DRIFT) mode with the scan range of 4,000–400 cm^{-1} and a resolution of 4 cm^{-1} over 64 scans. All data were processed with the standard OPUS software version 4.0. The relative amount of SCA grafting on PSi surfaces was measured by the intensity ratio at the wavenumber of 3,700 cm^{-1} , 3,400 cm^{-1} and 1,650 cm^{-1} for hydroxyl group, at the wavenumber of 2,900 cm^{-1} and 2,800 cm^{-1} for propyl moiety of silane (CH_2 -), at the wavenumber of 1,200 cm^{-1} for siloxane bridge (Si-O-Si). All of intensity ratio was compare with the intensity of KSCN at wavenumber of 2,150 cm^{-1} . The relative ratio was calculated from Equation 4.1-4.4.

Relative intensity ratio of hydroxyl group (-OH):

$$I_{\text{OH}} = \frac{I_{3,700}}{I_{2,100}} + \frac{I_{3,400}}{I_{2,100}} + \frac{I_{1,650}}{I_{2,100}} \quad (4.1)$$

Relative intensity ratio of propyl moiety group (CH_2 -):

$$I_{\text{CH}_2-} = \frac{I_{2,900}}{I_{2,100}} \quad (4.2)$$

Relative intensity ratio of siloxane group (Si-O-Si):

$$I_{\text{Si-O-Si}} = \frac{I_{1,200}}{I_{2,100}} \quad (4.3)$$

Relative grafting ratio:

$$\text{Relative grafting ratio} = \frac{I_{\text{Si-O-Si, modified}} - I_{\text{Si-O-Si, unmodified}}}{I_{\text{Si-O-Si, unmodified}}} \quad (4.4)$$

Sear number

The modified Sears number is a measure of the number of free silanol groups determined via titration of silica with potassium hydroxide solution in the range from pH 6 to pH 9 according to the following procedure: 10 g of unmodified

and modified PSi, each having a moisture level of $5\pm 1\%$, was transferred to a suitable glass container and placed in an oven at 105°C for 2 hours. The container was removed from the oven and placed in desiccators until analyzed. The 2.50 g of the dried silica was weighed at room temperature and put into a 250 ml titration vessel and mixed with 60 ml of methanol (analytical grade). Once the silica was completely wetted, 40 ml of deionized water was added. A Teflon coated stir bar was added to the titration vessel and the container was placed on a stir plate for 30 seconds to disperse the silica and methanol/water solution. Deionized water (100 ml) was used to flush the silica particles adhering to the edge of the vessel into the suspension. The temperature of the system was measured and allowed to come to room temperature.

The pH measurement device was calibrated by using buffer solutions (pH 4, 7 and 9) at room temperature. The pH meter was first used to measure the starting pH value of the suspension at room temperature, and then, as a function of the result, either sodium hydroxide solution (0.1 M) or hydrochloric acid solution (0.1 M) was used to adjust the pH value to 6. NaOH (0.1 M) was used for titration to a pH value of 9. Consumption of NaOH solution in ml to pH 9 is V. The titration with 0.1 M NaOH was continued until the pH of the solution was maintained for 60 seconds. The volume of NaOH was recorded and the Sears number was obtained in the unit ml/g.

Zeta Potential

Approximately 0.1 g of unmodified and SCA-modified PSi was dispersed in deionized water and stirred for 2 hours. The clear solution was added to Zeta cell for performing the test with Zeta sizer.

The grafting ratios via elementary analysis

The contents of C, H and N of the APTES-modified PSi samples were measured by elementary analysis technique. For each sample, three measurements were made.

4.2 Compound preparation

Polychloroprene (Neoprene; CR grade W) was purchased from DuPont Dow Elastomer Co., Ltd. Precipitated silica (PSi, Tokusil 233) was manufactured by Tokuyama Siam Silica Co., Ltd. Silane coupling agents (SCAs), i.e., 3-aminopropyl

triethoxysilane (APTES), 3-chloropropyl triethoxysilane (CPTES) and bis-(3-triethoxysilylpropyl) tetrasulfide (TESPT, or Si-69) were supplied by Evonic Co., Ltd. Magnesium oxide (MgO), N-(1,3-dimethylbutyl)-N'-phenyl-p-phenylenediamine (6-PPD), zinc oxide (ZnO), ethylene thiourea (ETU), stearic acid and sulfur (S₈) were purchased from local suppliers. All chemicals were used as-received without further purification. Lists materials used in this work are summarized in Table 4.1.

Table 4.1 Materials used in this work.

Chemical Name	Function	Grade/Manufacture or supplier
Chloroprene rubber (CR)	Raw material	W-type/Dupont Dow Elastomer Co., Ltd., USA
Magnesium oxide (MgO)	Cure activator/ Acid acceptor	Starmag # 150/Konoshima Chemical Co., Ltd., Osaka, Japan
Precipitated silica (PSi)	Reinforcing filler	Tokusil 233/Tokuyama Siam Silica Co., Ltd., Thailand
3-aminopropyltriethoxy silane (APTES)	Silane coupling agents	JJ-Degussa (Thailand) Co., Ltd., Thailand
3-chloropropyltriethoxy silane (CPTES)		
bis-(3-triethoxysilylpropyl) tetrasulfide (TESPT, Si-69)		
N-(1, 3-dimethylbutyl)-N'-phenyl-p-phenylenediamine (6-PPD)	Antioxidant	Santoflex 6-PPD/Flexsys Co., Ltd., USA
Stearic acid	Cure activator/ Softener	Commercial grade/Petch Thai Chemical Co., Ltd., Thailand
Ethylene thiourea (ETU)	Vulcanizing agent	ETU 22S/Kawakushi Co., Ltd., Japan

Table 4.1 Materials used in this work (cont.).

Chemical Name	Function	Grade/Manufacture or supplier
Sulfur (S ₈)	Vulcanizing agent	Commercial grade/Chemmin Co., Ltd., Thailand
Zinc oxide (ZnO)	Cure activator/Vulcanizing agent	Enery Product Co., Ltd./Thailand
Sodium hydroxide (NaOH)	Reagent	Analytical Grade/ Merck, Germany
Hydrochloric acid (HCl)	Reagent	Analytical Grade/ VWR international Ltd., UK
Ethyl alcohol (C ₂ H ₅ OH)	Solvent	Analytical Grade/Merck, Germany
Methyl alcohol (CH ₃ OH)	Solvent	Analytical Grade/Merck, Germany
Diethyl ether (C ₂ H ₅) ₂ O	Solvent	Analytical Grade/ VWR international Ltd., UK
Dichloromethane (CH ₂ Cl ₂)	Solvent	Analytical Grade/ VWR international Ltd., UK
Acetone	Solvent	Commercial Grade/RCI Labscan Ltd., Thailand
Toluene	Solvent	Commercial Grade/RCI Labscan Ltd., Thailand

4.2.1 Instruments

List of instruments used in this study is shown in Table 4.2.

Table 4.2 List of instruments used in the study.

Instruments	Model	Manufacture
2- roll mill	W100T	Collin, Germany
Hydraulic hot press	G30H	Wabash Genesis, USA
Rubber process analyzer	RPA 2000	Alpha Technologies, USA
Dynamic mechanical analyzer	Eplexor 25N	Gabo, Germany
Moving die rheometer	Rheo TECH MD+	TechPro, USA
Tensile tester	5566	Instron, USA
Shore A hardness tester	H17A	Cogenix Wallace, UK
Heat buildup flexometer	BF Goodrich flexometer Model II	Hurst Mfg., Div. of Emerson Electric Co., USA
DIN-type abrasion tester	6102	Zwick, Germany
Scanning electron microscope (SEM)	JSM 6400	EOL, Japan
Fourier transform infrared spectrophotometer	Equinox55	Bruker, Germany
²⁹ Si Solid state nuclear magnetic resonance spectrophotometer	DPX-300	Bruker Biospin, Germany
Particle size analyzer	Mastersizer 2000	Malvern instrument, UK
Zeta sizer	Zeta sizer nano ZS	Malvern instrument, UK
pH meter	-	Schott instrument, Germany
Ultrasonic bath	2510E-MTU	Becthai, Thailand
Brunauer Emmett and Teller (BET) tester	Quantachrome Nova 1200e	Quantachrome Instruments, USA

4.2.2 Compounding formulation

The PSi filled rubber compounds were prepared according to the compound formulations as illustrated in Table 4.3.

Table 4.3 Compound formulations used in this work.

Ingredients	Amount (phr)*
Polychloroprene (CR)	100
Magnesium oxide (MgO)	4
Precipitated silica (PSi)	40
Stearic acid	1
Antioxidant (6-PPD)	1
Zinc oxide (ZnO)	5
Ethylene thiourea (ETU)	0.3
Sulfur (S ₈)	2
APTES	varied**
CPTES	varied**
TESPT or Si-69	varied**

* phr: parts per hundred rubber

** varied from 0-8 %w of PSi

4.2.3 Surfaces treatment technique (in-situ technique)

Mixing was performed in the laboratory-scale internal mixer (Haake Rheomix 3000p) equipped with roller type rotors. The mixing conditions used were as follows; fill factor = 0.8, set chamber temperature = 50°C, rotor speed = 40 rpm and mixing time = 20 minutes. Loading of precipitated silica (PSi) was kept constant at 40 phr. The APTES, CPTES and TESPT were used as silane coupling agents (SCAs) with various loadings from 0 – 8 %w of PSi. A 2-stage mixing technique was used for preparing the compounds. The first stage was carried out using the mixing sequence as shown in Figure 4.1. The second stage as exhibited in Figure 4.2 was performed by mixing the masterbatch obtained from the first stage (Compound A) with zinc oxide

(ZnO), ethylene thiourea (ETU) and sulfur (S_8) as curing agents. The final mix denoted as Compound B was sheeted after being dumped from the mixer by a two-roll mill, and kept for 24 hours before being used.

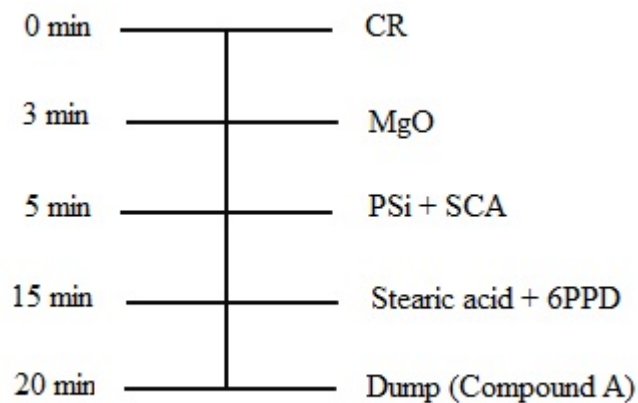


Figure 4.1 Mixing sequence used for preparing compound masterbatch (Compound A).

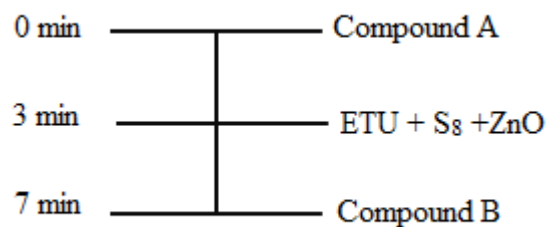


Figure 4.2 Mixing sequence used for preparing final CR compounds (Compound B).

4.2.4 Surfaces treatment technique (Pre-modified technique)

With this technique, the SCA-modified PSi from section 4.1 was mixed with CR using similar mixing procedure to that mentioned previously in Figure 4.1-4.2. The only difference was the substitute of PSi/silane by the SCA-modified PSi.

4.2.5 Characterization

Degree of the filler-filler interaction (Payne effect)

Approximately 5 g of rubber compounds were placed in the test chamber of the rubber process analyzer (RPA, 2000), and the test was performed at test frequency of 0.99 rad/sec, temperature of 100°C and %strain deformation range of 0.56%–1,199.98%. The storage modulus (G') as a function of shear strain was recorded at least 3 test specimens from different location of each compound was taken from the rubber compounds, so that the uniformity of rubber compounds could be monitored.

Cure characteristics of rubber compounds

Cure characteristics including scorch time (t_{s2}), cure time (t_{c99}), minimum torque (M_L) and maximum torque (M_H) of rubber compounds were measured using a moving die rheometer (MDR) at 155°C. Torque difference ($M_H - M_L$) was also calculated, and used as an indication of crosslink density in vulcanizates [10, 106].

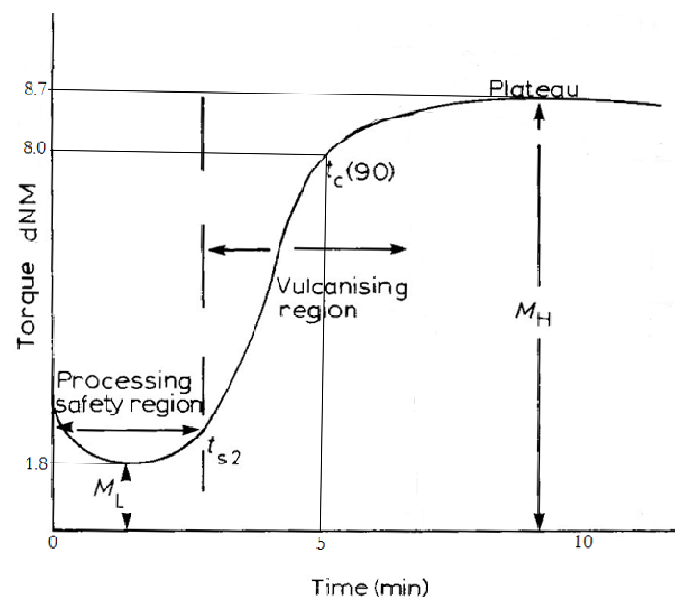


Figure 4.3 General characteristics of cure behavior [5].

According to ASTM D5289-95, approximately 5 g of rubber compounds were placed in the test cavity, and deformed under oscillating strain of 0.56%. The t_{cx} is simply the time to reach a given x % of state of cure. The t_{cx} can be calculated, as follows:

$$t_{cx} = \left[\left(\frac{x}{100} \right) \times (M_H - M_L) \right] + M_L \quad (4.5)$$

where:

t_{cx} = time to a given x % in state of cure (min)

M_L = minimum torque (dN.m)

M_H = maximum torque (dN.m)

x = percentage of state-of-cure (%)

Bound rubber content (BRC)

Bound rubber is defined as the rubber incapable of being extracted from an uncured filled rubber using good solvent for a rubber matrix, usually at room temperature. The BRC is known to be functions of rubber-filler interaction, filler surface area, molecular weight of the rubber, solvent used for the extraction, time and temperature for the extraction and filler loading in the composites [107]. The solubility method is usually used to determine the BRC, as illustrated in Equations 4.6.

Approximately 1 g of the rubber compound was immersed in 300 ml of toluene for 7 days, and then the insoluble portion was removed and dried at room temperature to a constant weight.

$$\%BRC = \frac{W_{fg} - W \left[m_f / (m_f + m_p) \right]}{W \left[m_p / (m_f + m_p) \right]} \times 100 \quad (4.6)$$

where

W_{fg} = the weight of filler-rubber gel (g)

W = the weight of the test specimen (g)

m_f = the weight of filler in the rubber compound (g)

m_p = the weight of polymer in the rubber compound (g)

4.3 Preparation of rubber vulcanizates

The Compound B was compression molded at 155°C under pressure of 15 MPa using a hydraulic hot press for the optimum cure time (t_{c99}) as pre-determined

from the moving die rheometer (MDR). Subsequently, the specimen was kept at room temperature for maturing overnight.

4.3.1 Characterization of vulcanization properties

Hardness

Hardness of rubber as measured using the Wallace H17 hardness tester with Shore A scale as per ASTM D2240-97. The square specimen with approximately 6 mm in thickness, and smooth surface was required. The measurement was performed at different positions on specimen surfaces. The average of 10 locations was calculated, and recorded as a hardness value of the test specimen.

Tensile properties

To measure tensile properties, the universal mechanical tester (Instron 5566) with load cell of 1 kN, a crosshead speed of 500 mm/min was used. The dumbbell shape specimens were prepared using die C according to ASTM D412-92 as illustrated in Figure 4.4. At least 5 test specimens were measured, and the average value was reported. Calculations of tensile properties are illustrated in Equations 4.7 – 4.9.

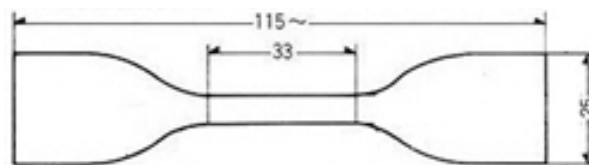


Figure 4.4 Dimensions of the tensile specimen as per ASTM D412 with die C.

Tensile strength

$$TS = \frac{F}{A} \quad (4.7)$$

where:

TS = tensile strength, the stress at rupture (MPa)

F = the force magnitude at rupture (N)

A = cross-sectional area of unstrained specimen (mm²)

Elongation at break

$$\%Eb = \frac{(L - L_0)}{L_0} \times 100 \quad (4.8)$$

where:

$\%Eb$ = the percentages of elongation from original bench mark distance (%)

L = observed distance between the extensometer clamps (mm)

L_0 = original distance between the extensometer clamps (mm)

$$\text{Modulus at 100\% (M100)} = \text{stress at 100\% elongation} \quad (4.9)$$

Compression set

A cured specimen is measured for its tendency to take a set from a constant strain under preselected standard conditions of temperature, time, percent deflection and recovery time as per ASTM D395 (Method B) at 100°C. The test specimen is a disc with 13 mm in diameter and 6.3 mm in thickness. The compression set could be calculated by Equation 4.10.

$$C_B = \left[\frac{(t_0 - t_i)}{t_0 - t_n} \right] \times 100 \quad (4.10)$$

where:

C_B = compression set (Method B) expressed as percentage of the original deflection

t_0 = original thickness of specimen (mm)

t_i = final thickness of specimen (mm)

t_n = thickness of the space bar used (i.e., 4.5 mm)

Heat build-up (HBU)

The HBU test was used to evaluate the temperature rise after submitting the rubber sample to dynamic compressive strain according to ASTM D623-93. The test specimen was cylindrical in shape with 17.8 and 25 mm in diameter and height. At the temperature controlled at 100 °C, the test specimen was placed in the oven on the platform for 20 minutes. The test was performed by compressing the specimen with

the static force of 245 N, and sinusoidal compressive amplitude of 2.2 mm at 30 Hz for 25 min. The temperature at the base of the specimen was monitored, and the temperature rise was reported as the heat build-up (HBU).

Abrasion resistance

The DIN abrasion test was performed based on ASTM D5963. A disc test piece in a suitable holder was traversed across a rotating drum covered with a sheet of the abradant. Test pieces were cylindrical in shape with a diameter of 16 ± 0.2 mm and a minimum thickness of 6 mm. Weight or volume loss can be related to unit distance travelled over the abradant, per 1000 cycles, or whatever is convenient.

To calculate the abrasion loss (A_A) the loss in mass shall be converted into volume loss using the density of the test rubber. Referred to Equation 4.11, the volume loss is corrected by the use of “ S_0/S ” ratio where S_0 is the “normal abrasiveness” of the abrasive sheet, and S is the abrasiveness of the abrasive sheet used for the test. Mathematically, A_A could be calculated as follows:

$$A_A = \frac{\Delta m_t \times S_0}{d_t \times S} \quad (4.11)$$

where:

- A_A = abrasion loss (mm^3)
- Δm_t = mass loss of the test piece (mg)
- d_t = density of the test rubber (mg/mm^3)
- S_0 = “normal abrasiveness” (i.e., 200 mg)
- S = abrasiveness (mg)

Crosslink density via Flory-Rehner equation

The degree of swelling could be used to determine the magnitude of crosslink density in rubber vulcanizates [108, 109]. In general, the crosslinked polymer, when placed in a good solvent, rather than dissolving completely, will absorb a portion of the solvent and subsequently swell. The Flory-Rehner equation is widely used to relate the amount of swelling to the crosslink density of polymer [10].

The vulcanized rubber sheets were cut into the dimensions of approximately 1.5 cm x 1.5 cm x 1 mm. Then, the test specimens were weighed, and

then immersed in 150 ml toluene for 7 days at room temperature. After 7 days, the test specimens were removed from the toluene and weighed accurately. It must be noted that the excess of toluene on the specimen after removed from the toluene was eliminated by towel paper. The number average molecular weight between crosslinks, M_C , can be calculated from the Flory-Rehner equation as shown in Equations 4.12-4.13 [108, 109]. The densities of toluene and CR are 0.87 and 1.23 g/cm³, respectively [110-112].

$$\left[\ln(1 - v_2) + v_2 + \lambda v_2^2 \right] = V_1 M_C \left[v_2^{1/3} - \frac{v_2}{2} \right] \quad (4.12)$$

$$v_2 = \frac{M_1 d_s}{M_1 (d_s - d_r) + M_2 d_r} \quad (4.13)$$

where:

- M_C = number average molecular weight between crosslink per unit volume (g/mol)
- v_2 = volume fraction of polymer in the swollen gel at equilibrium
- χ = interaction parameter of polymer-solvent,
i.e., 0.386 for CR-toluene [112]
- V_1 = the molar volume of the solvent (cm³/mol)
- M_1 = weight of the polymer before swelling (g)
- M_2 = weight of the polymer after swelling (g)
- d_s = density of solvent, i.e., 0.87 g/cm³ for toluene
- d_r = density of polymer, i.e., 1.23 g/cm³ for CR

Dynamic mechanical analysis (DMA)

Dynamic mechanical analyzer (DMA) with tension mode was utilized to determine viscoelastic properties as a function temperature of the specimens including storage modulus, loss modulus and damping factor at test frequency of 10 Hz and dynamic strain amplitude of 0.1 % strain. Temperature was scanned from -40°C to 80°C with a heating rate of 2°C/min.

Scanning Electron Microscope (SEM)

Phase morphology of the sample surfaces was observed using a scanning electron microscope (SEM). The fractured surface was prepared by a cryogenic fracturing technique. Thereafter, the samples were placed on the specimen stub, and sputter coated with gold to prevent electron bombardment on the sample surfaces.

CHAPTER V

RESULTS AND DISCUSSION

The experiment in this research is divided into 2 main parts. The first part concerns the surface modification of PSi with different loadings and types of silanes by silanization method. Moreover, the effect of pH on surface treatment of selected SCAs at optimum loading is studied. The second part aims to investigate the effect of surface treatment technique (i.e., in-situ and pre-modified), silane types (i.e., APTES, CPTES and TESPT) and silane loading (i.e., 0, 2, 4, 6, 8 %w/w of PSi) on viscoelastic and mechanical properties of PSi filled CR compounds and vulcanizates. Furthermore, the dispersion degree of filler in rubber matrix is evaluated.

The general formula of trialkoxysilane is $R'Si(OR)_3$. For the chosen silanes: APTES, CPTES and TESPT; R' corresponds to amino (NH_2), chloro (Cl), and mercapto (S) groups, respectively. The organo-functional group (R') easily attaches to the organic polymer matrix while the alkoxy group (OR) reacts through the hydrolysis and condensation reactions with silanol groups on silica surfaces. R' is responsible for the reaction with the CR matrix.

5.1 Characterization of PSi

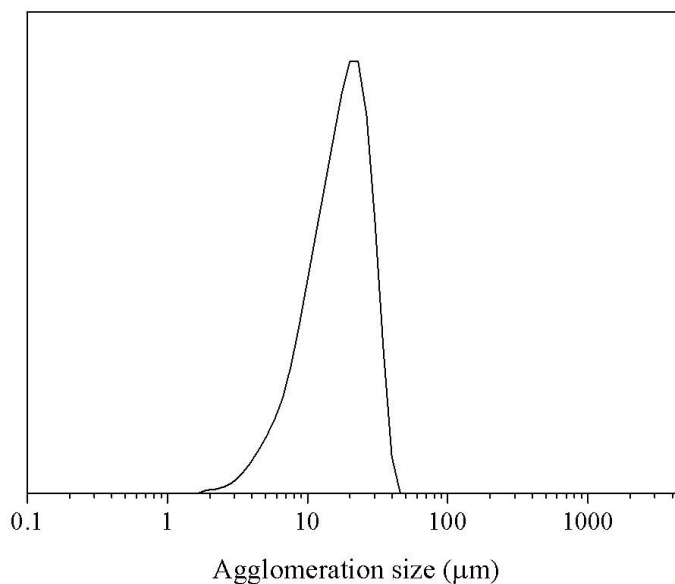
Physical characteristics of PSi were first characterized with respect to morphology, surface and adsorption characteristics in order to facilitate further comparison with surface-modified samples. Results obtained are shown in Table 5.1.

Table 5.1 Physical characteristics of PSi used in this work.

Characteristics	Values
N ₂ adsorption, BET surface area (m ² /g)	137.0±1.5
Average pore diameter (Å)	511.7±10.5
pH	5.9±0.2
Specific gravity (g/cm ³)	2.0±0.1
Water content (%)	5.0±0.3

PSi particle size and its distribution

Particle size analyzer was used to measure size and distribution of PSi agglomerations. The PSi used in this work shows uni-modal peak with the sizes range from 3 to 50 microns, as illustrated in Figure 5.1. The reported mean particle size, d(0.5) of PSi is of 18.3 microns.

**Figure 5.1** Particle size distribution of PSi used in the present study.

Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFT)

DRIFT is an infrared spectroscopy spectra technique, employed for examining the functional groups on PSi surfaces.

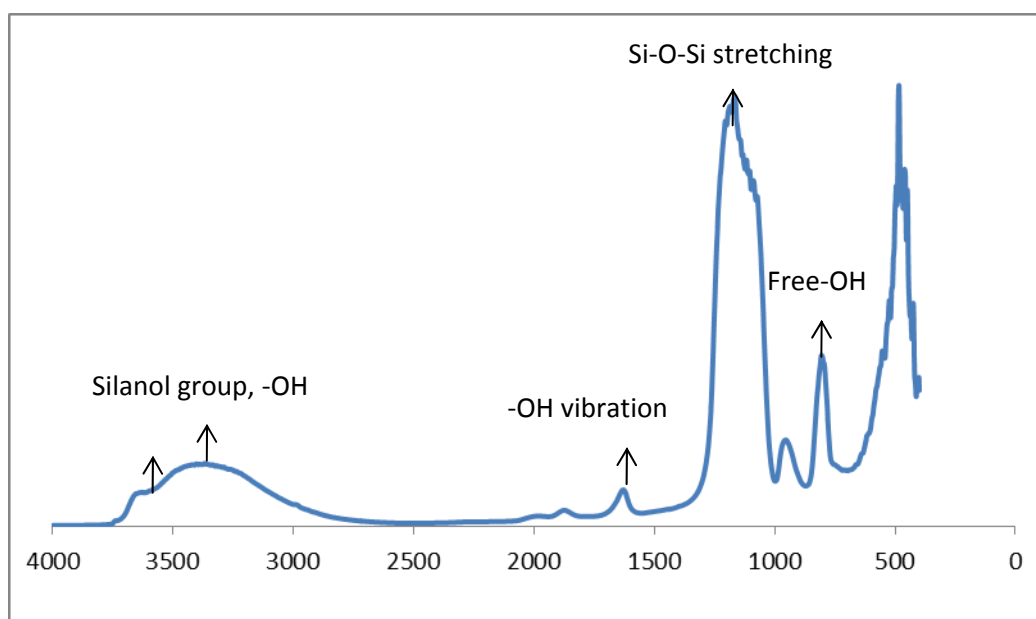


Figure 5.2 DRIFT spectra of PSi, Tokusil 233 used in the present study.

The results as exhibited in Figure 5.2 show that isolated hydroxyls are responsible for the narrow band at $3,700\text{ cm}^{-1}$ [113], internal hydroxyls give rise to the band at $3,440\text{ cm}^{-1}$, and tightly bound water peak or free hydrate peak shows at 1600 cm^{-1} [114]. Moreover, a strong band between $1,300$ and $1,000\text{ cm}^{-1}$ related to asymmetric stretching of Si-O-Si bonds in linear and cyclic forms are observed [115]; the peaks at 900 and 800 cm^{-1} are referred to Si-O bending [116-118].

Silicon Nuclear Magnetic Resonance spectroscopy (^{29}Si -NMR)

Figure 5.3 exhibits the ^{29}Si NMR spectra of as-received PSi. The PSi reveals three chemical shifts at -110 , -100 and -90 ppm , representing the siloxane bridges (O_4Si), isolated or vicinal silanols ($\text{O}_3\text{Si}(\text{OH})$) and germinal silanols ($\text{O}_2\text{Si}(\text{OH})_2$), respectively [72], with the intensities of $40 : 54 : 6$, from a Gaussian deconvolution of the spectrum [119].

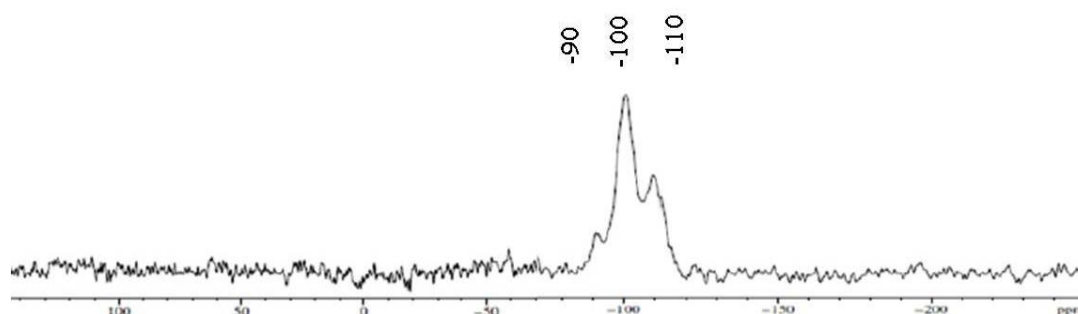


Figure 5.3 ^{29}Si NMR spectra of PSi used in the present study.

5.2 Surface modification of PSi with different SCA types

Physical characteristics

Physical characteristics of unmodified and modified PSi with 3 types of SCAs, including; surface area, average particle size by BET technique and mean average particle size, $d(0.5)$ with particle size distribution index (PDI) by particle size analyzer are tabulated in Table 5.2, Table 5.3 and Figure 5.4, respectively.

Table 5.2 Physical characteristics of unmodified and modified PSi with different SCA types by BET technique.

Parameter checked	Unmodified	SCA type		
		APTES	CPTES	TESPT
BET surface area (m^2/g)	137 ± 2	133 ± 6	144 ± 2	141 ± 2

The BET or nitrogen sorption measurement was carried out to determine the surface area in the unit of m^2 per 1 gram of silica and, where reasonable, the pore diameter. Referring to Table 5.2, a larger amount of nitrogen gas adsorbed on silica surfaces suggests the higher BET surface area, and thus higher reactivity with chemical reaction [120]. After silica surface modification with various SCA types, the

results of BET surface area show no significant change. This could be caused by nature of PSi structure [25].

Table 5.3 Physical characteristics of unmodified and modified PSi with different SCA types (8% w) by particle size analyzer technique.

Systems	Average agglomeration size (μm)	PDI
Unmodified	18.3 $\pm$ 0.1	3.1
APTES	25.6 $\pm$ 0.1	5.2
CPTES	20.4 $\pm$ 0.1	3.4
TESPT	27.9 $\pm$ 0.2	5.8

Table 5.3 reveals the physical characteristics (as measured by the particle size analyzer) of unmodified and modified PSi with various SCAs. Unexpectedly, a modification of PSi surfaces with SCAs significantly increases the average agglomeration size and increases the PDI value. These are due probably to the interaction development via H-bonds of silanol groups on PSi surfaces. Such interaction tends to cause silica clustering as evidenced by the increase in average particle size. Moreover, all SCAs affect the average particle size and PDI value of modified PSi. The modified PSi with CPTES shows smaller size and PDI (i.e., narrower size distribution) than those with APTES and TESPT, respectively. This means the CPTES-treated PSi gives a narrow variety of agglomerate size as evidenced in Figure 5.4. The unexpected increase in average particle size after surface modification by SCA is believed to be the result of linkage development between PSi with SCA as described in Figures 5.5 – 5.7.

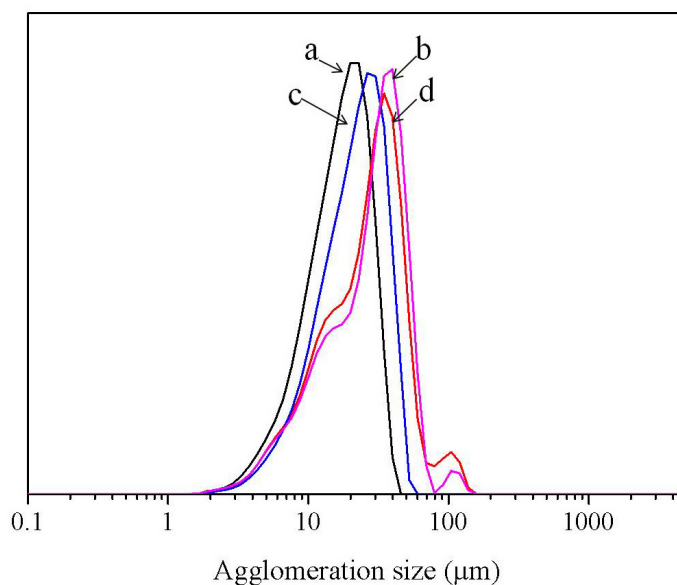


Figure 5.4 Particle size distribution (PSD) of: a) unmodified PSi; b) APTES-modified PSi; c) CPTES-modified PSi and d) TESPT-modified PSi.

The primary reaction step is the reaction of the first alkoxy group of silane (APTES, CPTES and TESPT) with silanol groups on the silica surfaces (see also Figures 5.5 – 5.7 for the reacting steps of APTES, CPTES and TESPT, respectively). Two possible mechanisms are: (i) direct reaction of silicon of silanol groups with alkoxy group of silane and (ii) hydrolysis of the alkoxy group to form reactive silanol groups. After hydrolysis, the activated silane is capable of reacting with silanol groups on silica surfaces to create the PSi-SCAs interaction.

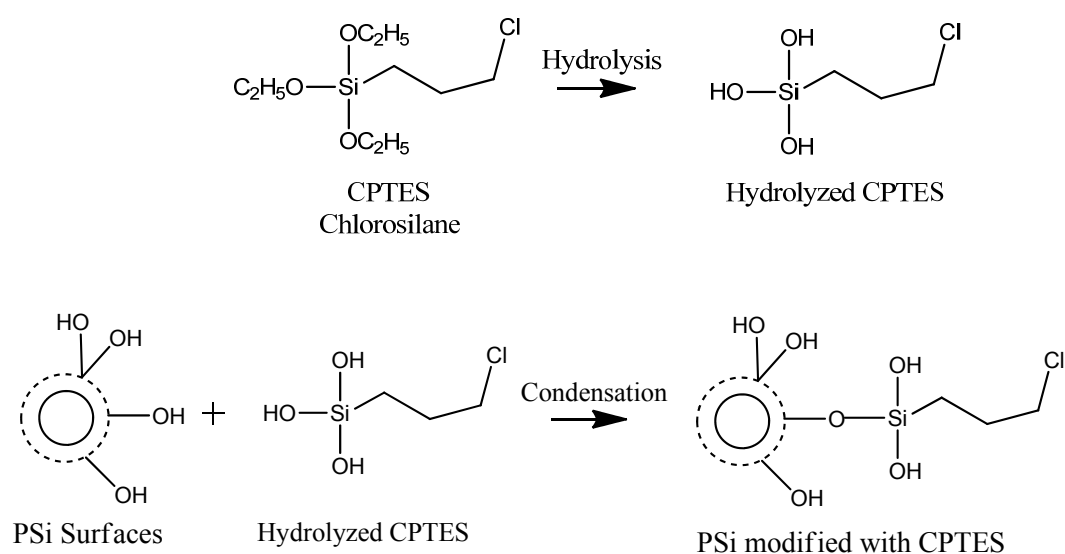


Figure 5.5 Proposed model of interaction development between PSi and CPTES leading to the increase in particle size of PSi after surface modification.

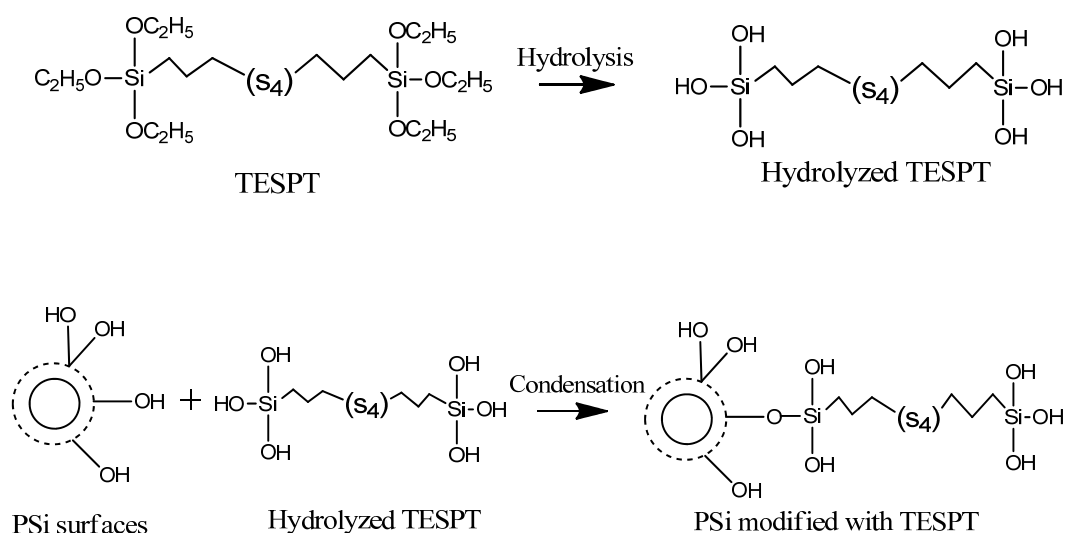


Figure 5.6 Proposed model of interaction development between PSi and TESPT leading to the increase in particle size of PSi after surface modification.

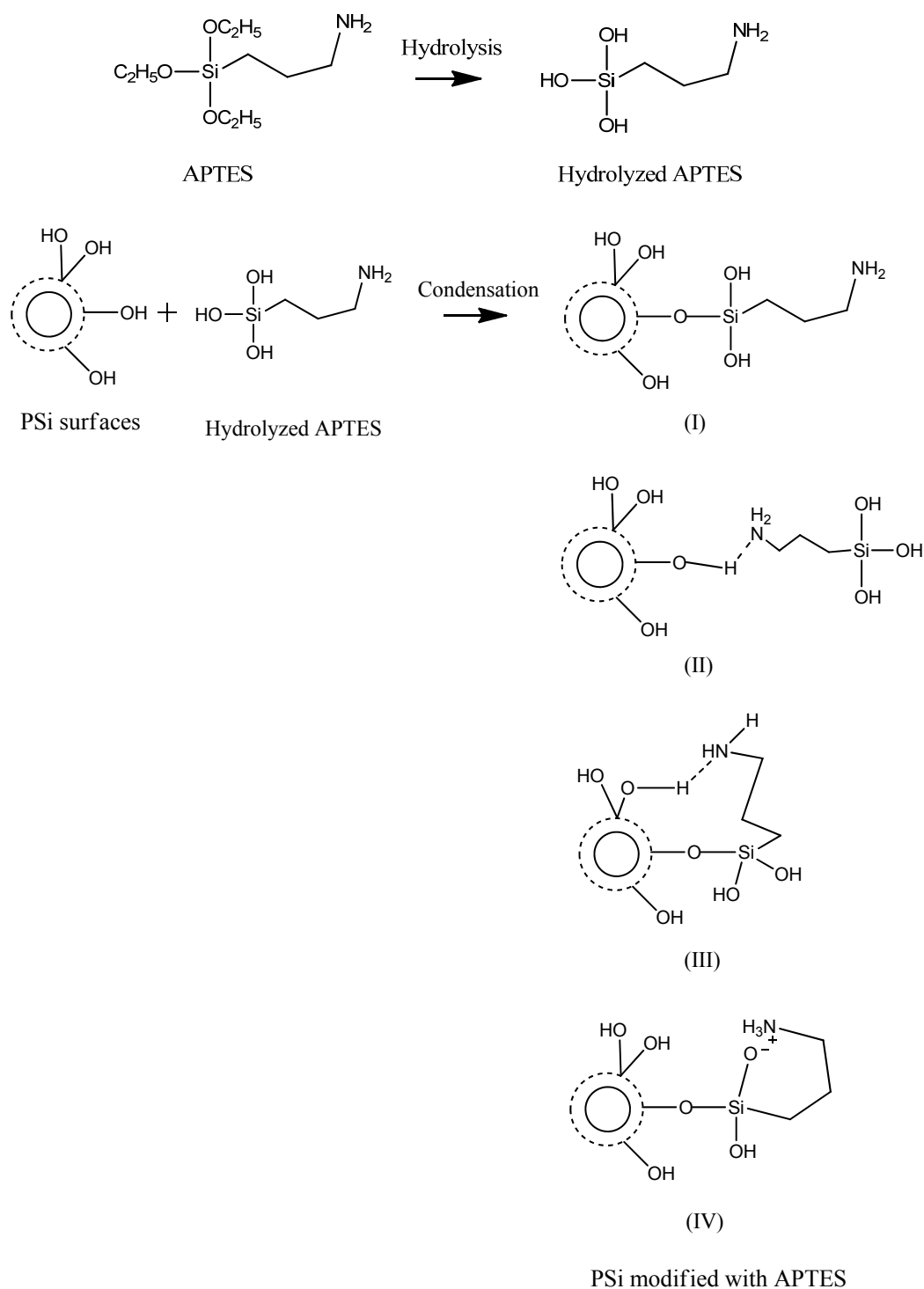
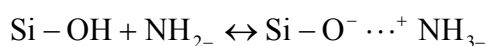


Figure 5.7 Proposed model of interaction development between PSi and APTES leading to the increase in particle size of PSi after surface modification.

In the case of silanization reaction by APTES, simultaneous 4 possible ways in hydrolysis-condensation reaction yielding 4 possible products are proposed as shown in Figure 5.7. (Product I): the APTES molecule after undergoing the hydrolysis reaction is chemisorbed as a monolayer on PSi surfaces by reacting with hydroxyl groups. The terminating NH_2 group of APTES might be protonated by deionized water or by the slight acidity of the acid to form NH_3^+ ion. The APTES monolayer might then undergo a vertical polymerization through covalent bond (Si-O-Si polysiloxane reticulation out of the plane of the substrate) [121] This vertical polymerization is favored by the hydrogen bonding between- NH_2 groups and Si-OH groups on the hydroxylated surfaces (Product II) and intramolecularly within the hydrolyzed molecule itself (Product III) [122, 123]. The head groups of hydrolyzed APTES molecules, $\text{Si}(\text{OH})_3$, in the presence of adsorbed water layer, might interact with the surface NH_2 groups of the monolayer. This interaction is described either as a hydrogen bond or as an ionic bond resulting from an acid-base type reaction, by considering that a proton transfer occurs from weakly acidic silanol group to basic amino group [4]. Reported pKa values for surface silanol groups are generally less than 9 lower than pKa of the acid-base couple $\text{RNH}_3^+/\text{RNH}_2$ (in the range 10-11). These values lead to the acid-base equilibrium [4]:



Such mechanism results in the layer-by-layer self-assembly of multi-layers with the formation of more or less $^{\delta+}\text{NH}_3$ - charged species. A poly-condensation reaction via formation of the Si-O-Si network in the plane of the substrate accompanies the ionic interaction and reinforces the assembly. (Product IV): the interaction between NH_2 -group and PSi surfaces occurs to form penta-coordinated silicon on the PSi surfaces [124].

Fourier Transform Infrared spectroscopy (FTIR)

In general, there are two regions of FTIR spectrum, namely, functional group region and the fingerprint region [125]. The functional group region is generally considered to range from $4,000\text{--}1,500\text{ cm}^{-1}$, which generally represents the band stretching vibrations as characteristics of typical functional groups in organic

molecules. The frequencies of these bands are reliable, and the presence of these bands can be used confidently to determine the nature of the components in organic molecule [125]. On the other hand, the fingerprint region, ranging of 1,500–400 cm^{-1} , usually involves bending molecular motions that are characteristics of a whole molecule or large fragments of a molecule. When dealing with unknown structures, the complexity of the FTIR spectra in this region causes difficulty in absorption bands assignment. Therefore, it is recommended to focus on identifying the characteristic features on the functional group region [126]. Furthermore, analyses of the peaks location and relative intensity to the rest of the spectrum have been performed to identify the presence of key functional components in the silane-grafted silica. In this work, the diffuse reflectance infrared fourier transform spectroscopic (DRIFT) technique was used to support the presence of surface silane functionalities grafted to PSi surfaces. The DRIFT results are given in Figure 5.8. Apart from the typical absorption bands of PSi, new vibrational mode is observed in the DRIFT-FTIR spectra of modified PSi with various SCAs. The vibration of unmodified PSi appears at approximately 3,700 and 3,400 cm^{-1} attributed to isolated hydroxyl and the vibration of OH stretching; at 1,650 cm^{-1} ascribed to the bending motion of adsorbed water (H-O-H) [113], and at 1,300–1,000 cm^{-1} assigned to the vibrations of the Si-O-Si bond of siloxane bridges and at 800 cm^{-1} assigned to bending motion of Si-O [13, 114, 116, 117]. The spectra of SCA-modified PSi with various SCAs reveal a new band at 2,900–2,800 cm^{-1} associated with the CH_2 vibrations of the propyl moiety of the silane group. Additionally, the increased intensity of the bands attributed to stretching vibration of O-H at around 3,700 cm^{-1} is observed. The presence of Si-O and –Si-O-Si– bridges, corresponding to the condensation of the hydroxyl groups of SCAs with the hydroxyl groups of PSi and of those silanols self-condensation, respectively, are not easily detected by FTIR technique, since the typical vibrations of these moieties at approximately 2,900–2,800 cm^{-1} , are masked by a large and intense silane spectrum. Except for the FTIR result of the modified PSi with APTES, the interesting shift in hydroxyl and H-bond stretching vibration at 3,400–3,645 cm^{-1} to the N-H stretching frequency at 3,200–3,500 cm^{-1} are observed [125]. There is a larger dipole moment associated with the N-H bond leading to a stronger intensity in the absorption band. In addition, the presence of N-H bonds in a molecule usually involved with hydrogen

bonding causes a peak shifting toward lower frequency, and peak broadening of all functional groups. The spectrum reveals the presence of primary amines by the broad band at 3,300–3,340 cm^{-1} and by the presence of an additional weak peak at frequency lower than 3,300 cm^{-1} , suggesting the formation of hydrogen bonding [126]. The broad band ranging from 3,340–3,550 cm^{-1} is widely recognized as an indication of intermolecular hydrogen bond [127].

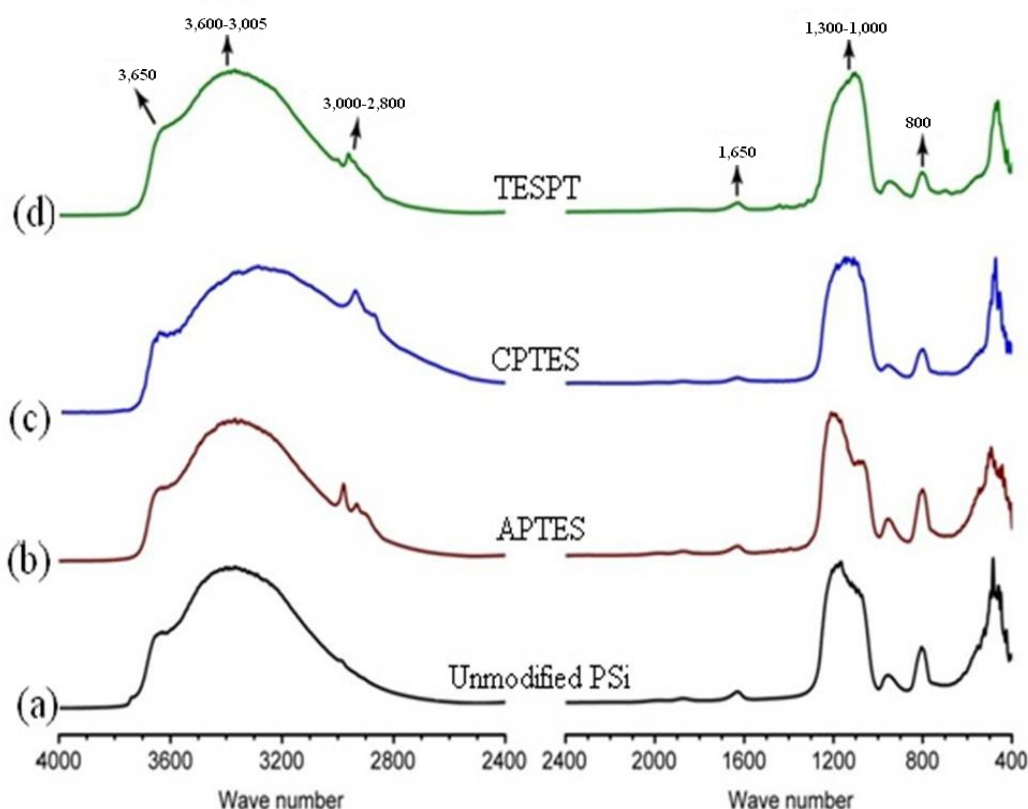


Figure 5.8 DRIFT spectra of unmodified and modified PSi with different SCAs.

In this part, the internal standard method is used to determine the silane grafting efficiency on silica surfaces. The relative peak ratios of PSi covered by various SCAs are tabulated in Table 5.4.

Table 5.4 Relative intensity ratio of PSi with various SCAs.

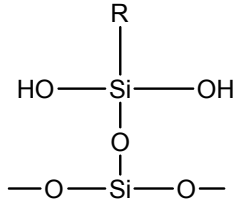
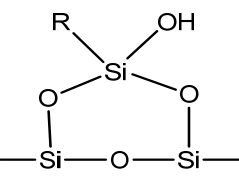
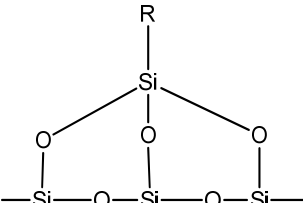
Systems	CH ₂	Si-O-Si	-OH	Relative grafting ratio (%)
Unmodified	0.00	3.23	11.66	-
APTES	0.46	6.00	8.82	85.8
CPTES	0.49	5.41	8.80	75.5
TESPT	0.55	6.17	8.96	91.0

As evidenced in Table 5.4, after surface modification with various SCAs, the relative peak ratio of propyl moiety of silane (CH₂ or CH₃) and siloxane bridge (Si-O-Si) increases while the silanol group or hydroxyl group decreases with respect to the unmodified one. The highest relative grafting ratio of SCA-modified PSi is found in the TESPT modified system, accounting for 91%. This might be due to the fact that the alkoxy groups of silanes are capable of reacting with silanol groups on the PSi surfaces resulting in siloxane bridge formation.

²⁹Si-NMR spectra

Figure 5.9 exhibits the ²⁹Si NMR spectra of unmodified and modified PSi with various SCA types. In unmodified PSi, three chemical shifts can be distinguished at -110, -100 and -90 ppm representing the siloxane bridges (O₄Si), isolated or vicinal silanols (O₃Si(OH)) and germinal silanols (O₂Si(OH)₂), respectively [72]. In the hydrolysis-condensation products, the observed chemical shifts (δ_{Si}) and commonly assigned chemical structures are summarized in Table 5.5. According to the simplified reaction mechanism scheme as shown previously in Figures 5.5-5.7, the reaction of the surface silanols with the functional groups of tri-alkoxysilanes is expected to yield three types of anchoring onto the silica surfaces [7]. These mono-, bi-, and tridentate structures (see Table 5.5) could occur from the reaction of one, two, and three alkoxy groups with the silanols on the silica surfaces respectively.

Table 5.5 ^{29}Si NMR spectroscopy of trialkoxysilanes: structures and chemical shifts (in ppm) of hydrolyzed/condensed species [25, 128].

Mono-dentate structure	Bi-dentate structure	Tri-dentate structure
 –50 to –45 ppm	 –55 ppm	 –70 to –60 ppm

The ^{29}Si -NMR spectra of hydrolysis-condensation products on silica surfaces after silanization reaction are exhibited in Figure 5.9: Figure 5.9 b), the ^{29}Si -NMR result of the APTES-modified PSi shows broader peak at –65.9 ppm with slightly low intensity representing the reaction of 3- alkoxy group of APTES with –OH (silanol group) to form tri-dentate structure on the PSi surfaces. According to Figure 5.9 c) illustrates the ^{29}Si -NMR of the CPTES-modified PSi, in which the chemical shifts are observed at –57.1 and –65.9 ppm, attributing to the reactions of 2- and 3-alkoxy groups of CPTES with –OH (silanol group) to form bi-dentate (T_2) and tri-dentate (T_3) structures on the PSi surfaces, respectively. Figure 5.9 d) exhibits ^{29}Si -NMR of the PSi modified with TESPT, in which the chemical shifts are observed at –48.4, –57.1 and –67.3 ppm representing the reactions of 1-, 2- and 3-alkoxy group of TESPT with –OH (silanol group) to form mono-dentate (T_1) bi-dentate (T_2) and tri-dentate (T_3) structures on PSi surfaces, respectively [129]. These chemical shifts are assigned to T_1 , T_2 , and, T_3 which explain the differences in the silane structure on PSi surfaces. The peak denoted T_3 as tridentate structure corresponds to silane molecules with all three –OH groups reacting with other hydroxyl groups. Similarly, peak T_2 of bi-dentate structure represents the silane molecules with one un-reacted hydroxyl group while peak T_1 of mono-dentate structure demonstrates the silane with two un-reacted hydroxyl groups [129, 130].

Resonance areas are resulted from each ^{29}Si NMR spectrum by de-convolution technique into three Gaussian curves using a curve fitting routine. Areas are derived by iteratively minimizing the sum of the deviations between the actual ^{29}Si

spectra and the sum spectrum of all simulated resonances [131]. Relative intensity area reported in Table 5.6 is the area of the -91 ppm resonance (O_2) divided by the sum of O_2 and the -100 ppm single silanol resonance area (O_3). The percentage of germinal hydroxyls per total hydroxyls presented is estimated from these areas as illustrated in Equation 5.1 [130].

$$\%O_2 = \left(\frac{2O_2}{2O_2 + O_3} \right) \times 100 \quad (5.1)$$

Table 5.6 Relative resonance area of ^{29}Si NMR signal of PSi with different SCAs.

Systems	Si-O-Si (O_4)	Si-OH (O_3)	HO-Si-OH (O_2)	T_1	T_2	T_3
Unmodified	40	54	6	-	-	-
APTES	74	12	4	-	10	-
CPTES	22	24	4	-	20	30
TESPT	20	50	5	3	16	6

As evidenced in Table 5.6, after the silanization reaction, the germinal hydroxyl (O_2) is resulted in every case with relative resonance areas accounting for 4, 4, and 5 of total hydroxyl signal for APTES, CPTES, and TESPT systems, respectively. Moreover, the isolated hydroxyl (O_3) is obtained with relative resonance area accounting for 12, 24, and 50 for APTES, CPTES, and TESPT systems, respectively. In other words, the number of hydroxyl group decreases after the silanization reaction. Moreover, the condensation product determined from ^{29}Si NMR is presented at the positions of T_1 , T_2 and T_3 . The relative resonance areas of T_1 , T_2 and T_3 increase after silanization reaction. This suggests the hydrolysis and condensation reactions between silanol groups on silica surfaces and $-\text{OH}$ or alkoxy groups of silane regardless of SCAs.

The system of PSi modified with APTES shows 3 peaks (O_4 , O_3 , and O_2) of typical ^{29}Si -NMR spectra of silica and 1 peak of condensation product (T_2). The

relative resonance area of PSi with APTES is 10 (T_2) which could be explained by the reaction of 2-OH groups and/or amino groups of APTES and PSi surfaces.

The system of PSi modified with CPTES demonstrates 3 peaks of silica and 2 peaks (T_2 and T_3) of condensation product. Two peaks of condensation product indicate that 2-OH or alkoxy group of CPTES could react with silanol groups on PSi surfaces to form bi- and tri-dentate structures on silica surfaces. This is evidenced by the reduction of relative resonance areas of O_2 and O_3 of PSi with respect to unmodified one. In this case, the highest relative resonance area ($T_3 = 30$) is resulted, that means all of alkoxy group of CPTES could react with silanol groups on silica surfaces. Thus, the surface energy of silica is reduced as confirmed by the relatively small particle size of the PSi modified with CPTES compared with other silane systems (see Table 5.3).

The system of PSi modified with TESPT exhibits 3 peaks of silica and 3 peaks of condensation product ($T_1=3$, $T_2 = 16$, and $T_3 = 6$). The formation of resulting 3 structures might be due to the relatively high molecular weight with long chain length of TESPT (steric hindrance). According to TESPT, its 6-OH groups are capable of reacting with a large amount of silanol groups on PSi surfaces despite the steric hindrance effect.

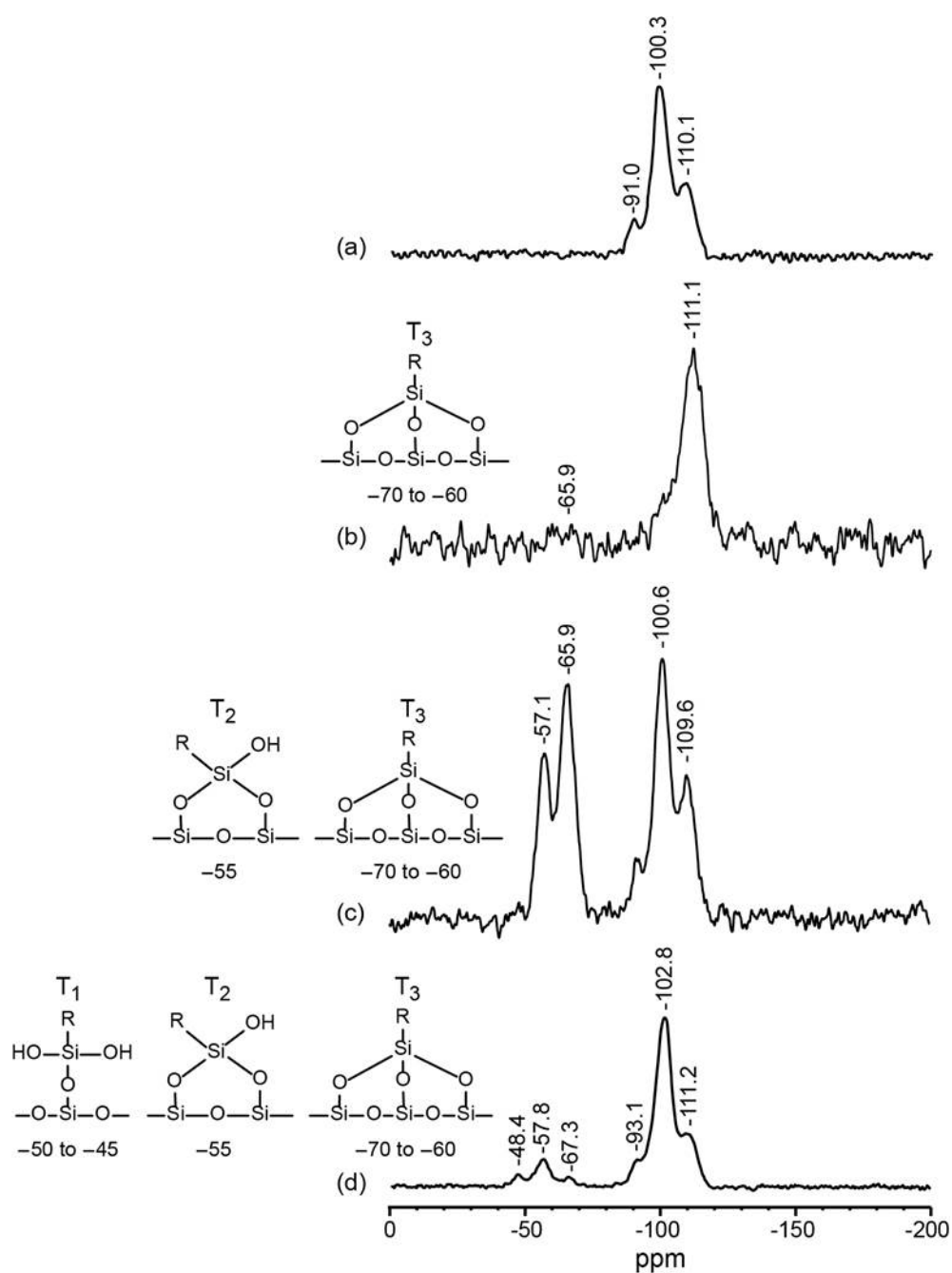


Figure 5.9 ^{29}Si -NMR spectra of PSi modified with various SCAs: (a) unmodified PSi (b) APTES, (c) CPTES and (d) TESPT.

Influence of SCA-modified PSi on Sear number

Sear number is a measure of the free silanol amount on PSi surfaces, determined via titration of silica with 0.1 M sodium hydroxide solutions in the pH range of 6–9 [33]. The acidic silanol groups on PSi surfaces react with sodium hydroxide (NaOH). The Sear number indicates a number of reactive centers on the PSi surfaces [132]. Referring to previous work [132], the Sear number on PSi surfaces is due either to the reaction of surface silanol groups with hydroxyl ions, or to an adsorption of hydroxyl ions by the surface silanol.

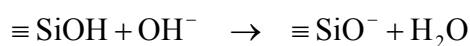


Table 5.7 Sear number of unmodified and modified PSi with various SCAs.

Systems	Sear number	Sear number/SA* (number of unreacted OH in 1 g of PSi per m ²)
Unmodified	10.82±0.10	0.079
APTES	8.67±0.30	0.065
CPTES	5.33±0.30	0.037
TESPT	5.05±0.21	0.036

*SA, specific surface area by N₂ adsorption technique

As mentioned in the literature review, the PSi surfaces consist of silanol groups leading to its acidic behavior [37, 133]. The larger the number of silanol groups, the higher the acidity of PSi [25, 49]. Therefore, the silanization reaction could reduce the acidity of PSi surfaces, due to the reduction of –OH group. In this work, based on the theory of acid-base titration, the concentration of acid is determined by titration with alkaline solution. The volume of alkaline consumption is calculated by stoichiometry to define the acid concentration. The acidity value is referred to remain acidity value or relative un-reacted silanol on PSi surfaces [33]. The Sear number results reveals in Table 5.7. Apparently, the unmodified PSi shows a large amount of acidity silanol on the PSi surfaces. After silane is incorporated, the system modified with APTES provides the highest Sear number on the PSi surfaces while those

modified with CPTES and TESPT show similarity in surface acidity. This could be attributed to the protonation of amino groups of APTES to form the zwitterion through the self-reaction of silanol, and the protonated amine might take place. Thus, the surfaces of PSi modified with APTES exhibit low acidity value. That means the surfaces of PSi modified with APTES provides a large number of un-reacted silanol.

The PSi modified with CPTES and that with TESPT provide comparable Sear number. This could be caused by a low molecular weight (i.e., low steric hindrance) of CPTES having high molecular mobility to react with other silanol molecules. The TESPT contains 6 hydroxyl groups capable of reacting with silanol groups on PSi surfaces, i.e., high efficiency in reducing the PSi surface acidity.

In order to measure the reactivity of hydroxyl ions, the number of $\equiv\text{SiO}^-$ ions formed per square millimeter of PSi surfaces (Sear number/SA*) is calculated by dividing the Sear number with the total area of surface exposed [25]. This number is related to the relative amount of unreacted silanol per gram of PSi. The higher the relative value of unreacted silanol, the lower the yield reaction. Therefore, the highest the yield reaction is presented in TESPT-modified PSi.

Zeta potential

Zeta potential analysis is a technique for determining the surface charge of particles in suspension [134, 135]. Zeta potential of unmodified and modified PSi with various SCAs is given in Table 5.8. The magnitude of zeta potential indicates the colloidal stability. Particles with zeta potential values greater than +30 mV or less than -30 mV typically show good colloidal stability. On the contrary, dispersions with low zeta potential value tend to aggregate due to Van der Waal inter-particle attractions [134, 136].

Table 5.8 Zeta potential of unmodified and modified PSi with various SCAs.

Systems	Zeta Potential (mV)
Unmodified	-16.60 ± 0.90
APTES	12.23 ± 1.03
CPTES	-25.10 ± 0.94
TESPT	-23.43 ± 0.61

According to Table 5.8, the unmodified PSi surfaces exhibit negative charge (about -16.60 mV) at neutral condition. The surface charge of PSi comes from the dissociation of the silanol groups [137]. After surface modification, the PSi with different SCAs reveals change in net charge. The modification PSi with aminosilane (APTES) shows zeta potential of +12.23 mV implying a net positive surface charge. According to previous work [138-140], the dissociation of NH_2 groups plays a significant role in alteration of solid surface charge, giving 4 possible products as shown in Figure 5.10.

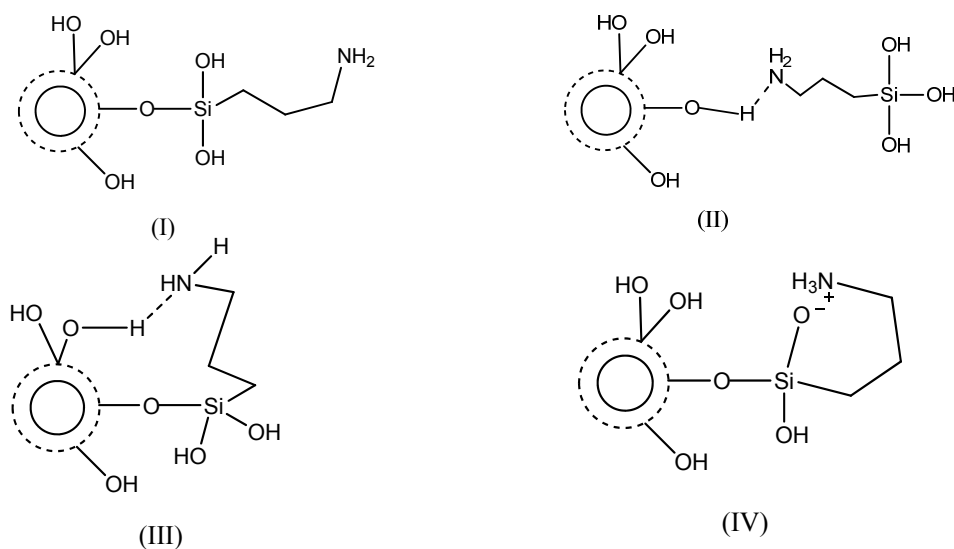


Figure 5.10 Possible products of PSi modified with APTES [139, 140].

At high H^+ ion density, the induction of NH_3^+ takes place, resulting in positive surface charge on modified silica [4]. The modification of PSi with chlorosilane (CPTES) and mercaptosilane (TESPT) are found to be sufficient for producing a net negative charge, i.e., the particles possess zeta potential of -25.10 mV and -23.43 mV, respectively. However, all modified PSi with 3 SCAs show relatively low strength of charge on the PSi surfaces. This means that, after the silanization reaction, the modified PSi still possesses a tendency of re-agglomeration.

5.3 Influence of SCA loading on surface modification of PSi

Particle size and its distributions

Figure 5.11 and Table 5.9 provide the particle size and its distribution of PSi modified with various SCA loadings. Results reveal that the modification of PSi with different SCA loading shows no significant difference in size diameter and specific surface area of PSi. The increment in the mean particle size as measured by the Malvern Mastersizer is probably attributed to the subsequent re-agglomeration of the modified PSi during the washing and drying steps.

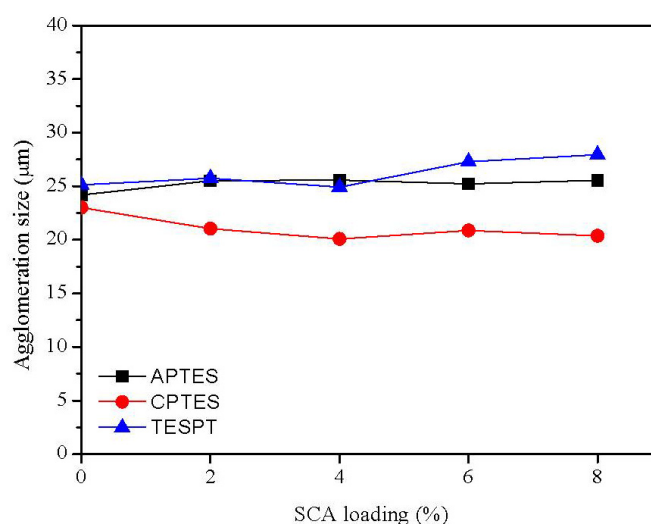


Figure 5.11 Agglomeration size of PSi modified with various SCA loadings.

Table 5.9 reveals the particle size of PSi modified with APTES at 0–8% wt of PSi. Results shows that the mean average particle size $d(0.50)$ slightly increases with increasing APTES loading, which could be due to the agglomeration formation via self-cyclization. The larger agglomeration size causes the lower surface area (SA) measured. Moreover, the increment of APTES loading exhibits the multi-modal agglomeration size of PSi as shown in the particle size distribution index result (see Table 5.9). A broad range of PDI suggests the broad sizes distribution [25].

Table 5.9 Particle size analysis of PSi modified with various SCA loadings.

Systems	Loading of SCAs (%)	SA ^a (m ² /g)	Agglomeration size (μm)	PSI ^b
APTES	0	0.359	18.3	3.1
	2	0.357	25.5	4.5
	4	0.345	25.6	5.6
	6	0.352	25.2	4.7
	8	0.354	25.5	5.2
CPTES	0	0.359	18.3	3.1
	2	0.391	20.0	3.8
	4	0.394	20.1	3.4
	6	0.377	20.4	3.3
	8	0.389	20.9	3.4
TESPT	0	0.359	18.3	3.1
	2	0.349	24.9	5.3
	4	0.355	25.7	4.8
	6	0.348	27.3	5.8
	8	0.344	27.9	3.4

a = specific surface area

b = particle size distribution index

In the system modified with CPTES, the results show no change in mean average agglomeration size by CPTES loading. as illustrated in Table 5.9. In the system with TESPT, the agglomeration size slightly increases with increasing TESPT loading, due probably to the steric hindrance of hydroxyl group of TESPT in silanization reaction [62, 96, 103]. By contrast, the agglomeration size of PSi modified with CPTES is smallest.

Determination of silane grafting efficiency of PSi by internal standard FTIR technique

In this part, the grafting ratios of SCA at various loadings on PSi surfaces are given in Table 5.10. The KSCN internal standard is used to calculate the relative quantity of grafting efficiency [141]. The ratios of CH₂, Si-O-Si (siloxane bridge) and -OH over that of KSCN (2,150 cm⁻¹) are calculated. Moreover, the ratio of siloxane bridge is used to quantify the relative grafting efficiency of silane on PSi surfaces after silanization. The results show that the TESPT-modified PSi exhibits the highest magnitude of relative grafting efficiency at any given TESPT loading as evidenced by the increment of relative ratio of CH₂ (propyl moiety of SCAs) and the number of siloxane bridge.

Table 5.10 Relative intensity ratios of PSi modified with various SCA loadings.

Systems	Loading of SCA (%)	CH ₂ -	Si-O-Si	-OH	Relative grafting ratio (%)
APTES	0	0.00	3.23	11.66	-
	2	0.36	4.51	10.28	36.6
	4	0.42	5.53	9.27	71.2
	6	0.43	5.63	8.98	74.3
	8	0.46	6.00	8.82	85.8
CPTES	0	0.00	3.23	11.66	-
	2	0.29	4.17	11.36	29.1
	4	0.34	4.42	11.06	36.8
	6	0.44	5.00	10.72	54.8
	8	0.49	5.41	8.80	67.5
TESPT	0	0.00	3.23	11.66	-
	2	0.36	4.18	10.74	29.4
	4	0.44	4.81	9.69	48.9
	6	0.53	5.57	9.06	72.4
	8	0.55	6.17	8.96	91.0

Sear number of PSi modified with various SCA loadings

The Sear number on PSi surfaces modified with various loadings of APTES, CPTES and TESPT is given in Table 5.11. It must be noted that the high magnitude of Sear number refers to the large number of un-reacted silanol group on the PSi surfaces [33].

Table 5.11 Sear number of PSi modified with various loadings of SCAs.

Loading of SCA (%)	Sear number		
	APTES	CPTES	TESPT
0	10.82 ± 0.10	10.82 ± 0.10	10.82 ± 0.10
2	8.95 ± 0.03	8.31 ± 0.12	7.55 ± 0.65
4	8.67 ± 0.13	7.81 ± 0.90	6.43 ± 0.29
6	8.08 ± 0.73	6.62 ± 0.42	6.07 ± 0.30
8	7.43 ± 0.30	5.33 ± 0.30	5.05 ± 0.21

The Sear number of all SCA-modified PSi decreases with increasing loading of SCA. At a given loading of SCA, APTES-modified PSi shows the highest un-reacted silanol group on the PSi surfaces. It could be caused by the reactions of alkoxy and amino groups which decrease the silanol deactivation efficiency. Both of CPTES and TESPT-modified PSi show a comparable value of un-reacted silanol groups. The sear number decreases with increasing loading of both CPTES and TESPT. This suggests the reaction of silanol group on PSi surfaces with hydroxyl/or alkoxy group of silane to develop SCA-PSi interaction (see Figure 5.5).

The Zeta potential of PSi with various SCA loadings

The zeta potential of unmodified and modified PSi with different type and loading of SCAs is tabulated in Table 5.12.

Table 5.12 reveals the zeta potential of PSi after silanization reaction. The net charge of modified PSi with APTES shows the positive charge, attributed to the electric charge of amino group. Thus, the particles behave like a cationic surface [142]. The higher magnitude of charge means the higher strength of charge on the PSi

surfaces. The increase in APTES loading contributes to the increased strength of surface charge giving more stability or more dispersibility of PSi in solution media.

Table 5.12 Zeta potential of PSi modified with various loadings of SCAs.

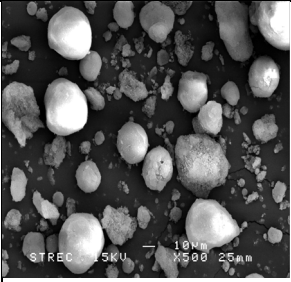
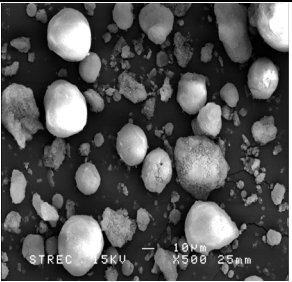
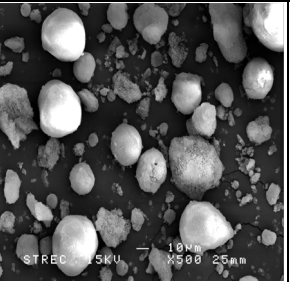
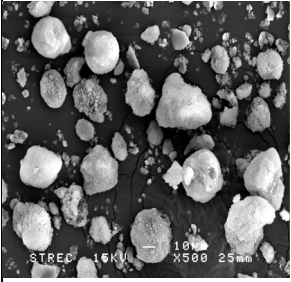
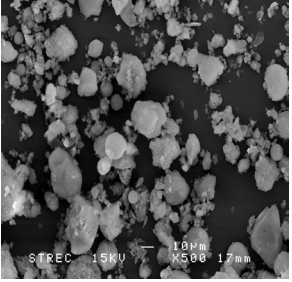
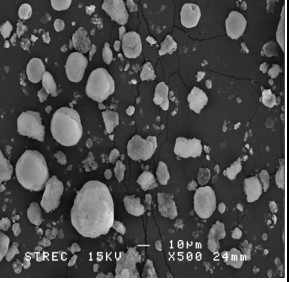
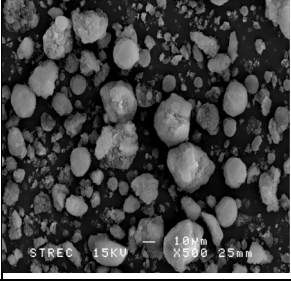
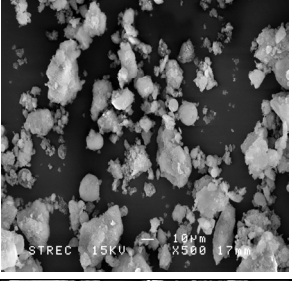
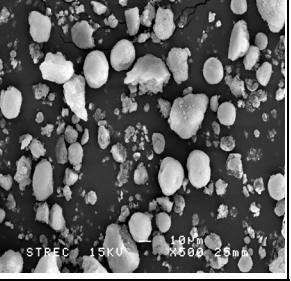
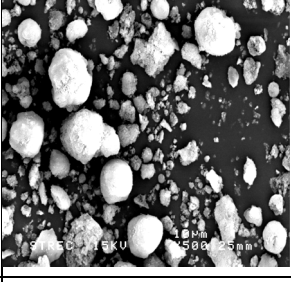
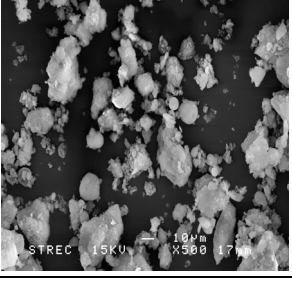
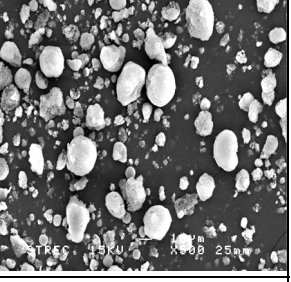
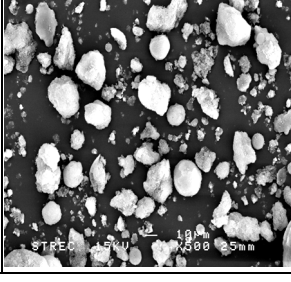
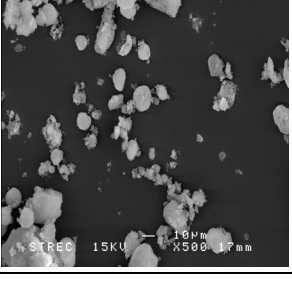
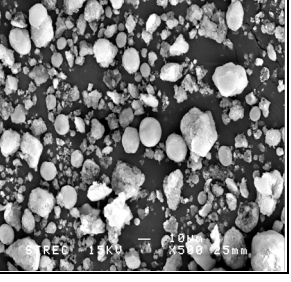
Loading of SCA (%)	Zeta Potential (mV)		
	APTES	CPTES	TESPT
0	-16.60 ± 0.90	-16.60 ± 0.90	-16.60 ± 0.90
2	0.16 ± 0.03	-18.97 ± 0.40	-14.10 ± 2.14
4	5.26 ± 0.34	-20.17 ± 0.73	-18.93 ± 0.66
6	5.88 ± 1.01	-21.17 ± 0.73	-20.27 ± 0.90
8	12.23 ± 1.03	-20.10 ± 0.94	-21.43 ± 0.61

For the zeta potential of CPTES and TESPT-modified PSi at 0–8% wt, the negative surface charge is observed. Moreover, the strength of charge increases with increased loadings of CPTES and TESPT. This could be caused by the presence of chloro-group of CPTES on the PSi surfaces. In other words, the surfaces of CPTES-modified PSi act as anionic surfaces. Furthermore, this explanation is applicable to the case of TESPT-modified PSi in which the thiol group acts as an anionic surface. The magnitude of charge increases with increased loading of TESPT, suggesting the increase in colloidal stability or dispersability of modified PSi in solution media.

5.4 Influences of SCA type and loading on morphology of modified PSi

Table 5.13 reveals the SEM micrographs of unmodified and SCA-modified PSi with various SCAs loadings. Compared with unmodified PSi, all types of SCA exhibit significant reduction in aggregate size. Moreover, the PSi particle size in all systems tends to reduce with increasing SCA loading. The CPTES-modified PSi exhibits the smallest particle size. This could be caused by high affinity to silanization reaction of CPTES on the PSi surfaces.

Table 5.13 SEM images of unmodified PSi and SCA-modified PSi with various SCAs loadings.

Systems Loading (%)	APTES	CPTES	TESPT
0			
2			
4			
6			
8			

5.5 Influence of pH on silanization reaction of PSi with APTES

As mentioned in the literature review, the action of alkoxy silane starts with hydrolysis reaction depending on pH and type of organo- and silicon-functional groups. The silicon functional group affects strongly the hydrolysis rate [4]. In this part, APTES having bi-functional active end chains consisting of alkoxy groups and organo-functional groups (-NH_2 , amino groups) is focused. The polarity of amino groups, is a primary amine giving different properties in different acid-base conditions [4]. Moreover, the characteristics of amine group at end chain may affect the reactivity with Cl- or C-atom on CR backbone leading to change in viscoelastic and mechanical properties of PSi filled CR. Thus, with APTES, the influence of pH on silanization reaction of modified PSi was investigated. Loading of APTES used was kept constant at 6 % by weight of PSi.

Particle size and its distribution

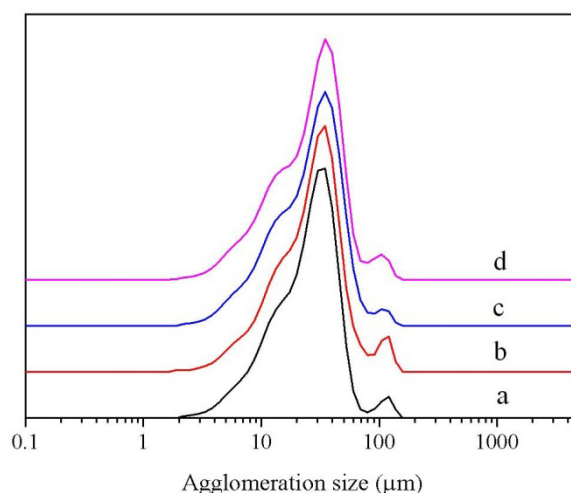


Figure 5.12 Agglomeration size of 6% APTES-modified PSi with various pH conditions of: (a) unmodified PSi, (b) pH 2, (c) pH 6 and (d) pH 12.

Figure 5.12 and Table 5.14 exhibit the aggregate size of PSi modified with 6 %wt APTES at pH of 2, 6 and 12. It can be seen that particle size is slightly affected by pH condition. It could be explained by the hydrolysis-condensation reaction of APTES which may possibly be caused by: i) direct condensation, ii) H-bond and iii) proton transfer as mentioned previously (section 5.2), thus the APTES tends to give

re-agglomeration of PSi via H-bond. However, the acid-base conditions exhibit no apparent effect on specific surface area (SA) and particle size distribution index (PSI) of modified PSi [143], suggesting the incapability of acid-base condition in changing the primary particle characteristics of PSi.

In the case of APTES-modified PSi under alkaline condition, alkoxy groups of APTES become highly reactive [4], and form silanol groups very quickly. Such silanol groups are so unstable that they would condense very quickly to give uncoordinated Si-O-Si networks [4]. Moreover, for the APTES-modified PSi with acidic condition (pH 2), the modified PSi provides small size molecules of dimers and low molecular weight oligomers, and therefore the rate of condensation to form higher molecular weight oligomers is minimized [144]. Although the rate of silane hydrolysis is affected by both steric and inductive effects of alkoxy groups of silane, such steric effect has been reported to be the dominant factor over the inductive effect [145].

Table 5.14 Particle size analysis of APTES-modified PSi prepared with different pH.

Systems	SA (m ² /g)	Agglomeration size (μm)	PSI ^c
Unmodified	137±2	18.3±0.1	3.1
pH 2	107±2	21. 1±0.1	4.3
pH 6	118±2	25. 6±0.1	5.2
pH 12	114±2	24.5±0.1	4.7

FTIR

The DRIFT spectra of PSi modified with APTES prepared with different pH conditions are illustrated in Figure 5.13. All silanization conditions demonstrate the isolated hydroxyl band at 3,650 cm⁻¹, the hydroxyl stretching vibration band at 3,400–3,200 cm⁻¹ with a broad peak, the APTES moiety (CH₂ stretching) band at 3,000–2,800 cm⁻¹ with small intensity, and siloxane bridge (Si-O-Si) band at 1,300–1,000 cm⁻¹ [126]. At pH 2, the DRIFT spectra show a sharp peak of siloxane bridge with higher intensity than that of neutral and alkaline conditions. This means, at very low pH (pH 2), the APTES could be hydrolyzed very quickly to become a stable silanol groups and then form strongly coordinate network of Si-O-Si. By contrast, at

high pH (pH 12), the silanol groups become highly reactive and form unstable silanol very quickly leading to the uncoordinated Si-O-Si networks afterwards [4]. Table 5.15 shows the relative grafting ratio of APTES at various pH. The relative intensity of CH₂, Si-O-Si and -OH demonstrates the efficiency of grafting APTES on PSi surfaces after silanization reaction. The peaks of propyl moiety (CH₂), siloxane bridge (Si-O-Si) and hydroxyl (OH) of APTES show high relative intensity under both acid and alkaline conditions compared with neutral condition. This supports the strong dependence of silanization reaction of APTES on pH.

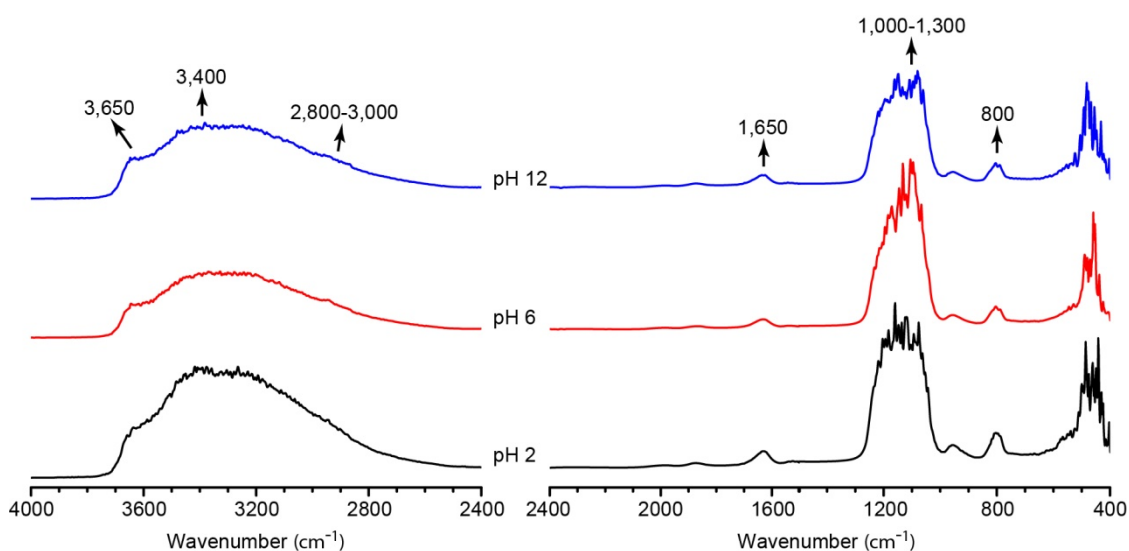


Figure 5.13 DRIFT spectra of 6% APTES-modified PSi prepared at different pH conditions.

Quantitative analysis by internal standard method

Ratios of APTES grafting at various pH conditions on modified PSi surfaces are given in Table 5.15. The intensity peak at 2,150 cm⁻¹ is used as a reference peak to calculate the relative grafting ratio of APTES on PSi surfaces. The results show that the amounts of -OH, CH₂ and Si-O-Si increase with changing pH conditions. Surprisingly, the increase of -OH in acid and alkaline condition may come from the dissociation of silicon dioxide (SiO₂) [25, 72]. Thus, the propyl moiety (CH₂) and siloxane bridge (Si-O-Si) may be increased by the silanization reaction.

Table 5.15 Relative intensity ratio of 6% APTES-modified PSi prepared with different pH.

Systems	CH ₂ -	Si-O-Si	-OH
Unmodified	0.00	3.23	11.66
pH 2	0.73	4.04	10.53
pH 6	0.43	3.36	8.98
pH 12	0.67	3.83	10.56

Sear number

Table 5.16 reveals the number of reactive silanol groups on PSi surfaces after silanization with APTES under various pH conditions. The Sear number is found in un-reacted OH or remained hydroxyl group on PSi surfaces [146]. Under acidic condition, the Sear number increases with increasing the power of hydronium ion (H^+). Such hydronium ion is capable of catalyzing the hydrolysis reaction of APTES as a primary step. Next, an intermolecular condensation between silanes on silica surfaces as a secondary reaction takes place to give the siloxane bridge [14]. On the other hand, with alkaline conditions, the amine groups of APTES may react with -OH groups of alkaline and/or silanol groups to form basic structure. This phenomenon leads to low sodium hydroxide consumption giving rise to the low Sear number [146]. Thus, the APTES modified PSi prepared with alkaline condition (pH 12) shows the lowest Sear number.

Table 5.16 Sear number of 6% APTES-modified PSi at different pH.

Systems	Sear number
Unmodified	10.82±0.10
pH 2	9.90±0.52
pH 6	8.16±0.73
pH 12	3.61±0.57

Zeta potential

Table 5.17 reveals the Zeta potential results of PSi modified with APTES under different pH condition. All pH conditions provide positive surface charge with different strength of PSi in the solution. In acidic solution (pH 2), the surface charge increases to +20.47 mV implying the increased stability of silanol groups while amines are protonated to soluble salt structure. This silane seems to be in zwitterions structure as shown below:



According to previous work [123, 140, 147], the dissociation of $-\text{NH}_2$ groups plays a significant role in surface charge of PSi. Under acidic condition (at high H^+ ion density), an induction of NH_3^+ takes place. Under strongly alkaline condition (pH 12), the surface charge reduces to +2.35 mV that means the aqueous solution of aminosilane is in the monomeric aminoalkylsiliconates structure as shown below:



Table 5.17 Zeta potential of 6% APTES-modified PSi prepared with different pH.

Systems	Zeta potential (mV)
Unmodified	-16.60±0.90
pH 2	20.47±0.41
pH 6	5.88±1.01
pH 12	2.35±1.67

Elementary analysis

Elementary analysis is used to determine the percentage weight of the elements existing in APTES modified PSi under different pH conditions. The amounts of C, H, and N are summarized in Table 5.18.

Table 5.18 Elementary analysis of unmodified and 6% APTES-modified PSi prepared with different pH.

Systems	%C	%H	%N
Unmodified	0.29	0.9	0.04
pH 2	1.39	0.6	0.49
pH 6	1.56	0.66	0.51
pH 12	1.49	0.43	0.47

Elementary analysis results of APTES-modified PSi with 6% of PSi or 6.8 mmol. The %N from amino group of APTES and %C of propyl moiety are greater than those of unmodified one. These results suggest the independence of acid-base condition on the %N.

5.6 Influences of SCA types on properties of rubber compounds with different surface treatment technique

In this part, 2 treatment methods of PSi, namely, in-situ and pre-treatment techniques are compared for their performance on rubber compounds. Furthermore, influences of type and loading of SCA on compound properties are reported and compared.

5.6.1 Payne effect and bound rubber content (BRC)

Payne effect is used to represent the degree of filler-filler interaction which is calculated from the difference in G' at low and high strains. The magnitude of Payne effect ($\Delta G'$) of CR compounds as affected by 2 treatment techniques is given in Table 5.19.

Table 5.19 Comparison of Payne effect ($\Delta G'$) of CR compounds prepared with different PSi surface treatment techniques.

Systems	Payne effect ($\Delta G'$) (kPa)	
	In-situ	Pre-modified
Unmodified	402.19 ± 5.72	402.19 ± 5.72
APTES	276.93 ± 5.98	344.02 ± 6.85
CPTES	319.21 ± 1.17	353.51 ± 9.75
TESPT	264.81 ± 3.67	320.55 ± 0.10

As illustrated in Table 5.19 the system with unmodified PSi shows the highest magnitude of $\Delta G'$. In the presence of SCA, the magnitude of $\Delta G'$ is decreased. Comparing among 3 SCAs used, the system with TESPT exhibits the lowest magnitude of $\Delta G'$. This means that alkoxy groups of TESPT react with silanol groups on PSi surfaces, resulting in reduced H-bonds between aggregates. The results are in good agreement with DRIFT results in which the TESPT exhibits the highest grafting ratio. However, as evidenced by mean averages particle size results, the agglomerate size of PSi in TESPT treated system is found to be largest. Thus, it is believed that such large agglomerate may be disrupted to be in aggregate size under high shear field during the mixing step. Comparing between 2 surface treatment techniques, the in-situ technique provides the lower magnitude of $\Delta G'$. It could be attributed to a large amount of SCA covering on PSi surfaces. This leads to low hydrophilicity and low magnitude of filler-filler network formation.

Table 5.20 Comparison of BRC of CR compounds prepared with different PSi surface treatment techniques.

Systems	BRC (%)	
	In-situ	Pre-modified
Unfilled	7.86 ± 0.11	7.86 ± 0.11
Unmodified	37.35 ± 0.78	37.35 ± 0.78
APTES	49.36 ± 0.09	51.84 ± 1.24
CPTES	39.89 ± 0.47	44.04 ± 1.87
TESPT	54.79 ± 0.63	52.43 ± 2.90

Table 5.20 shows the BRC of CR compounds. The unfilled CR compounds exhibits some extent of BRC because of a gel formation of CR. With an incorporation of unmodified PSi, a drastic increase in BRC is observed, due to the interaction between silanol groups of PSi and Cl groups of CR [70, 148, 149]. The silane modified systems exhibit bound rubber content (BRC) in the range of about 39 to 55% and the magnitude of BRC is found to be in the following order: TESPT $\cong$ APTES > CPTES. The superior interaction in the system with TESPT is due to the silanol-alkoxy interaction resulting in the reduced hydrophilicity and thus enhanced degree of PSi dispersion. The increased BRC in the system modified with APTES might be due to the strong interaction between amino groups of APTES and Cl-group of CR. On the contrary, CPTES shows the lowest BRC, attributed probably to its low reactivity of Cl-end group of CPTES on the PSi surface and Cl- groups on CR chains. The simplified model of the reinforcement of the PSi/SCAs filled CR compound is revealed in Figure 5.14.

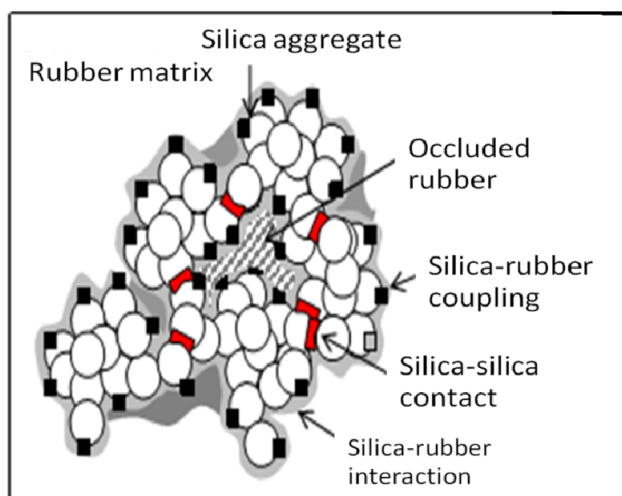


Figure 5.14 Proposed model of the reinforcement of the PSi/SCAs filled CR compound [62].

5.6.2 Cure characteristics

Results of scorch time (t_{s2}), and torque difference between the maximum and minimum torques ($M_H - M_L$) as an indication of crosslink density [12, 53, 54] are presented in Figures 5.15 and 5.16 respectively. Moreover, the crosslink density result via swelling technique is presented in Figure 5.17. The system with unmodified PSi exhibits the longest scorch time (t_{s2}). In the systems with SCA, the scorch time decreases while the torque difference (crosslink density) increases. The shortest scorch time is found in the system with CPTES. This could be caused by the lowest molecular weight of CPTES, capable of easily wetting and reacting with silanol groups on PSi surfaces, resulting in decreased magnitudes of curative adsorption on the PSi surfaces. As evidenced in Figure 5.16, the highest magnitude of torque difference is observed in the system with TESPT, which could be explained by the release of free sulfur from the mercapto group in TESPT during the curing process [150, 151]. The increased crosslink density in APTES system may be caused by the interaction of amino groups of APTES and Cl-atom of CR. Additionally, the increased magnitude of crosslink density as measured by the swelling technique (see Figure 5.17) agrees well with the that determine from torque difference. Comparing between 2 surface treatment techniques, the in-situ method shows higher magnitude of crosslink density than the

pre-treatment method. It could be attributed to the greater grafting efficiency of SCA on PSi surfaces.

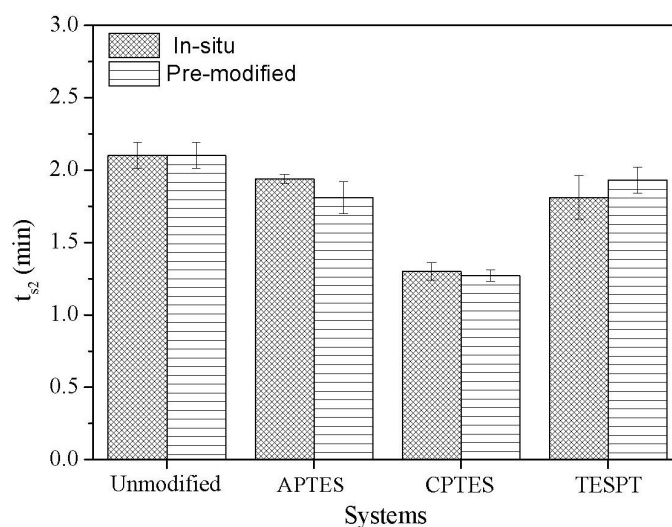


Figure 5.15 Influence of SCA type on the scorch time of PSi filled CR.

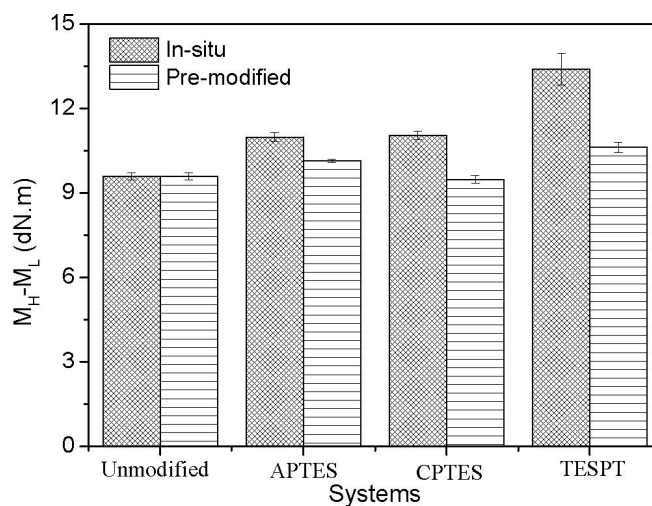


Figure 5.16 Influence of SCA type on torque difference of PSi filled CR (determined from curometer).

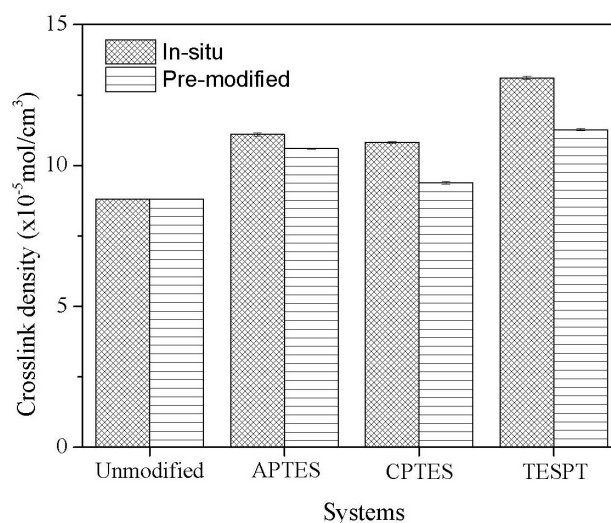


Figure 5.17 Influence of SCA type on crosslink density of CR cured specimens (measured from swelling technique).

5.6.3 Morphology

Figures 5.18 and 5.19 represent SEM micrographs of the fractured surfaces of CR cured specimens filled with PSi by different surfaces treatment technique. The micrographs of unfilled CR are shown in Figures 5.18a and 5.19a as a reference, in which white particles of metal oxide in CR matrix are observed. The unmodified PSi reveals the small aggregate size of PSi (see Figures 5.18b and 5.19b). With both surface treatment techniques (see Figure 5.18 (c-e) for in-situ and Figure 5.19 (c-e) for pre-treatment technique), the aggregation size of PSi is reduced with SCA treatment, suggesting the enhanced PSi dispersability by silane treatment. Among 3 SCAs, the system modified with TESPT (Figures 5.18e and 5.19e) demonstrates the smallest aggregation size of modified PSi, suggesting the enhanced PSi dispersability over the APTES (Figures 5.18c and 5.19c) and CPTES (Figures 5.18d and 5.19d) respectively. Comparing between 2 surface treatment techniques, the SEM micrographs illustrate no significant difference in PSi dispersion.

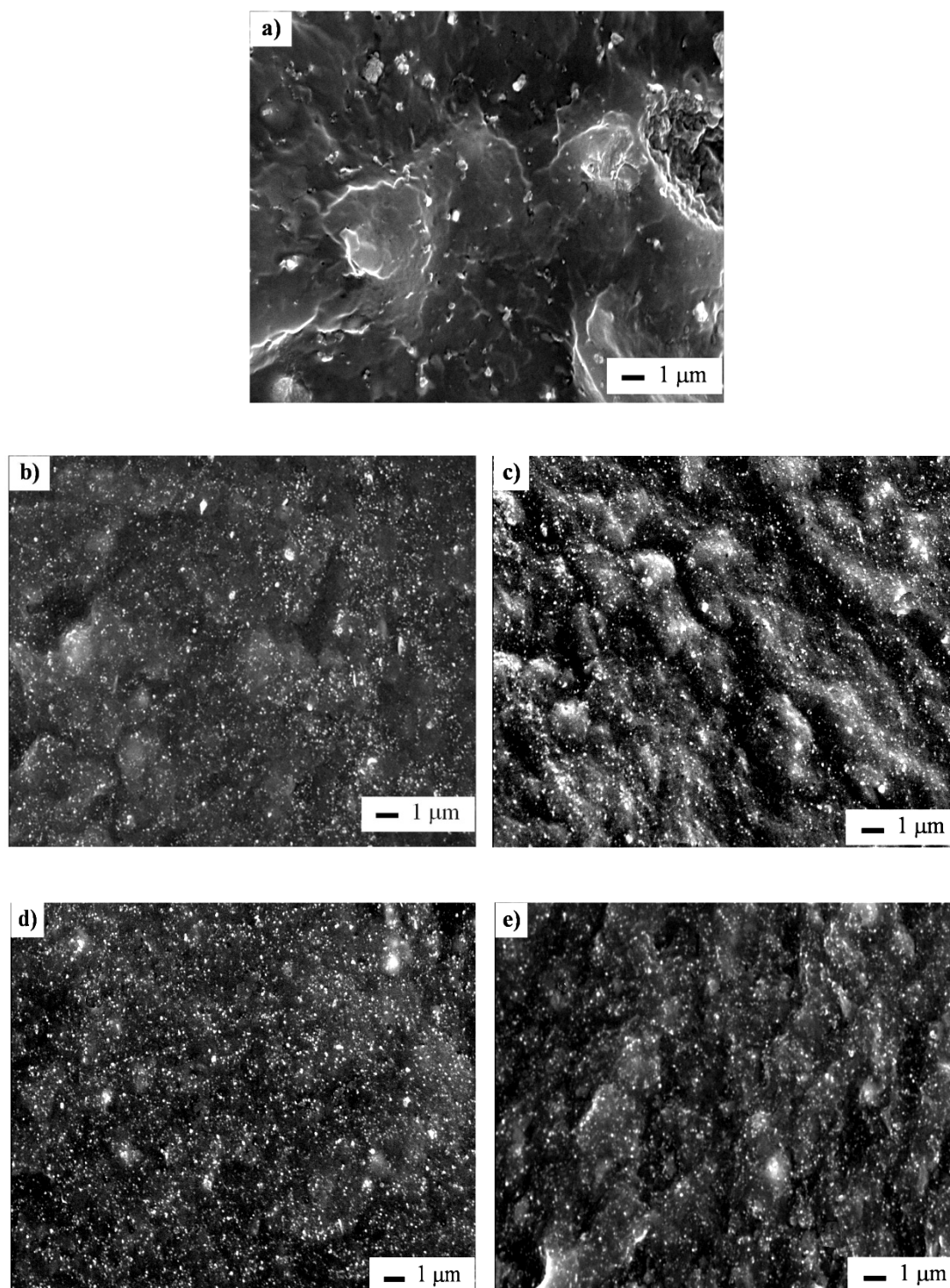


Figure 5.18 SEM micrographs of CR cured specimens with various SCA types by in-situ technique: a) Unfilled; b) Unmodified PSi; c) APTES-modified PSi; d) CPTES-modified PSi; and e) TESPT-modified PSi.

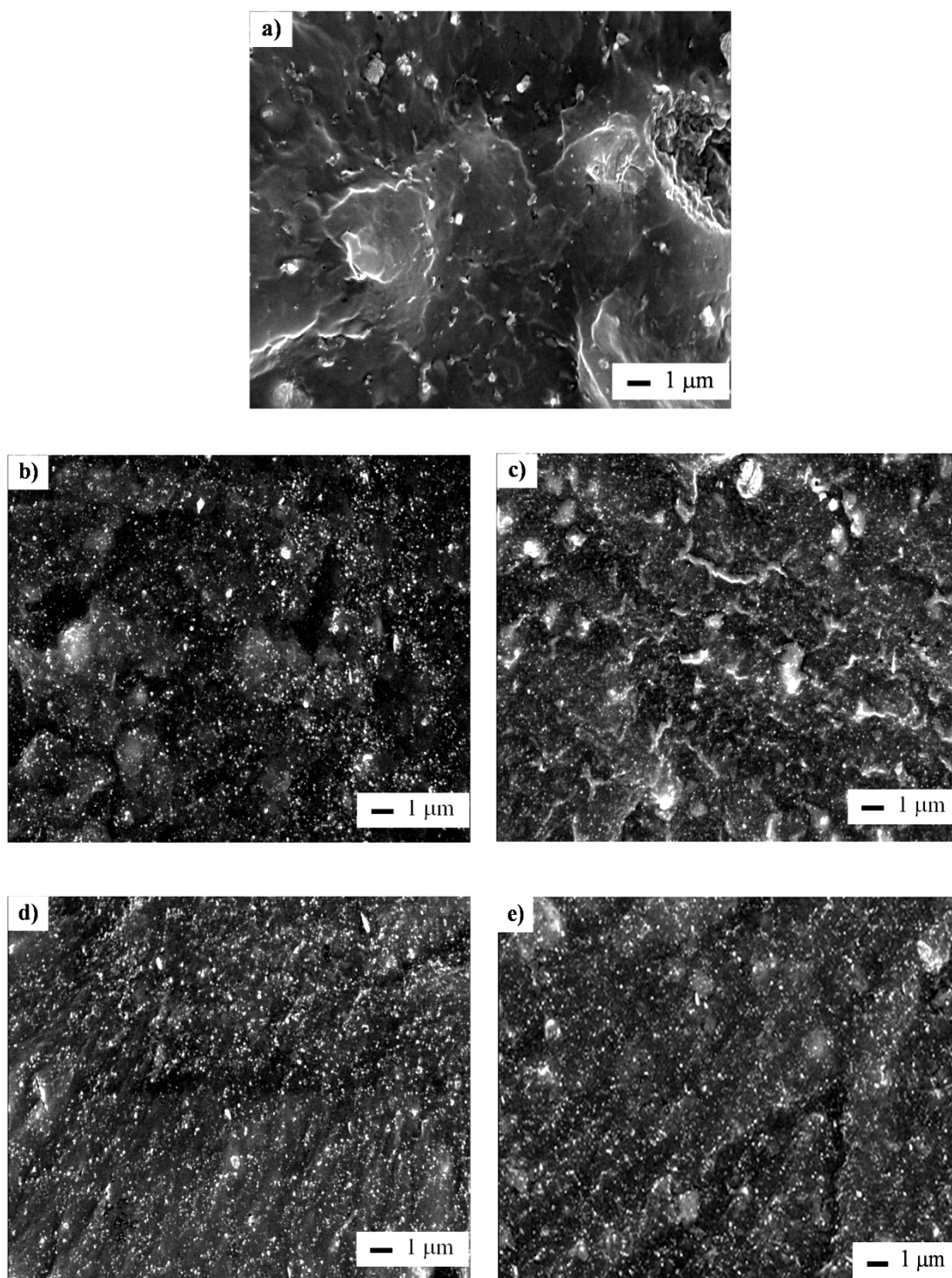


Figure 5.19 SEM micrographs of CR cured specimens with various SCA types by pre-modified technique: a) Unfilled; b) Unmodified PSi; c) APTES-modified PSi; d) CPTES-modified PSi; and e) TESPT-modified PSi.

5.6.4 Mechanical properties

In this part, mechanical properties including static and dynamic properties used to explain and compare the influence of SCA types are revealed. Results of hardness, tensile properties, abrasion loss and compression set are revealed in Figures 5.20-5.25. Moreover, influences of SCA types on dynamic properties via heat built-up and rolling resistance ($\tan\delta$ at 60°C) are presented in Figures 5.26-5.28.

Figures 5.20-5.25 shows hardness and tensile properties results of CR filled with unmodified and SCA-modified PSi. The results show that the CR filled with unmodified PSi provides the lowest hardness and modulus. Among the 3 SCAs, the TESPT gives the highest hardness and modulus, followed by APTES and CPTES, respectively. It is widely recognized that both modulus and hardness of the cured specimens depend strongly on crosslink density [150]. Thus, the results of modulus and hardness are synchronous with those of crosslink density. Similar to hardness and modulus results, the tensile strength is improved by SCA treatment of PSi surface as evidenced in Figure 5.22. Explanations are given by the combined effects of improved rubber-filler interaction, increased crosslink density and enhanced PSi dispersion. It is known that elongation at break depends strongly on crosslink density, i.e., the higher the crosslink density, the lower the elongation at break. Thus the elongation at break of the system modified with TESPT is lowest due to its highest crosslink density. On the other hand, the system with the unmodified PSi shows the highest elongation at break which is simply due to its lowest crosslink density. Comparing with 2 surface treatment techniques, the in-situ technique offers greater magnitudes of hardness and modulus while the magnitudes of tensile strength and elongation at break are lower than the pre-treatment technique. This can be explained by the poor filler dispersion causing stress concentration point giving poor tensile strength in the cured specimens.

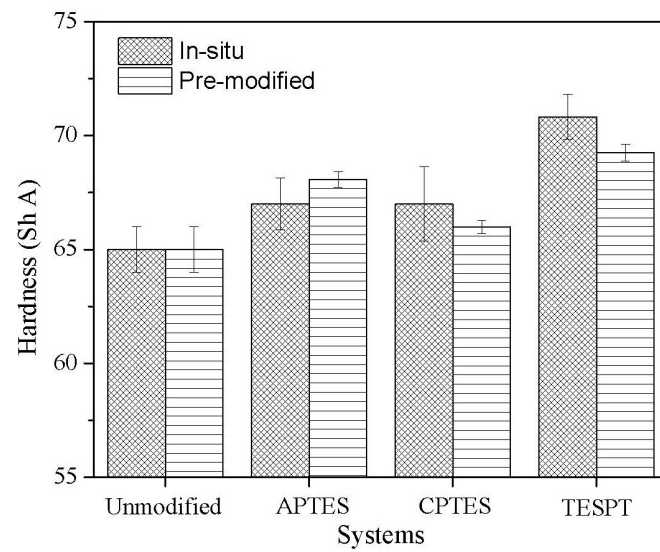


Figure 5.20 Influence of SCA type on hardness of CR cured specimens.

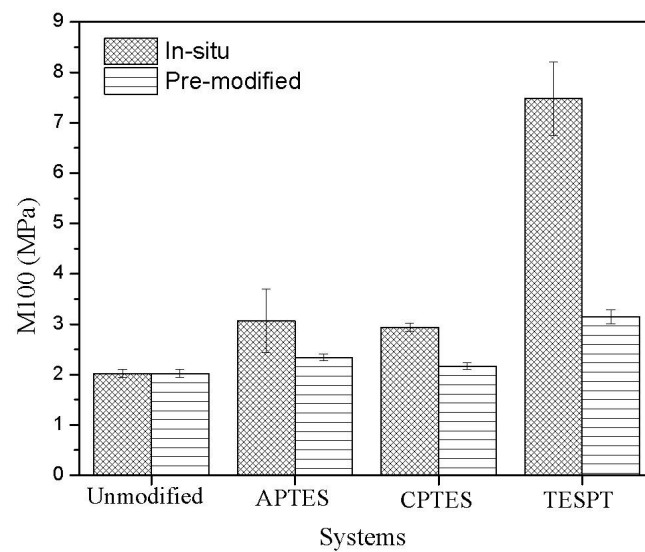


Figure 5.21 Influence of SCA type on 100% modulus of CR cured specimens.

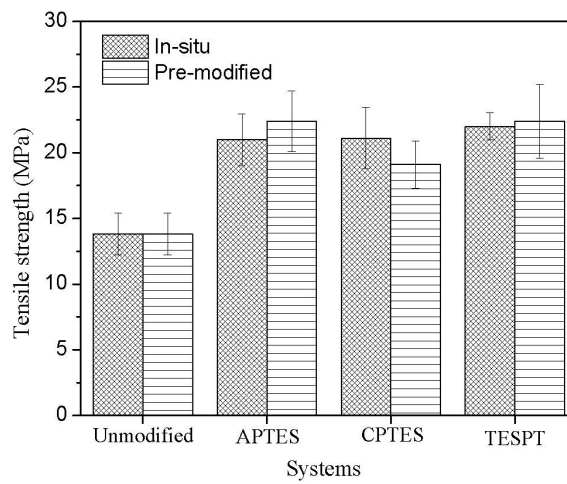


Figure 5.22 Influence of SCA type on tensile strength of CR cured specimens.

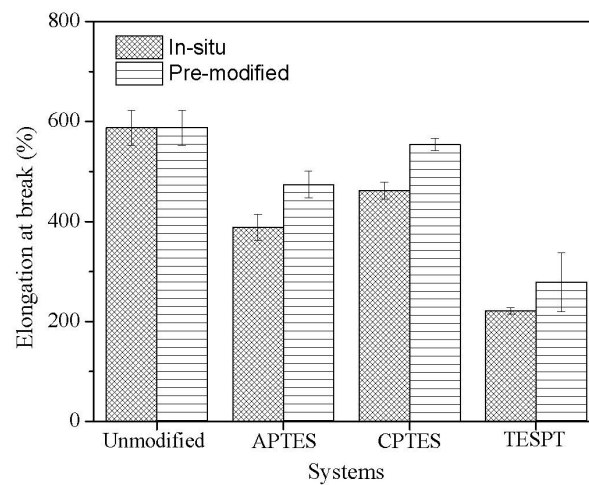


Figure 5.23 Influence of SCA type on elongation at break of CR cured specimens.

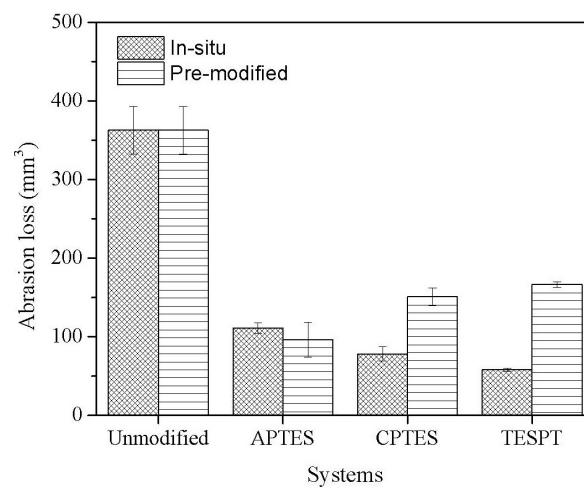


Figure 5.24 Influence of SCA type on abrasion loss of CR cured specimens.

Figure 5.24 shows the influence of SCA type on abrasion resistance of CR filled with unmodified and SCA-modified PSi prepared by different surface treatment techniques. The CR filled with unmodified PSi shows the highest volume loss. In the presence of SCA, the volume loss of CR cured specimens is decreased, and the lowest magnitude of volume loss is found in the system with TESPT and APTES prepared by in-situ and pretreatment technique respectively. Comparing between the systems with TESPT (in-situ) and APTES (pre-modified), the lowest magnitude of volume loss is observed in TESPT-modified system. Thus, enhancement magnitude in abrasion resistance of the system with TESPT is greater than the system with APTES when prepared by in-situ technique. This can be attributed to the increased crosslink density and enhanced filler dispersion in the system modified with TESPT. It has been reported that the system with good filler dispersion exhibits higher abrasion resistance than that with poor filler dispersion [152]. In other words, the enhancement in abrasion resistance could be due to the combined effect of reduced filler-filler interaction and increased rubber-filler interaction.

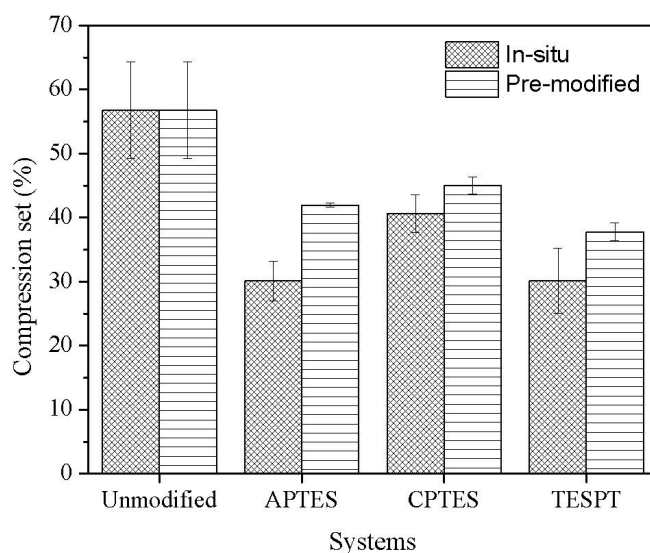


Figure 5.25 Influence of SCA type on compression set of CR cured specimens.

Compression set results as functions of SCA types and surface treatment technique are displayed in Figure 5.25. The CR filled with unmodified PSi demonstrates the highest compression set. When SCA is incorporated, the reduction of

compression set is observed. Both of surface treatment technique with TESPT and APTES provides comparable compression set. This could be caused by: (i) lowered filler network formation (as evidenced in Payne effect results); (ii) improved rubber-filler interaction (as evidenced in BRC results) and (iii) improved filler dispersion (i.e., state-of-mix) as evidenced in SEM micrographs.

The dynamic mechanical properties of CR filled with unmodified and SCA-modified PSi prepared from different surface treatment techniques as measured by heat build-up (HBU) are displayed in Figure 5.26. It is found that the CR filled with unmodified PSi exhibits the highest HBU. Both surface treatment techniques with TESPT and APTES exhibit relatively low HBU. By contrast, the system modified with CPTES demonstrates relatively high HBU, due to the low rubber-filler interaction as evidenced by low BRC and low crosslink density results as shown earlier (Table 5.20 and Figures 5.16-5.17). Such low interaction and crosslink density facilitate energy dissipation of cured specimens under cyclic deformation of the HBU.

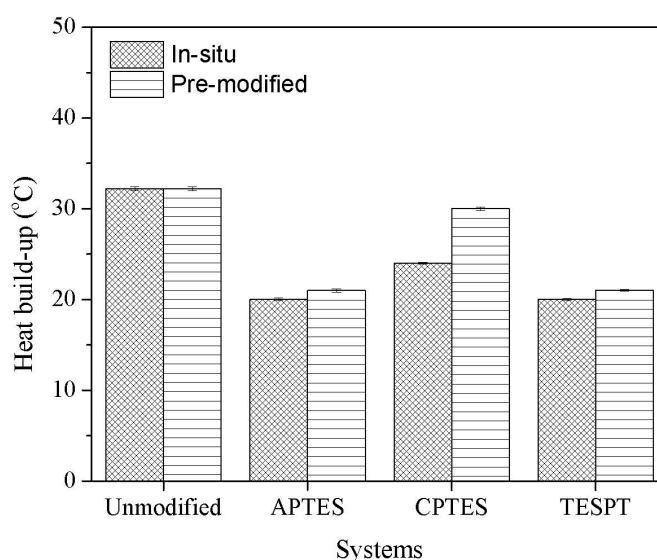


Figure 5.26 Influence of SCA type on heat build-up of CR cured specimens.

Figures 5.27 reveals the loss factor ($\tan\delta$) results of CR filled with unmodified and SCA-modified PSi prepared by different surface treatment technique, respectively. It can be seen that $\tan\delta$ peak is observed at the temperatures between -40 and -10°C. Regardless of SCA used, neither SCA type nor treatment technique give

significant effect on T_g . However, the magnitude of $\tan\delta_{\max}$ tends to increase when SCA is incorporated. This may be due to decrease in filler network (acting as elastic body). Therefore, the lower filler network in the systems with SCA gives a decrease in storage modulus and thus the increase of $\tan\delta_{\max}$ in CR cured specimens. Comparing among 3 SCAs, the magnitude of $\tan\delta_{\max}$ is in the following order: i.e., APTES > CPTES > TESPT.

Furthermore, the $\tan\delta$ at 60 °C results representing rolling resistance parameter of CR filled with unmodified and SCA-modified PSi prepared by different surface treatment technique are given in Figure 5.28. The results show that CR filled with unmodified PSi exhibits the highest magnitude of $\tan\delta$ at 60°C. Among 3 silanes used, the TESPT provides the lowest magnitude of $\tan\delta$ at 60 °C (see Figure 5.28), which could be caused by co-curing of mercapto group of TESPT with CR matrix i.e., the increased the rubber-filler interaction. These results are in accordance with the results of Payne effect, BRC and crosslink density as discussed earlier.

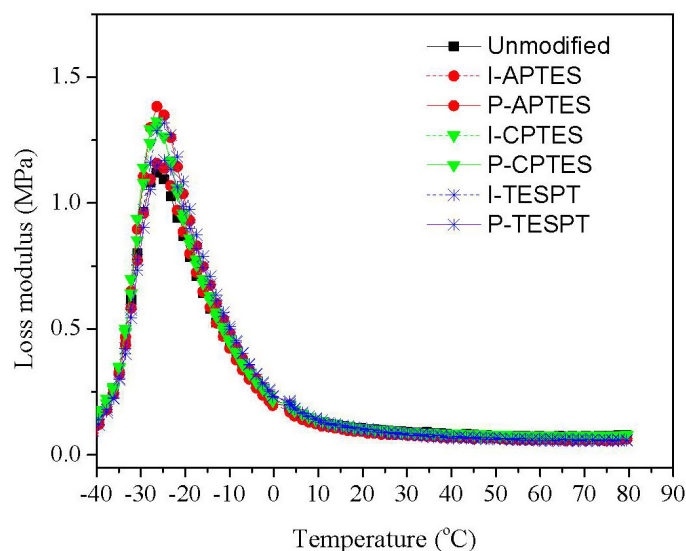


Figure 5.27 Influence of SCA type on $\tan\delta$ of CR cured specimens prepared with different surface treatment technique; I) in-situ and P) pre-modified technique.

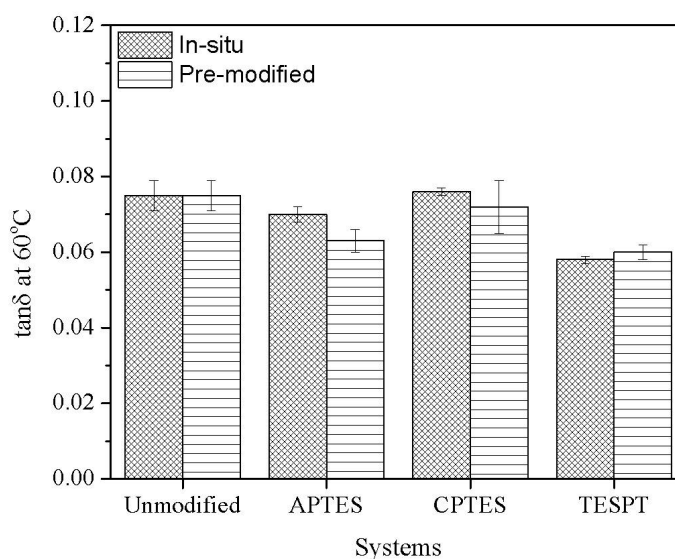


Figure 5.28 Influence of SCA type on $\tan\delta$ at 60°C of CR cured specimens.

From all the results as previously described, it could be summarized that the in-situ technique provides greater performance than that of pre-modified technique. Furthermore, the systems modified with TESPT and APTES show superior performance on compounds and vulcanizates properties as a result of: (i) improved filler-filler dispersion (ii) improved rubber-filler interaction and (iii) improved state-of-mix in the PSi filled CR composites.

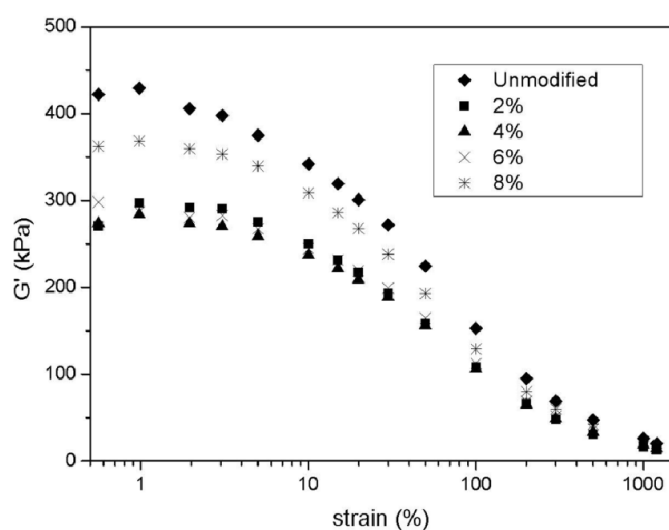


Figure 5.29 Payne effect of 40 phr PSi filled CR compounds modified with various loadings of APTES prepared with in-situ method.

5.7 Influences of SCA loading and surface treatment technique on properties of rubber compounds

5.7.1 Payne effect

Figure 5.29 shows the storage modulus (G') as a function of strain of CR compounds with various APTES loadings as prepared from the in-situ method. It is evident that the highest magnitude of storage modulus (G') at low strain is found in the system PSi without APTES system. This could be caused by the filler-filler networks formation via H-bonding. This phenomenon is called Payne effect. With increasing APTES content, magnitude of Payne effect reduces up to 6% APTES content and then increases (see Table 5.21). The reduction in Payne effect is due to the deactivation of silanol groups on PSi surfaces by APTES. This leads to the reduction in PSi network formation. On the contrary, the increase in Payne effect at APTES content higher than 6% APTES might be attributed to the high reactivity between amino and hydroxyl group of either APTES on PSi surfaces.

The summarized magnitude of Payne effect of the CR filled with various SCA loadings prepared by different surface treatment technique is given in Table 5.21. The results reveals that the unmodified PSi provides the highest magnitude of Payne effect indicating a strong filler-filler network due to H-bonds between PSi aggregates. With the presence of SCAs, both of systems modified with CPTES and TESPT, the Payne effect decreases with increasing loading of both SCAs. This might be due to the reaction between alkoxy groups of SCAs and silanol groups on PSi surfaces giving the reduction in filler-filler interaction or filler network. Furthermore, at similar SCA content, the TESPT possesses larger number of alkoxy groups than the APTES and the CPTES, respectively. The TESPT therefore has the highest capability of silanol deactivation and thus the lowest magnitudes of filler network. From this result, the in-situ technique is suitable for yielding good PSi dispersion as evidenced by lower magnitude of Payne effect.

Table 5.21 Payne effect comparison of CR compounds as affected by SCA loading and surface treatment technique.

Systems	Loading of SCA (%)	Payne effect ($\Delta G'$), kPa	
		In-situ	Pre-modified
APTES	0	370.43	370.43
	2	162.49	353.45
	4	167.45	328.53
	6	185.76	320.19
	8	233.48	367.46
CPTES	0	370.43	370.43
	2	229.42	350.78
	4	224.81	345.86
	6	212.06	335.51
	8	202.25	323.37
TESPT	0	370.43	370.43
	2	225.23	353.45
	4	204.96	335.99
	6	179.78	304.56
	8	194.28	291.22

5.7.2 BRC

The BRC comparison of the PSi filled CR with various SCA loadings prepared by different surface treatment technique is given in Table 5.22. It is evident that the system of PSi filled CR without SCA (0% SCA) exhibits the lowest magnitude of BRC. Apparently, the BRC is found to increase with increasing SCA loading, which could be caused by a large amount of SCA being adsorbed on PSi surfaces and thus the lowered PSi-PSi interaction. This provides the enhanced filler dispersion degree and also the increased rubber-filler interaction leading to the increased BRC. Comparing with 3 silanes used, the APTES and TESPT gives the highest BRC due probably to the strong interaction between amino groups of APTES and Cl atoms of

CR. Additionally, the increased magnitude of BRC in TESPT is due to the silanol-alkoxy interaction resulting in the reduced hydrophilicity and thus enhanced degree of PSi dispersion. By contrast, the system with CPTES shows the lowest BRC due partly to the lowest reactivity of Cl end groups of CPTES on the PSi surfaces and CR matrix as mentioned in section 5.3.1. After the incorporation of CPTES in the mixer, it is believed that PSi surfaces behave like an anionic surface (as evidenced by negative value in zeta potential results illustrated in Table 5.12) leading to low dipole-dipole interaction between Cl of CR matrix and chloro groups of CPTES on PSi surfaces [108]. This phenomenon is used for explaining the lowest BRC found in CPTES – modified PSi system.

Table 5.22 BRC of PSi filled CR compounds with various types and loadings of SCAs.

Systems	Loading of SCA (%)	BRC (%)	
		In-situ	Pre-modified
APTES	0	37.35 ± 0.78	37.35 ± 0.78
	2	39.84 ± 0.42	45.77 ± 3.30
	4	44.58 ± 0.78	50.33 ± 6.02
	6	46.02 ± 0.70	51.84 ± 1.24
	8	49.39 ± 0.09	53.46 ± 2.54
CPTES	0	37.35 ± 0.78	37.35 ± 0.78
	2	37.45 ± 0.72	44.04 ± 6.87
	4	38.98 ± 0.50	45.01 ± 1.00
	6	38.85 ± 0.99	45.44 ± 2.76
	8	39.89 ± 0.47	46.91 ± 0.92
TESPT	0	37.35 ± 0.78	37.35 ± 0.78
	2	54.79 ± 0.63	46.17 ± 0.88
	4	41.02 ± 0.47	47.00 ± 0.47
	6	46.18 ± 0.87	52.43 ± 2.90
	8	52.43 ± 2.90	54.79 ± 0.62

5.7.3 Cure characteristics

Cure characteristics of CR filled with PSi as functions of SCA loading and surface treatment technique, i.e., scorch time (t_{s2}) and the difference between maximum and minimum torques (M_H-M_L) are presented in Table 5.23. Moreover, in this section, the crosslink density results of CR cured specimens as determined from the swelling technique based on Flory-Rehner equation are given in Figure 5.30.

Table 5.23 Scorch time (t_{s2}) of CR compounds as affected by SCA loading and surface treatment technique.

Systems	Loading of SCA (%)	t_{s2} (min)	
		In-situ	Pre-modified
APTES	0	2.10±0.09	2.10±0.09
	20	3.03±0.02	2.57±0.09
	40	2.35±0.28	1.55±0.09
	60	1.94±0.03	1.81±0.09
	80	1.95±0.10	2.08±0.09
CPTES	0	2.10±0.09	2.10±0.09
	2	1.73±0.18	2.79±0.03
	4	1.31±0.10	2.56±0.31
	6	1.30±0.06	2.17±0.04
	8	1.35±0.13	2.32±0.06
TESPT	0	2.10±0.09	2.10±0.09
	2	1.86±0.08	1.85±0.12
	4	1.51±0.07	1.82±0.11
	6	1.81±0.25	1.93±0.03
	8	2.06±0.02	2.31±0.30

In the system with APTES as shown in Table 5.23, scorch time (t_{s2}) results of PSi filled CR tends to increase with APTES content up to 4% and then decrease. This might be due to the influence of bi-functional active chain ends of APTES easily

reacting with other APTES molecules in the early step. Thus, a large amount of activated silanol remained on PSi surfaces in the early stage leads to the increase in curative adsorption capacity on the PSi surfaces and thus decreases magnitude of torque difference of CR cured specimens. At higher APTES content (6 and 8%), the decrease in t_{s2} is observed which could be explained by higher reactivity of both end groups of APTES than that of each other on the PSi surfaces. This results in a large amount of curative remained and thus the increase in torque difference. In the system with CPTES, the t_{s2} decreases with increasing CPTES content. Likewise, the system with TESPT shows the decrease in the t_{s2} with TESPT loading up to 6% and then the increased t_{s2} is observed. The increase of t_{s2} in the case of large amount of TESPT content is due to the mercapto group need sufficient time to sulfur dissociation (cure retardation effect) and incorporation of curing agents. Results of torque difference as an indication of crosslink density of the rubber vulcanizates are shown in Table 5.23. It is apparent that the torque difference of the vulcanizates of all modified systems slightly increases with increasing SCA loading corresponding to the results of crosslink density determined from swelling technique as illustrated in Figure 5.29. Comparing with 2 surface treatment techniques, the in-situ technique with APTES and TESPT provides greater magnitude of crosslink density of CR matrix than CPTES.

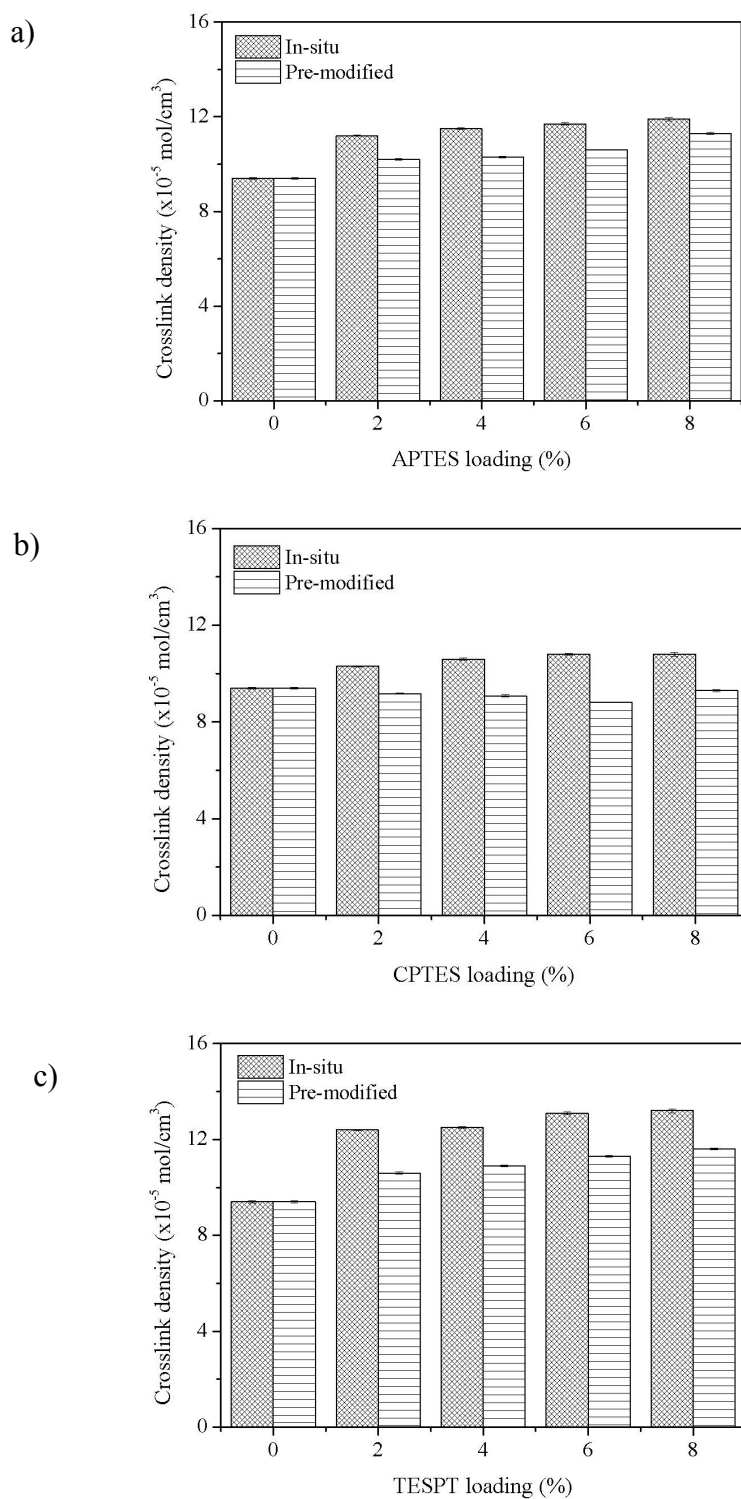


Figure 5.30 Crosslink density via swelling of CR cured specimens (prepared by different surface treatment techniques) with various loadings of SCAs: (a) APTES; (b) CPTES and (c) TESPT.

5.7.4 Morphology

Figures 5.31-5.36 illustrate SEM micrographs of unmodified and SCA-modified PSi filled CR at various loading with different surface treatment techniques. The results show that agglomerate size of PSi tends to reduce with increasing SCA loading. This could be caused by the deactivation of silanol groups on the PSi surfaces, leading to enhanced PSi dispersion. At a given SCA content, the smallest agglomerate size is found in the system with TESPT-modified PSi indicating the enhanced PSi dispersibility over the systems with APTES-modified, CPTES-modified and unmodified PSi, respectively.

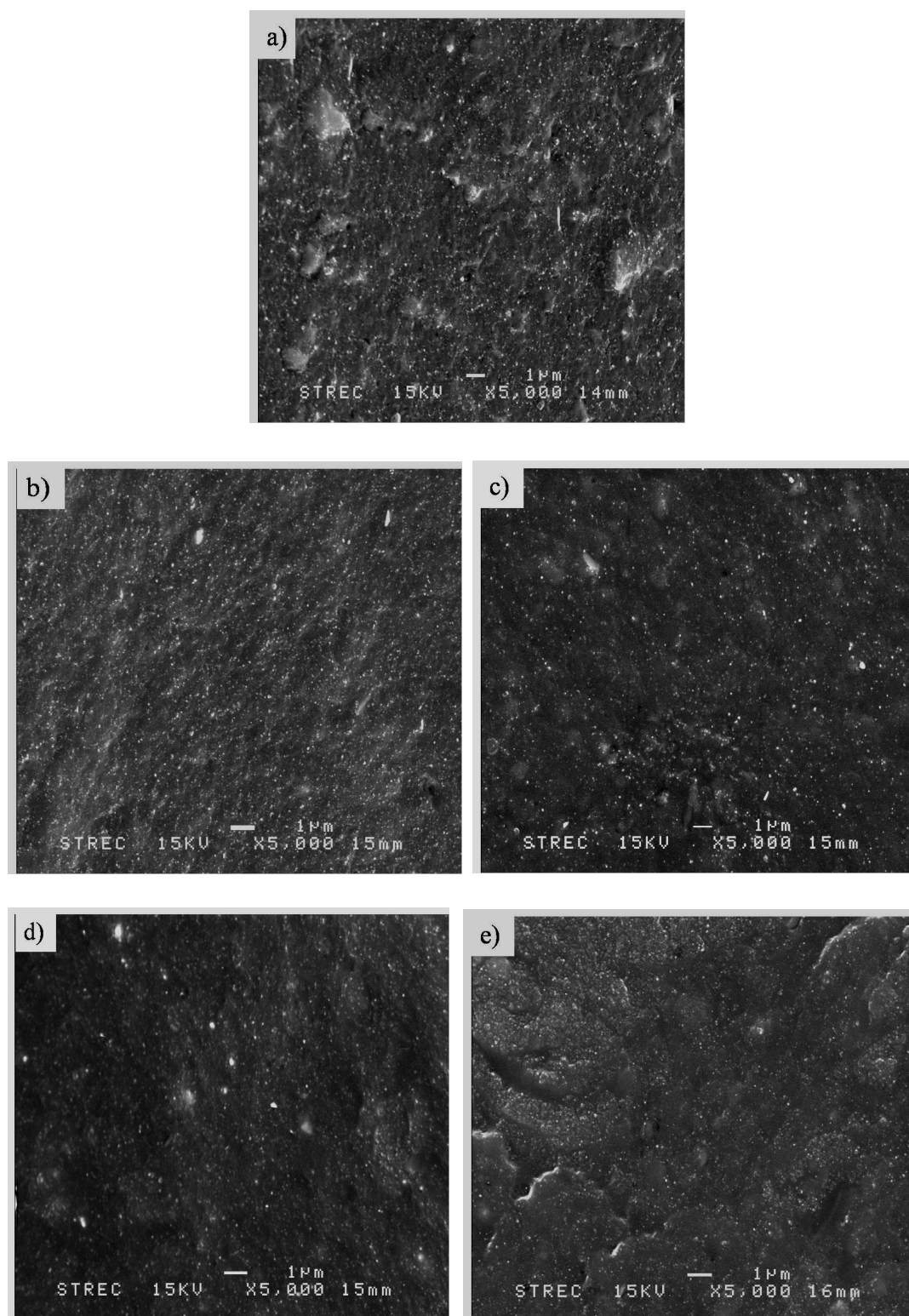


Figure 5.31 SEM images of APTES-modified PSi filled CR by in-situ technique with APTES loading of: a) 0%; b) 2%; c) 4%; d) 6% and e) 8%.

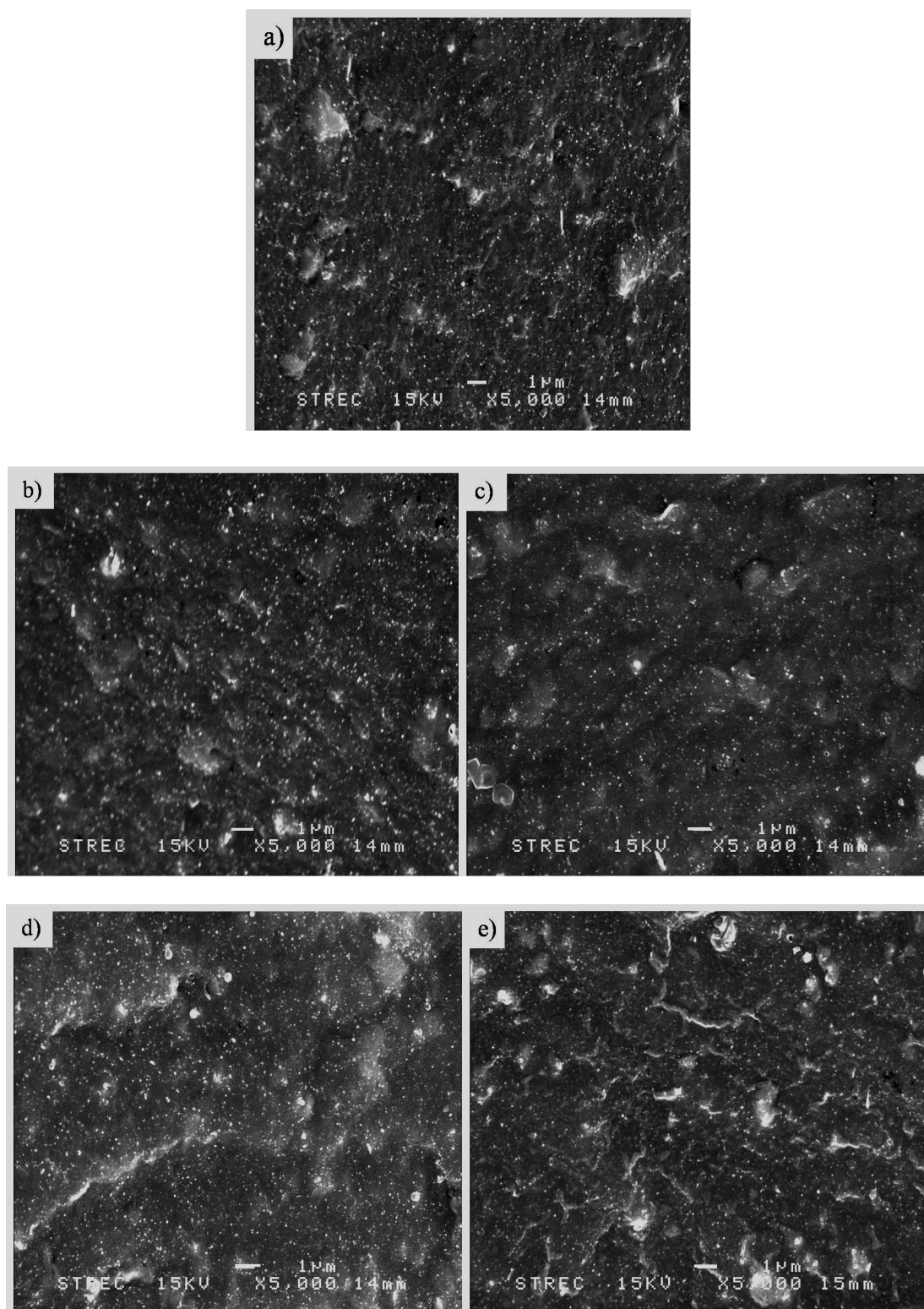


Figure 5.32 SEM images of APTES-modified PSi filled CR by pre-modified technique with APTES loading of: a) 0%; b) 2%; c) 4%; d) 6% and e) 8%.

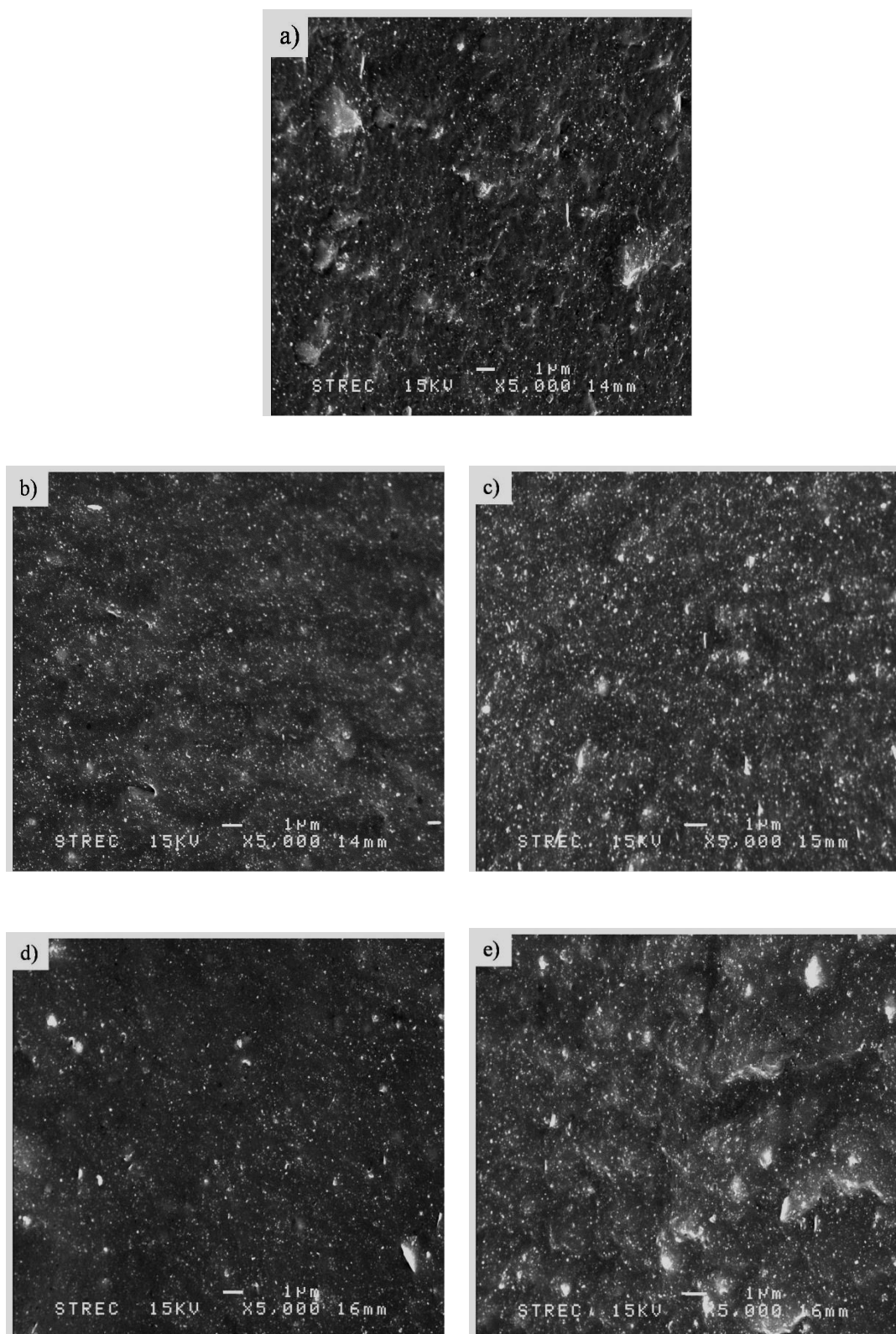


Figure 5.33 SEM images of CPTES-modified PSi filled CR by in-situ technique with CPTES loading of: a) 0%; b) 2%; c) 4%; d) 6% and e) 8%.

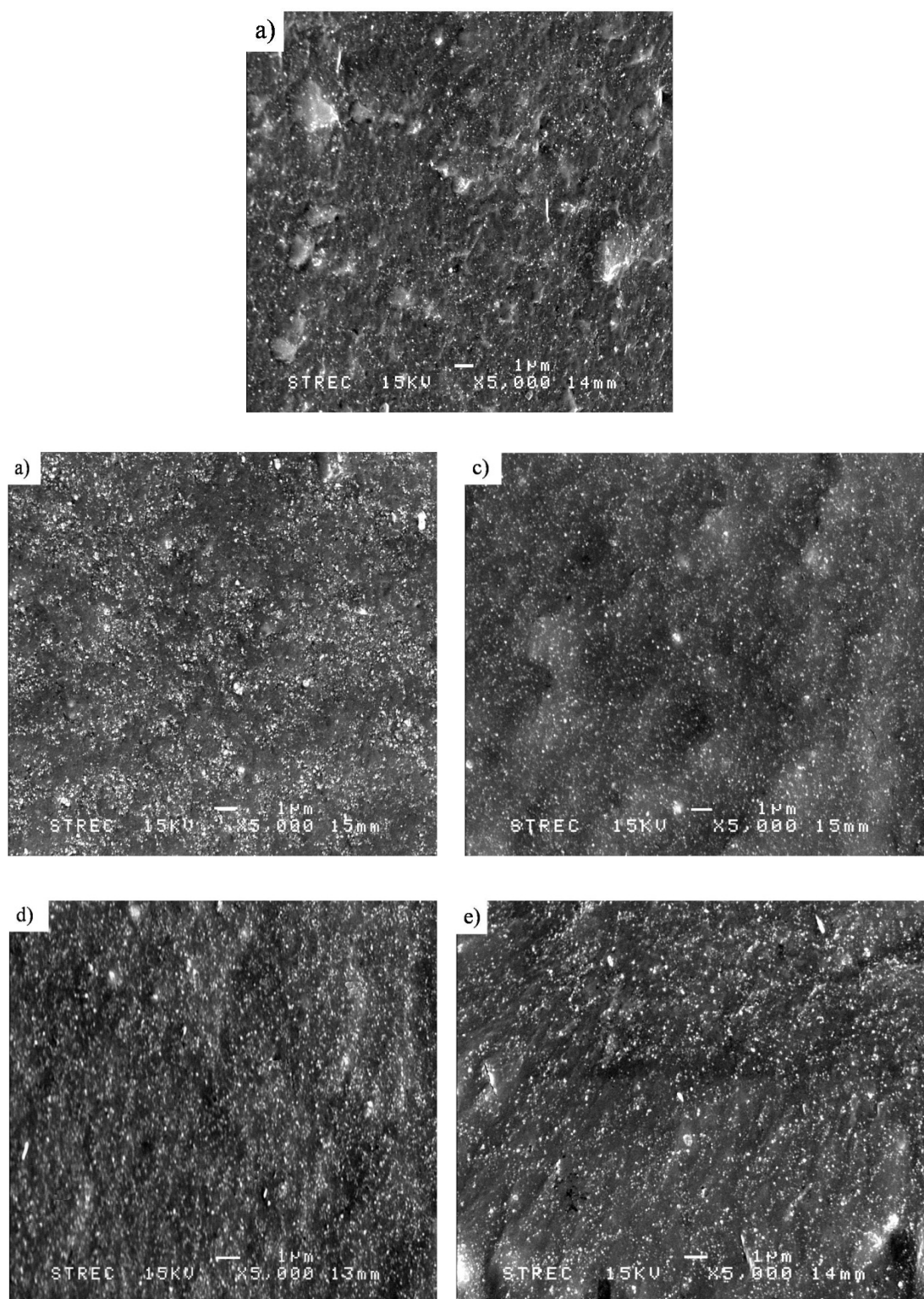


Figure 5.34 SEM images of CPTES-modified PSi filled CR by pre-modified technique with CPTES loading of: a) 0%; b) 2%; c) 4%; d) 6% and e) 8%.

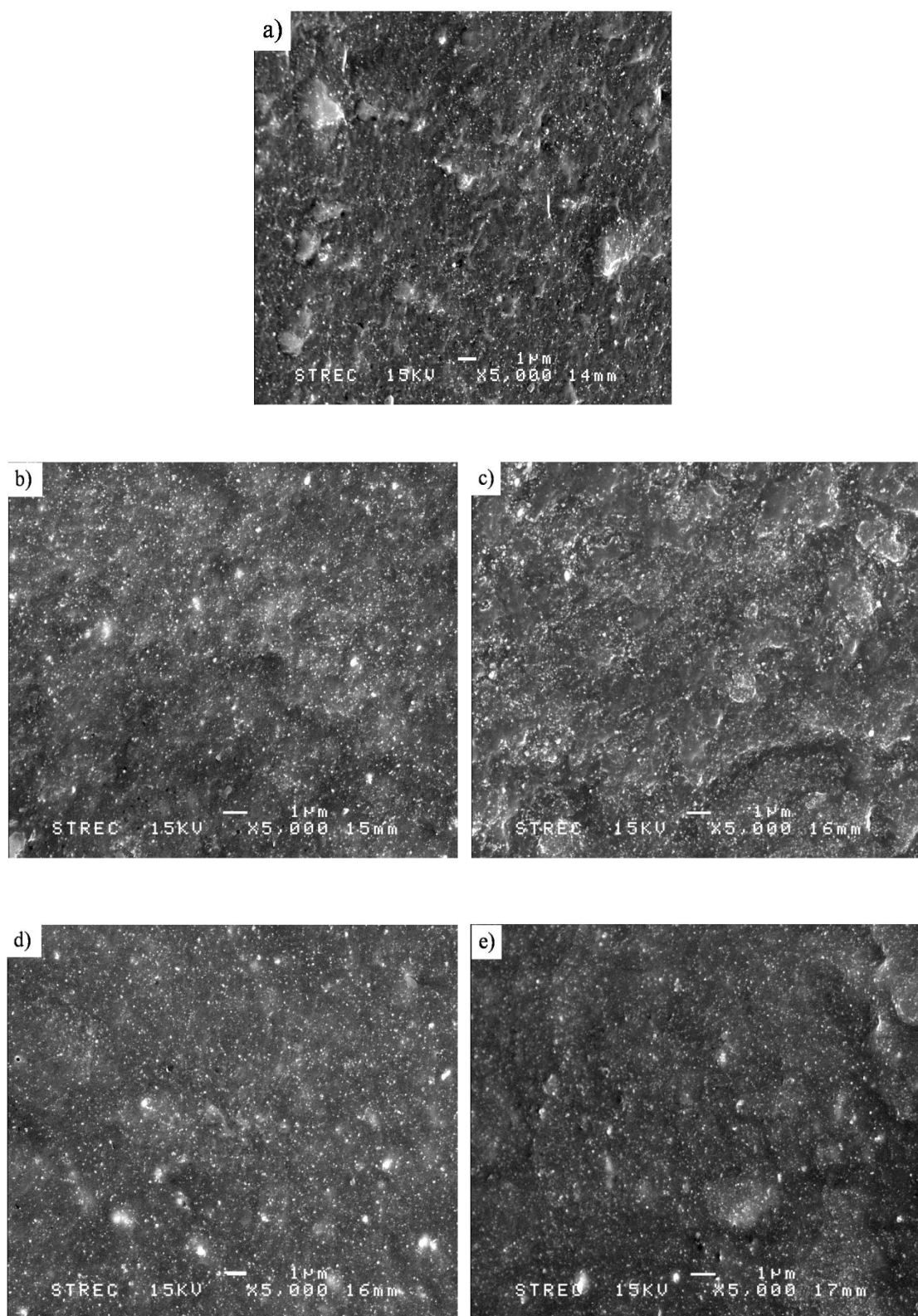


Figure 5.35 SEM images of TESPT-modified PSi filled CR by in-situ technique with CPTES loading of: a) 0%; b) 2%; c) 4%; d) 6% and e) 8%.

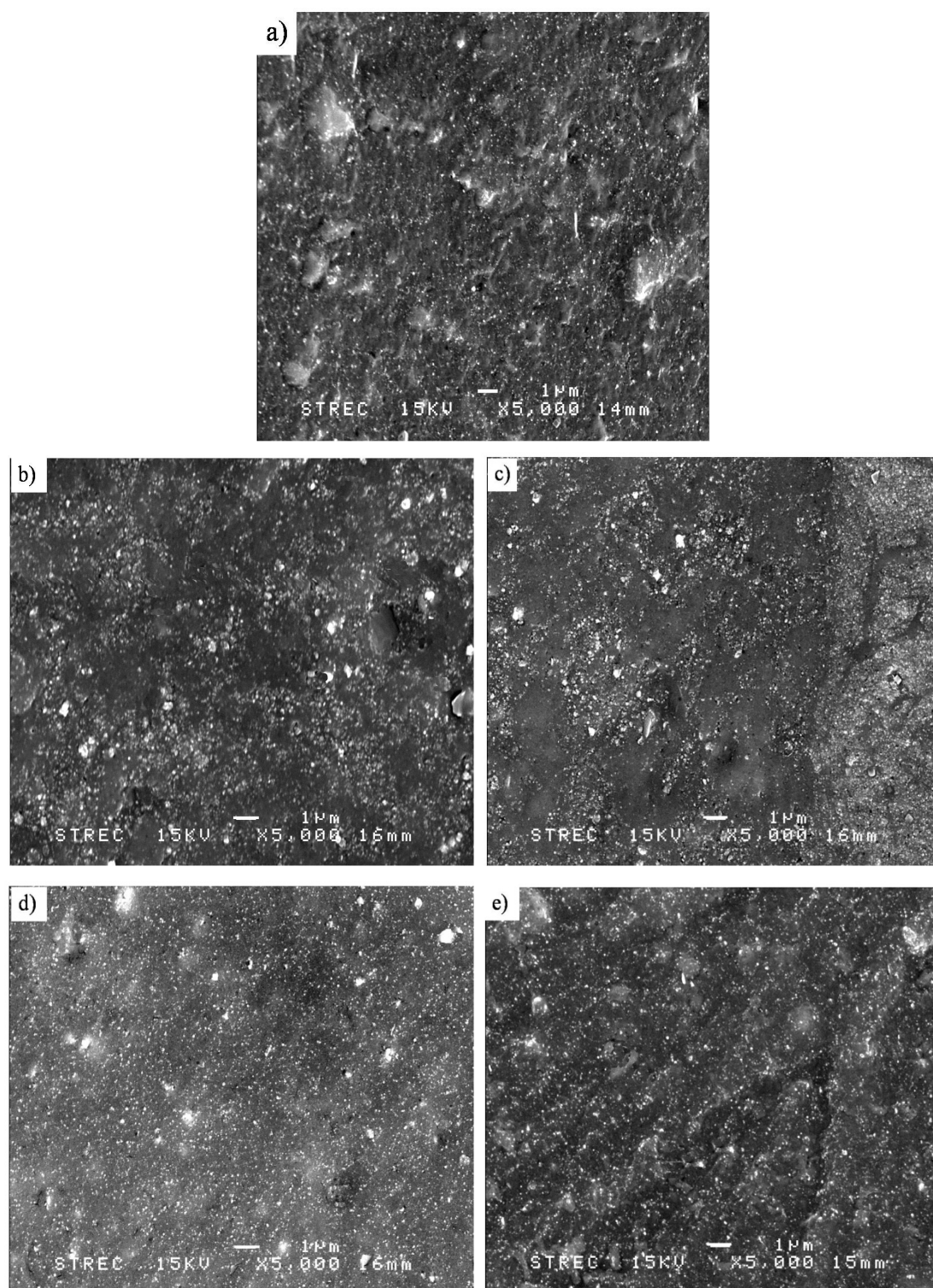
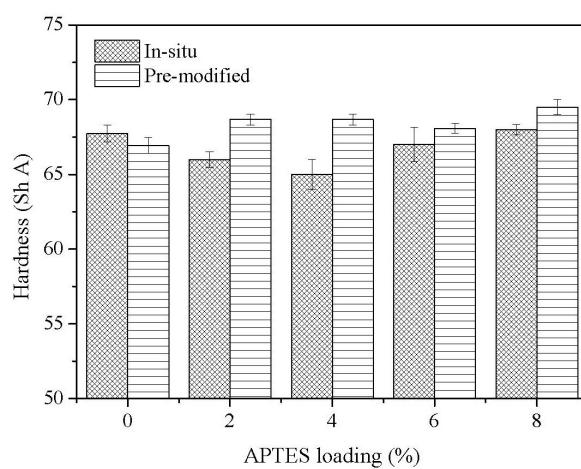


Figure 5.36 SEM images of TESPT-modified PSi filled CR by pre-modified technique with CPTES loading of: a) 0%; b) 2%; c) 4%; d) 6% and e) 8%.

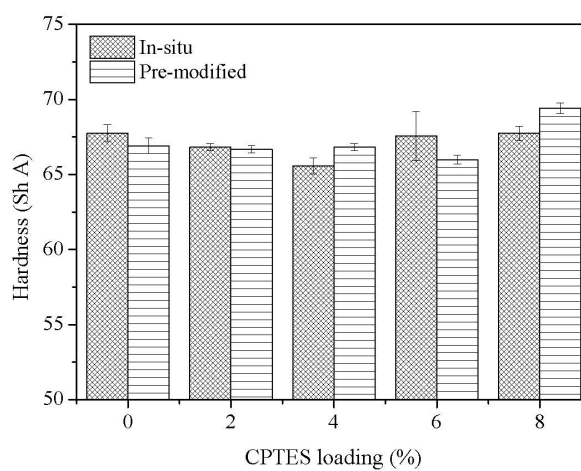
5.7.5 Mechanical properties

Results of hardness and tensile properties, i.e., tensile strength (TS), M100 and elongation at break (Eb) of CR cured specimens with various loadings of SCA as prepared by different surface treatment techniques are shown in Figures 5.37-5.40 respectively. The lowest hardness and M100 of CR cured specimens are found in the system with unmodified PSi or 0% SCA. This could be caused by the lowest in filler-filler dispersion degree as evidenced by the highest magnitude of Payne effect (see Table 5.21). In the presence of SCA system, hardness and M100 tend to increase with increasing TESPT loading. In the systems modified with APTES and CPTES, hardness and M100 decrease up to 4% SCA content and then increase. Similar to hardness and modulus results, the increase in SCA loading especially TESPT and APTES provides a similar trend of tensile strength. Explanations are given by the combined effects of improved rubber-filler interaction, increased crosslink density and enhanced PSi dispersion. The decrease in the Eb (see Figure 5.40) of cured specimens with all SCAs could be caused by the increase of crosslink density. Comparing with 2 surface treatment techniques, the in-situ technique provides greater mechanical properties than does the pre-modified technique.

(a)



(b)



(c)

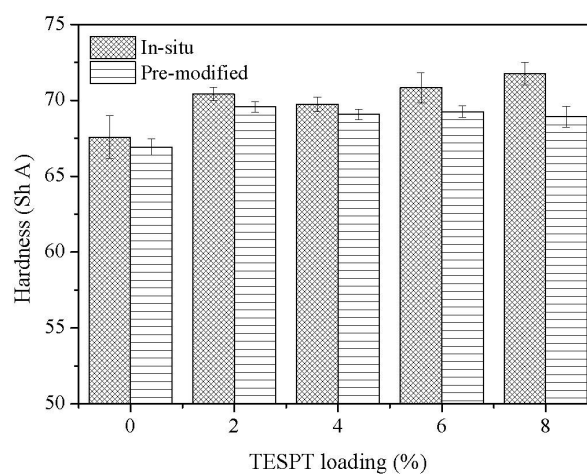
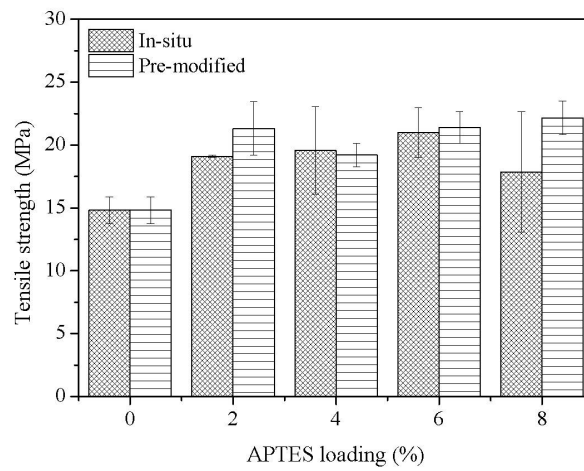
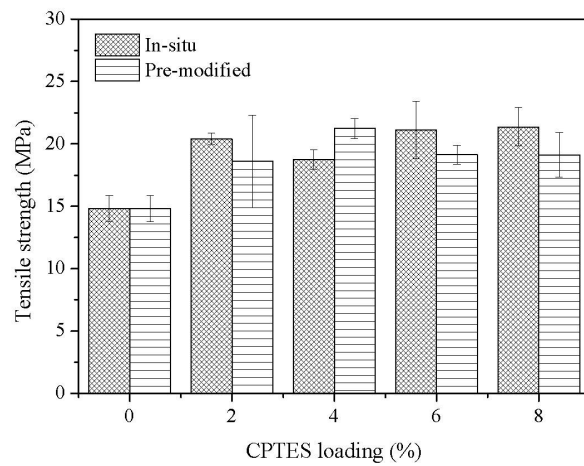


Figure 5.37 Hardness comparison of CR cured specimens (prepared by different surface treatment techniques) with various SCA loadings: (a) APTES; (b) CPTES and (c) TESPT.

(a)



(b)



(c)

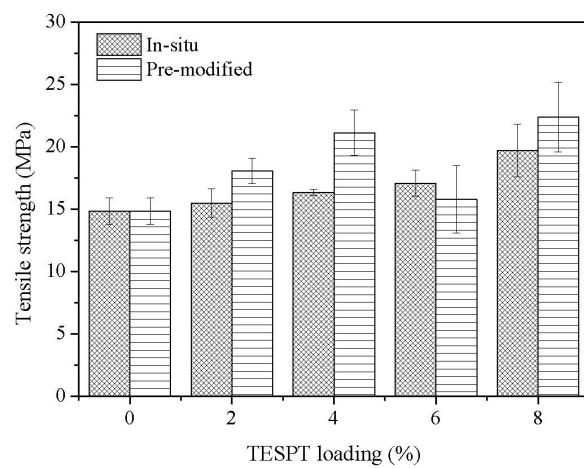
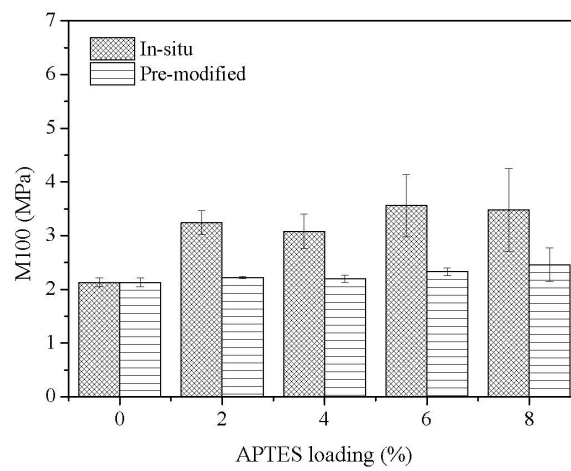
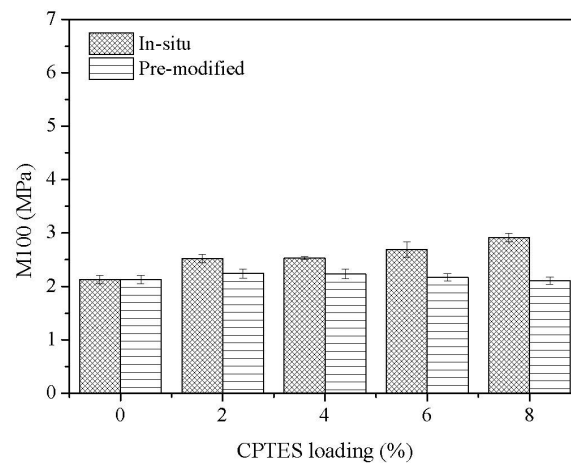


Figure 5.38 Tensile strength comparison of CR cured specimens (prepared by different surface treatment techniques) with various SCA loadings: (a) APTES; (b) CPTES and (c) TESPT.

(a)



(b)



(c)

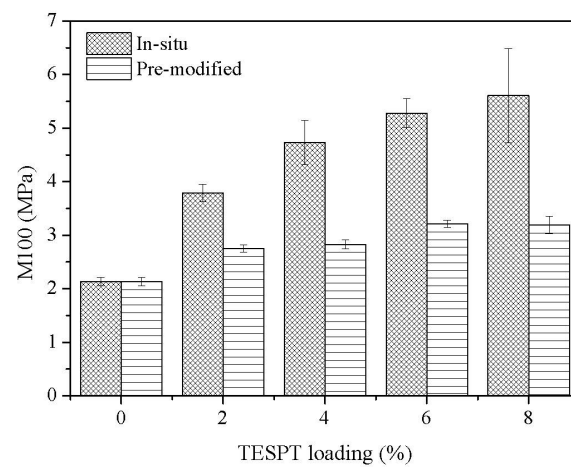
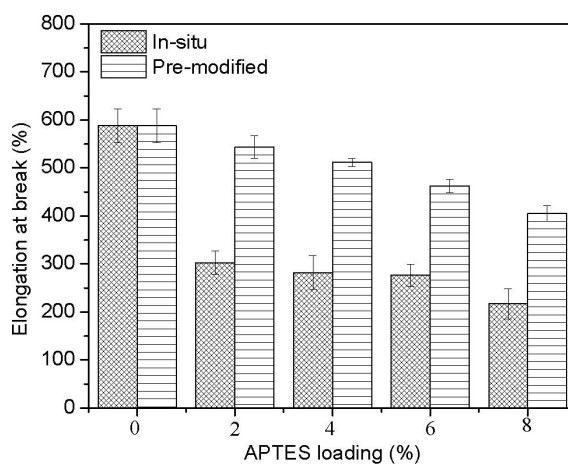
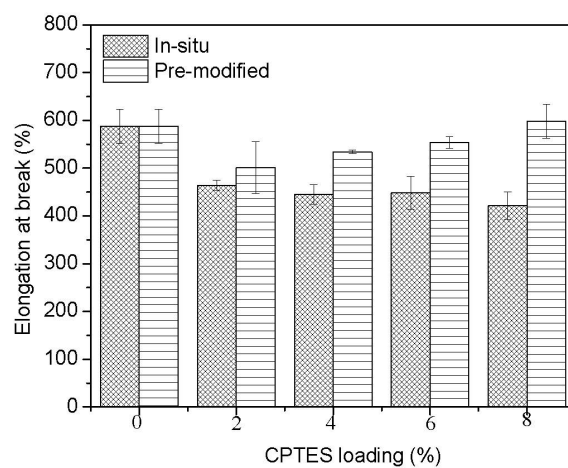


Figure 5.39 100% modulus (M100) comparison of CR cured specimens (prepared by different surface treatment techniques) with various SCA loadings: (a) APTES; (b) CPTES and (c) TESPT.

(a)



(b)



(c)

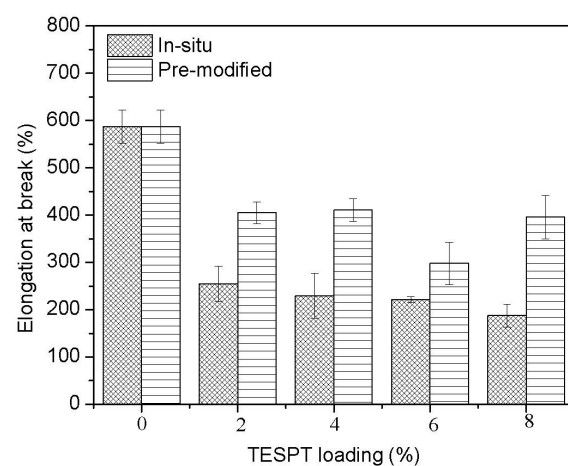
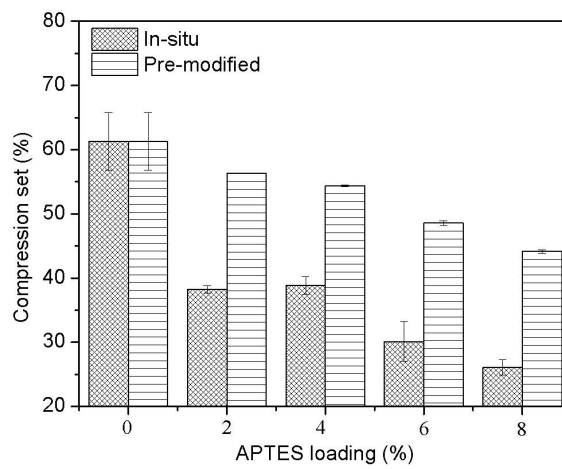


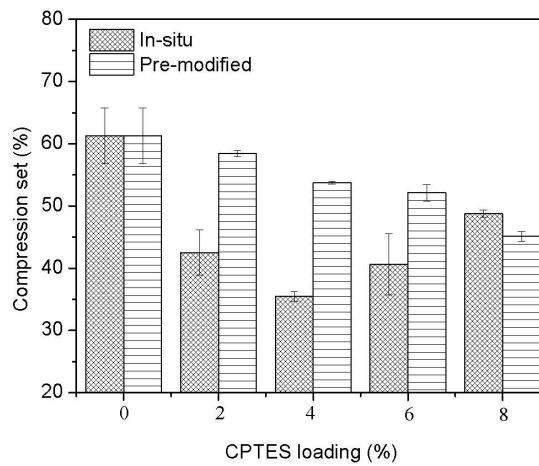
Figure 5.40 Elongation at break results comparison of CR cured specimens (prepared by different surface treatment techniques) with various SCA loadings: (a) APTES; (b) CPTES and (c) TESPT.

Figure 5.41 reveals compression set results of CR cured specimens with various loadings of SCA prepared with different surface treatment techniques. As evidenced in Figure 5.41, the system with unmodified PSi gives the highest magnitude of compression set. This could be caused by its low filler dispersion, low rubber-filler interaction and crosslink density as mentioned earlier. With the presence of SCA, the compression set tends to decrease. It is evident that the SCA increases the interaction between PSi and rubber. Furthermore, SCA loading affects the compression set of PSi filled CR. In both of APTES and TESPT systems (see Figure 5.41a and c), compression set decreases with increasing APTES and TESPT loading. It is believed that amino and mercapto groups of both SCAs improve rubber-filler interaction and thus increase crosslink density more effectively than chloro-group of CPTES. In the system modified with CPTES (see Figure 5.41b), compression set decreases up to 4% SCA content and then increases. It could be caused by the interaction between PSi and CR taking place through the hydrogen bonds, i.e., the hydrogen atom of the silanol group having a locally positive charge could interact with chlorine atom of CR which has a locally negative charge [148, 152]. Hence, the use of CPTES, chloro group of CPTES may interact with silanol group on the PSi surfaces resulting in their low rubber-filler interaction and then low crosslink density. Comparing with 2 surfaces treatment techniques, the in-situ technique gives lower magnitude of compression set than the pre-modified technique.

(a)



(b)



(c)

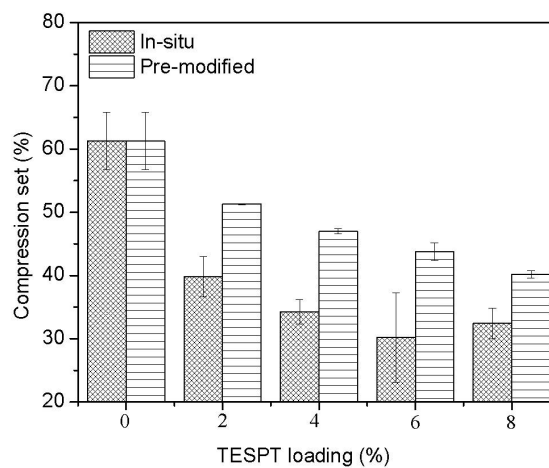
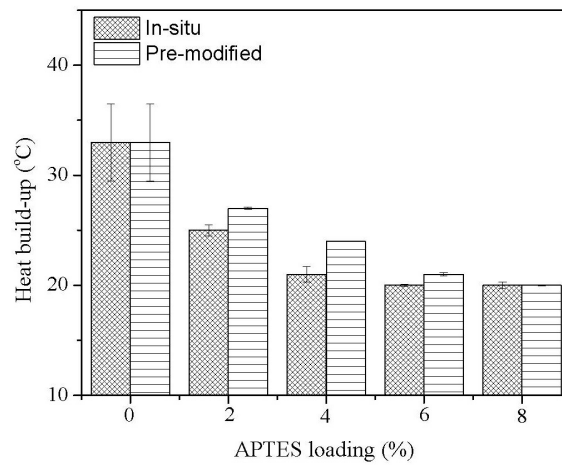


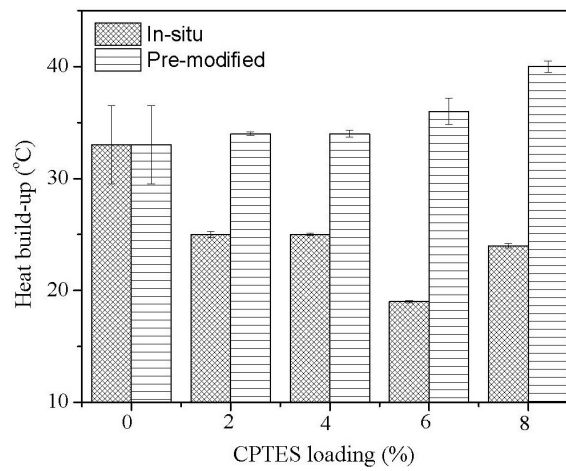
Figure 5.41 Compression set comparison of CR cured specimens (prepared by different surface treatment techniques) with various SCA loadings: (a) APTES; (b) CPTES and (c) TESPT.

Heat build-up (HBU) test is a measurement of temperature rise in the cured specimens as a result of viscoelastic nature of polymers. Part of the applied stress is dissipated by viscous flow between molecules and converted into thermal energy. Figure 5.42 shows the HBU comparison of CR cured specimens with various loadings of SCA prepared by different surface treatment techniques. The system with unmodified PSi exhibits the highest HBU, which may be due to the lowest magnitudes of rubber-filler interaction (as evidenced by the BRC results) and of crosslink density. Regardless of surface treatment techniques, the systems modified with APTES and TESPT show a decrease in the HBU with increasing APTES and TESPT loading. This is caused by the increased crosslink density and thus the elastic contribution of CR cured specimens. By contrast, the HBU of the system modified with CPTES depends on surface treatment technique. Comparing with 2 surfaces treatment techniques, the CPTES in pre-modified techniques provides the increase in HBU with increasing CPTES loading. The weak interaction between chloro end chain of CPTES and chloro group on CR backbone via dipole-dipole interaction is believed to be responsible. The higher energy loss during the cyclic deformation via molecular slippage of rubber molecule on PSi surfaces in the system with CPTES is therefore resulted.

(a)



(b)



(c)

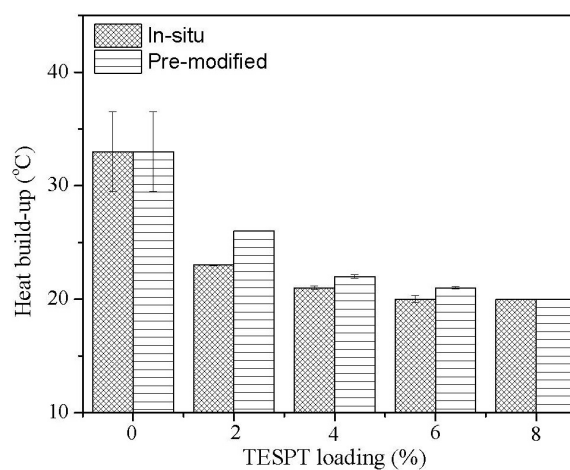
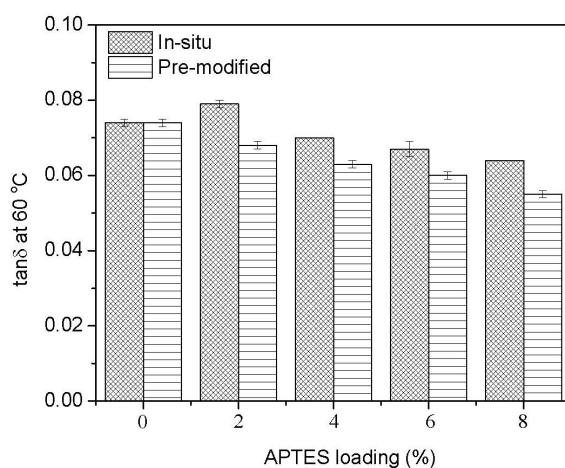


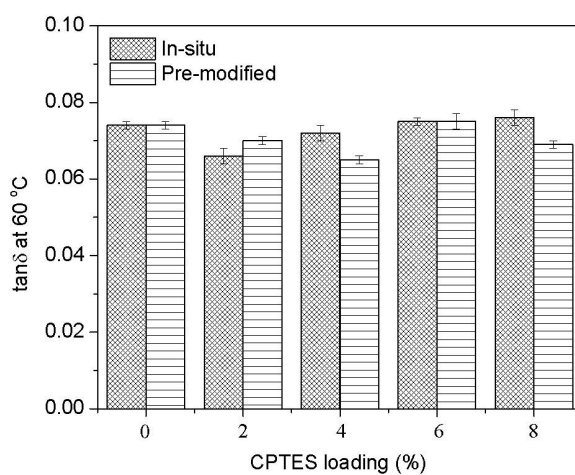
Figure 5.42 Heat build-up results of CR cured specimens (prepared by different surface treatment techniques) with various SCA loadings: (a) APTES; (b) CPTES and (c) TESPT.

Dynamic mechanical properties of CR cured specimens modified with various loadings of SCA and prepared with different surface treatment techniques are exhibited in Figure 5.43. It is evident that, regardless of surface treatment techniques, the systems modified with APTES and TESPT provide similar trend of $\tan\delta$ at 60 °C (as an indication of rolling resistance). The $\tan\delta$ decreases with increasing APTES and TESPT loading (see Figures 5.43a and 5.43c). These results suggest that the increase of SCA loading gives the increase in rubber-filler interaction. Also, the increases of APTES and TESPT loadings are capable of increasing the magnitude of crosslink density and thus a reduction in energy dissipation ($\tan\delta$). In other words, the surface treatment of PSi surfaces by APTES and TESPT could significantly reduce the rolling resistance in the applications subjected to cyclic deformation such as industrial rollers.

(a)



(b)



(c)

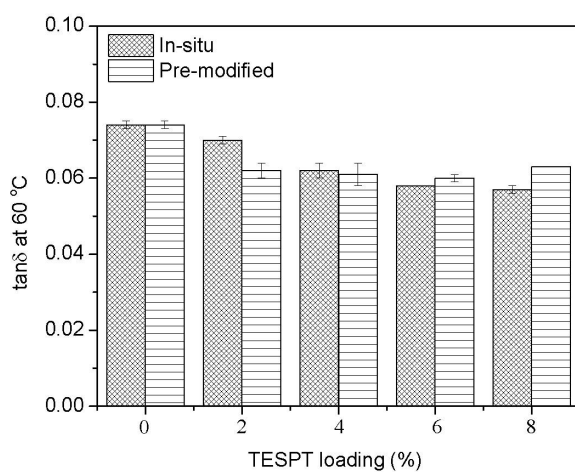
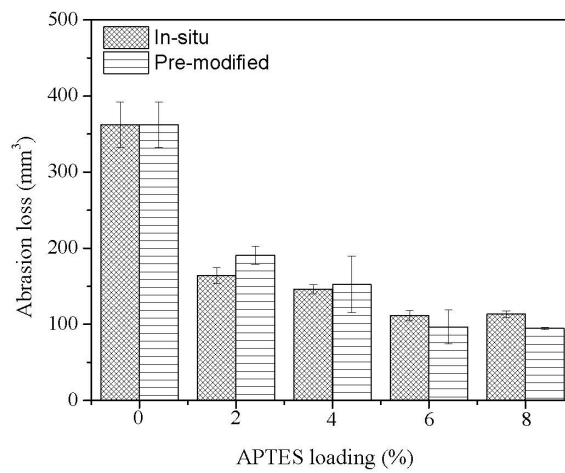


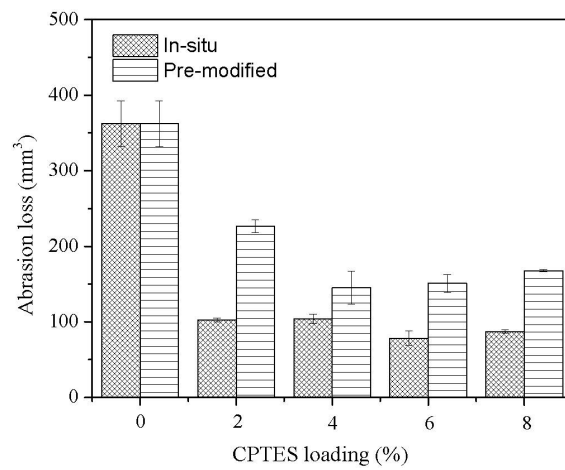
Figure 5.43 Comparison of $\tan\delta$ at 60°C in CR cured specimens (prepared by different surface treatment techniques) with various SCA loadings: (a) APTES; (b) CPTES and (c) TESPT.

Abrasion loss results of CR cured specimens with various loadings of SCA prepared by different surface treatment techniques are presented in Figure 5.44. It is found that, with both silane treatment techniques, the enhancement in abrasion resistance is observed. The magnitude of abrasion loss decreases with increasing SCA loading via various possible reasons; (i) improved filler-filler dispersion (ii) improved rubber-filler interaction and (iii) improved state-of-mix in the P*Si* filled CR composites. Among 3 SCAs, the TESPT (see Figure 5.44c) demonstrates the highest abrasion resistance in both surface treatment techniques followed by APTES and CPTES (see Figures 5.44 (a-b)), respectively. This result corresponds to the high reactivity of mercapto group of TESPT through the sulfur contribution effect.

(a)



(b)



(c)

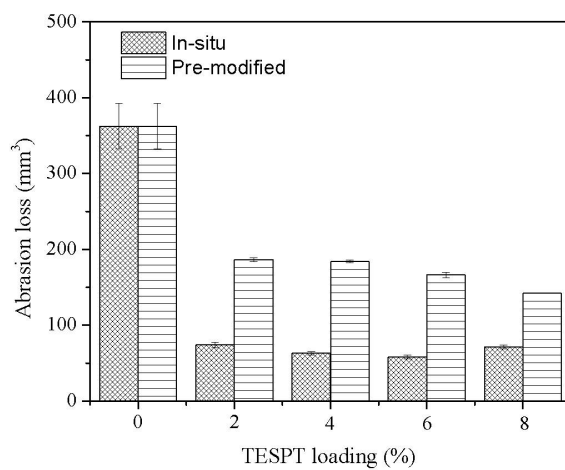


Figure 5.44 Abrasion loss of CR cured specimens (prepared by different surface treatment techniques) with various SCA loadings: (a) APTES; (b) CPTES and (c) TESPT.

5.8 Influence of pH condition of APTES system on properties of rubber compounds

In this section, the conditions with 3 different pH (pH = 2, 6 and 12) are used to modify the PSi surfaces with APTES. Then, the modified PSi is incorporated with CR and curatives. Influence of pH condition on properties of compounds and cured rubber is discussed.

Table 5.24 Payne effect and BRC of CR filled with 6% APTES-modified PSi prepared by different pH treatment conditions.

Systems	$\Delta G'$ (kPa)	BRC (%)
Unmodified	370.43 ± 0.20	37.35 ± 0.78
pH 2	354.04 ± 0.41	45.04 ± 6.30
pH 6	250.24 ± 0.13	51.84 ± 1.23
pH 12	404.20 ± 0.15	60.06 ± 7.20

5.8.1 Payne effect and BRC

Table 5.24 shows the influence of pH condition used for silanization reaction on properties of rubber compounds. The lowest Payne effect magnitude is found in APTES-modified PSi at pH 6. This is because, by preparing APTES at pH 6, the products immediately form oligomers retaining the solubility in water to the moderate concentrations [4]. Moreover, at pH 6 condition, there is no evidence of amine salt formation or penta-coordinate silicon, but most likely structure is an internal hydrogen-bonded seven-membered ring [4]. Thus, it is believed that, the PSi surfaces are covered by APTES resulting in low filler-filler network formation. Surprisingly, the APTES-modified PSi at pH 12 provides the highest Payne effect magnitude. Explanation is given by the high reactivity of $N^+ \cdots O \cdots H \cdots N^+$ interaction to form oligomer structure on the PSi surfaces as evidenced by mean average particle size result (see Table 5.14) resulting in high modulus at low strains. Regarding the influence of APTES-modified PSi at different pH condition on BRC, the highest BRC is found in the alkaline condition (pH 12). This might be due to the high reactivity of

amino groups and chloro groups of CR via N^+-Cl^- interaction or amino end groups and allylic carbon atom of CR via C-N interaction.

5.8.2 Cure characteristics

Table 5.25 reveals the cure characteristics, i.e., scorch time (t_{s2}), torque difference (M_H-M_L) and cure time (t_{c99}) of APTES-modified PSi at different pH condition. The results show that t_{s2} at pH 6 is shorter than that of pH 2 condition. This could be explained by the behavior of APTES-modified PSi at the acid condition (pH 2) which behaves like acidic surfaces as evidenced in zeta potential results (positive charge) leading to the curative adsorption on PSi surfaces. At pH 6, a mild positive charge which no ammonium salts character is resulted. Therefore, amino end chain of APTES under condition of pH 6 may behave like primary amine probably acting as accelerating substance in curing process [5]. In pH 12 conditions, the self-cyclization of APTES takes place giving low amount of silanol groups on the PSi surfaces as evidenced in Sear number and zeta potential results. The small amount of silanol groups on PSi surfaces leads to low magnitude of curing agent adsorption and thus, the decrease in scorch time (t_{s2}). Moreover, the torque difference (M_H-M_L), as crosslink density indicator, depends on acid-base condition. The highest magnitude of crosslink density is observed at pH 12. This could be caused by the relatively high reactivity of amino end chain contributes to the relatively high crosslink density of cured specimens as evidenced in Figure 5.45. With pH 6, the lowest crosslink density is observed. It is evident that the APTES-modified PSi may exist as zwitterions structure [4], which may reduce the reactivity of amino end chain to the CR backbone.

Table 5.25 Cure characteristics of CR filled with 6% APTES-modified PSi prepared by different pH treatment conditions.

Systems	t_{s2} (min)	M_H-M_L (dN.m)	t_{c99} (min)
Unmodified	2.10±0.09	8.49±0.12	66.55±0.97
pH 2	2.33±0.16	10.75±0.66	67.61±2.28
pH 6	1.80±0.11	8.09±0.06	70.30±5.74
pH 12	1.85±0.05	12.72±0.07	43.25±0.32

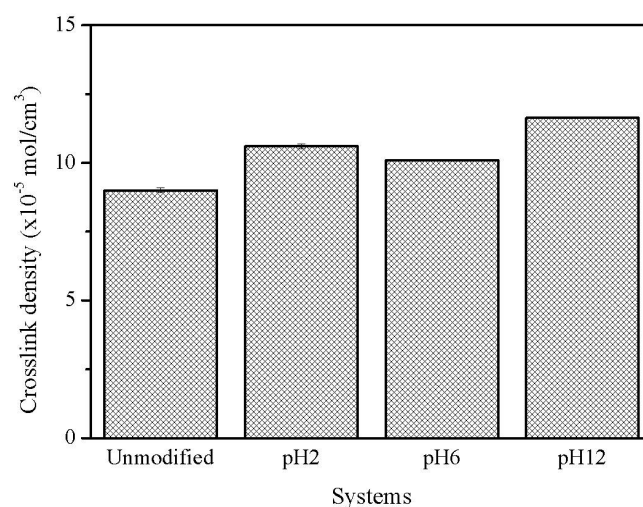


Figure 5.45 Crosslink density via swelling of CR cured specimens with 6% APTES-modified PSi at different pH condition.

5.8.3 Morphology

Figure 5.46 reveals SEM images of CR vulcanizates filled with APTES-modified PSi prepared with different pH conditions. The results show that the pH conditions affect on the PSi aggregate size and its dispersion degree in CR matrix. Among 3 pH conditions investigated, the pH 6 (see Figure 5.46b) provides the smallest PSi aggregate sizes. Explanation is given by the interaction between APTES and silanol groups on PSi surfaces, leading to low level of filler-filler network formation and thus the reduced PSi aggregation size and enhanced filler dispersion.

5.8.4 Mechanical properties

Hardness and tensile properties as a function of pH condition of APTES-modified PSi filled CR are given in Table 5.26. Apparently, the lowest hardness, M100 and strength but highest Eb are found in the modified system at pH 6. Explanations are given by the lowest crosslink density as illustrated previously in Table 5.25.

The influence of acid-base condition for PSi surface modification on compression set of CR cured specimens is given in Figure 5.47. It is evident that the lowest compression set is found in the modified system at pH 12. This can be attributed to the greatest crosslink density as discussed earlier in Table 5.25. On the

contrary, the highest compression set is observed in the modified system at pH 6. Again, the lowest crosslink density is responsible.

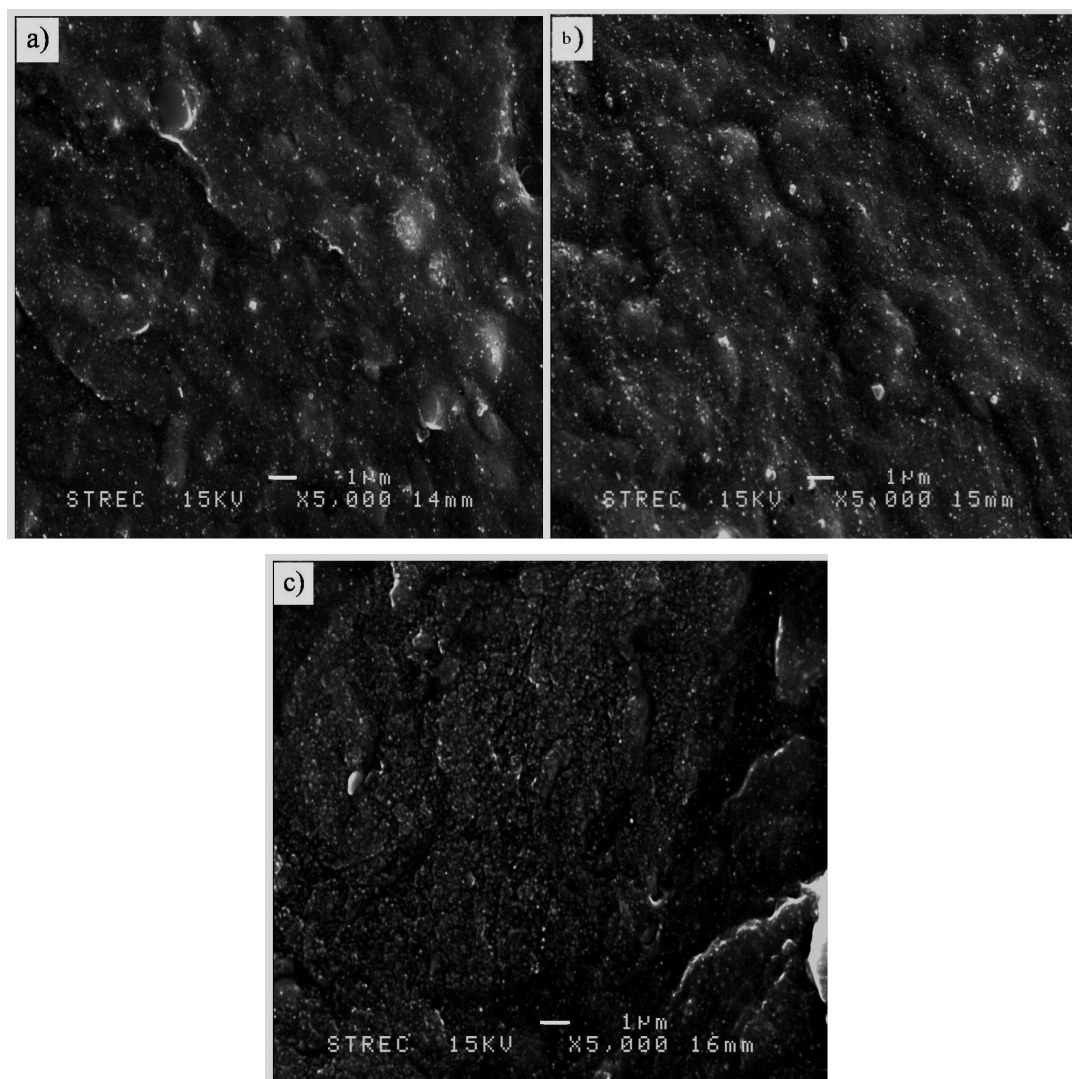


Figure 5.46 SEM images of CR filled with 6% APTES-modified PSi prepared by different pH treatment conditions: (a) pH 2; (b) pH 6 and (c) pH 12.

Table 5.26 Mechanical properties of CR filled with 6% APTES-modified PSi prepared by different pH treatment conditions.

Systems	Hardness (Sh A)	Tensile strength (MPa)	M100 (MPa)	Eb (%)
Unmodified	63.0±0.5	14.81±1.06	3.37±0.37	334±55
pH 2	65.8±1.8	20.68±0.68	4.44±0.63	303±21
pH 6	63.5±0.5	19.31±1.27	2.33±0.07	462±14
pH 12	66.5±0.8	21.22±3.98	4.18±0.65	276±48

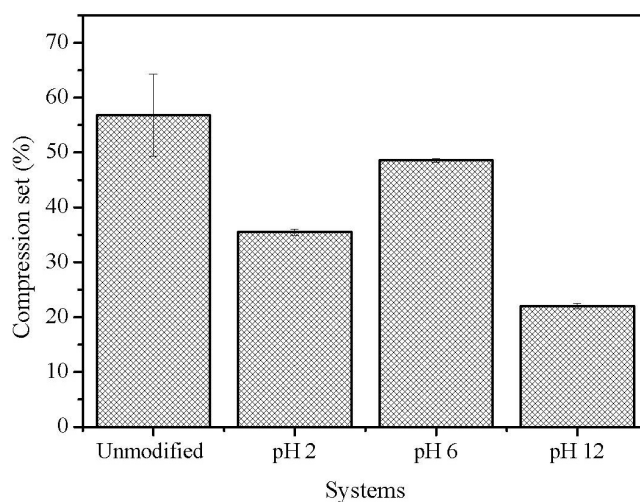


Figure 5.47 Compression set of CR filled with 6% APTES-modified PSi prepared by different pH treatment conditions.

Abrasion resistance results of CR filled with APTES-modified PSi prepared by different pH conditions are displayed in Figure 5.48. It is evident that lowest volume loss (or highest abrasion resistance) is found in the modified system at pH 12 which, could be due to the high magnitude of filler-rubber interaction and crosslink density as revealed previously in Tables 5.24-5.25 and Figure 5.45, respectively. The comparable abrasion resistance to the system modified at pH 12 is

found in the system modified at pH 6 which is believed to be due to its good dispersion in CR matrix as evidenced in the Payne effect results (see Table 5.24).

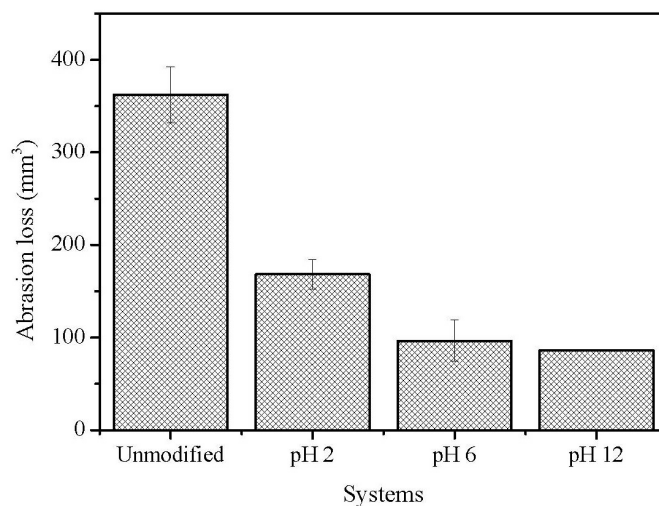


Figure 5.48 Abrasion loss of CR filled with 6% APTES-modified PSi by different pH treatment condition.

Figure 5.49 reveals HBU of CR cured specimens filled with APTES-modified PSi prepared by different pH condition. Clearly, the lowest magnitude of HBU is found in the modified system at pH 12 followed by pH 6 and pH 2, respectively. It might be due to the combined effect of greatest rubber-filler interaction (as evidenced by BRC) and crosslink density. In other words, the reduction in HBU is affected by increases in filler-rubber interaction and crosslink density.

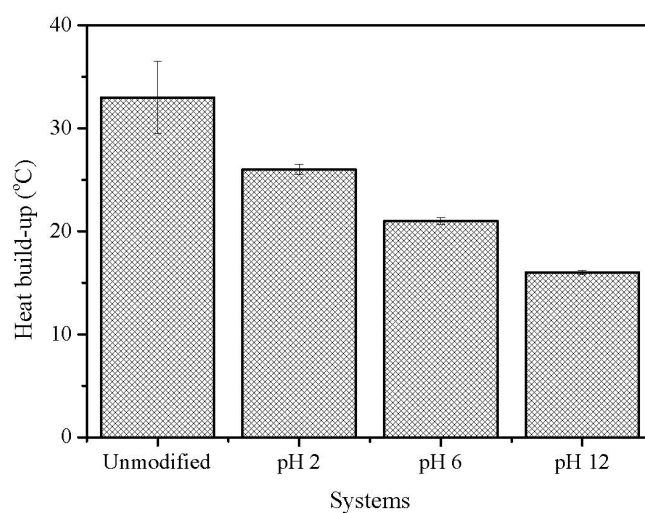


Figure 5.49 Heat build-up (HBU) of CR filled with 6% APTES-modified PSi prepared at different pH conditions.

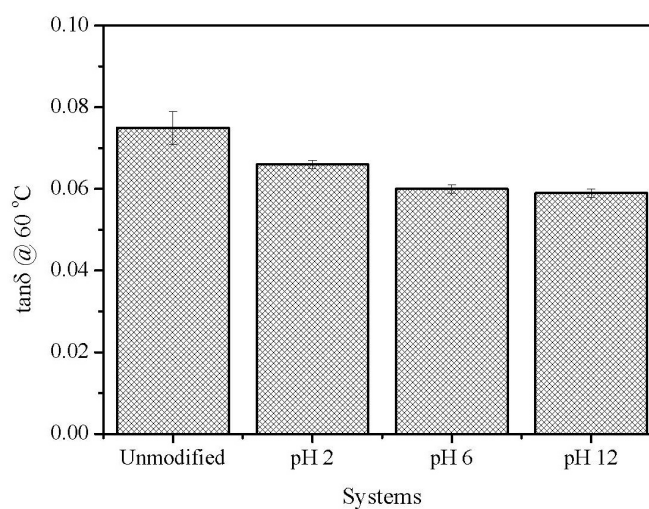


Figure 5.50 $\tan\delta$ at 60 °C of CR filled with 6% APTES-modified PSi prepared by different pH conditions.

Figure 5.50 shows the $\tan\delta$ at 60°C as affected by pH for PSi surface treatment of CR cured specimens. It is evident that the pH condition slightly affects the loss factor. The relatively low loss factor is found in APTES-modified PSi at pH 6 and pH 12. The results agree well with increased crosslink density and enhanced rubber-filler interaction as discussed earlier.

CHAPTER VI

CONCLUSIONS

Part 1:PSi Surface modification by silanization method

Influence of types and loading of SCA on PSi surface modification

Modification of PSi surfaces with 3 types of organo-alkoxysilane was carried out, and characterized by BET, particle size analysis, DRIFT and ^{29}Si NMR spectroscopy, elementary analysis, Sear number, and zeta potential. After being modified with SCA, the modified PSi shows an increase in aggregate size. The FTIR result exhibits wetted PSi surfaces with SCA. The ^{29}Si -NMR result of PSi suggests the difference in silane structure on the PSi surfaces. Furthermore, FTIR technique demonstrates the relative SCA grafting efficiency on PSi surfaces in the following order: TESPT > APTES > CPTES.

Influence of acid-base condition on PSi surface modification

In this part, the APTES is selected to further study for an influence of acid-base condition on silanization reaction. The sensitivity of amino-end chain to acid-base condition is focused. Acid-base conditions of APTES treatment show no significant effect on aggregate size of PSi. The largest amount of APTES grafted on PSi surface is found at pH 2 and pH 12 as evidenced by results of FTIR and elementary analysis.

Part 2: Effect of surface modification technique on properties of CR compounds and vulcanizates

Influence of surface treatment technique on Payne effect and bound rubber content of CR compounds

The magnitude of Payne effect as an indication of filler network level is in the following order: unmodified PSi > CPTES > APTES > TESPT. The bound rubber content (BRC) is found to increase after PSi surface modification with silanes. Among the 3 silanes, the TESPT gives the highest BRC whereas the CPTES shows the lowest.

Influence of surface treatment technique on mechanical and dynamic properties of CR vulcanizates

The TESPT-modified PSi gives the greatest hardness and modulus, followed by APTES and CPTES. Both TESPT and APTES show superior performance in compression set to CPTES. The systems modified with TESPT and APTES exhibit relatively low HBU.

Influence of acid-base condition on CR compounds and vulcanizates

Acid-base condition for PSi surfaces modification with APTES plays significant role on coupling efficiency. The modified PSi at pH 6 provides the highest efficiency in reducing the Payne effect ($\Delta G'$) while that at pH 12 gives the highest BRC. The CR filled with APTES-modified PSi prepared at pH 2 and pH 12 provides the best mechanical and dynamic properties of CR cured specimens.

Comments and suggestions

In this work, CR is used as rubber matrix, and is curable mainly with metal oxide. To effectively reinforce with precipitated silica (PSi), coupling agents are typically used. There are 3 silane types, namely, aminosilane (APTES), chlorosilane (CPTES) and mercaptosilane (TESPT) investigated as coupling agents in this work. In general, the TESPT is used in most sulfur curable rubber due to the capability of co-vulcanization with rubber matrix. However, the TESPT is sometimes used in CR systems despite the fact that the CR is usually crosslinked with metal oxide rather than

sulfur. Furthermore, in theory, the uses of APTES and CPTES are anticipated to give greater coupling efficiency via the interaction of either amino end group ($-\text{NH}_2$) of APTES or chloro group of CPTES with Cl atom of CR backbone. As a consequence, this research aims to clarify the level of coupling efficiency provided by those 3 silanes.

The results gained from this work reveal that, the TESPT still exhibits the greatest levels of coupling efficiency, PSi dispersion and crosslink density in CR cured with metal oxide. On the contrary, the poor performance of APTES is believed to be the result of self-cyclization. The PSi filled CR systems modified CPTES are suffered from poor dipole-dipole interaction in conjunction with low crosslink density.

The suggestion for the uses of silanes (among TESPT, APTES and CPTES) in PSi-filled CR systems is the utilization of TESPT as a first priority where applicable. The use of APTES with good coupling efficiency is possible if the self-cyclization could be minimized. Lastly, the used of CPTES is not recommended in the PSi-filled CR systems.

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APPENDICES

APPENDIX A

EFFECT OF SCAS TYPE ON MODIFIED PSi FILLED CR

Table A1 Strain sweep of modified PSi with 0% mSCAs type in CR compound.

Strain (%)	G' modulus (kPa)		
	No. 1	No. 2	No.3
0.56	362.49	296.46	414.74
0.98	400.27	370.33	390.29
1.95	380.31	356.66	363.26
3.07	359.57	342.35	345.65
5.02	335.35	319.97	333.51
10.04	301.89	287.82	294.05
15.07	279.51	264.27	269.04
19.95	259.29	246.56	252.4
29.99	230.19	219.6	223.65
49.94	187.53	178.91	181.76
100.02	129.31	124.23	124.79
200.04	84.567	79.97	80.884
300.06	64.279	60.282	60.299
499.97	44.529	41.821	42.005
999.94	23.608	22.974	23.064
1199.98	16.603	16.572	16.437

Table A2 Strain sweep of modified PSi with 2% mAPTES in CR compound.

Strain (%)	G' modulus (kPa)		
	No. 1	No. 2	No.3
0.56	339.37	417.68	384.54
0.98	355.92	372.55	379.2
1.95	345.11	366.33	371.36
3.07	323.94	344.62	339.1
5.02	311.97	332.52	330.17
10.04	284.8	300.6	297.64
15.07	264.41	279.55	275.23
19.95	249.55	261.11	257.48
29.99	225.36	233.39	229.48
49.94	186.85	190.83	187.4
100.02	129.73	130.77	127.88
200.04	81.219	82.386	81.486
300.06	59.593	58.741	60.033
499.97	40.792	40.797	40.381
999.94	21.828	22.081	21.57
1199.98	16.09	15.937	15.29

Table A3 Strain sweep of modified PSi with 4% mAPTES in CR compound.

Strain (%)	G' modulus (kPa)		
	No. 1	No. 2	No.3
0.56	336.22	338.23	337.225
0.98	328.2	355.92	342.06
1.95	325.57	331.34	328.455
3.07	305.33	302.59	303.96
5.02	296.4	295.37	295.885
10.04	265.01	263.94	264.475
15.07	244.8	244.39	244.595
19.95	229.52	228.87	229.195
29.99	205.54	204.55	205.045
49.94	168.03	167.26	167.645
100.02	112.81	113.3	113.055
200.04	67.973	70.128	69.0505
300.06	48.891	49.823	49.357
499.97	32.612	33.302	32.957
999.94	17.365	17.688	17.5265
1199.98	13.668	13.388	13.528

Table A4 Strain sweep of modified PSi with 6% mAPTES in CR compound.

Strain (%)	G' modulus (kPa)		
	No. 1	No. 2	No.3
0.56	365.98	349.44	357.71
0.98	342.61	325.15	333.88
1.95	337.29	321.1	329.195
3.07	315.33	297.48	306.405
5.02	304.96	292.17	298.565
10.04	278.57	265.96	272.265
15.07	257.43	246.04	251.735
19.95	241.71	231.23	236.47
29.99	216.03	206.91	211.47
49.94	176.38	170.22	173.3
100.02	118.82	115.9	117.36
200.04	71.5	72.676	72.088
300.06	52.118	52.318	52.218
499.97	35.621	35.754	35.6875
999.94	18.497	18.879	18.688
1199.98	13.563	13.809	13.686

Table A5 Strain sweep of modified PSi with 8% mAPTES in CR compound.

Strain (%)	G' modulus (kPa)		
	No. 1	No. 2	No.3
0.56	382.53	407.34	410.71
0.98	367.9	384.78	392.65
1.95	347.55	377.57	364.36
3.07	346.19	367.29	353.02
5.02	340.09	357.74	351.11
10.04	306.23	326.97	323.93
15.07	289.17	304.61	299.94
19.95	272.68	286.52	280.89
29.99	243.61	253.65	249.32
49.94	197.23	203.22	200.02
100.02	129.89	133.03	131.69
200.04	79.239	81.325	81.311
300.06	58.734	60.228	60.651
499.97	41.478	42.317	42.774
999.94	21.27	19.627	19.639
1199.98	15.083	14.009	13.859

Table A6 Strain sweep of modified PSi with 2% mCPTES in CR compound.

Strain (%)	G' modulus (kPa)		
	No. 1	No. 2	No.3
0.56	444.94	376.15	378.28
0.98	374.76	365.65	355.52
1.95	359.96	346.49	334.09
3.07	353.58	326.01	314.94
5.02	333.16	317.41	305.59
10.04	299.65	281.79	274.61
15.07	275.06	259.42	253.86
19.95	255.87	244.06	237.91
29.99	226.07	216.93	213.09
49.94	182.81	177.91	175.84
100.02	123.72	121.15	121.32
200.04	76.969	75.257	75.7
300.06	55.551	54.419	54.808
499.97	36.929	36.039	36.368
999.94	18.08	18.596	18.608
1199.98	13.382	15.011	15.208

Table A7 Strain sweep of modified PSi with 4% mCPTES in CR compound.

Strain (%)	G' modulus (kPa)		
	No. 1	No. 2	No.3
0.56	372.19	380.46	378.39
0.98	363.4	356.65	360.02
1.95	339.6	336.62	335.19
3.07	322.29	325.41	321.67
5.02	311.18	318.09	308.38
10.04	275.78	280.87	274.74
15.07	252.71	256.67	251.6
19.95	236.09	241.66	235.34
29.99	211.1	215.08	210.74
49.94	173.09	175.67	172.04
100.02	117.75	119.37	117.07
200.04	73.049	74.211	72.537
300.06	51.987	53.488	51.943
499.97	34.07	35.165	34.575
999.94	17.307	17.753	17.743
1199.98	13.863	14.045	14.593

Table A8 Strain sweep of modified PSi with 6% mCPTES in CR compound.

Strain (%)	G' modulus (kPa)		
	No. 1	No. 2	No.3
0.56	511.63	553.9	405.27
0.98	360.02	362.27	381.4
1.95	335.74	339.6	349.5
3.07	324.1	321.18	333.84
5.02	307.5	309.42	318.63
10.04	275.27	273.96	286.71
15.07	253.6	250.99	259.74
19.95	238.55	237.75	243.53
29.99	212.13	209.57	214.68
49.94	173.4	170.31	174.01
100.02	116.1	113.65	116.25
200.04	70.458	68.855	70.761
300.06	51.201	49.899	51.156
499.97	34.702	33.713	34.296
999.94	18.4	18.047	18.143
1199.98	14.561	14.437	14.174

Table A9 Strain sweep of modified PSi with 8% mCPTES in CR compound.

Strain (%)	G' modulus (kPa)		
	No. 1	No. 2	No.3
0.56	339.1	348.52	357.71
0.98	348.77	330.41	335.27
1.95	307.66	311.99	323.08
3.07	301.15	310.58	312.28
5.02	287.54	293.77	300.43
10.04	256.89	261.94	265.01
15.07	235.87	240.39	244.8
19.95	221.13	225.93	228.87
29.99	198.27	201.15	203.74
49.94	164.14	166.21	167.24
100.02	112.1	113.14	113.79
200.04	69.615	70.217	71.156
300.06	50.998	50.585	52.134
499.97	34.023	33.621	33.985
999.94	17.688	17.464	17.699
1199.98	14.773	14.837	14.739

Table A10 Strain sweep of modified PSi with 2% mTESPT in CR compound.

Strain (%)	G' modulus (kPa)		
	No. 1	No. 2	No.3
0.56	417.68	357.71	387.695
0.98	378.09	361.15	369.62
1.95	378.15	341.54	359.845
3.07	366.88	329.78	348.33
5.02	355.31	318.66	336.985
10.04	321.66	295.18	308.42
15.07	299.66	273.88	286.77
19.95	282.68	259.42	271.05
29.99	253.05	234.39	243.72
49.94	206.85	194.93	200.89
100.02	141.42	136.45	138.935
200.04	88.611	86.905	87.758
300.06	65.374	64.457	64.9155
499.97	44.737	43.48	44.1085
999.94	22.865	22.291	22.578
1199.98	16.606	16.556	16.581

Table A11 Strain sweep of modified PSi with 4% mTESPT in CR compound.

Strain (%)	G' modulus (kPa)		
	No. 1	No. 2	No.3
0.56	326.7	378.39	352.545
0.98	357.77	380.31	369.04
1.95	344.55	350.83	347.69
3.07	333.15	335.66	334.405
5.02	324.88	329.1	326.99
10.04	293.41	298.9	296.155
15.07	273.92	277.06	275.49
19.95	257.97	261.36	259.665
29.99	232.01	233.64	232.825
49.94	189.01	189.69	189.35
100.02	126.95	126.63	126.79
200.04	78.264	77.326	77.795
300.06	55.872	54.884	55.378
499.97	37.091	36.732	36.9115
999.94	19.873	19.598	19.7355
1199.98	15.04	15.067	15.0535

Table A12 Strain sweep of modified PSi with 6% mTESPT in CR compound.

Strain (%)	G' modulus (kPa)		
	No. 1	No. 2	No.3
0.56	337.04	337.04	337.04
0.98	315.02	327.09	321.055
1.95	308.77	308.77	308.77
3.07	289.48	302.91	296.195
5.02	284.65	295.09	289.87
10.04	263.46	271.23	267.345
15.07	246.34	254.24	250.29
19.95	233.15	240.03	236.59
29.99	209.88	216.18	213.03
49.94	172.87	177.27	175.07
100.02	117.02	118.72	117.87
200.04	73.141	73.343	73.242
300.06	52.456	54.189	53.3225
499.97	35.469	36.681	36.075
999.94	19.277	19.825	19.551
1199.98	16.366	16.621	16.4935

Table A13 Strain sweep of modified PSi with 8% mTESPT in CR compound.

Strain (%)	G' modulus (kPa)		
	No. 1	No. 2	No.3
0.56	351.51	306.02	328.765
0.98	325.15	290.5	307.825
1.95	303.27	272.69	287.98
3.07	297.33	280.05	288.69
5.02	290.38	266.38	278.38
10.04	262.24	245.24	253.74
15.07	242.02	228.74	235.38
19.95	228.77	215.95	222.36
29.99	204.81	195.4	200.105
49.94	167.21	161.66	164.435
100.02	111.79	109.26	110.525
200.04	69.285	66.306	67.7955
300.06	50.776	48.105	49.4405
499.97	34.95	33.136	34.043
999.94	19.494	18.792	19.143
1199.98	16.565	16.645	16.605

APPENDIX B

EFFECT OF SCAS TYPE ON PSi FILLED CR BY IN-SITU TECHNIQUE

Table B1 Strain sweep of PSi with 0% ISCA in CR compound by in-situ technique

Strain (%)	G' modulus (kPa)		
	No. 1	No. 2	No.3
0.56	317.79	288.37	280.52
0.98	324.02	313.78	297.15
1.95	308.22	319.78	280.7
3.07	301.46	317	283.91
5.02	284.86	300.46	272.38
10.04	261.61	272.24	246.91
15.07	242.76	253.81	230.58
19.95	226.91	237.48	215.55
29.99	206.04	213.05	194.61
49.94	170.8	175.33	161.77
100.02	118.21	121.26	112.59
200.04	72.836	75.337	70.378
300.06	53.843	55.377	52.131
499.97	37.483	38.471	36.128
999.94	21.364	21.169	20.143
1199.98	17.809	16.745	17.26

Table B2 Strain sweep of PSi with 2% I-APTES in CR compound by in-situ technique.

Strain (%)	G' modulus (kPa)		
	No. 1	No. 2	No.3
0.56	269.78	270.71	266.79
0.98	270.54	297.15	271.65
1.95	262.22	291.71	274.65
3.07	256.07	290.16	258.43
5.02	245.33	275.16	245.59
10.04	224.19	249.79	223.12
15.07	208.58	231.29	206.31
19.95	196.51	217.26	193.94
29.99	177.03	193.1	174.21
49.94	146.86	158.35	143.69
100.02	99.667	108.22	97.448
200.04	59.556	66.313	58.919
300.06	42.109	47.822	42.115
499.97	28.808	30.562	25.241
999.94	15.952	16.696	13.429
1199.98	13.072	12.652	11.275

Table B3 Strain sweep of PSi with 4% I-APTES in CR compound by in-situ technique.

Strain (%)	G' modulus (kPa)		
	No. 1	No. 2	No.3
0.56	281.86	273.81	316.09
0.98	267.21	283.85	293.82
1.95	267.21	273.55	295.56
3.07	263.4	270.22	291.92
5.02	255.16	258.53	275.89
10.04	233.13	237.27	251.4
15.07	217.88	221.71	234.63
19.95	205.28	208.8	220.11
29.99	186.05	188.67	197.72
49.94	153.01	156.11	161.3
100.02	103.82	106.36	108.1
200.04	62.277	64.853	65.692
300.06	46.087	48.648	48.383
499.97	31.618	33.423	33.695
999.94	17.752	18.632	19.087
1199.98	13.96	14.341	14.218

Table B4 Strain sweep of PSi with 6% I-APTES in CR compound by in-situ technique.

Strain (%)	G' modulus (kPa)		
	No. 1	No. 2	No.3
0.56	263.74	297.97	285.89
0.98	282.74	286.89	297.15
1.95	270.25	280.15	287.31
3.07	266.55	282.62	274.23
5.02	263.28	267.13	267.88
10.04	238.45	244.52	244.24
15.07	224.27	231.5	228.74
19.95	210.87	219.35	216.05
29.99	192.97	198.99	196.62
49.94	160.36	164.52	162.24
100.02	109.5	112.21	109.59
200.04	67.719	68.829	65.904
300.06	50.853	51.802	49.29
499.97	35.736	36.574	34.717
999.94	20.437	20.833	19.831
1199.98	14.828	15.059	14.937

Table B5 Strain sweep of PSi with 8% I-APTES in CR compound by in-situ technique.

Strain (%)	G' modulus (kPa)		
	No. 1	No. 2	No.3
0.56	376.32	362.39	407.34
0.98	351.48	368.11	375.87
1.95	351.7	359.41	368.77
3.07	348.13	353.18	355.5
5.02	327.97	339.45	340.43
10.04	299.11	308.57	307.62
15.07	279.17	285.9	285.53
19.95	264.29	267.8	268.09
29.99	233	238.02	238.59
49.94	190.93	192.82	194.34
100.02	128.02	128.91	130.43
200.04	79.433	79.705	81.476
300.06	59.633	59.683	60.95
499.97	42.991	42.516	43.74
999.94	22.535	21.897	22.114
1199.98	15.36	14.929	15.207

Table B6 Strain sweep of PSi with 2% I-CPTES in CR compound by in-situ technique.

Strain (%)	G' modulus (kPa)		
	No. 1	No. 2	No.3
0.52	411.47	368.79	394.61
0.95	376.9	388.07	401.38
1.95	354.66	363.68	368.77
3.04	346.38	345.68	362.17
4.97	333.74	336.15	342.99
9.99	302.28	304.95	308.36
15.07	281.37	283.59	288.26
19.95	266.59	265.55	273.19
30.06	240.59	240.32	243.92
49.97	197.91	197.53	199.44
100.08	135.12	133.44	134.92
200.15	83.736	81.684	82.761
300.11	62.081	60.339	61.162
499.98	42.465	41.064	41.992
999.92	23.109	22.626	22.889
1199.97	19.079	19.313	18.805

Table B7 Strain sweep of PSi with 4% I-CPTES in CR compound by in-situ technique.

Strain (%)	G' modulus (kPa)		
	No. 1	No. 2	No.3
0.56	405.27	452.99	428.02
0.98	393.61	406.92	388.07
1.95	372.07	362.16	368.77
3.07	362.17	350.39	358.55
5.02	351.33	333.37	342.45
10.04	313.98	304.1	309.22
15.07	294.12	284.82	288.47
19.95	278.09	267.8	271.7
29.99	250.37	242.03	244.18
49.94	205	199.76	201.72
100.02	139.81	136.4	137.11
200.04	87.13	83.529	85.465
300.06	63.976	61.683	63.696
499.97	43.812	42.062	43.701
999.94	24.44	23.45	24.648
1199.98	20.085	19.934	20.639

Table B8 Strain sweep of PSi with 6% I-CPTES in CR compound by in-situ technique.

Strain (%)	G' modulus (kPa)		
	No. 1	No. 2	No.3
0.56	402.66	338.23	340.25
0.98	372.55	405.81	361.97
1.95	371.44	349.26	341.5
3.07	353.05	344.45	331.17
5.02	340.43	329.96	311.36
10.04	306.45	298.47	283.51
15.07	284.81	279.43	263.84
19.95	268.52	263.28	248.96
29.99	241.24	237.4	225.61
49.94	198.73	195.61	187
100.02	135.18	133.67	128.2
200.04	84.515	83.045	79.743
300.06	62.462	61.082	59.169
499.97	42.25	41.731	40.037
999.94	23.485	23.301	22.713
1199.98	19.796	20.188	19.871

Table B9 Strain sweep of PSi with 8% I-CPTES in CR compound by in-situ technique.

Strain (%)	G' modulus (kPa)		
	No. 1	No. 2	No.3
0.56	314.07	299.98	320.11
0.98	288.28	302.69	283.85
1.95	280.7	297.77	296.66
3.07	285.06	285.76	275.07
5.02	268.41	270.33	267.55
10.04	243.03	244.35	242.77
15.07	225.98	227.11	225.69
19.95	212.92	213.82	213
29.99	192.44	194.11	193.15
49.94	159.35	161.76	160.4
100.02	108.48	110.37	110.59
200.04	66.341	66.795	68.311
300.06	49.609	49.538	51.139
499.97	33.579	33.469	34.803
999.94	18.608	18.54	19.129
1199.98	16.344	16.267	16.621

Table B10 Strain sweep of PSi with 2% I-TESPT in CR compound by in-situ technique.

Strain (%)	G' modulus (kPa)		
	No. 1	No. 2	No.3
0.56	352.77	325.15	303.9
0.98	307.15	284.64	267.77
1.95	289.94	274.33	263.64
3.07	281.57	275.84	253.97
5.02	271.21	262.18	241.27
10.04	243.44	236	221.23
15.07	224.99	218.48	205.5
19.95	211.18	205.46	194.56
29.99	189.81	184.74	175.44
49.94	155.4	152.39	146.26
100.02	103.41	103.05	99.679
200.04	61.81	63.719	61.676
300.06	44.302	47.332	45.12
499.97	30.006	31.894	30.156
999.94	16.561	16.812	16.195
1199.98	14.236	14.409	14.27

Table B11 Strain sweep of PSi with 4% I-TESPT in CR compound by in-situ technique.

Strain (%)	G' modulus (kPa)		
	No. 1	No. 2	No.3
0.56	303.95	277.33	341.17
0.98	260.56	267.77	317.11
1.95	253.18	289.27	290.61
3.07	264.03	282.93	294.74
5.02	251.37	257.22	272.28
10.04	229.52	234.05	244.8
15.07	213.34	218.64	227.25
19.95	201.75	205.92	212.15
29.99	181.83	184.14	188.51
49.94	150.53	150.96	154.93
100.02	102.34	101.99	103.36
200.04	62.969	62.089	63.56
300.06	46.868	45.968	47.135
499.97	31.415	30.923	31.775
999.94	16.436	16.212	16.886
1199.98	14.331	13.657	13.817

Table B12 Strain sweep of PSi with 6% I-TESPT in CR compound by in-situ technique.

Strain (%)	G' modulus (kPa)		
	No. 1	No. 2	No.3
0.56	274.14	256.4	281.21
0.98	263.27	259.45	251.37
1.95	243.18	243.83	249.73
3.07	238.68	242.91	248.82
5.02	226.93	229.73	239.4
10.04	202	204.76	212.73
15.07	187.63	193.28	195.65
19.95	177.91	183.06	183.43
29.99	159.2	163.24	164.81
49.94	132.18	134.82	135.26
100.02	90.083	91.766	90.573
200.04	56.064	57.047	55.207
300.06	41.53	41.943	40.771
499.97	28.335	28.266	27.696
999.94	14.97	14.774	14.601
1199.98	13	12.801	12.724

Table B13 Strain sweep of PSi with 8% I-TESPT in CR compound by in-situ technique.

Strain (%)	G' modulus (kPa)		
	No. 1	No. 2	No.3
0.56	303.9	266.73	299.65
0.98	247.26	253.91	290.5
1.95	273.87	262.54	273.87
3.07	261.31	245.59	262.2
5.02	248.59	237.02	256.3
10.04	225.05	213.34	229.41
15.07	207.93	199.34	210.19
19.95	196.38	185.43	197.62
29.99	174.66	166.88	176.51
49.94	143.16	137.68	143.91
100.02	96.599	94.506	96.343
200.04	58.934	58.007	58.526
300.06	43.576	42.704	43.225
499.97	29.604	28.955	29.151
999.94	15.439	15.1	15.322
1199.98	13.12	13.301	13.19

Table B14 Strain sweep of CR with 0% I-SCA by in-situ technique.

Strain (%)	G' modulus (kPa)		
	No. 1	No. 2	No.3
0.56	68.659	103.97	62.412
0.98	57.656	60.982	55.74
1.95	54.884	58.893	58.765
3.07	56.502	57.292	57.203
5.02	58.817	60.691	56.26
10.04	58.793	58.416	57.778
15.07	59.748	59.134	57.627
19.95	59.451	59.741	56.417
29.99	58.295	58.197	57.263
49.94	54.192	54.65	53.389
100.02	42.287	43.026	41.858
200.04	26.937	27.402	26.502
300.06	19.655	19.925	19.335
499.97	13.679	13.852	13.451
999.94	8.2537	8.2975	8.0775
1199.98	7.3421	7.3109	7.149

Table B15 Strain sweep of CR with 2% I-APTES by in-situ technique.

Strain (%)	G' modulus (kPa)		
	No. 1	No. 2	No.3
0.56	48.319	58.85	62.774
0.98	67.762	62.091	79.784
1.95	63.846	71.001	62.646
3.07	64.278	66.025	67.422
5.02	66.276	64.358	66.248
10.04	66.716	67.009	67.555
15.07	66.215	66.172	66.375
19.95	66.194	65.545	65.973
29.99	64.092	63.665	63.986
49.94	58.421	58.03	58.116
100.02	43.772	43.548	43.804
200.04	27.359	27.414	27.557
300.06	20.267	20.283	20.503
499.97	14.67	14.647	14.887
999.94	9.6281	9.6663	9.688
1199.98	8.646	8.7721	8.7142

Table B16 Strain sweep of CR with 4% I-APTES by in-situ technique.

Strain (%)	G' modulus (kPa)		
	No. 1	No. 2	No.3
0.56	117.7	98.651	106.7
0.98	103.12	96.463	99.457
1.95	89.164	95.219	83.66
3.07	97.718	95.719	95.37
5.02	96.807	97.603	99.585
10.04	95.552	95.525	97.786
15.07	94.498	94.515	96.429
19.95	93.067	93.304	94.736
29.99	89.742	89.001	92.162
49.94	80.008	79.732	80.972
100.02	58.595	58.283	59.627
200.04	37.954	37.367	38.791
300.06	29.418	29.123	30.426
499.97	22.612	22.562	23.257
999.94	11.918	11.767	12.112
1199.98	8.3381	8.2118	8.4724

Table B17 Strain sweep of CR with 6% I-APTES by in-situ technique.

Strain (%)	G' modulus (kPa)		
	No. 1	No. 2	No.3
0.56	153.01	107.89	162.82
0.98	125.29	139.9	144.14
1.95	146.96	142.55	153.56
3.07	143.58	141.53	148.47
5.02	142.33	145.53	150.87
10.04	144.62	143.42	149.72
15.07	143.45	141.59	147.47
19.95	141.57	138.95	143.11
29.99	134.72	133.09	136.91
49.94	121.13	119.33	122.72
100.02	92.12	90.637	93.551
200.04	63.98	62.898	65.922
300.06	50.949	50.18	53.005
499.97	35.573	35.302	36.437
999.94	13.507	13.664	13.665
1199.98	9.6961	9.6927	9.7166

Table B18 train sweep of CR with 8% I-APTES by in-situ technique.

Strain (%)	G' modulus (kPa)		
	No. 1	No. 2	No.3
0.56	175.76	139.28	181.2
0.98	160.77	175.19	180.73
1.95	155.72	171.72	153.01
3.07	156.85	148.84	155.11
5.02	155.35	156.43	155.35
10.04	152.37	154.93	154.82
15.07	149.61	152.09	150.53
19.95	146.97	149.7	149.75
29.99	140.89	143.69	143.34
49.94	126.77	128.48	129.15
100.02	99.305	97.61	99.994
200.04	74.569	67.964	71.483
300.06	66.09	54.583	56.697
499.97	40.725	37.229	37.596
999.94	10.532	14.096	13.63
1199.98	7.489	10.02	9.7585

Table B19 Strain sweep of CR with 2% I-CPTES by in-situ technique.

Strain (%)	G' modulus (kPa)		
	No. 1	No. 2	No.3
0.56	55.828	51.693	45.49
0.98	42.133	52.879	42.753
1.95	50.086	48.232	47.885
3.07	50.536	51.003	49.033
5.02	50.006	50.932	51.075
10.04	50.223	50.26	48.162
15.07	49.562	49.516	48.737
19.95	49.988	48.972	48.685
29.99	48.394	47.816	47.518
49.94	44.975	44.532	44.254
100.02	35.543	35.095	34.823
200.04	22.395	22.042	21.723
300.06	15.716	15.01	15.221
499.97	10.595	9.9669	10.3
999.94	6.1573	5.6963	5.9599
1199.98	5.476	5.0164	5.3214

Table B20 Strain sweep of CR with 4% I-CPTES by in-situ technique.

Strain (%)	G' modulus (kPa)		
	No. 1	No. 2	No.3
0.56	49.625	55.828	51.693
0.98	46.632	47.677	45.003
1.95	44.032	46.784	42.078
3.07	48.337	44.86	46.946
5.02	45.305	46.373	47.228
10.04	47.603	47.284	47.137
15.07	47.205	46.639	47.657
19.95	46.652	46.171	46.031
29.99	45.846	45.313	45.618
49.94	42.515	41.938	42.451
100.02	33.132	33.079	33.228
200.04	20.867	20.829	20.967
300.06	14.66	14.013	14.941
499.97	9.9562	9.2835	10.058
999.94	5.7934	5.3441	5.8043
1199.98	5.2154	4.8011	5.1514

Table B21 Strain sweep of CR with 6% I-CPTES by in-situ technique.

Strain (%)	G' modulus (kPa)		
	No. 1	No. 2	No.3
0.56	53.129	57.896	55.254
0.98	46.568	47.677	46.611
1.95	46.784	47.885	46.233
3.07	43.667	46.811	47.161
5.02	46.16	47.014	48.938
10.04	45.691	45.903	44.947
15.07	44.828	45.323	44.658
19.95	44.534	44.664	46.192
29.99	43.001	44.032	43.677
49.94	40.079	41.019	40.518
100.02	31.138	32.162	31.965
200.04	19.728	20.095	19.896
300.06	13.617	14.208	13.856
499.97	9.2902	9.6808	9.4225
999.94	5.4766	5.6868	5.5427
1199.98	4.9611	5.1006	5.0403

Table B22 Strain sweep of CR with 8% I-CPTES by in-situ technique.

Strain (%)	G' modulus (kPa)		
	No. 1	No. 2	No.3
0.56	38.253	40.133	39.286
0.98	40.503	56.547	43.878
1.95	39.629	58.893	47.334
3.07	43.318	42.969	44.017
5.02	43.595	45.091	42.834
10.04	42.822	44.46	43.034
15.07	44.021	43.131	42.99
19.95	42.426	43.221	42.396
29.99	41.4	41.135	41.42
49.94	38.862	38.947	38.456
100.02	30.22	30.301	30.308
200.04	18.888	18.901	18.808
300.06	13.048	13.42	13.163
499.97	8.8654	9.0345	8.8694
999.94	5.198	5.2791	5.2011
1199.98	4.7486	4.8295	4.7459

Table B23 Strain sweep of CR with 2% I-TESPT by in-situ technique.

Strain (%)	G' modulus (kPa)		
	No. 1	No. 2	No.3
0.56	39.286	126.13	47.557
0.98	54.33	54.33	56.547
1.95	53.939	56.141	49.895
3.07	51.353	55.64	52.858
5.02	53.639	54.218	54.218
10.04	53.723	55.573	54.236
15.07	53.9	55.01	53.646
19.95	53.784	55.188	53.869
29.99	52.924	53.518	52.58
49.94	49.331	49.971	48.996
100.02	38.588	38.994	38.141
200.04	24.566	24.759	24.446
300.06	17.505	17.688	17.32
499.97	11.676	11.833	11.564
999.94	6.4222	6.5179	6.4117
1199.98	5.7464	5.815	5.7233

Table B24 Strain sweep of CR with 4% I-TESPT by in-situ technique.

Strain (%)	G' modulus (kPa)		
	No. 1	No. 2	No.3
0.56	59.504	48.878	66.439
0.98	45.003	52.879	57.379
1.95	51.934	52.288	49.7
3.07	49.85	50.305	49.606
5.02	50.434	51.577	51.432
10.04	49.798	50.826	51.11
15.07	50.744	50.39	50.673
19.95	49.491	50.559	50.558
29.99	49.416	49.639	49.782
49.94	45.42	46.078	46.724
100.02	35.298	35.928	36.376
200.04	22.415	22.585	23.028
300.06	15.859	15.51	16.413
499.97	10.552	10.322	10.99
999.94	5.956	5.7849	6.1301
1199.98	5.2929	5.106	5.4966

Table B25 Strain sweep of CR with 6% I-TESPT by in-situ technique.

Strain (%)	G' modulus (kPa)		
	No. 1	No. 2	No.3
0.56	27.627	88.585	42.503
0.98	51.003	49.895	28.127
1.95	51.003	45.46	51.003
3.07	49.85	48.685	52.51
5.02	49.793	51.861	51.716
10.04	50.472	51.747	49.728
15.07	49.142	51.098	48.762
19.95	49.827	51.36	49.419
29.99	48.34	49.51	48.007
49.94	44.37	45.843	44.681
100.02	34.698	35.25	34.825
200.04	22.224	22.31	22.221
300.06	15.748	15.763	15.654
499.97	10.475	10.669	10.426
999.94	5.9418	5.9682	5.906
1199.98	5.2519	5.2145	5.1737

Table B26 Strain sweep of CR with 8% I-TESPT by in-situ technique.

Strain (%)	G' modulus (kPa)		
	No. 1	No. 2	No.3
0.56	58.386	49.625	54.0055
0.98	54.647	25.502	40.0745
1.95	35.02	30.272	32.646
3.07	46.399	45.271	45.835
5.02	47.493	45.129	46.311
10.04	45.458	47.007	46.2325
15.07	45.095	44.162	44.6285
19.95	45.368	44.138	44.753
29.99	44.367	43.088	43.7275
49.94	40.653	40.102	40.3775
100.02	32.399	31.592	31.9955
200.04	20.029	19.952	19.9905
300.06	14.058	13.554	13.806
499.97	9.4063	9.1135	9.2599
999.94	5.3279	5.2353	5.2816
1199.98	4.7636	4.6532	4.7084

APPENDIX C

EFFECT OF ACID-BASE CONDITION ON APTES-MODIFIED PSI

Table C1 Strain sweep of 6% APTES-modified PSi at pH 2 filled CR.

Strain (%)	G' modulus (kPa)		
	No. 1	No. 2	No.3
0.56	493	464.63	580.16
0.98	554.66	508.88	551.52
1.53	568.92	465.92	521.5
1.95	556.4	466.04	513.13
3.07	562.09	449.04	486.35
5.02	521.7	429.95	468.78
6.98	500.64	417.41	457.49
10.04	478.18	393.53	428.39
15.07	440.57	366.08	394.9
19.95	411.39	345.64	370.23
29.99	362.51	307.19	328.29
49.94	289.26	249.82	265.92
100.02	191.65	169.55	182.77
200.04	114.25	106.6	116.07
300.06	77.885	73.597	82.898
499.97	46.166	45.367	56.019
999.94	19.258	22.593	23.393
1199.98	14.241	16.034	16.393

Table C2 Strain sweep of 6% APTES-modified PSi at pH 6 filled CR.

Strain (%)	G' modulus (kPa)		
	No. 1	No. 2	No.3
0.56	382.53	407.34	410.71
0.98	367.9	384.78	392.65
1.95	347.55	377.57	364.36
3.07	346.19	367.29	353.02
5.02	340.09	357.74	351.11
10.04	306.23	326.97	323.93
15.07	289.17	304.61	299.94
19.95	272.68	286.52	280.89
29.99	243.61	253.65	249.32
49.94	197.23	203.22	200.02
100.02	129.89	133.03	131.69
200.04	79.239	81.325	81.311
300.06	58.734	60.228	60.651
499.97	41.478	42.317	42.774
999.94	21.27	19.627	19.639
1199.98	15.083	14.009	13.859

Table C3 Strain sweep of 6% APTES-modified PSi at pH 12 filled CR.

Strain (%)	G' modulus (kPa)		
	No. 1	No. 2	No.3
0.56	573	671.55	435.12
0.98	634.62	603.04	575.5
1.53	592.55	578.96	555.01
1.95	571.31	592.64	549.1
3.07	576.7	558.52	533.82
5.02	495.36	537.23	504.48
6.98	498.72	526.15	496.6
10.04	482.25	497.34	471.09
15.07	448.69	463.06	441.53
19.95	422.76	433.98	415.33
29.99	369.52	381.57	368.03
49.94	302.82	302.67	295.52
100.02	204.99	199.02	196.54
200.04	127.92	125.36	125.97
300.06	90.376	90.162	92.866
499.97	56.313	59.168	61.37
999.94	24.105	23.848	25.642
1199.98	16.96	16.676	17.452

APPENDIX D

STRAIN SWEEP TEST OF CR WITH SILANE

Table D1 strain sweep test of neat CR.

Strain (%)	G' modulus (kPa)		
	No. 1	No. 2	No.3
0.56	500	447.39	473.695
0.98	657.62	470.28	563.95
1.53	516.41	481.98	499.195
1.95	489.63	463.91	476.77
3.07	551.66	454.47	503.065
5.02	440.56	430.16	435.36
6.98	401.09	412.46	406.775
10.04	382.42	391.63	387.025
15.07	359.91	362.85	361.38
19.95	346.19	344.91	345.55
29.99	309.74	309.9	309.82
49.94	260.69	258.4	259.545
100.02	186.09	183.39	184.74
200.04	120.93	117.38	119.155
300.06	91	88.112	89.556
499.97	61.246	59.069	60.1575
999.94	27.629	26.919	27.274
1199.98	19.013	18.904	18.9585

Table D2 Strain sweep test of CR with 2% APTES.

Strain (%)	G' modulus (kPa)		
	No. 1	No. 2	No.3
0.56	505.34	794.8	650.07
0.98	444.19	398.28	421.235
1.53	417.62	392.18	404.9
1.95	408.57	410.54	409.555
3.07	402.09	418.11	410.1
5.02	382.53	378.95	380.74
6.98	370.21	365	367.605
10.04	346.98	348.13	347.555
15.07	321.48	324.51	322.995
19.95	307.46	307.57	307.515
29.99	276.86	278.18	277.52
49.94	230.84	230.09	230.465
100.02	159.19	158.71	158.95
200.04	97.909	98.27	98.0895
300.06	71.498	71.623	71.5605
499.97	47.747	47.606	47.6765
999.94	23.551	23.283	23.417
1199.98	17.032	16.584	16.808

Table D3 Strain sweep test of CR with 4% APTES.

Strain (%)	G' modulus (kPa)		
	No. 1	No. 2	No.3
0.56	436.29	463.06	449.675
0.98	428.65	455.66	442.155
1.53	411.04	436.78	423.91
1.95	415.86	432.25	424.055
3.07	404.43	421.64	413.035
5.02	381.46	399.48	390.47
6.98	369.13	386.67	377.9
10.04	351.82	367.23	359.525
15.07	328.36	341.23	334.795
19.95	311.31	323.53	317.42
29.99	282.4	289.39	285.895
49.94	233.04	238.34	235.69
100.02	160.48	163.9	162.19
200.04	98.41	102.47	100.44
300.06	71.935	74.204	73.0695
499.97	47.961	49.091	48.526
999.94	23.557	22.646	23.1015
1199.98	16.504	15.783	16.1435

Table D4 Strain sweep test of CR with 6% APTES.

Strain (%)	G' modulus (kPa)		
	No. 1	No. 2	No.3
0.56	406.69	459.03	432.86
0.98	449.9	447.61	448.755
1.53	399.22	433.76	416.49
1.95	405.48	422.42	413.95
3.07	389.8	415.26	402.53
5.02	371.51	400.07	385.79
6.98	364.4	385.75	375.075
10.04	345.6	366.06	355.83
15.07	325.2	340.87	333.035
19.95	306.5	322.69	314.595
29.99	276.91	287.87	282.39
49.94	230.07	234.94	232.505
100.02	158.7	160.21	159.455
200.04	99.337	100.12	99.7285
300.06	71.665	72.846	72.2555
499.97	48.083	48.14	48.1115
999.94	23.567	22.647	23.107
1199.98	16.581	15.995	16.288

Table D5 Strain sweep test of CR with 8% APTES.

Strain (%)	G' modulus (kPa)		
	No. 1	No. 2	No.3
0.56	426.82	372.46	399.64
0.98	433.91	411.07	422.49
1.53	414.11	397.13	405.62
1.95	416.65	388.03	402.34
3.07	394.93	374.88	384.905
5.02	376.8	357.81	367.305
6.98	364.62	347.35	355.985
10.04	346.87	328.65	337.76
15.07	323.5	308.99	316.245
19.95	305.75	290.95	298.35
29.99	273.74	262.83	268.285
49.94	225.39	217.97	221.68
100.02	154.79	151.74	153.265
200.04	96.986	96.365	96.6755
300.06	71.748	70.713	71.2305
499.97	48.178	46.66	47.419
999.94	22.98	22.302	22.641
1199.98	16.308	15.783	16.0455

Table D6 Strain sweep test of CR with 2% CPTES.

Strain (%)	G' modulus (kPa)		
	No. 1	No. 2	No.3
0.56	55.828	51.693	45.49
0.98	42.133	52.879	42.753
1.95	50.086	48.232	47.885
3.07	50.536	51.003	49.033
5.02	50.006	50.932	51.075
10.04	50.223	50.26	48.162
15.07	49.562	49.516	48.737
19.95	49.988	48.972	48.685
29.99	48.394	47.816	47.518
49.94	44.975	44.532	44.254
100.02	35.543	35.095	34.823
200.04	22.395	22.042	21.723
300.06	15.716	15.01	15.221
499.97	10.595	9.9669	10.3
999.94	6.1573	5.6963	5.9599
1199.98	5.476	5.0164	5.3214

Table D7 Strain sweep test of CR with 4% CPTES.

Strain (%)	G' modulus (kPa)		
	No. 1	No. 2	No.3
0.56	49.625	55.828	51.693
0.98	46.632	47.677	45.003
1.95	44.032	46.784	42.078
3.07	48.337	44.86	46.946
5.02	45.305	46.373	47.228
10.04	47.603	47.284	47.137
15.07	47.205	46.639	47.657
19.95	46.652	46.171	46.031
29.99	45.846	45.313	45.618
49.94	42.515	41.938	42.451
100.02	33.132	33.079	33.228
200.04	20.867	20.829	20.967
300.06	14.66	14.013	14.941
499.97	9.9562	9.2835	10.058
999.94	5.7934	5.3441	5.8043
1199.98	5.2154	4.8011	5.1514

Table D8 Strain sweep test of CR with 6% CPTES.

Strain (%)	G' modulus (kPa)		
	No. 1	No. 2	No.3
0.56	53.129	57.896	55.254
0.98	46.568	47.677	46.611
1.95	46.784	47.885	46.233
3.07	43.667	46.811	47.161
5.02	46.16	47.014	48.938
10.04	45.691	45.903	44.947
15.07	44.828	45.323	44.658
19.95	44.534	44.664	46.192
29.99	43.001	44.032	43.677
49.94	40.079	41.019	40.518
100.02	31.138	32.162	31.965
200.04	19.728	20.095	19.896
300.06	13.617	14.208	13.856
499.97	9.2902	9.6808	9.4225
999.94	5.4766	5.6868	5.5427
1199.98	4.9611	5.1006	5.0403

Table D9 Strain sweep test of CR with 8% CPTES.

Strain (%)	G' modulus (kPa)		
	No. 1	No. 2	No.3
0.56	38.253	40.133	39.286
0.98	40.503	56.547	43.878
1.95	39.629	58.893	47.334
3.07	43.318	42.969	44.017
5.02	43.595	45.091	42.834
10.04	42.822	44.46	43.034
15.07	44.021	43.131	42.99
19.95	42.426	43.221	42.396
29.99	41.4	41.135	41.42
49.94	38.862	38.947	38.456
100.02	30.22	30.301	30.308
200.04	18.888	18.901	18.808
300.06	13.048	13.42	13.163
499.97	8.8654	9.0345	8.8694
999.94	5.198	5.2791	5.2011
1199.98	4.7486	4.8295	4.7459

Table D10 Strain sweep test of CR with 2% TESPT.

Strain (%)	G' modulus (kPa)		
	No. 1	No. 2	No.3
0.56	47.557	126.13	39.286
0.98	56.547	54.33	54.33
1.95	49.895	56.141	53.939
3.07	52.858	55.64	51.353
5.02	54.218	54.218	53.639
10.04	54.236	55.573	53.723
15.07	53.646	55.01	53.9
19.95	53.869	55.188	53.784
29.99	52.58	53.518	52.924
49.94	48.996	49.971	49.331
100.02	38.141	38.994	38.588
200.04	24.446	24.759	24.566
300.06	17.32	17.688	17.505
499.97	11.564	11.833	11.676
999.94	6.4117	6.5179	6.4222
1199.98	5.7233	5.815	5.7464

Table D11 Strain sweep test of CR with 4% TESPT.

Strain (%)	G' modulus (kPa)		
	No. 1	No. 2	No.3
0.56	66.439	48.878	59.504
0.98	57.379	52.879	45.003
1.95	49.7	52.288	51.934
3.07	49.606	50.305	49.85
5.02	51.432	51.577	50.434
10.04	51.11	50.826	49.798
15.07	50.673	50.39	50.744
19.95	50.558	50.559	49.491
29.99	49.782	49.639	49.416
49.94	46.724	46.078	45.42
100.02	36.376	35.928	35.298
200.04	23.028	22.585	22.415
300.06	16.413	15.51	15.859
499.97	10.99	10.322	10.552
999.94	6.1301	5.7849	5.956
1199.98	5.4966	5.106	5.2929

Table D12 Strain sweep test of CR with 6% TESPT.

Strain (%)	G' modulus (kPa)		
	No. 1	No. 2	No.3
0.56	42.503	88.585	27.627
0.98	28.127	49.895	51.003
1.95	51.003	45.46	51.003
3.07	52.51	48.685	49.85
5.02	51.716	51.861	49.793
10.04	49.728	51.747	50.472
15.07	48.762	51.098	49.142
19.95	49.419	51.36	49.827
29.99	48.007	49.51	48.34
49.94	44.681	45.843	44.37
100.02	34.825	35.25	34.698
200.04	22.221	22.31	22.224
300.06	15.654	15.763	15.748
499.97	10.426	10.669	10.475
999.94	5.906	5.9682	5.9418
1199.98	5.1737	5.2145	5.2519

Table D13 Strain sweep test of CR with 8% TESPT.

Strain (%)	G' modulus (kPa)		
	No. 1	No. 2	No.3
0.56	58.386	49.625	44.628
0.98	54.647	25.502	36.589
1.95	35.02	30.272	57.792
3.07	46.399	45.271	41.06
5.02	47.493	45.129	45.129
10.04	45.458	47.007	44.354
15.07	45.095	44.162	43.242
19.95	45.368	44.138	42.747
29.99	44.367	43.088	42.183
49.94	40.653	40.102	39.215
100.02	32.399	31.592	30.754
200.04	20.029	19.952	19.282
300.06	14.058	13.554	13.516
499.97	9.4063	9.1135	9.0727
999.94	5.3279	5.2353	5.1956
1199.98	4.7636	4.6532	4.6819

APPENDIX E

PARTICLE SIZE BY PARTICLE SIZE ANALYZER

Table E1 Aggregates size of APTES-modified Psi at various loading.

Size (μm)	Volume (%)	Loading of APTES (% w)				
		0	2	4	6	8
0.01	0	0	0	0	0	0
0.011	0	0	0	0	0	0
0.013	0	0	0	0	0	0
0.015	0	0	0	0	0	0
0.017	0	0	0	0	0	0
0.02	0	0	0	0	0	0
0.023	0	0	0	0	0	0
0.026	0	0	0	0	0	0
0.03	0	0	0	0	0	0
0.035	0	0	0	0	0	0
0.04	0	0	0	0	0	0
0.046	0	0	0	0	0	0
0.052	0	0	0	0	0	0
0.06	0	0	0	0	0	0
0.069	0	0	0	0	0	0
0.079	0	0	0	0	0	0
0.091	0	0	0	0	0	0
0.105	0	0	0	0	0	0
0.12	0	0	0	0	0	0
0.138	0	0	0	0	0	0
0.158	0	0	0	0	0	0
0.182	0	0	0	0	0	0
0.209	0	0	0	0	0	0
0.24	0	0	0	0	0	0
0.275	0	0	0	0	0	0
0.316	0	0	0	0	0	0
0.363	0	0	0	0	0	0
0.417	0	0	0	0	0	0
0.479	0	0	0	0	0	0
0.55	0	0	0	0	0	0
0.631	0	0	0	0	0	0
0.724	0	0	0	0	0	0
0.832	0	0	0	0	0	0
0.955	0	0	0	0	0	0
1.096	0	0	0	0	0	0
1.259	0	0	0	0	0	0
1.445	0	0	0	0	0	0
1.66	0	0	0	0.01	0	0
1.905	0.08	0	0	0.08	0	0.02

Table E1 Aggregates size of APTES-modified PSi at various loading (Cont.).

Size (μm)	Volume (%)	Loading of APTES (% w)				
		0	2	4	6	8
2.188	0.1	0.09	0.08	0.07	0.08	0.09
2.512	0.16	0.13	0.11	0.09	0.11	0.12
2.884	0.27	0.18	0.17	0.16	0.17	0.19
3.311	0.46	0.26	0.26	0.25	0.27	0.3
3.802	0.73	0.42	0.42	0.38	0.45	0.49
4.365	1.06	0.68	0.63	0.61	0.73	0.78
5.012	1.44	1	0.89	0.93	1.07	1.13
5.754	1.88	1.31	1.17	1.23	1.39	1.45
6.607	2.46	1.62	1.5	1.48	1.68	1.73
7.586	3.3	1.98	1.91	1.75	2.02	2.06
8.71	4.36	2.53	2.47	2.21	2.53	2.56
10	5.57	3.27	3.16	2.91	3.24	3.25
11.482	6.76	4.07	3.88	3.74	4	3.98
13.183	7.95	4.68	4.4	4.44	4.57	4.51
15.136	9.14	5.08	4.68	4.91	4.89	4.78
17.378	10.34	5.46	4.97	5.26	5.13	4.94
19.953	11.21	6.22	5.67	5.83	5.61	5.34
22.909	11.21	7.57	6.99	6.94	6.59	6.28
26.303	9.81	9.33	8.76	8.63	8.06	7.81
30.2	7.05	10.72	10.38	10.22	9.49	9.47
34.674	3.71	10.81	11.1	10.65	10.13	10.41
39.811	0.95	9.1	10.38	9.23	9.43	9.81
45.709	0	6.13	8.22	6.41	7.41	7.55
52.481	0	3.14	5.2	3.62	4.74	4.49
60.256	0	1.17	2.26	1.96	2.47	1.96
69.183	0	0.38	0.35	1.17	1.11	0.81
79.433	0	0.25	0	0.73	0.57	0.72
91.201	0	0.4	0	0.76	0.53	0.92
104.713	0	0.72	0	1.35	0.72	1.09
120.226	0	0.93	0	1.54	0.63	0.82
138.038	0	0.37	0	0.44	0.14	0.16
158.489	0	0	0	0	0	0
181.97	0	0	0	0	0	0
208.93	0	0	0	0	0	0
239.883	0	0	0	0	0	0
275.423	0	0	0	0	0	0
316.228	0	0	0	0	0	0
363.078	0	0	0	0	0	0
416.869	0	0	0	0	0	0
478.63	0	0	0	0	0	0
549.541	0	0	0	0	0	0
630.957	0	0	0	0	0	0
724.436	0	0	0	0	0	0
831.764	0	0	0	0	0	0
954.993	0	0	0	0	0	0
1096.478	0	0	0	0	0	0

Table E1 Aggregates size of APTES-modified PSi at various loading (Cont.).

Size (μm)	Volume (%)	Loading of APTES (% w)				
		0	2	4	6	8
1258.925	0	0	0	0	0	0
1445.44	0	0	0	0	0	0
1659.587	0	0	0	0	0	0
1905.461	0	0	0	0	0	0
2187.762	0	0	0	0	0	0
2511.886	0	0	0	0	0	0
2884.032	0	0	0	0	0	0
3311.311	0	0	0	0	0	0
3801.894	0	0	0	0	0	0
4365.158	0	0	0	0	0	0
5011.872	0	0	0	0	0	0
5754.399	0	0	0	0	0	0
6606.934	0	0	0	0	0	0
7585.776	0	0	0	0	0	0
8709.636	0	0	0	0	0	0
10000	0	0	0	0	0	0
1258.925	0	0	0	0	0	0
1445.44	0	0	0	0	0	0
1659.587	0	0	0	0	0	0
1905.461	0	0	0	0	0	0
2187.762	0	0	0	0	0	0
2511.886	0	0	0	0	0	0
2884.032	0	0	0	0	0	0
3311.311	0	0	0	0	0	0
3801.894	0	0	0	0	0	0
4365.158	0	0	0	0	0	0
5011.872	0	0	0	0	0	0
5754.399	0	0	0	0	0	0
6606.934	0	0	0	0	0	0
7585.776	0	0	0	0	0	0
8709.636	0	0	0	0	0	0
10000	0	0	0	0	0	0

Table E2 Aggregates size of CPTES-modified PSi at various loading.

Size (μm)	Volume (%)	Loading of CPTES (% w)				
		0	2	4	6	8
0.01	0		0	0	0	0
0.011	0		0	0	0	0
0.013	0		0	0	0	0
0.015	0		0	0	0	0
0.017	0		0	0	0	0
0.02	0		0	0	0	0
0.023	0		0	0	0	0
0.026	0		0	0	0	0
0.03	0		0	0	0	0
0.035	0		0	0	0	0
0.04	0		0	0	0	0
0.046	0		0	0	0	0
0.052	0		0	0	0	0
0.06	0		0	0	0	0
0.069	0		0	0	0	0
0.079	0		0	0	0	0
0.091	0		0	0	0	0
0.105	0		0	0	0	0
0.12	0		0	0	0	0
0.138	0		0	0	0	0
0.158	0		0	0	0	0
0.182	0		0	0	0	0
0.209	0		0	0	0	0
0.24	0		0	0	0	0
0.275	0		0	0	0	0
0.316	0		0	0	0	0
0.363	0		0	0	0	0
0.417	0		0	0	0	0
0.479	0		0	0	0	0
0.55	0		0	0	0	0
0.631	0		0	0	0	0
0.724	0		0	0	0	0
0.832	0		0	0	0	0
0.955	0		0	0	0	0
1.096	0		0	0	0	0

Table E2 Aggregates size of CPTES-modified PSi at various loading (Cont.).

Size (μm)	Volume (%)	Loading of CPTES (% w)				
		0	2	4	6	8
208.93	0		0	0	0	0
239.883	0		0	0	0	0
275.423	0		0	0	0	0
316.228	0		0	0	0	0
363.078	0		0	0	0	0
416.869	0		0	0	0	0
478.63	0		0	0	0	0
549.541	0		0	0	0	0
630.957	0		0	0	0	0
724.436	0		0	0	0	0
831.764	0		0	0	0	0
954.993	0		0	0	0	0
1096.478	0		0	0	0	0
1258.925	0		0	0	0	0
1445.44	0		0	0	0	0
1659.587	0		0	0	0	0
1905.461	0		0	0	0	0
208.93	0		0	0	0	0
239.883	0		0	0	0	0
275.423	0		0	0	0	0
316.228	0		0	0	0	0
363.078	0		0	0	0	0
416.869	0		0	0	0	0
478.63	0		0	0	0	0
549.541	0		0	0	0	0
630.957	0		0	0	0	0
724.436	0		0	0	0	0
831.764	0		0	0	0	0
954.993	0		0	0	0	0
1096.478	0		0	0	0	0
1258.925	0		0	0	0	0
1445.44	0		0	0	0	0
1659.587	0		0	0	0	0
1905.461	0		0	0	0	0
2187.762	0		0	0	0	0
2511.886	0		0	0	0	0
2884.032	0		0	0	0	0
3311.311	0		0	0	0	0
3801.894	0		0	0	0	0
4365.158	0		0	0	0	0
5011.872	0		0	0	0	0
5754.399	0		0	0	0	0
6606.934	0		0	0	0	0
7585.776	0		0	0	0	0
8709.636	0		0	0	0	0
10000	0		0	0	0	0

Table E3 Aggregates size of TESPT-modified PSi at various loading.

Size (μm)	Volume (%)	Loading of TESPT (% w)				
		0	2	4	6	8
0.01	0		0	0	0	0
0.011	0		0	0	0	0
0.013	0		0	0	0	0
0.015	0		0	0	0	0
0.017	0		0	0	0	0
0.02	0		0	0	0	0
0.023	0		0	0	0	0
0.026	0		0	0	0	0
0.03	0		0	0	0	0
0.035	0		0	0	0	0
0.04	0		0	0	0	0
0.046	0		0	0	0	0
0.052	0		0	0	0	0
0.06	0		0	0	0	0
0.069	0		0	0	0	0
0.079	0		0	0	0	0
0.091	0		0	0	0	0
0.105	0		0	0	0	0
0.12	0		0	0	0	0
0.138	0		0	0	0	0
0.158	0		0	0	0	0
0.182	0		0	0	0	0
0.209	0		0	0	0	0
0.24	0		0	0	0	0
0.275	0		0	0	0	0
0.316	0		0	0	0	0
0.363	0		0	0	0	0
0.417	0		0	0	0	0
0.479	0		0	0	0	0
0.55	0		0	0	0	0
0.631	0		0	0	0	0
0.724	0		0	0	0	0
0.832	0		0	0	0	0
0.955	0		0	0	0	0
1.096	0		0	0	0	0
1.259	0		0	0	0	0
1.445	0		0	0	0	0
1.66	0		0.01	0	0.01	0
1.905	0.08		0.07	0	0.07	0

Table E3 Aggregates size of TESPT-modified PSi at various loading (Cont.).

Size (μm)	Volume (%)	Loading of TESPT (% w)				
		0	2	4	6	8
2.188	0.1		0.08	0.09	0.11	0.07
2.512	0.16		0.11	0.12	0.15	0.1
2.884	0.27		0.17	0.19	0.22	0.15
3.311	0.46		0.28	0.3	0.32	0.25
3.802	0.73		0.47	0.48	0.5	0.42
4.365	1.06		0.73	0.75	0.78	0.64
5.012	1.44		1.03	1.05	1.11	0.92
5.754	1.88		1.32	1.33	1.41	1.25
6.607	2.46		1.58	1.62	1.67	1.66
7.586	3.3		1.89	2	1.97	2.17
8.71	4.36		2.37	2.56	2.43	2.86
10	5.57		3.03	3.24	3.03	3.76
11.482	6.76		3.76	3.91	3.65	4.82
13.183	7.95		4.31	4.39	4.09	5.86
15.136	9.14		4.62	4.69	4.31	6.87
17.378	10.34		4.84	5.03	4.41	7.85
19.953	11.21		5.41	5.79	4.71	8.95
22.909	11.21		6.72	7.19	5.58	10.08
26.303	9.81		8.71	9.06	7.21	10.94
30.2	7.05		10.59	10.62	9.26	10.86
34.674	3.71		11.3	10.94	10.87	9.55
39.811	0.95		10.14	9.56	11.04	6.38
45.709	0		7.36	6.86	9.37	3.23
52.481	0		4.16	3.92	6.36	0.36
60.256	0		1.86	1.78	3.12	0
69.183	0		0.87	0.68	0.75	0
79.433	0		0.64	0.24	0.03	0
91.201	0		0.59	0.23	0.23	0
104.713	0		0.62	0.55	0.6	0
120.226	0		0.3	0.64	0.53	0
138.038	0		0.07	0.17	0.1	0
158.489	0		0	0	0	0
181.97	0		0	0	0	0
208.93	0		0	0	0	0
239.883	0		0	0	0	0
275.423	0		0	0	0	0
316.228	0		0	0	0	0
363.078	0		0	0	0	0
416.869	0		0	0	0	0
478.63	0		0	0	0	0
549.541	0		0	0	0	0
630.957	0		0	0	0	0
724.436	0		0	0	0	0
831.764	0		0	0	0	0
954.993	0		0	0	0	0
1096.478	0		0	0	0	0

Table E3 Aggregates size of TESPT-modified PSi at various loading (Cont.).

Size (μm)	Volume (%)	Loading of TESPT (% w)				
		0	2	4	6	8
1258.925	0		0	0	0	0
1445.44	0		0	0	0	0
1659.587	0		0	0	0	0
1905.461	0		0	0	0	0
2187.762	0		0	0	0	0
2511.886	0		0	0	0	0
2884.032	0		0	0	0	0
3311.311	0		0	0	0	0
3801.894	0		0	0	0	0
4365.158	0		0	0	0	0
5011.872	0		0	0	0	0
5754.399	0		0	0	0	0
6606.934	0		0	0	0	0
7585.776	0		0	0	0	0
8709.636	0		0	0	0	0
10000	0		0	0	0	0

Table E4 Aggregates size of 6% APTES-modified PSi at different pH condition.

Size (μm)	Systems		
	pH 2	pH 6	pH 12
0.01	0	0	0
0.011	0	0	0
0.013	0	0	0
0.015	0	0	0
0.017	0	0	0
0.02	0	0	0
0.023	0	0	0
0.026	0	0	0
0.03	0	0	0
0.035	0	0	0
0.04	0	0	0
0.046	0	0	0
0.052	0	0	0
0.06	0	0	0
0.069	0	0	0
0.079	0	0	0
0.091	0	0	0
0.105	0	0	0
0.12	0	0	0
0.138	0	0	0
0.158	0	0	0
0.182	0	0	0
0.209	0	0	0
0.24	0	0	0
0.275	0	0	0
0.316	0	0	0
0.363	0	0	0
0.417	0	0	0
0.479	0	0	0
0.55	0	0	0
0.631	0	0	0
0.724	0	0	0
0.832	0	0	0
0.955	0	0	0
1.096	0	0	0
1.259	0	0	0
1.445	0	0	0
1.66	0.01	0	0
1.905	0.08	0	0.02
2.188	0.07	0.08	0.09
2.512	0.09	0.11	0.12
2.884	0.16	0.17	0.19
3.311	0.25	0.27	0.3
3.802	0.38	0.45	0.49
4.365	0.61	0.73	0.78

Table E4 Aggregates size of 6% APTES-modified PSi at different pH condition (Cont.).

Size (μm)	Systems		
	pH 2	pH 6	pH 12
5.012	0.93	1.07	1.13
5.754	1.23	1.39	1.45
6.607	1.48	1.68	1.73
7.586	1.75	2.02	2.06
8.71	2.21	2.53	2.56
10	2.91	3.24	3.25
11.482	3.74	4	3.98
13.183	4.44	4.57	4.51
15.136	4.91	4.89	4.78
17.378	5.26	5.13	4.94
19.953	5.83	5.61	5.34
22.909	6.94	6.59	6.28
26.303	8.63	8.06	7.81
30.2	10.22	9.49	9.47
34.674	10.65	10.13	10.41
39.811	9.23	9.43	9.81
45.709	6.41	7.41	7.55
52.481	3.62	4.74	4.49
60.256	1.96	2.47	1.96
69.183	1.17	1.11	0.81
79.433	0.73	0.57	0.72
91.201	0.76	0.53	0.92
104.713	1.35	0.72	1.09
120.226	1.54	0.63	0.82
138.038	0.44	0.14	0.16
158.489	0	0	0
181.97	0	0	0
208.93	0	0	0
239.883	0	0	0
275.423	0	0	0
316.228	0	0	0
363.078	0	0	0
416.869	0	0	0
478.63	0	0	0
549.541	0	0	0
630.957	0	0	0
724.436	0	0	0
831.764	0	0	0
954.993	0	0	0
1096.478	0	0	0
1258.925	0	0	0
1445.44	0	0	0
1659.587	0	0	0
1905.461	0	0	0
2187.762	0	0	0

Table E4 Aggregates size of 6% APTES-modified PSi at different pH condition (Cont.).

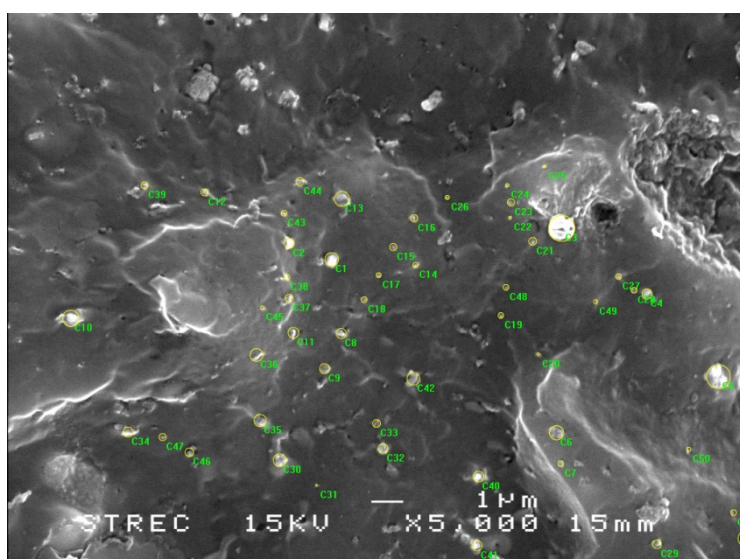
Size (μm)	Systems		
	pH 2	pH 6	pH 12
2511.886	0	0	0
2884.032	0	0	0
3311.311	0	0	0
3801.894	0	0	0
4365.158	0	0	0
5011.872	0	0	0
5754.399	0	0	0
6606.934	0	0	0
7585.776	0	0	0
8709.636	0	0	0
10000	0	0	0

APPENDIX F

PSI AGGLOMERATION SIZE BY PARTICLE ANALYSIS

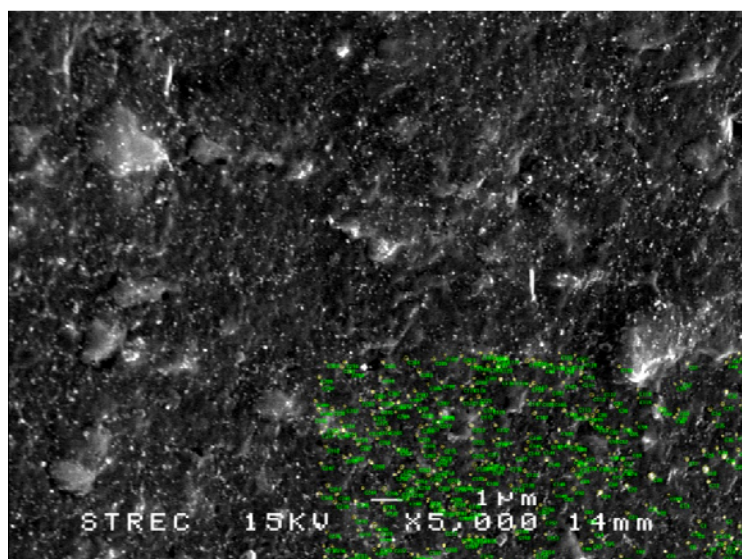
IMAGES

Table F5 Agglomeration size of unfilled CR.



	Features	Center X Pos.	Center Y Pos.	Area	Length	Radius
1	C1	5.526303	4.209345	0.042951	0.7346693	0.1169262
2	C2	4.80013	3.938568	0.0233196	0.5413352	0.0861561
3	C3	9.440256	3.6801	0.1541955	1.392005	0.2215445
4	C4	10.8926	4.80013	0.0233196	0.5413352	0.0861561
5	C5	12.1111	6.215553	0.129567	1.276004	0.2030824
6	C6	9.354099	7.175579	0.0475912	0.7733361	0.1230803
7	C7	9.427948	7.704824	0.0076145	0.3093344	0.0492321
8	C8	5.686308	5.477071	0.0233196	0.5413352	0.0861561
9	C9	5.403223	6.080165	0.0233196	0.5413352	0.0861561
10	C10	1.083106	5.218603	0.0629393	0.8893365	0.1415423
11	C11	4.873978	5.464763	0.02677	0.580002	0.0923101
12	C12	3.360091	3.064698	0.0118978	0.386668	0.0615401
13	C13	5.698616	3.175471	0.0524693	0.8120029	0.1292343
14	C14	6.954034	4.307809	0.0076145	0.3093344	0.0492321
15	C15	6.572486	4.000108	0.0118978	0.386668	0.0615401
16	C16	6.929418	3.507787	0.0118978	0.386668	0.0615401

	Features	Center X Pos.	Center Y Pos.	Area	Length	Radius
17	C17	6.326325	4.480121	0.0058299	0.2706676	0.043078
18	C18	6.080165	4.898594	0.0076145	0.3093344	0.0492321
19	C19	8.406381	5.169371	0.0076145	0.3093344	0.0492321
20	C20	9.046399	5.834004	0.0019036	0.1546672	0.024616
21	C21	8.947935	3.901644	0.0143963	0.4253348	0.0676941
22	C22	8.566386	3.495479	0.0019036	0.1546672	0.024616
23	C23	8.578694	3.237011	0.0118978	0.386668	0.0615401
24	C24	8.517154	2.941618	0.0029744	0.193334	0.03077
25	C25	9.157171	2.621609	0.0019036	0.1546672	0.024616
26	C26	7.495588	3.150855	0.0042832	0.2320008	0.036924
27	C27	10.41259	4.504737	0.0076145	0.3093344	0.0492321
28	C28	10.67106	4.73859	0.0076145	0.3093344	0.0492321
29	C29	11.06491	9.083323	0.0171328	0.4640016	0.0738481
30	C30	4.640126	7.643284	0.0385488	0.6960024	0.1107722
31	C31	5.267835	8.074065	0.0004759	0.0773336	0.012308
32	C32	6.400173	7.446355	0.0233196	0.5413352	0.0861561
33	C33	6.289401	7.015575	0.0143963	0.4253348	0.0676941
34	C34	2.05544	7.163271	0.0233196	0.5413352	0.0861561
35	C35	4.307809	6.966342	0.0343846	0.6573356	0.1046182
36	C36	4.246269	5.846312	0.0385488	0.6960024	0.1107722
37	C37	4.80013	4.873978	0.0143963	0.4253348	0.0676941
38	C38	4.763206	4.517045	0.0076145	0.3093344	0.0492321
39	C39	2.338525	2.941618	0.0118978	0.386668	0.0615401
40	C40	8.024833	7.926368	0.02677	0.580002	0.0923101
41	C41	8.000217	9.107939	0.0233196	0.5413352	0.0861561
42	C42	6.91711	6.252477	0.0385488	0.6960024	0.1107722
43	C43	4.713974	3.421631	0.0076145	0.3093344	0.0492321
44	C44	4.98475	2.880078	0.0143963	0.4253348	0.0676941
45	C45	4.344733	5.033982	0.0029744	0.193334	0.03077
46	C46	3.101622	7.507896	0.0171328	0.4640016	0.0738481
47	C47	2.646225	7.249427	0.0118978	0.386668	0.0615401
48	C48	8.492538	4.689358	0.0076145	0.3093344	0.0492321
49	C49	10.01873	4.935518	0.0042832	0.2320008	0.036924
50	C50	11.60647	7.458664	0.0042832	0.2320008	0.036924
51	C51	12.36957	8.54177	0.0076145	0.3093344	0.0492321
52	C52	12.5788	8.984859	0.0575853	0.8506697	0.1353883
					mean	0.074558196
					SD	0.041117168

Table F6 Agglomeration size of CR filled with unmodified PSi.

	Features	Center X Pos.	Center Y Pos.	Area	Length	Radius
1	C1	19.16346	13.59615	0.007261	0.302076	0.048077
2	C2	19.14423	14.03846	0.001162	0.120831	0.019231
3	C3	17.95192	14.09615	0.001162	0.120831	0.019231
4	C4	17.93269	13.78846	0.007261	0.302076	0.048077
5	C5	17.72115	13.32692	0.001162	0.120831	0.019231
6	C6	18.64423	13.19231	0.007261	0.302076	0.048077
7	C7	18.47115	12.94231	0.004647	0.241661	0.038462
8	C8	17.06731	12.07692	0.004647	0.241661	0.038462
9	C9	16.89423	13.17308	0.004647	0.241661	0.038462
10	C10	16.39423	12.76923	0.010456	0.362492	0.057692
11	C11	16.43269	12.19231	0.018589	0.483322	0.076923
12	C12	16.64423	11.82692	0.018589	0.483322	0.076923
13	C13	17.52885	11.80769	0.004647	0.241661	0.038462
14	C14	18.79808	12.01923	0.001162	0.120831	0.019231
15	C15	19.54808	11.96154	0.001162	0.120831	0.019231
16	C16	18.49038	12.51923	0.001162	0.120831	0.019231
17	C17	18.49038	11.46154	0.010456	0.362492	0.057692
18	C18	19.02885	11.09615	0.010456	0.362492	0.057692
19	C19	18.04808	11	0.018589	0.483322	0.076923
20	C20	18.74038	10.82692	0.004647	0.241661	0.038462
21	C21	18.29808	10.69231	0.001162	0.120831	0.019231
22	C22	18.89423	10.38462	0.018589	0.483322	0.076923
23	C23	18.43269	10.07692	0.018589	0.483322	0.076923
24	C24	18.39423	9.865385	0.004647	0.241661	0.038462
25	C25	17.875	9.807692	0.004647	0.241661	0.038462
26	C26	17.79808	10.07692	0.010456	0.362492	0.057692
27	C27	17.31731	10.09615	0.004647	0.241661	0.038462

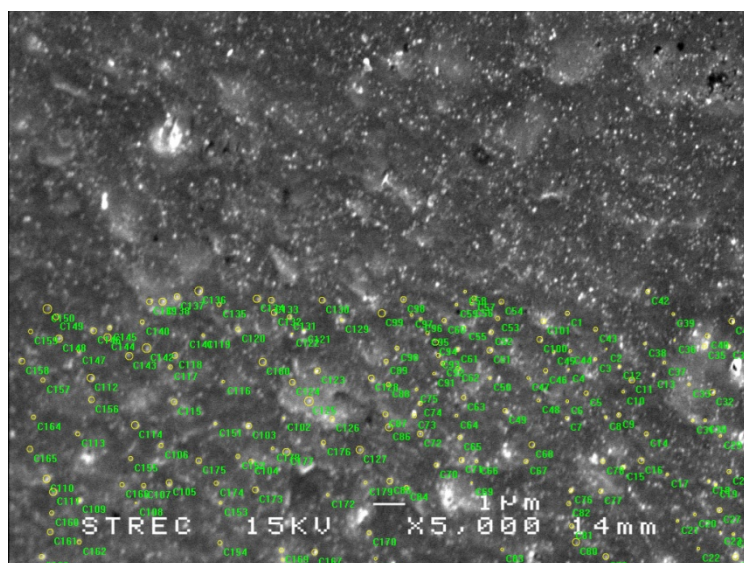
	Features	Center X Pos.	Center Y Pos.	Area	Length	Radius
28	C28	17.66346	10.73077	0.004647	0.241661	0.038462
29	C29	17.33654	10.73077	0.018589	0.483322	0.076923
30	C30	17.52885	10.57692	0.004647	0.241661	0.038462
31	C31	16.64423	10.5	0.004647	0.241661	0.038462
32	C32	16.06731	10.65385	0.004647	0.241661	0.038462
33	C33	18.80769	6.788462	0.010456	0.362492	0.057692
34	C34	17.86538	6.25	0.010456	0.362492	0.057692
35	C35	18.15385	5.5	0.004647	0.241661	0.038462
36	C36	17.69231	5.057692	0.010456	0.362492	0.057692
37	C37	17.17308	4.423077	0.010456	0.362492	0.057692
38	C38	19.38462	4.288462	0.029046	0.604152	0.096154
39	C39	18.55769	4.980769	0.010456	0.362492	0.057692
40	C40	19.65385	5.942308	0.004647	0.241661	0.038462
41	C41	18.21154	7.519231	0.029046	0.604152	0.096154
42	C42	18.80769	8.576923	0.029046	0.604152	0.096154
43	C43	17.36538	8.807692	0.004647	0.241661	0.038462
44	C44	16.86538	8.5	0.001162	0.120831	0.019231
45	C45	16.59615	8.480769	0.004647	0.241661	0.038462
46	C46	16.01923	8.788462	0.004647	0.241661	0.038462
47	C47	14.82692	9.057692	0.001162	0.120831	0.019231
48	C48	15.26923	9.076923	0.010456	0.362492	0.057692
49	C49	15.05769	9.730769	0.004647	0.241661	0.038462
50	C50	14.36538	9.942308	0.041826	0.724983	0.115385
51	C51	15.5	10.80769	0.018589	0.483322	0.076923
52	C52	14.69231	10.75	0.010456	0.362492	0.057692
53	C53	13.15385	10.90385	0.001162	0.120831	0.019231
54	C54	11.07692	11.73077	0.004647	0.241661	0.038462
55	C55	12.21154	9.057692	0.004647	0.241661	0.038462
56	C56	11.90385	8.634615	0.001162	0.120831	0.019231
57	C57	9.846154	10.23077	0.007261	0.302076	0.048077
58	C58	8.25	11.40385	0.010456	0.362492	0.057692
59	C59	9.384615	10.86538	0.004647	0.241661	0.038462
60	C60	8.115385	10.38462	0.004647	0.241661	0.038462
61	C61	8.442308	10	0.004647	0.241661	0.038462
62	C62	9.173077	9.884615	0.001162	0.120831	0.019231
63	C63	12	12.67308	0.010456	0.362492	0.057692
64	C64	11.78846	12.86538	0.004647	0.241661	0.038462
65	C65	11.61538	14.26923	0.018589	0.483322	0.076923
66	C66	13.57692	14.36538	0.004647	0.241661	0.038462
67	C67	12.76923	14.09615	0.018589	0.483322	0.076923
68	C68	15	14.17308	0.010456	0.362492	0.057692
69	C69	14.67308	13.21154	0.010456	0.362492	0.057692
70	C70	15.63462	13.13462	0.010456	0.362492	0.057692

	Features	Center X Pos.	Center Y Pos.	Area	Length	Radius
71	C71	14.59615	12.34615	0.014232	0.422907	0.067308
72	C72	14.44231	12.80769	0.004647	0.241661	0.038462
73	C73	14.28846	12.25	0.010456	0.362492	0.057692
74	C74	15.46154	8.519231	0.010456	0.362492	0.057692
75	C75	14.34615	8.942308	0.001162	0.120831	0.019231
76	C76	13.59615	8.923077	0.004647	0.241661	0.038462
77	C77	14.23077	7.673077	0.004647	0.241661	0.038462
78	C78	13.94231	7.826923	0.004647	0.241661	0.038462
79	C79	13.46154	8.307692	0.004647	0.241661	0.038462
80	C80	14.38462	6.576923	0.001162	0.120831	0.019231
81	C81	13.15385	6.903846	0.010456	0.362492	0.057692
82	C82	12.34615	7.326923	0.004647	0.241661	0.038462
83	C83	12	7.019231	0.001162	0.120831	0.019231
84	C84	11.73077	7.25	0.018589	0.483322	0.076923
85	C85	11.94231	7.788462	0.004647	0.241661	0.038462
86	C86	14.94231	4.711538	0.010456	0.362492	0.057692
87	C87	14.82692	4.403846	0.004647	0.241661	0.038462
88	C88	14.48077	3.923077	0.004647	0.241661	0.038462
89	C89	12.94231	4.5	0.014232	0.422907	0.067308
90	C90	12.63462	4.134615	0.010456	0.362492	0.057692
91	C91	11.73077	4.884615	0.018589	0.483322	0.076923
92	C92	11.34615	4.153846	0.018589	0.483322	0.076923
93	C93	11.86538	3.788462	0.010456	0.362492	0.057692
94	C94	10.13462	5.442308	0.018589	0.483322	0.076923
95	C95	10.21154	4.653846	0.05693	0.845813	0.134615
96	C96	9.288462	5.75	0.001162	0.120831	0.019231
97	C97	7.807692	5.711538	0.004647	0.241661	0.038462
98	C98	8.538462	4.038462	0.010456	0.362492	0.057692
99	C99	8	4.326923	0.010456	0.362492	0.057692
100	C100	7.769231	4.923077	0.001162	0.120831	0.019231
101	C101	7.576923	5.153846	0.001162	0.120831	0.019231
102	C102	7.153846	5.076923	0.001162	0.120831	0.019231
103	C103	6.711538	5.442308	0.018589	0.483322	0.076923
104	C104	7.615385	6.346154	0.010456	0.362492	0.057692
105	C105	6.980769	7.826923	0.010456	0.362492	0.057692
106	C106	6.134615	7.884615	0.018589	0.483322	0.076923
107	C107	5.711538	8.384615	0.018589	0.483322	0.076923
108	C108	5.403846	9.076923	0.001162	0.120831	0.019231
109	C109	5.326923	8.75	0.004647	0.241661	0.038462
110	C110	5.269231	8.346154	0.001162	0.120831	0.019231
111	C111	4.884615	8.134615	0.007261	0.302076	0.048077
112	C112	5.653846	6.673077	0	0	
113	C113	10.53846	12.55769	0.010456	0.362492	0.057692

	Features	Center X Pos.	Center Y Pos.	Area	Length	Radius
114	C114	9.673077	13.48077	0.004647	0.241661	0.038462
115	C115	9.096154	13.26923	0.001162	0.120831	0.019231
116	C116	6.115385	12.17308	0.001162	0.120831	0.019231
117	C117	4.134615	9.480769	0.010456	0.362492	0.057692
118	C118	3.096154	9.269231	0.010456	0.362492	0.057692
119	C119	3.615385	9.307692	0.001162	0.120831	0.019231
120	C120	2.884615	7.865385	0.004647	0.241661	0.038462
121	C121	3.846154	7.192308	0.001162	0.120831	0.019231
122	C122	3.442308	7.096154	0.004647	0.241661	0.038462
123	C123	3.923077	5.769231	0.010456	0.362492	0.057692
124	C124	3.673077	5.442308	0.018589	0.483322	0.076923
125	C125	4.826923	5.038462	0.010456	0.362492	0.057692
126	C126	2.942308	6.057692	0.004647	0.241661	0.038462
127	C127	1.826923	6.961538	0.018589	0.483322	0.076923
128	C128	2.096154	7.615385	0.004647	0.241661	0.038462
129	C129	2.365385	7.673077	0.001162	0.120831	0.019231
130	C130	2.25	9.423077	0.041826	0.724983	0.115385
131	C131	1.826923	9.596154	0.004647	0.241661	0.038462
132	C132	2.269231	10.5	0.001162	0.120831	0.019231
133	C133	2.057692	10.36538	0.010456	0.362492	0.057692
134	C134	3.057692	10.34615	0.001162	0.120831	0.019231
135	C135	2.769231	11.63462	0.004647	0.241661	0.038462
136	C136	9.5	7.653846	0.004647	0.241661	0.038462
137	C137	8.884615	8.057692	0.010456	0.362492	0.057692
138	C138	10.69231	8.384615	0.010456	0.362492	0.057692
139	C139	11.05769	7.942308	0.004647	0.241661	0.038462
140	C140	10.92308	7.538462	0.004647	0.241661	0.038462
141	C141	10.57692	7.865385	0.004647	0.241661	0.038462
142	C142	10.13462	8.192308	0.010456	0.362492	0.057692
143	C143	10.5	8.769231	0.001162	0.120831	0.019231
144	C144	10.36538	9.596154	0.018589	0.483322	0.076923
145	C145	10.84615	9.615385	0.001162	0.120831	0.019231
146	C146	12.19231	10.28846	0.010456	0.362492	0.057692
147	C147	12.48077	10.94231	0.004647	0.241661	0.038462
148	C148	12.38462	11.36538	0.004647	0.241661	0.038462
149	C149	9.615385	11.98077	0.010456	0.362492	0.057692
150	C150	9.5	11.40385	0.004647	0.241661	0.038462
151	C151	7.557692	11.13462	0.010456	0.362492	0.057692
152	C152	7.442308	9.980769	0.004647	0.241661	0.038462
153	C153	7.75	9.326923	0.001162	0.120831	0.019231
154	C154	7.423077	9.461538	0.010456	0.362492	0.057692
155	C155	6.538462	9.807692	0.001162	0.120831	0.019231
156	C156	5.673077	12.25	0.001162	0.120831	0.019231

	Features	Center X Pos.	Center Y Pos.	Area	Length	Radius
157	C157	6.442308	10.75	0.001162	0.120831	0.019231
158	C158	6	10.78846	0.001162	0.120831	0.019231
159	C159	4.980769	10.71154	0.001162	0.120831	0.019231
160	C160	5.730769	10.25	0.001162	0.120831	0.019231
161	C161	4.307692	10.36538	0.010456	0.362492	0.057692
162	C162	1.576923	5.25	0.001162	0.120831	0.019231
163	C163	1.038462	5.788462	0.010456	0.362492	0.057692
164	C164	1	6.115385	0.004647	0.241661	0.038462
165	C165	0.6346154	6.096154	0.001162	0.120831	0.019231
166	C166	0.6538462	5.826923	0.004647	0.241661	0.038462
167	C167	0.7307692	4.576923	0.001162	0.120831	0.019231
168	C168	1.096154	4.5	0.001162	0.120831	0.019231
169	C169	0.9615385	4.134615	0.004647	0.241661	0.038462
170	C170	1.076923	3.807692	0.001162	0.120831	0.019231
171	C171	10.46154	7	0.004647	0.241661	0.038462
172	C172	10.44231	6.576923	0.001162	0.120831	0.019231
173	C173	11.15385	6.442308	0.001162	0.120831	0.019231
174	C174	16.09615	6.788462	0.004647	0.241661	0.038462
175	C175	15.36538	5.692308	0.001162	0.120831	0.019231
176	C176	16.82692	4.884615	0.007261	0.302076	0.048077
177	C177	16.13462	4.807692	0.001162	0.120831	0.019231
178	C178	16.48077	3.634615	0.004647	0.241661	0.038462
179	C179	17.17308	4.25	0.001162	0.120831	0.019231
180	C180	14.5	5.692308	0.004647	0.241661	0.038462
181	C181	15.38462	5.711538	0.004647	0.241661	0.038462
182	C182	11.36538	5.076923	0.010456	0.362492	0.057692
183	C183	10.75	4.5	0.001162	0.120831	0.019231
184	C184	10.92308	4.307692	0.010456	0.362492	0.057692
185	C185	10.86538	3.865385	0.001162	0.120831	0.019231
186	C186	9.134615	3.923077	0.001162	0.120831	0.019231
187	C187	9.653846	5.25	0.004647	0.241661	0.038462
188	C188	5.538462	5.903846	0.001162	0.120831	0.019231
189	C189	5.230769	4.269231	0.001162	0.120831	0.019231
190	C190	5.269231	3.730769	0.004647	0.241661	0.038462
191	C191	4.288462	4.346154	0.001162	0.120831	0.019231
192	C192	4.730769	4.057692	0.001162	0.120831	0.019231
193	C193	3.769231	4.634615	0.018589	0.483322	0.076923
194	C194	3.769231	3.615385	0.004647	0.241661	0.038462
195	C195	3.384615	3.961538	0.010456	0.362492	0.057692
196	C196	2.846154	3.903846	0.004647	0.241661	0.038462
197	C197	3.057692	5.576923	0.001162	0.120831	0.019231
198	C198	2.346154	4.653846	0.004647	0.241661	0.038462
199	C199	0.5576923	4.057692	0.004647	0.241661	0.038462

	Features	Center X Pos.	Center Y Pos.	Area	Length	Radius
200	C200	0.3846154	5.269231	0.004647	0.241661	0.038462
201	C201	0.5961538	4.75	0.004647	0.241661	0.038462
202	C202	0.4423077	6.480769	0.004647	0.241661	0.038462
203	C203	1.134615	7.307692	0.010456	0.362492	0.057692
204	C204	0.9230769	7.653846	0.004647	0.241661	0.038462
205	C205	0.6153846	7.788462	0.010456	0.362492	0.057692
206	C206	0.8076923	8.557692	0.018589	0.483322	0.076923
207	C207	0.6538462	8.711538	0.001162	0.120831	0.019231
208	C208	0.8846154	10.21154	0.004647	0.241661	0.038462
209	C209	0.6730769	9.692308	0.001162	0.120831	0.019231
210	C210	1.634615	9.173077	0.001162	0.120831	0.019231
211	C211	1.461538	9.288462	0.001162	0.120831	0.019231
212	C212	0.8269231	11.17308	0.018589	0.483322	0.076923
213	C213	1.115385	11.23077	0.004647	0.241661	0.038462
214	C214	0.4615385	11.51923	0.004647	0.241661	0.038462
215	C215	0.8653846	12.01923	0.004647	0.241661	0.038462
216	C216	0.8846154	12.42308	0.004647	0.241661	0.038462
217	C217	0.8846154	13.23077	0.001162	0.120831	0.019231
218	C218	0.6538462	13.46154	0.004647	0.241661	0.038462
219	C219	0.5576923	13.30769	0.010456	0.362492	0.057692
220	C220	0.4230769	13.88462	0.001162	0.120831	0.019231
221	C221	0.3846154	13.53846	0.010456	0.362492	0.057692
222	C222	1.5	14.32692	0.001162	0.120831	0.019231
223	C223	1.730769	14.42308	0.010456	0.362492	0.057692
224	C224	2.269231	14.13462	0.010456	0.362492	0.057692
225	C225	2.5	14	0.004647	0.241661	0.038462
226	C226	2.884615	12.55769	0.004647	0.241661	0.038462
227	C227	4.461538	12.88462	0.004647	0.241661	0.038462
228	C228	4.596154	12.17308	0.004647	0.241661	0.038462
229	C229	4.923077	11.61538	0.004647	0.241661	0.038462
230	C230	4.038462	11.80769	0.010456	0.362492	0.057692
231	C231	3.75	11.55769	0.001162	0.120831	0.019231
232	C232	5.480769	14.26923	0.004647	0.241661	0.038462
233	C233	4.519231	14.48077	0.010456	0.362492	0.057692
234	C234	5.634615	13.78846	0.010456	0.362492	0.057692
235	C235	9	14.38462	0.004647	0.241661	0.038462
236	C236	8.461538	14.11538	0.001162	0.120831	0.019231
237	C237	8.25	14.51923	0.001162	0.120831	0.019231
238	C238	7.769231	14.09615	0.010456	0.362492	0.057692
239	C239	9.903846	14.5	0.004647	0.241661	0.038462
240	C240	6.769231	14.44231	0.004647	0.241661	0.038462
					mean	0.04337
					SD	0.020868

Table F7 Agglomeration size of CR filled with 2% APTES-modified PSi.

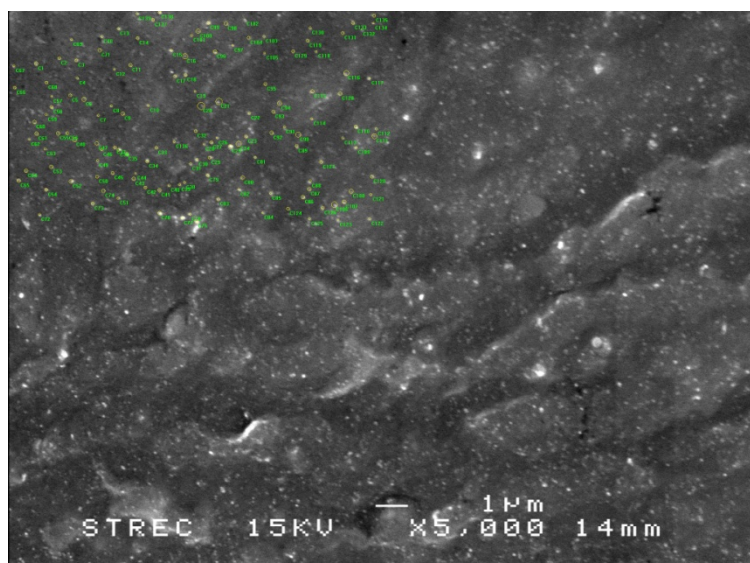
	Features	Center X Pos.	Center Y Pos.	Area	Length	Radius
1	C1	14.83654	8	0.010456	0.362492	0.057692
2	C2	15.875	8.942308	0.001162	0.120831	0.019231
3	C3	15.58654	9.211538	0.004647	0.241661	0.038462
4	C4	14.875	9.480769	0.001162	0.120831	0.019231
5	C5	15.33654	10.11538	0.010456	0.362492	0.057692
6	C6	14.83654	10.32692	0.004647	0.241661	0.038462
7	C7	14.81731	10.76923	0.004647	0.241661	0.038462
8	C8	15.85577	10.75	0.004647	0.241661	0.038462
9	C9	16.20192	10.69231	0.010456	0.362492	0.057692
10	C10	16.31731	10.07692	0.004647	0.241661	0.038462
11	C11	16.54808	9.769231	0.018589	0.483322	0.076923
12	C12	16.22115	9.403846	0.004647	0.241661	0.038462
13	C13	17.125	9.634615	0.001162	0.120831	0.019231
14	C14	16.93269	11.19231	0.010456	0.362492	0.057692
15	C15	16.31731	12.07692	0.010456	0.362492	0.057692
16	C16	16.79808	11.90385	0.018589	0.483322	0.076923
17	C17	17.49038	12.26923	0.004647	0.241661	0.038462
18	C18	18.58654	12.44231	0.004647	0.241661	0.038462
19	C19	18.77885	12.53846	0.004647	0.241661	0.038462
20	C20	18.22115	13.32692	0.004647	0.241661	0.038462
21	C21	17.75962	13.5	0.004647	0.241661	0.038462
22	C22	18.31731	14.23077	0.004647	0.241661	0.038462
23	C23	18.89423	13.78846	0.001162	0.120831	0.019231
24	C24	19.24038	13.84615	0.004647	0.241661	0.038462
25	C25	19.29808	14.46154	0.018589	0.483322	0.076923
26	C26	19.66346	13.09615	0.004647	0.241661	0.038462

	Features	Center X Pos.	Center Y Pos.	Area	Length	Radius
27	C27	18.875	13.21154	0.014232	0.422907	0.067308
28	C28	19.125	12.19231	0.010456	0.362492	0.057692
29	C29	18.89423	11.25	0.004647	0.241661	0.038462
30	C30	18.49038	10.82692	0.004647	0.241661	0.038462
31	C31	18.16346	10.84615	0.004647	0.241661	0.038462
32	C32	18.68269	10.09615	0.018589	0.483322	0.076923
33	C33	18.06731	9.884615	0.004647	0.241661	0.038462
34	C34	19.125	8.865385	0.004647	0.241661	0.038462
35	C35	18.47115	8.865385	0.010456	0.362492	0.057692
36	C36	17.68269	8.711538	0.001162	0.120831	0.019231
37	C37	17.41346	9.307692	0.004647	0.241661	0.038462
38	C38	16.89423	8.807692	0.004647	0.241661	0.038462
39	C39	17.64423	8.019231	0.004647	0.241661	0.038462
40	C40	18.54808	8.596154	0.010456	0.362492	0.057692
41	C41	19.20192	8.211538	0.018589	0.483322	0.076923
42	C42	16.97115	7.423077	0.010456	0.362492	0.057692
43	C43	15.58654	8.423077	0.010456	0.362492	0.057692
44	C44	14.91346	9	0.004647	0.241661	0.038462
45	C45	14.47115	9.019231	0.004647	0.241661	0.038462
46	C46	14.25962	9.519231	0.010456	0.362492	0.057692
47	C47	13.79808	9.711538	0.004647	0.241661	0.038462
48	C48	14.06731	10.30769	0.004647	0.241661	0.038462
49	C49	13.18269	10.57692	0.010456	0.362492	0.057692
50	C50	12.77885	9.711538	0.004647	0.241661	0.038462
51	C51	12.77885	8.980769	0.018589	0.483322	0.076923
52	C52	12.81731	8.5	0.010456	0.362492	0.057692
53	C53	12.99038	8.134615	0.010456	0.362492	0.057692
54	C54	13.08654	7.692308	0.014232	0.422907	0.067308
55	C55	12.125	8.365385	0.001162	0.120831	0.019231
56	C56	12.29808	7.75	0.004647	0.241661	0.038462
57	C57	12.35577	7.596154	0.010456	0.362492	0.057692
58	C58	12.125	7.423077	0.004647	0.241661	0.038462
59	C59	11.89423	7.769231	0.004647	0.241661	0.038462
60	C60	11.56731	8.192308	0.010456	0.362492	0.057692
61	C61	11.91346	8.961538	0.010456	0.362492	0.057692
62	C62	11.93269	9.461538	0.010456	0.362492	0.057692
63	C63	12.08654	10.23077	0.010456	0.362492	0.057692
64	C64	11.89423	10.71154	0.004647	0.241661	0.038462
65	C65	11.99038	11.28846	0.010456	0.362492	0.057692
66	C66	12.43269	11.92308	0.004647	0.241661	0.038462
67	C67	13.74038	11.92308	0.010456	0.362492	0.057692
68	C68	13.89423	11.48077	0.018589	0.483322	0.076923
69	C69	12.29808	12.48077	0.001162	0.120831	0.019231

	Features	Center X Pos.	Center Y Pos.	Area	Length	Radius
70	C70	11.35577	12.01923	0.010456	0.362492	0.057692
71	C71	12.02885	11.88462	0.014232	0.422907	0.067308
72	C72	10.93269	11.19231	0.018589	0.483322	0.076923
73	C73	10.77885	10.71154	0.010456	0.362492	0.057692
74	C74	10.93269	10.38462	0.010456	0.362492	0.057692
75	C75	10.83654	10.01923	0.004647	0.241661	0.038462
76	C76	14.93269	12.69231	0.010456	0.362492	0.057692
77	C77	15.72115	12.71154	0.010456	0.362492	0.057692
78	C78	15.77885	11.92308	0.010456	0.362492	0.057692
79	C79	15.85577	14.44231	0.018589	0.483322	0.076923
80	C80	15.06731	14.05769	0.029046	0.604152	0.096154
81	C81	14.95192	13.63462	0.010456	0.362492	0.057692
82	C82	14.875	13.03846	0.010456	0.362492	0.057692
83	C83	13.10577	14.25	0.004647	0.241661	0.038462
84	C84	10.56731	12.61538	0.010456	0.362492	0.057692
85	C85	10.125	12.44231	0.018589	0.483322	0.076923
86	C86	10.10577	11.01923	0.029046	0.604152	0.096154
87	C87	10.00962	10.67308	0.014232	0.422907	0.067308
88	C88	10.08654	9.884615	0.010456	0.362492	0.057692
89	C89	10.02885	9.269231	0.010456	0.362492	0.057692
90	C90	10.31731	8.923077	0.010456	0.362492	0.057692
91	C91	11.29808	9.596154	0.004647	0.241661	0.038462
92	C92	11.52885	9.326923	0.010456	0.362492	0.057692
93	C93	11.41346	9.115385	0.010456	0.362492	0.057692
94	C94	11.33654	8.769231	0.018589	0.483322	0.076923
95	C95	11.125	8.519231	0.007261	0.302076	0.048077
96	C96	10.95192	8.153846	0.004647	0.241661	0.038462
97	C97	10.70192	8.038462	0.004647	0.241661	0.038462
98	C98	10.49038	7.634615	0.018589	0.483322	0.076923
99	C99	9.913462	8	0.029046	0.604152	0.096154
100	C100	14.10577	8.692308	0.018589	0.483322	0.076923
101	C101	14.20192	8.211538	0.014232	0.422907	0.067308
102	C102	7.307692	10.76923	0.001162	0.120831	0.019231
103	C103	6.384615	10.98077	0.018589	0.483322	0.076923
104	C104	6.442308	11.92308	0.010456	0.362492	0.057692
105	C105	4.269231	12.48077	0.018589	0.483322	0.076923
106	C106	4.057692	11.5	0.010456	0.362492	0.057692
107	C107	3.596154	12.55769	0.010456	0.362492	0.057692
108	C108	3.384615	13.01923	0.001162	0.120831	0.019231
109	C109	1.865385	12.94231	0.010456	0.362492	0.057692
110	C110	1.019231	12.38462	0.029046	0.604152	0.096154
111	C111	1.192308	12.73077	0.029046	0.604152	0.096154
112	C112	2.192308	9.711538	0.029046	0.604152	0.096154

	Features	Center X Pos.	Center Y Pos.	Area	Length	Radius
113	C113	1.846154	11.19231	0.010456	0.362492	0.057692
114	C114	3.365385	10.96154	0.029046	0.604152	0.096154
115	C115	4.403846	10.34615	0.018589	0.483322	0.076923
116	C116	5.711538	9.807692	0.004647	0.241661	0.038462
117	C117	4.307692	9.423077	0.010456	0.362492	0.057692
118	C118	4.423077	9.115385	0.018589	0.483322	0.076923
119	C119	5.173077	8.576923	0.004647	0.241661	0.038462
120	C120	6.096154	8.423077	0.010456	0.362492	0.057692
121	C121	7.846154	8.442308	0.001162	0.120831	0.019231
122	C122	7.538462	8.538462	0.001162	0.120831	0.019231
123	C123	8.211538	9.519231	0.018589	0.483322	0.076923
124	C124	7.538462	9.826923	0.018589	0.483322	0.076923
125	C125	7.980769	10.32692	0.041826	0.724983	0.115385
126	C126	8.596154	10.78846	0.010456	0.362492	0.057692
127	C127	9.326923	11.61538	0.029046	0.604152	0.096154
128	C128	9.634615	9.711538	0.018589	0.483322	0.076923
129	C129	8.846154	8.173077	0.004647	0.241661	0.038462
130	C130	8.326923	7.653846	0.018589	0.483322	0.076923
131	C131	7.461538	8.096154	0.010456	0.362492	0.057692
132	C132	7.057692	7.980769	0.018589	0.483322	0.076923
133	C133	6.980769	7.653846	0.018589	0.483322	0.076923
134	C134	6.596154	7.615385	0.029046	0.604152	0.096154
135	C135	5.596154	7.769231	0.010456	0.362492	0.057692
136	C136	5.057692	7.403846	0.035145	0.664568	0.105769
137	C137	4.480769	7.557692	0.018589	0.483322	0.076923
138	C138	4.096154	7.692308	0.029046	0.604152	0.096154
139	C139	3.75	7.692308	0.018589	0.483322	0.076923
140	C140	3.557692	8.230769	0.010456	0.362492	0.057692
141	C141	4.711538	8.576923	0	0	
142	C142	3.673077	8.923077	0.041826	0.724983	0.115385
143	C143	3.211538	9.134615	0.029046	0.604152	0.096154
144	C144	2.634615	8.634615	0.029046	0.604152	0.096154
145	C145	2.692308	8.384615	0.010456	0.362492	0.057692
146	C146	2.269231	8.461538	0.018589	0.483322	0.076923
147	C147	1.865385	9	0.004647	0.241661	0.038462
148	C148	1.346154	8.673077	0.029046	0.604152	0.096154
149	C149	1.269231	8.096154	0.018589	0.483322	0.076923
150	C150	1.038462	7.884615	0.041826	0.724983	0.115385
151	C151	5.5	10.92308	0.004647	0.241661	0.038462
152	C152	6.096154	11.78846	0.010456	0.362492	0.057692
153	C153	5.634615	13.01923	0.004647	0.241661	0.038462
154	C154	5.615385	14.07692	0.010456	0.362492	0.057692
155	C155	3.25	11.84615	0.010456	0.362492	0.057692

	Features	Center X Pos.	Center Y Pos.	Area	Length	Radius
156	C156	2.211538	10.28846	0.018589	0.483322	0.076923
157	C157	0.923077	9.769231	0.010456	0.362492	0.057692
158	C158	0.365385	9.269231	0.018589	0.483322	0.076923
159	C159	0.596154	8.480769	0.010456	0.362492	0.057692
160	C160	1.153846	13.28846	0.010456	0.362492	0.057692
161	C161	1.115385	13.78846	0.018589	0.483322	0.076923
162	C162	1.884615	14.05769	0.010456	0.362492	0.057692
163	C163	0.884615	14.44231	0.010456	0.362492	0.057692
164	C164	0.673077	10.75	0.010456	0.362492	0.057692
165	C165	0.576923	11.59615	0.018589	0.483322	0.076923
166	C166	3.019231	12.53846	0.010456	0.362492	0.057692
167	C167	8.134615	14.32692	0.018589	0.483322	0.076923
168	C168	7.288462	14.51923	0.004647	0.241661	0.038462
169	C169	7.25	14.26923	0.010456	0.362492	0.057692
170	C170	9.576923	13.80769	0.010456	0.362492	0.057692
171	C171	9.75	14.5	0.004647	0.241661	0.038462
172	C172	8.480769	12.80769	0.004647	0.241661	0.038462
173	C173	6.557692	12.67308	0.018589	0.483322	0.076923
174	C174	5.519231	12.5	0.010456	0.362492	0.057692
175	C175	5.057692	11.90385	0.018589	0.483322	0.076923
176	C176	8.365385	11.42308	0.010456	0.362492	0.057692
177	C177	7.384615	11.67308	0.029046	0.604152	0.096154
178	C178	7.019231	11.57692	0.004647	0.241661	0.038462
179	C179	9.480769	12.48077	0.004647	0.241661	0.038462
180	C180	6.75	9.288462	0.029046	0.604152	0.096154
					mean	0.058498
					SD	0.021341

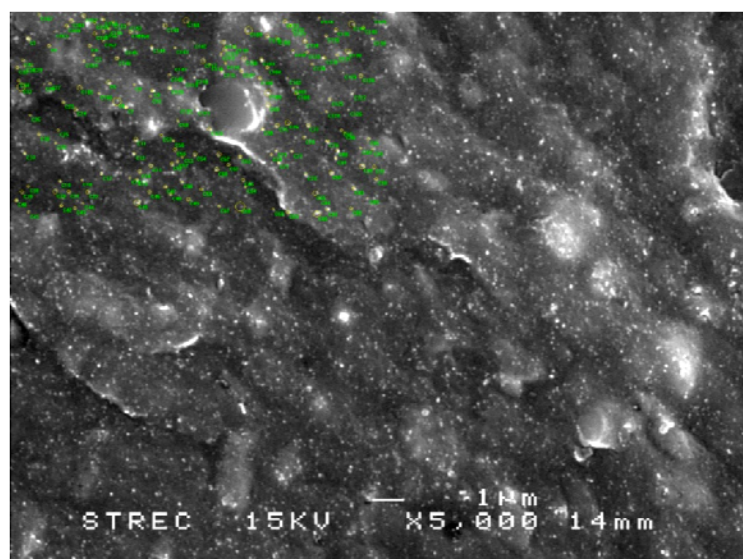
Table F8 Agglomeration size of CR filled with 4% APTES-modified PSi.

	Features	Center X Pos.	Center Y Pos.	Area	Length	Radius
1	C1	0.740385	1.384615	0.007261	0.302076	0.048077
2	C2	1.346154	1.240385	0.004647	0.241661	0.038462
3	C3	1.798077	1.298077	0.004647	0.241661	0.038462
4	C4	1.826923	1.769231	0.002614	0.181246	0.028846
5	C5	1.634615	2.221154	0.004647	0.241661	0.038462
6	C6	2	2.326923	0.010456	0.362492	0.057692
7	C7	2.375	2.75	0.002614	0.181246	0.028846
8	C8	2.721154	2.5	0.002614	0.181246	0.028846
9	C9	3.019231	2.701923	0.007261	0.302076	0.048077
10	C10	3.692308	2.490385	0.002614	0.181246	0.028846
11	C11	3.221154	1.423077	0.007261	0.302076	0.048077
12	C12	2.798077	1.538462	0.001162	0.120831	0.019231
13	C13	2.903846	0.461539	0.002614	0.181246	0.028846
14	C14	3.413462	0.711539	0.004647	0.241661	0.038462
15	C15	4.298077	1.028846	0.002614	0.181246	0.028846
16	C16	4.663462	1.192308	0.014232	0.422907	0.067308
17	C17	4.394231	1.721154	0.004647	0.241661	0.038462
18	C18	4.673077	1.682692	0.004647	0.241661	0.038462
19	C19	4.923077	2.115385	0.001162	0.120831	0.019231
20	C20	5.086538	2.5	0.029046	0.604152	0.096154
21	C21	5.557692	2.384615	0.023527	0.543737	0.086538
22	C22	6.355769	2.692308	0.002614	0.181246	0.028846
23	C23	6.269231	3.307692	0.004647	0.241661	0.038462
24	C24	6.076923	3.5	0.014232	0.422907	0.067308
25	C25	5.855769	3.567308	0.007261	0.302076	0.048077
26	C26	5.5	3.346154	0.001162	0.120831	0.019231

	Features	Center X Pos.	Center Y Pos.	Area	Length	Radius
27	C27	5.355769	3.461538	0.004647	0.241661	0.038462
28	C28	5.153846	3.509615	0.001162	0.120831	0.019231
29	C29	5.307692	3.865385	0.004647	0.241661	0.038462
30	C30	4.980769	3.913462	0.002614	0.181246	0.028846
31	C31	4.807692	4.028846	0.002614	0.181246	0.028846
32	C32	4.942308	3.163462	0.004647	0.241661	0.038462
33	C33	3.903846	3.605769	0.004647	0.241661	0.038462
34	C34	3.663462	3.961538	0.004647	0.241661	0.038462
35	C35	3.125	3.769231	0.004647	0.241661	0.038462
36	C36	2.903846	3.663462	0.004647	0.241661	0.038462
37	C37	2.817308	3.596154	0.004647	0.241661	0.038462
38	C38	4.644231	4.519231	0.002614	0.181246	0.028846
39	C39	4.519231	4.576923	0.002614	0.181246	0.028846
40	C40	4.240385	4.596154	0.002614	0.181246	0.028846
41	C41	3.990385	4.721154	0.007261	0.302076	0.048077
42	C42	3.615385	4.653846	0.004647	0.241661	0.038462
43	C43	3.307692	4.423077	0.007261	0.302076	0.048077
44	C44	3.355769	4.278846	0.001162	0.120831	0.019231
45	C45	2.75	4.269231	0.004647	0.241661	0.038462
46	C46	2.461538	3.653846	0.002614	0.181246	0.028846
47	C47	2.336538	3.490385	0.007261	0.302076	0.048077
48	C48	1.75	3.394231	0.010456	0.362492	0.057692
49	C49	2.355769	3.942308	0.002614	0.181246	0.028846
50	C50	2.346154	4.365385	0.004647	0.241661	0.038462
51	C51	2.894231	4.932692	0.002614	0.181246	0.028846
52	C52	1.653846	4.490385	0.007261	0.302076	0.048077
53	C53	1.134615	4.105769	0.007261	0.302076	0.048077
54	C54	1	4.711538	0.004647	0.241661	0.038462
55	C55	1.317308	3.221154	0.007261	0.302076	0.048077
56	C56	1.557692	3.221154	0.004647	0.241661	0.038462
57	C57	1.144231	2.25	0.001162	0.120831	0.019231
58	C58	1.144231	2.528846	0.004647	0.241661	0.038462
59	C59	1	2.730769	0.002614	0.181246	0.028846
60	C60	0.692308	2.923077	0.007261	0.302076	0.048077
61	C61	0.75	3.230769	0.007261	0.302076	0.048077
62	C62	0.557692	3.384615	0.001162	0.120831	0.019231
63	C63	0.971154	3.634615	0.002614	0.181246	0.028846
64	C64	0.471154	4.211538	0.007261	0.302076	0.048077
65	C65	0.278846	4.471154	0.007261	0.302076	0.048077
66	C66	0.173077	2.019231	0.004647	0.241661	0.038462
67	C67	0.153846	1.442308	0.002614	0.181246	0.028846
68	C68	1.009615	1.884615	0.004647	0.241661	0.038462
69	C69	1.673077	0.75	0.002614	0.181246	0.028846

	Features	Center X Pos.	Center Y Pos.	Area	Length	Radius
70	C70	2.471154	0.673077	0.002614	0.181246	0.028846
71	C71	2.413462	1.028846	0.007261	0.302076	0.048077
72	C72	0.826923	5.365385	0.002614	0.181246	0.028846
73	C73	2.230769	5.076923	0.004647	0.241661	0.038462
74	C74	2.509615	4.740385	0.007261	0.302076	0.048077
75	C75	4.961538	5.538462	0.007261	0.302076	0.048077
76	C76	4.798077	5.355769	0.002614	0.181246	0.028846
77	C77	4.586538	5.461538	0.002614	0.181246	0.028846
78	C78	3.990385	5.326923	0.007261	0.302076	0.048077
79	C79	5.259615	4.326923	0.004647	0.241661	0.038462
80	C80	6.182692	4.394231	0.007261	0.302076	0.048077
81	C81	6.509615	3.855769	0.002614	0.181246	0.028846
82	C82	6.076923	4.701923	0.001162	0.120831	0.019231
83	C83	5.538462	4.961538	0.004647	0.241661	0.038462
84	C84	6.701923	5.317308	0.001162	0.120831	0.019231
85	C85	6.913462	4.807692	0.002614	0.181246	0.028846
86	C86	7.769231	4.903846	0.007261	0.302076	0.048077
87	C87	7.932692	4.692308	0.007261	0.302076	0.048077
88	C88	7.961538	4.480769	0.002614	0.181246	0.028846
89	C89	7.605769	3.557692	0.004647	0.241661	0.038462
90	C90	7.644231	3.259615	0.014232	0.422907	0.067308
91	C91	7.278846	3.057692	0.002614	0.181246	0.028846
92	C92	6.942308	3.211538	0.007261	0.302076	0.048077
93	C93	6.990385	2.653846	0.004647	0.241661	0.038462
94	C94	7.153846	2.432692	0.010456	0.362492	0.057692
95	C95	6.778846	1.923077	0.004647	0.241661	0.038462
96	C96	5.451923	1.067308	0.007261	0.302076	0.048077
97	C97	5.913462	0.903846	0.001162	0.120831	0.019231
98	C98	5.740385	0.326923	0.007261	0.302076	0.048077
99	C99	5.278846	0.307692	0.004647	0.241661	0.038462
100	C100	5.009615	0.528846	0.010456	0.362492	0.057692
101	C101	4.836538	0.634615	0.002614	0.181246	0.028846
102	C102	6.240385	0.211539	0.00029	0.060415	0.009615
103	C103	6.740385	0.663462	0.002614	0.181246	0.028846
104	C104	6.336538	0.701923	0.004647	0.241661	0.038462
105	C105	6.759615	1.105769	0.001162	0.120831	0.019231
106	C106	8.596154	5.105769	0.018589	0.483322	0.076923
107	C107	8.855769	5.028846	0.007261	0.302076	0.048077
108	C108	9.038462	4.75	0.010456	0.362492	0.057692
109	C109	9.173077	3.596154	0.002614	0.181246	0.028846
110	C110	9.163462	3.048077	0.007261	0.302076	0.048077
111	C111	9.653846	3.298077	0.014232	0.422907	0.067308
112	C112	9.701923	3.105769	0.002614	0.181246	0.028846

	Features	Center X Pos.	Center Y Pos.	Area	Length	Radius
113	C113	8.817308	3.346154	0.002614	0.181246	0.028846
114	C114	8	2.836538	0.002614	0.181246	0.028846
115	C115	8.019231	2.115385	0.007261	0.302076	0.048077
116	C116	8.913462	1.634615	0.014232	0.422907	0.067308
117	C117	9.528846	1.769231	0.001162	0.120831	0.019231
118	C118	8.125	1.057692	0.001162	0.120831	0.019231
119	C119	7.894231	0.778846	0.004647	0.241661	0.038462
120	C120	9.586538	4.365385	0.004647	0.241661	0.038462
121	C121	9.557692	4.836538	0.002614	0.181246	0.028846
122	C122	9.528846	5.480769	0.002614	0.181246	0.028846
123	C123	8.692308	5.509615	0.001162	0.120831	0.019231
124	C124	7.375	5.211538	0.004647	0.241661	0.038462
125	C125	7.942308	5.480769	0.002614	0.181246	0.028846
126	C126	8.288462	5.192308	0.004647	0.241661	0.038462
127	C127	8.25	3.980769	0.004647	0.241661	0.038462
128	C128	8.75	2.173077	0.007261	0.302076	0.048077
129	C129	7.509615	1.057692	0.004647	0.241661	0.038462
130	C130	7.961538	0.442308	0.002614	0.181246	0.028846
131	C131	8.817308	0.576923	0.004647	0.241661	0.038462
132	C132	9.307692	0.480769	0.00029	0.060415	0.009615
133	C133	9.086538	0.307692	0.004647	0.241661	0.038462
134	C134	9.625	0.317308	0.001162	0.120831	0.019231
135	C135	9.644231	0.115385	0.004647	0.241661	0.038462
136	C136	4.375	3.442308	0.002614	0.181246	0.028846
137	C137	3.817308	0.230769	0.004647	0.241661	0.038462
138	C138	3.990385	0.028846	0.004647	0.241661	0.038462
139	C139	3.394231	0.067308	0.002614	0.181246	0.028846
					mean	0.037977
					SD	0.013808

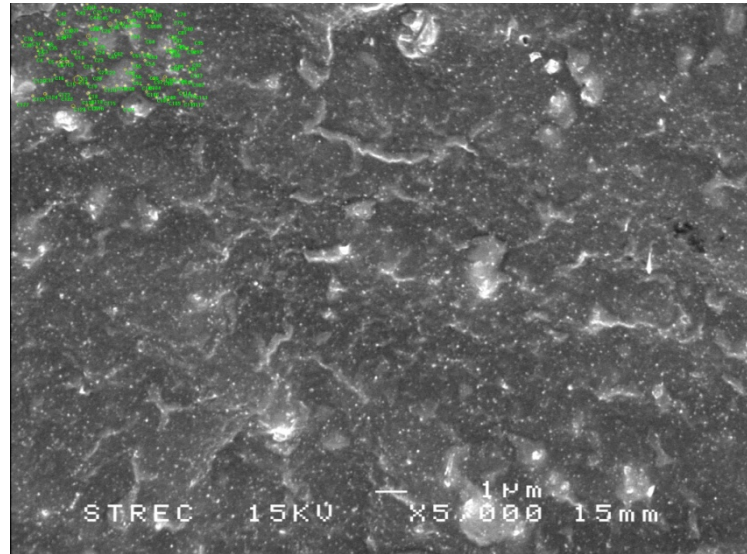
Table F9 Agglomeration size of CR filled with 6% APTES-modified PSi.

	Features	Center X Pos.	Center Y Pos.	Area	Length	Radius
1	C1	0.3653846	0.6442308	0.0026141	0.1812457	0.0288461
2	C2	0.4903846	1.115385	0.0011618	0.1208305	0.0192307
3	C3	0.6153846	1.144231	0.0026141	0.1812457	0.0288461
4	C4	0.8557692	0.8076923	0.0011618	0.1208305	0.0192307
5	C5	1.278846	0.9519231	0.0011618	0.1208305	0.0192307
6	C6	1.173077	1.211538	0.0011618	0.1208305	0.0192307
7	C7	1.442308	1.375	0.0046473	0.241661	0.0384615
8	C8	1.596154	1.519231	0.0026141	0.1812457	0.0288461
9	C9	1.173077	1.721154	0.0026141	0.1812457	0.0288461
10	C10	0.9903846	1.855769	0.0026141	0.1812457	0.0288461
11	C11	0.7115385	1.971154	0.0026141	0.1812457	0.0288461
12	C12	0.5480769	1.971154	0.0011618	0.1208305	0.0192307
13	C13	1.086538	2.125	0.0026141	0.1812457	0.0288461
14	C14	1.134615	2.384615	0.0011618	0.1208305	0.0192307
15	C15	0.7403846	2.336538	0.0026141	0.1812457	0.0288461
16	C16	0.5192308	2.490385	0.0011618	0.1208305	0.0192307
17	C17	0.3846154	2.615385	0.0026141	0.1812457	0.0288461
18	C18	0.125	2.442308	0.0002904	0.0604152	0.0096153
19	C19	1.432692	2.25	0.0011618	0.1208305	0.0192307
20	C20	1.692308	1.884615	0.0011618	0.1208305	0.0192307
21	C21	1.759615	2.057692	0.0026141	0.1812457	0.0288461
22	C22	1.326923	2.086538	0.0011618	0.1208305	0.0192307
23	C23	2.269231	2.009615	0.0026141	0.1812457	0.0288461
24	C24	1.932692	2.576923	0.0026141	0.1812457	0.0288461
25	C25	2.240385	2.634615	0.0046473	0.241661	0.0384615
26	C26	2.326923	2.567308	0.0046473	0.241661	0.0384615

	Features	Center X Pos.	Center Y Pos.	Area	Length	Radius
27	C27	2.461538	2.461538	0.0046473	0.241661	0.0384615
28	C28	2.519231	2.067308	0.0026141	0.1812457	0.0288461
29	C29	2.817308	2.615385	0.0046473	0.241661	0.0384615
30	C30	3	2.567308	0.0011618	0.1208305	0.0192307
31	C31	3.230769	2.644231	0.0026141	0.1812457	0.0288461
32	C32	3.480769	2.634615	0.0011618	0.1208305	0.0192307
33	C33	3.644231	2.759615	0.0002904	0.0604152	0.0096153
34	C34	3.788462	2.740385	0.0026141	0.1812457	0.0288461
35	C35	3.682692	2.451923	0.0026141	0.1812457	0.0288461
36	C36	3.75	2.317308	0.0046473	0.241661	0.0384615
37	C37	3.375	1.865385	0.0026141	0.1812457	0.0288461
38	C38	2.961538	1.836538	0.0026141	0.1812457	0.0288461
39	C39	3.519231	1.567308	0.0026141	0.1812457	0.0288461
40	C40	3	1.596154	0.0011618	0.1208305	0.0192307
41	C41	2.980769	1.480769	0.0026141	0.1812457	0.0288461
42	C42	2.711538	1.557692	0.0046473	0.241661	0.0384615
43	C43	2.826923	1.384615	0.0011618	0.1208305	0.0192307
44	C44	3.153846	1.163462	0.0002904	0.0604152	0.0096153
45	C45	3.076923	0.8942308	0.0046473	0.241661	0.0384615
46	C46	3.230769	1.028846	0.0002904	0.0604152	0.0096153
47	C47	3.057692	0.7596154	0.0026141	0.1812457	0.0288461
48	C48	2.769231	0.8461538	0.0026141	0.1812457	0.0288461
49	C49	2.653846	0.9326923	0.0026141	0.1812457	0.0288461
50	C50	2.673077	0.75	0.0002904	0.0604152	0.0096153
51	C51	2.5	0.6730769	0.0011618	0.1208305	0.0192307
52	C52	2.317308	0.7596154	0.0046473	0.241661	0.0384615
53	C53	2.211538	0.8365385	0.0026141	0.1812457	0.0288461
54	C54	2.173077	0.5865385	0.0011618	0.1208305	0.0192307
55	C55	1.817308	1.076923	0.0046473	0.241661	0.0384615
56	C56	1.836538	1.336538	0.0026141	0.1812457	0.0288461
57	C57	2.086538	1.298077	0.0026141	0.1812457	0.0288461
58	C58	2.307692	1.471154	0.0011618	0.1208305	0.0192307
59	C59	2.192308	1.471154	0.0002904	0.0604152	0.0096153
60	C60	1.490385	0.7115385	0.0026141	0.1812457	0.0288461
61	C61	1.798077	0.5769231	0.0011618	0.1208305	0.0192307
62	C62	1.682692	0.4038462	0.0072614	0.3020762	0.0480769
63	C63	1.538462	0.4807692	0.0011618	0.1208305	0.0192307
64	C64	1.894231	0.2115385	0.0026141	0.1812457	0.0288461
65	C65	2.201923	0.2115385	0.0011618	0.1208305	0.0192307
66	C66	2.105769	0.1730769	0.0011618	0.1208305	0.0192307
67	C67	1.605769	0.0576923	0.0026141	0.1812457	0.0288461
68	C68	1.144231	0.2980769	0.0026141	0.1812457	0.0288461
69	C69	1.317308	0.6826923	0.0026141	0.1812457	0.0288461

	Features	Center X Pos.	Center Y Pos.	Area	Length	Radius
70	C70	2.865385	2.028846	0.0011618	0.1208305	0.0192307
71	C71	3.336538	2.259615	0.0011618	0.1208305	0.0192307
72	C72	4.182692	2.086538	0.0011618	0.1208305	0.0192307
73	C73	4.144231	2.326923	0.0011618	0.1208305	0.0192307
74	C74	4.038462	2.528846	0.0011618	0.1208305	0.0192307
75	C75	4.692308	2.548077	0.0011618	0.1208305	0.0192307
76	C76	4.711538	2.644231	0.0072614	0.3020762	0.0480769
77	C77	5.057692	2.75	0.0046473	0.241661	0.0384615
78	C78	5.269231	2.557692	0.0046473	0.241661	0.0384615
79	C79	5.25	2.25	0.0026141	0.1812457	0.0288461
80	C80	5.144231	2.144231	0.0046473	0.241661	0.0384615
81	C81	4.894231	2.019231	0.0011618	0.1208305	0.0192307
82	C82	4.788462	2.028846	0.0026141	0.1812457	0.0288461
83	C83	4.576923	1.913462	0.0072614	0.3020762	0.0480769
84	C84	4.192308	1.519231	0.0941083	1.087474	0.1730769
85	C85	4.317308	1.461538	0	0	
86	C86	4.346154	1.432692	0.0046473	0.241661	0.0384615
87	C87	4.519231	1.413462	0.0026141	0.1812457	0.0288461
88	C88	4.298077	1.086538	0.0026141	0.1812457	0.0288461
89	C89	4.144231	1.105769	0	0	
90	C90	3.846154	0.4807692	0.0002904	0.0604152	0.0096153
91	C91	3.692308	0.4326923	0.0002904	0.0604152	0.0096153
92	C92	3.884615	0.125	0.0002904	0.0604152	0.0096153
93	C93	3.25	0.0576923	0.0002904	0.0604152	0.0096153
94	C94	3.740385	0.9711538	0.0011618	0.1208305	0.0192307
95	C95	3.615385	1.192308	0.0072614	0.3020762	0.0480769
96	C96	4.355769	0.6153846	0.0026141	0.1812457	0.0288461
97	C97	4.307692	0.4519231	0.0046473	0.241661	0.0384615
98	C98	4.480769	0.2788462	0.0026141	0.1812457	0.0288461
99	C99	5.019231	0.3269231	0.0011618	0.1208305	0.0192307
100	C100	5.230769	0.2403846	0.0026141	0.1812457	0.0288461
101	C101	5.269231	0.4519231	0.0011618	0.1208305	0.0192307
102	C102	5.442308	0.6730769	0.0011618	0.1208305	0.0192307
103	C103	5.038462	0.9230769	0.0026141	0.1812457	0.0288461
104	C104	5.346154	1.221154	0.0011618	0.1208305	0.0192307
105	C105	4.855769	1.461538	0.0011618	0.1208305	0.0192307
106	C106	5.403846	1.038462	0.0046473	0.241661	0.0384615
107	C107	5.788462	0.9903846	0.0026141	0.1812457	0.0288461
108	C108	5.826923	1.134615	0.0026141	0.1812457	0.0288461
109	C109	5.826923	1.567308	0.0002904	0.0604152	0.0096153
110	C110	5.375	1.913462	0.0011618	0.1208305	0.0192307
111	C111	5.567308	1.846154	0.0002904	0.0604152	0.0096153
112	C112	5.692308	1.855769	0.0011618	0.1208305	0.0192307

	Features	Center X Pos.	Center Y Pos.	Area	Length	Radius
113	C113	5.817308	2.019231	0.0026141	0.1812457	0.0288461
114	C114	5.634615	2.336538	0.0046473	0.241661	0.0384615
115	C115	5.663462	2.701923	0.0002904	0.0604152	0.0096153
116	C116	4.836538	0.6923077	0.0002904	0.0604152	0.0096153
117	C117	4.019231	0.7115385	0.0002904	0.0604152	0.0096153
118	C118	3.980769	1.75	0.0026141	0.1812457	0.0288461
119	C119	3.826923	1.769231	0.0011618	0.1208305	0.0192307
120	C120	3.913462	1.923077	0.0011618	0.1208305	0.0192307
121	C121	3.884615	2.096154	0.0026141	0.1812457	0.0288461
122	C122	3.740385	2.125	0.0011618	0.1208305	0.0192307
123	C123	2.836538	2.336538	0.0011618	0.1208305	0.0192307
124	C124	1.663462	2.490385	0.0011618	0.1208305	0.0192307
125	C125	2.759615	0.1057692	0.0011618	0.1208305	0.0192307
126	C126	2.759615	0.4903846	0.0026141	0.1812457	0.0288461
					mean	0.026365
					SD	0.016195

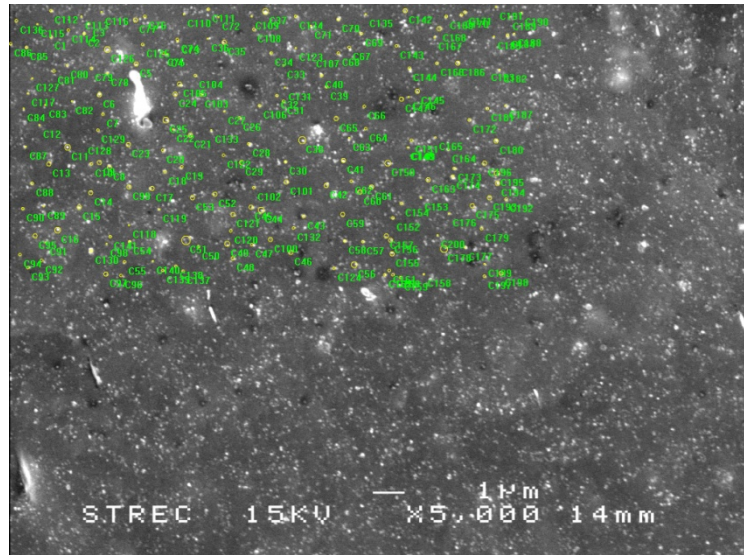
Table F10 Agglomeration size of CR filled with 8% APTES-modified PSi.

	Features	Center X Pos.	Center Y Pos.	Area	Length	Radius
1	C1	0.8365385	1.201923	0.0011618	0.1208305	0.0192307
2	C2	0.7307692	1.278846	0.0011618	0.1208305	0.0192307
3	C3	0.7019231	1.173077	0.0011618	0.1208305	0.0192307
4	C4	0.6826923	1.432692	0.0011618	0.1208305	0.0192307
5	C5	0.9903846	1.480769	0.0011618	0.1208305	0.0192307
6	C6	1.240385	1.567308	0.0011618	0.1208305	0.0192307
7	C7	1.346154	1.557692	0.0072614	0.3020762	0.0480769
8	C8	1.336538	1.394231	0.0026141	0.1812457	0.0288461
9	C9	1.509615	1.557692	0.0046473	0.241661	0.0384615
10	C10	1.711538	1.365385	0.0011618	0.1208305	0.0192307
11	C11	1.605769	1.221154	0	0	
12	C12	1.932692	1.605769	0.0011618	0.1208305	0.0192307
13	C13	1.798077	1.932692	0.0002904	0.0604152	0.0096153
14	C14	1.798077	2.038462	0.0351454	0.6645677	0.1057692
15	C15	1.480769	2.076923	0.0011618	0.1208305	0.0192307
16	C16	1.173077	1.913462	0.0011618	0.1208305	0.0192307
17	C17	0.9038462	1.971154	0.0002904	0.0604152	0.0096153
18	C18	2.067308	2.403846	0.0046473	0.241661	0.0384615
19	C19	2.048077	2.134615	0.0011618	0.1208305	0.0192307
20	C20	2.182692	1.923077	0	0	
21	C21	2.326923	1.759615	0.0026141	0.1812457	0.0288461
22	C22	2.538462	1.769231	0.0011618	0.1208305	0.0192307
23	C23	2.221154	1.432692	0.0026141	0.1812457	0.0288461
24	C24	2.25	1.230769	0.0026141	0.1812457	0.0288461
25	C25	2.278846	1.086538	0.0011618	0.1208305	0.0192307
26	C26	2.413462	0.6538462	0.0002904	0.0604152	0.0096153

	Features	Center X Pos.	Center Y Pos.	Area	Length	Radius
27	C27	2.192308	0.5769231	0.0011618	0.1208305	0.0192307
28	C28	2.096154	0.6057692	0.0026141	0.1812457	0.0288461
29	C29	2.076923	0.8846154	0.0104564	0.3624915	0.0576923
30	C30	1.798077	0.9903846	0.0002904	0.0604152	0.0096153
31	C31	1.567308	0.6346154	0.0011618	0.1208305	0.0192307
32	C32	1.432692	0.6634615	0.0011618	0.1208305	0.0192307
33	C33	1.375	0.7980769	0.0046473	0.241661	0.0384615
34	C34	1.230769	0.8365385	0.0011618	0.1208305	0.0192307
35	C35	1	1.105769	0.0002904	0.0604152	0.0096153
36	C36	0.8942308	1	0.0011618	0.1208305	0.0192307
37	C37	0.5576923	1	0.0002904	0.0604152	0.0096153
38	C38	0.3173077	1.038462	0.0026141	0.1812457	0.0288461
39	C39	0.3461538	0.8653846	0.0002904	0.0604152	0.0096153
40	C40	0.625	0.7307692	0.0011618	0.1208305	0.0192307
41	C41	1.25	0.4423077	0.0011618	0.1208305	0.0192307
42	C42	1.240385	0.2019231	0.0002904	0.0604152	0.0096153
43	C43	1.740385	0.1730769	0.0002904	0.0604152	0.0096153
44	C44	2.096154	0.2980769	0.0002904	0.0604152	0.0096153
45	C45	2.336538	0.3076923	0.0011618	0.1208305	0.0192307
46	C46	2.644231	0.5576923	0.0104564	0.3624915	0.0576923
47	C47	2.798077	0.4519231	0.0011618	0.1208305	0.0192307
48	C48	2.942308	0.5288462	0.0026141	0.1812457	0.0288461
49	C49	3.086538	0.375	0.0046473	0.241661	0.0384615
50	C50	3.201923	0.5096154	0.0026141	0.1812457	0.0288461
51	C51	3.221154	1.317308	0.0011618	0.1208305	0.0192307
52	C52	3.5	1.307692	0.0011618	0.1208305	0.0192307
53	C53	3.653846	1.355769	0.0011618	0.1208305	0.0192307
54	C54	3.576923	1.528846	0.0026141	0.1812457	0.0288461
55	C55	3.230769	1.596154	0.0011618	0.1208305	0.0192307
56	C56	3.230769	1.875	0.0011618	0.1208305	0.0192307
57	C57	3.240385	2.048077	0.0011618	0.1208305	0.0192307
58	C58	3.048077	2.201923	0.0011618	0.1208305	0.0192307
59	C59	2.826923	2.201923	0.0026141	0.1812457	0.0288461
60	C60	3.057692	1.769231	0.0026141	0.1812457	0.0288461
61	C61	2.586538	1.336538	0.0011618	0.1208305	0.0192307
62	C62	2.740385	1.269231	0.0002904	0.0604152	0.0096153
63	C63	3.192308	0.8076923	0.0026141	0.1812457	0.0288461
64	C64	3.576923	0.9423077	0.0002904	0.0604152	0.0096153
65	C65	3.625	0.5288462	0.0011618	0.1208305	0.0192307
66	C66	3.778846	0.5288462	0.0011618	0.1208305	0.0192307
67	C67	3.721154	0.3269231	0.0011618	0.1208305	0.0192307
68	C68	3.769231	0.2211538	0.0011618	0.1208305	0.0192307
69	C69	3.596154	0.125	0.0002904	0.0604152	0.0096153

	Features	Center X Pos.	Center Y Pos.	Area	Length	Radius
70	C70	3.471154	0.1057692	0.0011618	0.1208305	0.0192307
71	C71	3.355769	0.25	0.0026141	0.1812457	0.0288461
72	C72	3.230769	0.1826923	0.0002904	0.0604152	0.0096153
73	C73	2.663462	0.125	0.0011618	0.1208305	0.0192307
74	C74	2.451923	0.0961538	0.0011618	0.1208305	0.0192307
75	C75	2.182692	0.1538462	0	0	
76	C76	2.038462	0.0192307	0.0026141	0.1812457	0.0288461
77	C77	1.913462	0.0480769	0.0002904	0.0604152	0.0096153
78	C78	4.413462	0.2115385	0.0002904	0.0604152	0.0096153
79	C79	4.326923	0.4326923	0.0002904	0.0604152	0.0096153
80	C80	4.596154	0.5961538	0.0002904	0.0604152	0.0096153
81	C81	4.432692	0.7019231	0.0002904	0.0604152	0.0096153
82	C82	4.182692	0.8173077	0	0	
83	C83	4.307692	0.9134615	0.0011618	0.1208305	0.0192307
84	C84	4.490385	1.105769	0.0002904	0.0604152	0.0096153
85	C85	4.384615	1.067308	0.0002904	0.0604152	0.0096153
86	C86	4.105769	1.182692	0.0011618	0.1208305	0.0192307
87	C87	4.240385	1.201923	0.0026141	0.1812457	0.0288461
88	C88	4.259615	1.307692	0.0011618	0.1208305	0.0192307
89	C89	4.346154	1.605769	0.0002904	0.0604152	0.0096153
90	C90	4.230769	1.663462	0.0002904	0.0604152	0.0096153
91	C91	4.701923	1.673077	0.0011618	0.1208305	0.0192307
92	C92	4.817308	1.567308	0.0011618	0.1208305	0.0192307
93	C93	4.836538	1.211538	0.0011618	0.1208305	0.0192307
94	C94	4.682692	1.221154	0.0011618	0.1208305	0.0192307
95	C95	4.875	0.9711538	0.0002904	0.0604152	0.0096153
96	C96	3.682692	1.913462	0.0002904	0.0604152	0.0096153
97	C97	3.798077	2.019231	0.0011618	0.1208305	0.0192307
98	C98	4.057692	2.057692	0.0026141	0.1812457	0.0288461
99	C99	4.105769	1.971154	0.0046473	0.241661	0.0384615
100	C100	4.355769	2	0.0011618	0.1208305	0.0192307
101	C101	4.528846	2.028846	0.0011618	0.1208305	0.0192307
102	C102	4.817308	2.096154	0.0002904	0.0604152	0.0096153
103	C103	4.769231	1.846154	0.0011618	0.1208305	0.0192307
104	C104	3.663462	2.173077	0.0011618	0.1208305	0.0192307
105	C105	3.480769	2.182692	0.0002904	0.0604152	0.0096153
106	C106	3.615385	2.355769	0.0026141	0.1812457	0.0288461
107	C107	3.875	2.509615	0.0011618	0.1208305	0.0192307
108	C108	4.067308	2.432692	0.0002904	0.0604152	0.0096153
109	C109	4.192308	2.586538	0.0011618	0.1208305	0.0192307
110	C110	4.596154	2.394231	0.0011618	0.1208305	0.0192307
111	C111	4.596154	2.625	0.0011618	0.1208305	0.0192307
112	C112	4.807692	2.625	0.0026141	0.1812457	0.0288461

	Features	Center X Pos.	Center Y Pos.	Area	Length	Radius
113	C113	4.903846	2.432692	0.0011618	0.1208305	0.0192307
114	C114	4.461538	2.317308	0.0011618	0.1208305	0.0192307
115	C115	2.471154	2.586538	0	0	
116	C116	2.153846	2.721154	0.0026141	0.1812457	0.0288461
117	C117	2.038462	2.721154	0.0026141	0.1812457	0.0288461
118	C118	2.125	2.548077	0.0011618	0.1208305	0.0192307
119	C119	1.894231	2.567308	0.0002904	0.0604152	0.0096153
120	C120	2.480769	2.230769	0.0026141	0.1812457	0.0288461
121	C121	2.980769	2.759615	0.0011618	0.1208305	0.0192307
122	C122	1.336538	2.471154	0.0002904	0.0604152	0.0096153
123	C123	1.259615	2.355769	0.0002904	0.0604152	0.0096153
124	C124	0.9230769	2.423077	0.0046473	0.241661	0.0384615
125	C125	0.5961538	2.480769	0.0026141	0.1812457	0.0288461
126	C126	0.6057692	1.990385	0.0002904	0.0604152	0.0096153
127	C127	0.1634615	2.625	0.0002904	0.0604152	0.0096153
128	C128	1.673077	2.75	0.0072614	0.3020762	0.0480769
					mean	0.021106875
					SD	0.012423019

Table F11 Agglomeration size of CR filled with 8% CPTES-modified PSi.

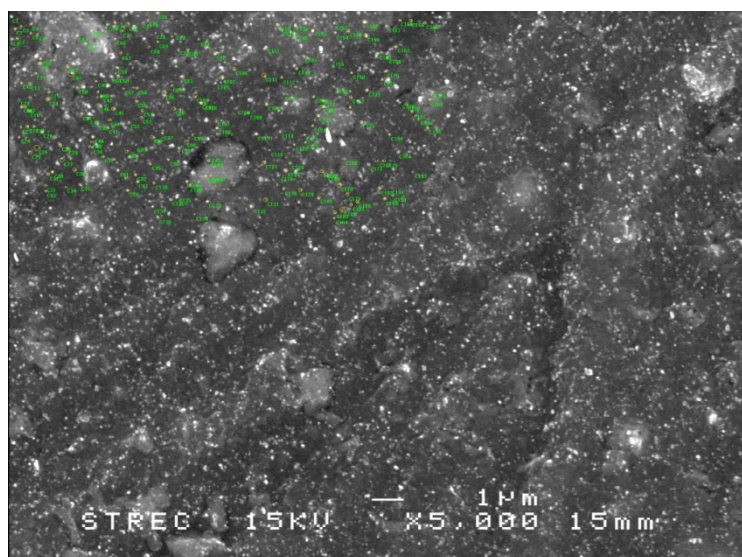
	Features	Center X Pos.	Center Y Pos.	Area	Length	Radius
1	C1	1.115385	0.8653846	0.0046473	0.241661	0.0384615
2	C2	2	0.7884615	0.0046473	0.241661	0.0384615
3	C3	2.134615	0.5192308	0.0011618	0.1208305	0.0192307
4	C4	4.211538	1.326923	0.0011618	0.1208305	0.0192307
5	C5	3.384615	1.596154	0.0104564	0.3624915	0.0576923
6	C6	2.403846	2.423077	0.0104564	0.3624915	0.0576923
7	C7	2.5	2.942308	0.0046473	0.241661	0.0384615
8	C8	2.673077	4.365385	0.0104564	0.3624915	0.0576923
9	C9	2.403846	4.230769	0.0104564	0.3624915	0.0576923
10	C10	2.192308	4.269231	0.0046473	0.241661	0.0384615
11	C11	1.557692	3.826923	0.0185893	0.4833219	0.076923
12	C12	0.8076923	3.230769	0.0011618	0.1208305	0.0192307
13	C13	1.057692	4.269231	0.0104564	0.3624915	0.0576923
14	C14	2.173077	5.038462	0.0104564	0.3624915	0.0576923
15	C15	1.865385	5.423077	0.0104564	0.3624915	0.0576923
16	C16	1.288462	6.038462	0.0185893	0.4833219	0.076923
17	C17	3.807692	4.923077	0.0104564	0.3624915	0.0576923
18	C18	4.153846	4.480769	0.0046473	0.241661	0.0384615
19	C19	4.596154	4.346154	0.0046473	0.241661	0.0384615
20	C20	4.096154	3.903846	0.0046473	0.241661	0.0384615
21	C21	4.826923	3.5	0.0104564	0.3624915	0.0576923
22	C22	4.365385	3.346154	0.0011618	0.1208305	0.0192307
23	C23	3.173077	3.75	0.0104564	0.3624915	0.0576923
24	C24	4.423077	2.403846	0.0104564	0.3624915	0.0576923
25	C25	4.173077	3.096154	0.0185893	0.4833219	0.076923
26	C26	6.134615	3.038462	0.0046473	0.241661	0.0384615
27	C27	5.730769	2.865385	0.0011618	0.1208305	0.0192307
28	C28	6.384615	3.730769	0.0046473	0.241661	0.0384615
29	C29	6.192308	4.230769	0.0104564	0.3624915	0.0576923

	Features	Center X Pos.	Center Y Pos.	Area	Length	Radius
30	C30	7.365385	4.211538	0.0046473	0.241661	0.0384615
31	C31	7.307692	2.596154	0.0046473	0.241661	0.0384615
32	C32	7.134615	2.442308	0.0046473	0.241661	0.0384615
33	C33	7.307692	1.634615	0.0011618	0.1208305	0.0192307
34	C34	6.980769	1.307692	0.0046473	0.241661	0.0384615
35	C35	5.730769	1.019231	0.0104564	0.3624915	0.0576923
36	C36	5.288462	0.9230769	0.0011618	0.1208305	0.0192307
37	C37	6.826923	0.1923077	0.0185893	0.4833219	0.076923
38	C38	7.807692	3.634615	0.0290457	0.6041524	0.0961538
39	C39	8.461538	2.211538	0.0046473	0.241661	0.0384615
40	C40	8.326923	1.903846	0.0046473	0.241661	0.0384615
41	C41	8.903846	4.173077	0.0104564	0.3624915	0.0576923
42	C42	8.442308	4.846154	0.0104564	0.3624915	0.0576923
43	C43	7.846154	5.673077	0.0046473	0.241661	0.0384615
44	C44	6.711538	5.5	0.0185893	0.4833219	0.076923
45	C45	6.442308	5.423077	0.0104564	0.3624915	0.0576923
46	C46	7.5	6.634615	0.0104564	0.3624915	0.0576923
47	C47	6.461538	6.423077	0.0046473	0.241661	0.0384615
48	C48	5.961538	6.788462	0.0072614	0.3020762	0.0480769
49	C49	5.807692	6.403846	0.0142324	0.4229067	0.0673076
50	C50	5.038462	6.480769	0.0046473	0.241661	0.0384615
51	C51	4.711538	6.307692	0.0418259	0.7249829	0.1153846
52	C52	5.480769	5.076923	0.0104564	0.3624915	0.0576923
53	C53	4.884615	5.173077	0.0104564	0.3624915	0.0576923
54	C54	3.211538	6.346154	0.0046473	0.241661	0.0384615
55	C55	3.076923	6.884615	0.0046473	0.241661	0.0384615
56	C56	9.192308	6.961538	0.0185893	0.4833219	0.076923
57	C57	9.423077	6.346154	0.0046473	0.241661	0.0384615
58	C58	8.942308	6.326923	0.0046473	0.241661	0.0384615
59	C59	8.884615	5.615385	0.0104564	0.3624915	0.0576923
60	C60	9.346154	5.019231	0.0104564	0.3624915	0.0576923
61	C61	9.653846	4.884615	0.0104564	0.3624915	0.0576923
62	C62	9.115385	4.730769	0.0046473	0.241661	0.0384615
63	C63	9.057692	3.576923	0.0011618	0.1208305	0.0192307
64	C64	9.5	3.326923	0.0046473	0.241661	0.0384615
65	C65	8.711538	3.057692	0.0104564	0.3624915	0.0576923
66	C66	9.461538	2.730769	0.0046473	0.241661	0.0384615
67	C67	9.057692	1.153846	0.0046473	0.241661	0.0384615
68	C68	8.769231	1.307692	0.0046473	0.241661	0.0384615
69	C69	9.384615	0.7884615	0.0046473	0.241661	0.0384615
70	C70	8.769231	0.4038462	0.0046473	0.241661	0.0384615
71	C71	8.038462	0.5769231	0.0011618	0.1208305	0.0192307
72	C72	5.576923	0.3461538	0.0011618	0.1208305	0.0192307
73	C73	4.5	0.9807692	0.0011618	0.1208305	0.0192307
74	C74	4.480769	0.9423077	0.0046473	0.241661	0.0384615
75	C75	4.115385	1.307692	0.0046473	0.241661	0.0384615
76	C76	3.615385	0.3269231	0.0046473	0.241661	0.0384615
77	C77	3.365385	0.4230769	0.0104564	0.3624915	0.0576923

	Features	Center X Pos.	Center Y Pos.	Area	Length	Radius
78	C78	2.615385	1.846154	0.0011618	0.1208305	0.0192307
79	C79	2.192308	1.711538	0.0046473	0.241661	0.0384615
80	C80	1.538462	1.634615	0.0011618	0.1208305	0.0192307
81	C81	1.192308	1.788462	0.0046473	0.241661	0.0384615
82	C82	1.673077	2.596154	0.0011618	0.1208305	0.0192307
83	C83	0.9615385	2.692308	0.0011618	0.1208305	0.0192307
84	C84	0.3846154	2.788462	0.0011618	0.1208305	0.0192307
85	C85	0.4615385	1.153846	0.0046473	0.241661	0.0384615
86	C86	0.0384615	1.057692	0.0046473	0.241661	0.0384615
87	C87	0.4423077	3.807692	0.0011618	0.1208305	0.0192307
88	C88	0.6153846	4.788462	0.0046473	0.241661	0.0384615
89	C89	0.9230769	5.403846	0.0011618	0.1208305	0.0192307
90	C90	0.3653846	5.461538	0.0046473	0.241661	0.0384615
91	C91	0.9807692	6.365385	0.0011618	0.1208305	0.0192307
92	C92	0.8653846	6.846154	0.0046473	0.241661	0.0384615
93	C93	0.5	7.038462	0.0046473	0.241661	0.0384615
94	C94	0.2884615	6.692308	0.0046473	0.241661	0.0384615
95	C95	0.6923077	6.192308	0.0104564	0.3624915	0.0576923
96	C96	2.980769	7.25	0.0046473	0.241661	0.0384615
97	C97	2.576923	7.211538	0.0104564	0.3624915	0.0576923
98	C98	2.596154	6.403846	0.0011618	0.1208305	0.0192307
99	C99	3.192308	4.884615	0.0104564	0.3624915	0.0576923
100	C100	6.961538	6.288462	0.0104564	0.3624915	0.0576923
101	C101	7.384615	4.75	0.0104564	0.3624915	0.0576923
102	C102	6.519231	4.903846	0.0046473	0.241661	0.0384615
103	C103	5.115385	2.423077	0.0046473	0.241661	0.0384615
104	C104	4.961538	1.903846	0.0046473	0.241661	0.0384615
105	C105	4.538462	2.134615	0.0104564	0.3624915	0.0576923
106	C106	6.673077	2.711538	0.0046473	0.241661	0.0384615
107	C107	8.076923	1.346154	0	0	
108	C108	6.519231	0.6730769	0.0046473	0.241661	0.0384615
109	C109	6.461538	0.3269231	0.0011618	0.1208305	0.0192307
110	C110	4.653846	0.2692308	0.0011618	0.1208305	0.0192307
111	C111	5.307692	0.1346154	0.0046473	0.241661	0.0384615
112	C112	1.115385	0.1730769	0.0046473	0.241661	0.0384615
113	C113	1.923077	0.3269231	0.0011618	0.1208305	0.0192307
114	C114	1.576923	0.6923077	0.0046473	0.241661	0.0384615
115	C115	0.75	0.5384615	0.0011618	0.1208305	0.0192307
116	C116	2.461538	0.2115385	0.0011618	0.1208305	0.0192307
117	C117	0.5	2.384615	0.0011618	0.1208305	0.0192307
118	C118	3.192308	5.903846	0.0011618	0.1208305	0.0192307
119	C119	4	5.480769	0.0011618	0.1208305	0.0192307
120	C120	5.903846	6.057692	0.0046473	0.241661	0.0384615
121	C121	5.961538	5.615385	0.0104564	0.3624915	0.0576923
122	C122	5.711538	4.038462	0.0046473	0.241661	0.0384615
123	C123	7.634615	1.173077	0.0011618	0.1208305	0.0192307
124	C124	8.653846	7.057692	0.0046473	0.241661	0.0384615
125	C125	3.557692	1.076923	0.0046473	0.241661	0.0384615

	Features	Center X Pos.	Center Y Pos.	Area	Length	Radius
126	C126	2.615385	1.211538	0.0185893	0.4833219	0.076923
127	C127	0.6153846	1.980769	0.0011618	0.1208305	0.0192307
128	C128	2	3.673077	0	0	
129	C129	2.365385	3.365385	0.0046473	0.241661	0.0384615
130	C130	2.192308	6.596154	0.0046473	0.241661	0.0384615
131	C131	7.346154	2.230769	0.0011618	0.1208305	0.0192307
132	C132	7.576923	5.980769	0.0046473	0.241661	0.0384615
133	C133	5.384615	3.365385	0.0011618	0.1208305	0.0192307
134	C134	7.634615	0.3269231	0.0046473	0.241661	0.0384615
135	C135	9.5	0.2692308	0.0011618	0.1208305	0.0192307
136	C136	0.1923077	0.4423077	0.0046473	0.241661	0.0384615
137	C137	4.634615	7.134615	0.0046473	0.241661	0.0384615
138	C138	4.442308	7	0.0046473	0.241661	0.0384615
139	C139	4.096154	7.115385	0.0046473	0.241661	0.0384615
140	C140	3.826923	6.865385	0.0011618	0.1208305	0.0192307
141	C141	2.692308	6.211538	0.0046473	0.241661	0.0384615
142	C142	10.54808	0.1730769	0.0104564	0.3624915	0.0576923
143	C143	10.31731	1.115385	0.0046473	0.241661	0.0384615
144	C144	10.66346	1.711538	0.0046473	0.241661	0.0384615
145	C145	10.875	2.326923	0.0104564	0.3624915	0.0576923
146	C146	10.64423	2.480769	0.0011618	0.1208305	0.0192307
147	C147	10.45192	2.538462	0.0104564	0.3624915	0.0576923
148	C148	10.58654	3.826923	0	0	
149	C149	10.625	3.826923	0.0011618	0.1208305	0.0192307
150	C150	10.08654	4.25	0.0185893	0.4833219	0.076923
151	C151	10.72115	3.634615	0.0046473	0.241661	0.0384615
152	C152	10.22115	5.711538	0.0046473	0.241661	0.0384615
153	C153	10.97115	5.173077	0.0011618	0.1208305	0.0192307
154	C154	10.45192	5.326923	0.0046473	0.241661	0.0384615
155	C155	10.20192	6.673077	0.0104564	0.3624915	0.0576923
156	C156	10.16346	6.307692	0.0104564	0.3624915	0.0576923
157	C157	10.04808	6.192308	0.0104564	0.3624915	0.0576923
158	C158	11.04808	7.211538	0.0011618	0.1208305	0.0192307
159	C159	10.43269	7.307692	0.0046473	0.241661	0.0384615
160	C160	10.22115	7.230769	0.0046473	0.241661	0.0384615
161	C161	10.125	7.115385	0.0046473	0.241661	0.0384615
162	C162	10.00962	7.230769	0.0046473	0.241661	0.0384615
163	C163	11.16346	4.692308	0.0104564	0.3624915	0.0576923
164	C164	11.70192	3.884615	0.0011618	0.1208305	0.0192307
165	C165	11.35577	3.557692	0.0011618	0.1208305	0.0192307
166	C166	11.39423	1.576923	0.0046473	0.241661	0.0384615
167	C167	11.33654	0.8846154	0.0011618	0.1208305	0.0192307
168	C168	11.45192	0.6538462	0.0104564	0.3624915	0.0576923
169	C169	11.64423	0.3269231	0.0046473	0.241661	0.0384615
170	C170	12.04808	0.2884615	0.0046473	0.241661	0.0384615
171	C171	12.14423	0.2115385	0.0046473	0.241661	0.0384615
172	C172	12.25962	3.096154	0.0046473	0.241661	0.0384615
173	C173	11.85577	4.384615	0.0046473	0.241661	0.0384615

	Features	Center X Pos.	Center Y Pos.	Area	Length	Radius
174	C174	11.81731	4.596154	0.0046473	0.241661	0.0384615
175	C175	12.33654	5.384615	0.0104564	0.3624915	0.0576923
176	C176	11.72115	5.596154	0.0011618	0.1208305	0.0192307
177	C177	12.14423	6.5	0.0011618	0.1208305	0.0192307
178	C178	11.58654	6.538462	0.0290457	0.6041524	0.0961538
179	C179	12.58654	6	0.0046473	0.241661	0.0384615
180	C180	12.97115	3.653846	0.0104564	0.3624915	0.0576923
181	C181	12.74038	2.788462	0.0046473	0.241661	0.0384615
182	C182	13.06731	1.75	0.0011618	0.1208305	0.0192307
183	C183	12.74038	1.711538	0	0	
184	C184	13.27885	0.8269231	0.0046473	0.241661	0.0384615
185	C185	12.91346	0.8653846	0.0011618	0.1208305	0.0192307
186	C186	11.95192	1.576923	0.0104564	0.3624915	0.0576923
187	C187	13.22115	2.711538	0.0011618	0.1208305	0.0192307
188	C188	13.45192	0.7884615	0.0011618	0.1208305	0.0192307
189	C189	13.31731	0.3461538	0.0011618	0.1208305	0.0192307
190	C190	13.64423	0.2307692	0.0011618	0.1208305	0.0192307
191	C191	12.97115	0.076923	0.0011618	0.1208305	0.0192307
192	C192	13.24038	5.211538	0.0046473	0.241661	0.0384615
193	C193	12.79808	5.173077	0.0104564	0.3624915	0.0576923
194	C194	13.00962	4.788462	0.0104564	0.3624915	0.0576923
195	C195	12.99038	4.519231	0.0142324	0.4229067	0.0673076
196	C196	12.66346	4.25	0.0104564	0.3624915	0.0576923
197	C197	12.66346	7.269231	0.0046473	0.241661	0.0384615
198	C198	13.10577	7.192308	0.0104564	0.3624915	0.0576923
199	C199	12.66346	6.942308	0.0011618	0.1208305	0.0192307
200	C200	11.41346	6.173077	0.0011618	0.1208305	0.0192307
					mean	0.040767227
					SD	0.017694347

Table F12 Agglomeration size of CR filled with 8% TESPT-modified PSi.

	Features	Center X Pos.	Center Y Pos.	Area	Length	Radius
1	C1	0.0673076	0.1442308	0.0011618	0.1208305	0.0192307
2	C2	0.1730769	0.4615385	0.0011618	0.1208305	0.0192307
3	C3	0.3461538	0.3942308	0.0011618	0.1208305	0.0192307
4	C4	0.6057692	0.3557692	0.0011618	0.1208305	0.0192307
5	C5	0.5961538	0.5865385	0.0011618	0.1208305	0.0192307
6	C6	0.7884615	0.6153846	0.0002904	0.0604152	0.0096153
7	C7	0.2403846	0.7115385	0.0026141	0.1812457	0.0288461
8	C8	0.0961538	0.7596154	0.0011618	0.1208305	0.0192307
9	C9	0.8461538	1.394231	0.0046473	0.241661	0.0384615
10	C10	0.8653846	1.269231	0.0026141	0.1812457	0.0288461
11	C11	0.7115385	1.663462	0.0026141	0.1812457	0.0288461
12	C12	0.3461538	1.903846	0.0011618	0.1208305	0.0192307
13	C13	0.5673077	1.942308	0.0026141	0.1812457	0.0288461
14	C14	1.048077	2.355769	0.0072614	0.3020762	0.0480769
15	C15	1.086538	2.153846	0.0026141	0.1812457	0.0288461
16	C16	0.5480769	2.663462	0.0046473	0.241661	0.0384615
17	C17	0.4423077	2.538462	0.0026141	0.1812457	0.0288461
18	C18	0.3653846	2.548077	0.0011618	0.1208305	0.0192307
19	C19	0.2884615	2.346154	0.0002904	0.0604152	0.0096153
20	C20	0.8942308	3.221154	0.0046473	0.241661	0.0384615
21	C21	0.7019231	3.076923	0.0011618	0.1208305	0.0192307
22	C22	0.5288462	3.076923	0.0011618	0.1208305	0.0192307
23	C23	0.3365385	3.096154	0.0011618	0.1208305	0.0192307
24	C24	0.2980769	3.355769	0.0011618	0.1208305	0.0192307
25	C25	0.5865385	3.778846	0.0072614	0.3020762	0.0480769
26	C26	0.7692308	3.644231	0.0142324	0.4229067	0.0673076

	Features	Center X Pos.	Center Y Pos.	Area	Length	Radius
27	C27	1.442308	3.971154	0.0104564	0.3624915	0.0576923
28	C28	1.576923	3.663462	0.0011618	0.1208305	0.0192307
29	C29	1.384615	3.576923	0.0046473	0.241661	0.0384615
30	C30	1.182692	4.288462	0.0026141	0.1812457	0.0288461
31	C31	1.067308	4.355769	0.0046473	0.241661	0.0384615
32	C32	0.9807692	4.663462	0.0026141	0.1812457	0.0288461
33	C33	0.9807692	4.807692	0.0002904	0.0604152	0.0096153
34	C34	1.528846	4.682692	0.0002904	0.0604152	0.0096153
35	C35	1.903846	4.625	0.0026141	0.1812457	0.0288461
36	C36	1.769231	4.230769	0.0072614	0.3020762	0.0480769
37	C37	2.528846	3.875	0.0026141	0.1812457	0.0288461
38	C38	2.230769	3.644231	0.0011618	0.1208305	0.0192307
39	C39	2.211538	3.490385	0.0011618	0.1208305	0.0192307
40	C40	2.259615	3.355769	0.0011618	0.1208305	0.0192307
41	C41	2.644231	3.105769	0.0026141	0.1812457	0.0288461
42	C42	2.384615	3.009615	0.0002904	0.0604152	0.0096153
43	C43	2.144231	2.855769	0.0002904	0.0604152	0.0096153
44	C44	2.682692	2.903846	0.0026141	0.1812457	0.0288461
45	C45	2.798077	2.605769	0.0072614	0.3020762	0.0480769
46	C46	2.413462	2.5	0.0011618	0.1208305	0.0192307
47	C47	2.490385	2.269231	0.0011618	0.1208305	0.0192307
48	C48	2.394231	2.153846	0.0011618	0.1208305	0.0192307
49	C49	2.346154	1.865385	0.0011618	0.1208305	0.0192307
50	C50	1.836538	2.038462	0.0002904	0.0604152	0.0096153
51	C51	1.942308	2.75	0.0011618	0.1208305	0.0192307
52	C52	3.221154	2.961538	0.0011618	0.1208305	0.0192307
53	C53	3.538462	2.836538	0.0026141	0.1812457	0.0288461
54	C54	3.567308	2.644231	0.0026141	0.1812457	0.0288461
55	C55	3.413462	2.403846	0.0011618	0.1208305	0.0192307
56	C56	3.423077	2.057692	0.0026141	0.1812457	0.0288461
57	C57	3.067308	2.057692	0.0002904	0.0604152	0.0096153
58	C58	2.932692	1.75	0.0026141	0.1812457	0.0288461
59	C59	2.884615	1.5	0.0011618	0.1208305	0.0192307
60	C60	2.721154	1.75	0.0026141	0.1812457	0.0288461
61	C61	1.673077	1.663462	0.0185893	0.4833219	0.076923
62	C62	1.576923	1.451923	0.0026141	0.1812457	0.0288461
63	C63	2.067308	0.8557692	0.0011618	0.1208305	0.0192307
64	C64	1.836538	0.6442308	0.0026141	0.1812457	0.0288461
65	C65	2.211538	0.5	0.0026141	0.1812457	0.0288461
66	C66	2.846154	0.7307692	0.0002904	0.0604152	0.0096153
67	C67	2.990385	1.134615	0.0011618	0.1208305	0.0192307
68	C68	3.75	0.9615385	0.0026141	0.1812457	0.0288461
69	C69	3.980769	0.8173077	0.0011618	0.1208305	0.0192307

	Features	Center X Pos.	Center Y Pos.	Area	Length	Radius
70	C70	3.903846	0.5769231	0	0	
71	C71	3.019231	0.5288462	0.0026141	0.1812457	0.0288461
72	C72	3.182692	0.3557692	0.0072614	0.3020762	0.0480769
73	C73	2.846154	0.3076923	0.0026141	0.1812457	0.0288461
74	C74	2.634615	0.3557692	0.0011618	0.1208305	0.0192307
75	C75	3.951923	0.0384615	0.0011618	0.1208305	0.0192307
76	C76	3.711538	0.2211538	0.0002904	0.0604152	0.0096153
77	C77	3.548077	0.2884615	0	0	
78	C78	4.442308	0.5961538	0.0011618	0.1208305	0.0192307
79	C79	4.548077	1	0.0002904	0.0604152	0.0096153
80	C80	4.778846	1.028846	0.0026141	0.1812457	0.0288461
81	C81	5.086538	0.7596154	0.0002904	0.0604152	0.0096153
82	C82	5.509615	1.125	0.0046473	0.241661	0.0384615
83	C83	4.634615	1.75	0.0011618	0.1208305	0.0192307
84	C84	4.346154	1.990385	0.0011618	0.1208305	0.0192307
85	C85	4.153846	2.182692	0.0104564	0.3624915	0.0576923
86	C86	4.413462	2.605769	0.0072614	0.3020762	0.0480769
87	C87	4.115385	3.269231	0.0011618	0.1208305	0.0192307
88	C88	3.826923	3.355769	0.0046473	0.241661	0.0384615
89	C89	3.394231	3.586538	0.0002904	0.0604152	0.0096153
90	C90	3.153846	3.75	0.0046473	0.241661	0.0384615
91	C91	2.932692	4.25	0.0011618	0.1208305	0.0192307
92	C92	3.394231	4.365385	0.0026141	0.1812457	0.0288461
93	C93	3.432692	4.557692	0.0011618	0.1208305	0.0192307
94	C94	3.182692	4.778846	0.0026141	0.1812457	0.0288461
95	C95	3.788462	4.076923	0.0026141	0.1812457	0.0288461
96	C96	4.269231	3.961538	0.0011618	0.1208305	0.0192307
97	C97	4.576923	3.625	0	0	
98	C98	4.711538	3.461538	0.0011618	0.1208305	0.0192307
99	C99	4.913462	3.288462	0.0011618	0.1208305	0.0192307
100	C100	5.567308	3.115385	0.0026141	0.1812457	0.0288461
101	C101	5.548077	2.903846	0.0011618	0.1208305	0.0192307
102	C102	5.201923	2.471154	0.0046473	0.241661	0.0384615
103	C103	5.125	2.451923	0.0011618	0.1208305	0.0192307
104	C104	4.980769	2.259615	0.0104564	0.3624915	0.0576923
105	C105	5.528846	1.913462	0.0002904	0.0604152	0.0096153
106	C106	6.019231	1.538462	0.0046473	0.241661	0.0384615
107	C107	5.692308	1.769231	0.0046473	0.241661	0.0384615
108	C108	6.403846	2.721154	0.0026141	0.1812457	0.0288461
109	C109	6.076923	2.586538	0.0011618	0.1208305	0.0192307
110	C110	6.884615	2.480769	0.0026141	0.1812457	0.0288461
111	C111	6.817308	1.711538	0.0104564	0.3624915	0.0576923
112	C112	7.278846	1.778846	0.0011618	0.1208305	0.0192307

	Features	Center X Pos.	Center Y Pos.	Area	Length	Radius
113	C113	7.336538	2.221154	0.0002904	0.0604152	0.0096153
114	C114	7.240385	3.221154	0.0011618	0.1208305	0.0192307
115	C115	6.605769	3.278846	0.0011618	0.1208305	0.0192307
116	C116	6.961538	3.711538	0.0011618	0.1208305	0.0192307
117	C117	6.807692	4.038462	0.0046473	0.241661	0.0384615
118	C118	7.221154	4.365385	0	0	
119	C119	7.403846	4.25	0.0046473	0.241661	0.0384615
120	C120	7.519231	4.057692	0.0026141	0.1812457	0.0288461
121	C121	7.913462	3.5	0.0002904	0.0604152	0.0096153
122	C122	7.625	3.557692	0.0011618	0.1208305	0.0192307
123	C123	7.894231	3.307692	0.0011618	0.1208305	0.0192307
124	C124	8.105769	3.067308	0.0011618	0.1208305	0.0192307
125	C125	8.240385	2.778846	0.0026141	0.1812457	0.0288461
126	C126	8.355769	2.548077	0.0046473	0.241661	0.0384615
127	C127	8.355769	2.375	0.0011618	0.1208305	0.0192307
128	C128	8.134615	2.278846	0.0011618	0.1208305	0.0192307
129	C129	7.778846	4.778846	0.0046473	0.241661	0.0384615
130	C130	7.326923	4.75	0.0011618	0.1208305	0.0192307
131	C131	6.855769	5.038462	0.0104564	0.3624915	0.0576923
132	C132	6.509615	5.230769	0.0011618	0.1208305	0.0192307
133	C133	5.307692	5.076923	0.0026141	0.1812457	0.0288461
134	C134	4.961538	5.432692	0.0002904	0.0604152	0.0096153
135	C135	4.509615	4.932692	0.0002904	0.0604152	0.0096153
136	C136	4.326923	5.028846	0.0026141	0.1812457	0.0288461
137	C137	3.836538	5.230769	0.0011618	0.1208305	0.0192307
138	C138	3.884615	4.586538	0.0026141	0.1812457	0.0288461
139	C139	3.980769	5.509615	0.0002904	0.0604152	0.0096153
140	C140	4.807692	4.663462	0.0046473	0.241661	0.0384615
141	C141	4.778846	4.538462	0.0002904	0.0604152	0.0096153
142	C142	5.413462	4.384615	0.0026141	0.1812457	0.0288461
143	C143	5.269231	4.413462	0.0026141	0.1812457	0.0288461
144	C144	5.355769	3.990385	0.0011618	0.1208305	0.0192307
145	C145	5.298077	3.865385	0.0002904	0.0604152	0.0096153
146	C146	7.682692	1.528846	0.0026141	0.1812457	0.0288461
147	C147	7.865385	1.192308	0.0026141	0.1812457	0.0288461
148	C148	7.615385	0.5961538	0.0026141	0.1812457	0.0288461
149	C149	7.259615	0.4903846	0.0026141	0.1812457	0.0288461
150	C150	7.163462	0.3557692	0.0011618	0.1208305	0.0192307
151	C151	6.875	0.9519231	0.0011618	0.1208305	0.0192307
152	C152	7.634615	0.3557692	0.0002904	0.0604152	0.0096153
153	C153	8.125	0.5	0.0011618	0.1208305	0.0192307
154	C154	8.701923	0.5865385	0.0002904	0.0604152	0.0096153
155	C155	8.586538	1.298077	0.0002904	0.0604152	0.0096153

	Features	Center X Pos.	Center Y Pos.	Area	Length	Radius
156	C156	8.682692	2.028846	0.0002904	0.0604152	0.0096153
157	C157	9.125	2.298077	0.0046473	0.241661	0.0384615
158	C158	9.144231	1.644231	0.0011618	0.1208305	0.0192307
159	C159	9.528846	0.6442308	0.0072614	0.3020762	0.0480769
160	C160	9.057692	0.5192308	0.0026141	0.1812457	0.0288461
161	C161	8.682692	0.3269231	0.0002904	0.0604152	0.0096153
162	C162	9.490385	0.2884615	0.0046473	0.241661	0.0384615
163	C163	10.08654	0.3942308	0.0002904	0.0604152	0.0096153
164	C164	10.41346	0.2307692	0.0011618	0.1208305	0.0192307
165	C165	10.72115	0.25	0.0046473	0.241661	0.0384615
166	C166	11.09615	0.3076923	0.0046473	0.241661	0.0384615
167	C167	10.33654	0.9326923	0.0026141	0.1812457	0.0288461
168	C168	10.10577	1.230769	0.0011618	0.1208305	0.0192307
169	C169	9.846154	1.125	0.0011618	0.1208305	0.0192307
170	C170	10.04808	1.605769	0.0011618	0.1208305	0.0192307
171	C171	9.961538	1.826923	0.0011618	0.1208305	0.0192307
172	C172	9.557692	2.115385	0.0046473	0.241661	0.0384615
173	C173	9.403846	2.951923	0.0026141	0.1812457	0.0288461
174	C174	10.36538	3.769231	0.0011618	0.1208305	0.0192307
175	C175	10.01923	4	0.0026141	0.1812457	0.0288461
176	C176	9.846154	4	0.0011618	0.1208305	0.0192307
177	C177	9.615385	4.105769	0.0011618	0.1208305	0.0192307
178	C178	8.817308	4.644231	0.0104564	0.3624915	0.0576923
179	C179	9.028846	4.894231	0.0046473	0.241661	0.0384615
180	C180	9.298077	5.086538	0.0046473	0.241661	0.0384615
181	C181	9.134615	5.173077	0.0046473	0.241661	0.0384615
182	C182	8.903846	5.307692	0.0142324	0.4229067	0.0673076
183	C183	8.701923	5.365385	0.0046473	0.241661	0.0384615
184	C184	8.682692	5.528846	0.0011618	0.1208305	0.0192307
185	C185	8.278846	4.961538	0.0026141	0.1812457	0.0288461
186	C186	8.471154	4.365385	0.0072614	0.3020762	0.0480769
187	C187	8.355769	4.278846	0.0046473	0.241661	0.0384615
188	C188	8.942308	3.942308	0.0026141	0.1812457	0.0288461
189	C189	10.01923	5.019231	0.0026141	0.1812457	0.0288461
190	C190	10.24038	4.923077	0.0011618	0.1208305	0.0192307
191	C191	10.18269	4.721154	0.0002904	0.0604152	0.0096153
192	C192	9.884615	4.740385	0.0026141	0.1812457	0.0288461
193	C193	10.78846	4.288462	0.0002904	0.0604152	0.0096153
194	C194	10.15385	3.288462	0.0011618	0.1208305	0.0192307
195	C195	11.17308	3.105769	0.0011618	0.1208305	0.0192307
196	C196	10.94231	2.875	0.0011618	0.1208305	0.0192307
197	C197	10.75962	2.701923	0.0026141	0.1812457	0.0288461
198	C198	10.60577	2.480769	0.0046473	0.241661	0.0384615

	Features	Center X Pos.	Center Y Pos.	Area	Length	Radius
199	C199	10.45192	2.432692	0	0	
200	C200	11.22115	2.375	0.0011618	0.1208305	0.0192307
201	C201	11.29808	2.144231	0.0026141	0.1812457	0.0288461
					mean	0.026098841
					SD	0.012701417

APPENDIX G

DRIFT-FTIR SPECTRA

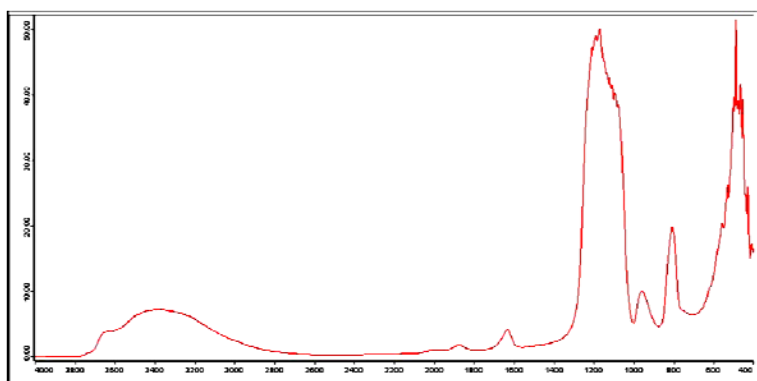


Figure G1 Unmodified PSi.

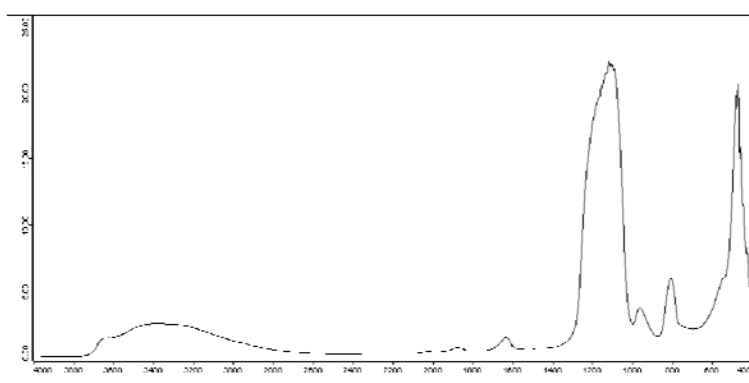


Figure G2 2% APTES-modified PSi.

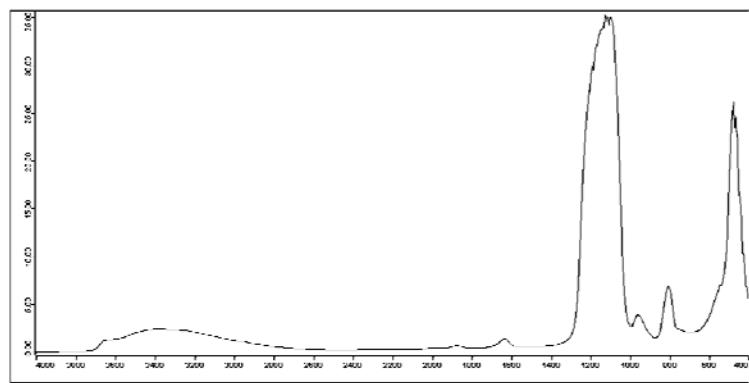


Figure G3 4% APTES-modified PSi.

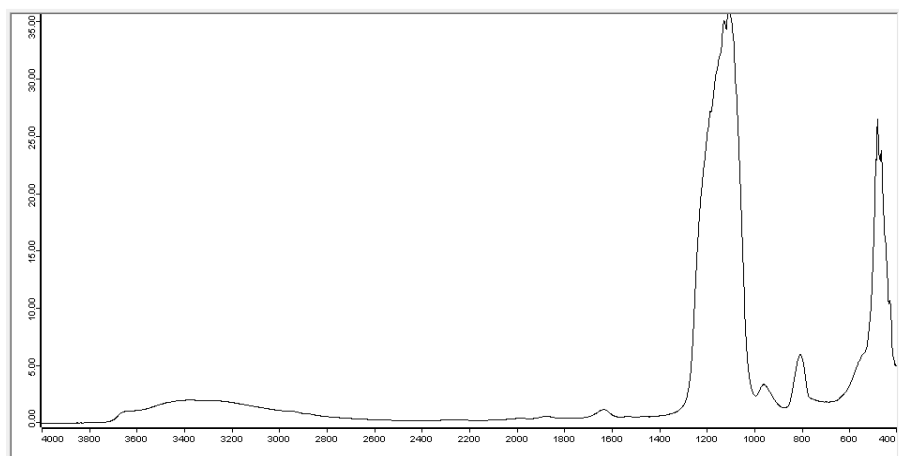


Figure G4 6% APTES-modified PSi.

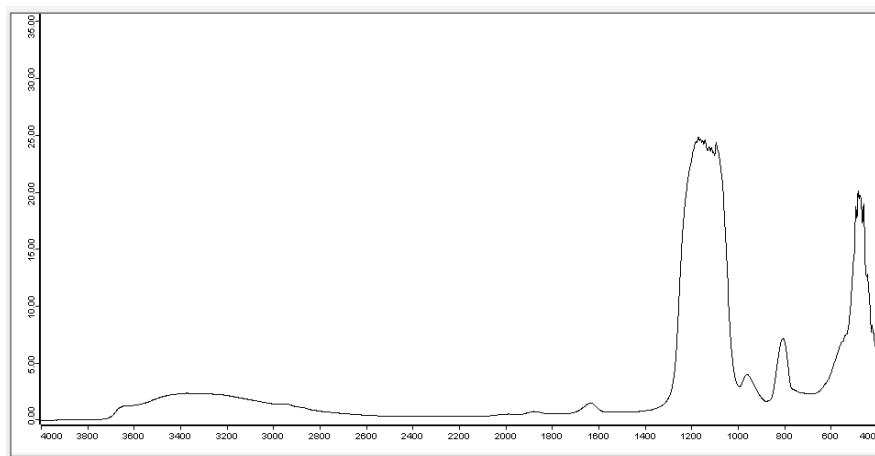


Figure G5 8% APTES-modified PSi.

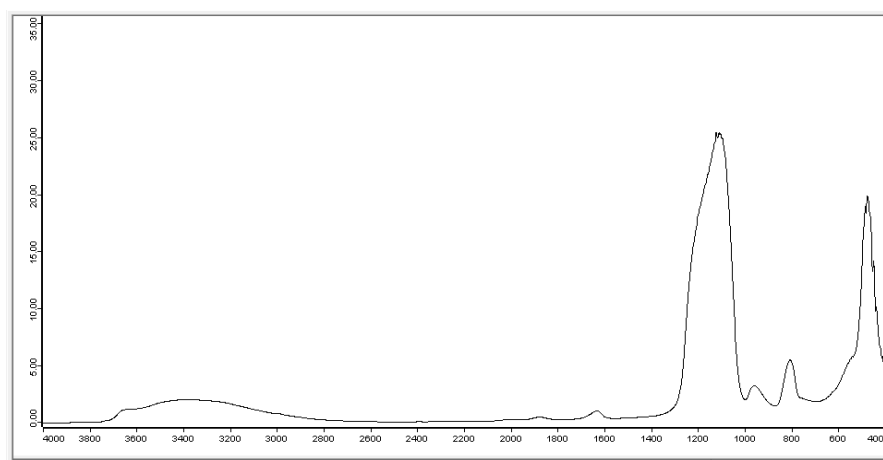


Figure G6 2% CPTES-modified PSi.

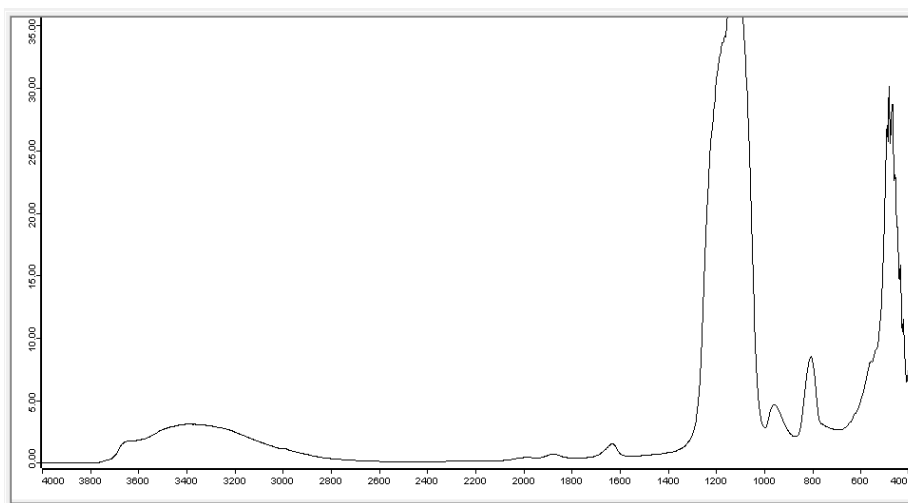


Figure G7 4% CPTES-modified PSi.

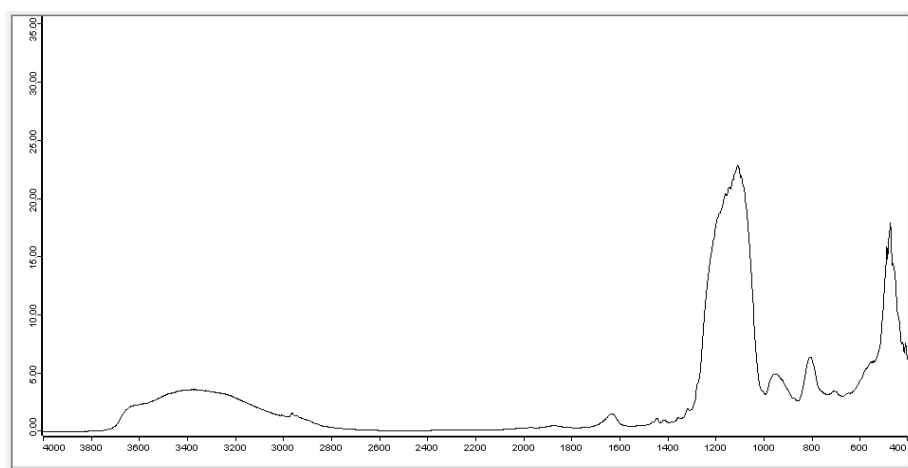


Figure G8 6% CPTES-modified PSi.

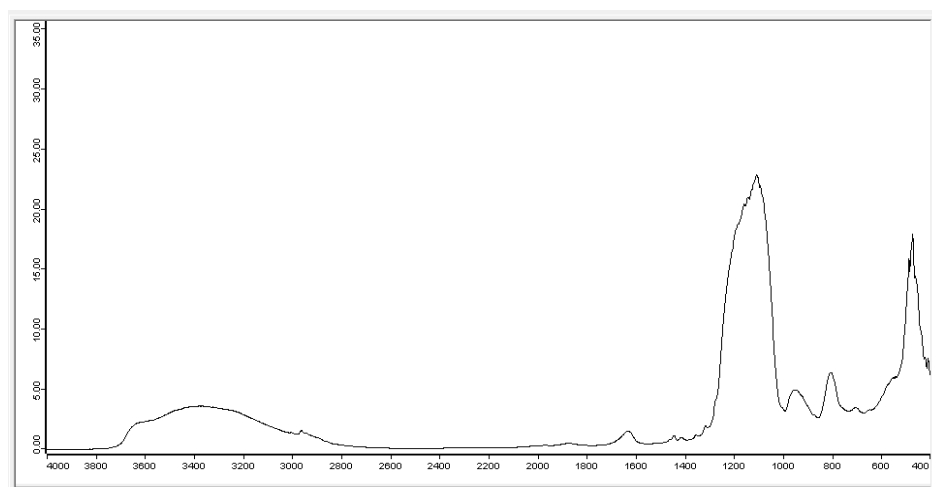


Figure G9 8% CPTES-modified PSi.

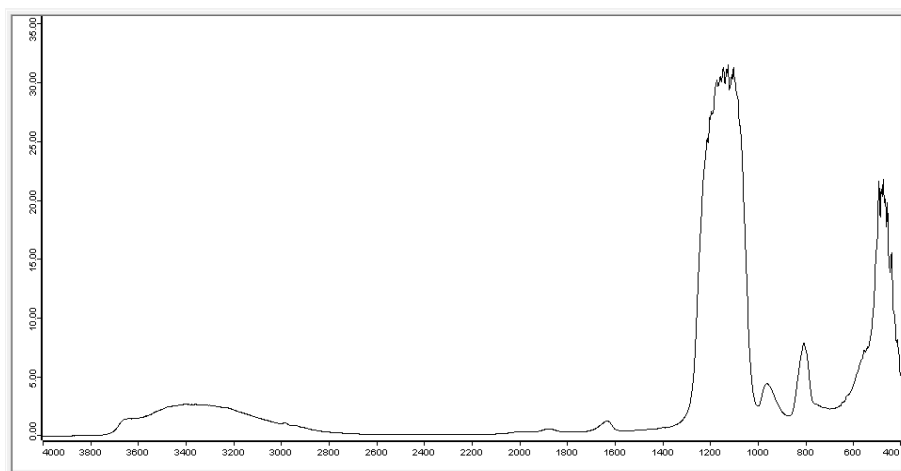


Figure G10 2% TESPT-modified PSi.

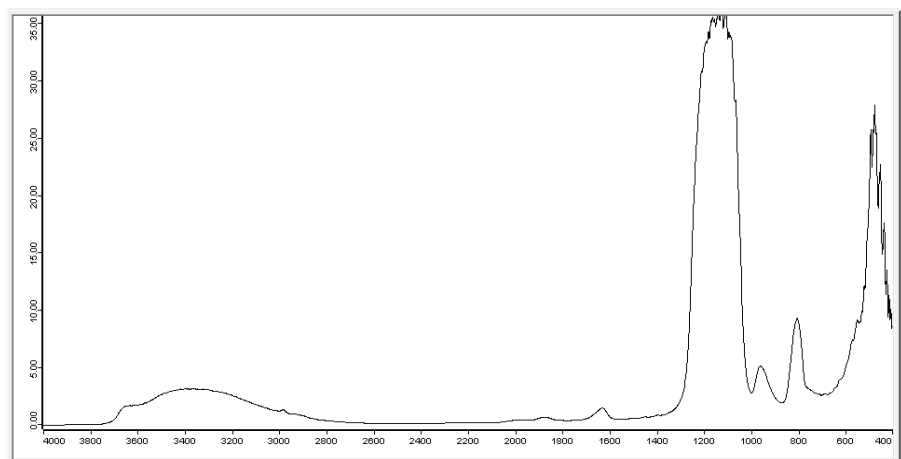


Figure G11 4% TESPT-modified PSi.

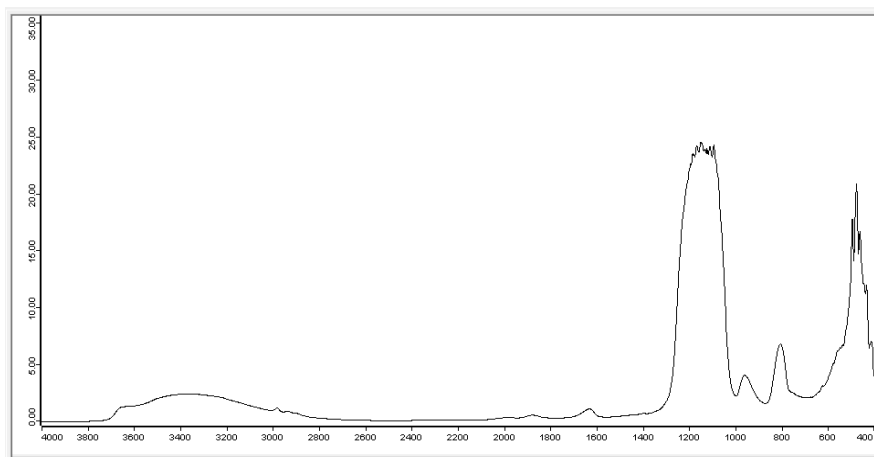


Figure G12 6% TESPT-modified PSi.

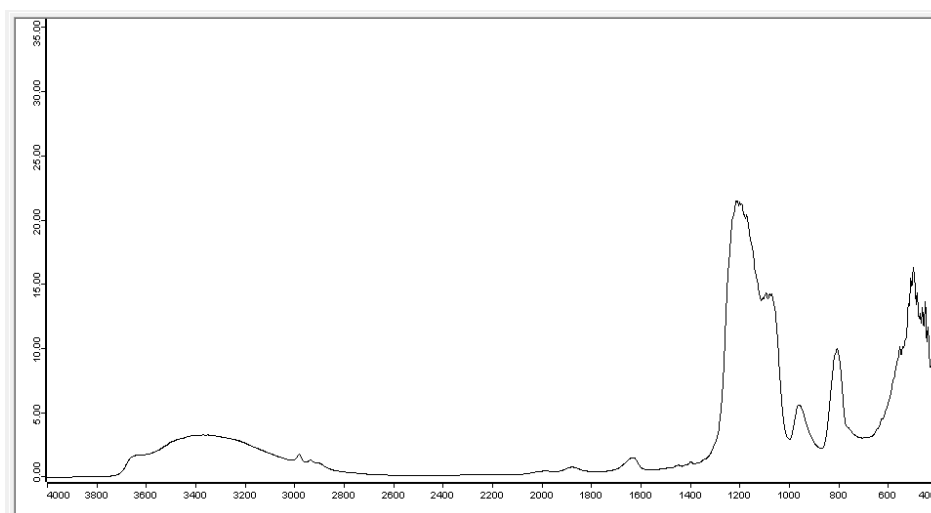


Figure G13 8% TESPT-modified PSi.

APPENDIX H

RELATIVE GRAFTING RATIO OF SCA-MODIFIED PSi

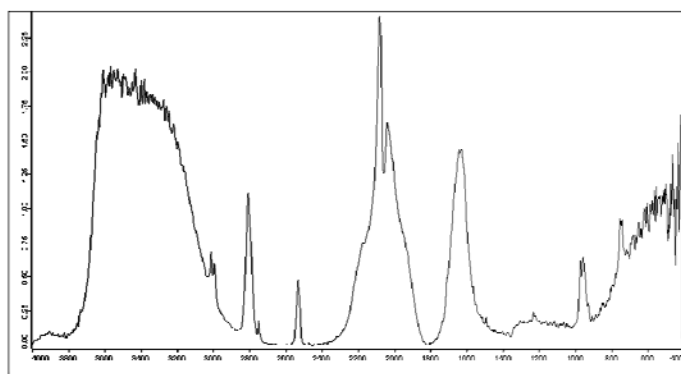


Figure H1 DRIFT of unmodified PSi with 0.1 g KSCN.

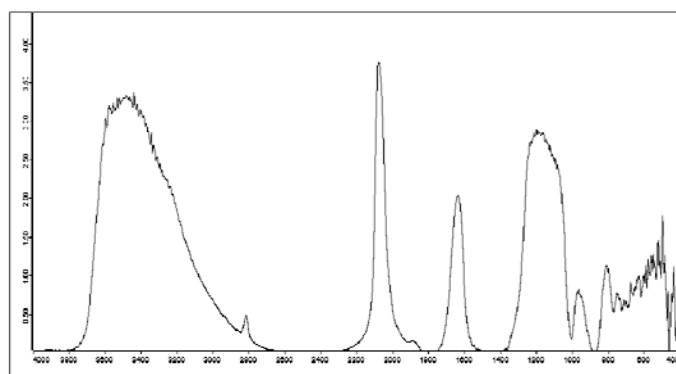


Figure H2 DRIFT of 2% APTES-modified PSi with 0.1 g KSCN.

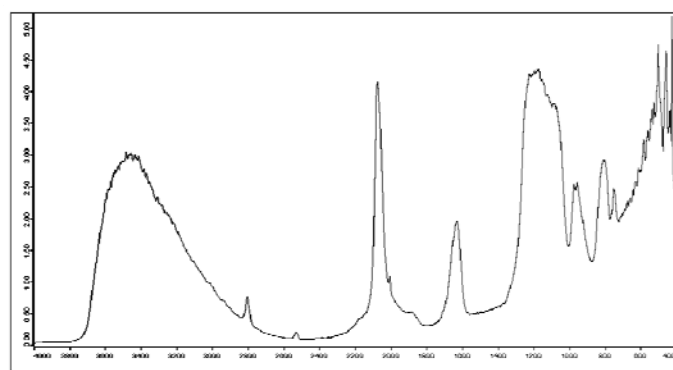


Figure H3 DRIFT of 4% APTES-modified PSi with 0.1 g KSCN.

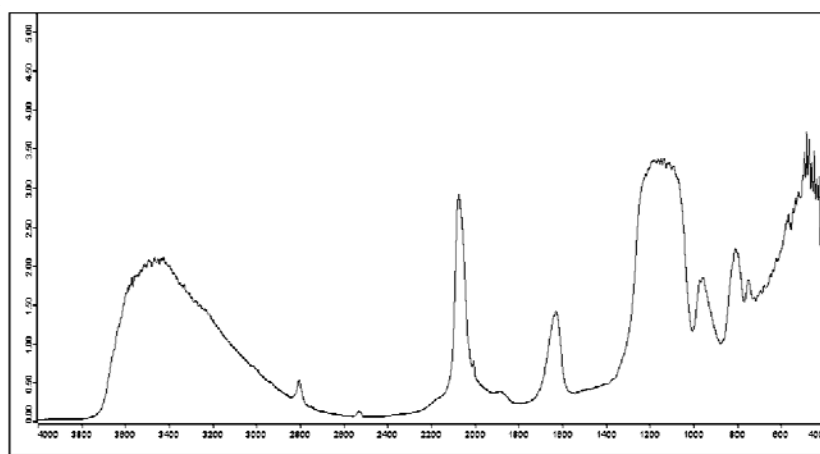


Figure H4 DRIFT of 6% APTES-modified PSi with 0.1 g KSCN.

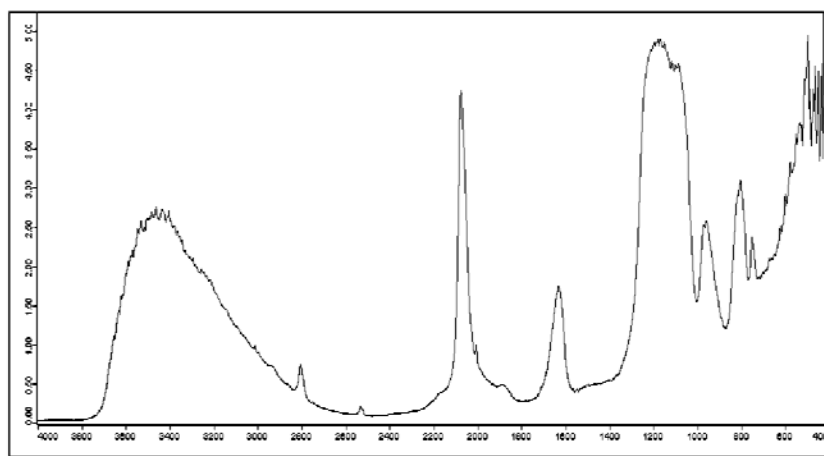


Figure H5 DRIFT of 8% APTES-modified PSi with 0.1 g KSCN.

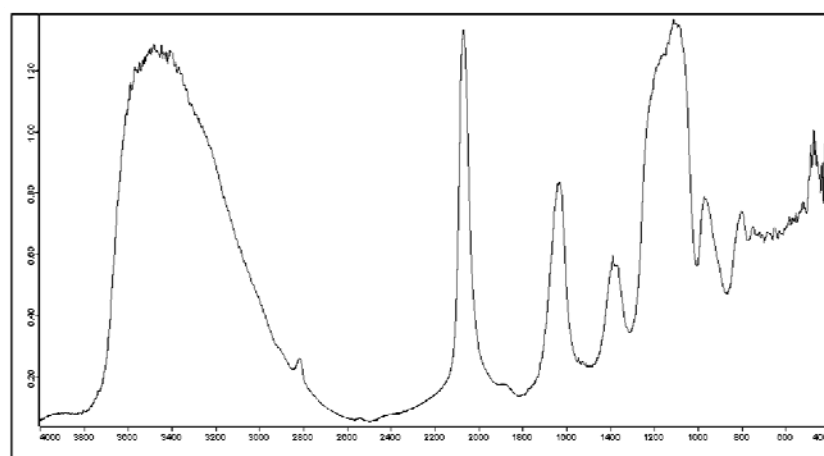


Figure H6 DRIFT of 2% CPTES-modified PSi with 0.1 g KSCN.

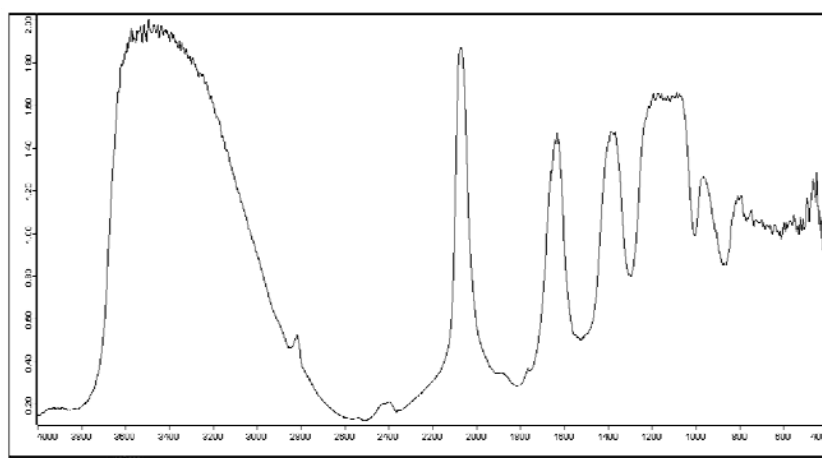


Figure H7 DRIFT of 4% CPTES-modified PSi with 0.1 g KSCN.

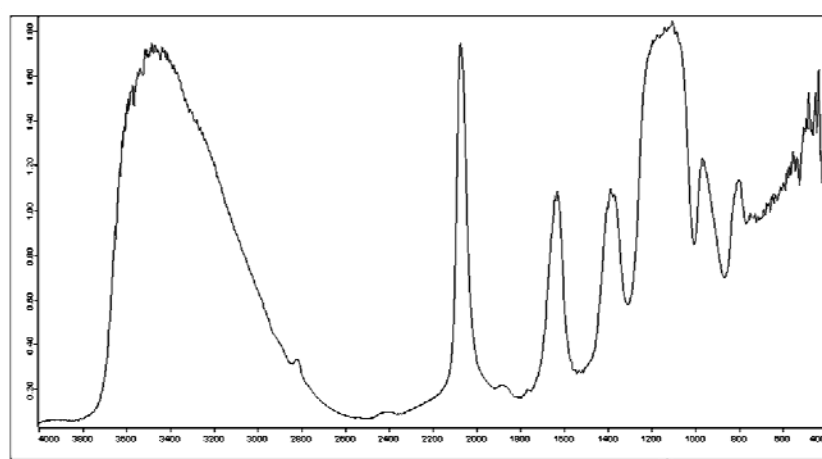


Figure H8 DRIFT of 6% CPTES-modified PSi with 0.1 g KSCN.

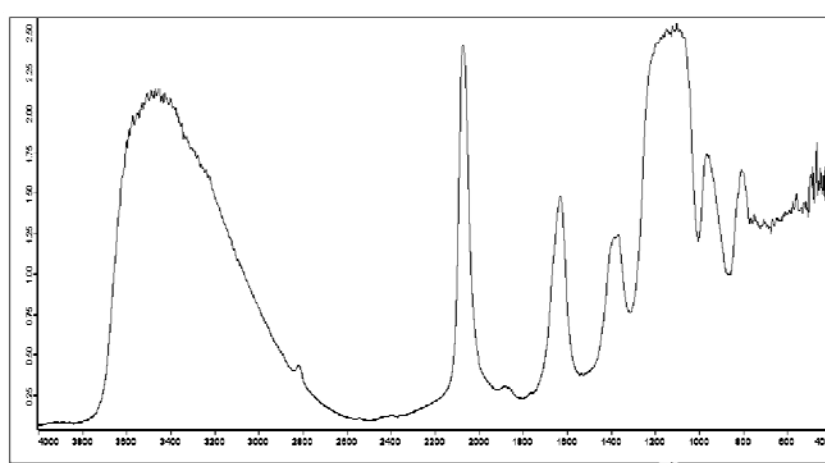


Figure H9 DRIFT of 8% CPTES-modified PSi with 0.1 g KSCN.

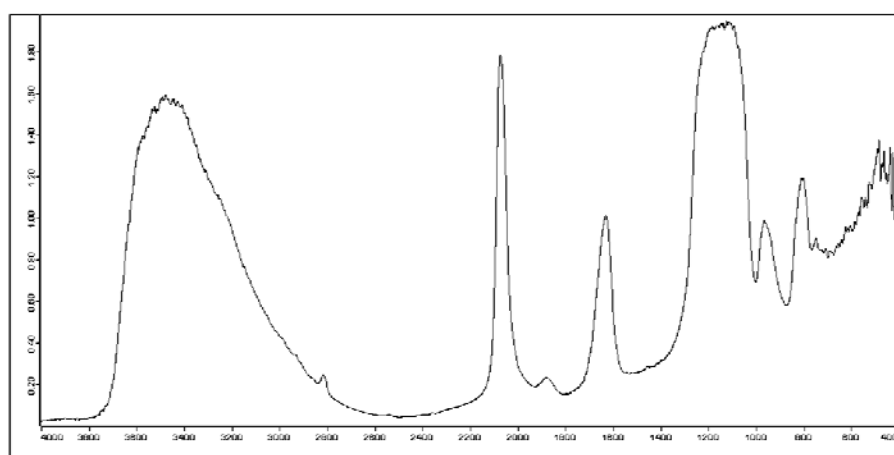


Figure H10 DRIFT of 2% TESPT-modified PSi with 0.1 g KSCN.

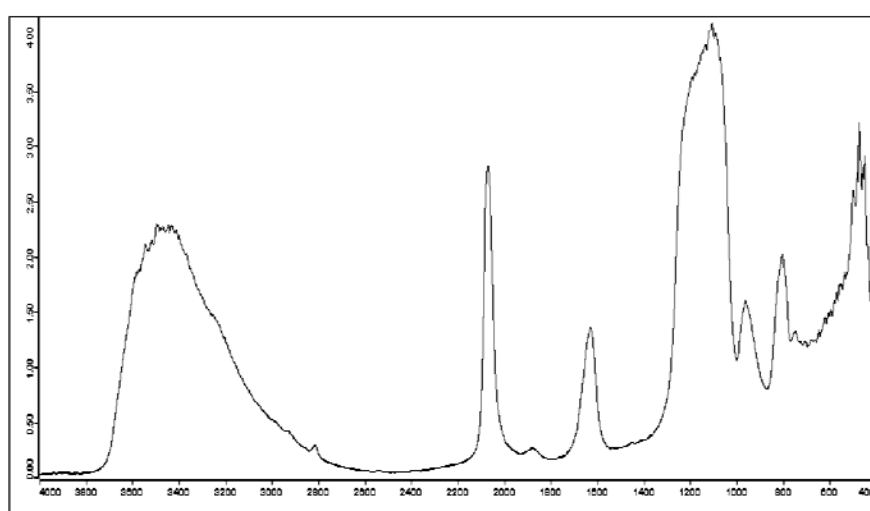


Figure H11 DRIFT of 4% TESPT-modified PSi with 0.1 g KSCN.

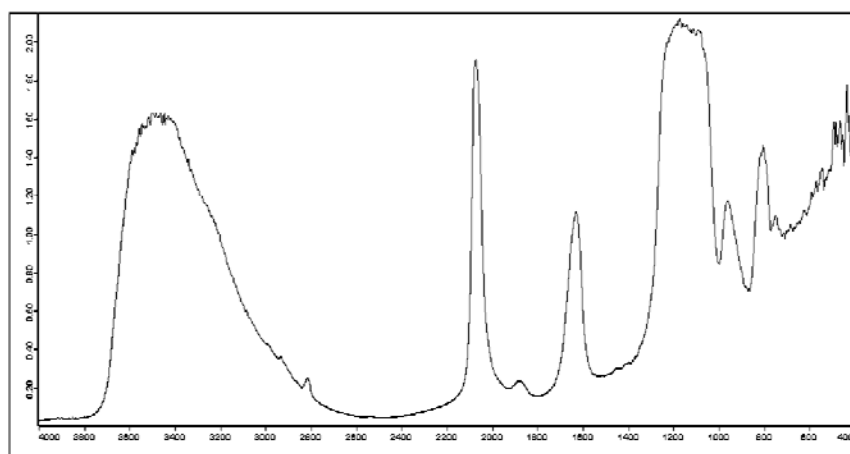


Figure H12 DRIFT of 6% TESPT-modified PSi with 0.1 g KSCN.

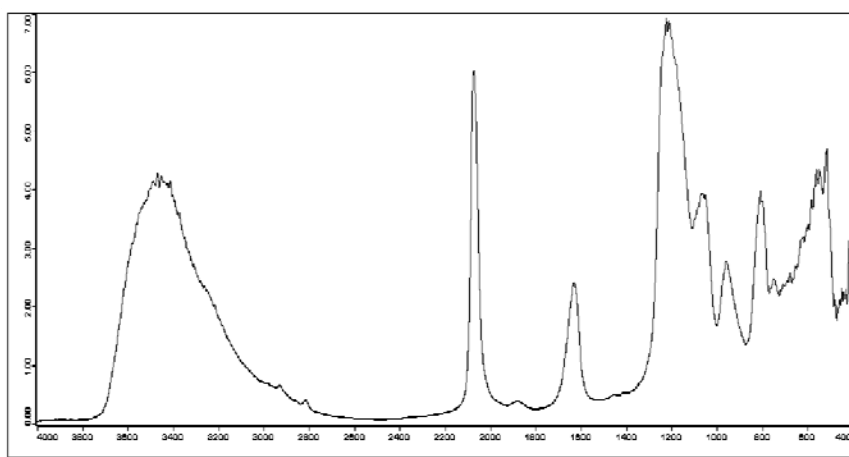


Figure H13 DRIFT of 8% TESPT-modified PSi with 0.1 g KSCN.

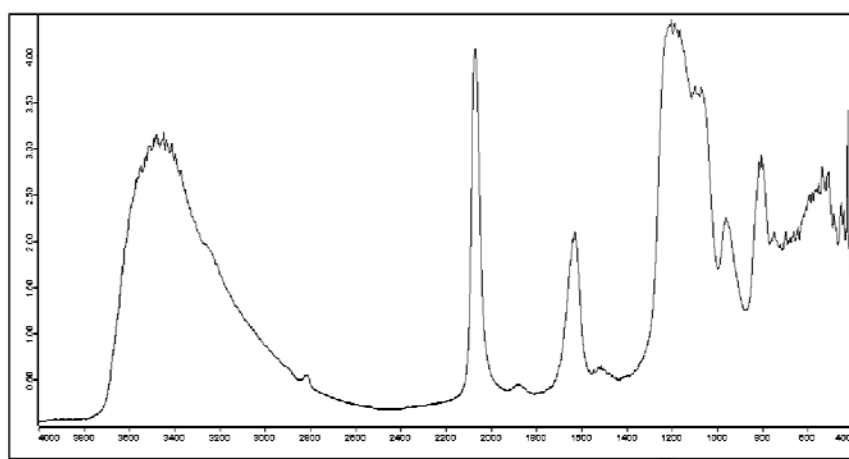


Figure H14 DRIFT of APTES-modified PSi at pH 2 with 0.1 g KSCN.

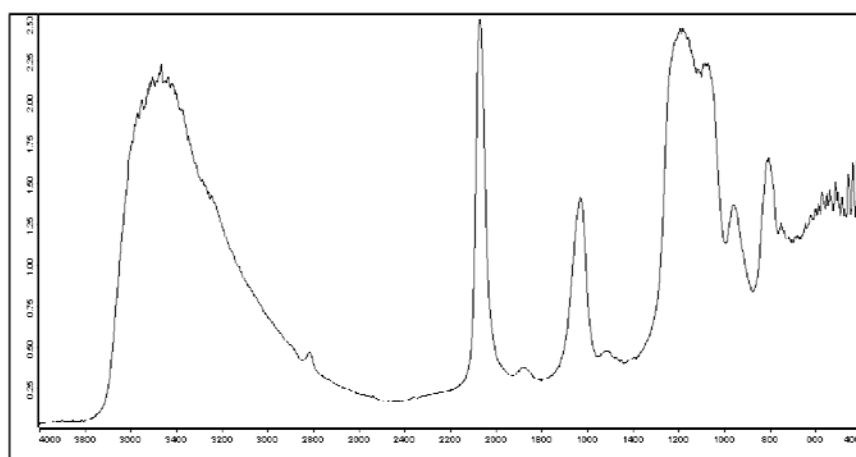


Figure H15 DRIFT of APTES-modified PSi at pH 6 with 0.1 g KSCN.

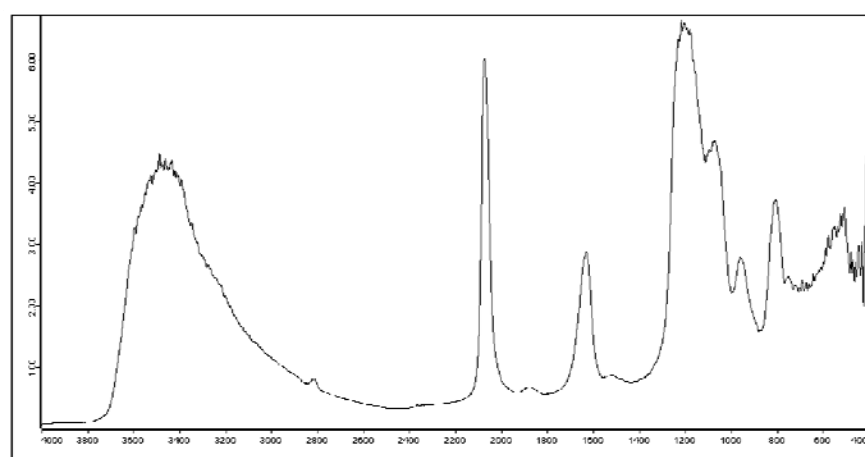


Figure H16 DRIFT of APTES-modified PSi at pH 12 with 0.1 g KSCN.

APPENDIX I

CURE CHARACTERISTIC OF MODIFIED PSi FILLED CR

Table I1 Cure properties of modified PSi with APTES filled CR.

Loading (%)	M _L (dN.m)	t _{s2} (min)	M _H (dN.m)	M _H -M _L (dN.m)	t _{c99} (min)
0	2.64 ± 0.04	2.10 ± 0.09	11.13 ± 0.12	8.49 ± 0.12	66.55 ± 0.97
2	2.51 ± 0.11	2.57 ± 0.03	7.78 ± 0.06	7.78 ± 0.06	68.83 ± 1.35
4	2.48 ± 0.16	1.55 ± 0.24	11.38 ± 0.72	8.90 ± 0.52	74.91 ± 4.43
6	2.36 ± 0.16	1.81 ± 0.11	10.45 ± 0.06	9.09 ± 0.07	70.30 ± 5.74
8	2.55 ± 0.49	2.08 ± 0.02	11.79 ± 0.32	9.24 ± 0.13	71.78 ± 0.04

Table I2 Cure properties of modified PSi with CPTES filled CR.

Loading (%)	M _L (dN.m)	t _{s2} (min)	M _H (dN.m)	M _H -M _L (dN.m)	t _{c99} (min)
0	2.64 ± 0.04	2.10 ± 0.09	11.13 ± 0.12	8.49 ± 0.12	66.55 ± 0.97
2	2.52 ± 0.01	2.79 ± 0.02	11.35 ± 0.03	8.83 ± 0.01	72.28 ± 0.26
4	2.47 ± 0.03	2.55 ± 0.32	11.37 ± 0.17	8.90 ± 0.65	71.90 ± 1.19
6	2.32 ± 0.04	2.17 ± 0.04	10.15 ± 0.03	8.39 ± 0.14	74.95 ± 1.04
8	2.04 ± 0.23	2.32 ± 0.06	9.99 ± 0.28	7.95 ± 0.06	75.96 ± 1.18

Table I3 Cure properties of modified PSi with TESPT filled CR.

Loading (%)	M _L (dN.m)	t _{s2} (min)	M _H (dN.m)	M _H -M _L (dN.m)	t _{c99} (min)
0	2.71 ± 0.02	2.10 ± 0.09	11.25 ± 0.10	8.54 ± 0.17	74.83 ± 1.14
2	2.22 ± 0.13	1.85 ± 0.12	11.85 ± 0.07	9.63 ± 0.57	73.11 ± 1.33
4	2.36 ± 0.39	1.82 ± 0.11	11.77 ± 0.42	9.41 ± 0.44	64.34 ± 2.86
6	2.57 ± 0.14	1.93 ± 0.03	11.97 ± 0.09	9.40 ± 0.18	62.88 ± 0.20
8	2.51 ± 0.01	2.31 ± 0.02	11.93 ± 0.16	9.42 ± 0.56	67.44 ± 0.17

Table I4 Cure properties of PSi with APTES filled CR by in-situ technique.

Loading (%)	M _L (dN.m)	t _{s2} (min)	M _H (dN.m)	M _H -M _L (dN.m)	t _{c99} (min)
0	1.83 ± 0.11	2.10 ± 0.09	11.54 ± 0.14	9.71 ± 0.18	65.83 ± 5.78
2	3.22 ± 0.02	2.03 ± 0.02	11.99 ± 0.02	8.77 ± 0.10	72.26 ± 0.02
4	2.19 ± 0.42	1.95 ± 0.10	12.78 ± 0.32	10.59 ± 0.44	71.81 ± 0.70
6	1.80 ± 0.02	1.94 ± 0.03	12.69 ± 0.07	10.89 ± 0.16	76.37 ± 0.60
8	1.89 ± 0.18	1.85 ± 0.28	13.00 ± 0.15	11.11 ± 0.19	70.96 ± 2.56

Table I5 Cure properties of PSi with CPTES filled CR by in-situ technique.

Loading (%)	M _L (dN.m)	t _{s2} (min)	M _H (dN.m)	M _H -M _L (dN.m)	t _{c99} (min)
0	2.50 ± 0.31	2.10 ± 0.09	15.63 ± 0.12	13.13 ± 0.36	63.07 ± 1.73
2	2.22 ± 0.67	1.73 ± 0.18	13.74 ± 0.04	11.52 ± 1.22	63.85 ± 4.19
4	2.41 ± 0.27	1.45 ± 0.10	15.55 ± 0.12	13.14 ± 0.36	72.47 ± 0.42
6	2.18 ± 0.21	1.36 ± 0.06	15.38 ± 0.37	13.20 ± 0.32	77.34 ± 0.97
8	2.23 ± 0.36	1.30 ± 0.06	14.78 ± 0.31	12.55 ± 0.45	71.26 ± 0.56

Table I6 Cure properties of PSi with TESPT filled CR by in-situ technique.

Loading (%)	M _L (dN.m)	t _{s2} (min)	M _H (dN.m)	M _H -M _L (dN.m)	t _{c99} (min)
0	3.28 ± 0.52	2.10 ± 0.09	13.06 ± 0.12	9.78 ± 0.80	75.35 ± 0.70
2	3.49 ± 0.33	1.86 ± 0.08	13.28 ± 0.05	9.79 ± 0.20	72.55 ± 1.09
4	2.43 ± 0.50	1.51 ± 0.24	12.30 ± 0.52	9.87 ± 0.02	70.08 ± 0.19
6	3.34 ± 0.51	1.81 ± 0.11	13.17 ± 0.11	9.83 ± 0.41	66.32 ± 0.58
8	3.04 ± 0.94	2.06 ± 0.02	12.94 ± 0.27	9.90 ± 0.03	73.53 ± 0.53

APPENDIX J

EFFECT OF PH ON SILANIZATION OF APTES-MODIFIED PSi

Table J1 Strain sweep of with 6% APTES modified PSi at pH 2 filled CR.

Strain (%)	G' (kPa)		
	No.1	No.2	No.3
0.56	493	464.63	580.16
0.98	554.66	508.88	551.52
1.53	568.92	465.92	521.5
1.95	556.4	466.04	513.13
3.07	562.09	449.04	486.35
5.02	521.7	429.95	468.78
6.98	500.64	417.41	457.49
10.04	478.18	393.53	428.39
15.07	440.57	366.08	394.9
19.95	411.39	345.64	370.23
29.99	362.51	307.19	328.29
49.94	289.26	249.82	265.92
100.02	191.65	169.55	182.77
200.04	114.25	106.6	116.07
300.06	77.885	73.597	82.898
499.97	46.166	45.367	56.019
999.94	19.258	22.593	23.393
1199.98	14.241	16.034	16.393

Table J2 Strain sweep of 6% APTES modified PSi at pH 6 filled CR.

Strain (%)	G' (kPa)		
	No. 1	No. 2	No.3
0.56	365.98	349.44	357.71
0.98	342.61	325.15	333.88
1.95	337.29	321.1	329.195
3.07	315.33	297.48	306.405
5.02	304.96	292.17	298.565
10.04	278.57	265.96	272.265
15.07	257.43	246.04	251.735
19.95	241.71	231.23	236.47
29.99	216.03	206.91	211.47
49.94	176.38	170.22	173.3
100.02	118.82	115.9	117.36
200.04	71.5	72.676	72.088
300.06	52.118	52.318	52.218
499.97	35.621	35.754	35.6875
999.94	18.497	18.879	18.688
1199.98	13.563	13.809	13.686

Table J3 Strain sweep of 6% APTES modified PSi at pH 12 filled CR.

Strain (%)	G' (kPa)		
	No.1	No.2	No.3
0.56	573	671.55	435.12
0.98	634.62	603.04	575.5
1.53	592.55	578.96	555.01
1.95	571.31	592.64	549.1
3.07	576.7	558.52	533.82
5.02	495.36	537.23	504.48
6.98	498.72	526.15	496.6
10.04	482.25	497.34	471.09
15.07	448.69	463.06	441.53
19.95	422.76	433.98	415.33
29.99	369.52	381.57	368.03
49.94	302.82	302.67	295.52
100.02	204.99	199.02	196.54
200.04	127.92	125.36	125.97
300.06	90.376	90.162	92.866
499.97	56.313	59.168	61.37
999.94	24.105	23.848	25.642
1199.98	16.96	16.676	17.452

Table J4 Cure properties of CR filled with 6% APTES-modified PSi at various pH conditions

Systems	M _L (dN.m)	t _{s2} (min)	M _H (dN.m)	M _H -M _L (dN.m)	t _{c99} (min)
pH 2	2.58 ± 0.07	2.33 ± 0.16	13.33 ± 0.72	10.75 ± 0.66	67.61 ± 2.28
pH 6	2.36 ± 0.02	1.81 ± 0.11	10.45 ± 0.04	8.09 ± 0.06	70.3 ± 5.54
pH 12	2.40 ± 0.03	1.85 ± 0.05	15.11 ± 0.05	12.72 ± 0.07	43.25 ± 0.32

APPENDIX K

CROSSLINK DENSITY

Table K1 Comparison on crosslink density via swell of CR compounds as affected by SCA loading and surface treatment technique.

SCA	Loading of SCAs (%)	Crosslink density ($\times 10^{-4}$ mol/cm ³ $\pm 10^{-7}$ SD)	
		In-situ	Pre-treatment
APTES	0	0.94 $\pm$ 4.37	0.94 $\pm$ 4.37
	2	1.12 $\pm$ 2.15	1.02 $\pm$ 3.44
	4	1.15 $\pm$ 3.09	1.02 $\pm$ 2.7
	6	1.17 $\pm$ 4.71	1.06 $\pm$ 1.38
	8	1.19 $\pm$ 7.07	1.13 $\pm$ 5.22
CPTES	0	0.94 $\pm$ 4.37	0.94 $\pm$ 4.37
	2	1.03 $\pm$ 2.17	0.917 $\pm$ 2.57
	4	1.06 $\pm$ 4.09	0.908 $\pm$ 4.59
	6	1.08 $\pm$ 3.15	0.881 $\pm$ 1.47
	8	1.08 $\pm$ 7.65	0.930 $\pm$ 5.07
TESPT	0	0.94 $\pm$ 4.37	0.94 $\pm$ 4.37
	2	1.24 $\pm$ 1.57	1.06 $\pm$ 3.93
	4	1.25 $\pm$ 3.14	1.09 $\pm$ 2.75
	6	1.31 $\pm$ 5.79	1.13 $\pm$ 2.98
	8	1.32 $\pm$ 8.22	1.16 $\pm$ 3.42

APPENDIX L

DMA RESULTS

Table L1 Temperature sweep test results of CR cured specimens at various APTES loadings by pre-modified technique.

Temperature (°C)	tanδ				
	0% APTES	2% APTES	4% APTES	6% APTES	8% APTES
-59.1	0.05221	0.0316	0.03014	0.03148	0.03231
-58.6	0.05233	0.03266	0.03057	0.0324	0.0367
-57.6	0.05133	0.0357	0.03204	0.03157	0.03962
-55.8	0.05093	0.03709	0.03495	0.03178	0.04095
-54.2	0.05162	0.03915	0.03738	0.03304	0.04367
-52.6	0.05268	0.04124	0.03876	0.0339	0.04621
-51.2	0.05474	0.04411	0.04102	0.03543	0.04929
-49.9	0.05725	0.04752	0.04344	0.03791	0.05218
-48.4	0.06106	0.05128	0.04583	0.04095	0.05586
-47	0.0657	0.05635	0.04916	0.04439	0.06035
-45.5	0.07206	0.06176	0.05313	0.04992	0.06682
-43.9	0.08108	0.06983	0.05863	0.05777	0.0756
-42.4	0.09244	0.08172	0.06821	0.06826	0.08769
-40.9	0.11043	0.10147	0.08315	0.0867	0.10731
-39.5	0.1363	0.13461	0.11458	0.12052	0.13624
-37.7	0.18971	0.18988	0.16644	0.17832	0.18643
-36.2	0.24995	0.25857	0.22733	0.245	0.24679
-34.9	0.33553	0.34988	0.30957	0.33	0.32985
-33.5	0.46108	0.48157	0.4292	0.4682	0.4591
-32.2	0.61752	0.65794	0.59371	0.64992	0.62213
-30.8	0.80068	0.88719	0.79325	0.89616	0.83608
-29.4	0.96403	1.08946	0.99413	1.10612	1.02285
-27.9	1.08214	1.2519	1.15403	1.29961	1.17186
-26.4	1.12082	1.31363	1.23159	1.38376	1.2388
-24.8	1.09374	1.27592	1.22105	1.34992	1.2289
-23.3	1.02743	1.18296	1.15279	1.26066	1.17224
-21.8	0.942147	1.07999	1.06071	1.14426	1.08546
-20.5	0.868005	0.972194	0.962317	1.03676	0.996935
-19	0.785726	0.869721	0.872365	0.931737	0.90801
-17.5	0.711365	0.781092	0.786178	0.830928	0.820739
-16	0.64181	0.702514	0.70681	0.748168	0.745986
-14.4	0.579782	0.630789	0.635574	0.674073	0.671341

Table L1 Temperature sweep test results of CR cured specimens at various APTES loadings by pre-modified technique (Cont.).

Temperature (°C)	tanδ				
	0% APTES	2% APTES	4% APTES	6% APTES	8% APTES
-13	0.526219	0.570261	0.573093	0.600608	0.600724
-11.4	0.473651	0.510414	0.516218	0.538537	0.539028
-10	0.428685	0.459056	0.462778	0.485142	0.484817
-8.5	0.385006	0.407612	0.413702	0.42789	0.430094
-7.1	0.346029	0.363711	0.370804	0.3835	0.385004
-5.6	0.310188	0.324764	0.330625	0.339356	0.340638
-4	0.277174	0.288696	0.293891	0.303078	0.301943
-2.5	0.248049	0.258551	0.263549	0.267991	0.266629
-1.1	0.226077	0.231729	0.235765	0.23961	0.240252
-0.3	0.207331	0.210458	0.214715	0.218767	0.213766
3.5	0.190879	0.193292	0.195043	0.198441	0.195188
3.6	0.181396	0.185626	0.186731	0.187174	0.182136
4.6	0.170387	0.168105	0.16944	0.168806	0.174176
6.4	0.154269	0.152458	0.151817	0.159222	0.154968
7.8	0.145001	0.142909	0.140302	0.142356	0.142703
9.4	0.135245	0.133038	0.132299	0.131654	0.129986
10.8	0.129397	0.125968	0.125259	0.1247	0.124706
12.3	0.122061	0.119512	0.120656	0.120353	0.113854
13.8	0.117293	0.114663	0.113711	0.11424	0.108938
15.5	0.113627	0.111013	0.110487	0.10894	0.104872
16.6	0.110141	0.105784	0.105651	0.104088	0.099354
18.1	0.107941	0.10521	0.102983	0.098514	0.094758
19.6	0.105721	0.10118	0.100795	0.095819	0.092586
21.1	0.101555	0.09695	0.095207	0.091171	0.087574
22.6	0.100793	0.095277	0.093217	0.093951	0.086213
24.2	0.09894	0.095751	0.091532	0.089304	0.083842
25.8	0.095018	0.091323	0.088329	0.087081	0.079295
27.2	0.093651	0.087277	0.085744	0.08459	0.078614
28.7	0.093279	0.084475	0.082958	0.084477	0.078851
30.1	0.089909	0.083947	0.082137	0.07877	0.077246
31.6	0.089618	0.08373	0.079169	0.078969	0.071821
33.1	0.088882	0.080969	0.079263	0.076482	0.071408
34.5	0.090181	0.081384	0.077896	0.074092	0.070957
36	0.084594	0.080366	0.076025	0.07257	0.06895
37.6	0.084717	0.078701	0.07649	0.072814	0.067491
38.9	0.083089	0.075559	0.074396	0.071991	0.066376
40.4	0.080583	0.074173	0.073191	0.070643	0.06315
41.9	0.081262	0.078681	0.069844	0.069048	0.063127
43.4	0.082692	0.073613	0.072331	0.067693	0.065422
45	0.080401	0.075048	0.068623	0.063593	0.064136

Table L1 Temperature sweep test results of CR cured specimens at various APTES loadings by pre-modified technique (Cont.).

Temperature (°C)	tanδ				
	0% APTES	2% APTES	4% APTES	6% APTES	8% APTES
46.5	0.078493	0.071689	0.069105	0.071793	0.062652
48	0.077621	0.071462	0.07007	0.068375	0.060863
49.6	0.07624	0.069054	0.065433	0.067677	0.06144
50.9	0.076381	0.072924	0.066401	0.063814	0.062353
52.3	0.07542	0.069808	0.067055	0.061568	0.060372
53.7	0.075784	0.071335	0.067444	0.061234	0.058198
55.3	0.075028	0.07256	0.066914	0.060095	0.056857
56.7	0.075739	0.070345	0.066013	0.061177	0.055536
58.2	0.074006	0.06842	0.064484	0.058902	0.055891
59.8	0.074796	0.066211	0.06449	0.059869	0.054492
61.2	0.073542	0.069268	0.061519	0.062137	0.053796
62.7	0.073382	0.067316	0.063746	0.059035	0.056013
64.2	0.075773	0.067212	0.060853	0.059832	0.054876
65.7	0.072377	0.06683	0.059234	0.056747	0.056532
67.3	0.074539	0.06584	0.061589	0.0576	0.053074
68.7	0.072793	0.069029	0.062645	0.05988	0.052317
70.3	0.074356	0.067529	0.06402	0.057674	0.053217
71.7	0.073351	0.06925	0.06403	0.061948	0.051814
73.2	0.07483	0.06969	0.063804	0.058339	0.054705
74.6	0.074633	0.066798	0.060094	0.057004	0.054636
76.3	0.075926	0.069454	0.065938	0.058342	0.05396
77.7	0.077048	0.07119	0.062546	0.05919	0.055134
79.5	0.076782	0.06854	0.065329	0.06212	0.056969

Table L2 Temperature sweep test results of CR cured specimens at various CPTES loadings by pre-modified technique.

Temperature (°C)	tanδ				
	0% CPTES	2% CPTES	4% CPTES	6% CPTES	8% CPTES
-59.1	0.05221	0.03189	0.02949	0.05833	0.04168
-58.6	0.05233	0.03265	0.02968	0.06678	0.04043
-57.6	0.05133	0.03345	0.02939	0.06432	0.04005
-55.8	0.05093	0.03542	0.02972	0.06549	0.04
-54.2	0.05162	0.03791	0.03145	0.06753	0.04117
-52.6	0.05268	0.05013	0.03265	0.07005	0.04203
-51.2	0.05474	0.05097	0.03419	0.07294	0.04461
-49.9	0.05725	0.05337	0.03618	0.07706	0.04661
-48.4	0.06106	0.05567	0.03887	0.08068	0.05115
-47	0.0657	0.05904	0.0429	0.08666	0.0551
-45.5	0.07206	0.06418	0.04857	0.09139	0.06063
-43.9	0.08108	0.07331	0.05862	0.09898	0.06794
-42.4	0.09244	0.08573	0.07412	0.10833	0.0789
-40.9	0.11043	0.1129	0.09568	0.12594	0.09478
-39.5	0.1363	0.15505	0.13614	0.15531	0.12167
-37.7	0.18971	0.21757	0.19098	0.20422	0.17467
-36.2	0.24995	0.27944	0.25351	0.25997	0.23451
-34.9	0.33553	0.37271	0.34483	0.35131	0.32037
-33.5	0.46108	0.50561	0.49122	0.50132	0.44078
-32.2	0.61752	0.71714	0.68198	0.69734	0.60457
-30.8	0.80068	0.94147	0.92515	0.93623	0.79323
-29.4	0.96403	1.15161	1.13196	1.14047	0.99669
-27.9	1.08214	1.30082	1.29375	1.29218	1.1249
-26.4	1.12082	1.33069	1.34061	1.32508	1.17584
-24.8	1.09374	1.25634	1.28242	1.26474	1.15476
-23.3	1.02743	1.15463	1.18508	1.15767	1.08317
-21.8	0.942147	1.04079	1.05823	1.03981	0.994192
-20.5	0.868005	0.935123	0.960855	0.93713	0.907421
-19	0.785726	0.842457	0.860565	0.840015	0.818163
-17.5	0.711365	0.757678	0.768903	0.755296	0.741011
-16	0.64181	0.67892	0.69467	0.68204	0.670424
-14.4	0.579782	0.611792	0.626406	0.613908	0.603309
-13	0.526219	0.553681	0.565552	0.550025	0.546958
-11.4	0.473651	0.492595	0.507091	0.49444	0.485991
-10	0.428685	0.445269	0.452771	0.445626	0.440442
-8.5	0.385006	0.400835	0.408405	0.403437	0.393996
-7.1	0.346029	0.35623	0.360073	0.35908	0.353665
-5.6	0.310188	0.3183	0.322891	0.323329	0.315833
-4	0.277174	0.282411	0.288319	0.287287	0.283049
-2.5	0.248049	0.251094	0.257929	0.260266	0.254666

Table L2 Temperature sweep test results of CR cured specimens at various CPTES loadings by pre-modified technique (Cont.).

Temperature (°C)	tanδ				
	0% CPTES	2% CPTES	4% CPTES	6% CPTES	8% CPTES
-1.1	0.226077	0.228121	0.234592	0.234274	0.230157
-0.3	0.207331	0.205118	0.209818	0.21511	0.207358
3.5	0.190879	0.195741	0.196101	0.197662	0.192036
3.6	0.181396	0.189603	0.186574	0.190596	0.183008
4.6	0.170387	0.167205	0.168153	0.177717	0.169939
6.4	0.154269	0.152445	0.155044	0.162006	0.155018
7.8	0.145001	0.144507	0.141588	0.15063	0.144787
9.4	0.135245	0.135819	0.134753	0.139852	0.136316
10.8	0.129397	0.133551	0.130099	0.132714	0.127658
12.3	0.122061	0.123698	0.124307	0.124823	0.12366
13.8	0.117293	0.119986	0.118051	0.122937	0.118292
15.5	0.113627	0.113677	0.114694	0.116903	0.113953
16.6	0.110141	0.108679	0.108294	0.11493	0.111162
18.1	0.107941	0.108255	0.10715	0.10878	0.107758
19.6	0.105721	0.104434	0.103346	0.105639	0.105941
21.1	0.101555	0.100021	0.100246	0.103491	0.10089
22.6	0.100793	0.099669	0.096068	0.099201	0.099532
24.2	0.09894	0.093987	0.090407	0.099489	0.095939
25.8	0.095018	0.091862	0.093746	0.097955	0.093367
27.2	0.093651	0.087692	0.088349	0.095236	0.092196
28.7	0.093279	0.086576	0.088731	0.092579	0.091934
30.1	0.089909	0.089838	0.089047	0.09122	0.087014
31.6	0.089618	0.08826	0.083504	0.089674	0.086939
33.1	0.088882	0.084969	0.082589	0.087236	0.084867
34.5	0.090181	0.080925	0.077916	0.087293	0.083083
36	0.084594	0.075667	0.076024	0.084304	0.082598
37.6	0.084717	0.07411	0.075662	0.085541	0.080484
38.9	0.083089	0.07302	0.069658	0.085718	0.080512
40.4	0.080583	0.068811	0.070907	0.082366	0.081067
41.9	0.081262	0.067966	0.071522	0.086005	0.078214
43.4	0.082692	0.068398	0.06634	0.082209	0.076199
45	0.080401	0.067009	0.068173	0.07955	0.074034
46.5	0.078493	0.065604	0.064632	0.077091	0.073849
48	0.077621	0.062568	0.065648	0.078524	0.074825
49.6	0.07624	0.062509	0.066233	0.080468	0.074011
50.9	0.076381	0.062922	0.065407	0.076914	0.072374
52.3	0.07542	0.064562	0.06387	0.076358	0.070516
53.7	0.075784	0.067497	0.064182	0.075177	0.072745
55.3	0.075028	0.06493	0.061228	0.07569	0.072819
56.7	0.075739	0.064843	0.065122	0.077265	0.071104

Table L2 Temperature sweep test results of CR cured specimens at various CPTES loadings by pre-modified technique (Cont.).

Temperature (°C)	tanδ				
	0% CPTES	2% CPTES	4% CPTES	6% CPTES	8% CPTES
58.2	0.074006	0.061203	0.063914	0.074922	0.068223
59.8	0.074796	0.065982	0.065633	0.072198	0.068975
61.2	0.073542	0.069567	0.06572	0.077621	0.069643
62.7	0.073382	0.067316	0.067543	0.07441	0.068946
64.2	0.075773	0.067212	0.062999	0.074784	0.070522
65.7	0.072377	0.06683	0.065898	0.07453	0.069609
67.3	0.074539	0.06584	0.068966	0.072724	0.068869
68.7	0.072793	0.069029	0.066089	0.077071	0.067476
70.3	0.074356	0.067529	0.067451	0.074075	0.070631
71.7	0.073351	0.06925	0.069158	0.073332	0.069711
73.2	0.07483	0.06969	0.066837	0.073819	0.070788
74.6	0.074633	0.066798	0.063961	0.074754	0.070925
76.3	0.075926	0.069454	0.068541	0.075211	0.075308
77.7	0.077048	0.07119	0.066131	0.074116	0.073439
79.5	0.076782	0.06854	0.065133	0.076778	0.073422

Table L3 Temperature sweep test results of CR cured specimens at various TESPT loadings by pre-modified technique.

Temperature (°C)	tanδ				
	0% TESPT	2% TESPT	4% TESPT	6% TESPT	8% TESPT
-59.1	0.05221	0.05439	0.04042	0.0427	0.04358
-58.6	0.05233	0.05545	0.04336	0.04908	0.04375
-57.6	0.05133	0.05502	0.04403	0.05215	0.04379
-55.8	0.05093	0.05519	0.0454	0.05338	0.04341
-54.2	0.05162	0.05631	0.04712	0.05517	0.04433
-52.6	0.05268	0.05606	0.04887	0.05789	0.04582
-51.2	0.05474	0.05775	0.05031	0.06023	0.04769
-49.9	0.05725	0.05902	0.05316	0.06324	0.05018
-48.4	0.06106	0.06047	0.05593	0.06505	0.05375
-47	0.0657	0.06312	0.05924	0.06904	0.05806
-45.5	0.07206	0.06691	0.06386	0.07387	0.06376
-43.9	0.08108	0.07506	0.07161	0.07988	0.07066
-42.4	0.09244	0.08986	0.08488	0.09239	0.08102
-40.9	0.11043	0.12977	0.11114	0.11347	0.09703
-39.5	0.1363	0.16851	0.15055	0.15018	0.12051
-37.7	0.18971	0.21649	0.20325	0.20051	0.16995
-36.2	0.24995	0.26847	0.26918	0.26197	0.22362
-34.9	0.33553	0.35005	0.36476	0.34065	0.2986
-33.5	0.46108	0.49921	0.51847	0.45617	0.40053
-32.2	0.61752	0.69007	0.70235	0.63027	0.54319
-30.8	0.80068	0.92772	0.92135	0.84007	0.73485
-29.4	0.96403	1.13284	1.11748	1.06194	0.90157
-27.9	1.08214	1.2966	1.28436	1.23202	1.05363
-26.4	1.12082	1.3331	1.33129	1.31549	1.14974
-24.8	1.09374	1.28044	1.2748	1.29608	1.17137
-23.3	1.02743	1.16516	1.18684	1.21433	1.13394
-21.8	0.942147	1.06538	1.07204	1.10741	1.06348
-20.5	0.868005	0.964026	0.961809	1.0026	0.986876
-19	0.785726	0.870526	0.874886	0.910941	0.900746
-17.5	0.711365	0.780244	0.788483	0.817824	0.820253
-16	0.64181	0.699546	0.713799	0.737497	0.744954
-14.4	0.579782	0.629614	0.639925	0.666222	0.677452
-13	0.526219	0.565705	0.578637	0.593248	0.611035
-11.4	0.473651	0.50676	0.514241	0.53767	0.549004
-10	0.428685	0.451484	0.464699	0.489325	0.499586
-8.5	0.385006	0.407157	0.411506	0.434834	0.448629
-7.1	0.346029	0.356516	0.368648	0.386188	0.403112
-5.6	0.310188	0.319786	0.328467	0.341823	0.359967
-4	0.277174	0.281973	0.29179	0.301597	0.320274
-2.5	0.248049	0.25255	0.252268	0.275609	0.287739

Table L3 Temperature sweep test results of CR cured specimens at various TESPT loadings by pre-modified technique (Cont.).

Temperature (°C)	tanδ				
	0% TESPT	2% TESPT	4% TESPT	6% TESPT	8% TESPT
-1.1	0.226077	0.232531	0.238841	0.238391	0.258639
-0.3	0.207331	0.208084	0.21297	0.221281	0.233249
3.5	0.190879	0.190723	0.193577	0.205241	0.213477
3.6	0.181396	0.183337	0.188403	0.19573	0.201683
4.6	0.170387	0.166057	0.172687	0.179568	0.18494
6.4	0.154269	0.147495	0.157222	0.160896	0.167892
7.8	0.145001	0.1442	0.14354	0.149965	0.153417
9.4	0.135245	0.128927	0.139652	0.140344	0.144838
10.8	0.129397	0.123252	0.127633	0.129239	0.136583
12.3	0.122061	0.11503	0.114024	0.114055	0.126612
13.8	0.117293	0.110637	0.109307	0.105633	0.12258
15.5	0.113627	0.108	0.106442	0.095821	0.116711
16.6	0.110141	0.111604	0.102656	0.090455	0.113642
18.1	0.107941	0.102062	0.099846	0.091	0.108859
19.6	0.105721	0.094684	0.092691	0.089727	0.105891
21.1	0.101555	0.092763	0.091187	0.083684	0.101973
22.6	0.100793	0.091401	0.084929	0.084056	0.098796
24.2	0.09894	0.082379	0.080196	0.078437	0.094871
25.8	0.095018	0.087357	0.081501	0.077266	0.090081
27.2	0.093651	0.085942	0.075815	0.073853	0.088324
28.7	0.093279	0.077386	0.074668	0.069293	0.087373
30.1	0.089909	0.076297	0.070709	0.06983	0.084712
31.6	0.089618	0.0771	0.070195	0.066022	0.083082
33.1	0.088882	0.0695	0.069653	0.063602	0.079406
34.5	0.090181	0.075248	0.067662	0.064825	0.080479
36	0.084594	0.068591	0.066223	0.063769	0.079423
37.6	0.084717	0.070866	0.062813	0.06373	0.075723
38.9	0.083089	0.064872	0.063647	0.065256	0.074499
40.4	0.080583	0.064131	0.063537	0.061255	0.072289
41.9	0.081262	0.067737	0.060869	0.058538	0.07431
43.4	0.082692	0.065935	0.061232	0.062027	0.068191
45	0.080401	0.06238	0.065419	0.060465	0.069908
46.5	0.078493	0.063475	0.062283	0.056351	0.069039
48	0.077621	0.06237	0.059359	0.057461	0.06823
49.6	0.07624	0.062002	0.056643	0.060748	0.067327
50.9	0.076381	0.066841	0.065042	0.060211	0.065517
52.3	0.07542	0.064687	0.062475	0.063107	0.065599
53.7	0.075784	0.062367	0.061116	0.063297	0.063915
55.3	0.075028	0.053414	0.061422	0.059579	0.064903
56.7	0.075739	0.06002	0.060019	0.058746	0.064063

Table L3 Temperature sweep test results of CR cured specimens at various TESPT loadings by pre-modified technique (Cont.).

Temperature (°C)	tanδ				
	0% TESPT	2% TESPT	4% TESPT	6% TESPT	8% TESPT
58.2	0.074006	0.060944	0.062451	0.057988	0.062414
59.8	0.074796	0.060283	0.063198	0.05718	0.063585
61.2	0.073542	0.064941	0.056245	0.056385	0.063299
62.7	0.073382	0.056799	0.057696	0.055589	0.062109
64.2	0.075773	0.062671	0.060131	0.054794	0.063758
65.7	0.072377	0.059695	0.058656	0.053998	0.061614
67.3	0.074539	0.058323	0.059231	0.053203	0.060532
68.7	0.072793	0.060747	0.055275	0.052408	0.06122
70.3	0.074356	0.059703	0.058095	0.051612	0.060694
71.7	0.073351	0.060998	0.058864	0.050817	0.060889
73.2	0.07483	0.057543	0.055327	0.056356	0.058502
74.6	0.074633	0.057518	0.057359	0.058204	0.059803
76.3	0.075926	0.059717	0.060711	0.059413	0.058202
77.7	0.077048	0.059526	0.058735	0.059294	0.061241
79.5	0.076782	0.060336	0.06174	0.057637	0.05854

Table L4 Temperature sweep test results of CR cured specimens at various APTES loadings by in-situ technique.

Temperature (°C)	tanδ				
	0% APTES	2% APTES	4% APTES	6% APTES	8% APTES
-58.8	0.07741	0.05202	0.02952	0.04107	0.06644
-58.8	0.07517	0.06512	0.02758	0.04128	0.06327
-57.3	0.07324	0.06656	0.02677	0.04254	0.0616
-55.6	0.07322	0.06709	0.02616	0.04389	0.06366
-54	0.07382	0.0675	0.02697	0.04581	0.06452
-52.6	0.07584	0.0679	0.0278	0.04723	0.06677
-51.3	0.07857	0.06962	0.02929	0.04932	0.06897
-49.8	0.0821	0.07179	0.03033	0.05204	0.07273
-48.3	0.08577	0.07396	0.03268	0.05567	0.07598
-46.8	0.09067	0.07818	0.03783	0.05984	0.08069
-45.3	0.0963	0.08276	0.04315	0.06478	0.08499
-43.8	0.10447	0.08795	0.05133	0.07168	0.09188
-42.2	0.11339	0.09525	0.06378	0.08234	0.09835
-40.9	0.12878	0.10886	0.08635	0.09988	0.11503
-39.2	0.15152	0.12988	0.13356	0.13289	0.13751
-37.6	0.19777	0.16752	0.17926	0.18108	0.18187
-36.1	0.25649	0.22124	0.24175	0.24014	0.24238
-34.8	0.34227	0.28615	0.32762	0.31917	0.32153
-33.5	0.47377	0.38436	0.44388	0.4362	0.4292
-32.2	0.64804	0.51026	0.59919	0.58292	0.57813
-30.8	0.88096	0.67085	0.79457	0.77271	0.75558
-29.4	1.10419	0.8526	0.96594	0.95969	0.91255
-27.9	1.28542	0.9989	1.09017	1.09421	1.03651
-26.3	1.36925	1.08006	1.15084	1.15689	1.08367
-24.9	1.33742	1.08819	1.13136	1.13909	1.06815
-23.4	1.23252	1.0332	1.05936	1.06862	1.00567
-21.8	1.11097	0.951022	0.97185	0.97158	0.924093
-20.3	0.999421	0.862081	0.887603	0.886221	0.842392
-18.9	0.895239	0.780647	0.800812	0.799459	0.764143
-17.3	0.798524	0.700269	0.71752	0.724255	0.695891
-15.8	0.711725	0.628543	0.65066	0.648606	0.623335
-14.3	0.638086	0.562755	0.582749	0.586219	0.559543
-12.8	0.569858	0.504473	0.524439	0.523932	0.502652
-11.2	0.508616	0.451149	0.468547	0.470458	0.448882
-10	0.457752	0.411354	0.421511	0.423488	0.404311
-8.5	0.406228	0.365879	0.374112	0.376969	0.360412
-6.9	0.361404	0.321701	0.334261	0.337132	0.318953
-5.5	0.321757	0.28652	0.29656	0.300559	0.283936
-4	0.285893	0.256554	0.263916	0.265945	0.25576
-2.5	0.255517	0.2288	0.237065	0.237448	0.227822

Table L4 Temperature sweep test results of CR cured specimens at various APTES loadings by in-situ technique (Cont.).

Temperature (°C)	tanδ				
	0% APTES	2% APTES	4% APTES	6% APTES	8% APTES
-1	0.231402	0.206044	0.213178	0.213603	0.204504
-0.3	0.208395	0.189534	0.191202	0.196305	0.185458
3.9	0.190372	0.170017	0.176727	0.178231	0.169762
3.8	0.179458	0.160481	0.167978	0.170153	0.159762
4.6	0.164934	0.1517	0.15273	0.154705	0.148215
6.3	0.149902	0.138011	0.140794	0.140719	0.135036
7.9	0.139619	0.125817	0.132056	0.130584	0.125461
9.6	0.13021	0.120821	0.122558	0.124042	0.115702
11	0.123351	0.114187	0.116948	0.114444	0.112792
12.4	0.115942	0.106644	0.108643	0.11115	0.105679
13.9	0.111919	0.103726	0.104302	0.10601	0.101947
15.3	0.105864	0.099343	0.101154	0.101775	0.097488
16.8	0.102736	0.096564	0.097064	0.096887	0.095852
18.3	0.101345	0.093234	0.095835	0.092955	0.092702
19.8	0.097958	0.089665	0.091916	0.093725	0.089179
21.3	0.092979	0.089512	0.087204	0.086493	0.089002
22.7	0.091542	0.087184	0.086778	0.08601	0.08416
24.2	0.087074	0.086023	0.085145	0.081699	0.08266
25.7	0.086671	0.084033	0.081483	0.081259	0.079724
27.3	0.083653	0.080645	0.080773	0.08043	0.077198
28.8	0.082976	0.082699	0.081583	0.080893	0.077292
30.1	0.080185	0.081654	0.079566	0.077268	0.078283
31.6	0.077617	0.080966	0.076818	0.076973	0.075811
33.2	0.07685	0.078731	0.076041	0.075536	0.07432
34.7	0.076668	0.079837	0.074806	0.074005	0.073321
36.1	0.075356	0.078884	0.07534	0.073982	0.069945
37.7	0.075721	0.080949	0.075348	0.070599	0.070685
39.2	0.071244	0.078979	0.073884	0.068513	0.070264
40.6	0.074276	0.076529	0.071551	0.070589	0.070276
42.1	0.073248	0.079524	0.071626	0.070628	0.069938
43.5	0.070962	0.076866	0.071438	0.070509	0.067346
45	0.068956	0.076726	0.070523	0.068932	0.067563
46.6	0.069594	0.0779	0.073126	0.06942	0.066688
48	0.073746	0.076244	0.071578	0.066957	0.065438
49.5	0.07129	0.078457	0.06854	0.067233	0.066619
50.9	0.06836	0.078272	0.07314	0.067737	0.065681
52.5	0.069547	0.077527	0.067087	0.069137	0.065401
53.9	0.068577	0.079434	0.069506	0.06895	0.06657
55.4	0.068281	0.080029	0.071733	0.06719	0.06696
57	0.068721	0.080872	0.070727	0.067483	0.065286

Table L4 Temperature sweep test results of CR cured specimens at various APTES loadings by in-situ technique (Cont.).

Temperature (°C)	tanδ				
	0% APTES	2% APTES	4% APTES	6% APTES	8% APTES
58.5	0.069203	0.078971	0.070427	0.0672	0.063644
60	0.067411	0.079763	0.070229	0.069587	0.064184
61.3	0.066491	0.077203	0.070342	0.064139	0.063991
63	0.068104	0.077432	0.069753	0.065771	0.064572
64.3	0.067126	0.077708	0.067673	0.063558	0.06405
65.9	0.067593	0.077131	0.072221	0.064571	0.064385
67.4	0.070388	0.078696	0.071577	0.063294	0.06484
69	0.068087	0.078024	0.070624	0.066245	0.06437
70.3	0.069599	0.081211	0.06868	0.066418	0.062877
71.8	0.068732	0.077356	0.071172	0.0637	0.064321
73.2	0.068782	0.07889	0.070251	0.065473	0.065616
74.6	0.070632	0.078166	0.070358	0.06644	0.064271
76.3	0.070395	0.076699	0.072119	0.066653	0.062016
78.1	0.068933	0.079508	0.068065	0.065157	0.064136
79.9	0.071338	0.077733	0.070361	0.066043	0.064822

Table L5 Temperature sweep test results of CR cured specimens at various CPTES loadings by in-situ technique.

Temperature (°C)	tanδ				
	0% CPTES	2% CPTES	4% CPTES	6% CPTES	8% CPTES
-59.3	0.07741	0.04265	0.07462	0.10066	0.07689
-58.9	0.07517	0.04396	0.07304	0.09753	0.07498
-57.6	0.07324	0.04375	0.07232	0.09563	0.07346
-56.1	0.07322	0.04521	0.07331	0.09635	0.07215
-54.3	0.07382	0.04677	0.07409	0.0971	0.07398
-52.8	0.07584	0.04856	0.07672	0.0998	0.07453
-51.3	0.07857	0.05122	0.07962	0.10337	0.07821
-49.8	0.0821	0.05369	0.08299	0.10649	0.07852
-48.3	0.08577	0.05814	0.08721	0.11045	0.08428
-47	0.09067	0.0627	0.09326	0.1158	0.08608
-45.6	0.0963	0.06755	0.09922	0.12242	0.09366
-43.8	0.10447	0.07597	0.10678	0.13125	0.09601
-42.5	0.11339	0.08655	0.12091	0.13977	0.10799
-41	0.12878	0.10473	0.14012	0.15422	0.12004
-39.6	0.15152	0.13606	0.18029	0.17871	0.15452
-37.7	0.19777	0.18936	0.22162	0.22146	0.2174
-36.4	0.25649	0.2546	0.28512	0.26819	0.26936
-35.1	0.34227	0.35293	0.39004	0.34524	0.35252
-33.7	0.47377	0.48059	0.54094	0.48661	0.48462
-32.3	0.64804	0.68322	0.73048	0.64035	0.66676
-30.8	0.88096	0.93535	0.97649	0.85219	0.8874
-29.4	1.10419	1.18089	1.1712	1.07944	1.10971
-28	1.28542	1.35697	1.31193	1.23818	1.26158
-26.4	1.36925	1.42672	1.3398	1.30171	1.32317
-24.9	1.33742	1.38554	1.27666	1.26273	1.28253
-23.3	1.23252	1.27453	1.17465	1.16914	1.18635
-21.8	1.11097	1.15458	1.06442	1.05885	1.07312
-20.4	0.999421	1.04121	0.961752	0.957332	0.978412
-18.9	0.895239	0.935927	0.867168	0.859838	0.881304
-17.4	0.798524	0.839647	0.77685	0.775101	0.797207
-15.9	0.711725	0.755267	0.702808	0.698889	0.714926
-14.4	0.638086	0.674755	0.630629	0.631069	0.643867
-12.9	0.569858	0.607354	0.57225	0.564956	0.581537
-11.4	0.508616	0.54036	0.514861	0.507664	0.52333
-10	0.457752	0.488098	0.464096	0.459659	0.474487
-8.5	0.406228	0.434927	0.412765	0.409724	0.422416
-7	0.361404	0.386214	0.366092	0.365127	0.379228
-5.6	0.321757	0.342495	0.328373	0.327947	0.337357
-4	0.285893	0.302855	0.289419	0.292643	0.304605
-2.6	0.255517	0.269089	0.260352	0.264273	0.26973

Table L5 Temperature sweep test results of CR cured specimens at various CPTES loadings by in-situ technique (Cont.).

Temperature (°C)	tanδ				
	0% CPTES	2% CPTES	4% CPTES	6% CPTES	8% CPTES
-1.1	0.231402	0.240344	0.234277	0.235854	0.244939
-0.3	0.208395	0.219344	0.215057	0.215904	0.224436
3.3	0.190372	0.19621	0.197625	0.199253	0.205805
3.4	0.179458	0.185979	0.188921	0.190339	0.195594
4.6	0.164934	0.170555	0.175053	0.176607	0.179912
6.4	0.149902	0.156724	0.159643	0.162037	0.169853
7.8	0.139619	0.147985	0.146554	0.15054	0.155442
9.4	0.13021	0.133871	0.135663	0.140956	0.144907
10.9	0.123351	0.126416	0.126645	0.134358	0.134048
12.3	0.115942	0.119494	0.122554	0.124477	0.129424
14	0.111919	0.112678	0.113584	0.119904	0.123791
15.1	0.105864	0.109747	0.110617	0.114886	0.118641
16.7	0.102736	0.106419	0.10664	0.112091	0.114723
18.3	0.101345	0.100377	0.103621	0.106812	0.114291
19.7	0.097958	0.098716	0.101626	0.105626	0.109886
21.1	0.092979	0.095928	0.095486	0.103769	0.104973
22.8	0.091542	0.09188	0.096379	0.099003	0.102844
24.3	0.087074	0.091584	0.094927	0.097828	0.100697
25.8	0.086671	0.088841	0.090885	0.094949	0.098379
27.2	0.083653	0.083602	0.090691	0.094279	0.094437
28.8	0.082976	0.082345	0.085069	0.090186	0.095176
30.1	0.080185	0.083325	0.086349	0.089986	0.094098
31.7	0.077617	0.083137	0.087104	0.087888	0.09263
33.1	0.07685	0.079105	0.083599	0.086553	0.090829
34.6	0.076668	0.077297	0.082159	0.086291	0.087194
36.1	0.075356	0.078345	0.083455	0.086318	0.085801
37.6	0.075721	0.078549	0.081303	0.08307	0.085638
39.1	0.071244	0.078319	0.078828	0.084424	0.083524
40.5	0.074276	0.075038	0.08043	0.082254	0.084375
42	0.073248	0.076131	0.078315	0.080515	0.084249
43.5	0.070962	0.071908	0.078329	0.082394	0.085338
45	0.068956	0.072822	0.07621	0.080101	0.083205
46.5	0.069594	0.072115	0.075773	0.080968	0.080595
48.1	0.073746	0.072974	0.07461	0.07919	0.081278
49.4	0.07129	0.06869	0.077203	0.079719	0.079728
50.9	0.06836	0.068453	0.074589	0.078017	0.077687
52.4	0.069547	0.06957	0.074423	0.07966	0.078692
54	0.068577	0.067803	0.074311	0.076829	0.076268
55.5	0.068281	0.067085	0.074934	0.077147	0.076662
56.9	0.068721	0.066747	0.073463	0.07462	0.076512

Table L5 Temperature sweep test results of CR cured specimens at various CPTES loadings by in-situ technique (Cont.).

Temperature (°C)	tanδ				
	0% CPTES	2% CPTES	4% CPTES	6% CPTES	8% CPTES
58.3	0.069203	0.067689	0.074268	0.074493	0.07768
59.8	0.067411	0.066673	0.070275	0.076038	0.075371
61.4	0.066491	0.063784	0.070383	0.074963	0.073588
63	0.068104	0.063218	0.071702	0.076007	0.074428
64.3	0.067126	0.065129	0.069606	0.074378	0.074653
65.6	0.067593	0.064996	0.070786	0.075484	0.071978
67.3	0.070388	0.064759	0.070432	0.076783	0.074387
68.7	0.068087	0.064405	0.071612	0.072818	0.074499
70.2	0.069599	0.067485	0.070932	0.074058	0.075024
71.7	0.068732	0.066374	0.070805	0.07677	0.076658
73.2	0.068782	0.063191	0.071584	0.077643	0.073507
74.8	0.070632	0.064392	0.069113	0.075602	0.07465
76.2	0.070395	0.067924	0.071084	0.07624	0.074446
77.8	0.068933	0.064506	0.070604	0.076499	0.072971
79.5	0.071338	0.063578	0.070148	0.07853	0.074813

Table L6 Temperature sweep test results of CR cured specimens at various TESPT loadings by in-situ technique.

Temperature (°C)	tanδ				
	0% TESPT	2% TESPT	4% TESPT	6% TESPT	8% TESPT
-60.4	0.07741	0.04428	0.02934	0.03335	0.07341
-59.5	0.07517	0.0465	0.03046	0.03969	0.07305
-57.4	0.07324	0.04685	0.0307	0.06054	0.07452
-55.8	0.07322	0.04828	0.03177	0.06806	0.08025
-54.5	0.07382	0.0502	0.03327	0.07572	0.08279
-52.8	0.07584	0.05255	0.03475	0.0776	0.08687
-51.4	0.07857	0.05481	0.03683	0.08153	0.09041
-50	0.0821	0.05678	0.03936	0.08453	0.09586
-48.5	0.08577	0.05942	0.04214	0.08745	0.10718
-47	0.09067	0.06333	0.04551	0.09249	0.12991
-45.4	0.0963	0.06676	0.05101	0.09784	0.13774
-43.9	0.10447	0.0725	0.05932	0.10407	0.1592
-42.5	0.11339	0.08105	0.07141	0.11361	0.21677
-41	0.12878	0.09639	0.09231	0.12678	0.29029
-39.2	0.15152	0.12764	0.12584	0.14177	0.38994
-37.8	0.19777	0.17504	0.1831	0.17952	0.52341
-36.5	0.25649	0.23448	0.24759	0.22718	0.68583
-35.1	0.34227	0.31935	0.33685	0.30502	0.85873
-33.8	0.47377	0.44654	0.46347	0.42306	1.02254
-32.3	0.64804	0.60355	0.64002	0.57667	1.14766
-30.8	0.88096	0.81154	0.84495	0.77419	1.22136
-29.3	1.10419	1.00108	1.04881	0.97323	1.23683
-27.9	1.28542	1.18519	1.22628	1.16171	1.21081
-26.5	1.36925	1.24921	1.30406	1.2858	1.15458
-25	1.33742	1.22692	1.28464	1.3191	1.08372
-23.4	1.23252	1.14356	1.20138	1.27085	1.00839
-21.9	1.11097	1.04977	1.09451	1.18388	0.933226
-20.5	0.999421	0.955863	0.999109	1.08553	0.862381
-19	0.895239	0.862364	0.899331	0.976197	0.795788
-17.6	0.798524	0.774069	0.809847	0.874799	0.731034
-16.1	0.711725	0.695212	0.725263	0.789254	0.676565
-14.5	0.638086	0.622747	0.644896	0.708418	0.620974
-13.1	0.569858	0.56065	0.579246	0.636089	0.574409
-11.6	0.508616	0.500603	0.519515	0.565676	0.527551
-10.1	0.457752	0.450093	0.471587	0.510067	0.484847
-8.7	0.406228	0.401518	0.420885	0.452096	0.437157
-7.1	0.361404	0.360415	0.374211	0.404121	0.389408
-5.6	0.321757	0.323284	0.333119	0.357368	0.347903
-4.1	0.285893	0.285644	0.296022	0.319442	0.312227
-2.6	0.255517	0.255599	0.264566	0.28208	0.276518

Table L6 Temperature sweep test results of CR cured specimens at various TESPT loadings by in-situ technique (Cont.).

Temperature (°C)	tanδ				
	0% TESPT	2% TESPT	4% TESPT	6% TESPT	8% TESPT
-1	0.231402	0.230325	0.237456	0.253848	0.249428
-0.3	0.208395	0.206931	0.214653	0.230434	0.226828
2.8	0.190372	0.194287	0.197547	0.208677	0.206048
3.2	0.179458	0.184088	0.18773	0.197865	0.193456
4.7	0.164934	0.169689	0.172969	0.181008	0.17978
6.3	0.149902	0.15488	0.156357	0.163635	0.163875
7.8	0.139619	0.14354	0.14713	0.152305	0.15191
9.3	0.13021	0.133629	0.134078	0.140597	0.140357
10.7	0.123351	0.123072	0.125854	0.127503	0.130652
12.2	0.115942	0.11831	0.11964	0.120097	0.122037
13.8	0.111919	0.114828	0.114434	0.116448	0.116353
15.2	0.105864	0.109628	0.108185	0.110923	0.110697
16.8	0.102736	0.1046	0.103061	0.10628	0.106865
18.1	0.101345	0.103416	0.100524	0.103748	0.103435
19.5	0.0979582	0.099172	0.096743	0.098152	0.099607
21	0.0929785	0.097989	0.094092	0.095012	0.095746
22.6	0.091542	0.09574	0.091528	0.093731	0.093571
24.2	0.0870742	0.091375	0.089723	0.089082	0.09092
25.7	0.0866705	0.087278	0.08662	0.08548	0.087436
27.1	0.0836534	0.087071	0.082911	0.082802	0.084623
28.7	0.0829763	0.082546	0.081517	0.081878	0.081277
30	0.0801854	0.082732	0.078654	0.079391	0.080228
31.6	0.0776171	0.081379	0.078449	0.0771	0.076532
33	0.0768499	0.080214	0.078306	0.076618	0.075115
34.6	0.0766681	0.0798	0.074133	0.073991	0.072461
36	0.075356	0.075368	0.074758	0.071175	0.072541
37.5	0.0757214	0.073216	0.073485	0.071856	0.070759
39	0.0712437	0.073414	0.072893	0.067319	0.071705
40.4	0.0742763	0.072422	0.07305	0.065934	0.069841
41.9	0.073248	0.075543	0.068503	0.070361	0.070165
43.3	0.070962	0.071319	0.071586	0.065988	0.066602
44.9	0.0689559	0.069934	0.06753	0.066406	0.06243
46.4	0.0695937	0.068826	0.069433	0.063639	0.06448
47.8	0.0737464	0.06875	0.06521	0.063355	0.065851
49.3	0.0712896	0.067362	0.062502	0.061581	0.064286
50.8	0.0683595	0.066851	0.065165	0.064454	0.063171
52.3	0.0695468	0.067006	0.063513	0.063557	0.062226
53.8	0.0685772	0.068373	0.065407	0.059776	0.060747
55.2	0.0682807	0.065957	0.061317	0.05923	0.060169
56.7	0.0687212	0.06323	0.062424	0.059105	0.060577

Table L6 Temperature sweep test results of CR cured specimens at various TESPT loadings by in-situ technique (Cont.).

Temperature (°C)	tanδ				
	0% TESPT	2% TESPT	4% TESPT	6% TESPT	8% TESPT
58.2	0.0692034	0.065562	0.064443	0.057935	0.055893
59.7	0.0674114	0.059971	0.062479	0.057875	0.058512
61.2	0.0664906	0.062842	0.059772	0.057342	0.055863
62.7	0.0681037	0.0643	0.058445	0.057498	0.055463
64.3	0.0671263	0.062325	0.060903	0.05584	0.05596
65.8	0.0675929	0.063507	0.061396	0.056772	0.057808
67.2	0.0703875	0.065886	0.057639	0.055024	0.053032
68.8	0.0680868	0.063864	0.056935	0.057209	0.054971
70.1	0.0695987	0.063576	0.057848	0.05524	0.055891
71.7	0.0687315	0.061734	0.059307	0.056622	0.05454
73.1	0.0687822	0.061984	0.058838	0.057825	0.053877
74.6	0.0706322	0.063278	0.058463	0.056528	0.055213
76.1	0.0703949	0.065364	0.057943	0.054847	0.056183
77.6	0.0689325	0.064051	0.058717	0.057063	0.055717
79.4	0.0713384	0.062533	0.060221	0.057431	0.056663

Table L7 Temperature sweep test results of CR cured specimens at 6% APTES with various pH conditions.

Temperature (°C)	tanδ			
	Unmodified	pH 2	pH 6	pH 12
-60.4	0.07741	0.040	0.031	0.043
-60	0.07517	0.042	0.032	0.044
-57.9	0.07324	0.043	0.032	0.044
-55.5	0.07322	0.043	0.032	0.043
-54.3	0.07382	0.044	0.033	0.044
-52.9	0.07584	0.044	0.034	0.044
-50.9	0.07857	0.045	0.035	0.046
-49.8	0.0821	0.046	0.038	0.047
-48.5	0.08577	0.046	0.041	0.048
-46.9	0.09067	0.047	0.044	0.050
-45.4	0.0963	0.049	0.050	0.051
-44.2	0.10447	0.051	0.058	0.054
-42.2	0.11339	0.057	0.068	0.057
-41	0.12878	0.062	0.087	0.063
-39.4	0.15152	0.071	0.121	0.070
-38.1	0.19777	0.089	0.178	0.087
-36.2	0.25649	0.141	0.245	0.120
-34.6	0.34227	0.206	0.330	0.177
-33.7	0.47377	0.279	0.468	0.242
-32	0.64804	0.423	0.650	0.352
-30.7	0.88096	0.567	0.896	0.498
-29.4	1.10419	0.778	1.106	0.703
-28.2	1.28542	1.014	1.300	0.940
-26.1	1.36925	1.276	1.384	1.174
-25	1.33742	1.375	1.350	1.333
-23.4	1.23252	1.392	1.261	1.363
-21.9	1.11097	1.315	1.144	1.298
-20.6	0.999421	1.224	1.037	1.190
-19	0.895239	1.112	0.932	1.086
-17.5	0.798524	1.002	0.831	0.971
-16	0.711725	0.899	0.748	0.863
-14.6	0.638086	0.806	0.674	0.770
-13	0.569858	0.733	0.601	0.684
-11.5	0.508616	0.661	0.539	0.614
-10.1	0.457752	0.602	0.485	0.548
-8.6	0.406228	0.539	0.428	0.484
-7.1	0.361404	0.481	0.384	0.433
-5.6	0.321757	0.425	0.339	0.383
-4.1	0.285893	0.377	0.303	0.342
-2.6	0.255517	0.336	0.268	0.300

Table L7 Temperature sweep test results of CR cured specimens at 6% APTES with various pH conditions (Cont.).

Temperature (°C)	tanδ			
	Unmodified	pH 2	pH 6	pH 12
-1	0.231402	0.284	0.240	0.269
-0.4	0.208395	0.250	0.219	0.236
4.4	0.190372	0.222	0.198	0.210
4.6	0.179458	0.209	0.187	0.196
4.6	0.164934	0.198	0.169	0.188
6.1	0.149902	0.180	0.159	0.169
7.8	0.139619	0.162	0.142	0.154
9.5	0.13021	0.148	0.132	0.142
10.8	0.123351	0.143	0.125	0.136
12.2	0.115942	0.133	0.120	0.130
13.9	0.111919	0.124	0.114	0.119
15.3	0.105864	0.119	0.109	0.116
17	0.102736	0.114	0.104	0.111
18	0.101345	0.110	0.099	0.102
19.5	0.097958	0.109	0.096	0.102
21.2	0.092979	0.104	0.091	0.101
22.8	0.091542	0.102	0.094	0.096
24.2	0.087074	0.098	0.089	0.095
25.6	0.086671	0.092	0.087	0.088
27.5	0.083653	0.095	0.085	0.089
28.4	0.082976	0.091	0.084	0.087
30.1	0.080185	0.089	0.079	0.082
31.6	0.077617	0.087	0.079	0.086
33.2	0.07685	0.083	0.076	0.081
34.3	0.076668	0.085	0.074	0.077
35.8	0.075356	0.080	0.073	0.077
37.5	0.075721	0.079	0.073	0.075
39.2	0.071244	0.084	0.072	0.077
40.4	0.074276	0.078	0.071	0.076
41.7	0.073248	0.079	0.069	0.073
43.7	0.070962	0.078	0.068	0.073
44.9	0.068956	0.074	0.064	0.070
46.3	0.069594	0.075	0.072	0.068
47.7	0.073746	0.071	0.068	0.068
49.7	0.07129	0.069	0.068	0.066
50.9	0.06836	0.070	0.064	0.069
52.4	0.069547	0.069	0.062	0.057
54	0.068577	0.068	0.061	0.065
55.1	0.068281	0.067	0.060	0.064
56.9	0.068721	0.066	0.061	0.060

Table L7 Temperature sweep test results of CR cured specimens at 6% APTES with various pH conditions (Cont.).

Temperature (°C)	tanδ			
	Unmodified	pH 2	pH 6	pH 12
58.7	0.069203	0.063	0.059	0.058
59.8	0.067411	0.066	0.060	0.059
60.9	0.066491	0.067	0.062	0.054
62.6	0.068104	0.062	0.059	0.055
64.3	0.067126	0.058	0.060	0.055
65.8	0.067593	0.060	0.057	0.053
67.3	0.070388	0.058	0.058	0.053
68.5	0.068087	0.065	0.060	0.051
70.5	0.069599	0.057	0.058	0.056
71.8	0.068732	0.054	0.062	0.053
73.4	0.068782	0.055	0.058	0.049
74.4	0.070632	0.054	0.057	0.051
75.9	0.070395	0.057	0.058	0.051
77.3	0.068933	0.052	0.059	0.049
79.4	0.071338	0.053	0.062	0.047

APPENDIX M

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Material properties

Comparison of coupling effectiveness among amino-, chloro-, and mercapto silanes in chloroprene rubber

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ABSTRACT

Organoalkoxysilane was grafted onto the surface of precipitated silica (PSi), and the modified PSi was characterized by particle size analysis, DRIIFT and ²⁹Si NMR spectroscopy. There were 3 types of organoalkoxysilane used in this work, namely, 3-aminopropyl triethoxysilane (APTES), 3-chloropropyl triethoxysilane (CPTES) and bis (3-triethoxysilylpropyl) tetrasulfide (TESPT). The magnitude of the Payne effect, bound rubber content and mechanical properties of chloroprene rubber (CR) filled with unmodified and silane-modified PSi were investigated. Results reveal that the type of silane coupling agent (SCA) affects not only compound processability, but also mechanical properties of the CR vulcanizates. Among the 3 SCAs, it is evident that APTES and TESPT are capable of reducing the filler-filler interaction more efficiently than CPTES, as evidenced by Payne effect results, leading to superior compound processability. Mechanical properties of the CR vulcanizates filled with APTES-modified and TESPT-modified PSi are also greater than those filled with CPTES-modified PSi. This might be ascribed to the combined effects of enhanced rubber-filler interaction and improved filler dispersion.

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1. Introduction

The use of particulate fillers to achieve desirable reinforcement has been widely accepted by the rubber industry. Generally, carbon black (CB) and precipitated silica (PSi) are used as reinforcing fillers. The latter is typically used in light-colored products. The magnitude of PSi reinforcement is greatly influenced by its specific surface area [1]. The surface chemistry of PSi is dramatically different

from that of CB, due mainly to the presence of silanol groups. Thus, the interactions between PSi and rubber matrix must be taken into consideration to obtain maximum reinforcement efficiency [2]. The surface of PSi is polar and hydrophilic due to the abundance of silanol groups, resulting in strong filler-filler interaction via hydrogen bonds. This in turn causes poor filler dispersion in the rubber matrix [3]. Moreover, the silanol groups on the PSi surface are reactive to both cure activator (soluble zinc) and alkaline accelerators, causing detrimental effects on cure efficiency, such as undesirably long cure time in association with slow cure rate, as well as low crosslink density in sulfur-cured compounds [4,5]. Bi-functional silane coupling agents (SCAs) are commonly used to chemically modify the silica surfaces in order to enhance

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the interaction with hydrocarbon rubbers. The presence of silane not only leads to enhancement in silica dispersion, but also prevents adsorption of curatives on the silica surface [6]. Remarkable improvements in mechanical properties such as tensile strength [7], tear strength [8] and abrasion resistance [7] of silica-reinforced rubber vulcanizates can, therefore, result. Reductions of rolling resistance [9] and heat build-up [10] are also reported. Currently, there are many types of organosilane commercially available. So far, mercapto or polysulfide silane, namely bis(3-triethoxysilylpropyl) tetrasulfide (TESPT or Si-69), is still one of the most widely used general purpose silanes in the rubber industry [11]. The presence of sulfur atoms in TESPT is beneficial, particularly in a system cured by sulfur vulcanization, due to a co-vulcanization phenomenon. However, there are still some other silanes including bis(3-triethoxysilylpropyl) disulfide (TESPD), 3-thiocyanatopropyl triethoxysilane (Si-264), 3-methacryloxypropyl trimethoxysilane (MPTMS), and 3-mercaptopropyl trimethoxysilane (MPS) being used in the rubber industry for improving the performance of PSi in rubber compounds [12–14].

Many attempts have been made to study the role of silane coupling agent in improving the reinforcement efficiency of silica, and most of the published works have been carried out on the sulfur-curable rubbers such as NR and SBR [15,16]. Little attention has been given to the role of silane coupling agent in a functionally active rubber such as polychloroprene (CR). Recently, it has been reported that Si-69 is capable of improving the mechanical properties of silica-filled CR by the sulfur contribution effect [7]. It is, therefore, interesting to intensively investigate the role of silane coupling agent in silica-filled CR. In this work, 3 types of silanes (i.e., 3-aminopropyl triethoxysilane (APTES), 3-chloropropyl triethoxysilane (CPTES) and bis (3-triethoxysilylpropyl) tetrasulfide (TESPT) were used to modify silica surface. The coupling efficiency and the effect of each silane on viscoelastic and mechanical properties of PSi-filled CR vulcanizates were investigated.

2. Material and methods

2.1. Materials

Polychloroprene (Neoprene; CR grade W) was purchased from DuPont Dow Elastomer Co., Ltd., USA. Precipitated silica (PSi, Tokusil 233) was manufactured by Tokuyama Siam Silica Co., Ltd., Thailand. Silane coupling agents (SCAs), i.e., 3-aminopropyl triethoxysilane (APTES), 3-chloropropyl triethoxysilane (CPTES) and bis (3-triethoxysilylpropyl) tetrasulfide (TESPT) were supplied by Evonik Co., Ltd., Germany. Magnesium oxide (MgO), N-(1,3-dimethylbutyl)-N'-phenyl-p-phenylenediamine (6-PPD), zinc oxide (ZnO), ethylene thiourea (ETU), stearic acid and sulfur (S_8) were purchased from local suppliers. All chemicals were used as-received without further purification.

2.2. Silanization of PSi surfaces

Approximately 25 g of PSi was dispersed in 1:4 water:ethanol mixture under continuous stirring for 1

hour, and pH of the dispersion was adjusted to 2 by 1.0 M hydrochloric acid (HCl). 1.5 g of silane (APTES, CPTES or TESPT) was added, and the mixture was refluxed at 80 °C for 5 hours to allow the silanization reaction on PSi surfaces. The modified PSi was then separated by centrifugation technique (30 min at 6,000 rpm), and washed 3 times with toluene. Finally, the modified PSi was dried in an oven at 80 °C for 15 hours. Surface chemistry of the unmodified and modified PSi was characterized by Fourier Transform Infrared spectroscopy (FTIR; Bruker, Bruker Equinox55, Germany) using the diffuse reflectance mode under a wavenumber of 4,000–400 cm^{-1} with a resolution of 4 cm^{-1} . ^{29}Si solid-state nuclear magnetic resonance, (^{29}Si -NMR, Bruker; DPX-300, Germany) was also used to study changes in chemical structure of silanes on the PSi surface. The test was performed at room temperature, and the spectra were acquired in the cross 3-polarization mode using a contact time of 10 ms and high power dipolar decoupling to reduce line broadening. Spectra were recorded at a frequency of 60 MHz and scanning rate of 4,000 ns^{-1} . A pulse repetition time of 5 s over 10,000–30,000 scans was used to gain sufficiently high signal to noise (S/N) ratio.

Measurement of agglomerate size was carried out by a particle size analyzer (Malvern Mastersizer 2000, Malvern Instruments Ltd, UK). Approximately 1 g of the sample was dispersed in 20 ml of distilled water and the suspension was sonicated in a water bath for 30 min prior to being measured.

2.3. Preparation and testing of rubber compounds and rubber vulcanizates

Rubber compounds were prepared using a laboratory-scale internal mixer (Haake Rheomix 90, Germany) equipped with roller rotors. The mixing conditions used were as follows; fill factor = 0.8, chamber temperature = 50 °C, rotor speed = 40 rpm and mixing time = 20 min. The compound recipe is given in Table 1. Loading of precipitated silica (PSi) was kept constant at 40 phr. A 2-stage mixing technique was used for preparing the compounds. In the first mixing stage, MgO, unmodified (or modified PSi), stearic acid and 6-PPD were incorporated sequentially into raw CR with total mixing time of 20 min. In the second stage, ZnO, ETU and sulfur were charged into the rubber mix, and further mixed for 7 min in order to achieve good dispersion and distribution of all ingredients.

Table 1
Compounding recipe.

Ingredient	Loading (phr ^a)	Function
CR	100	Raw rubber
MgO	4	Curative/Acid acceptor
PSi	40	Reinforcing filler
Stearic acid	2	Cure activator/Softener
6-PPD	2	Antioxidant
ZnO	5	Curative
ETU	0.5	Cure accelerator
Sulfur	0.5	Curative

^a Parts per hundred of rubber.

The extent of filler-filler interaction was evaluated using a rubber process analyzer (RPA 2000; Alpha Technologies, USA). Storage modulus (G') of the rubber compounds was measured at swept strains from 0.56% to 200% at 100 °C and 1.7 Hz. The difference in G' at low and high strains ($\Delta G'$), widely known as the "Payne effect" is used to represent the degree of filler-filler interaction. For a measurement of bound rubber content (BRC), small pieces of 1 g of uncured specimens were immersed in 150 ml of toluene for a total of 7 days at room temperature. The insoluble portion was then filtered and dried in an oven at 80 °C for 24 h. The percentage of BRC was determined by Equation (1).

$$\%BRC = \frac{W_g - W[m_f/(m_f + m_p)]}{W[m_p/(m_f + m_p)]} \times 100 \quad (1)$$

where W_g is the weight of filler-rubber gel; W is the weight of the test specimen. m_f and m_p are the weights of filler and polymer in the rubber compound, respectively.

Vulcanization of the rubber compounds was conducted using a hydraulic hot press (Wabash Genesis Series; model G30H, USA) at 155 °C. Mechanical properties of the CR vulcanizates were measured as per ISO standards. Hardness was measured using a durometer with Shore A scale (Wallace Instruments; model H17A, UK) as per ISO 7619-1. Tensile properties were determined by universal mechanical tester (Instron, model 5566, USA) following ISO 37 (Type I). Compression set was determined as per ISO 815 at 100 °C for 22 h. To measure the degree of heat dissipation under cyclic deformation, a heat build-up (HBU) test was performed using a flexometer (BF Goodrich Instruments, model II, USA) with reference to ISO 4666. The degree of filler dispersion was examined by scanning electron microscope (SEM) (JEOL, model JSM 6400, Japan). To

determine particle size of PSi dispersed in the CR matrix, the SEM images were analyzed using an Image-Pro® Express Version 6 (Media Cybernetics, Inc, USA). Crosslink density was determined by swelling based on the Flory-Rehner equation (Equation (2 and 3)) [15–17]. The cured specimens with dimensions of approximately 1.5 cm × 1.5 cm × 1 mm were weighed and then immersed in 60 ml toluene for 7 days at room temperature. Thereafter, the swollen specimens were removed from toluene, and weighed accurately.

$$[\ln(1 - v_2) + v_2 + \chi v_2^2] = V_1 n \left[\frac{v_2^{1/3}}{2} - \frac{v_2}{2} \right] \quad (2)$$

$$v_2 = \frac{M_1 d_s}{M_1 (d_s + d_r) + M_2 d_r} \quad (3)$$

where n is the number of elastically active chains per unit volume; v_2 is the volume fraction of polymer in the swollen gel at equilibrium; χ is the interaction parameter of polymer-solvent (the interaction parameter between CR and toluene = 0.386) [18]; V_1 is the molar volume of the solvent; M_1 is the weight of the polymer before swelling (g); M_2 is the weight of the polymer after swelling (g); d_s is the density of solvent (0.87 g/cm³) [19–21]; d_r is the density of polymer (1.23 g/cm³) [19–21].

3. Results and discussion

3.1. Characterization of unmodified and silane-modified PSi

Fig. 1 shows DRIFT spectra of unmodified and silane-modified PSi. For unmodified PSi, isolated surface hydroxyls are responsible for the band at 3,650 cm⁻¹ [22]. A

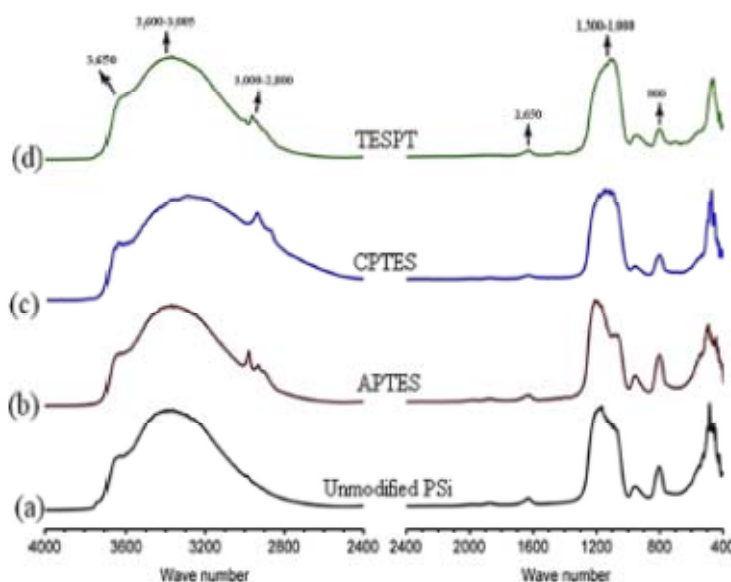


Fig. 1. DRIFT spectra of unmodified and silane-modified PSi: (a) unmodified; (b) APTES-modified PSi; (c) CPTES-modified PSi and (d) TESPT-modified PSi.

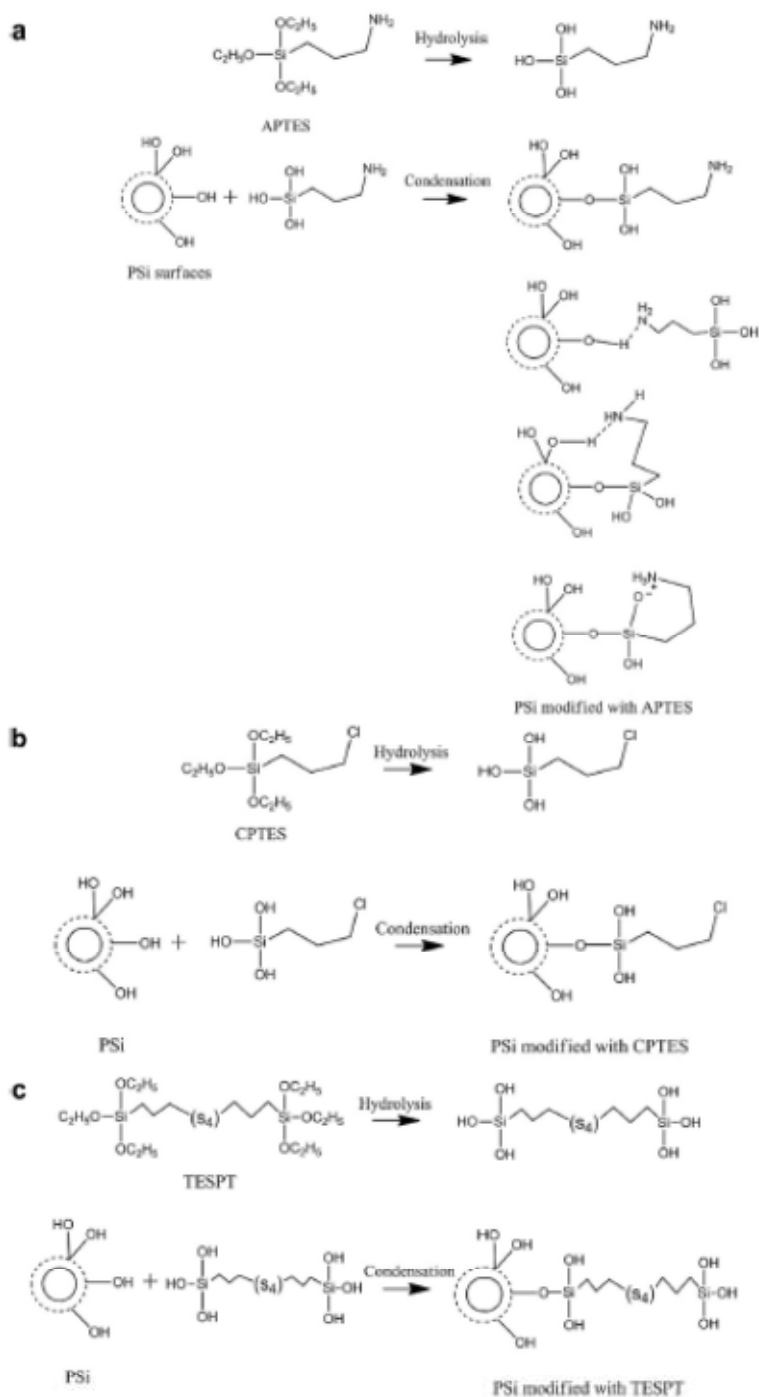


Fig. 2. Model of interaction development between PSi and silanes: (a) APTES-modified PSi; (b) CPTES-modified PSi and (c) TESPT-modified PSi.

broad O-H stretching band at the wavenumber of $3,600\text{--}3,000\text{ cm}^{-1}$ corresponds to the vibration of silanol groups and the hydrogen-bonding interaction between water and adjacent silanols. A band at $1,650\text{ cm}^{-1}$ arises from the O-H bending of the physically adsorbed water [23]. Moreover, a strong and broad band found in the $1,300\text{--}1,000\text{ cm}^{-1}$ region and a band near 800 cm^{-1} are assigned to the asymmetric stretching and symmetric stretching of Si-O-Si, respectively [24–26]. For silane-modified PSi, new bands are found at $3,000\text{--}2,800\text{ cm}^{-1}$, attributed to the C-H stretching of CH_3 and CH_2 , respectively. These results suggest that some silanol groups on silica surfaces are deactivated by silanes. The model of interaction development between silanol groups of PSi surfaces and silanes via a silanization reaction is illustrated in Fig. 2 [27–30].

Fig. 3 shows the ^{29}Si NMR spectra of unmodified and silane-modified PSi. The unmodified PSi exhibits 3 chemical shifts at -110 , -100 and -90 ppm, representing the siloxane bridges (O_4Si), isolated or vicinal silanols ($\text{O}_2\text{Si}(\text{OH})$) and geminal silanols ($\text{O}_2\text{Si}(\text{OH})_2$), respectively

[27]. When SCA is incorporated, additional peaks are observed between -70 to -40 ppm corresponding to monodentate (T_1), bidentate (T_2) and tridentate (T_3) structures, as shown in Figs. 3b–3d. The results imply differences in silane structure on the PSi surfaces. Peak T_3 corresponds to silane molecules for which all 3 $-\text{OH}$ groups react with silanol groups on the PSi surfaces [30,31]. Similarly, peak T_2 demonstrates the silane molecules with 1 unreacted hydroxyl group, and peak T_1 represents the silane molecules with 2 unreacted hydroxyl groups.

Fig. 4 shows the effect of silane type on average agglomerate size of PSi. It is evident that the average agglomerate size of PSi after surface modification appears to increase, which is believed to be the result of re-agglomeration of PSi via silane linkage [32]. Details of interaction development will be discussed subsequently.

3.2. Properties of PSi-filled CR

Table 2 contains the magnitude of the Payne effect ($\Delta G'$) and bound rubber content (BRC) of the rubber compounds.

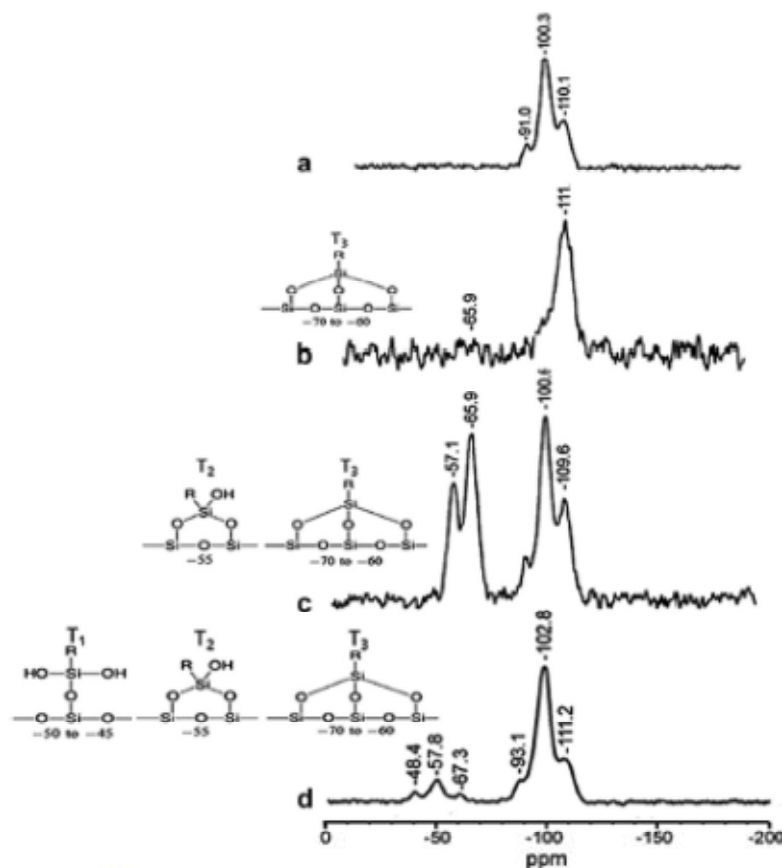


Fig. 3. ^{29}Si NMR spectra of unmodified and silane-modified PSi: (a) unmodified PSi; (b) APTES-modified PSi; (c) OPES-modified PSi and (d) TESPT-modified PSi.

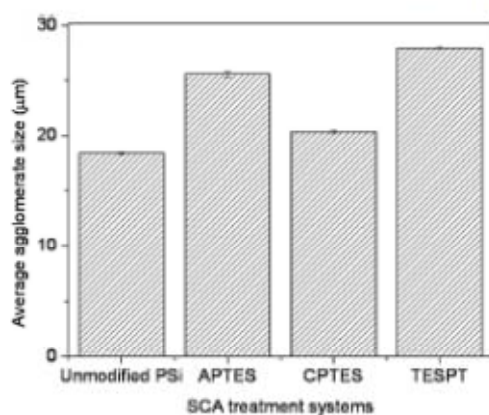


Fig. 4. Influence of silane type on average agglomerate size of PSI.

The magnitude of the Payne effect is in the following order: unmodified PSI > CPTES > APTES > TESPT. For unmodified PSI, strong filler-filler networks exist due to H-bonds between PSI aggregates. In the presence of SCAs, the alkoxy groups of SCAs could react with the silanol groups on PSI surfaces leading to the reduction of filler-filler interaction or filler network. Since TESPT possesses a greater amount of alkoxy groups than APTES and CPTES, compared at the same silane content, it has the highest ability to wet PSI surfaces, resulting in the lowest magnitudes of filler network and, thus, the Payne effect. Table 2 also represents BRC of the CR compounds. Obviously, BRC is found to increase after modification with silanes. Among the 3 silanes, APTES gives the highest BRC which might be due to the strong interaction between amino groups of APTES and Cl atoms of CR. On the contrary, CPTES shows the lowest BRC, attributed probably to its low dipole-dipole interaction between chloro-groups of CPTES and Cl atoms of CR.

Fig. 5 shows crosslink density (ρ) of the CR vulcanizates. Apparently, TESPT provides greater crosslink density than APTES and CPTES. This is possibly due to the sulfur donor effect of TESPT during the curing process. In conjunction with ETU, the donated sulfur is capable of co-curing at the double bonds of CR and, thereafter promoting C-S linkage formation. Compared with CPTES, APTES gives higher crosslink density because the amino group of APTES behaves as an electron donor reacting with allylic carbon of CR via nucleophilic addition reaction to promote the formation of C-N linkages.

Figs. 6a–6e displays SEM micrographs of the unfilled and PSI-filled CR. White particles found in the unfilled CR

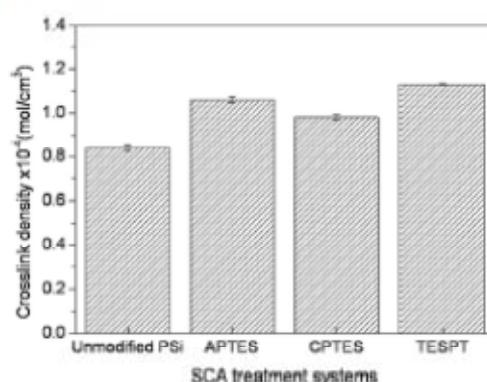


Fig. 5. Influence of silane type on crosslink density of CR vulcanizates.

(Fig. 6a) are metal oxides [33]. Without SCAs, relatively small aggregation size of PSI is observed (Fig. 6b). However, the addition of SCAs further reduces the aggregation size of PSI, as shown in Figs. 6c–6e. Obviously, the smallest aggregation size is found in the system with TESPT-modified PSI, indicating the enhanced PSI dispersibility over the systems with APTES-modified, CPTES-modified and unmodified PSI. The results demonstrate the capability of SCAs to reduce the filler-filler interaction, leading to the enhanced degree of PSI dispersion.

To quantitatively determine the degree of PSI dispersion, the SEM images were analyzed by image analysis software (Image-Pro® Express Version 6), and the results are shown in Fig. 7. Again, the smallest aggregation size is found in the system with TESPT-modified PSI, followed by the systems with APTES-modified, CPTES-modified and unmodified PSI. The results confirm that TESPT has a greater capability of reducing the filler-filler interaction, leading to lowered possibility of re-agglomeration than other silanes. In other words, the effectiveness of silanes in improving the degree of PSI dispersion is in the following order: TESPT > APTES > CPTES, which is in good accordance with the Payne effect results discussed previously.

Influence of silane type on hardness and tensile properties of the PSI-filled CR is illustrated in Table 3. The CR filled with unmodified PSI shows the lowest hardness and 100% modulus. Among the three silanes, TESPT gives the highest hardness and modulus, followed by APTES and CPTES. It is widely recognized that both modulus and hardness of the cured specimens depend strongly on crosslink density. Similar to hardness and modulus results, TESPT-modified PSI gives the highest tensile strength, followed by APTES-modified, CPTES-modified and unmodified PSI. Explanations are given by the combined effects of improved rubber-filler interaction, higher crosslink density and enhanced PSI dispersion. It is well known that elongation at break depends strongly on crosslink density, i.e., the higher the crosslink density, the lower the elongation at break, hence the elongation at break of the system with TESPT is the lowest due to its highest crosslink density. On the other hand, the system with the unmodified PSI shows

Table 2
Influence of silane type on magnitude of Payne effect and bound rubber content of rubber compounds.

SCA treatment systems	$\Delta G'$ (kPa)	BBRC
Unmodified PSI	370.43	41.6 ± 0.8
APTES	320.19	45.7 ± 3.1
CPTES	345.50	44.0 ± 2.7
TESPT	304.56	46.2 ± 0.9

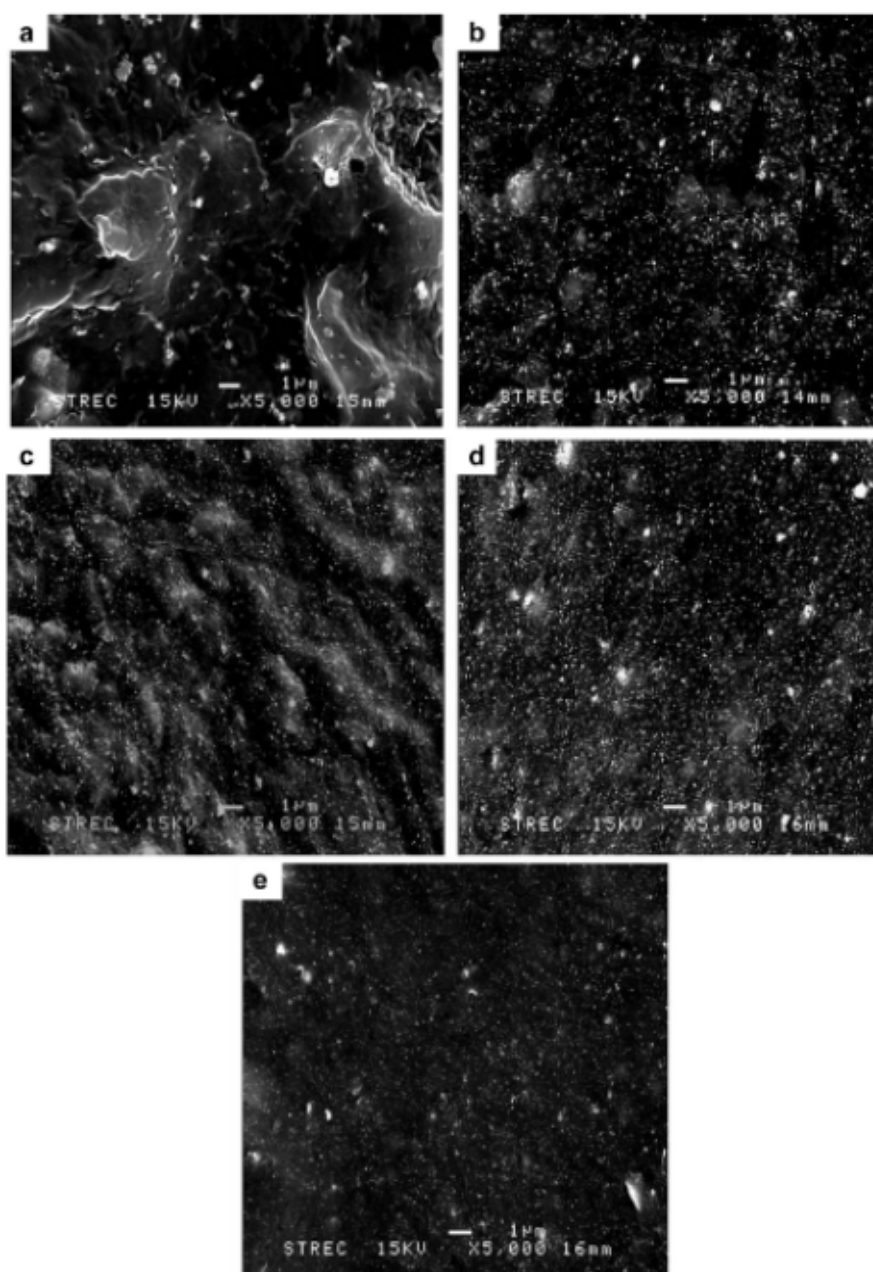


Fig. 6. SEM images of unfilled and PSI-filled CR specimens: (a) unfilled; (b) unmodified PSI; (c) APTES-modified PSI; (d) CPTES-modified PSI and (e) TESPT-modified PSI.

the highest elongation at break which is simply due to its lowest crosslink density.

Fig. 8 shows the influence of silane type on compression set of the CR vulcanizates. Apparently, both TESPT and APTES show greater performance in compression set than

CPTES. This could be caused by the improved magnitudes of filler dispersion, rubber-filler interaction and crosslink density, as mentioned earlier. Regarding the influence of silane type on heat build-up (HBU), the systems modified with TESPT and APTES exhibit relatively low HBU, as

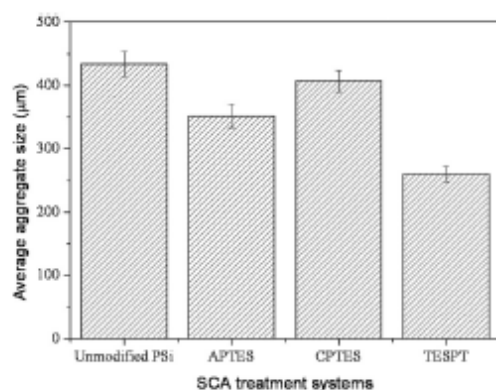


Fig. 7. Influence of silane type on average aggregate size of PSi dispersed in CR matrix.

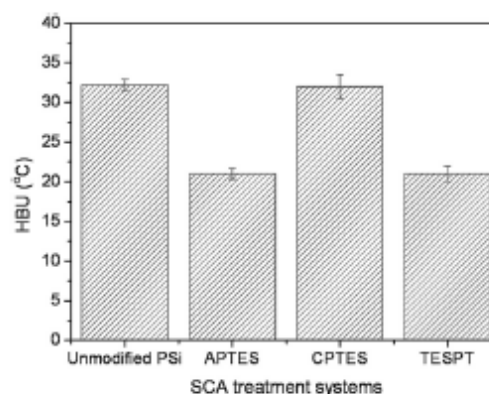


Fig. 9. Influence of silane type on heat build-up of the CR vulcanizates.

Table 3
Hardness and tensile properties of CR filled with various silane modified PSi.

SCA treatment systems	Hardness (Shore A)	100% modulus (MPa)	Tensile strength (MPa)	Elongation at break (%)
Unmodified PSi	66.9 ± 0.5	2.1 ± 0.1	13.8 ± 1.6	550 ± 35
APTES	68.1 ± 0.3	2.3 ± 0.1	22.4 ± 2.3	474 ± 27
CPTES	66.3 ± 0.3	2.2 ± 0.1	19.1 ± 1.8	511 ± 12
TESPT	69.3 ± 0.4	3.2 ± 0.1	22.4 ± 2.8	298 ± 45

evidenced in Fig. 9. By contrast, the system modified with CPTES demonstrates relatively high HBU, due to the low level of rubber-filler interaction, as evidenced by the BRC results, and crosslink density which facilitate the energy dissipation process under cyclic deformation.

4. Conclusions

Modification of PSi surfaces with 3 types of organo-alkoxy silane was carried out, and characterized by

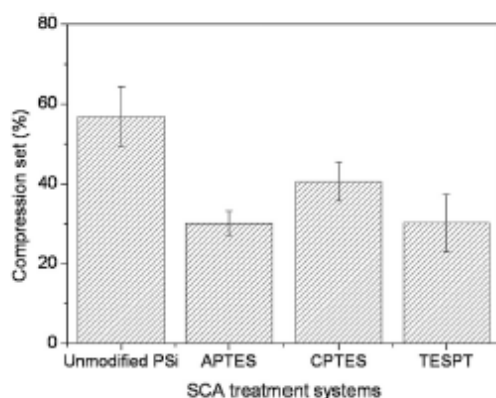


Fig. 8. Influence of silane type on compression set of the CR vulcanizates.

particle size analyzer, DRIFT and ^{29}Si NMR spectroscopy. Coupling efficiency of each silane and its effect on properties of CR were compared. Results show that the silane treatment of PSi is capable of significantly enhancing the reinforcement efficiency of silica-filled CR composites. In the systems treated with APTES and TESPT, the combined enhancements in rubber-filler interaction, filler dispersion and crosslink density are dominantly responsible for the improvement in mechanical properties. The results also suggest that the use of TESPT silane is still effective, even in the CR system with low sulfur curability.

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1. C. Siri Wong, P. Saeoui, C. Sirisinha, "Comparison of coupling effectiveness among amino-, chloro-, and mercapto silane in chloroprene rubber", Poster of the international congress for innovation in chemistry (PERCH-CIC congress VIII) at Jomtien Palm Beach Hotel & Resort, Chonburi, Thailand, 2012.

2. C. Siriwong, P. Saeoui, C. Sirisinha, "Comparison of coupling effectiveness among amino-, chloro-, and mercapto silane in chloroprene rubber", Oral presentation of the 4st international conference on Multi-Functional Materials and Structures at Eastin Grand Hotel, Sathorn, Bangkok, Thailand, 2013.
3. C. Siriwong, P. Saeoui, C. Sirisinha, "Comparison of coupling effectiveness among amino-, chloro-, and mercapto silane in chloroprene rubber", Proceeding in Advanced Materials Research vol. 747 (2013) 530 – 533 Trans Tech Publications, Switzerland.
4. C. Siriwong, P. Saeoui, C. Sirisinha, "Comparison of coupling effectiveness among amino-, chloro-, and mercapto silane in chloroprene rubber" Polymer testing 38 (2014) 64 – 72