

**IMPROVEMENT OF MECHANICAL PROPERTIES OF
POLYOLEFINIC THERMOPLASTIC ELASTOMER WITH
PINEAPPLE LEAF FIBER**

ASAMA KALAPAKDEE

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PINEAPPLE LEAF FIBER**

Asama Kalapakdee

.....
Miss Asama Kalapakdee
Candidate

T. Amornsakchai

.....
Assoc. Prof. Taweechai Amornsakchai,
Ph.D. (Polymer Physics)
Major advisor

Sombat Thanawan

.....
Assoc. Prof. Sombat Thanawan,
Ph.D. (Polymer Materials and Composites)
Member

Patcharee Lertrit

.....
Prof. Patcharee Lertrit,
M.D., Ph.D. (Biochemistry)
Dean
Faculty of Graduate Studies
Mahidol University

P. Sunintaboon

.....
Assoc. Prof. Panya Sunintaboon,
Ph.D. (Polymer Science)
Program Director
Master of Science Program in Polymer
Science and Technology
Faculty of Science
Mahidol University

Thesis
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**IMPROVEMENT OF MECHANICAL PROPERTIES OF
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on
July 16, 2015



Miss Asama Kalapakdee
Candidate



Assoc. Prof. Sunan Saikrasun
Ph.D. (Physical Chemistry)
Chair



Assoc. Prof. Taweechai Amornsakchai
Ph.D. (Polymer Physics)
Member



Assoc. Prof. Sombat Thanawan
Ph.D. (Polymer Materials and Composites)
Member



Prof. Patcharee Lertrit,
M.D., Ph.D. (Biochemistry)
Dean
Faculty of Graduate Studies
Mahidol University



Prof. Skorn Mongkolsuk,
Ph.D. (Biological Science)
Dean
Faculty of Science
Mahidol University

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Asama Kalapakdee

IMPROVEMENT OF MECHANICAL PROPERTIES OF POLYOLEFINIC
THERMOPLASTIC ELASTOMER WITH PINEAPPLE LEAF FIBER

ASAMA KALAPAKDEE 5336705 SCPO/M

M.Sc (POLYMER SCIENCE AND TECHNOLOGY)

THESIS ADVISORY COMMITTEE: TAWEECHAI AMORNSAKCHAI, Ph.D.
(POLYMER PHYSICS), SOMBAT THANAWAN, Ph.D. (POLYMER MATERIALS
AND COMPOSITE)

ABSTRACT

Uniaxial composite systems of pineapple leaf fiber (PALF) and Santoprene, a thermoplastic elastomer, were studied. PALF filled Santoprene composites were prepared by melt processing on a two-roll mill at various PALF contents. The molten mixture was sheeted out using a narrow nip with some stretching to give prepreg with PALF preferentially aligned along the machine direction. Wide angle x-ray scattering patterns revealed that the prepreps had matrix orientation and the matrix orientation still remained after moulding at 175 °C but not at 195 °C. Secant modulus at 10% strain and tear strength in the longitudinal direction increased significantly with increasing PALF content of up to 15%, while tensile strength and elongation at break decreased. The effect of PALF content was less significant in the transverse direction. To improve the compatibility of PALF with the Santoprene matrix, two compatibilizers including maleic anhydride grafted polypropylene (MAPP) and maleic anhydride grafted styrene-ethylene/butylene-styrene (MASEBS) were used. The mechanical properties increased with increasing compatibilizer content. In addition, PALF surface was also modified with various chemical methods. Modified PALF resulted in composites with lower tensile properties due to poor interfacial adhesion between the PALF fiber and Santoprene matrix.

KEY WORDS: PINEAPPLE LEAF/ NATURAL FIBER/ THERMOPLASTIC
ELASTOMER/ MATRIX ORIENTATION

75 pages

การปรับปรุงสมบัติเชิงกลของแซนโตพรีน ด้วยเส้นใยใบสับปะรด

IMPROVEMENT OF MECHANICAL PROPERTIES OF SANTOPRENE WITH PINEAPPLE LEAF FIBER (PALF)

อสมมา ภาพักดิ์ดี 5336705 SCPO/M

วท.ม. (วิทยาศาสตร์และเทคโนโลยีพอลิเมอร์)

คณะกรรมการที่ปรึกษาวิทยานิพนธ์: ทวีชัย อมรศักดิ์ชัย, Ph.D. (POLYMER PHYSICS),
สมบัติ ชนะวันต์, Ph.D. (POLYMER MATERIALS AND COMPOSITE)

บทคัดย่อ

งานวิจัยนี้เป็นการเตรียมคอมโพสิตระหว่างยางเทอร์โมพลาสติกแซนโตพรีนกับเส้นใยใบสับปะรด โดยคอมโพสิตถูกผสมด้วยเครื่องผสมสองลูกกลิ้งที่ปริมาณเส้นใยใบสับปะรดร้อยละ 3, 5, 9 และ 15 โดยน้ำหนัก งานวิจัยนี้ส่วนแรกเป็นการศึกษาผลของอุณหภูมิเตรียมชิ้นงานต่อการเสริมแรงของเส้นใยใบสับปะรดในยางเทอร์โมพลาสติกแซนโตพรีน โดยเตรียมตัวอย่างที่อุณหภูมิแตกต่างกันคือที่ 175 และ 195 องศาเซลเซียส จากผลการศึกษาด้วยการเลี้ยวเบนของรังสีเอกซ์ ซึ่งให้เห็นว่าระบบที่เตรียมที่อุณหภูมิ 175 องศาเซลเซียสยังมีการจัดเรียงตัวของโมเลกุลยางเทอร์โมพลาสติกแซนโตพรีนในคอมโพสิต และการศึกษาการเรียงตัวของเส้นใยสับปะรดโดยใช้กล้องจุลทรรศน์อิเล็กตรอน โดยผลจาก 2 กระบวนการนี้ส่งผลให้สมบัติเชิงกลของคอมโพสิต (การทนต่อแรงดึง, ความทนทานต่อแรงฉีกขาด) มีค่าเพิ่มมากขึ้น และยังได้ศึกษาผลของการเติมสารเสริมสภาพเข้ากันได้ 2 ชนิด คือ พอลิพรอพิลีนที่กราฟต์ด้วยมาเลอิกแอนไฮไดรด์ (MAPP) และ ยางเอสบีเอสที่กราฟต์ด้วยมาเลอิกแอนไฮไดรด์ (MASEBS) ในระบบคอมโพสิตที่ปริมาณเส้นใยสับปะรดร้อยละ 9 โดยน้ำหนัก พบว่าสมบัติเชิงกลมีค่าเพิ่มขึ้นเนื่องจากการยึดติดที่ดีระหว่างเส้นใยใบสับปะรดและยางเทอร์โมพลาสติกแซนโตพรีน นอกจากนี้ยังได้ศึกษาการปรับปรุงพื้นผิวของเส้นใยใบสับปะรดด้วยวิธีการทางเคมีหลายวิธีแต่กลับพบว่า เส้นใยที่ผ่านการปรับปรุงผิวทำให้คอมโพสิตที่ได้มีสมบัติเชิงกลน้อยกว่าระบบที่ไม่ได้ปรับปรุงพื้นผิว อาจเนื่องมาจากการยึดติดที่ไม่ดีระหว่างเส้นใยใบสับปะรดและยางเทอร์โมพลาสติกแซนโตพรีน

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LIST OF ABBREVIATIONS

PALF	Pineapple leaf fiber
TPE	Thermoplastic elastomer
MAPP	Maleic anhydride-grafted-polypropylene
MASEBS	Maleic anhydride grafted-styrene-ethylene/butylene-styrene
OM	Optical Microscope
SEM	Scanning Electron Microscope
DMA	Dynamic Mechanical Analyzer
WAXS	Wide-angle X-ray scattering
Un-PALF	untreated pineapple leaf fiber
Na-PALF	NaOH treated pineapple leaf fiber
BZDA-PALF	Benzene diazonium salt treated pineapple leaf fiber
Ami-PALF	Amino silane treated pineapple leaf fiber
Iso-PALF	Isocyanate treated pineapple leaf fiber

CHAPTER I

INTRODUCTION

The reinforcement of rubber has been used in many applications such as automotive parts, tyre and hoses etc. Rubber products commonly contain a reinforcing agent such as silica, carbon black and fiber etc. The fiber-reinforced in rubber to improved Young's modulus [1]. There are many advantages with short fibers as reinforced in rubber including design flexibility, high low-strain modulus, anisotropy in technical properties and stiffness, good damping, ease in processing and production economy. Many types of fibers such as rayon, nylon, cotton linter, polyester, aramid fiber and cellulose are used [2]. In addition, natural fiber such as jute, sisal, flax, coir and pineapple leaf fiber (PALF) have also been studied for rubber reinforcement [3]. Normal rubber systems are very complicated in processing. They require a complex system of chemicals for crosslinking. Recently, interests have been paid to thermoplastic elastomer (TPE) in many applications due to it ease of process and recycling [4]. They do not require crossliking system as do conventional rubbers. These materials exhibit some of the physical properties of elastomers at lower temperatures and are processable at elevated temperature [5]. TPE have a disadvantage of melting at elevated temperatures. This inherent property prevents TPE from applications requiring exposure to temperature above the melting point [5]. Thermoplastic elastomers have been classified into two main categories [2]:

(1) Block and graft copolymer such as polystyrene thermoplastic elastomer, thermoplastic polyurethane (TPU) elastomer, polyester thermoplastic elastomer, polyamide thermoplastic elastomer and graft copolymers.

(2) Thermoplastic elastomers from rubber-plastic blends such as NR-HDPE, NR-LDPE, EPDM-PP (Santoprene), EPDM-PE etc.

Thermoplastic elastomers (TPEs) from rubber-plastic blends are copolymer of a thermoplastic and thermoset rubber, giving rise to a two-phase morphology. The morphology of TPEs is shown in Figure 1.1. The properties of

thermoplastic elastomers reflect the properties of both thermoplastics and elastomers. In Santoprene (EPDM-PP blend) is one of a commercially important TPE used in various applications, to address the demands of engineering applications in more severe environmental conditions, enhancement of the performance properties of this polymer is required.

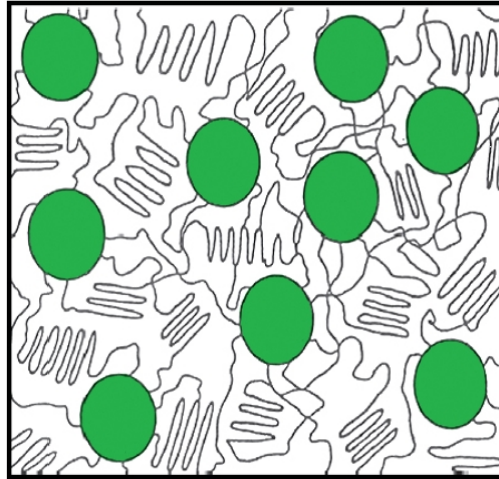


Figure 1.1 Molecular structure of soft (amorphous rubber) and hard phases (crystalline thermoplastic) in a thermoplastic elastomer [2].

Properties of thermoplastic elastomer can also be improved by the addition of vastly available natural fibers such as flax, hemp, sisal and pineapple leaf fiber (PALF) [6]. Natural fiber can be used in most application for example mat, rope, sack etc. According to natural fiber have good mechanical properties and mostly local availability [7]. Many work have report the improvement of mechanical properties by using natural fibers as reinforcement. The composites of white rice husk ash (WRHA) as filler for polypropylene (PP)/ethylene-propylene-diene terpolymer (EPDM) were improved the tensile modulus and flexural modulus [8]. Another study carried out by Anuar et.al [9] has shown the high tensile strength of thermoplastic elastomer composites reinforced kenaf fiber. Thailand is currently the world's largest pineapple export producer [10]. Its cultivation in Thailand is about 240,000 acres [11]. After harvesting, a large amount of pineapple leaf waste remains causing various problems for farmers [12]. Therefore, it is good chance to add value of Pineapple leaf waste by used in many applications such as rubber industry, plastic industry and food industry

[6]. Due to pineapple leaf fiber (PALF) has many advantages such as low cost, environmental friendly, high mechanical properties. PALF reinforced polymer composites exhibit better mechanical properties, such as stiffness, impact strength, flexible strength and modulus when compared to the pure polymer [6]. The superior mechanical properties of pineapple leaf fiber are associated with its high cellulose content and comparatively low microfibrillar angle than other natural fibers. Therefore, it is more interested to use PALF as a reinforcing agent in composite application.

Therefore, the purpose of this study is to prepare (PALF) reinforced Santoprene thermoplastic elastomer composites. Effects of fiber, Santoprene orientation, PALF modifications and compatibilizers on mechanical properties of the composites were studied. In this study, Santoprene and PALF were chosen to form a composite system. The composites were prepared using a two-roll-mill mixer. The mechanical properties, dynamic mechanical properties and morphologies of the composites were characterized.

CHAPTER II

OBJECTIVES

TPE has been used in many applications due to its ease of process and recycling. There are many products of fiber-reinforced TPE such as automotive part and hoses. Therefore, in this work, Santoprene TPE was used as matrix. Due to superior mechanical properties and abundantly available of PALF, it is chosen as reinforcement in TPE for many applications. So, PALF reinforced Santoprene TPE was investigated. For San/PALF composites, the fiber orientation, chain orientation of matrix and interfacial adhesion were also an important factor to improvement of mechanical properties. In this work, addition to quantity and fiber orientation of PALF, the chain orientation of Santoprene was investigated. To improve the compatibility between PALF and Santoprene matrix, the compatibilizer loading and surface treatments were carried out. The main objectives of this work are focused as follows:

- (a) The effect of PALF content and fiber orientation on improvement of mechanical properties of San/PALF composites.
- (b) The effect of compression moulding temperature on Santoprene chain orientation existing in San/PALF composites.
- (c) The effect of compatibilizers on the mechanical properties of San/PALF composites.
- (d) The effect of PALF surface modification on mechanical properties of San/PALF composites.

CHAPTER III

LITERATURE REVIEW

3.1 Thermoplastic elastomes (TPEs)

TPE provided a new horizon to the field of polymer technology. TPEs can be defined as a class of polymer, which combine the service properties of rubber with the processing properties of thermoplastics. The conventional rubber must be vulcanized to give useful properties. Vulcanization is a slow, irreversible process and takes place on heating. In TPE can be processible melt to a rubber-like solid is reversible [4].

3.1.1 Advantages and disadvantages of TPEs

The advantages of TPEs over conventional thermoset rubbers [4] are:

1. Simple processing with fewer steps. TPEs have the processing simplicity of a thermoplastic, giving more efficient processing and significantly lower cost for the finished rubber articles.
2. Recycle of TPEs scrap. After processing, the TPEs scrap can be recycled to give finished product with same properties as virgin material.
3. Shorter fabrication times. The TPEs moulding cycle is shorter than thermoset rubber, leading to lower finished part costs.
4. Lower quality control costs, because of the greater reproducibility and consistency of the properties of TPEs resins.
5. Lower energy consumption. This is a result of the lower cycle times and simple processing of TPEs.
6. Lower density than thermoset rubber.

As all materials do, TPE have some practical disadvantages [4] are:

1. The limited number of low hardness TPEs.

2. Melting at elevated temperatures. Some applications of TPEs require brief exposure to temperature above the melting point. A thermoset rubber probably would be suitable for such a brief exposure.

3. Drying prior to processing. In conventional rubber processing, this step is never used, but this is quite common to the thermoplastic fabricator

4. Unfamiliar processing equipment.

3.2 Santoprene TPE

Santoprene TPE is a family of high-performance elastomer which consists of a fine dispersion of highly vulcanized EPDM rubber in a matrix of polypropylene as the continuous phase. The particles of vulcanized EPDM are distributed uniformly throughout the polypropylene matrix as shown in figure 3.1. The properties of Santoprene are considerably improved over those of typical polymer blends. Tensile strengths are much improved. Compression and tension set, in particular are more in line with crosslinked elastomers than the blend.

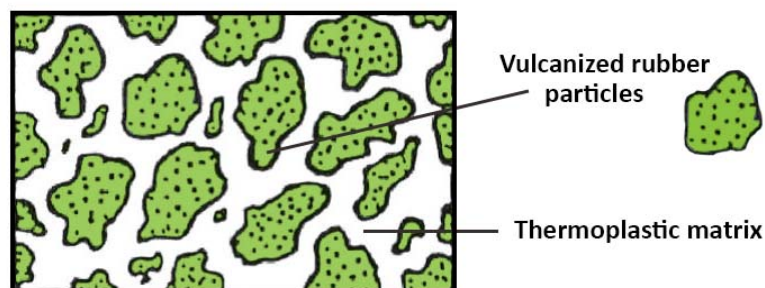


Figure 3.1 Morphology of thermoplastic vulcanite.

3.2.1 Performance and product characteristics of Santoprene TPE

1). Performance characteristics of properly processed Santoprene rubber include:

2). Withstands transient temperatures up to 150°C and continuous temperatures to 135 °C.

3). Fluid resistance equivalent to polychloroprene for aqueous-base fluids, oils, and hydrocarbons.

- 4). Low compression and tension set.
- 5). Outstanding dynamic fatigue resistance.
- 6). Good tear strength.
- 7). Excellent ozone and good weathering resistance.

Santoprene rubber is processed with conventional thermoplastic equipment to make extruded, injection molded, blow moulded or thermoformed products.

3.2.2 Applications of Santoprene TPE

The performance characteristics of Santoprene rubber make it exceptionally well-suited for processing into a wide variety of end-use applications. Some typical applications are given below:

- 1). Appliances: pump gaskets, supports, boots, hose connectors, plugs, sump boots, baffles.
- 2). Automotive: rack-and-pinion boots, air ducts, cable covers, bushings, windshield spacers, tubing, grommets, gaskets, body seals for windows and doors, body plugs, weather stripping, lamp covers, suspension dust covers, air bag doors.
- 3). Building and construction: glazing gaskets, weather stripping for doors and windows, bulb seals, expansion joints, setting blocks.
- 4). Business machines: rollers for printers, computer feet, vibration isolators.
- 5). Electrical/electronic: moulded connectors, power transmission and distribution components, linemen's accessories, mining cable, control cable, power-limited circuit cable, submersible cable, coiled cords, flexible cords.
- 6). Fluid delivery: plumbing seals, filter and pump seals, hose and tubing, pie seals.
- 7). Food contact: diaphragms, valve seals, closure seals, hose and tubing.
- 8). Hardware: caster wheels, tool grips, industrial rollers.
- 9). Medical devices: closures, gaskets, stoppers, plunger tips.
- 10). Sporting goods: bat grips, rifle stock cushions, scuba diving equipment, sky pole handles

3.3 Natural Fiber reinforced polymer composites

3.3.1 Natural fiber

Natural fibers can be divided based on their origins i.e., whether they are derived from plants, animals or minerals as shown in figure 3.2.

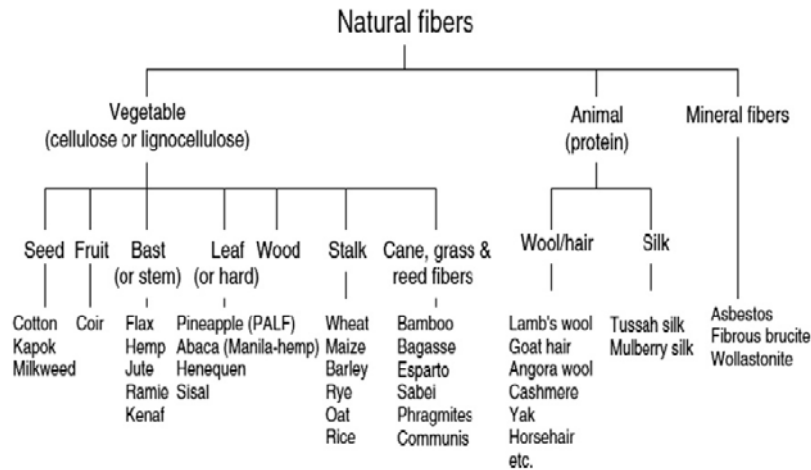


Figure 3.2 Classification of natural fibers [7]

The most common natural plant fibers can be divided into categories with refer to the source of the fiber such as leaf or hard fibers, seed, fruit, wood, cereal straw and other. Natural fiber can be used in most application for example mat, rope, suck etc. According to natural fiber have a good mechanical properties and mostly local availability. Recently, plant fibers have been used as reinforcing filler in material composites.

The plant fibers are composed of cellulose, hemicelluloses, lignin, waxes, and several water-soluble compounds; where cellulose, hemicelluloses, and lignin are the major constituents. The main constituent of any plant fiber is cellulose. The natural fibers are composed of a rigid crystalline cellulose microfibril reinforced amorphous lignin, and hemicelluloses matrix. Cellulose is the natural homopolymer (polysaccharides), where D-glucopyranose rings are connected to each other with β -1,4-glycosidic linkages, as can be seen in Fig. 3.3.[7].

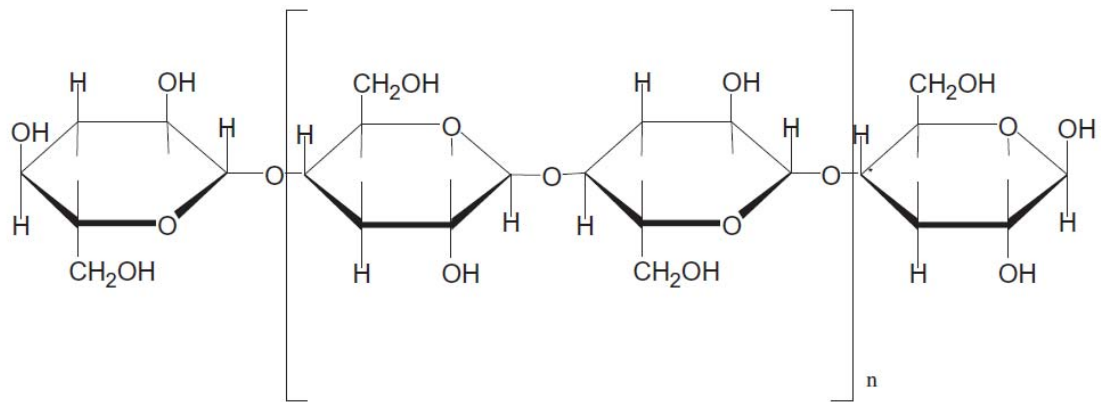


Figure 3.3. Chemical structure of cellulose [7]

Generally, natural fibers have a good the mechanical properties because of the cellulose content and the microfibrillar angle. In the case of the tensile strength and Young's modulus were increase with increasing of cellulose content and oriented parallel axis of the fiber. The mechanical properties of natural fiber and synthetic fiber are shown in table 1.1

Table 3.1 The mechanical properties of natural fiber and synthetic fiber [7]

Fibers	Density (g/cm^3)	Tensile strength (MPa)	Young's modulus (GPa)	Elongation at break (%)
Ramie	1.5	400-938	61.4-128	1.2-3.8
PALF	1.44	413-1627	34.5-82.5	1.6
Flax	1.5-3	450-1100	27.6	2.7-3.2
Jute	1.3-1.45	393-773	13-26.5	7-8
Hemp	-	690	-	1.6
Sisal	1.45	468-640	9.4-22	3-7
Cotton	1.5-1.6	287-800	5.5-12.6	7-8
Coir	1.15	131-175	4-6	15-40
E-glass	2.5	2000-3500	70	2.5
S-glass	2.5	4570	86	2.8
Aramid	1.4	3000-3150	63-67	3.3-3.7
Carbon	1.7	4000	230-240	1.4-1.8

3.3.2 PALF

PALF is obtained from the leaves of the plant (*Anannus comosus*) belonging to the Bromeliaceae family. The pineapple plant has a very short stem which first produces a rosette of leaves but which latter elongated and bear numerous spirally arranged fibrous leaves [6]. The leaves are 3ft. long, 2 to 3 inch wide sword shaped, dark green in color and bear spines of claws on their margins as shown in figure 3.3. The leaves of the pineapple plant yield strong, white fine silky fibers [6]. PALF is multicellular lignocellulosic in nature, comprising mainly polysaccharides and lignin and other compounds such as fat, wax, pectin, uronic anhydride, pentosan, coloring matter, inorganic substances[12] etc. It has a ribbon-like structure and is cemented together by gummy matters like lignin and pentosan, which contribute to the strength of the fiber. PALF contains about 70–82% of cellulose, [6] the arrangement of molecules in the fibers is similar to cotton cellulosic fibers. The molecular chains of cellulose lie parallel and in three-dimensional arrangements in the crystalline region of fibers. The other portions of the molecular chains are believed to lie in a less ordered state in the amorphous regions.



Figure 3.4 Pineapple leaf

Natural fibers are abundantly available in Thailand such as pineapple leaf, coir, bamboo, bagasses, etc. One of available natural fiber is pineapple leaf fiber

(PALF) because it is largely cultivated in tropical countries, mainly for its fruits. Its cultivation in Thailand is substantial about 240,000 acres (600,000 rai) [10]. Pineapple is export products in Thailand. These pineapple leaves are going to waste because of lack of knowledge about their economic uses. However, pineapple leaf waste left over in fields. Therefore, it is a good chance to add value of PALF wastes by using in many applications that large demand natural fiber such as rubber industry, plastic industry, food industry, etc. The superior mechanical properties of pineapple leaf fiber are associated with its high cellulose content and comparatively low microfibrillar angle than other natural fibers as shown in table 1.1. Therefore, it is more interested to use PALF as a reinforcing agent in composite application.

3.3.3 Mechanical properties of PALF reinforced polymer composites

PALF was used as reinforcement fiber in polymer matrix. Many Researches reported PALF fiber reinforced in polymer composites.

Liu et al [14] have reported green composites from soy base plastic and pineapple leaf fiber PALF. The mechanical properties (tensile, flexural and impact properties) improved with increases amount of fiber (at 30 wt %). The addition of compatibilizer (PEA-g-GMA) will improve the dispersion of pineapple leaf fiber in soy base plastic and mechanical properties. In addition, water absorption of compatibilized composites was reduced, compared with uncompatibilized indicating that the interfacial adhesion occurred between fiber and matrix.

The mechanical properties of pineapple leaf fiber reinforced polypropylene composites have been reported by *Arib et al* [15]. The tensile properties increased insignificantly compared with pure polypropylene. The flexural properties of the composites increased but the value lower than the other researcher.

3.4 Surface modifications of natural fibers

The quality of the fiber-matrix interface is significant for the application of natural fibers as reinforcement fibers for polymer. The hydroxyl groups, which occur throughout the structure of natural fibers, make them hydrophilic. But many polymer matrices are hydrophobic so that PALF-polymer composites have poor interfaces [12].

A lot of method used to solve this incompatibility bonding properties of natural fiber reinforced composites. Physical and chemical methods can be used to optimize this interface.

3.4.1 Compatibilizing promotion

It is important that most commercial polymer blends are immiscible systems. The phase separated typically exhibited by immiscible system usually lead to poor blends properties. This type of modification, typically referred to as blend compatibilization, is mostly based on interfacial modification. Compatibilization aims at modifying the interfacial properties, which is highly critical for the performance of immiscible polymer blends. An efficient compatibilization assists in the development of the required morphology during the compounding stage and help to preserve this optimized phase structure during the subsequent forming steps. J. K. Sameni et al [16] studies effects of processing parameters and graft copoly(propylene/maleic anhydride) on mechanical properties of thermoplastic natural rubber composites reinforced with wood fibres. They indicated that the compatibilizer increased the tensile strength and Young's modulus, but reduced the strain.

3.4.2 Alkali treatment

Natural fibers are hydrophilic and have poor compatibility with hydrophobic polymers due to the hydroxyl group (-OH) presented in cellulose the main composition of natural fibers. Alkali treatment is most popular used chemical treatments of natural fiber. This treatment removed hemicellulose and lignin covering the external surface of the fiber. S. V. Prasad et al [17] studies alkali treatment of fiber can be improved flexural and impact strength which increase by 40% as compared to untreated fiber composites. J. P. Siregar et al [18] study of the effect of the alkali treatment on the mechanical properties of pineapple leaf fibre (PALF) reinforced high impact polystyrene (HIPS) composites. The composites at 4% of alkali treatment showed the highest mechanical properties compared untreated fiber.

3.4.3 Silane treatment

Silanes are used as coupling agents to improved interfacial adhesion between fiber and matrix. The silane coupling agents reduce the number of cellulose hydroxyl groups in the fiber and matrix. M. Abdelmouleh et al. [19] studies effect of silane coupling agents in natural fibre reinforced polyethylene and natural rubber composites. The composites of silane coupling agent treatment showed the improvement the interfacial adhesion between fiber and matrix. Ifuku S. et al [20] showed the effect of silane coupling agent improved dispersibility of fibers and compatibility of fiber and polypropylene glycol matrix. Threepopnatkul et al [21] studies surface treatment on performance of pineapple leaf fiber (PALF) was pre-treated with sodium hydroxide and modified with two different functionalities such as γ -aminopropyl trimethoxy silane (PALF/Z-6011) and γ -methacryloxy propyl trimethoxy silane (PALF/Z-6030). polycarbonate composites. The composites of PALF/Z-6011 showed the highest tensile strength and impact strength. Reaction between PALF and γ -aminopropyl trimethoxy silane (Z-6011) is shown in Figure 3.5.

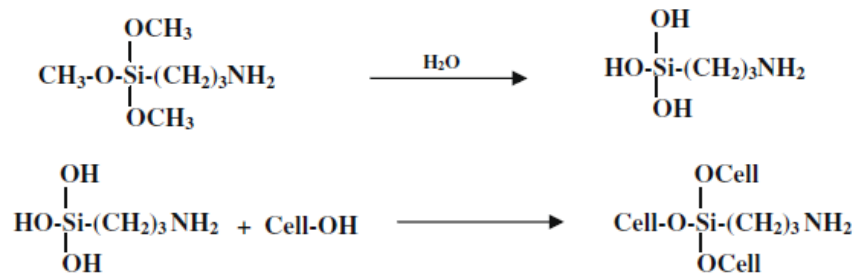


Figure 3.5 Reaction between PALF and γ -aminopropyl trimethoxy silane [21].

3.4.4 Benzenediazonium salt treatment

Recently, many researches presented the improvement compatibility by treated natural fiber with benzenediazonium salt. Rahman M.R. et al [22] have reported the abaca treatment with benzenediazonium salt on properties of PP based composites. Young's modulus, flexural strength, flexural modulus, impact strength and hardness of treated abaca-PP composites were improved, compared with untreated abaca composites systems.

3.4.5 Isocyanates treatment

Recently, many researches presented the improvement of mechanical properties of natural fiber composites by treated natural fiber with isocyanate group. The better performance is due to the formation of isocyanate linkage between –OH group of the fiber and –NCO groups as shown in Scheme 1.1 [23]. Isocyanates have a highly reactive functional group that readily reacts with various other functional entities [23]. R.G.RAJ et al. [23] studied isocyanate treated wood fiber reinforced polyethylene. They indicated that treated fiber composites to the significant improvement in mechanical properties of polyethylene-wood fiber composites. V.G. Geethamma et al [3] also presented the higher tensile properties of isocyanate solution treat coir fibers reinforced natural rubber when compared alkali treated composites.



Figure 3.6 Isocyanates treated cellulose [23]

CHAPTER IV

MATERIALS AND METHODS

4.1 Materials

All of materials used in this study were:

4.1.1 Polymer Matrix

Santoperne TPE (691-73W175) was purchased from Advanced Elastomer Systems. The elastomer contains 18 wt% PP and 82 wt% EPDM. The specific gravity and the brittle point of this material are 0.98 and < -60 °C, respectively.

4.1.2 Reinforcement agent

Pineapple leaves were collected from cultivation areas in Kok Kwai District, Amphor Ban Rai, Uthai Thani Province, Thailand. The fresh pineapple leaves were cut a length of 6 mm and milled. Then, the mill pineapple leaves were filtered to remove water and dried in oven at 80°C. The dried pineapple leaves were spinned and glided to remove non-fiber and separate the fiber part. The method was used following the milling technique developed in this laboratory [12]. PALF has diameter as small as 3 up to 80 μm and average diameter of approximately 3-20 μm . The chemical compositions of different parts of pineapple leaf fiber are shown in Table 4.1.

Table 4.1 Chemical composition (%) of different parts of ground pineapple leaf fiber.

Composition	Dry matter	Lignin	Hemicellulose	Cellulose
WGL	90.38 \pm 0.11	4.57 \pm 0.13	34.38 \pm 0.66	46.65 \pm 0.83
PALF	92.43 \pm 0.10	1.98 \pm 0.08	19.80 \pm 0.21	70.98 \pm 0.93
NFM	89.37 \pm 0.48	7.70 \pm 0.16	36.53 \pm 0.23	43.69 \pm 0.78

4.1.3 Compatibilizers

Maleic anhydride-grafted-polypropylene (MAPP, trade name P613) and maleic anhydride grafted-styrene-ethylene/butylene-styrene (MASEBS, from Aldrich). Compatibilizers were used as in this work.

4.1.4 Other chemicals

All chemicals used in this work are presented in Table 4.2

Table 4.2 The chemicals used in this work.

Chemical name	Manufacture
Sodium Hydroxide	AGC chemical
Sodium Nitrite	CARLO ERBA
Aniline	Panreac Quimical
3-aminopropyl trimethoxysilane	Sigma-Aldrich
Octadecyl isocyanate	Sigma-Aldrich

4.2 Instruments

All instrument used in this work are shown in Table 4.3

Table 4.3 Instruments, model and manufacture were used in the experiment

Instrument	Model	Manufacture
Two-roll-mill	W100T	Collin
Compression molding machine	Mach group	Mach group (1992) Co.,Ltd
Tensile testing machine	Instron 5566	Instron
Scanning Electron Microscope (SEM)	TM-1000	Hitachi
Optical Microscope (OM)	BX51TRF	Olympus
Dynamic Mechanical Analyzer (DMA)	Q800	TA Instrument
Hardness Tester (shore A)	H17A	Wallace
Abrasion tester	6102	Zwick
WAXS		Synchrotron Light Research Institute

4.3 Experimental procedure

4.3.1 Modification of PALF

4.3.1.1 Alkali treatment

In this research was used as Sodium hydroxide (NaOH). PALF were soaked in 10% w / v NaOH solution at room temperature in a fume hood for 30 minutes. After that, PALF were washed with distilled water until the pH about 7. The PALF were dried in vacuum oven at 80 °C for 24 h.

4.3.1.2 Amino silane treatment

3-aminopropyl trimethoxysilane was also used for surface modification. The ethanol-water (90/10 w / w) mixture was prepared in the first step and then amino silane was added. The solution was stirred for 1 minute and left for 1 h for their hydrolysis. After that, PALF were immersed in solution for 1 h at room temperature. The solution was separated from the mixture by evaporation. At last, PALF were dried in vacuum oven at 80 °C for 24 h.

4.3.1.3 Benzene diazonium salt (BZDA) treatment

Benzene diazonium salt was prepared by the standard diazotization method. The method is the reaction of aniline solution and Sodium Nitrite solution (NaNO_2) at temperature below 5°C. The solution was kept in freezer before using to treat of PALF. PALF were immersed in 5%NaOH solution and kept solution in freezer until the temperature of the mixture is about 0-5°C. The solution of benzene diazonium salt was poured into the mixture with constant stirring and kept for 10 min. After that, PALF were washed with soap solution and water. Finally, PALF were dried in vacuum oven at 80 °C for 24 h.

4.3.1.4 Isocyanate treatment

Isocyanate treatment was used in this work is Octadecyl isocyanate. Before soaking the PALF was prepared of 2%isocyanate in dichloromethane solution. The solution was kept in freezer. After that, PALF were immersed in solution with constant stirring and kept solution in freezer until the temperature of solution is room temperature for 2 h. At last, PALF were dried in vacuum oven at 80 °C for 24 h.

4.3.2 Preparation of San/PALF composites

4.3.2.1 San/PALF composites with various PALF contents.

The Santoprene and PALF were mixed with various contents of PALF. The raw materials were dried for 24 h in a vacuum oven at 70°C. Loading of PALF were varied at 0, 3, 5, 9, 15 wt%. Approximately 50 g of Santoprene and PALF fiber were melt mixed for 25 min on two roll mill, temperature of the front and rear roll at 180°C and 175°C, respectively. The compositions of San/PALF composites are present in Table 4.3. The prepage composites were kept in a desicator for 24 h. Then, the San/PALF prepage was compressed temperatures. At first compression temperature, the prepage mixture was compression moulded at 175°C under pressure of 500 psi for 5 min in hot pressed, followed by cooling pressed under pressure of 1,000 psi for 5 min. The second compression temperature, the prepage composite was compressed at 195°C and pressure and time in compression same as the first compression temperature. The specimens of 1 mm thickness were used for tensile and tear test. For abrasion resistance sample test, the prepage of composites were shaped by compression moulding with two compression temperatures (175°C and 195°C). The abrasion resistance samples are cylindrical shape with a diameter of 16 ± 0.2 mm and minimum thickness of 6 mm according to ASTM D963-97.

Table 4.4 The composition of San/PALF composites

Sample code	Santoprene (wt.%)	PALF (wt.%)
San0PALF	100	0
San3PALF	97	3
San5PALF	95	5
San9PALF	91	9
San15PALF	85	15

4.3.2.2 Preparation of compatibilizers on San/PALF composites.

The effect of compatilizer on mechanical properties in San/PALF composites was studied. The Santoprene and PALF were mixed with fixed PALF loading at 9 wt.% with and without the PP-g-MA and SEBS-g-MA. The contents of compatibilizer were 0, 0.1, 0.5, 0.75 and 1 (times of PALF). All materials were dried for 24 h in a vacuum oven at 70°C. After that, all material were mixed on two-roll mill machine for 25 min, temperature of the front and rear roll at 180°C and 175°C, respectively. The formulations of compatibilizer San/9PALF composites are present in Table 4.4. Then, the obtained mixtures of two systems were compression molded at 175°C under a pressure of 500 psi for 5 min, followed by cooling under pressure of 1,000 psi for 5 min. The sheet of 1 mm thickness were used for tensile and tear test. For prepare abrasion resistance sample, two compatibilizers system using the same step in preparation as described above with the compressed temperature at 175°C.

Table 4.5 Formulation of compatibilized San/9PALF composites

Sample code	Santoprene (wt.%)	PALF (wt.%)	MAPP / MASEBS (times of PALF)
San9PALF/0.1 MAPP	91	9	0.1
San9PALF/0.5 MAPP	91	9	0.5
San9PALF/0.75 MAPP	91	9	0.75
San9PALF/1 MAPP	91	9	1
San9PALF/0.1 MASEBS	91	9	0.1
San9PALF/0.5 MASEBS	91	9	0.5
San9PALF/0.75 MASEBS	91	9	0.75
San9PALF/1MASEBS	91	9	1

4.3.2.3 Preparation of treated PALF containing composites.

Before mixing all materials were dried for 24 h in a vacuum oven at 70°C. Santoprene and treated PALF with fixed PALF loading at 9 wt.% were prepared by melt blending on a two-roll mill at 180°C (front roll) and 175°C (rear roll) for 25 min. After that, the obtained mixtures were compression molded at 195°C under a pressure of 500 psi for 5 min, followed by cooling under pressure of 1,000 psi for 5 min. The sheet of 1 mm thickness was used for tensile test.

4.4 Composites characterizations

4.4.1 Structure and morphological characterization

4.4.1.1 PALF orientation

The observed PALF alignment in matrix, a piece of prepreg was extracted with toluene in a Soxhlet apparatus over night to remove the matrix. The specimens were observed under optical microscope (OM, Olympus BX51TRF).

4.4.1.2 Crystalline structure and orientation

The crystalline structure and PP orientation in Santoprene matrix were observed by WAXS. WAXS were performed at Beamline BL 2.2 at the Synchrotron Light Research Institute (Public Organization) (SLRI), Thailand. X-ray energy was 8 keV. The patterns were recorded with a Mar detector and data analysed according to standard procedure with a self-developed program, Saxsit [].

4.4.1.3 Morphology of PALF and composites

The morphology of shape and size of PALF and fractured surfaces of the composites were observed by scanning electron microscope (SEM) (Hitachi Tabletop Microscope; model TM 1000) at room temperature.

4.4.2 Mechanical properties

4.4.2.1 Tensile properties

The tensile properties of the Santoprene composites with various contents of PALF and compatibilizer/modification of PALF system were studied. Samples of appropriate shape were punched out from the molded sheet in the

longitudinal direction and transverse direction. The two directions are shown in Figure 4.1. The sample was dumb-bell-shaped according to Die type2 (ISO 37). Tensile testing was carried out using a universal testing machine (Instron 5569). The crosshead speed of 500 mm/min was used with load cell at 1 kN. Mean value of at least 5 specimens as determined. Ultimate tensile strength, modulus at low strain (10% and 20% strain) and elongation at break were measured.

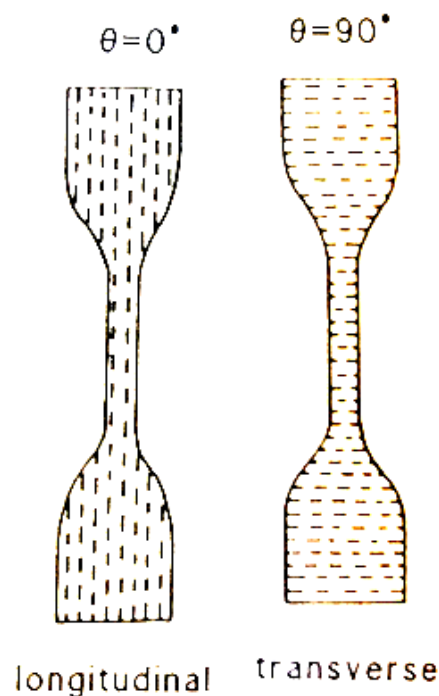


Figure 4.1 The longitudinal and transverse directions of fiber orientation in the tensile test.

(a) Modulus at low strain and ultimate tensile strength

Modulus at 10% and 20% strain and ultimate tensile strength were calculated from Equation 4.1.

$$\sigma = \frac{F}{A} \quad (4.1)$$

Where

σ = The modulus at low strain and ultimate tensile strength (MPa)

F = Corresponding force at 10 and 20% strain and at max force (N)

A = Cross section area of specimen (mm²)

(b) The percentage of elongation at break

The percentage elongation at break was calculated from Equation 4.2.

$$\text{Elongation at break (\%)} = \frac{(l - l_0) \times 100}{l_0} \quad (4.2)$$

Where

l = The distance between the gauge marks at break (mm)

l₀ = The initial gauge length (mm)

4.4.2.2 Tear strength

Tear strength was carried out by using a universal testing machine (Instron 5569). Samples of appropriate shape were punched out from the molded sheet in the longitudinal direction and transverse direction. The sample was a razor-nicked test piece with a crescent shaped according to Die B (ASTM D624 and ISO 34). The crescent shaped (Die B) is shown in Figure 4.2. The rate of jaw separation was of 500 mm/min was used with load cell 1 kN. Mean value of at least 6 specimens as determined.

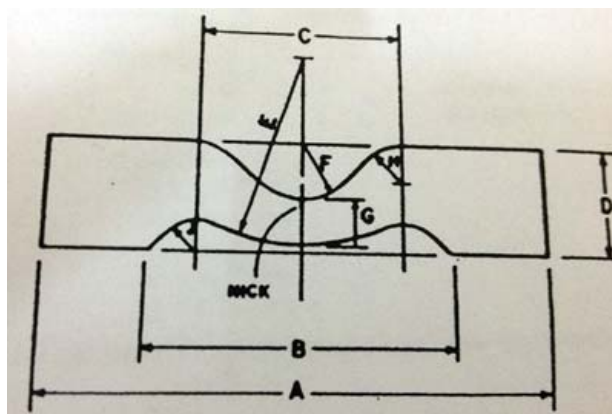


Figure 4.2 Crescent test piece die (Die B)

Tear strength was calculated by following Equation 4.3.

$$\text{Tear strength} = F/d \quad (4.3)$$

Where

F = The maximum force (N)

d = The mean thickness of each test piece (mm)

4.4.2.3 Hardness

The hardness of composite sheets was determined as indentation hardness using a durometer type A (Shore A) (Wallace, H17A) according to ISO 7619. The hardness specimen with a thickness at least 0.6 mm.

4.4.3 Abrasion resistance

The abrasion loss of composites was observed by using a rotary drum abrader (Zwick Model 6102). The samples are cylindrical in shape with a diameter of 16 ± 0.2 mm and minimum thickness of 6 mm (ASTM D5963, ISO 4649). Mean value of at least 3 specimens was determined. Abrasion loss was calculated by following Equation 4.4.

$$A_A = \frac{\Delta m_t \cdot S_0}{d_t \cdot S} \quad (4.4)$$

Where

A_A = abrasion loss in mm^3

Δm_t = mass loss of the test piece in mg

d_t = density of the test rubber in mg/m^3

S_0 = “normal abrasiveness” = 200 mg

S = abrasiveness in mg

4.4.4 Dynamic mechanical thermal analysis (DMTA)

The dynamic mechanical thermal analysis was carried out by Dynamic mechanical analyzer (DMA) (Q800, TA Instrument) with bending mode. The temperature range used to determine the dynamic properties was from -100 to 140 °C,

at a heating rate of 5°C/min, at frequency of 10 Hz and amplitude of 50 μm. The sample test specimens were about 30 mm length, 5 mm width and 1 mm thickness.

4.4.5 Water absorption

Water absorption of San/PALF composites was observed by immersion of composites specimen at 1, 7, 14, 31 days in distilled water. The percentage of water absorption was calculated by following Equation 4.5.

$$\% \text{Water absorption} = \frac{W_f - W_i}{W_i} \times 100 \quad (4.5)$$

Where

W_i = initial weight of the sample before immersion

W_f = final weight of the sample after immersion in water for a predetermined time.

CHAPTER V

RESULTS AND DISCUSSION

In this work, the results are presented in three parts. For the first part, the effect of compression moulding temperature (175°C and 195°C) and various PALF content on mechanical properties and morphology of Santoprene composites are presented. The second part deals with the effect of compatibilizer (MAPP and MASEBS) on mechanical properties of San/PALF composites. In the last part, the effect of PALF surface modifications on tensile properties of San/PALF composites is reported.

Part I: The effects of Santoprene orientation.

Due to Santoprene is thermoplastic elastomer which consists of dispersion phase of ethylene-propylene-diene monomer (EPDM rubber) in matrix polypropylene (PP) as the continuous phase. It is well known that chain orientation in PP influenced their mechanical properties. In this part concentrated the effect of compression moulding temperature and effect of PALF loading on San/PALF composites.

5.1 The effect of Santoprene orientation on San/PALF composites.

In this study, the effect of matrix orientation on Santoprene composites were observed by optical microscope (OM) and wide-angle x-ray scattering (WAXs). The effect of compression temperature (175°C and 195°C) and the effect of addition PALF on San/PALF composites were investigated.

5.1.1 The orientation of PALF in prepreg

The preferred orientation of PALF in San/PALF prepreg is shown in Figure 5.1. It can be seen that PALF in the prepreg is aligned in the direction of pulling out of the two-roll-mill machine. This shows that the prepreg of aligning PALF in the San/PALF prepreg have been carried out successfully.

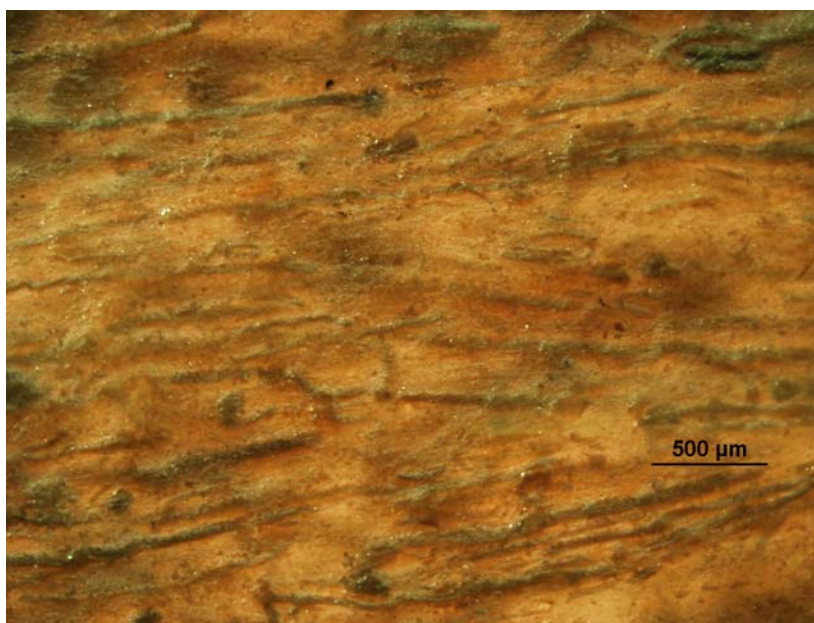


Figure 5.1 Optical micrograph of solvent washed San15PALF prepreg displaying highly aligned fibers.

5.1.2 WAXs of Santoprene composites

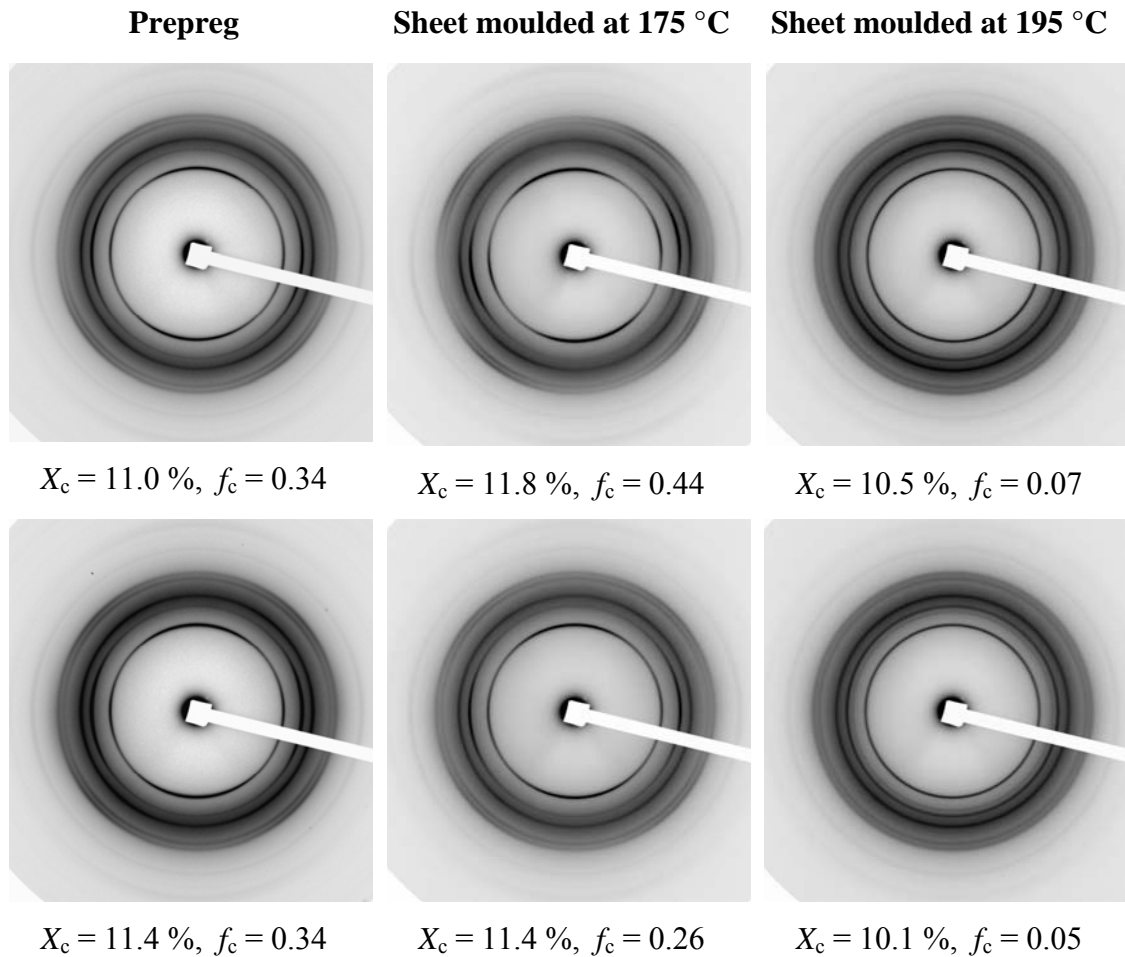


Figure 5.2 WAXS patterns of San0PALF (top row) and San9PALF (bottom row) prepreps and compressed sheets. Numbers under each pattern indicates sample's crystallinity (X_c) and orientation function (f_c) of polypropylene phase in the matrix.

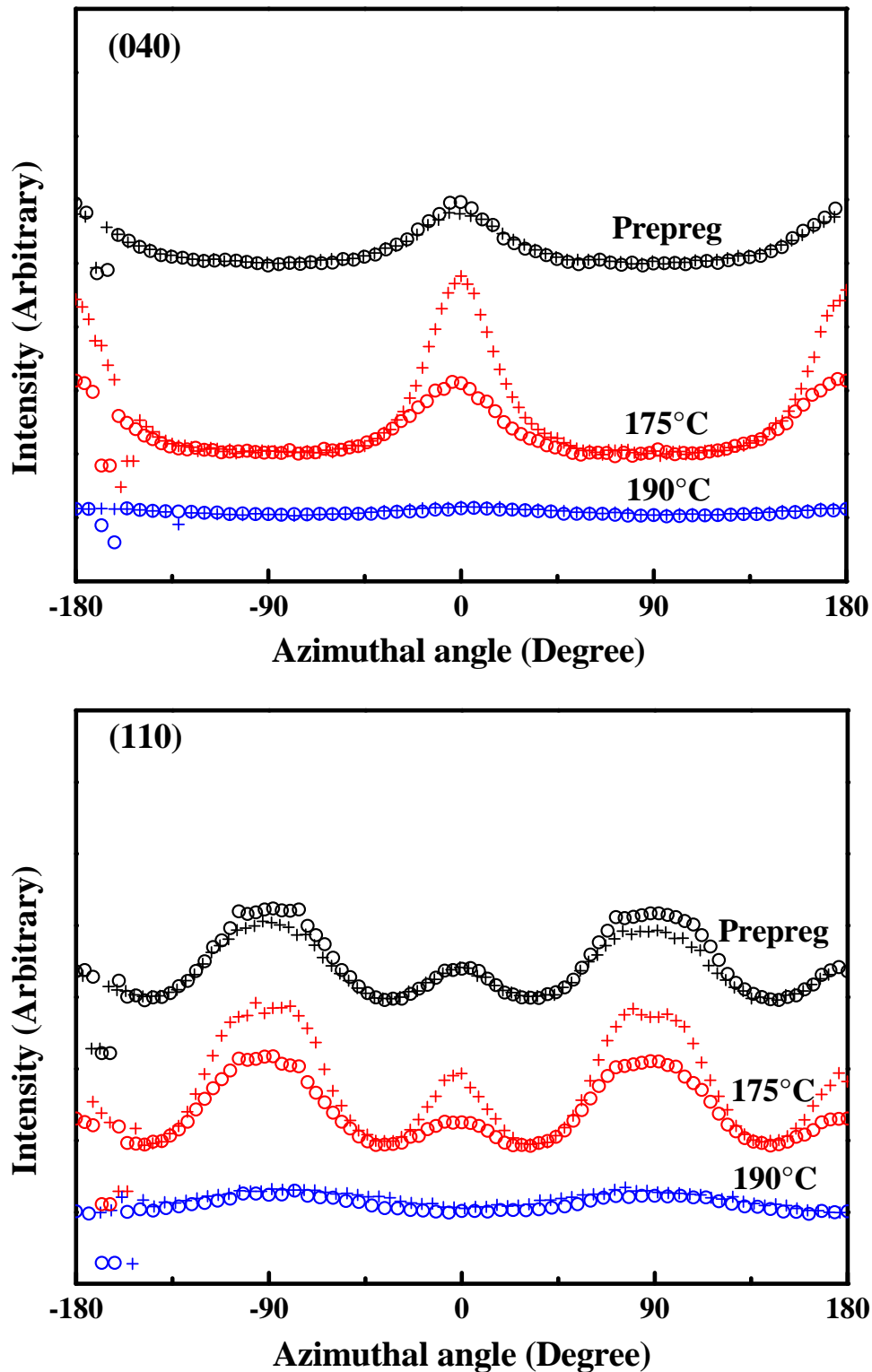


Figure 5.3 Azimuthal scan of the (040) (top) and (110) (bottom) reflections of the WAXS patterns in Fig. 8 for San0PALF (+) and San9PALF (O) prepregs and sheets compressed at 175 and 195 °C

From Figure 5.2 shows WAXS patterns of San0PALF and San9PALF prepreg and compressed sheet compressed at 175°C and 195°C. Figure 5.3 displays azimuthal scans of the (040) and (110) reflections of WAXS patterns in Figure 5.2. It can be seen that San0PALF prepreg and San9PALF prepreg show matrix orientation. The reflections seen in the patterns belong to PP phase in Santoprene rubber. The compressed sheet for compressed at 175°C shows matrix orientation while the compressed sheet at 195°C does not. So, it can be summarized that at compression temperature of 175°C, Santoprene matrix can be flow and fuse to form composites sheet but chain relaxation is slow to relax within compression time. The composites sheet compressed at 195°C, chain had more energy and together with the lower matrix viscosity, chain relaxation easily from composites within compression time [28].

5.2 The effect of compression moulding temperature and various PALF contents on mechanical properties of San/PALF composites.

In this study, the effect of compression temperature (175°C and 195°C) and the effect of PALF loading on tensile properties, tear strength, hardness and abrasion resistance of San/PALF composites were investigated.

5.2.1 Tensile properties

The stress-strain curves of San/PALF composites with various PALF contents at low compression temperature (175°C) compared at high compression temperature (195°C) are shown in Figure 5.4. The effect of Santoprene orientation are shown in the San/PALF composites at compressed with low temperature (175°C) can be seen from the neat Santoprene and San/PALF composites with less PALF content (3-5 wt.%). The elongation of neat Santoprene at low compression temperature (175°C) were lower than that of neat Santoprene at high compression temperature (195°C) because of Santoprene memories orientation in the system. In the longitudinal directions, stress is increased sharply with increasing of PALF content indicated on both compression temperatures. On the other hand, the extension decreased. At 9 and 15 wt.%, yielding-like behavior was observed. The yield-like behavior is not a yield point when semi-crystalline polymers deformed but is a result

of fiber debonding. In the transverse direction, PALF content shows no significant effect on the shape except lower extension.

Compression temperature at 175°C

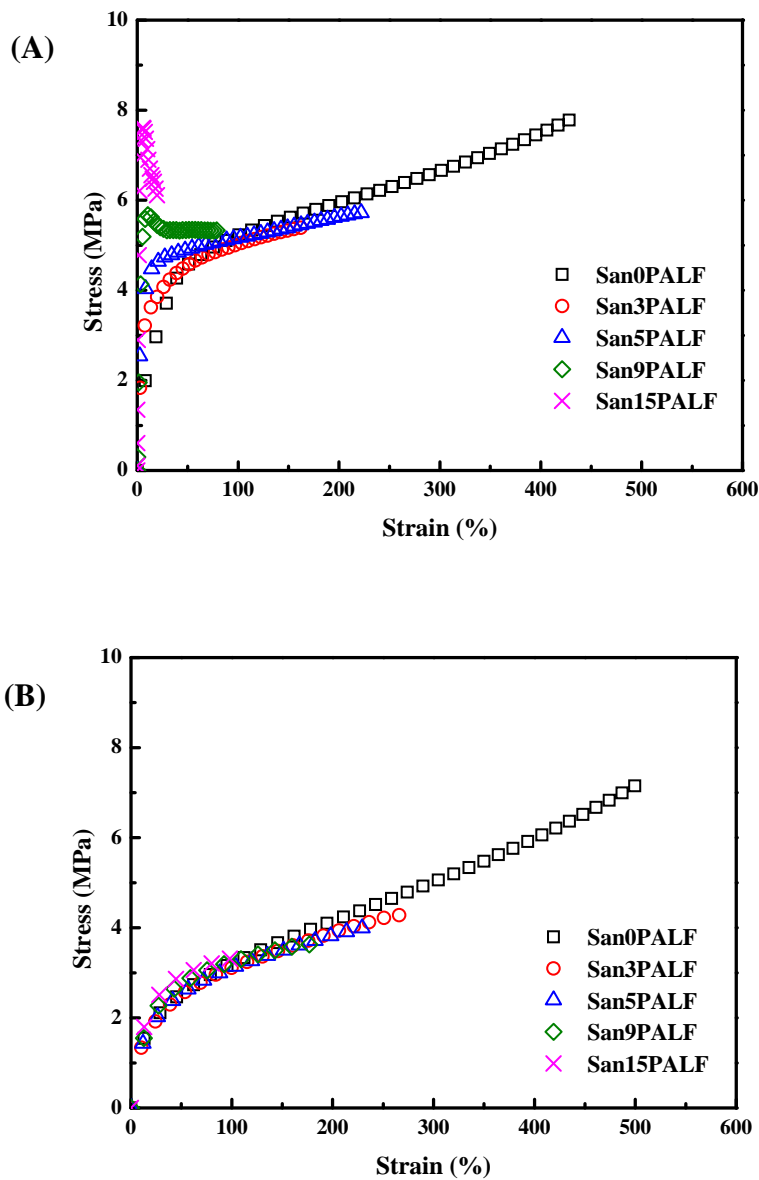


Figure 5.4 Stress-strain curves of San/PALF composites with various PALF contents in the longitudinal direction (A) and Transverse direction (B).

Compression temperature at 195°C

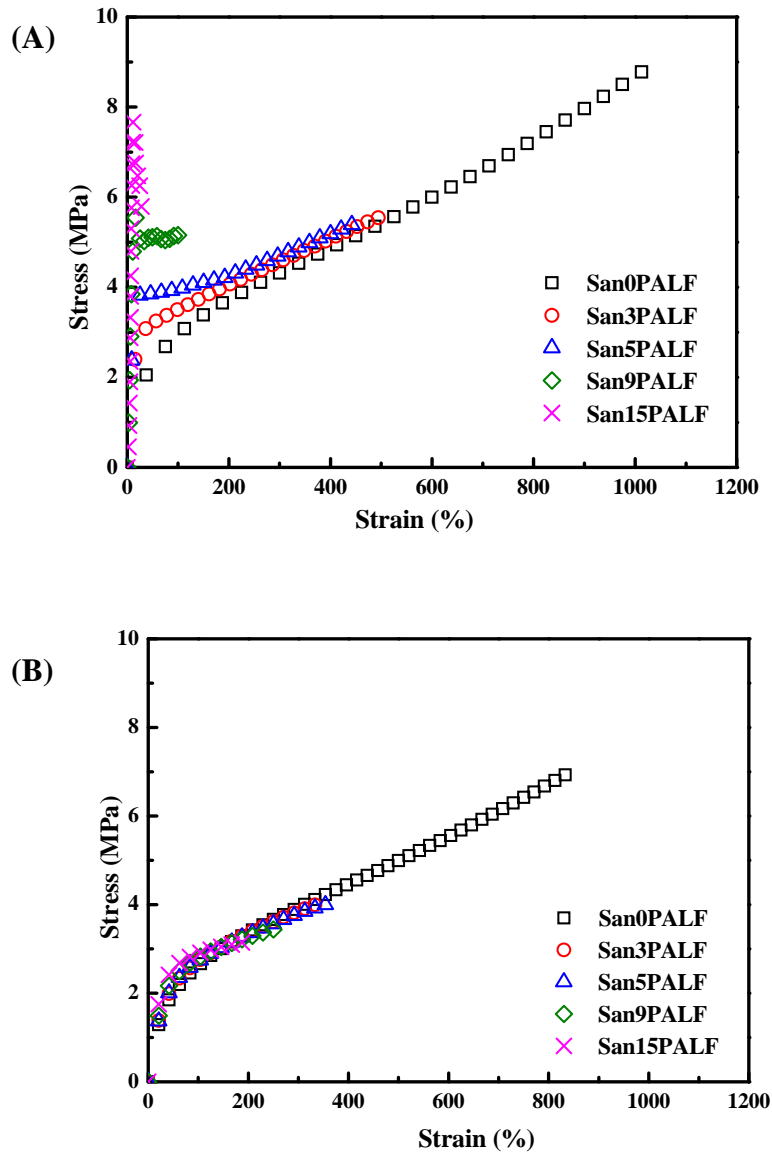


Figure 5.4 Stress-strain curves of San/PALF composites with various PALF contents in the longitudinal direction (A) and Transverse direction (B). (cont.)

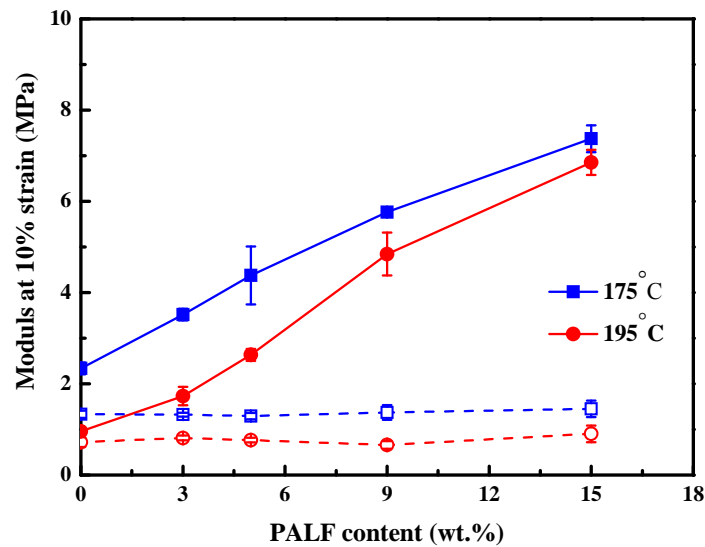


Figure 5.5 Modulus at 10% strain of composites containing different amounts of PALF compression moulded at 175°C and 195°C. (Closed symbols represent longitudinal direction and opened symbols transverse direction).

From the results shown in Figure 5.5, it is seen that the modulus at 10% strain of San/PALF composites containing different amounts of PALF compressed at 175°C and 195°C in the longitudinal and transverse directions. In longitudinal direction, the modulus at 10% strain increased with increasing PALF contents for both compression temperatures. It was found that composites compressed at 175°C modulus at 10% strain were better than those compressed at 195°C in both directions. The modulus of composites compressed at 175°C with 15 wt.% PALF content was improved from 2 MPa to 7.5 MPa as well as the composites compressed at 195°C with the same PALF content was improved from 1 MPa to 6.5 MPa. No significant difference in modulus the transverse direction for both compression temperatures is observed.

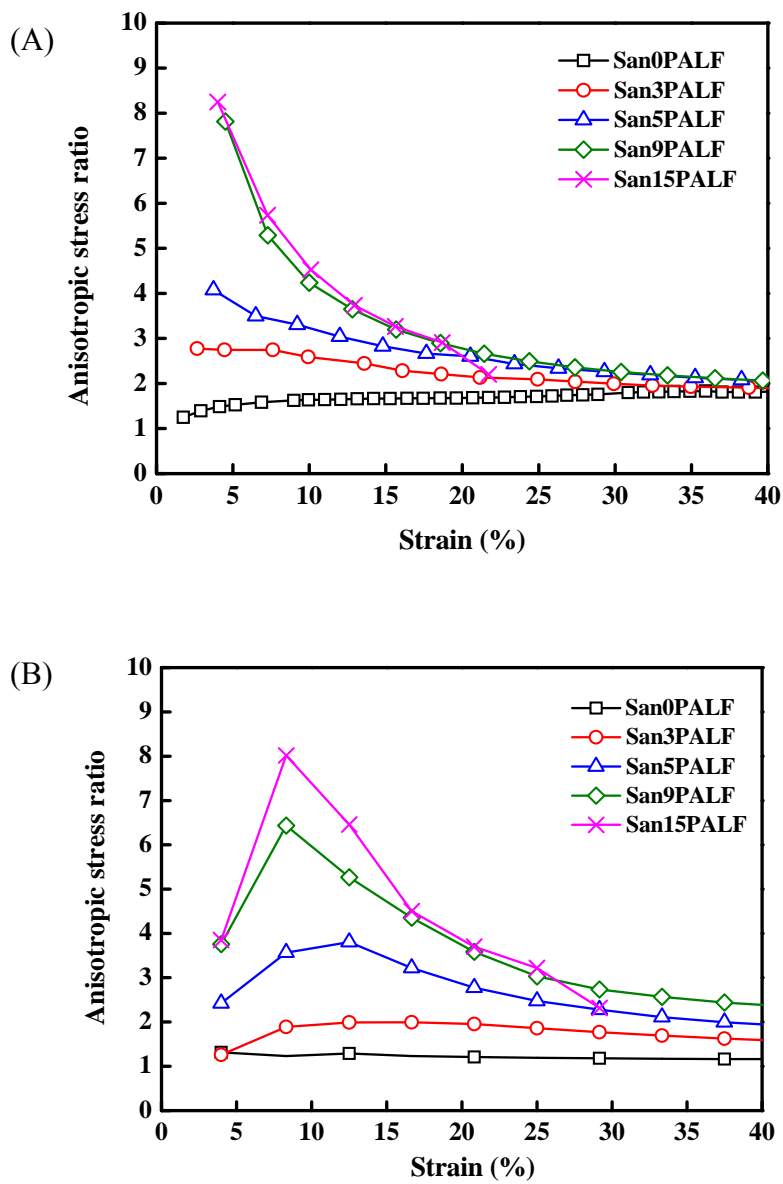


Figure 5.6 Anisotropic stress ratios in low strain region of composites containing different amounts of PALF compression moulded at 175°C (A) and 195°C (B).

Figure 5.6 displays stress ratio anisotropy in low strain region of composites containing different amount of PALF compression temperature at 175°C and 195°C. It was found that stress ratio anisotropy of neat Santoprene increases with increasing strain at 175°C (Figure 5.6-A). The stress ratio anisotropy of San/PALF composites starts from the maximum stress ratio anisotropy values at the low strain and drops when increasing strain. At 195°C (Figure 5.6-B), less change in the stress

ratio anisotropy of neat Santoprene is observed with increasing strain. For all San/PALF composites, the stress ratio anisotropy increases with increasing strain. At 9 and 15 wt.% PALF, maximum stress ratio anisotropy is observed at values about 8% strain.

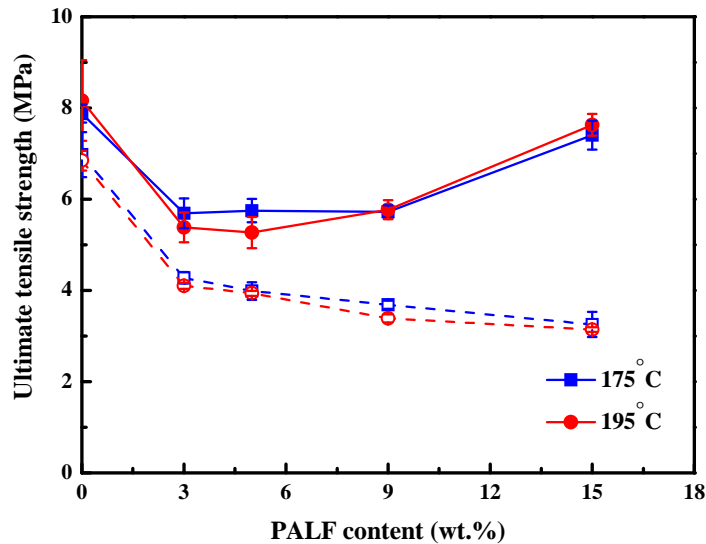


Figure 5.7 Ultimate tensile strength of composites containing different amounts of PALF compression moulded at 175°C and 195°C. (Closed and opened symbols represent longitudinal and transverse direction).

Figure 5.7 shows the ultimate tensile strength of composites containing different amounts of PALF compressed at 175°C and 195°C in longitudinal and transverse directions. It can be seen that ultimate tensile strength of neat Santoprene at both compression temperatures in the two directions are nearly the same. In longitudinal direction, the ultimate tensile strength decreases sharply with increase PALF loading up to 9 wt.% PALF and then shows a slight increase for composites containing 15 wt.% PALF at two compression temperature. In transverse direction, the ultimate tensile strength decrease with increasing PALF loading for both compression temperatures. The ultimate tensile strength at two compression temperature in longitudinal direction was better than that transverse direction. The decreased in ultimate tensile strength at low PALF loading is due to the amount of

fiber is not enough to restrain the matrix. High matrix strains result at relatively low composite stress [3].

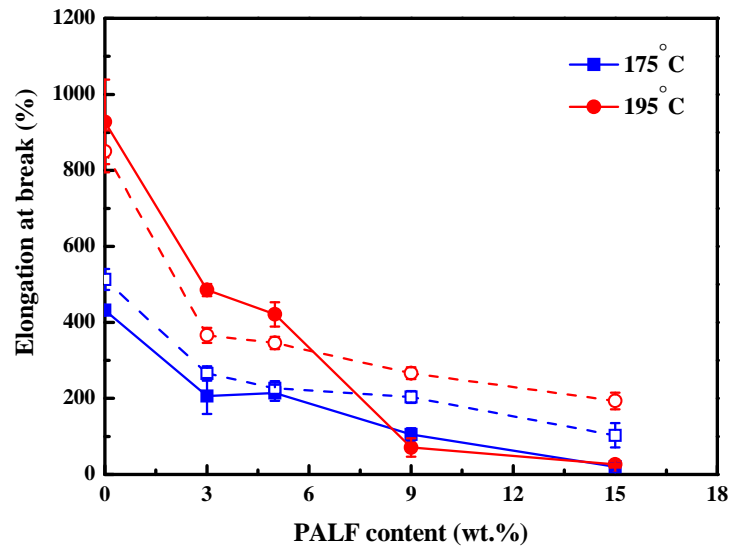


Figure 5.8 Elongation at break of composites containing different amounts of PALF compression moulded at 175°C and 195°C. (Closed and opened symbols represent longitudinal and transverse direction).

Figure 5.8 displays elongation at break of composites containing different amounts of PALF compression temperature at 175°C and 195°C in longitudinal and transverse directions. It is found that the elongation at break decreases sharply with increasing PALF loading at both compression temperatures. The elongation at break of composites compression temperature at 195°C is higher than that of the composites compression temperature at 175°C in both directions. The drop in elongation at break with increases amount of fiber is due to the poor interfacial adhesion between fiber and matrix [24].

5.2.2 Tear strength

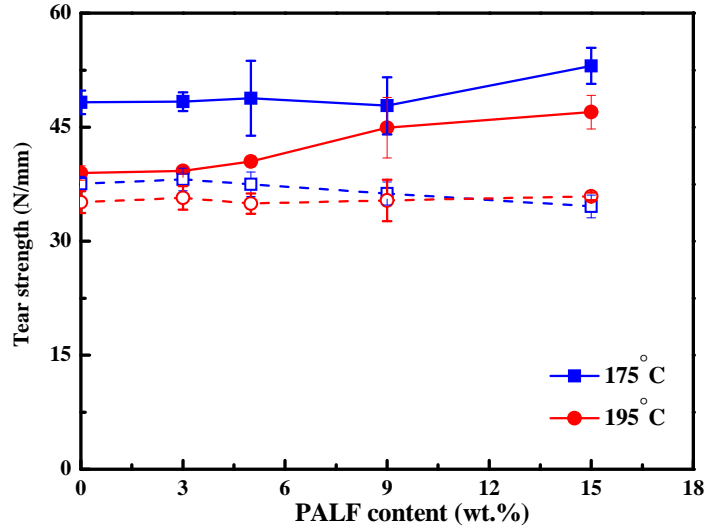


Figure 5.9 Tear strengths of composites containing different amount of PALF compression moulded at 175°C and 195°C. (Closed and opened symbols represent longitudinal and transverse direction).

Tear strength of the composites containing different amount of PALF compression moulded at 175°C and 195°C in two directions are presented in Figure 5.9. In longitudinal direction, the tear strength of composites compression temperature at 175°C are not changed with PALF loading up to 9 wt.% PALF and then the tear strength shows a slightly increase for composites containing 15 wt.% PALF. The composites compression temperature at 195°C in longitudinal direction showed the lowest values of tear strength compared to that of composites compression temperature at 175°C. In transverse direction, no significant change in tear strength with addition of PALF for both compression temperatures is observed. The tear strength in longitudinal direction is higher than that in transverse direction. This is because the fibers hinder crack propagation of matrix and the tear strength to become higher [25].

5.2.3 Hardness

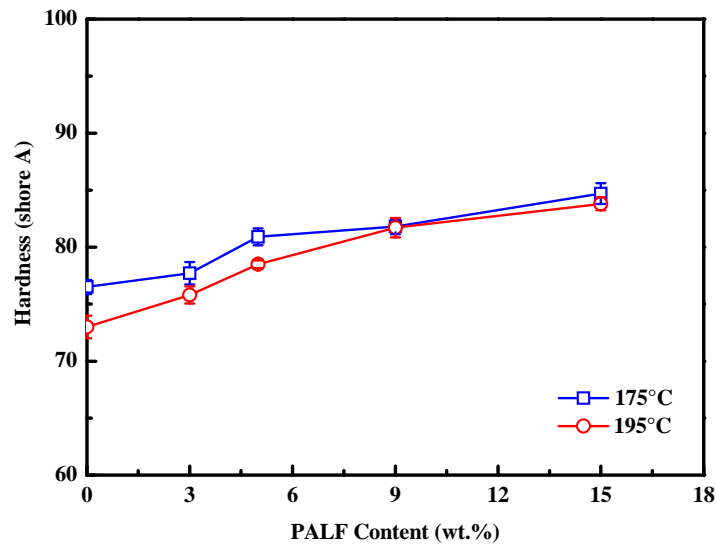


Figure 5.10 Hardness of composites containing different amount of PALF compression moulded at 175°C and 195 °C.

Figure 5.10 shows the hardness of composites containing different amounts of PALF compressed at 175°C and 195°C. It is found that the hardness increases with increasing PALF loading in two compression temperatures. The hardness of composites compressed at 175°C shows slightly higher value than that at compressed 195°C.

5.2.4 Abrasion resistance

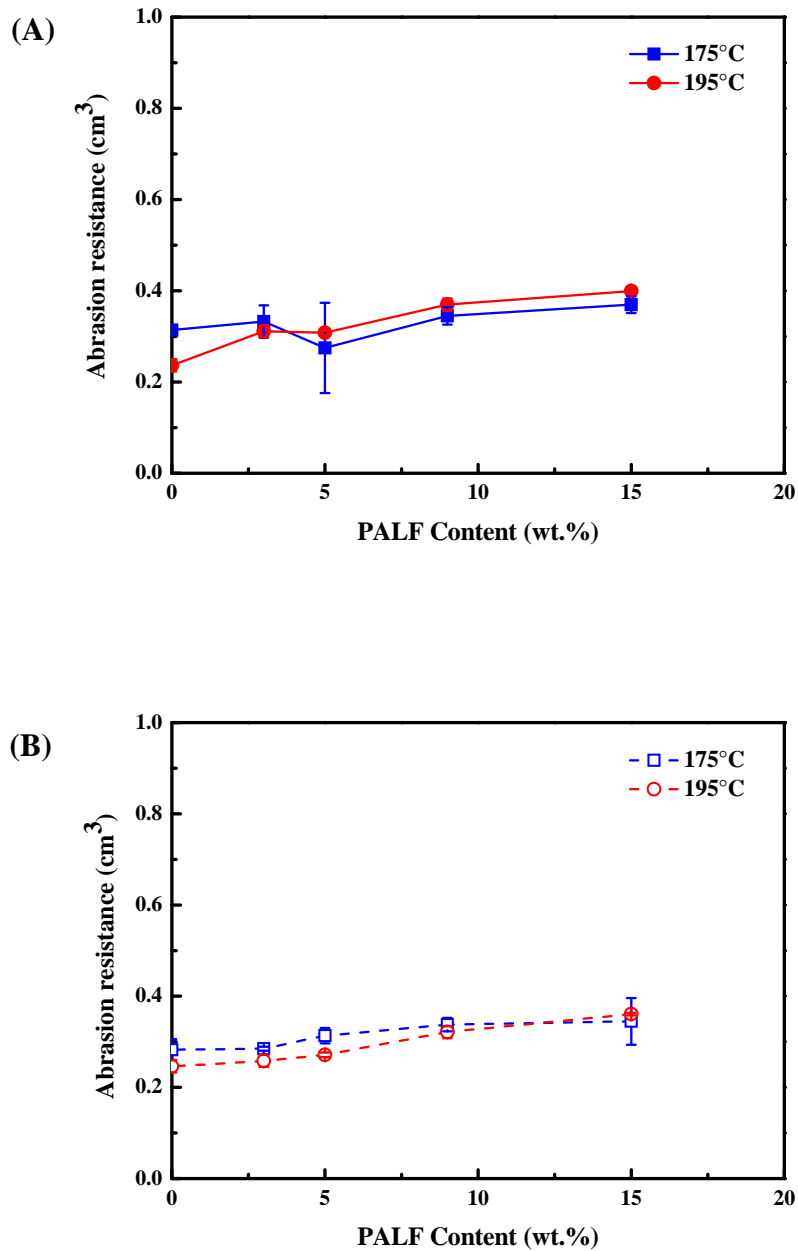


Figure 5.11 Abrasion resistance of composites containing different amounts of PALF compression moulded at 175°C and 195°C in longitudinal direction (A) and transverse direction (B).

Figure 5.11 displays abrasion resistance of composites containing different amount of PALF compressed at 175 and 195 °C in longitudinal and transvers

directions. In longitudinal direction (Figure 5.11-A), the abrasion resistance slightly increases with increasing amount of PALF for two compression temperatures. The abrasion resistance of neat Santoprene compressed at 175°C is higher than that at 195°C. With addition PALF up to 5 wt.% ,the abrasion resistance value of composites compressed at 175°C is lower than that composites compressed at 195°C. In transverse direction (Figure 5.11-B), the abrasion resistance of the composites compressed at 175°C is higher than that composites compressed at 195°C.

5.3 Fracture surface of San/PALF composites.

The interfacial adhesion between fiber and matrix was investigated by scanning electron microscopy (SEM). The SEM image of cryogenic and tensile fractured surfaces for San/PALF composites are shown in Figures 5.12 and 5.13.

Cryogenic and tensile fractured surface for neat Santoprene compressed at 175° and 195°C are shown in Figure 5.12. Neat Santoprene for cryogenic and tensile fracture surface compressed at 175°C and 195°C are show smooth and flat fracture surfaces. This is typical fracture surface of brittle materials. This indicates that compression temperatures show less effect on the fracture surface at temperature below T_g . Moreover, tensile fracture does not show any sign of large scale yielding. This is typical fracture surface of rubber.

Figure 5.13 shows the cryogenic and tensile fractured surfaces of San9PALF sheets compressed at 175°C and 195°C. The composites of San/9PALF for cryogenic and tensile fracture have a three points to discuss, i.e. surface matrix fracture surface, number of pull-out fiber, length of pull-out fiber. The pull-out fiber can be seen in both cases. The cryogenic fracture composites shows shorter pull-out fiber as tensile facture composites shows more fiber breakage and fiber pull-out. At low temperature as cryogenic fracture, the Santoprene matrix is glassy and did not deform. And at room temperature as tensile fracture, the Santoprene matrix is rubbery and deform.

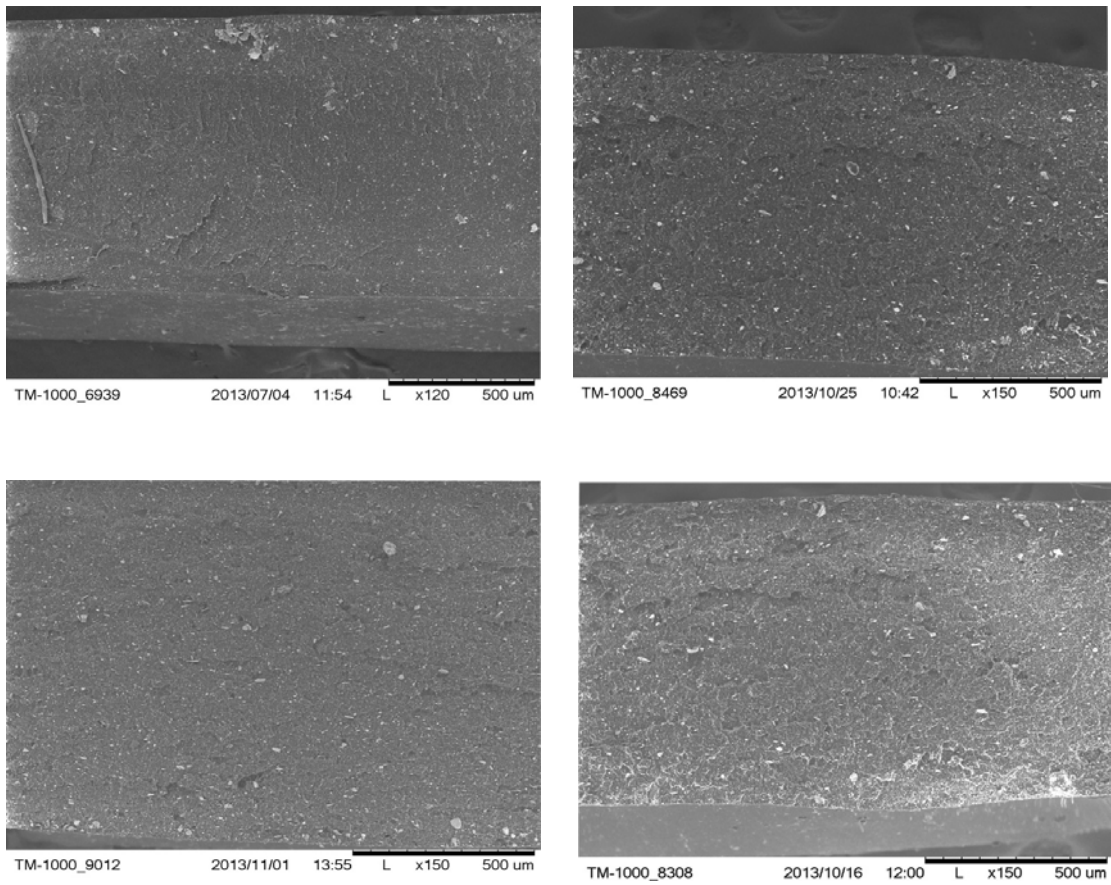


Figure 5.12 SEM images of cryogenic (top row) and tensile (bottom row) fractured surfaces of San0PALF sheets compressed at 175 °C (left column) and 195 °C (right column).

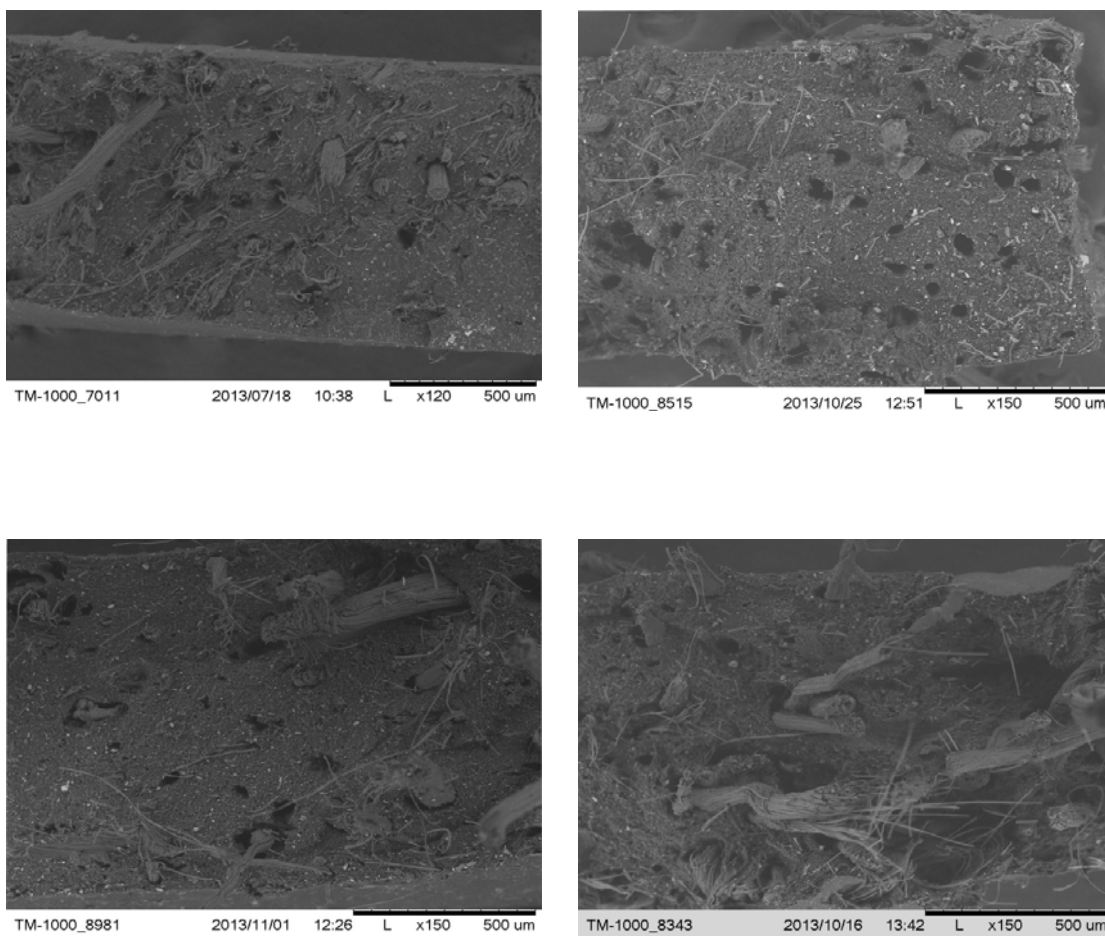


Figure 5.13 SEM images of cryogenic (top row) and tensile (bottom row) fractured surfaces of San9PALF sheets compressed at 175 °C (left column) and 195 °C (right column).

5.4 Dynamic mechanical properties of San/PALF composites.

The results of dynamic mechanical properties of San/PALF composites with different amount of PALF compression moulded at 175°C (A) and 195°C (B) are presented in Figures 5.14 and 5.15 as the variation of storage modulus and tan delta with temperature. All materials exhibit a sharply drop in storage modulus at around -50°C for two compression temperatures at 175°C and 195°C. The effect of PALF loading shows the stiffness at high temperature for both systems. It was found that storage modulus of San/PALF composites increased with increasing PALF loading for

two compression temperatures. Moreover, compression temperature slightly affect to the dynamic mechanical properties.

Figure 5.15 displays of $\text{Tan } \delta$ of composites containing different amount of PALF compression moulded at 175°C (A) and 195°C (B). The neat Santoprene shows the peaks at about -40°C presents glass transitions of the EPDM rubber and peaks at about 0°C attributed to glass transitions of PP part in Santoprene [24]. It is seen that $\text{tan } \delta$ peaks corresponding to EPDM parts decrease with increasing PALF loading at two compression temperatures. Whereas no significant change for T_g s of PP part in Santoprene is observed. The results indicate that the decreases of T_g is due to increase in chain mobility in EPDM rubber part [26].

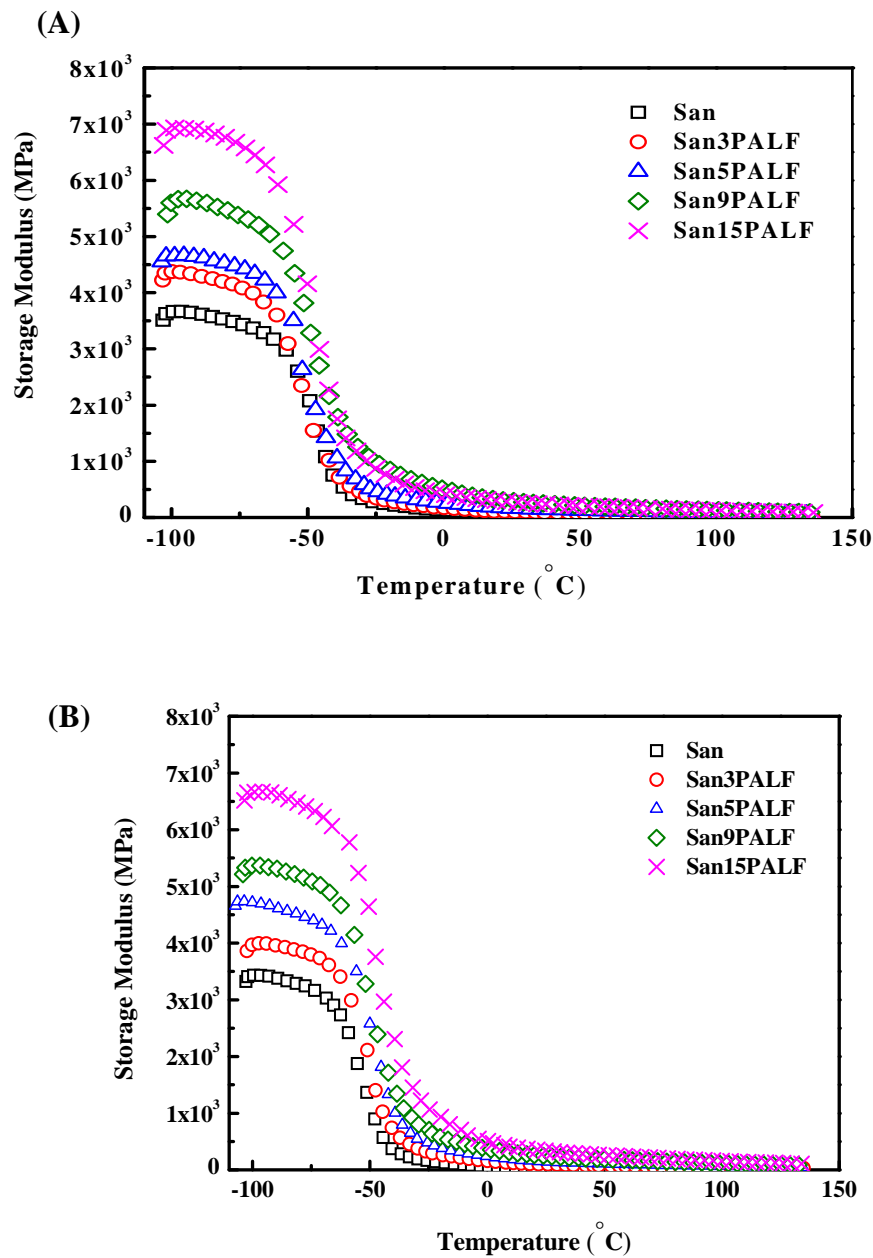


Figure 5.14 Dynamic storage modulus of composites containing different amount of PALF compression moulded at 175°C (A) and 195°C (B).

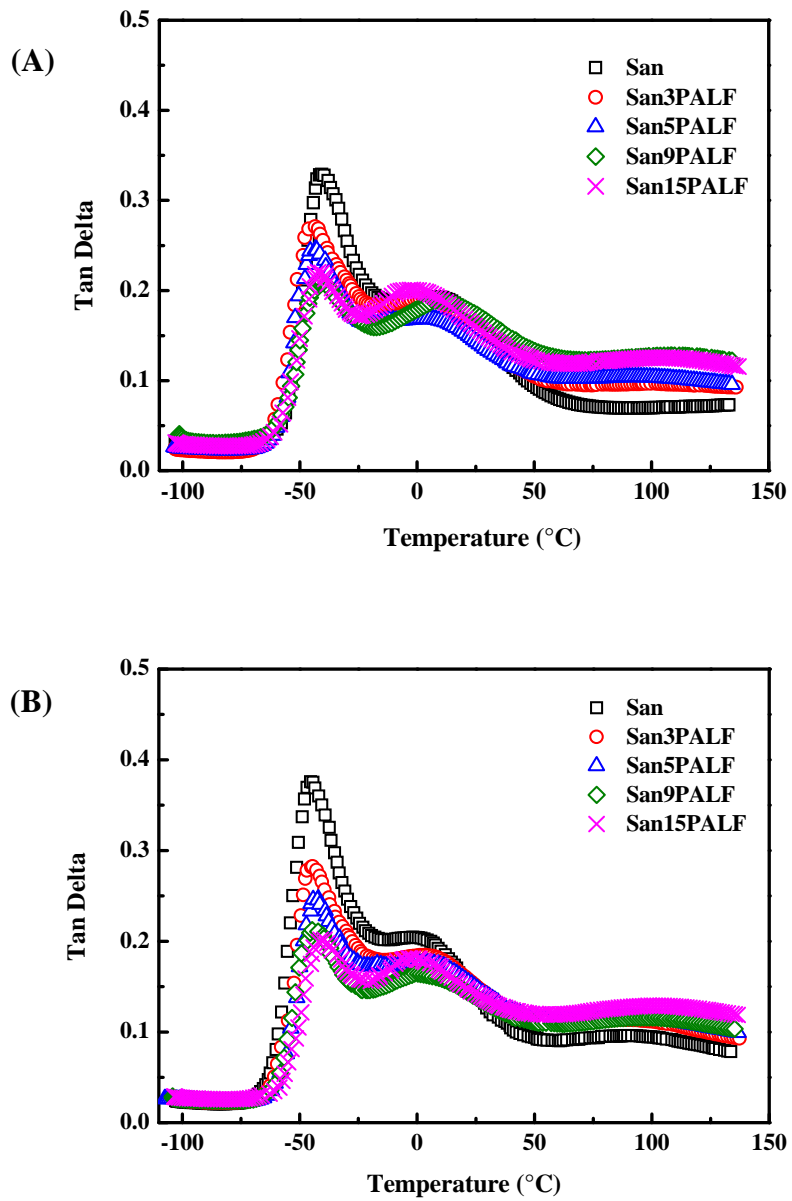


Figure 5.15 Tan Delta of composites containing different amount of PALF compression moulded at 175°C (A) and 195°C (B).

5.5 Water absorption of San/PALF composites.

The results of water absorption after immersion for 1, 7, 14 and 31 days of San/PALF composites with different amounts of PALF compression moulded at 175°C and 195°C are shown in Figure 5.16 and Table 5.1. It can be seen the composites compression at two temperatures show an increase in percentage of water absorption with increasing PALF loading and immersion times. This is due to that PALF contains lignin (lower hydrophobic) and has long and well fibrous structure resulting in easy reach of water into composites [27]. Moreover, compression temperature slightly affect to water absorption.

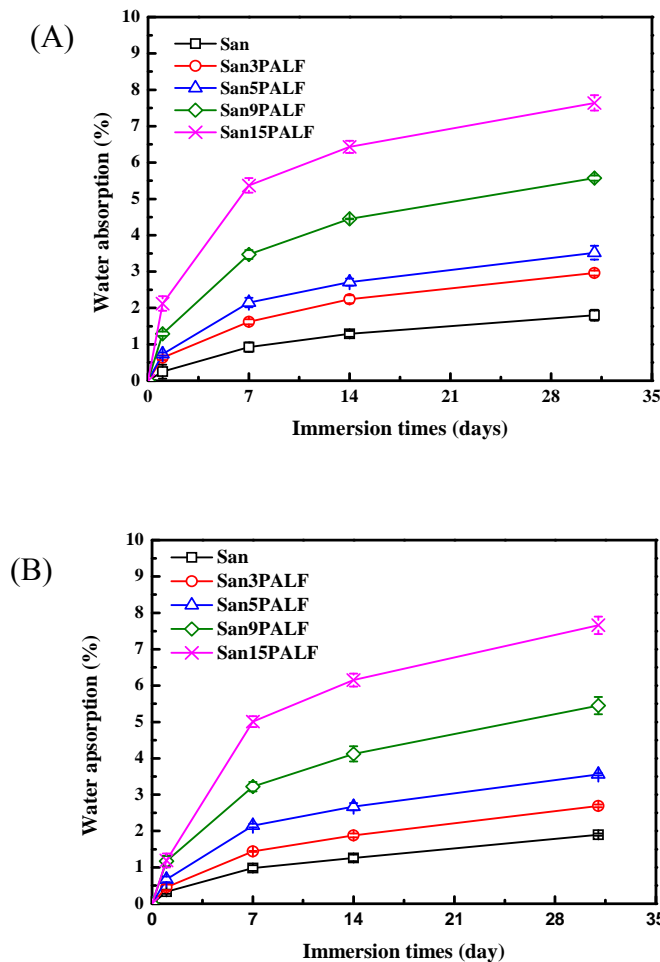


Figure 5.16 Water absorption of composites containing different amounts of PALF compression moulded at 175°C (A) and 195°C (B).

Table 5.1 Water absorption of composites containing different amounts of PALF compression moulded at 175°C and 195°C.

Sample	Water absorption (%)			
	1 day	7 days	14 days	31 days
Compressed at 175°C				
San0PALF	0.33 ± 0.06	0.98 ± 0.08	1.26 ± 0.09	1.90 ± 0.03
San3PALF	0.45 ± 0.08	1.44 ± 0.01	1.88 ± 0.05	2.69 ± 0.04
San5PALF	0.67 ± 0.08	2.15 ± 0.05	2.67 ± 0.10	3.56 ± 0.03
San9PALF	1.17 ± 0.15	3.22 ± 0.13	4.12 ± 0.21	5.45 ± 0.24
San15PALF	1.19 ± 0.19	5.01 ± 0.15	6.15 ± 0.18	7.66 ± 0.24
Compressed at 195°C				
San0PALF	0.25 ± 0.19	0.92 ± 0.13	1.29 ± 0.08	1.80 ± 0.15
San3PALF	0.63 ± 0.06	1.62 ± 0.07	2.24 ± 0.11	2.96 ± 0.07
San5PALF	0.73 ± 0.04	2.15 ± 0.13	2.71 ± 0.10	3.52 ± 0.19
San9PALF	1.29 ± 0.06	3.47 ± 0.12	4.45 ± 0.10	5.57 ± 0.07
San15PALF	2.12 ± 0.20	5.37 ± 0.20	6.43 ± 0.17	7.64 ± 0.21

Part II: study of the effect of compatibilizers on properties of San/PALF composites

In this part, improvement of interfacial adhesion between Santoprene matrix and PALF by compatibility promotion was investigated. Normally, Santoprene thermoplastic rubber is hydrophobic but PALF natural fiber is hydrophilic. Therefore, the composites are expected to have poor interfacial adhesion. In this work were used two compatibilizers i.e., maleic anhydride grafted polypropylene (MAPP) and maleic anhydride grafted styrene-ethylene/butylene-styrene (MASEBS) were used for compatibility improvement of PALF with the Santoprene matrix.

5.6 The effect of compatibilizer on mechanical properties of San/PALF composites

In this study, the effects compatibilizers (MAPP and MASEBS) on tensile properties, tear strength, hardness and abrasion resistance of San/PALF composites were investigated.

5.6.1 Tensile properties

In this study, various amounts of compatibilizer from 0 to 1 times of PALF fiber were blended with Santoprene matrix at fixed 9 wt% PALF content. The longitudinal and transverse direction stress-strain curves of 9 wt% PALF-Santoprene composites (San9PALF) with different amounts of two compatibilizer shown in Figures 5.17 and 5.18.

Figures 5.17 A and B show longitudinal and transverse stress-strain curves of 9%wt PALF-Santoprene composites (San9PALF) containing MAPP and MASEBS, respectively. In the longitudinal direction, the stress increases sharply with the addition of both types of compatibilizers. By adding the compatibilizer with equal amount (1 times) of PALF loading, the stress of two compatibilizer systems is found to increase. In the transverses direction, the stress are increased when MAPP loading up to 1 times of PALF when compared to the corresponding uncompatibilized system.

On the contrary, composites the containing MASEBS compatibilizer system display higher stress with increasing MASEBS loading.

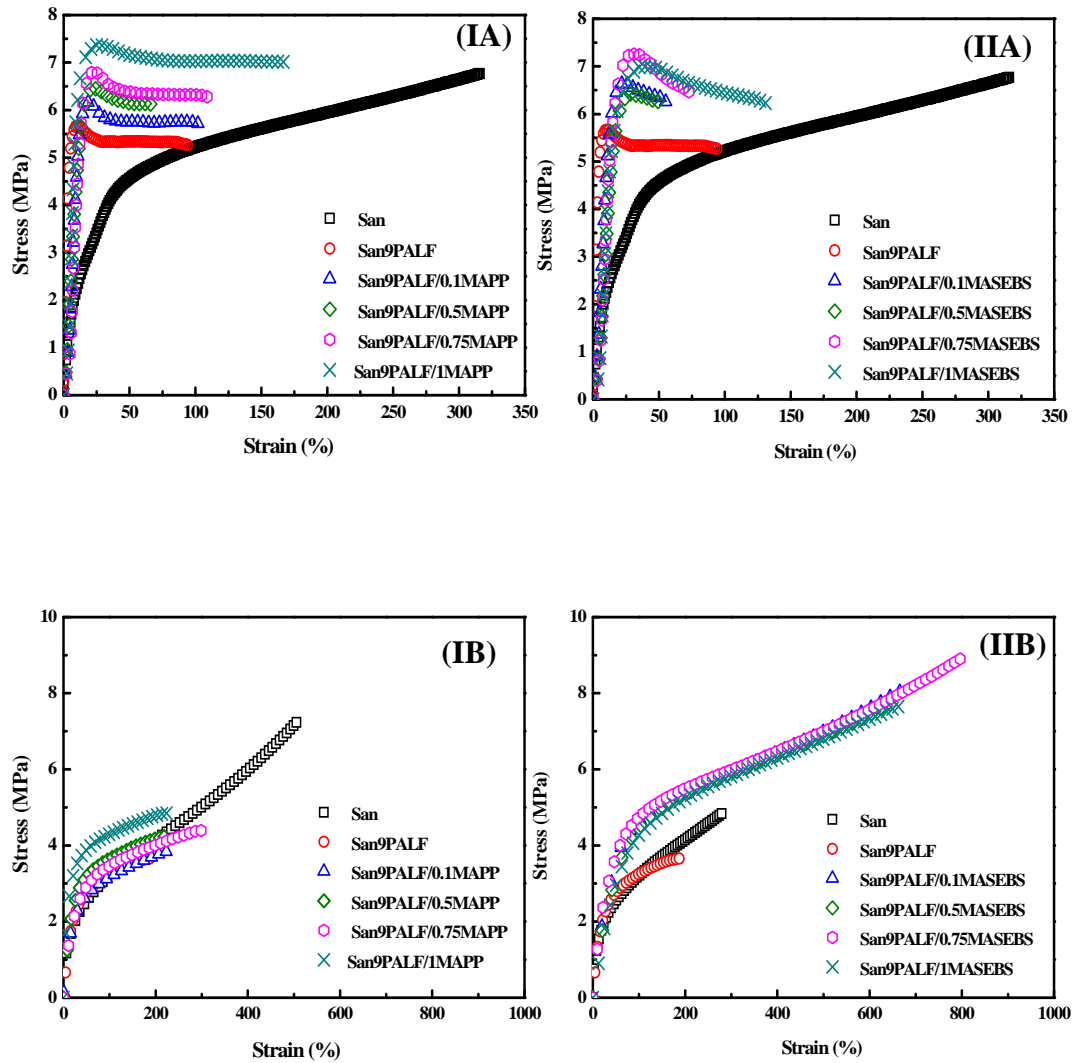


Figure 5.17 Stress-strain of San/9PALF composites with the presences of MAPP (column A) and MASEBS (column B) in the longitudinal direction (A) and transverse direction (B)

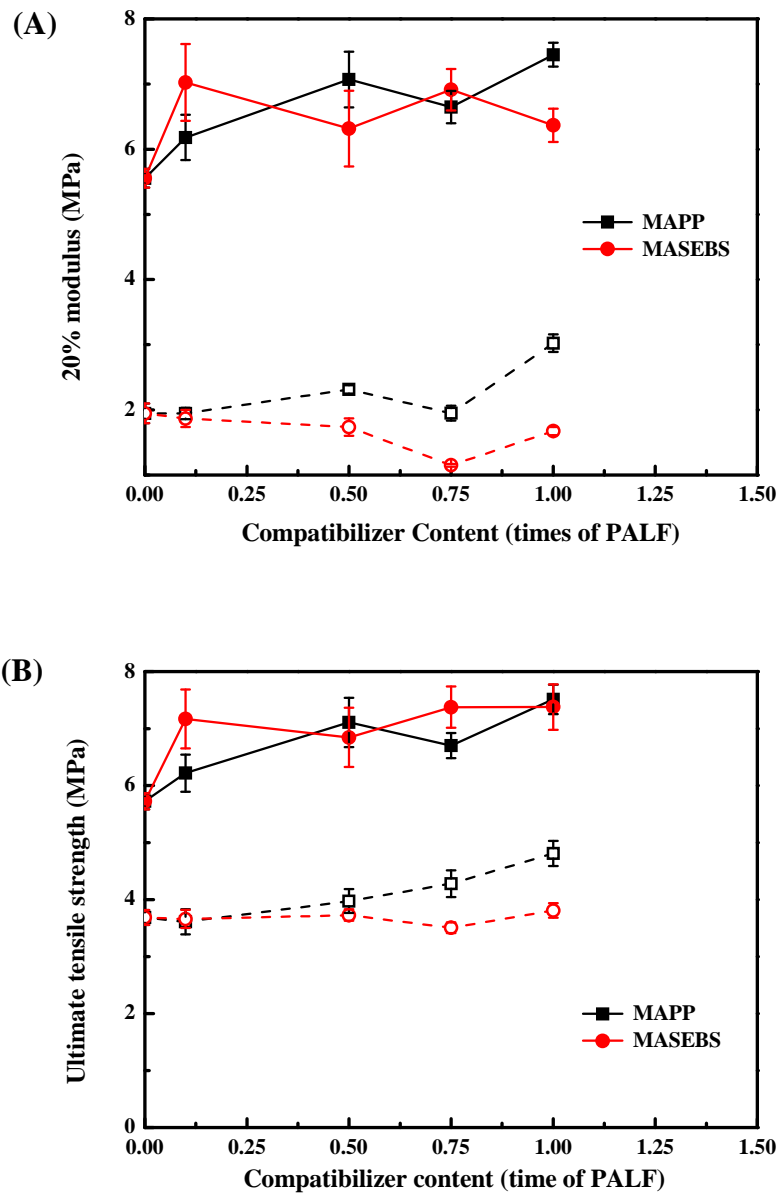


Figure 5.18 Effect of variation amounts of compatibilizers (MAPP and MASEBS) on tensile properties, (A) modulus at 20 % strain, (B) tensile strength (Closed opened symbols represent longitudinal and transverse direction, respectively).

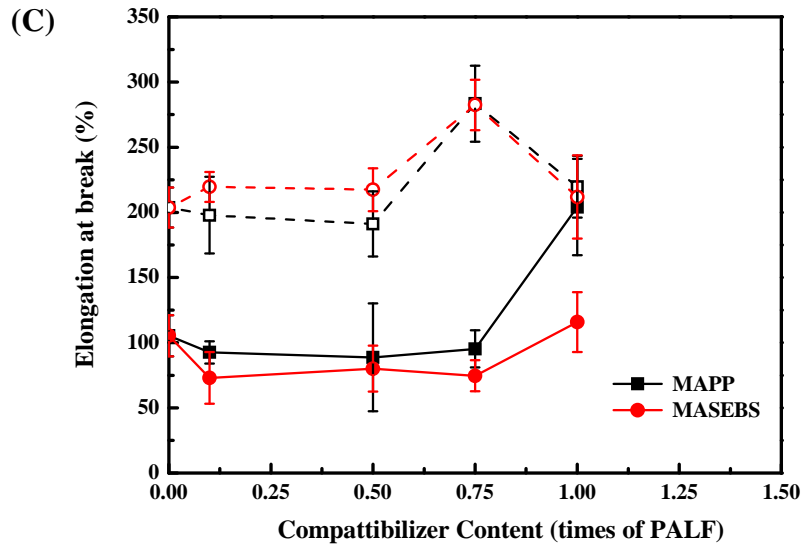


Figure 5.18 Effect of variation amounts of compatibilizers (MAPP and MASEBS) on tensile properties, (A) modulus at 20 % strain, (B) tensile strength and (C) elongation at break of San/9PALF composites. (Closed opened symbols represent longitudinal and transverse direction, respectively). (cont.)

Figure 5.18 shows that the 20% modulus (A), ultimate tensile strength (B) and elongation at break (C) of San/9PALF composites with various compatibilizer (MAPP and MASEBS) contents in longitudinal and transverse direction. It is seen that after strain modulus, ultimate tensile strength and elongation at break increase with increasing compatibilizer loading in both systems. This result can be observed in two directions. The composites containing MAPP are slightly stiffer than that of MASEBS. The increasing of these tensile properties can be attributed to the improvement of the interfacial adhesion between the PALF fiber and Santoprene matrix. This may be due to esterification reaction between hydroxyl groups of fiber and the maleic anhydride molecules of MAPP [16].

5.6.2 Tear strength

The results of tear strength of San/9PALF composites with different amounts of MAPP and MASEBS in the longitudinal direction are presented in Figures 5.19. It is seen that composites containing MAPP exhibit an improvement in tear

strength with increasing compatibilizer loading. This slight improvement in tear strength for the composites containing of MASEBS is also observed with increasing compatibilizer content up to 0.75 times of PALF. The SEBS composites shows slightly higher tear strength when compared to that of composites with MAPP. The increase in these properties can be attributed to the improvement of interfacial between the fiber and matrix.

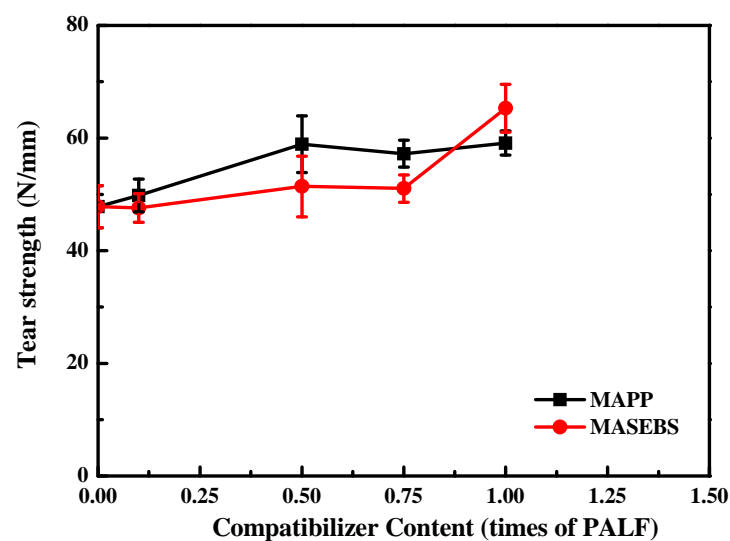


Figure 5.19 Longitudinal tear strength of San/9 PALF composites with the presence of different amount of MAPP and MASEBS.

5.6.3 Hardness

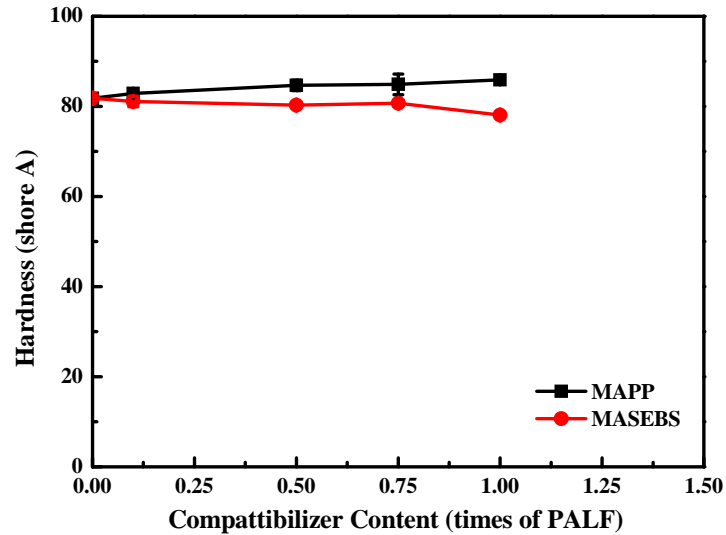


Figure 5.20 Longitudinal tear strength of San/9 PALF composites with the presence of different amount of MAPP and MASEBS.

Figure 5.20 displays hardness of containing different amount of MAPP and MASEBS in longitudinal direction. The hardness of composites containing MAPP show slightly increased with increasing of MAPP loading. In case of composites containing MASEBS, no significant effect on hardness is seen. The hardness of MAPP composites the compatibilizer loading show slightly higher value that of the MASEBS composites. It is due to PP phase in MAPP is more rigid than the SEBS phase in MASEBS composites.

5.6.4 Abrasion resistance

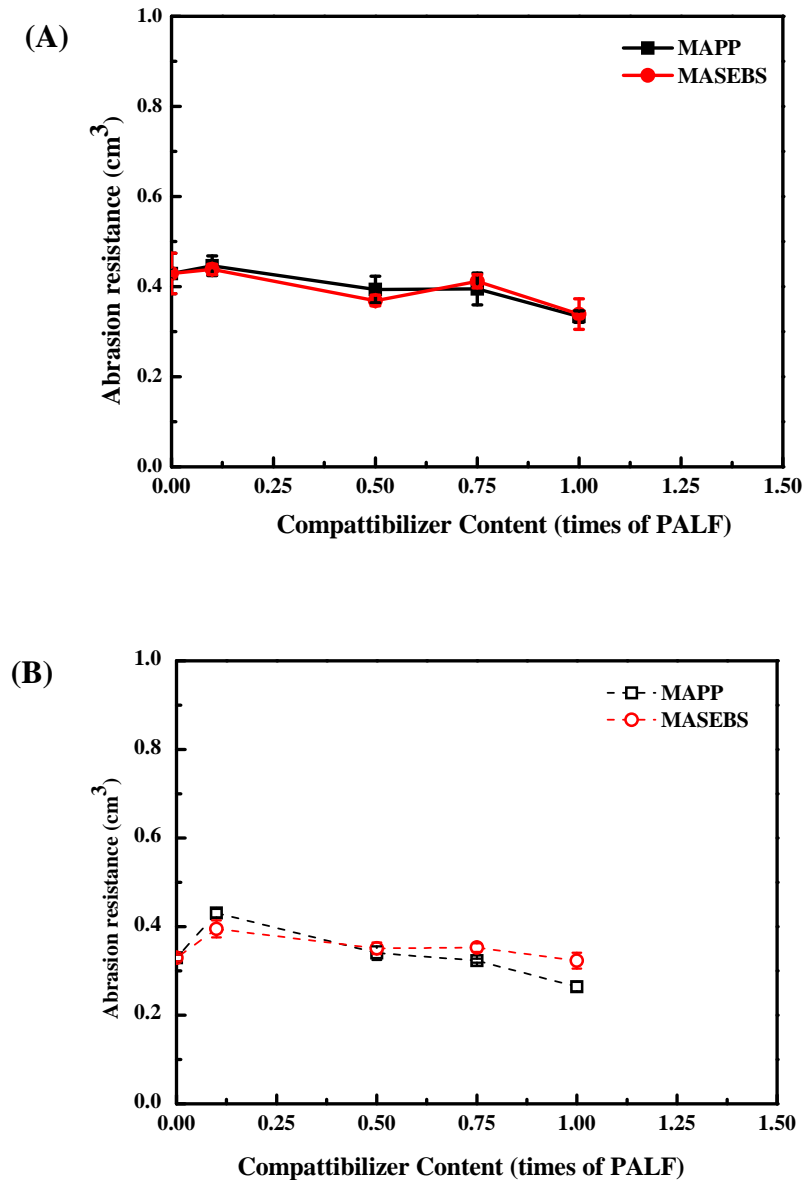


Figure 5.21 Abrasion resistances of San/9 PALF composites with different amount of MAPP and MASEBS in longitudinal direction (A) and transvers direction (B).

Figure 5.21 displays abrasion resistance of San/9PALF composites with different amount of MAPP and MASEBS in longitudinal direction and transverse directions. In longitudinal direction (Figure 5.21-A), the abrasion for the two systems resistance slightly decreased with increasing amount of compatibilizer. The abrasion resistance values of the two systems are nearly the same. In transverse direction

(Figure 5.21-B), the abrasion resistance of MASEBS composites increases with increasing MASEBS loading while the abrasion resistance of MAPP composites decrease with increasing MAPP loading. At a less amount of compatibilizer composites used MAPP is higher than composites used MASEBS but at a many amount of compatibilizer composites used MASEBS is higher than composites used MAPP.

5.7 Morphology

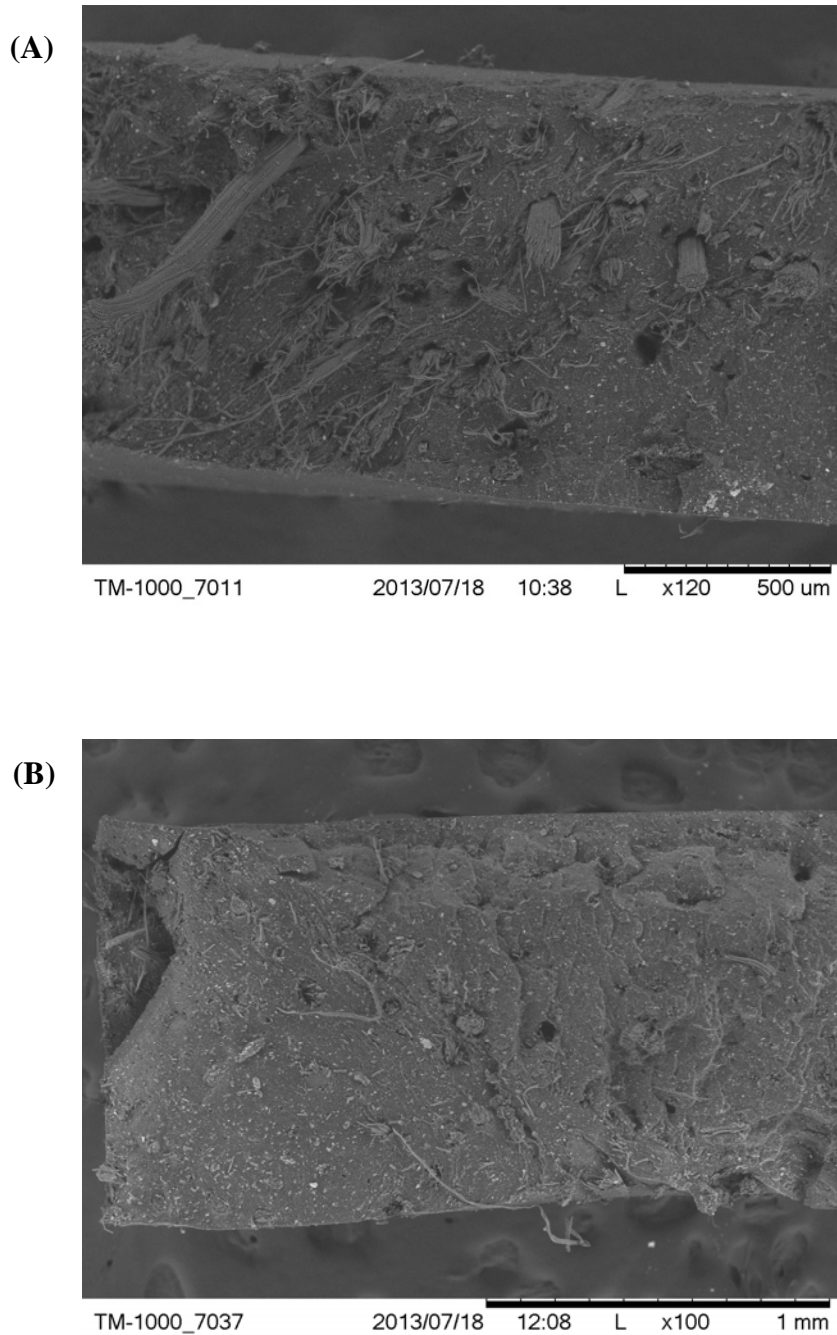


Figure 5.22 SEM image of cryogenic fractured surfaces of San9PALF composites (A), San9PALF/1 MASEEBS (B) and San9PALF/1MAPP (C).

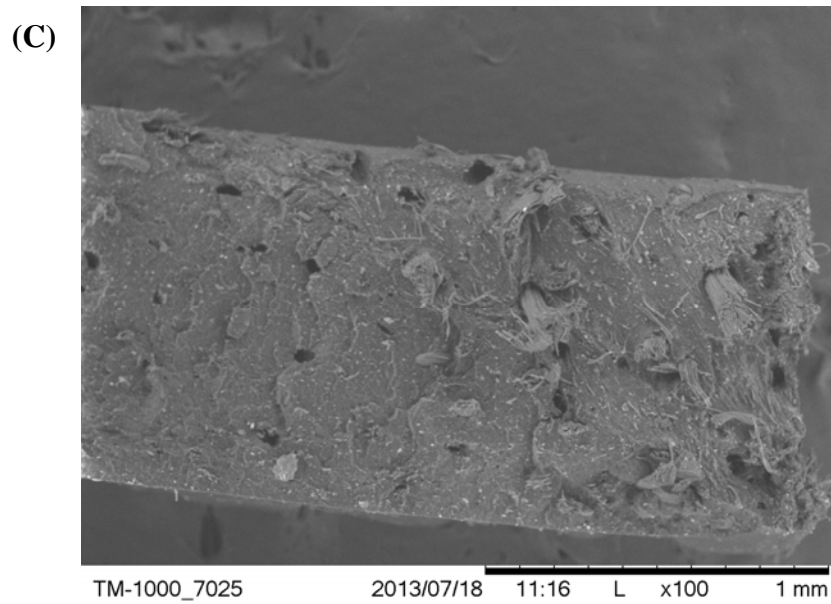


Figure 5.22 SEM image of cryogenic fractured surfaces of San9PALF composites (A), San9PALF/1 MASEEBS (B) and San9PALF/1MAPP (C).(cont.)

The effect of compatibilizer on the interfacial adhesion between fiber and matrix are characterized by Scanning electron microscopy (SEM). The SEM images of cryogenic fractured surfaces for San/9PALF composites and the composites containing of MASEBS and MAPP are shown in Figures 5.22A, B and C, respectively.

It is found that from Figure 5.22A there are a number of pull-out fibers. Cryogenic fracture surfaces of the composites containing of MASEBS and MAPP compatibilizers as shown in Figures 5.22B and 5.22C, show rather smooth surface when compared with the uncompatibilized system. The results confirm the improvement of interfacial adhesion between the PALF fiber and Santoprene matrix.

5.8 Dynamic mechanical properties

Figure 5.23(A) displays the storage modulus and tan delta curves with temperature range from -100 to 140 °C of Santoprene, San9PALF composites, San9PALF/1MAPP composites and San9PALF/1MASEBS composites. All materials exhibit a sharply drop in storage modulus at around -50°C. The storage modulus of the composite containing MAPP is greater while that containing MASEBS is lower when compared to that of composites without compatibilizer. For Figure 5.23–B, the neat Santoprene shows the peaks at about – 40°C glass transitions of the EPDM rubber and peaks at about 0°C attribut to glass transitions of PP part in Santoprene [24]. The glass transitions of EPDM part decrease with increasing compatibilizer. This may be due to increase in chain mobility in EPDM rubber part [26]. The composites with compatibilizer glass transition of PP part shift to high temperature. This may be due to that the MAPP hinders the mobility of PP part [26]. The results confirm the improvement of interfacial adhesion between the PALF fiber and Santoprene matrix.

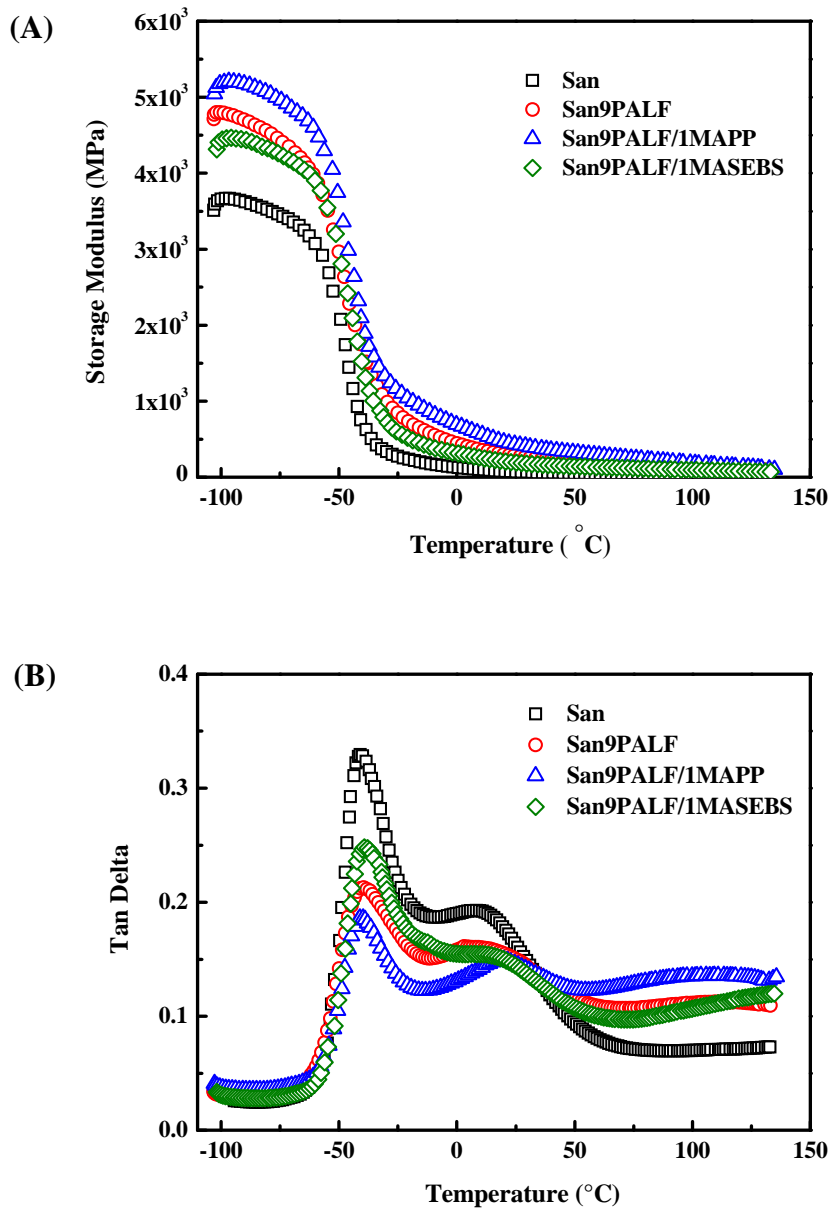


Figure 5.23 Dynamic storage modulus (A) and Tan delta (B) of Santoprene, San9PALF composites, San9PALF/IMAPP composites and San9PALF/IMASEBS composites.

5.9 Water absorption

The results of water absorption after immersion for 1, 7, 14 and 31 days of San/9PALF composites with different amount of MAPP and MASEBS are shown in Figure 5.24 and Table 5.1. All composites with compatibilizers (MAPP and MASEBS) display lower percentage of water absorption with the increasing immersion time. The composites with compatibilizer lower percentage of water absorption than the composite without compatibilizer. This is due to that the compatibilizer may reduce wetting with matrix [9], Resulting from the improvement of interfacial adhesion between the PALF fiber and Santoprene matrix.

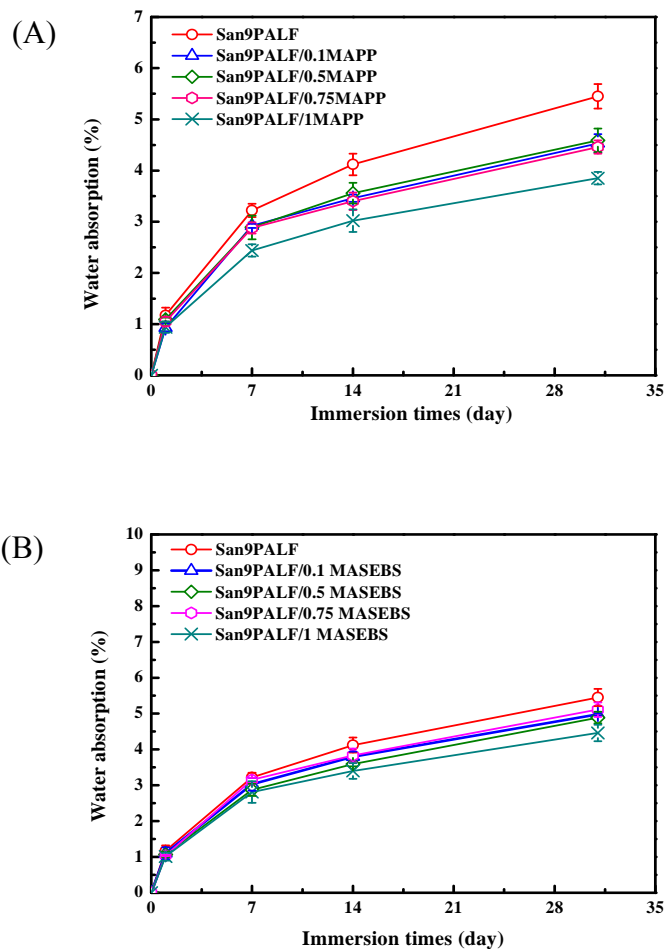


Figure 5.24 Water absorption of San/9PALF composites with different amount of MAPP (A) and MASEBS (B).

Table 5.2 Water absorption of San/9PALF composites with different amount of MAPP and MASEBS.

Sample	Water absorption (%)			
	1 day	7 days	14 days	31 days
San9PALF/xMAPP (x=times of PALF)				
San9PALF	1.17 ± 0.15	3.22 ± 0.13	4.12 ± 0.21	5.45 ± 0.24
0.1	0.93 ± 0.09	2.92 ± 0.04	3.46 ± 0.07	4.53 ± 0.18
0.5	1.09 ± 0.04	2.89 ± 0.23	3.56 ± 0.20	4.59 ± 0.23
0.75	1.05 ± 0.09	2.88 ± 0.11	3.40 ± 0.17	4.46 ± 0.13
1	0.94 ± 0.11	2.44 ± 0.12	3.02 ± 0.22	3.85 ± 0.12
San9PALF/xMASEBS (x=times of PALF)				
0.1	1.10 ± 0.17	3.03 ± 0.18	3.80 ± 0.14	4.98 ± 0.03
0.5	1.07 ± 0.08	2.87 ± 0.17	3.59 ± 0.06	4.89 ± 0.16
0.75	1.04 ± 0.02	3.15 ± 0.06	3.83 ± 0.19	5.11 ± 0.20
1	1.01 ± 0.11	2.81 ± 0.30	3.40 ± 0.22	4.46 ± 0.23

Part III: The effect of chemical modification of PALF surface on mechanical properties of San/PALF composites.

Generally, natural fiber is hydrophilic but thermoplastic elastomer rubber is hydrophobic. Therefore, composites of PALF fiber and Santoprene thermoplastic elastomer can be expected to have poor interfacial adhesion. To circumvent this problem, there are many methods to improve the interfacial adhesion of San/PALF composite such as adding of compatibilizer, surface treatment. In this part, the use of chemical treatments i.e. alkali treatment, amino silane treatment, benzene diazonium salt (BZDA) treatment and isocyanate treatment to improve interfacial adhesion were carried out.

5.10 Morphology of PALF chemical modification

The SEM images of PALF fibers before and after treatments are shown in Figure 5.25. The un-PALF (Figure 5.25 A) shows the large fiber bundle than single fiber. The fiber after treated with NaOH, amino silane and isocyanate shown in Figure 5.25 (B-D). The treated fibers have single fiber more than un-treated. It can be clean and smooth surface of fibers.

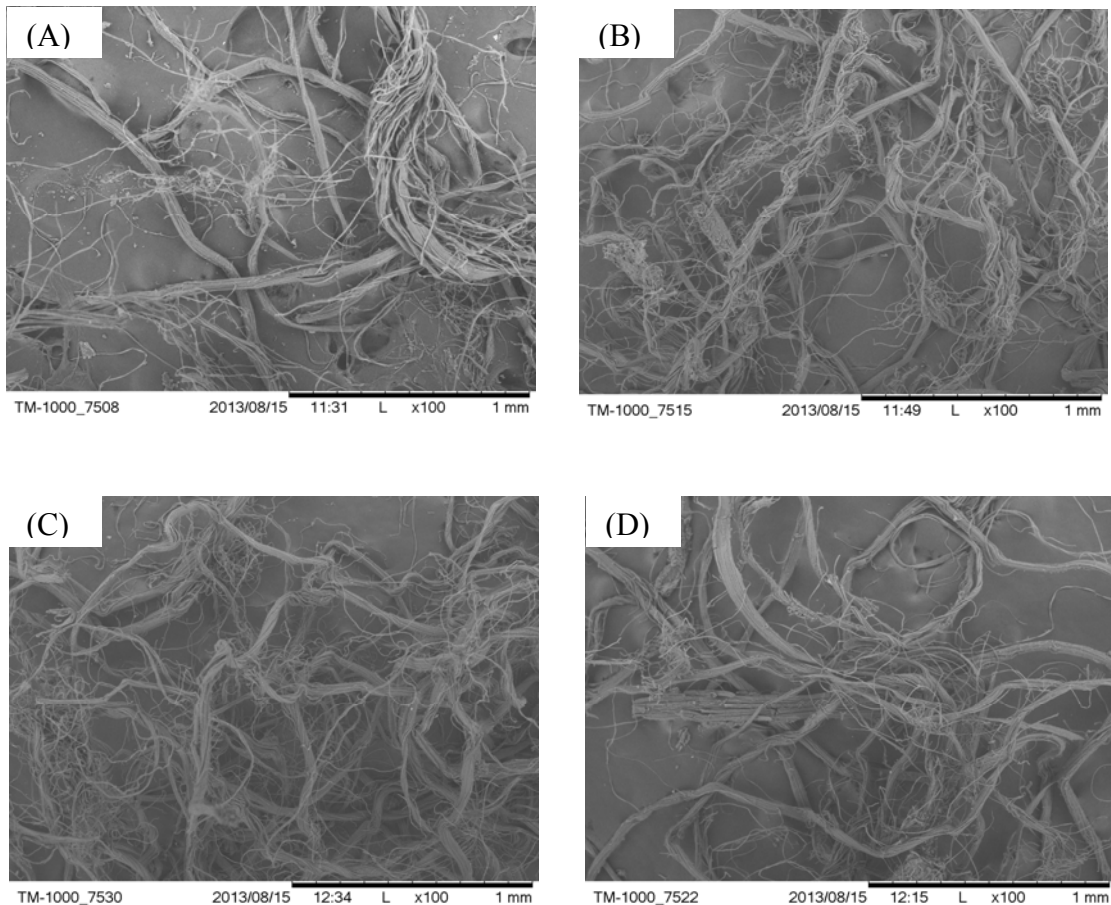


Figure 5.25 SEM images of PALF fibers (A) un-PALF, (B) Na-PALF, (C) Ami-PALF and (D) Iso-PALF

5.11 The effect of PALF chemical modifications on tensile properties

5.11.1 Tensile properties of PALF modification

Stress-strain curves of the composites containing modified PALFs with alkali and benzene diazonium salt (BZDA) are shown in Figure 5.26. It is seen that the slope of PALF modified (Na-PALF and BZDA-PALF) are lower than that of unmodified (un-PALF) system. This can be explained that the poor interfacial adhesion between PALF modified and Santoprene matrix. This result shows that PALF surface modification with alkali (NaOH) to remove impurity from surface such as lignin, wax and hemi-cellulose did not improve the tensile properties in case of santoprene matrix. However, other researches [18, 27] have reported that the mechanical properties (fiber modification with alkali and benzene diazonium salt)

can be improved. From the results shown in Figure 5.27 (A), untreatedPALF system shows the highest modulus at low strain (4.8 MPa). The modulus of Na-PALF (3.6 MPa) and BZDA-PALF (3.4 MPa) have a nearly the same values. For the Figures 5.27 (B) and (C), neat Santoprene shows the highest ultimate tensile strength and elongation at break. In case of the San/PALF composites, the ultimate tensile strength of un-PALF is higher than that of Na-PALF and BZDA-PALF. In contrast, the elongation at break of Na-PALF and BZDA-PALF composites system was higher than that of Un-PALF. This arises from that the PALF modification composites have a rubbery behavior as seen from stress-strain curve.

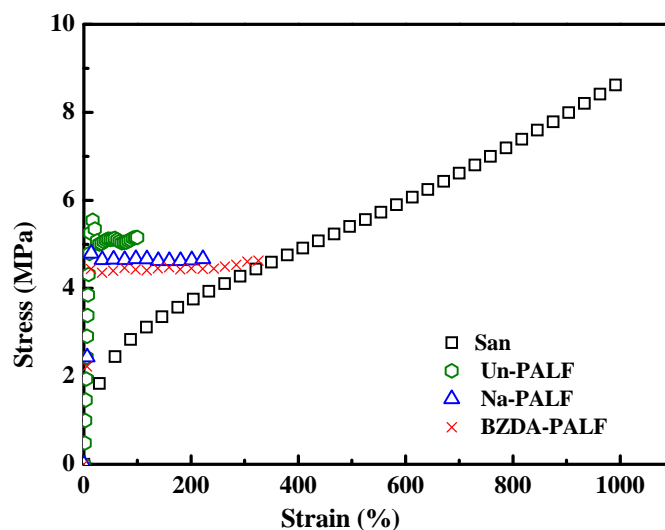


Figure 5.26 Stress-strain curves of San, Un-PALF, Na-PALF and BZDA-PALF composites.

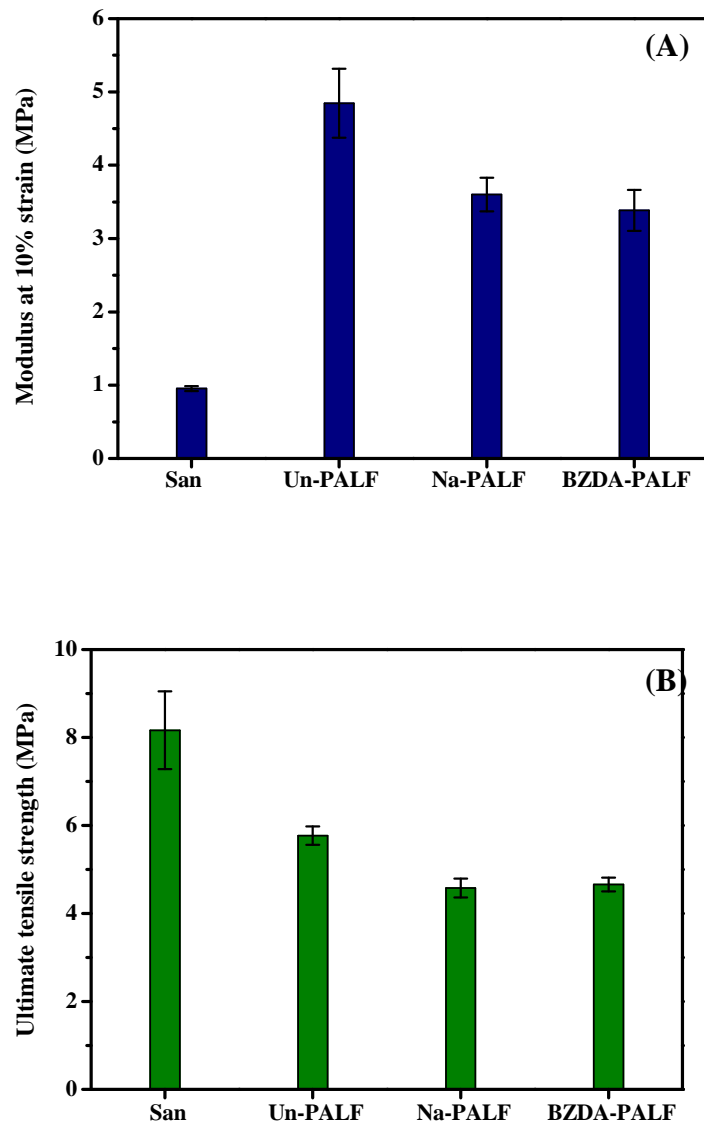


Figure 5.27 Tensile properties (A) modulus at 10% strain, (B) ultimate tensile strength and (C) elongation at break of San, un-PALF, Na-PALF and BZDA-PALF composites.

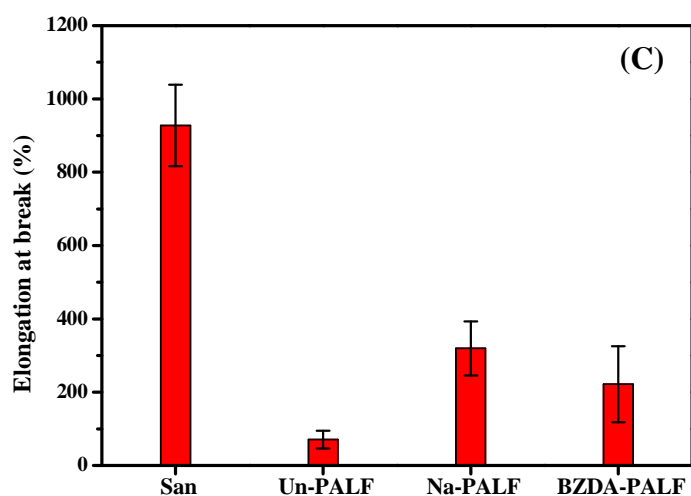


Figure 5.27 Tensile properties (A) modulus at 10% strain, (B) ultimate tensile strength and (C) elongation at break of San, un-PALF, Na-PALF and BZDA-PALF composites. (cont.)

5.11.2 Amino silane treatment on tensile properties

Figure 5.28 shows stress-strain curves of amino silane treated PALF composites. The rapid increase in stress of all composites is observed at low strain. The curve of PALF modification was lower than un-modification. From Figure 5.27 (A), the modulus at 10% of un-PALF (4.8 MPa) was higher than Na-PALF (3.6 MPa) and Ami-PALF (4.04 MPa). In case of Ami-PALF with adding two compatibilizers (MAPP and MASEBS), the lower of modulus at 10% strain is observed. From Figure 5.29 (B) the ultimate tensile strength of neat santoprene shows highest value. The ultimate tensile strengths of PALF modification with amino silane (Ami-PALF, Ami-PALF/0.5MAPP and Ami-PALF/0.5 MASEBS) were not significantly changed. From Figure 5.29 (C) the elongation at break of neat Santoprene is highest, while the un-PALF shows the lower elongation at break compared with modification PALF systems (Na-PALF, Ami-PALF, Ami-PALF/0.5MAPP and Ami-PALF/0.5MASEBS). The results indicate that the tensile properties were not improved by the modification. This indicates the poor interfacial adhesion between Santoprene matrix and PALF filler. M. Abdelmouleh et al [19] has reported that the mechanical properties of PE/short fiber natural fiber increased with using silane coupling agent treated fiber.

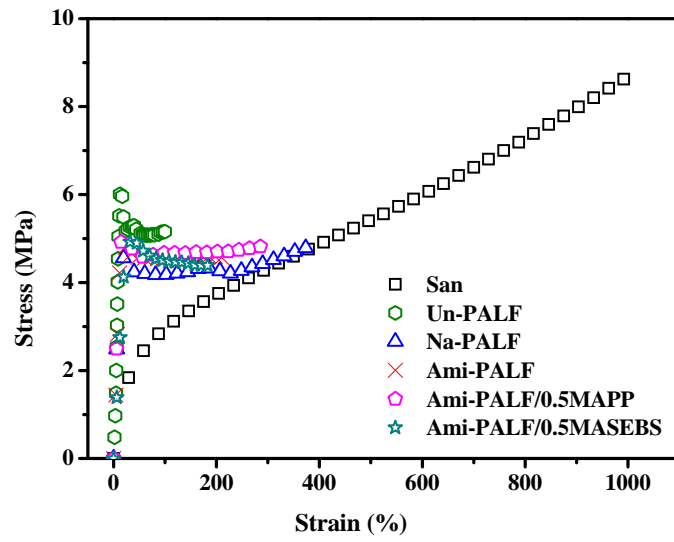


Figure 5.28 Effect of amino silane treated on stress-strain curves of San/PALF composites.

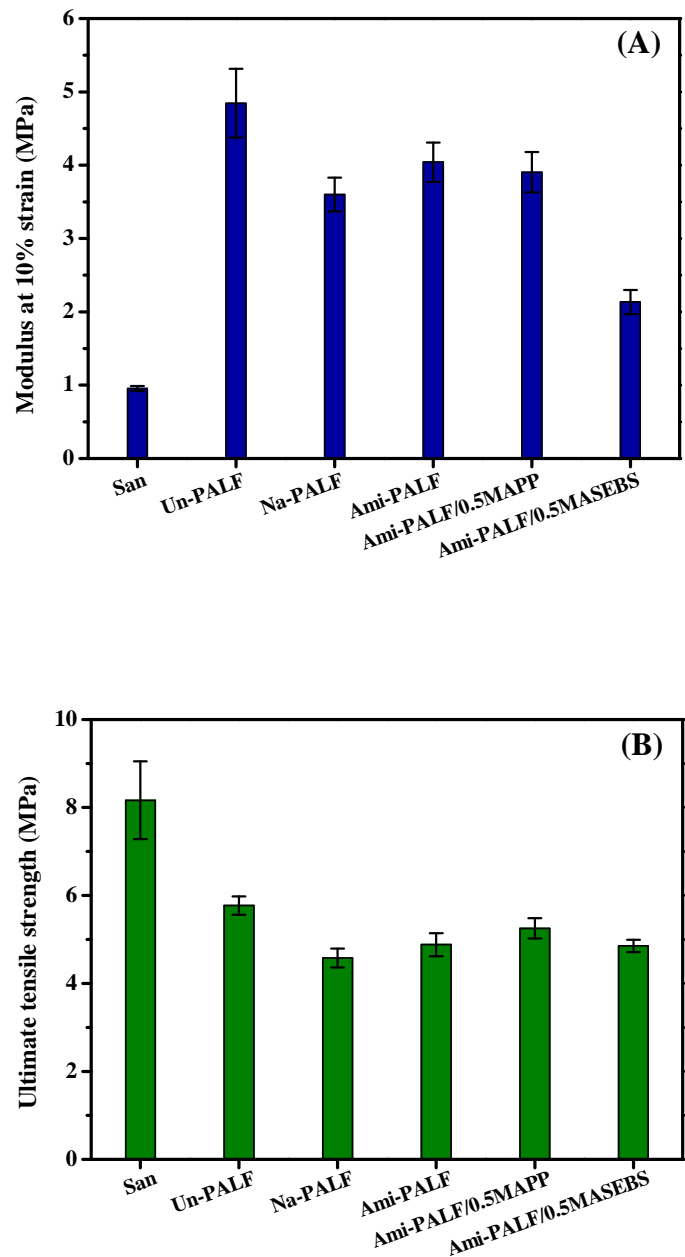


Figure 5.29 Effect of amino silane treated on tensile properties (A) modulus at 10% strain, (B) ultimate tensile strength and (C) elongation at break of San/PALF composites.

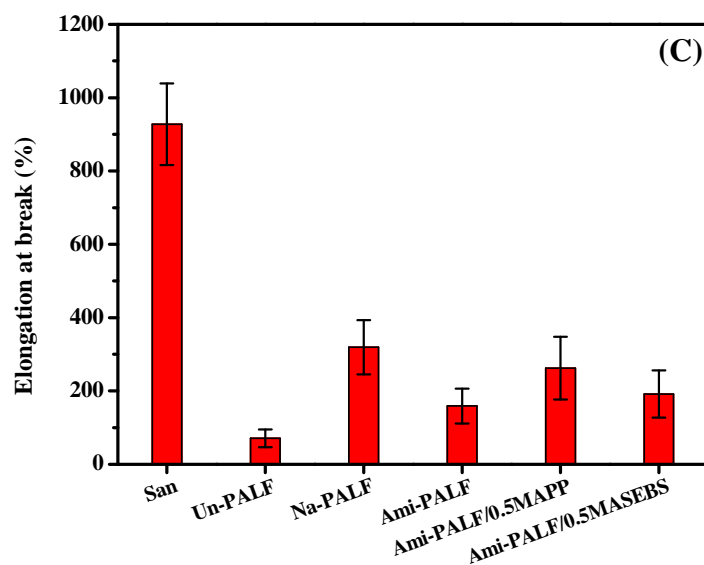


Figure 5.29 Effect of amino silane treated on tensile properties (A) modulus at 10% strain, (B) ultimate tensile strength and (C) elongation at break of San/PALF composites. (cont.)

5.11.3 Effect of isocyanate treatment on tensile properties

Figure 5.30 displays of stress-strain curves of PALF modification with isocyanate on tensile properties San/PALF composites. The result shows that the slope of Iso-PALF is lower than that of un-PALF. This corresponds to the modulus at 10% strain in Figure 5.31 (A) Iso-PALF (3.61 MPa) has lower than un-PALF (4.84 MPa). The ultimate tensile strength (Figure 5.31 (B)) of the neat Santprene is the highest compared among all samples examined. The un-PALF composites show higher tensile strength than that of Iso-PALF. On the other hand, the elongation at break in Figure 5.31 (C) of Iso-PALF is higher than un-PALF. For this system PALF modification with isocyanate cannot improve tensile properties in San/PALF composites.

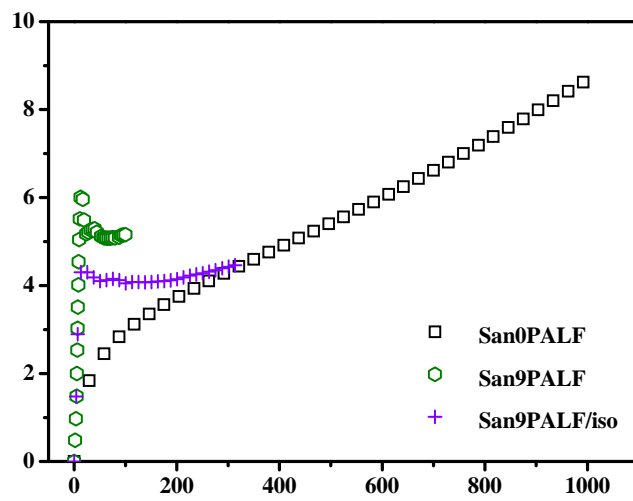


Figure 5.30 Effect of isocyanate treatment on stress-strain curves of on San/PALF composites.

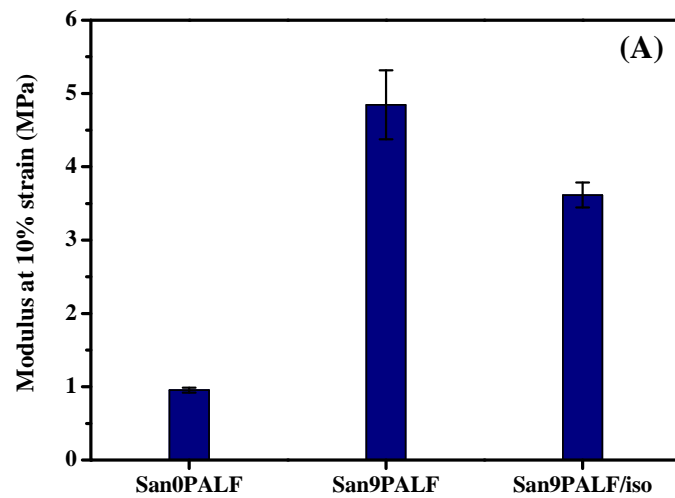


Figure 5.31 Effect of isocyanate treatment on tensile properties (A) modulus at 10% strain, (B) ultimate tensile strength and (C) elongation at break of San/PALF composites.

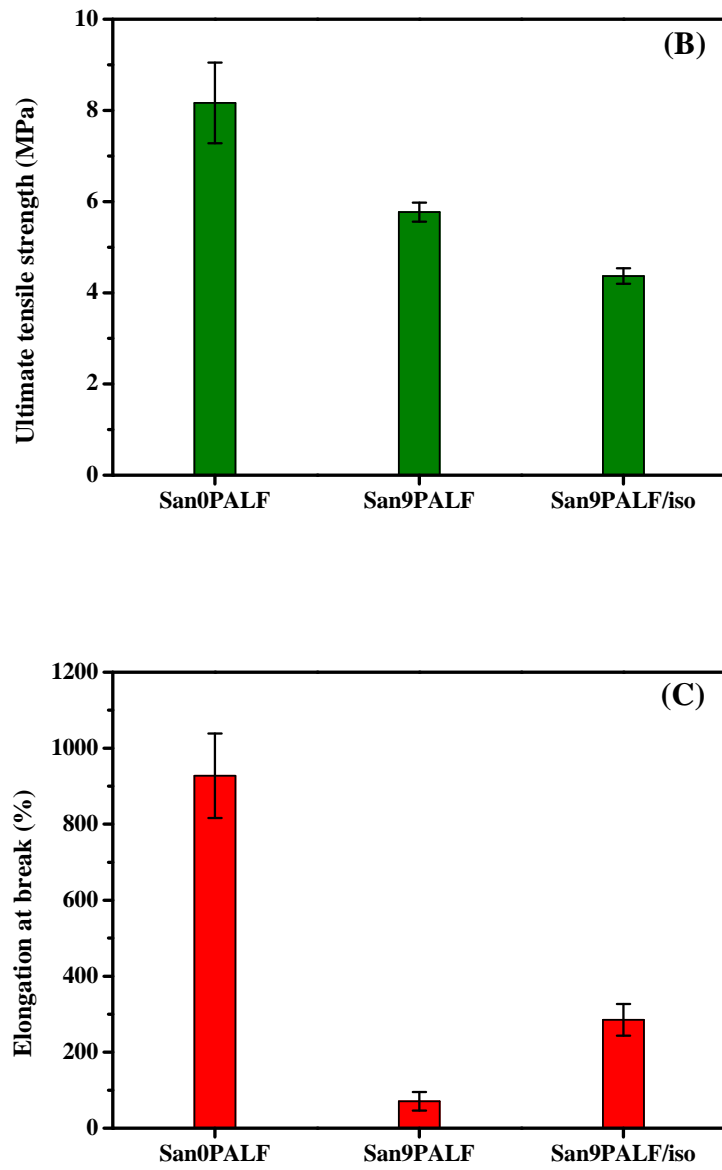


Figure 5.31 Effect of isocyanate treatment on tensile properties (A) modulus at 10% strain, (B) ultimate tensile strength and (C) elongation at break of San/PALF composites. (cont.)

CHAPTER VI

CONCLUSIONS

The objective of this thesis is to improvement mechanical properties of Santoprene by using PALF reinforcement. From the results in this thesis the conclusions can be drawn as follows;

1). The addition of PALF fibers can significantly improve the mechanical properties of San/PALF composites in the longitudinal direction. The compression temperature also effects on mechanical properties in longitudinal direction. San/PALF composites prepared at low compression temperature show matrix orientation.

2). The addition of compatibilizer (MAPP and MASEBS) could improve the mechanical properties of San/PALF composites. The improvement of these mechanical properties can be attributed to the improvement of the interfacial adhesion between the PALF fiber and Santoprene matrix

3). The chemical treatments of PALF with alkali, amino silane, benzene diazonium salt (BZDA) and isocyanate provide smooth surface and small fibers than untreated PALF. Whereas, the tensile properties of composites filled with treated PALFs were not significant improved as compared to that of untreated PALF.

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BIOGRAPHY

NAME Asama Kalapakdee

DATE OF BIRTH 23 July 1987

PLACE OF BIRTH Bangkok, Thailand

INSTITUTIONS OF ATTENDED Maharakham University 2006-2010
Bachelor of Science (Chemistry)
Mahidol University 2010-2014
Master of Science (Polymer Science and
Technology)

RESEARCH GRANT Recipient of a Teaching Assistance Scholarship
from the Department of Chemistry,
Faculty of Science, Mahidol University
in the academic year of 2011-2013.

HOME ADDRESS 11/49 M.6 Plutalaung , Sattahip,
Chonburi 20180 Thailand

PRESENTATION 2013: 1st International Conference on Natural
Fiber (ICNF2013), Guimaraes, Portugal.
2013: The Internationnal congress for Innovation
in chemistry (PERCH-CIC congress VIII),
Chonburi, Thailand.