IMPROVEMENT OF BONDING BETWEEN NATURAL RUBBER AND NITRILE RUBBER BY CHLORINATION OF NATURAL RUBBER SURFACE

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ABSTRACT

Natural rubber (NR) and nitrile butadiene rubber (NBR) exhibit different mechanical properties. NR is known as a better dynamic and mechanical material than nitrile rubber. NR contains some poor properties such as low oil and weathering resistance. Encasing NR with nitrile rubbers is one way to combine the good properties of these two kinds of rubbers. However, the adhesion between them is naturally poor. It is probably improved by chemical surface treatment especially chlorination of the NR surface.

In this research, a NR sheet was chlorinated in a mixture of sodium hypochlorite and hydrochloric acid solution. The available free chlorine was 0.15% mole approximately. The chlorination time was covered a range of 0-30 minutes. The degree of chlorination determined by X-ray absorption spectroscopy (XAS) increased with chlorination time up to 10 minutes and leveled off afterwards. The surface properties of the chlorinated NR sheet investigated by Atomic Force Microscopy (AFM) showed the surface stiffness and roughness increased steeply with treatment time. Adhesion between chlorinated NR and NBR shows the maximum peel strength at 1 min of chlorination time. That proved their adhesion depended not only on the amount of chlorine substitution on the NR surface but that surface properties also played an important role in the adhesion of NR//NBR. Other parameters such as the effect of chlorination on uncured NR, carbon black loading in NR compound, precuring of NR sheets before chlorination, filler type in NBR compound, as well as the stability of bonding were also studied in this work.

KEY WORDS: NATURAL RUBBER/ NITRILE RUBBER/ CHLORINATION/ ADHESION STRENGTH/ SURFACE MODIFICATION

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การปรับปรุงสมบัติการยึดติดระหว่างยางธรรมชาติกับยางไนไตรล์โดยวิธีคลอริเนชั่นบนพื้นผิวของยางธรรมชาติ (IMPROVEMENT OF BONDING BETWEEN NATURAL RUBBER AND NITRILE RUBBER BY CHLORINATION OF NATURAL RUBBER SURFACE)

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บทคัดย่อ

ยางธรรมชาติและยางไนไตรล์ส่วนใหญ่มักมีความแตกต่างกันทางด้านสมบัติทางกลและสมบัติทางกลเชิงพลวัตร ยางธรรมชาติเป็นที่รู้จักกันดีว่าเป็นยางที่มีสมบัติเชิงกลที่ดีกว่ายางไนไตรล์ แต่คุณสมบัติบางประการของยางธรรมชาตินั้นด้อยกว่ามาก อาทิเช่น ความทนทานต่อสภาพอากาศและความทนทานต่อน้ำมัน ข้อดีข้อเสียที่แตกต่างกันนั้น ทำให้เกิดแนวความคิดนำไปประยุกต์ใช้กับผลิตภัณฑ์ที่ต้องการ ดังนั้นการยึดติดยางธรรมชาติกับยางไนไตรล์เข้าไว้ด้วยกันจึงเป็นอีกทางเลือกหนึ่งซึ่งจะคงไว้ด้วยคุณสมบัติที่ดีของยางทั้งสองชนิด แต่อย่างไรก็ตามการทำให้ยางทั้งสองชนิดเข้ากันหรือติดกันได้นั้นเป็นเรื่องที่ยาก ดังนั้นจึงจำเป็นที่จะต้องปรับปรุงการยึดติดให้ดีขึ้น การปรับปรุงการยึดติดของยางธรรมชาติและยางไนไตรล์ให้ดีขึ้นในงานวิจัยนี้ทำได้โดยใช้วิธีคลอริเนชั่นบนพื้นผิวของยางธรรมชาติ

ในงานวิจัย ยางธรรมชาติที่ผ่านการขึ้นรูปแล้วถูกนำมาทำการคลอริเนชั่นในสารละลายที่มีส่วนผสมของโซเดียมไฮโปรคลอไรท์และกรดไฮโดรคลอริก สารละลายที่เตรียมได้นี้มีสารคลอรีนอิสระอยู่ประมาณ 0.15 % โมล แผ่นยางธรรมชาติถูกคลอริเนทที่เวลาต่างๆตั้งแต่ 0-30 นาที ปริมาณของจำนวนคลอรีนบนผิวยางธรรมชาติสามารถตรวจสอบได้จากเครื่องกำเนิดลำแสงซินโครตรอนโดยใช้เทคนิคการดูดกลืนรังสีเอ็กซ์พลังงานต่ำ (X-ray Absorption Spectroscopy หรือ XAS) จากการศึกษาด้วยเทคนิคนี้พบว่า ปริมาณของคลอรีนบนผิวยางธรรมชาติเพิ่มมากขึ้น แปรผันตามเวลาที่ใช้ในการคลอริเนชั่น จนกระทั่งที่เวลาประมาณ 10 นาทีหลังจากนั้น ปริมาณคลอรีนเริ่มคงที่ คุณสมบัติเชิงพื้นผิวบนยางธรรมชาติที่ถูกคลอริเนทแล้วสามารถตรวจสอบได้จากเครื่องจุลทรรศน์แรงอะตอม (Atomic Force Microscopy หรือ AFM) จากการศึกษาด้วยเครื่องมือนี้พบว่า ความแข็งและความขรุขระของผิวยางธรรมชาติเพิ่มขึ้นตามเวลาที่ถูกคลอริเนท การยึดติดระหว่างยางธรรมชาติและยางไนไตรล์แสดงค่าความทนต่อการดึงลอกสูงสุด ที่เวลาคลอริเนชั่น 1 นาที ซึ่งสามารถบอกได้ว่าการยึดติดของยางทั้งสองชนิดไม่ได้ขึ้นอยู่เพียงปริมาณของคลอรีนที่เข้ามาแทนที่บนผิวยางธรรมชาติเท่านั้น แต่ยังขึ้นอยู่กับสมบัติเชิงพื้นผิว ซึ่งมีบทบาทสำคัญมากต่อความแข็งแรงของการยึดติดของยางธรรมชาติและยางไนไตรล์ ตัวแปรอื่นๆเช่น อิทธิพลของการคลอริเนชั่นกับยางธรรมชาติที่ยังไม่แข็งตัว (uncure) ปริมาณของสารเขม่าดำ (carbon black) ในยางธรรมชาติ ปริมาณการแข็งตัว (precuring) ของยางธรรมชาติก่อนทำการคลอริเนชั่น และอิทธิพลของชนิดสารตัวเติม ในยางไนไตรล์ นอกจากนั้นยังศึกษาเสถียรภาพของการยึดติดของยางธรรมชาติและยางไนไตรล์ ด้วยวิธีการทดสอบในรูปแบบต่างๆอีกด้วย

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LIST OF ABBREVIATIONS

AFM	=	Atomic Force Microscopy
CB-N330	=	Carbon black
Cl-NR	=	Chlorinated Natural Rubber
EXAFS	=	Edge X-ray Absorption Fine Structure
FTIR-ATR	=	Attenuated Total Reflectance Fourier Transform Infrared Spectroscopy
Hi-sil ® 233-S	=	Silica
MDR	=	Moving Die Rheometer
NaOCl	=	Sodium hypochlorite solution
NBR	=	Nitrile Rubber
NEXAFS	=	Near-edge X-ray Absorption Fine Structure
NH_4OH	=	Ammonium hydroxide
NR	=	Natural Rubber
ODR	=	Oscillating Disk Rheometer
S	=	Sulphur
TMTD	=	Tetramethylthiuramdisulfide
TBBS	=	Tert-Butyl-Benzothiazol Sulfonamide
XAS	=	X-ray Absorption Spectroscopy
XANES	=	X-ray Absorption Near-edge Spectroscopy
ZnO	=	Zinc oxide
Ge	=	Germanium crystal)

CHAPTER 1
INTRODUCTION

Each polymer possesses its own advantages and disadvantages in properties. For example, NR has excellent mechanical properties but relatively poor oil resistance, whereas NBR or other synthetic rubbers possess those properties in an opposite trend. In Thailand is well known to be the biggest NR producer in the world. The main application is used in tyre industry 60 percent of production. Other productions are found in mechanical goods (such as hoses, mechanical belting, rubber belt, leaked tyre, inner tube) which requiring good mechanical and dynamic properties and the latex products such as gloves, condom, underwear laces. Because of a lot of NR in Thailand and also possesses good dynamic and mechanical properties thus NR applied production necessary for consideration investment of research and development. However, some properties such as oil resistance and weathering resistance of the NR are much lower than those of synthetic rubbers. Encasing NR with synthetic rubbers is one of an alternative solution to combine good properties of the two rubbers. This idea could be applied for various kinds of products including, hoses for transportation of oil, bridge bearing, and dock fender for marine port. Unfortunately, the adhesion between NR and synthetic rubber is very poor due to their different chemical structure and solubility parameter values [42]. Thus improvement of the adhesion between the two rubbers before the development and application of the product is necessary.

The aim of this research is to improve the adhesion between NR and NBR via surface modification. The chlorination is one of the most common chemical treatments. For example, NR latex film surface is often chemically modified by chlorination to reduce surface frictional resistance. This is particularly so in the manufacturer of examination and household NR latex gloves to improve donning property and to reduce surface tackiness [30]. In addition, surface modification via the chlorination was carried out to improve the interfacial adhesion between rubber and reinforcing agent in composites [32].

In practice, the chlorination can be carried out by using various chemicals including plasma chlorination, trichloroisocyanuric acid (TCI) and Sodium hypochlorite solution. In this work chlorination by using sodium hypochlorite solution is considered. Sodium hypochlorite can provide available chlorine in acidified solution. This method is not good for health and safety hazards. In addition, it is beset with poor reproducibility of chlorination levels, possible deterioration in physical properties ozone, wear and heat aging resistance. In spite of all these, chlorination remains the simplest and convenient way to modify NR surfaces. Besides, this research also interested in the studies of effects of various factors such as the effect of vulcanization system, the effect of filler types in NBR, the effect of cure extent of NR, the effect of surface viscosity on the adhesion NR and NBR.

CHAPTER 2
OBJECTIVES

The objectives of the present work were:

1. To study the surface modification of natural rubber via chlorination method by using the mixture of sodium hypochlorite and hydrochloric acid solution and using X-ray absorption spectroscopy (XAS) technique to characterize the modified surface.

2. To investigate structure of the chlorinated NR surface by using Atomic Force Microscopy (AFM), contact angle measurement and ATR-FTIR techniques.

3. To study the role of various factors influencing the interfacial adhesion of NR//NBR laminate including chlorination time, effect of filler content and pre-curing of the NR compound

4. To investigate durability of NR//NBR bonding under dynamic flex, heat and ozone.

CHAPTER 3
LITERATURE REVIEW

3.1 The theory of adhesion

There are theories attempting to predict the strength of adhesive bond and attempting to describe the theory relating basic physical and chemical properties of materials to the actual physical strength of an adhesive bond [1]. They are also theories predicting the strength of interaction and interfaces. The first thing to describe and explain of those that has to fundamentally known in the adhesion science. However, there are no theories making the complete connection among adhesion, the physical properties of the adhesive and adherend, and the practical strength of an adhesive bond.

The definition of adhesion is defined as the molecular attraction exerted between bodies in contact or following ASTM D907 is 'the state in which two surfaces are held together by interfacial forces which may consist of valence forces or interlocking forces or both'.

There are various types of theories of adhesion to discuss the mechanisms of adhesion. It was common to discuss individually of adsorption theory, mechanical theory, diffusion theory, electrostatic theory and dispersive theory. These could be termed "classical" theories of adhesion [2].

3.1.1 Adsorption theory

The adsorption theory could be another of chemical theory because of involving in chemical bonding such as ionic bonding and covalent bonding. When the two materials come into contact some forces must act between them. Depending on the chemical nature of the two these forces may be primary chemical bonds (covalent,

ionic or metallic), hydrogen bonds or van der Waals interactions (orientation, induction or dispersion). Thus adsorption will occur. The adsorption theory sees this adsorption as being responsible for the adhesive between two phases.

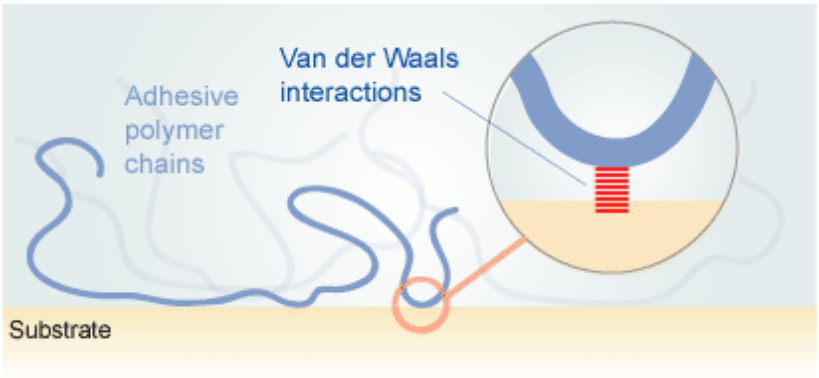

Figure 3.1 The schematic of the adsorption theory of adhesion [3]

Table 3.1 Chemical bond energy [4]

Bond type	**Bond energy (KJ/mol)**
Primary bond	
Ionic	600-1100
Covalent	70-950
Metallic	110-350
Secondary bond	
Hydrogen	10-50
Dipole interaction	4-20
London dispersion	0.08-40

Calculation of the adhesion expected to result from secondary bonds (hydrogen bond, dipole interaction and London dispersion) alone generally give predicted bond strengths considerably greater than measured strengths. In these calculations the

importance of the contribution of ubiquitous dispersion forces is apparent. This has led to the view that 'wetting and bonding are synonymous'.

The absorption theory is the most influential of the adhesion theories and seems to offer scope to rationalize a wide range of experimental results.

3.1.2 Mechanical theory

This theory like the absorption theory dates back to the earliest scientific work on adhesion, that of McBain and Hopkins in 1925 who considered that there were two kinds of adhesion, mechanical and specific. Specific adhesion involved *'some species of interaction'* between the smooth non-porous surface and the adhesive. This interaction might be *'chemical or adsorption or mere wetting'*. Specific adhesion has developed into the model we today describe in terms of the adsorption theory. In contrast, mechanical adhesion was only considered possible with porous materials. It occurred *'whenever any liquid material solidifies in situ to form a solid film in the pores'*. They cite as examples adhesion to wood, unglazed porcelain, pumice and charcoal. McBain and Hopkins mechanical adhesion was very much a common sense concept, *'It is obvious that a good joint must result when a strong continuous film of partially embedded adhesive is formed in situ'*. When they consider whether mechanical adhesion can act as a mechanism of adhesion on its own, in the absence of adsorption effects, their position was somewhat ambiguous. On one hand they wrote that '*A liquid which wets a surface and is then solidified possibly always makes a joint'*. Neglecting the equivocality of the 'possibly always', this seems to mean that 'whenever wetting occurs, some form of adhesion must result'. This would be accepted today. By contrast, elsewhere in the paper McBain and Hopkins talk of mechanical adhesion as being *'independent of adhesive action'* They found no evidence of adsorption of adhesive from solution onto filter paper, and concluded that the adhesive adsorption did not occur during the bonding of wood. McBain and Hopkins distinguish adhesion to porous surfaces from adhesion to surfaces which are merely rough. Roughness, they report, has little influence on adhesion, '*provided that the roughening has been carried out without pitting the surfaces appreciably'* If metal surfaces are '*rather deeply furrowed'* the joints are decidedly weaker than those obtained with

smooth surfaces. This reduction may be a result of either an increase in average adhesive film thickness, or there being insufficient adhesive to bridge the gap between the surfaces. [5]**.** McBain and Hopkins regarded adhesion to porous substrates as being due to mechanical interlocking of the adhesive into the pores of the substrate. Charcoal and wood were among the porous substrates they considered.

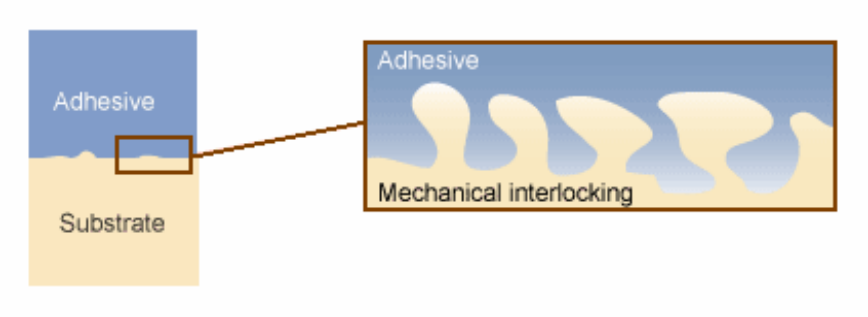

Figure 3.2 The schematic drawing of mechanical interlocking. [6]

Mechanical interlocking bonds materials together by allowing the adhesive or sealant to take advantage of the microscopic roughness of the substrates to lock them together [6] More recently work on adhesion to porous anodic films on aluminum and titanium and to microporous surfaces have shown that features such as pore penetration exert a profound influence on adhesion to such surfaces. The term ‘microporous keying’ has been used in this context.

3.1.3 Diffusion theory

Some materials may merge at the joint by diffusion when an adhesive contains an adherent solvent the adhesive can diffuse into the adherent surface (substrate) with an interchange of molecules. The theory is only really applicable to polymers where a movement and entanglement of long molecules can occur. This can be viewed as a molecular interlock enabled adhesion. For plastics, the theory includes for effects of contact time, influence of time and temperature on bonding rate, and the influences of polymer molecular weight and polymer structure. While the diffusion theory applies well for cases of self-adhesion or autohesion, it does not fit well in providing an

explanation for polymer-polymer adhesion. High molecular weight thermoplastic polymers often display very high melt viscosity and will not diffuse easily within the time scale of most bonding operations.

The original of this associated with Voyutskii and other Russian workers. Voyutkii's classical work was done on rubber to rubber adhesion. It was agued that the development of adhesion with time, the effects of molecular weight, polarity and cross-linking proved that adhesion was associated with the interdiffusion of polymer chains.

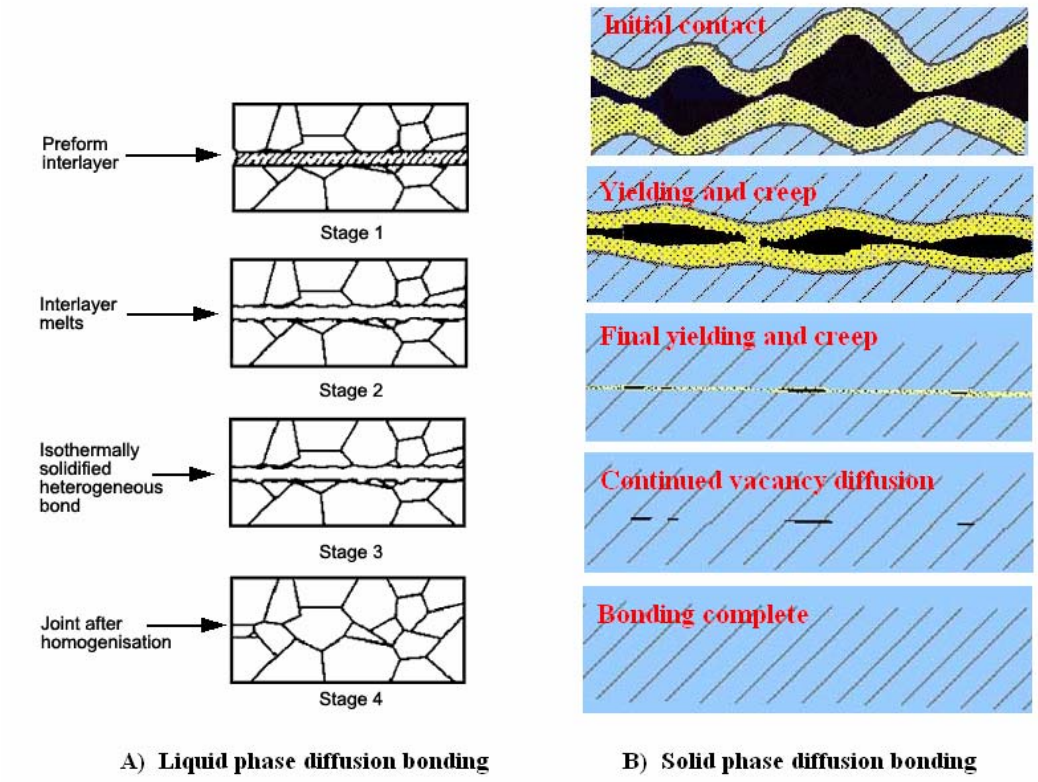

Figure 3.3 Schematic of the mechanism of diffusion bonding. A) is the mechanism of liquid phase diffusion bonding and, B) is the mechanism of solid phase diffusion bonding. [7]

More recently work on molecular dynamics has studied the mechanisms and kinetics of interdiffusion between compatible and incompatible polymers and has related the strength of the bond formed to this process. The diffusion theory of

adhesion is shown schematically in Figure 3.3 where A) is the diagram of liquid phase diffusion bonding and B) is the diagram of solid phase of diffusion theory. Both stages show solubility into one another that are formed a result of diffusion bonding, no longer have a true interface, but rather than an interphase.

3.1.4 Electrostatic theory

Electrostatic theory is basically very simple. It is the same basic theory as magnetism. The law states that like charges will repel, unlike charges will attract. [8] Some conducting materials may pass electrons to form a difference in electrical charge at the join. This results in a structure similar to a capacitor and creates an attractive electrostatic force between the materials and another word is if the adhesive and substrate have different electronic band structures, there is likely to be some electron transfer on contact to balance Fermi levels which will result in the formation of a double layer of electrical charge at the interface [9].

Deryaguin's and co-worker said that the electrostatic forces arising from such contact or junction potentials may contribute significantly to the intrinsic adhesion. This theory essentially treats the adhesion or substrate system as a capacitor which is charged due to the contact of the two different materials. Separation of two parts of the capacitor, as during interface rupture, leads to a separation of charge and to a potential difference which increases until a discharge occur an adhesion is due to the existence of these attractive forces across the electrical double layers and energy.

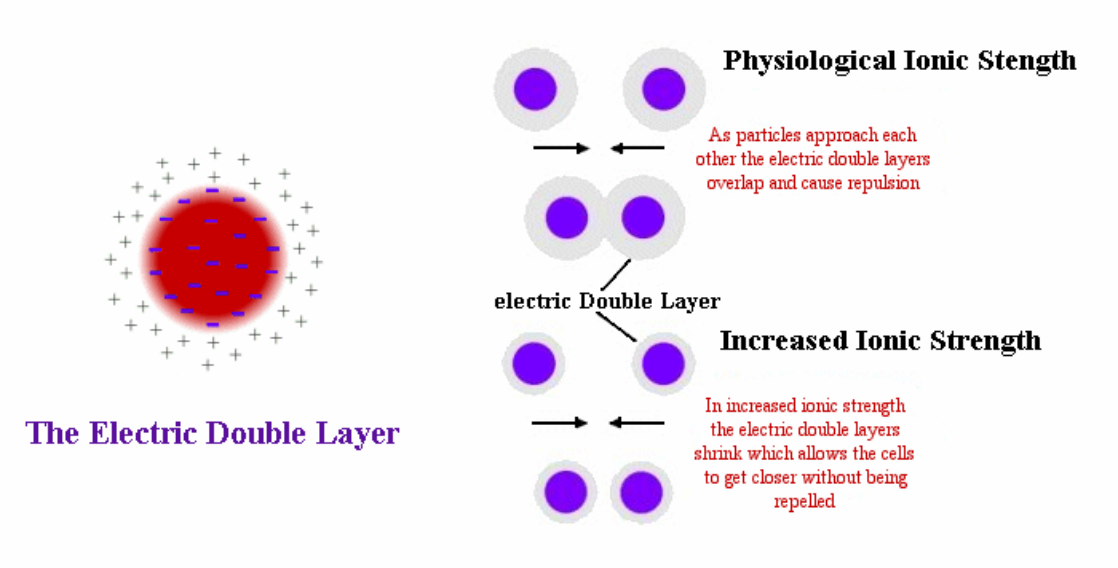

Figure 3.4 The picture of electrostatic charge and adhesion [10]

3.1.5 Wettability and adhesion theory

The study of adhesion can not be separated from the study of wettability and contact angle phenomena. For good adhesion to take place, the adhesive and the adherence must come into intimate contact [1] obtaining intimate contact of the adhesive, the interfacial flaws must be minimized or eliminated. Intimate contact occurs when the adhesive spontaneously spreads over the surface to maximize interfacial contact with other phases. It seems inherently reasonable that the energy of an interface or interface tension between phase 1 and 2 should be related the individual values of surface energy. A sample view of the relationship of wetting and adhesion is provided in Figure 3.5. That shows the contact angle of a drop of an epoxy adhesive on a variety of surfaces.

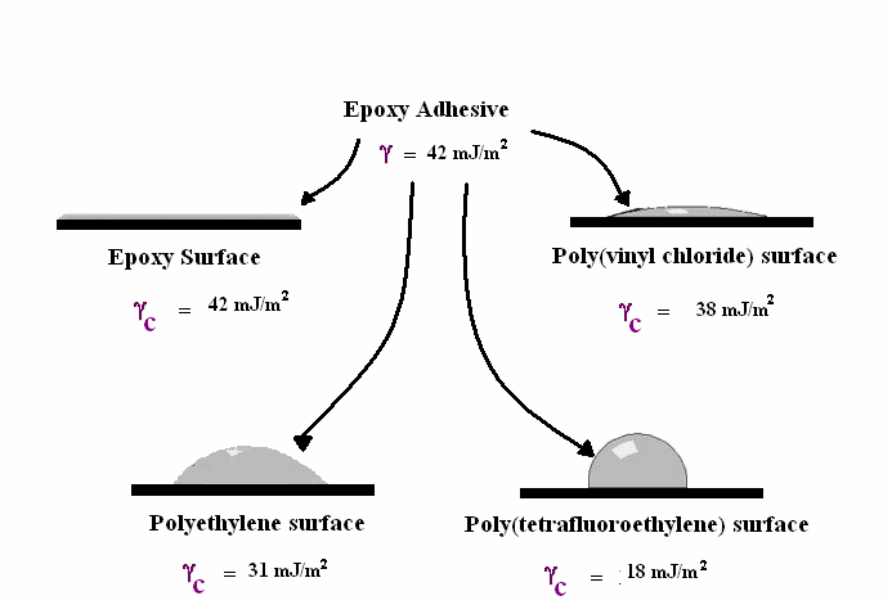

Figure 3.5 The schematic drawing of the observation of the contact angle of an epoxy adhesive (uncured) on four surfaces of varying critical wetting tensions which surface tension decreases, the contact angle of the liquid epoxy on that surface increases. [1]

The surface energy of a typical epoxy resin is about 42 mJ /m^2. The drop has a low profile on materials such as cured epoxy composite or polyvinyl chloride (PVC), although wetting would not be spontaneous on PVC. On polyethylene, which has a critical wetting tension of about 31 mJ /m^2, the drop has an even higher profile. The adhesive has a very high contact angle on polytetrafluoroethylene (PTFE) with a critical wetting of 18 mJ /m^2. Therefore, it might predict that an epoxy adhesive would have poor adhesion to PTFE. Low surface energy materials such as PTFE have poor adherability.

3.1.6 The weak boundary layer theory

Bikerman's theory, simply stated that if a proper adhesive bond is made, the bond fails in either the adherend or adhesive, whichever is cohesively weaker. Bond fails at less than their expected strength because materials of low cohesive strength

exist at the interface. This is low cohesive strength materials from the weak boundary layer, therefore, if the adhesive bond has low cohesive strength materials at the interface, then the adhesive bond is weaker than expected. However, it is not true that in proper adhesive bond, failure always occurs in either the adhesive or adherend.

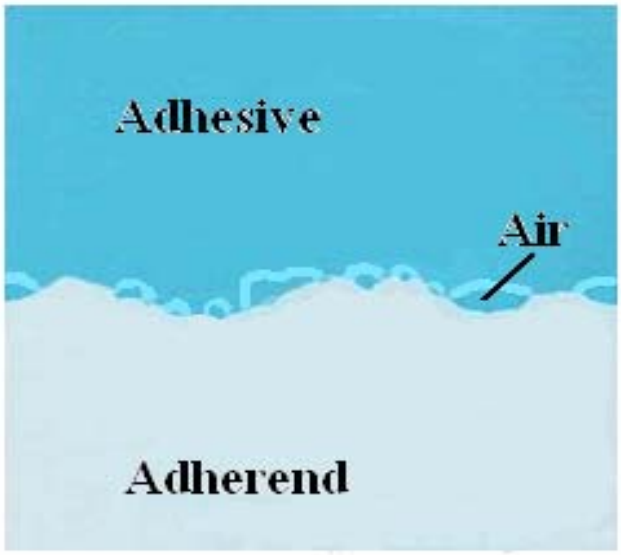

Figure 3.6 The schematic drawing of result in poor adhesion because of weak boundary layer [11].

3.2 Rubber to rubber bonding

Bonding of raw rubber or rubber compounds and their covulcanisation is important in industrial operations such as tyre building, while bonding of vulcanized rubbers to unvulcanised rubbers is also important in conventional (hot) retreading processes. There are a wide variety of variables affecting rubber to rubber bonding, such as the chemical composition of the rubbers, their compatibility or incompatibility, their molecular weights and their distributions, additives, crystalline and amorphous contents, surface nature and chemistry, crosslink densities, etc. [12]

3.2.1 Bonding of unvulcanised rubbers

3.2.1.1 Tack or autohesion [12]

When two rubber surfaces of the same or different rubbery polymer are brought into contact, they adhere with the strength that depends on the time of contact. This effect can be attributed either to increased interdiffusion of molecules across the interface or to an increase in the true contact area with time. Uncured rubbers at a temperature above their T_g can easily flow into intimate contact resulting in firm adhesion because of their molecular mobility. The ability of two uncured rubber surfaces to adhere together upon contact after the application of moderate pressure for a relatively short time is known as absolute tack.

Interdiffusion of chain segments across the interface is considered to be a major factor for developing tack. Tackiness between surfaces of the same rubber or rubber compounds having the same composition is referred to as autohesion or autohesive tack. The green strength of an unvulcanised rubber compound is the upper limit of the tack. The ratio of the absolute tack divided by green strength is sometimes referred to as relative tack. When the relative tack is close to one it may be assumed that almost complete contact and interdiffusion has taken place between the two surfaces and that the tack is green strength limited.

Amorphous polymers can not develop a strong higher tack because they do not crystallise under strain rely completely on chain entanglements to provide green strength and hence significant chain interdiffusion is required to develop high tack. Polymeric molecules from the two contacting surfaces must diffuse a sufficient distance across the interface to become entangled so as to develop a strong tack, which can resist stress. After sufficient interdiffusion, if the rubber is capable of strain crystallization, it can boost the tack to much higher levels. Therefore, a strain crystallizing rubber like natural rubber (NR) can develop very high tack. The advantage in this case stems from the fact that strain crystallization dose not occur during the interdiffusion or bond froming step and hence it dose not interfere with this step. Moreover, in the case of strain crystallizing rubbers less interdiffusion may be sufficient to develop good tack.

3.2.1.2 Testing of tack or autohesion levels [12]

The most commonly used sample testing for the bond strength is the 180^{o} peel test at a constant strain rate. It gives a direct measure of the energy per unit area required to separate the surfaces. Further, whereas the tensile test gives only a single estimate of the bond strength, peel test yields a trace, which shows how the force varies along the whole distance peeled. In either case, before testing, two test specimens are brought together under a light pressure (few kPa) for short time (usually a few seconds or minutes).

3.2.2 Bonding of vulcanized rubbers to unvulcanised rubbers

The processing and technology of vulcanized rubbers to unvulcanised rubbers bonding, it is usually found in tyre industry. In the conventional retreading process, an unvulcanised tread compound is extruded as a thick strip and a thin layer of a calendered cushion compound is bonded to this strip by passing between a pair of rollers. Then the compound strip with cushion is fixed on to the buffed casing of a tyre, after applying a solution of the cushion compound in naphtha, and vulcanized in a tyre mould. Since the assembly has to be kept in the mould for a long time, some deterioration in the quality of the rubber/reinforcement is inevitable and hence procured retreading is becoming more popular these days. Further, the actual retreading process in the case of the conventional may take place only after a few days of preparing the tread compound and hence the compounding ingredients have to be properly selected. Chances of blooming are high if any ingredient is added above its solubility limit at room temperature. Here the bonding between the vulcanized casing and the unvulcanised tread takes place in the tyre mould. Roughening the casing surface or wiping the surfaces by solvent naphtha improves bonding.

3.2.3 Bonding of vulcanized rubbers

The bonding of vulcanized rubber to vulcanized rubber is very important in many applications. Technological fabrication of large structures such as airplane,

hovercraft loop and inflatable objects need bond strength of vulcanized rubbers improvement. The bond must possess adequate strength, and must be capable of withstanding harsh environmental conditions such as extended periods of water immersion, severe tyre running conditions.

G.R. Hamed and co-worker [13] have studied the bond strength of vulcanized rubber to polyester cord using RFL (resorcinol/formaldehyde/latex) adhesives modified with Chlororesorcinolic resin. The adhesives were used to bond a tyre body stock (NR/SBR/BR blend) to polyethylene terephthalate (PET). In practice, an adhesive is applied by dipping cord into the adhesive and then subjecting the coated cord to a brief heat treatment. The adhesive dries, the RF further to react and good bonding between the adhesive and cord develops. Standard H-test specimens were prepared by embedding adhesive-coated, heat treated cords into the rubber and then vulcanizing.

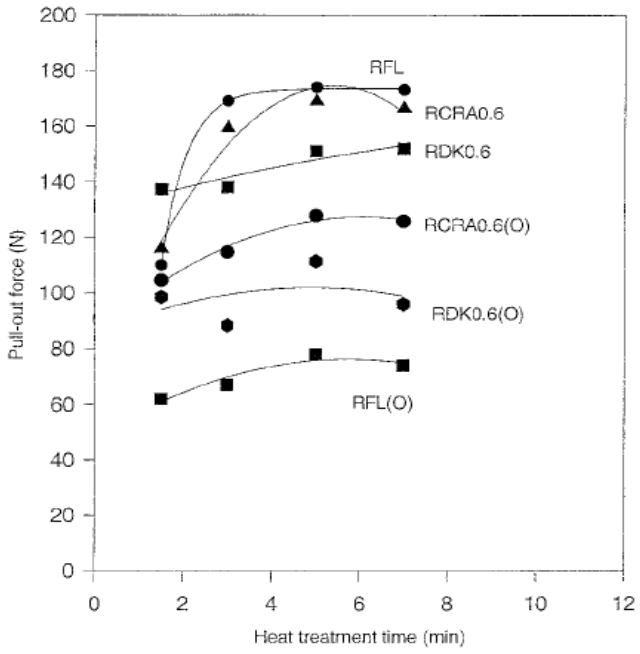

Figure 3.7 Pull-out forces for the three adhesives. Dipped PET cords were subjected to heat treatment at 233^{o}C before building test specimens and curing normally at 160^{o}C for 18.5 min. Curves labeled with suffix (O) are results for specimens that, after normal cure, were subjected to 170^{o}C for 90 min (i.e. overcure) before pull-out testing.

The effects of heat treatment time and overcure on pull-out adhesion were studied. Overcure conditions were used to simulate long service. It was found that, pull-out forces increased with longer heat treatment and decreased with overcure.

3.3 Factors affecting adhesion

There are a several variety of variables affecting rubber to rubber bonding.

3.3.1 Influence of vulcanization system

The composition of vulcanization systems and the dynamics of vulcanization can affect the bond strength significantly. After vulcanization, the rubber loses its capacity for cohesion. Therefore, the fusion of separate layers can only take place in the initial stage of vulcanization. In general, a system which vulcanizes more slowly promotes favourable conditions for autohesion.

In the case of different rubbery compounds, the unvulcanised boundary layer dose not promotes bond strength. The process of covulcanisation is possible if the two phases vulcanize at an identical rate. The bond strength depends upon the interface crosslinking as they differ in the cure rate as well as the curing system. Therefore, the bond strength is found to be highly dependent upon the degree of interface crosslinking.

Anil K. Bhowmick and Bidyut Chakraborty [57] have studied the bond strength in various rubber to rubber joints. They investigated the adhesion between various dissimilar rubbers during vulcanization and the effect of vulcanizing systems. It was found that the bond strength of two rubbers during vulcanization were increased due to diffusion of compounding ingredients across the interface that was important role in determining the interfacial adhesion. Adjustment of the vulcanizing ingredients, the cure rate, the cure time of these two systems are brought closer to each other, the joint must be expected to show higher strength.

3.3.2 Influence of filler type

Filler type is another significant factor affecting on bond strength of rubber to rubber. The extent of reinforcement of rubbers by the filler and the extent of decrease in surface mobility of rubber molecules due to the presence of the filler decreased the tack of rubber. These two parameters affect the tack of rubbers that have different chain mobility which one is higher that means more influence by reinforcement effect in another hand by chain mobility effect. When the rubber is mixed with carbon black, bound rubber is formed on surface filler. The amount of bound rubber increases with increase in surface area and structure. Hence the tack is reduced with decrease in the particle size or increase in the structure of carbon black.

Lippo and co-worker [15] have studied the bond strength of effect of filler orientation of particulate-filler composite to differently oriented fiber reinforced composite substrate. Commercially available fiber-reinforced composite (FRC) materials with continuous unidirectional silanated E-glass fibers, approximately 15 μm in diameter, preimpregnated with a polymer-monomer matrix of PMMA. The FRC substrate was first placed in cavity prepared in an acrylic resin block with different directions. The fiber direction of the substrate were (A) in the perpendicular to the bonding surface; (B) along the bonding surface longitudinal to the load and; (C) along the bonding surface, transverse to load. The results of fiber-filler differently orientations are shown in the Figure 3.8.

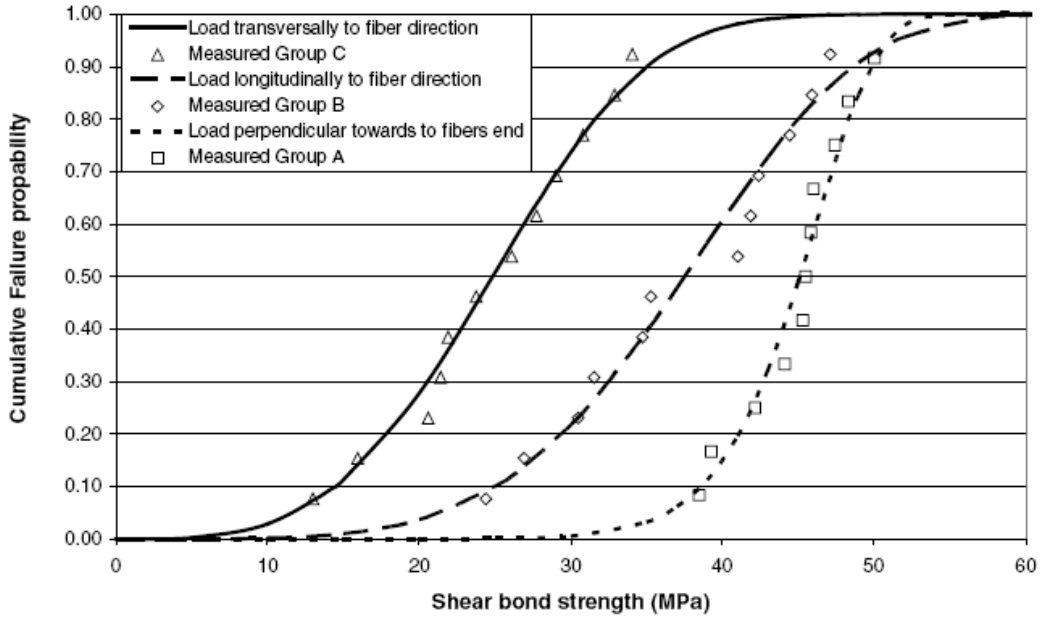

Figure 3.8 The cumulative failure probability of FRC to particulate filler composite loaded with the fibers placed in different directions.

From the Figure, it was found that the fiber of direction of the FRC substrate had a significant effect on the bond strength values. Group A where the fiber were placed perpendicular to the surface showed the highest bond strength values, Group B demonstrated lower strength values and Group C where the fibers were located transverse to the load produced the lowest bond strength values.

3.3.3 Effect of surface roughness

The roughness of surface is also the significant factor affecting adhesion. Roughness on the surfaces is well known that created roughening the heterogeneities on the surface, which will favour its interaction with the adhesive and will eliminate some mould release products present on the rubber surface and also improves the mechanical interlocking on their interfaces.

A number of researchers have studied the effect of surface roughness on bond strength. One is found that a mechanical roughening of the rubber surfaces using sandpaper was found to improve the bonding strength.

Shahid and Hashim [40] have studied the effect of surface roughness on the strength of cleavage joints. Standard steel/steel cleavage specimens have been presented. Cleavage joints with different surface roughness were mechanically tested and examined; it was found that the cleavage strength appears to increases linearly with the Ra value. The plots are shown in Figure 3.9.

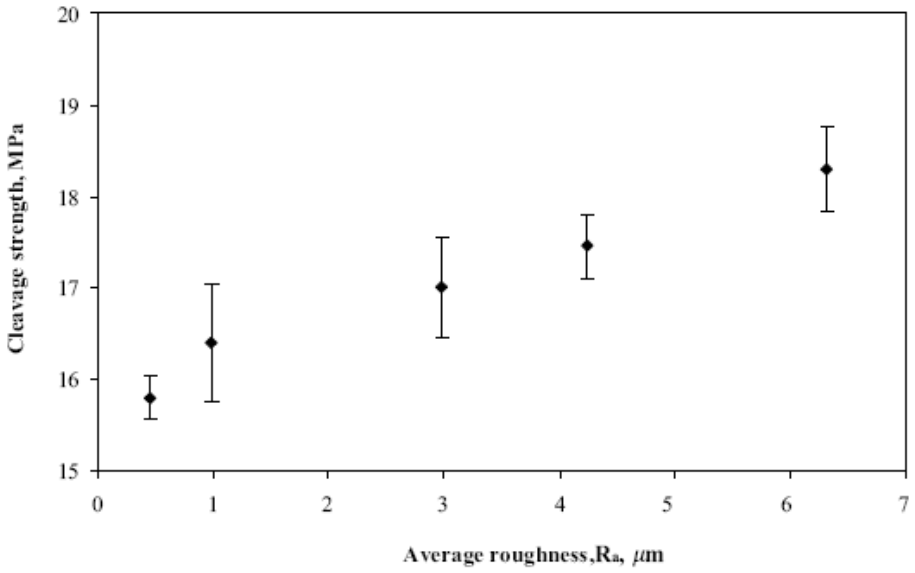

Figure 3.9 Graph showing the variation of cleavage strength with average roughness.

3.3.4 Effect of durability

Durability is concerned to the long term effects of surface preparation techniques for composite bonded joints. A number of researchers have studied the effect of time on prepared and modified surface before to be bonded in many fabrications such as footwear, automotive and aircraft industry. The bond strength has found to be dropped dramatically for application in moisture-changing environments [16].

Most research on bonding durability has considered surface adhesion as the critical factor for good bonds. Maria D. and co-workers [17] have studied the effect of durability of the halogenation in synthetic rubber. Halogenation with trichloroisocyanuric acid (TCI) solution is a common surface treatment for rubber materials to improve their adhesion to polyurethane adhesives. The time of chlorination is one key aspect in the footwear industry. It has been established [18] that for synthetic vulcanized styrene-butadiene rubbers, a minimum of 6 hrs is required to produce an adequate adhesive joint.

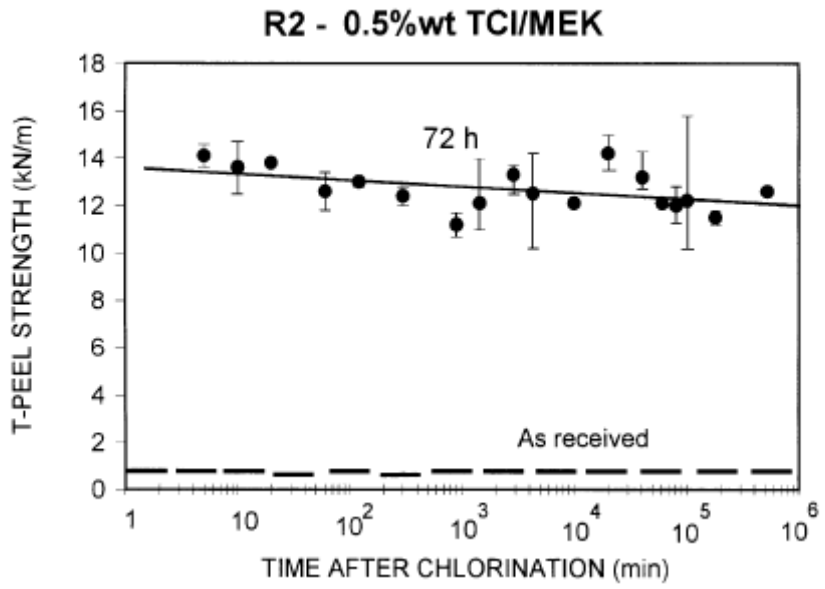

Figure 3.10 T-peel strength values of chlorinated R2 rubber/polyurethane adhesive joints as a function of the time from halogenation treatment.

3.3.5 Effect of tackifiers

Improvement of the bond strength of specimens can also be improved by addition of tackifiers. Tackifiers are resins like phenol-formaldehyde, coumarone-indene, wood rosin and maleated liquid BR. Tackifiers generally have MW in the range 500-2000 with broad MW distribution. The amount of tackifying resins that are added to rubbers varies widely depending upon the end use. The resin concentration is always

found to be higher on the surface of the compound compared to the bulk due to the solubility/insolubility of the resin in the rubber at mixing and ambient temperatures. Hence the presence of the resin can assist tack formation even when its total concentration is low.

Pimanchan and Nattakarn [19] have studied the effect of tackifier on tack and peel strength of natural rubber latex-based adhesives. They have studied the five ratios of NR latex to rosin-ester tackifier which were mixed and coated on PET films to produce adhesive tapes samples for probe tack and 180^{o} peel tests.

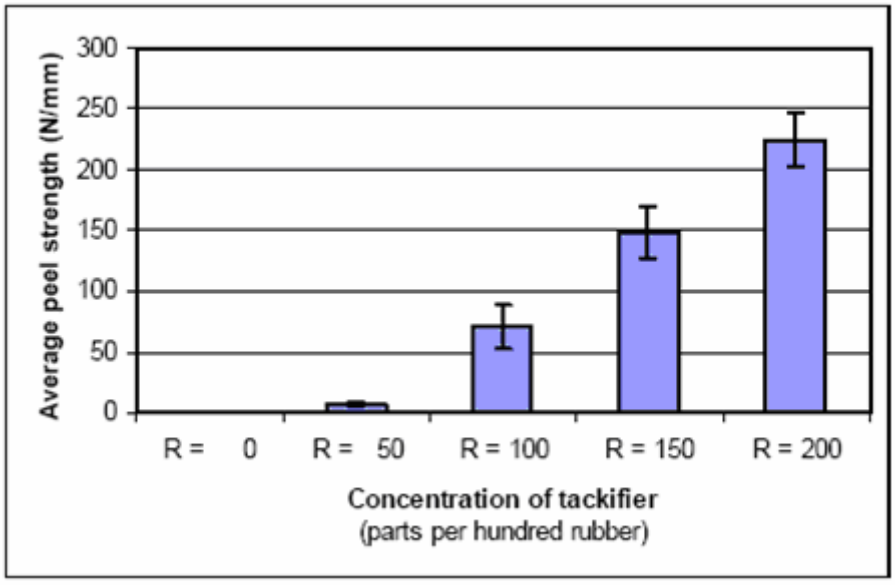

Figure 3.11 The peel strength with different concentrations of tackifier for natural rubber latex to rosin-ester blend

From Figure 3.11, it was found that higher concentration of tackifier increases peel strength in linear fashion. Peel strength is the measure of force needed to separate adhesive from the substrate when they had already well bonded together. Tackifier helps the NR-based adhesive to wet on the substrate better, producing higher adhesion between substrate and adhesive.

3.3.6 Effect of polymer viscosity

Polymer viscosity is the important factor to bonding strength. The adhesion of high polymers is very closely connected with their viscosity. The fact that high polymer viscosity is influenced by such properties of its macromolecules as size, branching, flexibility, presence of polar groups and in general, by all properties of macromolecules affecting macrobrownian and microbrownian motion.

Enzhi and co-worker [20] have studied the effect of wood surface roughness, adhesive viscosity and processing pressure on adhesion strength of protein adhesive, and to seek the relative importance of the individual factors in determining adhesion strength. Adhesive viscosity had greater effect on adhesion strength than surface roughness. Contact angle, which was found to be mainly determined by adhesive viscosity and surface roughness, was a major factor controlling adhesive penetration. A smaller contact angle, resulting from lower viscosity and rougher surface, produced deeper penetration, while a larger contact angle, resulting from higher viscosity and smoother surface, produced shallower penetration. An optimum penetration is needed to enhance adhesion strength by developing a three-dimensional interactive zone at the interface. Too deep or too much penetration would result in ‘dry-out’ at the interface; less penetration would limit the formation of the three-dimensional zone at the interface. Both cases resulted in reduced adhesion strength. Contact angles ranging from 35 to 47° provided the optimum penetration needed for good adhesion. The results of this research could be used as reference to determine optimum process parameters in plywood manufacturing when an aqueous based adhesive is used.

3.3.7 Effect of polarity of polymer

Most of polymers have differently polarity individual of themselves. Therefore, their bonded joints were deservedly considered to adhesion strength. The role of the thermodynamic factor in creating an adhesion bond between partly or wholly compatible polymers is discussed. The importance of this factor depends on the fact that polymers brought into contact will diffuse into each other only if they are wholly or partly mutually soluble. This mutual solubility is confined to a surface layer and is

determined by the local diffusion. In considering the mechanism of formation of an adhesion bond between two polymers it is necessary to take their surface properties into account. In the adhesion theory, of diffusion is regarded as the motive force in the creation of an adhesion bond [21].

3.3.8 Effect of surface modification

Surface of polymeric materials is the one affecting to the bond strength at their interface. In general, different polymers have the different surface energy which bonding them together might be difficult to good bond. The nature of the polymeric surface is involved in the phenomena of adhesion, adhesive joint strength, wettability, and spreading of a polymer in contact with another phase.

Many researches have found that modification on rubber surfaces can increase the adhesion strength of the different rubbers bonding. For example, Tyczkowski and co-worker [22] have studied plasma chlorination on styrene-butadiene rubber surfaces. Styrene-butadiene rubbers (SBR) were exposed to action of plasma generated in various reaction mixtures containing moieties. As chlorine precursors, trichloromethane ($CHCl_3$), tetrachloromethane (CCl_4), and chlorine (Cl_2) were used. The composite vulcanized butadiene-styrene rubber was subjected to various plasma treatments. The plasma treatment was carried out in the reactor that is more convenient for industrial applications. To determine the adhesion strength of rubber surfaces, T-peel tests were carried out. Adhesive joints were made using the rubber samples with the surface mechanically roughed before the modifying treatment and strips of standard leather (box cow, chrome tanned, non-pigmented). The results is shown in the Figure 3.12.

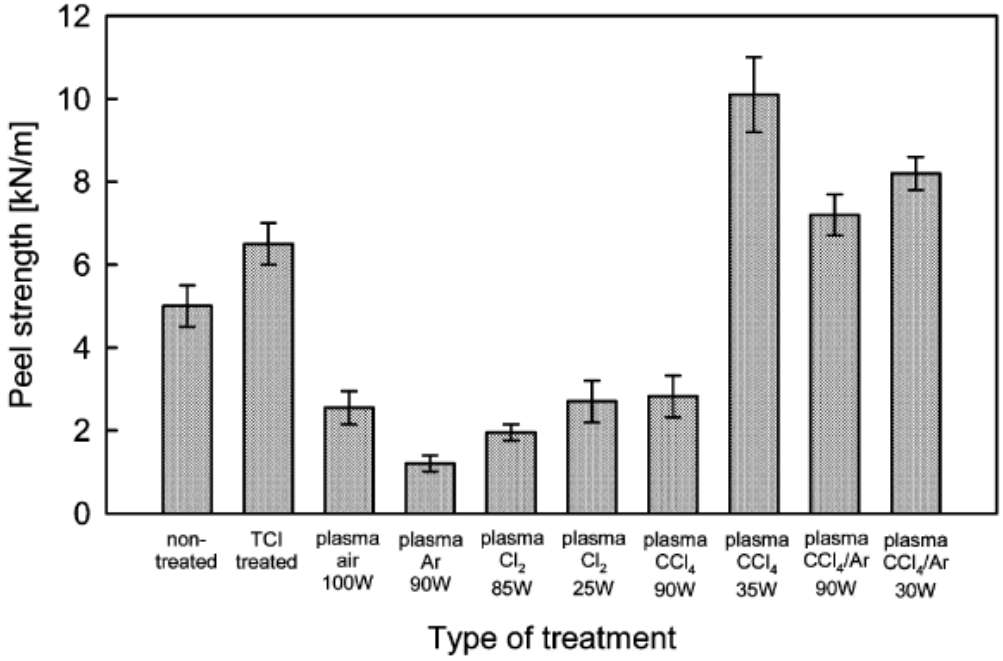

Figure 3.12 Measurements of the T-peel strength for a composite vulcanized rubber (SBR compounds) after various types of the surface treatment

In Figure 3.12, the selected results of peel strength are shown. It was found that the treatment at low-power pure CCl_4 plasma improves the adhesion strength approximately 100% in relation to the non-treated rubber. However, the treatments by air, argon and chlorine plasma evidently deteriorate the adhesion properties of the rubber surface, giving the peel strength values even below the value for the non-treated sample.

3.3.9 Effect of Blooming

The blooming of rubber is a serious problem affecting adhesion of rubber to rubber bonding. Blooming of ingredients such as sulphur and antioxidants was often found in unvulcanised rubbers. Some of the bloomed materials can be melted at about 90^{o}C while others remain as large flakes. While the former creates a little problem during the bonding of unvulcanised pieces via crosslinking, the latter leads to severe

loss of bonding strength. Sulphur blooming may be prevented by the use of insoluble sulphur, and controlling the mixing temperature as insoluble sulphur gets converted to the soluble form at 90^{o}C. In conventional retreading compounds, the amount of soluble sulphur used is below its solubility limit to control the sulphur blooming during storage.

3.3.10 Effect of aging

Unvulcanised rubber compounds were aged in the laboratory (oven) or external atmosphere, exposed to ozone or UV radiation including sunlight, suffer a reduction in their subsequent cured interfacial adhesion. The reduction in bond strength is dependent upon the rubber used. The exposure of uncured rubber surfaces causes an appreciable reduction in the subsequent vulcanized properties. In the case of tire industry, it was found that tire manufacturers blend into the tire polymer certain chemical ingredients which inhibit damage from ozone and ultraviolet light. The need to protect rubber against UV damage is why tires are black. For this purpose, a common type of UV stabilizer called a "competitive absorber" is used. Competitive absorbers work by capturing and absorbing harmful UV light wave energy (instead of the adjacent molecule of tire polymer that's why it's called "competitive"). Competitive absorbers have the added ability to convert harmful UV light wave energy into heat so it can dissipate harmlessly. All tire manufacturers use the same competitive absorber, carbon black, an extremely inexpensive compound. All other UV stabilizers are prohibitively expensive. This is why tires are black and why tires are not available in designer colors. All UV stabilizers are sacrificial, meaning they are gradually "used up" to where they can no longer protect against UV damage. As carbon black loses the ability to do its job, it turns gray. This is why rubber grays as it ages [23]. Tire manufacturers use waxes to protect against ozone. When tires are in use (regularly running up and down the road for example) they flex. Flexing causes the protective waxes to migrate to the surface where they form a physical barrier between the air (ozone and oxygen) and the tire polymer. This process the wax migrating to the surface of the tire during flexing is called "blooming". When tires are not regularly used (a parked RV, boat trailer, or classic car, etc), blooming does not occur. Ozone begins

eating away the protective wax and before long reaches the tire polymer. Often by this time, the surface carbon black has lost its ability to protect against UV. With UV light and ozone working in concert, degradation starts. The tire dries, checks, and will eventually crack.

3.3.11 Effect of moisture and humidity

Many researches have been reported that moisture and humidity have effective to adhesion of materials bonding. Mohamed and co-workers [24] had studied the effect of moisture and temperature ageing on reliability of interfacial adhesion with black copper oxide surface. They have studied the adhesion performance of copper alloy substrate with bare surface, black oxide coating and black oxide with debleeding treatment. The interfacial adhesion of substrate with polyimide tape and glob top resin was measured. Moisture absorption and desorption studied at different aging time were carried out to understand the property changes due to moisture. The results show that the black oxide coating improved significantly the interfacial bond strength in dry condition.

Some data has revealed that chemistry of moisture attack at polyimide and glass interface which the interaction between polyimide coatings and the oxide surface of a silicon wafer. The top most surface is in fact hydroxilated due to ubiquitous presence of moisture under ambient conditions. The polyimide can in fact bond chemically to this surface giving rise to good adhesion. The presence of fluorine, however, not only prevents this bonding from occuring but also provides a chemical mechanism for further disrupting bonds that have already formed [58]. The picture of moisture can interact with polyimide/glass is shown the Figure 3.13

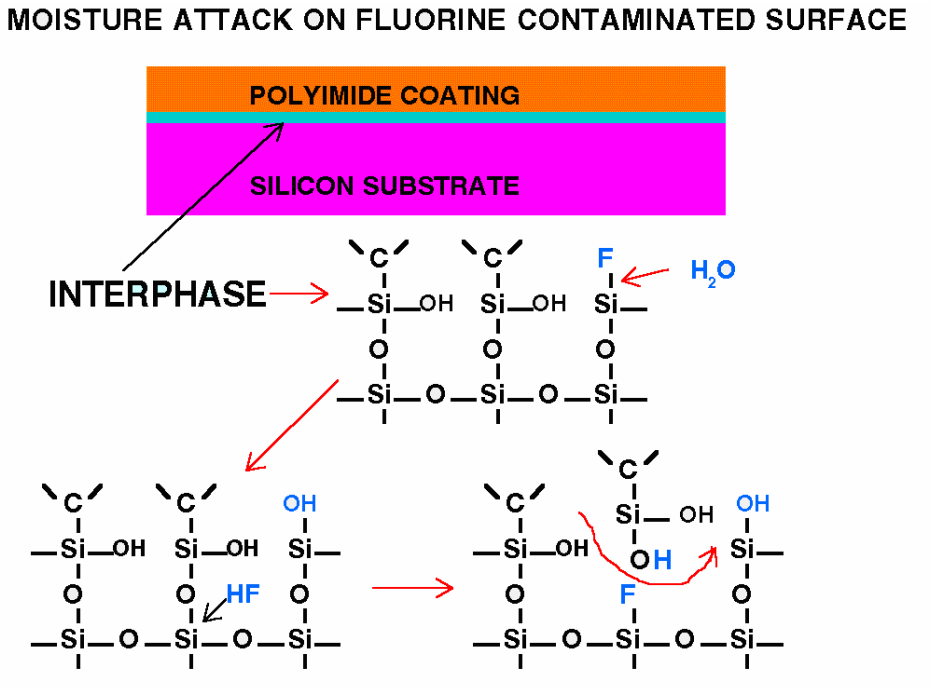

Figure 3.13 Schematic of polyimide/glass interface with fluorine contamination [58]

Fluorine to form HF (hydrofluoric acid) leaving a stable SiOH bond behind. It is well known that HF can readily attack and etch glass which is shown in the second step. After this reaction, the group anchoring the polyimide chain is now detached from the surface which will cause the adhesion at this point to drop dramatically. In addition, the contaminant fluorine atom is situated as it was initially and can now react with the next water molecule that comes along and repeat the whole degradation process over again. Thus, even though the amount of fluorine present may be very small, each fluorine atom can be used over and over again, leading to a large scale weakening of the polyimide/glass interface.

3.3.12 Effect of other ingredients

Petrochemicals and silicone oils can remove the protective waxes and increase the rate of degradation. Common automotive "protectants" and "tire dressings" are typically devoid UV stabilizers of any type. They contain petrochemicals and/or

silicone oils which dissolve away the protective waxes and can actually aggress the sidewall. In the event of warranty sidewall failure, one of the first things tire manufacturers look for is evidence of the use of these types of products. When found, this is often causing for not warranting the sidewall failure.

3.4 Adhesion strength improvement

The bonding strength between two materials can be improved in many ways, by adhesive between interfacial of materials and modification on material surfaces.

3.4.1 Improvement via adhesive

An adhesive is a compound that adheres or bonds two items together. Adhesives may come from either natural or synthetic sources. Some modern adhesives are extremely strong, and are becoming increasingly important in modern construction and industry.

3.4.1.1 Adhesive category

Natural adhesives Adhesives based on vegetable (natural resin), food (animal hide and skin), and mineral sources (inorganic materials).

Synthetic adhesives Adhesives based on elastomers, thermoplastic, and thermosetting adhesives.

Drying adhesives These adhesives are a mixture of ingredients (typically polymers) dissolved in a solvent. Glues such as white glue, and rubber cements are members of the drying adhesive family. As the solvent evaporates, the adhesive hardens. Depending on the chemical composition of the adhesive, they will adhere to different materials to greater or lesser degrees. These adhesives are typically weak and are used for household applications. Some intended for small children are now made non-toxic.

Contact adhesives Contact adhesive is one which must be applied to both surfaces and allowed some time to dry before the two surfaces are pushed together.

Some contact adhesives require as long as 24 hours to dry before the surfaces are to be held together. Once the surfaces are pushed together the bond forms very quickly hence it is usually not necessary to apply pressure for a long time. This means that there is no need to use clamps, which is convenient. Natural rubber and polychloroprene (Neoprene) are commonly used contact adhesives. Both of these elastomers undergo strain crystallization. When an adhesive bond containing either of these materials is pulled apart, the elastomer is strained, develops crystallites, and actually becomes stronger than in the original, unstressed, state. Contact adhesives find use in laminates, such as bonding Formica to a wooden counter, and in footwear, for example attachment of an outsole to an upper.

Hot adhesives (thermoplastic adhesives) A glue gun, an example of a hot adhesive. Also known as "hot melt" adhesives, these adhesives are thermoplastics; they are applied hot and simply allowed to harden as they cool. These adhesives have become popular for crafts because of their ease of use and the wide range of common materials to which they can adhere.

Reactive adhesives A reactive adhesive works by chemical bonding with the surface material. They are applied in thin films. Reactive adhesives are less effective when there is a secondary goal of filling gaps between the surfaces. These include two-part epoxy, peroxide, silane, metallic cross-links, or isocyanate. Such adhesives are frequently used to prevent loosening of bolts and screws in rapidly moving assemblies, such as automobile engines. They are largely responsible for the quieter running modern car engines.

UV and Light Curing Adhesives Typically, these adhesives fully cure in seconds upon exposure to UV or visible light of the proper wavelengths, intensity, and duration. Some formulations are "fixtured" with UV light, but require additional time or curing mechanisms to achieve full cure. UV curing adhesives can be formulated with a wide variety of properties (low to high viscosity, flexible to rigid, clear to colored, adhesion to glass/plastics/metals/ceramics, depth of cure to >1/2").

Pressure sensitive adhesives Pressure sensitive adhesives (PSAs) form a bond by the application of light pressure to marry the adhesive with the adherend. They are designed with a balance between flow and resistance to flow. The bond forms because the adhesive is soft enough to flow, or wet, the adherend. The bond has strength

because the adhesive is hard enough to resist flow when stress is applied to the bond. Once the adhesive and the adherend are in close proximity, molecular interactions such as van der Waals forces become involved in the bond, contributing significantly to its ultimate strength.

Pressure sensitive adhesives (PSAs) are designed for either permanent or removable applications. Examples of permanent applications include safety labels for power equipment, foil tape for HVAC duct work, automotive interior trim assembly, and sound/vibration damping films. Some high performance permanent PSAs exhibit high adhesion values and can support kilograms of weight per square centimeter of contact area, even at elevated temperature. Permanent PSAs may be initially removable (for example to recover mislabeled goods) and build adhesion to a permanent bond after several hours or days.

Removable adhesives are designed to form a temporary bond, and ideally can be removed after months or years without leaving residue on the adherend. Removable adhesives are used in applications such as surface protection films, masking tapes, bookmark and note papers, price marking labels, promotional graphics materials, and for skin contact (wound care dressings, EKG electrodes, athletic tape, analgesic and transdermal drug patches, etc.). Some removable adhesives are designed to repeatedly stick and unstick. They have low adhesion and generally can not support much weight. Pressure sensitive adhesives are manufactured with either a liquid carrier or in 100% solid form. Articles are made from liquid PSAs by coating the adhesive and drying off the solvent or water carrier. They may be further heated to initiate a crosslinking reaction and increase molecular weight. 100% solid PSAs may be low viscosity polymers that are coated and then reacted with radiation to increase molecular weight and form the adhesive; or they may be high viscosity materials that are heated to reduce viscosity enough to allow coating, and then cooled to their final form.

3.4.1.2 Mechanisms of adhesion

The strength of attachment, or adhesion, between an adhesive and its substrate depends on many factors, including the means by which this occurs. Adhesion may

occur either by mechanical means, in which the adhesive works its way into small pores of the substrate, or by one of several chemical mechanisms.

In some cases, an actual chemical bond occurs between adhesive and substrate. In others electrostatic forces, as in static electricity, hold the substances together. A third chemical method involves van der Waal's forces which develop between each's molecules. A fourth chemical means involves the moisture-aided diffusion of the glue into the substrate, followed by hardening.

3.4.2 Improvement via surface modification

Polymeric materials such as rubbers and plastics are used for a legion of applications in a host of technological fields. However, polymers are innately hydrophobic, low surface energy materials and thus do not adhere well to other materials. This necessitates surface modification to render them adhesionable.

The nature of the polymeric surface is involved in the phenomena of adhesion, adhesive joint strength, wettability, and spreading of a polymer in contact with another phase. At present, there is a considered body of experimental information on the wetting of polymer, polymer melt surface tension, interfacial tension between different pairs of polymer melts, and the modification of polymer surfaces by additives and chemical reactions.

The way to modifying on polymeric surfaces usually is divided in two types, physical and chemical methods.

3.4.2.1 Physical modification [25]

The activities aimed at physically modifying polymer surfaces can be divided into two main categories, the first involved with chemically altering the surface layer, the second with depositing an extraneous layer on top o f the existing material, thereby generating a sharp interface.

3.4.2.1.1 Plasma treatments

The plasma technology provides several varieties for surface treatment**.** Some of the applications are cleaning of contaminated devices, plasma activation of plastic parts, etching of PTFE, silicon and coating of layers similar to PTFE. That is why this plasma technology is used for various applications, where materials have to be combined or where surfaces need special modification.

Radio-frequency, low-pressure plasma treatment is an efficient, environmentally friendly method of surface preparation prior to bonding, deposition and coating. Plasma treatment provides increased bond strength, wettability, permeability, hydrophobicity, and biocompatibility. Plasma cleaning removes organic and inorganic materials that prohibit desired bond strengths without affecting the bulk properties. Plasma treatment can add functional groups to a surface at the molecular level, changing surface chemistries for improved lubricity and surface adhesion.

Low pressure plasma technique

Plasma is a partially ionized gas containing ions, electrons, atoms and neutral species. To be able to ionize the gas in a controlled and qualitative way the process acts under vacuum conditions. Therefore a vacuum vessel is pumped down to a pressure in the range of 10^{-2} to 10^{-3} mbar with the use of high vacuum pumps. The gas which is than introduced in the vessel is ionized with help of a high frequency generator. The formed environment is the so called 4^{th} state of matter. This means that if sufficient energy is supplied that solids can be melted to liquids, liquids can be vaporized into a gas, and gases are ionized into plasma. A specific characteristic of plasma is the visible grow discharge with colours ranging from blue-white to dark purple depending on the type of gas. The high reactive particles react with the surface of the substrate. The advantage of this plasma is that it is a well controlled and reproducible technique.

Tyczkowski and co-worker [22] have studied plasma chlorination modified on styrene-butadiene rubber surfaces. Styrene-butadiene rubbers (SBR) were exposed to action of plasma generated in various reaction mixtures containing moieties. As chlorine precursors, trichloromethane ($CHCl_3$), tetrachloromethane (CCl_4), and

chlorine (Cl_2) were used. The composite vulcanized butadiene-styrene rubber was subjected to various plasma treatments. The plasma treatment was carried out in the af reactor that is more convenient for industrial applications. To determine the adhesion strength of rubber surfaces, T-peel tests were carried out. Adhesive joints were made using the rubber samples with the surface mechanically roughed before the modifying treatment and strips of standard leather (box cow, chrome tanned, non-pigmented).

. It was found that the treatment at low-power pure CCl_4 plasma improves the adhesion strength approximately 100% in relation to the non-treated rubber. However, the treatments by air, argon and chlorine plasma evidently deteriorate the adhesion properties of the rubber surface, giving the peel strength values even below the value for the non-treated sample.

3.4.2.1.2 UV treatments

UV lamps are widely used for the treatment of polymer surfaces and the apparatus involves essentially a lamp and sample illumination devices, such as the possibility of selectively irradiating tiny areas or moving the sample below the photon source. Most applications involve the photon-activate cross-linking or fragmentation of polymer coatings. Sensitizers are typically added to enhance the photon yield of the processes. Lamps operating between 250 and 400 nm wavelengths are most frequent.

Maria and co-worker [27] have studied the effectiveness of the treatment with ultraviolet light (UV) on several polymeric surfaces. In this study, a low pressure mercury vapour lamp was used as a source of UV radiation for the surface treatment of a difficult-to-bond block styrene-butadiene-styrene rubber (S6), the treatment time ranging from 10 s to 30 min. The UV-treated S6 rubber surfaces were characterized by contact angle measurements (ethylene glycol, 25°C), ATR-IR spectroscopy, XPS, Scanning Electron Microscopy (SEM), and Atomic Force Microscopy (AFM). T-peel tests on UV-treated S6 rubber/polyurethane (PU) adhesive/ leather joints (before and after ageing) were carried out to quantify adhesion strengths. The UV treatment of S6 rubber produced improved wettability, the formation of C—O, C=O and COO^- moieties, and ablation (removal of a thin rubber layer from the surface). The extent of these modifications increased with increasing treatment time. The extended UV

treatment produced greater surface modifications, as well as the incorporation of nitrogen moieties at the surface. Furthermore, noticeable ablation of S6 rubber surface occurred. Peel strength values increased with increased treatment time of UV treatment of S6 rubber. Also, with increasing treatment time, the adhesive joints showed different loci of failure: adhesional failure for the as-received and 2 min-UV treated S6 rubber/polyurethane adhesive/leather joints changed to mixed failure (cohesive in the treated S6 rubber + adhesive failure) for the 30 min-UV treated S6 rubber/polyurethane adhesive/leather joint.

3.4.2.1.3 Ion beam treatments

Polymer materials are used in different fields of industries, from microelectronice to medicine. Ion beam implantation is method of surface modification when surface properties must be significantly changed and bulk properties of material must be saved.

Ion beams can be used for two different purposes, namely to directly alter the surface composition of the material or to sputter off target species which are then deposited on the surface. Ion beam sources have found increasing applications in the past two decades. Initially developed for space propulsion, their value for surface cleaning, etching, and thin film deposition was quickly realized. One area of technology that has demonstrated vast promise is gridless ion source technology. Gridless ion sources can produce ion beams with easy operation and maintenance. The high throughput, broad energy distribution, and ease of operation make gridless ion source technology well-suited to the surface modification of polymers. This application note relates some processes performed on an Advanced Energy Linear Ion Source (LIS) on polyfluorotetraethylene. Using argon and argon/oxygen ion beams, surface roughness was induced as visible in SEM images of untreated and ion beam treated samples as in the Figure 3.14.

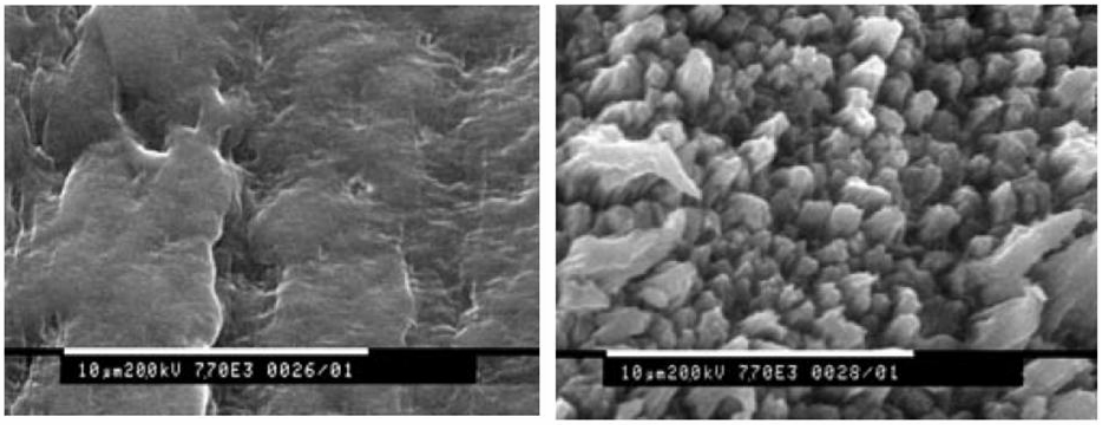

Figure 3.14 (Left) SEM image of surface of untreated PTFE, (Right) SEM image of treated PTFE surface with an argon/oxygen ion beam from an Advanced Energy Linear Ion Source.

The treatment conditions were an applied voltage and power of 3000 V and 1.3 kW at 2.2 mTorr chamber pressure with an O_2/Argon flow ratio of 2:1. This treatment generated an adhesion force of 90g/mm^2. From this image, it is clear that the surface topography has been significantly altered; the PTFE surface is now much rougher and several surface features visible in the SEM. From the image, it is clear that modifications to polymers using ion beam treatment can be localized at the surface, allowing surface properties to be specifically tailored without altering the bulk properties of the material. In addition, the adhesion force measurements suggest that the surface properties of this sample have been successfully altered to be more compatible with typical adhesives. [28]

3.4.2.2 Chemical modification [25]

Chemical modification is the treatments that modify the chemical composition of polymer surface either by direct reaction with a given solution (wet treatment) or by the covalent bonding of suitable macromolecular chains to the sample surface (surface grafting).

3.4.2.2.1 Wet treatments

Wet treatments were the first surface modification techniques used in order to improve surface properties of polymers. The chemical composition of the solution employed in the treatment was, in general, from general wet chemistry knowledge. The treating polymer on surfaces can also be called “wet chemical methods”. This term means that a solution is applied to the polymer’s surface that results in either a cleaning of the surface or an actual surface preparation. The simplest wet chemical method is solvent wiping, although this method is usually infective because the weak boundary layers often quickly reform after treatment. [1].

Solvent wiping does not increase surface energy nor modify surface morphology. Priming is a method of surface preparation often used to increase the surface energy of polymers. In priming, a coating is applied, usually one with a higher surface energy and compatible with the polymer to be primed. Chemical and morphological modification of polymer surfaces can also be obtained by aggressive chemical treatment.

The C=C bonds in the polymer structure cause the poor resistance to thermal and oxidative degradation when exposed to harsh operating systems. The study of chemical modification has been an interesting field to improve or develop the structure of general diene polymers such as natural rubber, polybutadiene, acrylonitrile-butadiene rubber, etc., to increase its thermal and oxidative resistance

The chemical modification of rubber is used to improve the chemical and mechanical properties of rubbers. The chemical modification reactions currently under study include halogenations (fluorination, chlorination, bromination), hydrogenation and graft copolymerization of natural rubber.

<u>Chlorination chemical modification method</u>

Chlorination with halogenating agents in organic solutions is a common surface treatment for styrene–butadiene rubber materials to improve their adhesion to polyurethane adhesives. Chlorination of rubber products is a simple and effective means of reducing surface friction and tack in application such as gloves and

windshield wiper blades. Samples are easily chlorinated by placing them in an aqueous free-chlorine solution for several minutes at room temperature. The chlorination of rubber is extremely complex, however, involving substitution, addition, and cyclization.

Chlorination methods have many ways to carry out the free chlorine groups to functional on rubber surfaces such as by sodium hypochlorite solution [29, 30] and trichloroisocyanuric acid [31, 32, 33]

In 1987, C.W. Extrand and A.N. Gent [29] had studied contact angle and spectroscopic of chlorinated and unchlorinated natural rubber surfaces. Chlorination of the rubber surfaces was affected by immersing samples for various times in a stirred aqueous solution containing 0.3 % free chlorine and then neutralizing them in 2% ammonium solution. The chlorination solution consisted of 100 parts by volume of distilled water, 6 parts of 5.25% NaOCl and 1 part of 37% HCl. After treatment, they had found that contact angles on chlorinated NR surface were decreased to compare with untreated NR surfaces.

In 1998, C.C. Ho and M.C. Khew [30] had studied the surface of chlorinated unvulcanised natural rubber latex films. NR latex film surface is often chemically modified by chlorination to reduce surface frictional resistance. This is particularly so in the manufacture of examination and household NR latex gloves to improve donning property and to reduce surface tackiness. NR latex film was chlorinated by chlorine gas generated in situ from acidified hypochlorite solution at room temperature and was characterized by FTIR-ATR, SEM-EDX and contact angle techniques. Chlorinated and oxygenated structures were found on the film surface after chlorination. The hydrophiclicity of the surface improved after chlorination. Cracking of the surface was noted and the surface mean roughness, R_a, of the chlorinated surface increased with extent of chlorination. Surface roughening and hardening both would result in a reduction in the adhesive friction of the chlorinated surface against a substrate.

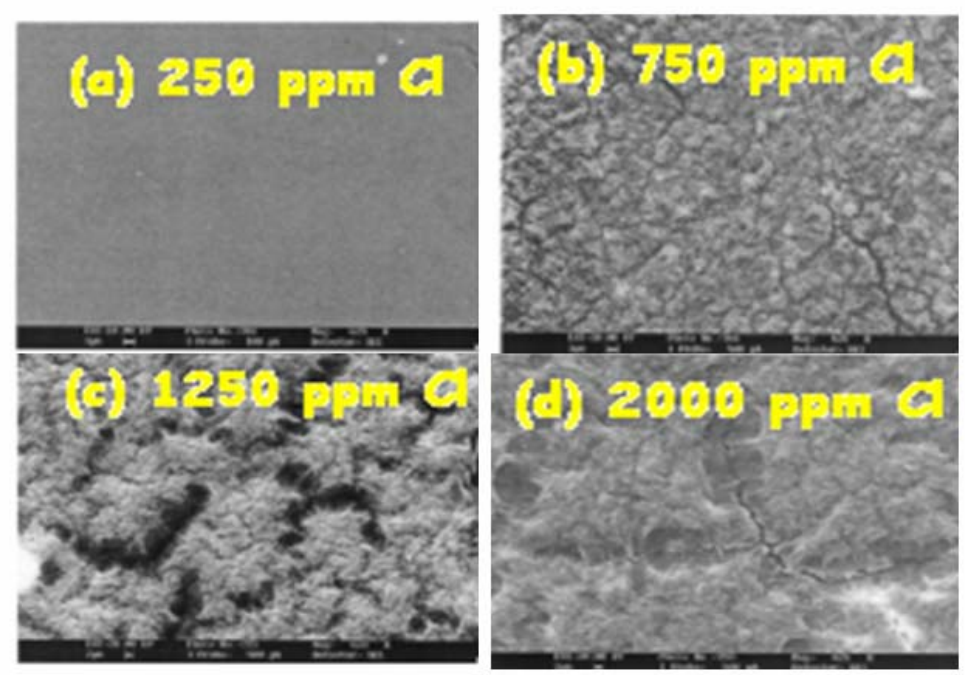

Figure 3.15 Scanning electron micrographs of NR latex films chlorinated at various chlorine dosages, (a) 250; (b) 750; (c) 1250; (d) 2000; ppm, Magnification at 2500 times.

Another usual way to chlorination rubber by wet chemical treatment is trichloroisocyanuric acid (TCI) solutions. Halogenation with trichloroisocyanuric acid is a common surface treatment for rubber materials to improve their adhesion to polyurethane adhesives in the footwear and automotive industry [32].

Maria D. and co-worker had studied the halogenation in synthetic rubber in many ways and methods. Synthetic vulcanized styrene-butadiene rubbers were used to the halogenation methods. Chlorination of a synthetic vulcanized styrene-butadiene rubber with trichloroisocyanuric acid in different solvents such as butanone, Ethyl, propyl and butyl acetates (EA, PA, BA), ethyl methyl ketone (MEK) have been used in researches. It was found that chlorination produced improved wettability of SBR and also the removal of paraffin wax from the surface. The improved surface modifications of SBR rubber treated allowed and increase in adhesion to polyurethane adhesive and failure was cohesive in the chlorinated layer. The peel strength of SBR treated and

polyurethane adhesive joints were affected with chlorine concentration in TCI solution and chlorination times.

Surface oxidation and Etching

Surface treatment of various polymers by oxidizing solution was showing the surface roughness and introduction of oxygen containing functional group. Surface oxidation and etching is the chemicals are used to eliminate oxides, to attack the surface layer of the material and/or to create reactive sites. The processes depend on the plastics or rubbers. The most used are:

- Chromic or sulfo-chromic acid etching, for polyolefins, polystyrene, ABS, polyacetal, polyphenylene ether. These treatments have two effects:
    - Forming surface irregularities for a mechanic anchorage.
    - Creating reactive sites such as hydroxyl, carbonyl, carboxylic.
- Oxidation by flame treatment for polyolefins: exposition to a flame of methane, propane or butane and oxygen in excess during a very short time (less than 0.2 seconds) to create oxidation and reactive sites such as hydroxyl, carbonyl, carboxyl. Particularly used for polyethylene and polypropylene.
- Oxidation by high hot-air treatment for polyolefins: exposition to a blast of hot air (roughly 500°C) during a short time to oxidize the surface and create reactive sites such as hydroxyl, carbonyl, carboxyl, amides. Rather similar to flame treatment, it is particularly used for polyethylene and polypropylene
- Iodine treatment for the polyamides: improves the chemical reactivity of the surface.
- Sodium naphthalene etching or Tetra Etch for PTFE: improves the surface roughness and creates unsaturated bonds, carbonyl and carboxyl groups.
- Sulphuric acid etching for some rubbers: creates reactive sites favourable for the chemical adhesion.

- Surface grafting of chemical species to improve the chemical bond ability. Can be helped by simultaneous gamma or other irradiation. It is particularly used for polyethylene.

3.4.2.2.2 Surface grafting

Surface modification via surface graft polymerization has been widely studied that involving the covalent bonding of suitable macromolecular chain to sample surface. It is a very simple method to obtain functionalized polymers with specific properties, by introducing specific monomers only on polymer surface. The surface graft polymerization of monomers can be initiated by trapped free radicals or polymeric peroxides generated in the surface region of substrate polymer. It is well known that surface grafting may proceed by a free radical abstracts hydrogen atom from the polymer. Macro radical are then formed and the radical can act as grafting site for vinyl polymerization. Therefore, a fundamental step in grafting is the creation of active site on the polymer surface.

3.5 Failure of the adhesive joint

When subjected to loading, debonding may occur at different locations in the adhesive joint. The major fracture types are the following.

3.5.1 Cohesive fracture

Cohesive “fracture" is obtained if a crack propagates in the bulk polymer which constitutes the adhesive. In this case, the surfaces of both adherents after debonding will be covered by fractured adhesive. The crack may propagate in the centre of the layer or near an interface. For this last case, the “cohesive” fracture can be said to be “cohesive near the interface”. Most quality control standards consider that a “good” adhesive bonding must be “cohesive”.

3.5.2 Interfacial fracture

The fracture is “adhesive” or “interfacial” when debonding occurs between the adhesive and the adherent. In most cases, the occurrence of “interfacial” fracture for a given adhesive goes along with smaller fracture toughness. The “interfacial” character of a fracture surface is usually detected by visual inspection, but advanced surface characterization techniques such as spectrophotometry allows identifying the precise location of the crack path in the interphase.

3.5.3 Other types of fracture

The “mixed” fracture type which occurs if the crack propagates at some spots in a “cohesive” and in others in an “interfacial” manner. “Mixed” fracture surfaces can be characterized by a certain percentage of “adhesive” and “cohesive” areas.

The “alternating crack path” fracture type which occurs if the crack jumps from one interface to the other. This type of fracture appears in the presence of tensile pre-stresses in the adhesive layer.

Fracture can also occur in the adherent if the adhesive is tougher than the adherent. In this case the adhesive remains intact and is still bonded to one substrate and the remnants of the other. For example, when one removes a price label, adhesive usually remains on the label and the surface. This is cohesive failure. If, however, a layer of paper remains stuck to the surface, the adhesive has not failed. Another example is when someone tries to pull apart Oreo cookies and all the filling remains on one side. The goal in this case is an adhesive failure, rather than a cohesive failure. [34]

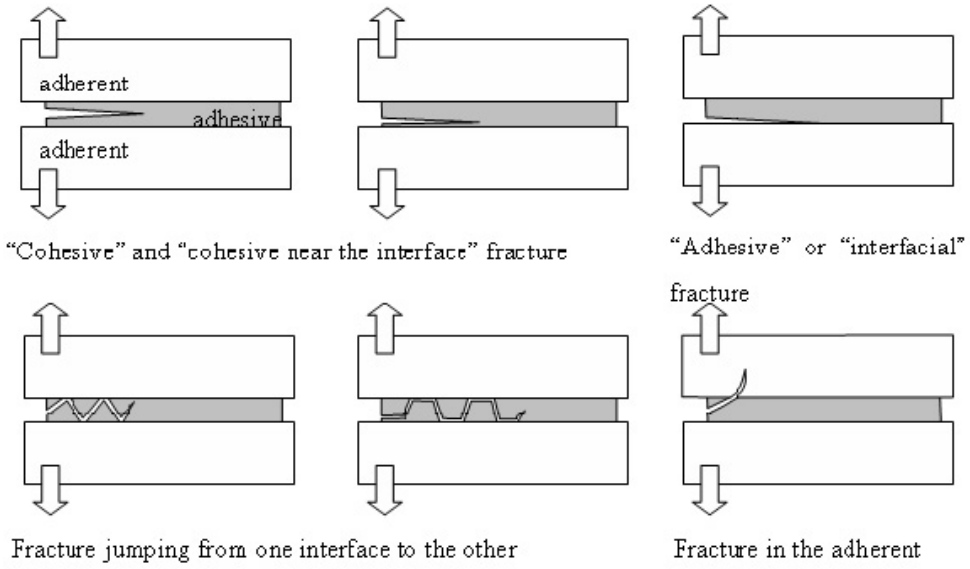

Figure 3.16 Various types of failure of adhesive joint [34]

3.6 Characterization methods

3.6.1 Surface properties

This section is appropriate to review and describe about the methods of characterizing surfaces of chemical modification on natural rubber surfaces.

3.6.1.1 Contact angle measurement [35]

Contact angle determinations have been used extensively to investigate the polarity of material surfaces and their properties. The contact angle is the angle at which a liquid/vapor interface meets the solid surface. The contact angle is specific for any given system and is determined by the interactions across the three interfaces. Most often the concept is illustrated with a small liquid droplet resting on a flat horizontal solid surface. The shape of the droplet is determined by the Young-Laplace equation. The contact angle plays the role of a boundary condition. Contact angle is measured using a contact angle goniometer. The contact angle is not limited to a liquid/vapour interface; it is equally applicable to the interface of two liquids or two vapours.

The theoretical description of contact arises from the consideration of a thermodynamic equilibrium between the three phases: the liquid phase of the droplet (L), the solid phase of the substrate (S), and the gas/vapor phase of the ambient (V) (which will be a mixture of ambient atmosphere and an equilibrium concentration of the liquid vapor). The V phase could also be another (immiscible) liquid phase. At equilibrium, the chemical potential in the three phases should be equal. It is convenient to frame the discussion in terms of the interfacial energies. We denote the solid-vapor interfacial energy as γ_{SV}, the solid-liquid interfacial energy as γ_{SL} and the liquid-vapor energy (i.e. the surface tension) as simply γ, we can write an equation that must be satisfied in equilibrium (known as the Young-Dupré equation):

$$0 = \gamma_{\mathrm{SV}} - \gamma_{\mathrm{SL}} - \gamma\cos\theta \qquad \text{Equation 3.1}$$

Where, θ is the experimental contact angle. Thus the contact angle can be used to determine an interfacial energy (if other interfacial energies are known). This equation can be rewritten as

$$\gamma(1+\cos\theta) = \Delta W_{\mathrm{SLV}} \qquad \text{Equation 3.2}$$

Where ΔW_{SLV} is the adhesion energy per unit area of the solid and liquid surfaces when in the medium V [35]

3.6.1.2 Atomic Force Microscopy (AFM) [36]

The Atomic Force Microscope (AFM) is being used to solve processing and materials problems in a wide range of technologies affecting the electronics, telecommunications, biological, chemical, automotive, aerospace, and energy industries. The materials being investigating include thin and thick film coatings, ceramics, composites, glasses, synthetic and biological membranes, metals, polymers, and semiconductors. The AFM is being applied to studies of phenomena such as abrasion, adhesion, cleaning, corrosion, etching, friction, lubrication, plating, and polishing. By using AFM one can not only image the surface in atomic resolution but

also measure the force at nano-newton scale. The publications related to the AFM are growing speedily since its birth.

The force between the tip and the sample surface is very small, usually less than 10^{-9} N. According to the interaction of the tip and the sample surface, the AFM can be classified as repulsive or Contact mode and attractive or Non-contact mode. Now the Tapping mode shows a prosperous future to image the micro-world.

The principles on how the AFM works are very simple. An atomically sharp tip is scanned over a surface with feedback mechanisms that enable the piezo-electric scanners to maintain the tip at a constant force (to obtain height information), or height (to obtain force information) above the sample surface. Tips are typically made from Si_3N_4 or Si, and extended down from the end of a cantilever. The nanoscope AFM head employs an optical detection system in which the tip is attached to the underside of a reflective cantilever. A diode laser is focused onto the back of a reflective cantilever. As the tip scans the surface of the sample, moving up and down with the contour of the surface, the laser beam is deflected off the attached cantilever into a dual element photodiode. The photodetector measures the difference in light intensities between the upper and lower photodetectors, and then converts to voltage. Feedback from the photodiode different signal, through software control from the computer, enables the tip to maintain either a constant force or constant height above the sample. In the constant force mode the piezo-electric transducer monitors real time height deviation. In the constant height mode the deflection force on the sample is recorded. The latter mode of operation requires calibration parameters of the scanning tip to be inserted in the sensitivity of the AFM head during force calibration of the microscope. Some AFM's can accept full 200 mm wafers. The primary purpose of these instruments is to quantitatively measure surface roughness with a nominal 5 nm lateral and 0.01nm vertical resolution on all types of samples. Depending on the AFM design, scanners are used to translate either the sample under the cantilever or the cantilever over the sample. By scanning in either way, the local height of the sample is measured. Three dimensional topographical maps of the surface are then constructed by plotting the local sample height versus horizontal probe tip position. In order to obtain good AFM results, the vibration isolation platform is needed.

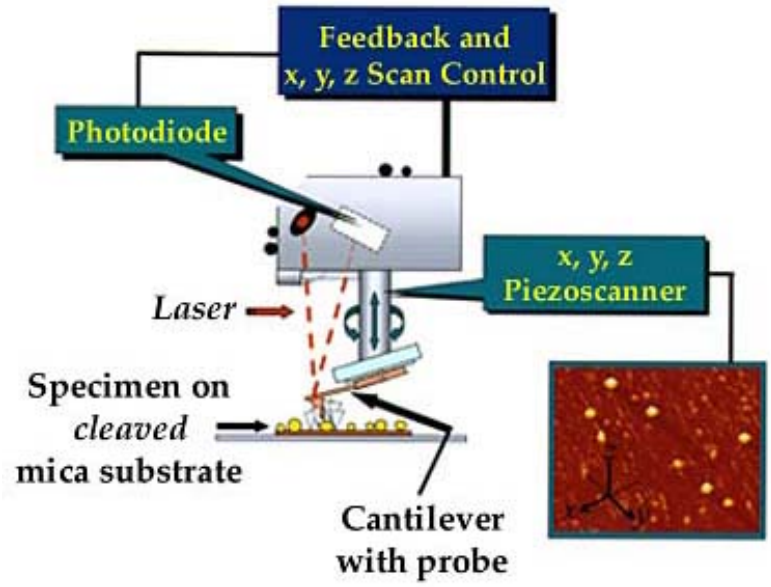

Figure 3.17 Schematic of Atomic Force Microscopy (AFM) [53]

Force Curves

In contact mode, force curve of a located sample surface during measurement was obtained by using the force calibration mode. Force curves (force-versus-distance curve) typically show the deflection of the free end of the AFM cantilever as the fixed end of the cantilever is brought vertically towards and then away from the sample surface. Experimentally, this is done by applying a triangle-wave voltage pattern to the electrodes for the z-axis scanner. This causes the scanner to expand and then contract in the vertical direction, generating relative motion between the cantilever and sample. The deflection of the free end of the cantilever is measured and plotted at many points as the z-axis scanner extends the cantilever towards the surface and then retracts it again. By controlling the amplitude and frequency of the triangle-wave voltage pattern, the researcher can vary the distance and speed that the AFM cantilever tip travels during the force measurement. The schematic below describes the anatomy of this measurement mode.

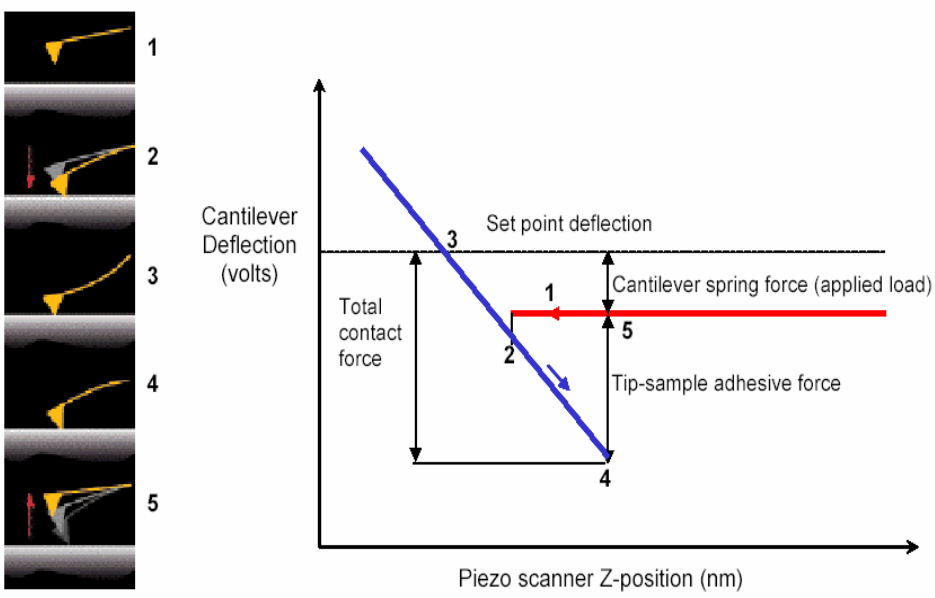

Figure 3.18 Show force measurement via cantilever deflection

1: The cantilever starts not touching the surface. In this region, if the cantilever feels a long-range attractive (or repulsive) force it will deflect downwards (or upwards) before making contact with the surface.

2: As the probe tip is brought very close to the surface, it may jump into contact if it feels sufficient attractive force from the sample.

3: Once the tip is in contact with the surface, cantilever deflection will increase as the fixed end of the cantilever is brought closer to the sample. If the cantilever is sufficiently stiff, the probe tip may indent into the surface at this point. In this case, the slope or shape of the contact part of the force curve can provide information about the elasticity of the sample surface.

4: After loading the cantilever to a desired force value, the process is reversed. As the cantilever is withdrawn, adhesion or bonds formed during contact with the surface may cause the cantilever to adhere to the sample some distance past the initial contact point on the approach curve (2).

5: A key measurement of the AFM force curve is the point at which the adhesion is broken and the cantilever comes free from the surface. This can be used to measure the rupture force required to break the bond or adhesion.

One of the first uses of force measurements was to improve the quality of AFM images by monitoring and minimizing the attractive forces between the tip and sample. Force measurements were also used to demonstrate similarly reduced capillary forces for samples in vacuum and in reduced humidity environments.

3.6.1.3 X-ray absorption near-edge spectroscopy (XANES)

X-ray Absorption Near Edge Structure (XANES) is a type of absorption spectroscopy which indicates the absorption peaks due to the photoabsorption cross section in the X-ray Absorption Spectra (XAS) observed in the energy region, extending over a range of about 100 eV, between the edge region and the EXAFS (edge x-ray absorption fine structure) region. While direct photoemission spectroscopy offers an experimental approach to the occupied electronic bands of a solid state, XANES (*x-ray absorption near-edge spectroscopy*) or NEXAFS (*near-edge x-ray absorption fine structure*) is a technique to characterize surfaces by evaluation of unoccupied electronic states. In contrast to inverse photoemission spectroscopy the experimental setup simply requires a monochromatically tunable light source and an electron energy analyzer so that XANES measurements can be performed at each synchrotron radiation source of sufficient energy. Due to the sharp transitions in molecular systems near-edge absorption spectroscopy is one of the preferred experimental techniques to study organic thin films [37].

In the XANES region, starting about 5 eV beyond the absorption threshold, because of the low kinetic energy range (5-150 eV) the photoelectron backscattering amplitude by neighbor atoms is very large so that multiple scattering events become dominant in the XANES spectra. The different energy range between XANES and EXAFS can be also explained in a very simply manner by the comparison between the photoelectron wavelength λ and the interatomic distance of the photoabsorber-backscatterer pair. The photoelectron kinetic energy is connected with the wavelength λ by the following relation:

$$E_{kinetic} = h\nu - E_{binding} = \hbar^2 k^2/(2m) = (2\pi)^2\hbar^2/(2m\lambda^2)$$

Equation 3.3

That means that for high energy the wavelength is shorter than interatomic distances and hence the EXAFS region corresponds to a single scattering regime; while for lower E, λ is larger than interatomic distances and the XANES region is associated with a multiple scattering regime.

Bostick and co-workers [38, 39] had studied Arsenic (As) sorption on sulfide minerals by using XANES investigation. The results is shown in Figure 3.19

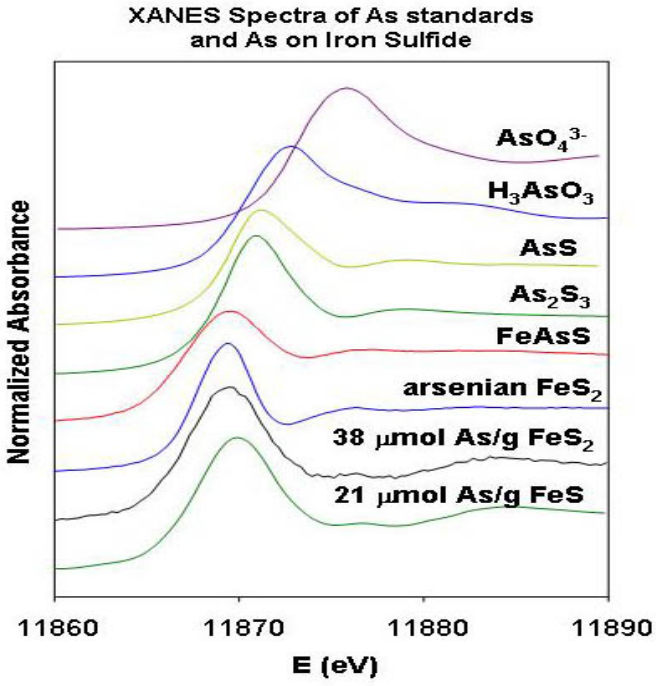

Figure 3.19 XANES spectra of Arsenic standard and Arsenic reacted with iron sulfide minerals

XANES spectra of As standards and As reacted with iron sulfide minerals. The oxidized As species have higher absorption edges than reduced species. The very low edge positions of As on the surfaces is indicative of highly reduced, zero-valent, As species such as FeAsS or arsenian pyrite.

3.6.2 Adhesion strength characterization

A very large number of tests of adhesion have been proposed. Many are codified in standards such as British Standard, I.S.O and A.S.T.M [2]. Many more are to be found in the literature. Some are based on a fundamental analysis of the joint. A number of fracture mechanics test have been adapted for the measurement of adhesion. The one method had been used to rubber to rubber adhesion is T-peel test.

Peel Test

Peel tests are used to measure the fracture resistance of a thin layer bonded on a thick substrate or of two layers bonded together. They consist in measuring the force needed for tearing an adherent layer from a substrate or for tearing two adherent layers one from another. Whereas the structure is not symmetrical, various mode mixities can be introduced in these tests.

The substrate is rigid and the flexible member is peeled at a defined angle, but where both materials bonded are flexible, such as laminated plastic film, a T-peel can be done. It is possible to use the climbing drum peel test for relatively rigid materials. It is evident that the 'peel angle', 90^{o} or 180^{o} or whatever is a formal angle between the lines of action on substrate and peeled strip, cannot be the actual angle at the point of fracture. All tests of adhesion are important to standardize the test piece dimensions and details of test method in order to ensure that results are comparable. It is usual to express the results as 'peel strength', the average peel force per unit width of the strip peeled.

In many adhesion tests, each piece tested gives only a single estimate of strength such as stress at failure in shear tests and tensile tests. An advantage of a peel test is that each strip peeled yields a trace which shows how the force varies along the whole distance peeled [2].

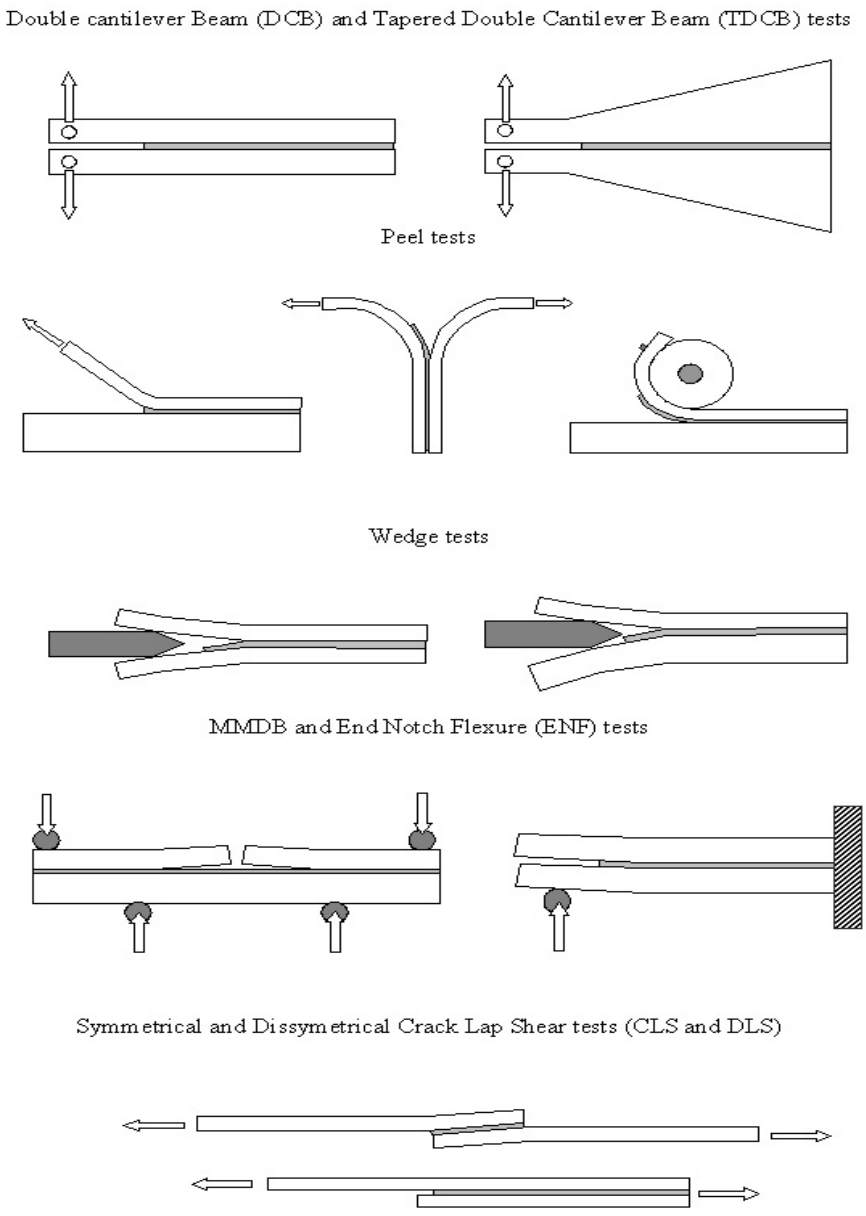

Figure 3.20 Many varieties of the adhesion test methods. [34]

CHEPTER 4
MATERIALS AND METHODS

4.1 Materials and Chemicals

Materials and chemical reagents used in this study are listed in the Table 4.1

Table 4.1 Materials and chemical reagents used in this study

Materials	Characteristics		Suppliers
NR (STR5L)	Specific gravity	0.92	Chalong Latex Industy Co.,Ltd.
NBR (N230S)	Acrylonitrile content, mole%	33	JSR
	Specific gravity	0.98	
	ML1+4, 100 ^{o}C	63	
Carbon black (N330)	Pour density, Kg/m^3	375	Thai Carbon Black Co.,Ltd
ZnO	Specific gravity	5.6	Unithai Oxide Co.,Ltd
	White powder		

Table 4.1 Materials and chemical reagents used in this study (continued)

Materials	Characteristics	Suppliers
Stearic acid	Specific gravity 0.84 White powder	China National Chemicals
TMTD	Specific gravity 1.425 Powder	Flexsys
TBBS	Specific gravity 1.28 Pellet	Flexsys
Sulphur	325 mesh grade	The Siam Chemicals Co.,Ltd.
Silica	Hi-Sil® 233-S	PPG-Siam Silica Co.,Ltd., Thailand
NaOCl	6-14 % active chlorine	Merck

4.2 Instruments

The instruments used in this study are shown in Table 4.2

Table 4.2 The instrument, manufacturer and model

Instrument	Manufacturer	Model
Internal mixer	Chaichareon Karnchang	-
Brabender	Brabender Mix	Banbury Rotor 3106
Two roll mill	Lab Tech Engineering Company	Model LRM 150
Hydrauric press	Wabash MPI	G30H-15-CX
MDR	Tech Pro, USA	Rheo Tech MD^{+}
Tensile Tester	Instron Tensile Testing Machine	Instron 5569
Hardness Tester	Wallace	H17A
FTIR-ATR Spectroscopy	Bruker	Equinox 55
AFM	Digital Instruments Inc.	Nanoscope IIIa ModelNS3a(multimode)
Contact angle Meter	Kruss GmbH	G-23 Strage
Flex meter	Wallact	300 rpm

Table 4.2 The instrument, manufacturer and model (continued)

Instrument	Manufacturer	Model
ODR	Monsanto	Rheometer 100s
Mooney viscometer	Monsanto	Rheometer 1500
Synchrotron light	Siam synchrotron	BL8 XAS
Ozone tester	Toyozeiki	-

4.3 Preparation of Specimens

In this work, chlorinated NR/NBR laminates were prepared and used as specimens for studying the adhesion by T-peel test. These specimens preparation was described as below;

4.3.1 Rubber Compounding and Mixing Procedures

NR, NBR and their ingredients were incorporated in an internal mixer using the fill factor of 0.6 at compounding temperature of 50^{o}C with a rotor speed 50 rpm. After that curing agents were added to the rubber compound by using a Two-roll mill. The compounding formulations of NR and NBR were shown in Table 4.3.

Table 4.3 The formulation of Rubber compounding

Compounds	NR	CB-NBR	Si-NBR
Rubber	100	100	100
Carbon black	40	40	-
Silica	-	-	30
Zinc oxide	3	3	3
Stearic acid	1	1	1
Sulfur	1.5	0.5	0.5
TBBS	2	-	-
TMTD	-	2	2

4.3.2 Rubber sheeting

Curing behaviors of the rubber compounds from 4.3.1 were determined by using the Moving Die Rheometer. A small piece of rubber compounds was placed on the die rotor at a temperature of 155^{o}C. Cure characteristic was obtained from the cure

curve. The optimum cure time was determined from 90% cure time (t_{90}). Curing of the rubber compounds were carried out in a hydraulic compression mould (2 mm thick), at 155°C.

The cure time used was t90 + 50% of t90. This was to ensure the complete vulcanization of the rubber. Noteworthy, undryed cloth was used as a backing strip during the compression moulding to reinforce the rubber strips and to prevent deformation of the rubber subsequent peel test.

4.3.3 Determination of available Chlorine Content

This section part was the determination of chlorine available in chlorination process of the entire study by following ASTM D 2022. Chlorine available was obtained from sodium hypochlorite solution (NaOCl) that contained chlorine concentration in wide range. Therefore, the amount of chlorine available from the solution must be known. This can be determined by using the following steps.

4.3.3.1 Standardization of titrant $Na_2S_2O_3$

To determine the concentration of $Na_2S_2O_3$, the standard of KIO_3 solution was prepared to titrate with $Na_2S_2O_3$ solution. Starch solution was used as an indicator for this titration. The chemical reactions occurred during the titration can be illustrated follow as below:

$$IO_3^-(aq) + 6H_3O^+(aq) + 5I^-(aq) \rightarrow 3I_2(aq) + 9H_2O$$

Equation 4.1

$$2S_2O_3^{2-}(aq) + I_2(aq) \rightarrow S_4O_6^{2-}(aq) + 2I^-(aq)$$ Equation 4.2

The entire equation 4.1+4.2

$$6S_2O_3^{2-}(aq) + 6H_3O^+(aq) \rightarrow 3S_4O_6^{2-}(aq) + 9H_2O$$ Equation 4.3

4.3.3.2 Iodometric Titration

In this step, the sodium hypochlorite solution was titrated with known concentration of $Na_2S_2O_3$ solution. The available chlorine is defined as the chlorine gas that occurred from the chemical reaction between NaOCl solution and KI in diluted acid. The product from this reaction is Iodine. One mole of the iodine means that there was one mole of chlorine in the sodium hypochlorite solution. The chemical reactions occurred during the titration can be illustrated as below:

$$ClO^-(aq) + 2H_3O^+(aq) + 2I^-(aq) \rightarrow Cl^-(aq) + 3H_2O + I_2(aq) \quad \text{Equation 4.4}$$

From equation 4.2

$$2\,S_2O_3{}^{2-}(aq) + I_2(aq) \rightarrow S_4O_6{}^{2-}(aq) + 2\,I^-(aq)$$

The entire equation 4.4+4.2

$$ClO^-(aq) + 2S_2O_3{}^{2-}(aq) + 2H_3O^+(aq) \rightarrow Cl^-(aq) + S_4O_6{}^{2-}(aq) + 3H_2O \quad \text{Equation 4.5}$$

The calculation of available chlorine in sodium hypochlorite solution can see in the Appendix A.

4.3.4 Chlorination Process

Chlorination of NR surface was performed by immersing the samples in the sodium hypochlorite solution, containing of 0.15% of free chlorine. This solution was prepared by mixing 100 parts by volume of distilled water, with 2 parts of 7.3% NaOCl and 1 part of 37% HCl. The treated specimens were then neutralized in 2% ammonium solution for 20 seconds before rinsing in deionized water for 10 seconds. Finally, the specimens were dried at room temperature for 1 day

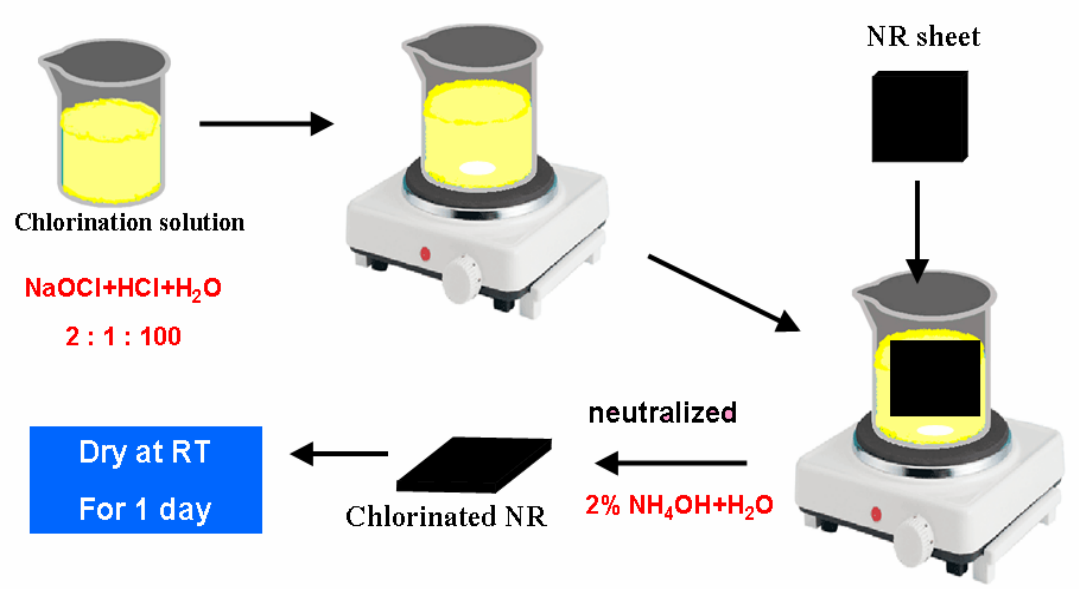

Figure 4.1 Chlorination process of Natural rubber sheet

4.3.5 Adhesion of rubber sheets

Chlorinated of NR sheets were pressed together with NBR sheets, NBR compound had been pre-pressed in 2mm of thickness at 80°C, they were adhered in 4 mm thick mould. The cure temperature was performed at 155°C at 15 tons-forces with t_{c90}+50% of t_{c90} of longer cure time of rubber. Afterward, the laminated was then cooled to room temperature before cutting into strips of 150x 30x 4 mm^3 for T-peel test.

Figure 4.2 Preparation of NR//NBR sheet

4.4 Peel strength measurement

The strength of interfacial adhesion between the chlorinated NR and NBR was determined by using T-peel test. Peel specimens (Figure 4.3) were then test with an Instron Tensile Testing Machine Model 5569. The measurement was carried out at a crosshead speed of 50 mm/min. At least 5 specimens were tested for each sample before average values were determined by using the equation 4.6.

$$\text{Peel strength} = \frac{2F}{W} \ (\text{J/m}^2) \qquad \text{Equation 4.6}$$

Where

F = Force required to separate the rubber sample (N)

W = Width of the specimen (m)

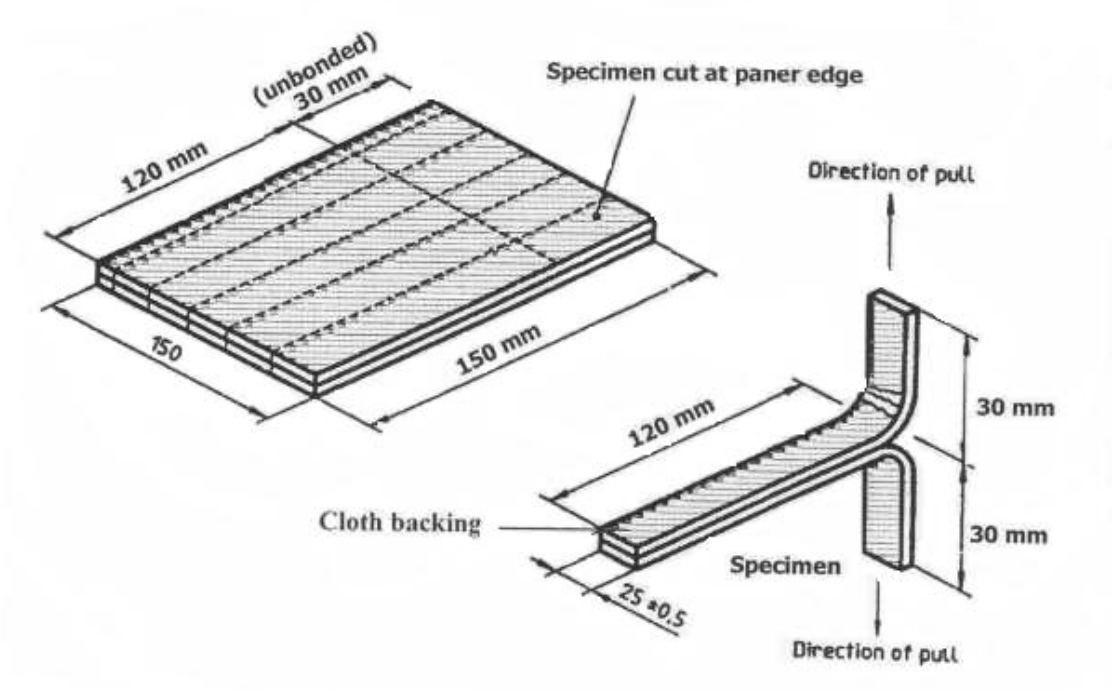

Figure 4.3 Peel test specimen

Figure 4.4 Instron Tensile Testing Machine Model 5569 and T-peel measurement

4.5 Characterization of Chlorinated NR surfaces

In this study, the chlorinated NR surfaces were characterized by various techniques such as FTIR-ATR, AFM, XAS and contact angle measurement.

4.5.1 Determination of Chlorine groups by Fourier Transform Infrared Spectroscopy (FTIR)

To investigate the chemical structure of NR surfaces after chlorination, the FTIR spectra of the sample were examined by using a Bruker model Equinox 55, FT-IR spectrophotometer with attenuated total internal reflectance (ATR) accessory with 16 scans at a resolution of 4 cm^{-1} over the scan range from 4000 to 500 cm^{-1}. A strip of chlorinated NR at different time was placed onto the single reflection crystal

(Germanium crystal used). The penetration depth of the measurement was about 5-10 µm from the surface.

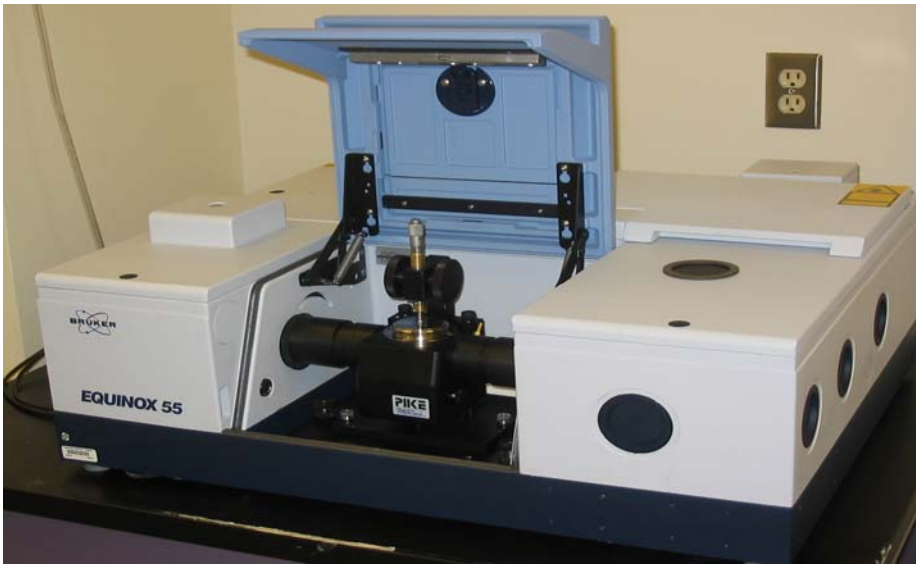

Figure 4.5 The model of FTIR-ATR , Bruker Equinox 55

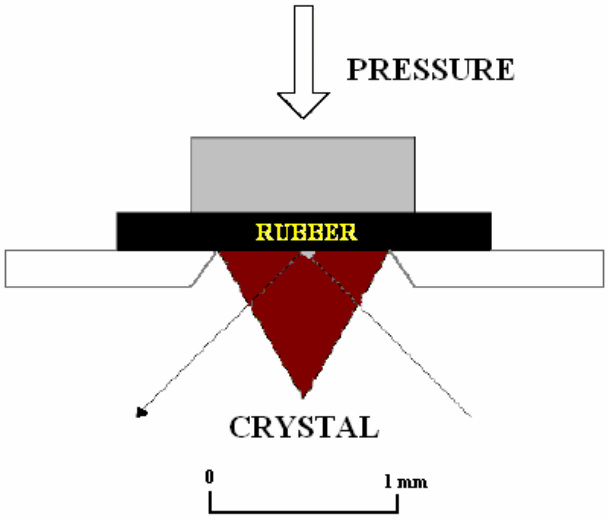

Figure 4.6 Single Reflection ATR [55]

4.5.2 Determination of surface properties of chlorinated NR surface by Atomic Force Microscopy (AFM)

In this experiment, AFM [Nanoscope IIIa model (Digital Instrument Company) (Figure 4.7)] was used to investigate morphology and surface properties of materials by using scanning probe microscopy. Chlorinated NR surfaces at various times were characterized in tapping mode and contact mode. The surface hardness and surface roughness was obtained from this technique. In addition, the adhesion force on the chlorinated NR surface was also determined.

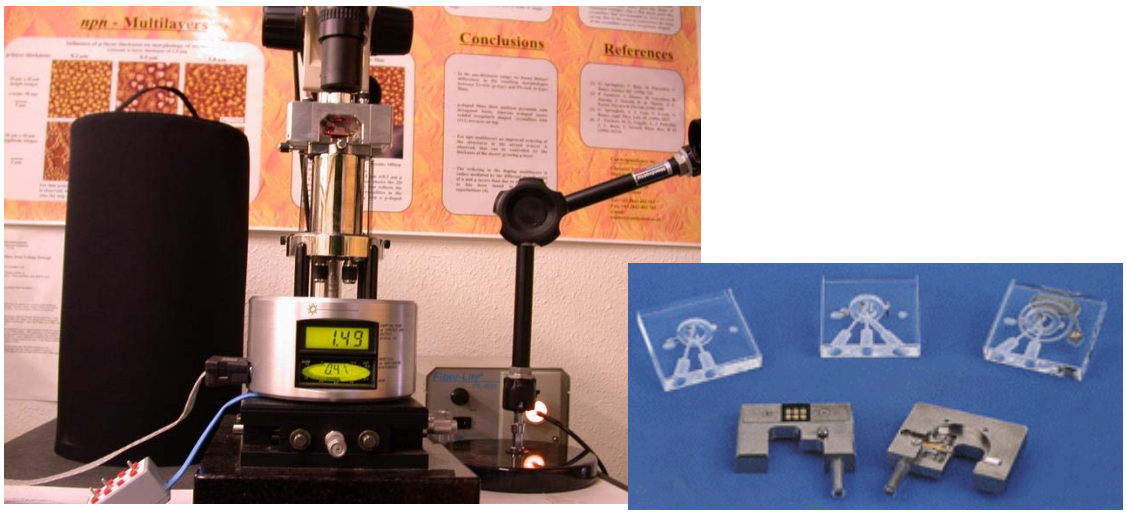

Figure 4.7 Nanoscope IIIa; multimode NS3a model, Digital Instruments Inc.

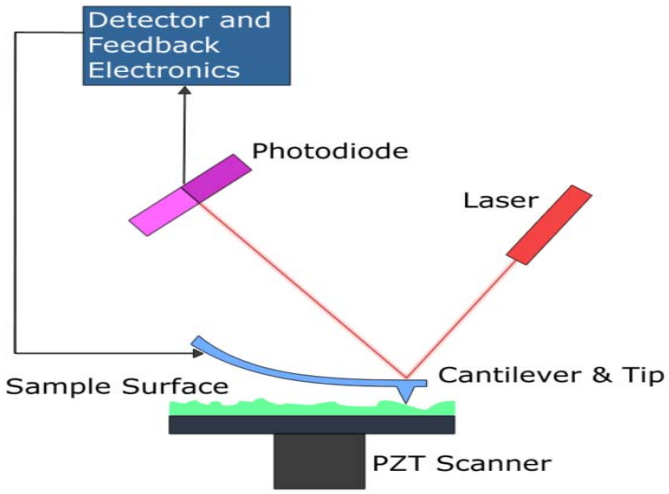

Figure 4.8 The diagram of Atomic Force Microscopy (AFM)

4.5.3 Determination of chlorine population of chlorinated NR surface by X-ray absorption Spectroscopy (XAS)

XANES measurements were performed at BL-8, National Synchrotron Research Center.The degree of chlorination was determined by this technique. The chlorinated NR films were cut and pasted with Kapton tape on top of the sample frame. XANES experiment was carried out by using synchrotron light source at the Siam Photon Laboratory. The XANES measurements were carried out in transmission mode at the XAS beamline, BL-8. A 10-cm-long and 40-cm-long ionization chambers were employed for monitoring the x-ray beam intensity before and after the sample. The image of instrument is shown in the Figure 4.9 [56].

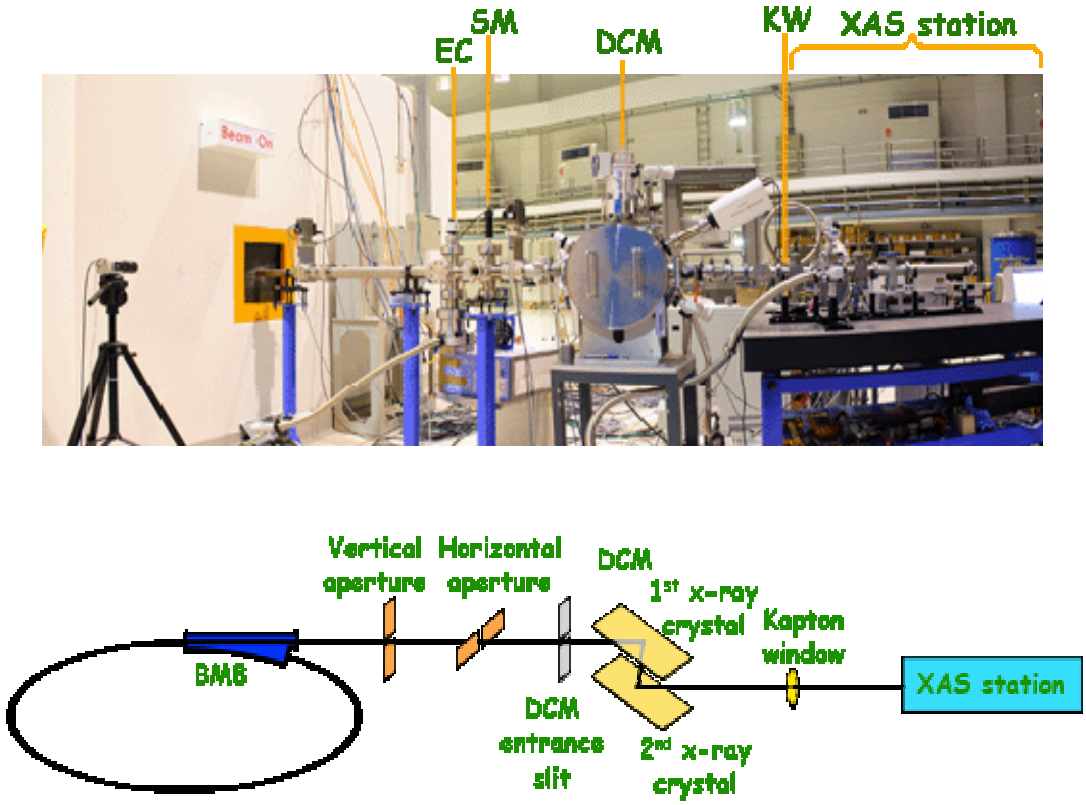

Figure 4.9 (Above) Optical beamline of BL-8. Evacuation chamber (EC), Screen monitor (SM), Double crystal monochromator (DCM), and Kapton window (KW) and Layout of the beamline BL-8 (below).

4.5.4 Contact angle measurement

A Kruss G23 Contact Angle Goniometer was used in this work. Water was used as a test liquid. The sample compartment and the sample were saturated by the test liquid for 30 min before a drop of the test liquid was placed onto the sample surface. The contact angles were monitored as a function of chlorination time. The initial contact angle was obtained by extrapolating the curve to zero time. The average of the initial contact angles determined from five locations on the same film surface was calculated.

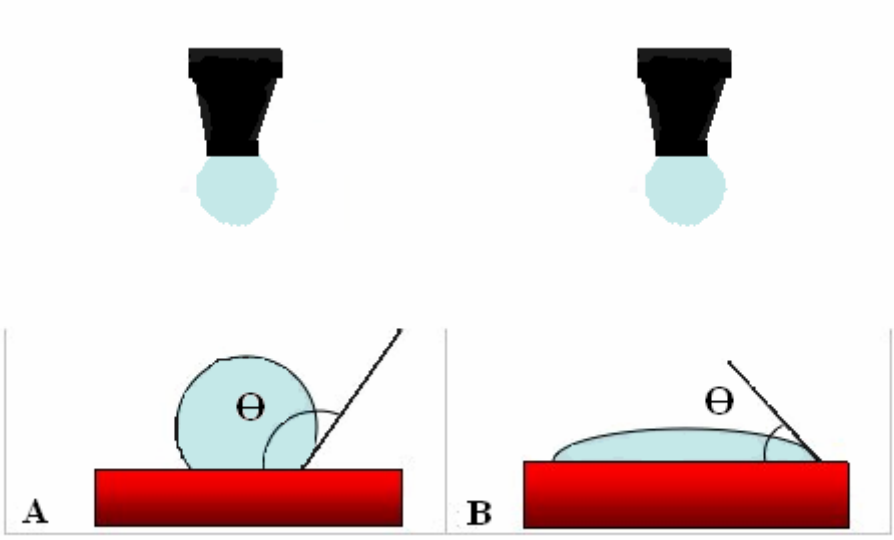

Figure 4.10 Contact angle measurements of water droplets.

4.6 Determination of vulcanization characteristics

Cure characteristics of rubber compounds were investigated and carried out using the Moving Die Rheometer (MDR). A piece of rubber compounds about 10g was placed on die at 155^{o}C. The cure characteristics were monitored from cure curve as shown in Figure 4.11. The optimum cure time used was obtained from the time to reach 90% cure (t_{90}).

This experiment, the effect of cure extent of NR before chlorination to adhesion with NBR by varying cure time was studied. Different cure times were obtained via cure curve. The different maximum and minimum toques are used as indicator of cure extent.

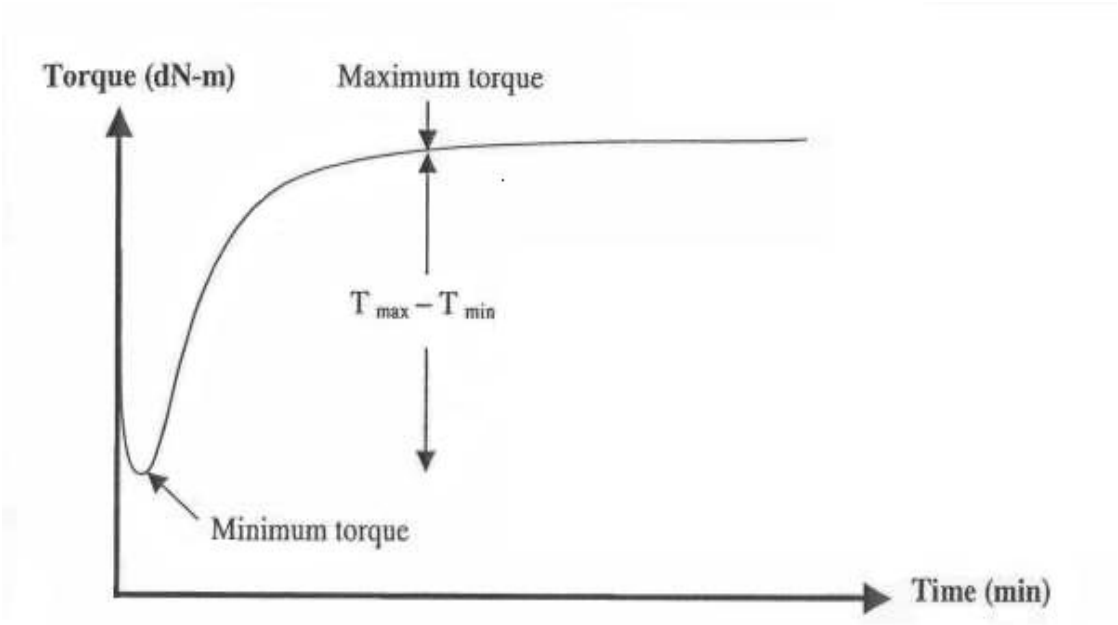

Figure 4.11 Characteristic of cure curve of rubber compound

$$\text{Cure rate} = \frac{T_{max} - T_{min}}{t_{c90} - t_{s2}} \qquad \text{Equation 4.7}$$

Where

T_{max} = the maximum torque (lb/m^2)

T_{min} = the minimum torque (lb/m^2)

T_{s2} = scorch time at 2% of maximum torque

T_{c90} = cure time at 90% of maximum torque

4.7 Determination of viscosity of rubber compound

Mooney viscometer (Monsanto model 1500) with small rotor was used to measure the Mooney viscosity of rubber compounds. The measurement was carried out at 100^{o}C. The specimen consisted of two pieces of the materials having a combined mass about 25g. The Mooney viscosity was determined in according with the ASTM D1646-87 standard method and the value was reported as (MS 1+4) in Mooney unit.

4.8 Stability of NR//NBR bonding

This experimental part aim to evaluate of stability of interfacial bonding of the NR//NBR laminate by using heat ageing test, ozone test and flexural testing.

4.8.1 Heat Ageing

Heat ageing test on NR//NBR laminate was performed to examine the influence of heat on physical properties of the laminate. The method of measurement was based on ASTM D572-88 standard method. The specimens were placed in an hot oven at 100^{o}C for 2 days. At the end of the ageing period, the specimens were removed from the oven and cooled to room temperature and then allowed to rest neither less than 16 hours nor more than 96 hours before the determination of T-peel test.

4.8.2 Storage time

In this part, effect of storage time on stability of the chlorinated NR sheets was investigated. The cured NR sheets were chlorinated by using sodium hypochlorite solution for 1 minute of chlorination time. These chlorinated cured NR sheets were divided into three parts, part one is the chlorinated specimens of 1 day leaving. Afterward, the 1 day chlorinated NR sheets were laminated with carbon black filled in

NBR sheets. Other parts were prepared to storage in two systems, closed air and opened air systems.

Closed air systems: The chlorinated NR specimens were kept in desiccators of the entire keeping times to avoid humidity and contamination. These specimens were kept at 1, 2, 3 and 4 weeks before bonding with carbon black filled NBR sheets.

Opened air systems the chlorinated NR specimens were kept to barely expose to environment surrounding of the entire keeping times at room temperature. These chlorinated cured NR sheets were kept at 1, 2, 3 and 4 weeks before bonding with carbon black filled NBR sheets.

4.8.3 Ozone ageing

In this experiment, effect of ozone on bonding strength of the NR//NBR laminate is of interest. The specimens were exposed to ozone (at 50 pphm about 25% of O_3 g) for 3 days. After that, the specimens were removed and rested at room temperature for 1 day before carried out the T-peel test.

4.8.4 Flex tester

Flexural test was used to perform the specimens for studying the stability of bonding within repeated flexing, the action of flexing repeatedly under the same conditions. The chlorinated NR//NBR specimens were measured at 1000, 2500, 5000 cycles of repeated flexing at room temperature.

CHAPTER 5
RESULTS AND DISCUSSION

Adhesion improvement between NR and NBR was the aim of this thesis. NR was previously modified by chlorination on surface prior to adhering with NBR. The effect of chlorination time on NR surface properties was investigated. Several techniques such as contact angle measurement, FTIR-ATR, and AFM as well as peel strength of chlorinated NR and NBR bonding were conducted and the results were presented and discussed. The effect of filler type in NBR layer (carbon black and silica) on peel strength of chlorinated NR and NBR was also determined. In addition, the effect of cure extent of NR compound before chlorination on peel strength was also within the scope of work.

On relating to real service, the stability or durability of bond strength between NR and NBR was investigated by studying the effect of storage time, heat and ozone resistances, and flex resistance.

5.1 Effect of surface preparation of chlorinated NR on peel strength

Generally the topological structure of material surfaces affects the bond strength of adhered surfaces significantly [40]. Scrubbing of NR surface was used to modify surface roughness prior to press together with NBR during vulcanization. Sand paper no 80 was used to scrub NR surface for 10 cycles. Afterwards the scrubbed NR surface was chlorinated in chlorinate solution for 30 minutes. Table 5.1 shows the peel strength of scrubbed- and un-scrubbed NR for NR//NBR bonding

Table 5.1 The effect of surface scrubbing of chlorinated NR and NBR bonding on peel strength.

Peel strength (J/m^2) of Cl-NR //NBR	
Un-scrubbed NR	**Scrubbed NR**
7,340 (±544)	11,390 (±636)

It is clear that scrubbing of NR surface before chlorination shows much higher peel strength of NR//NBR bonding than un-scrubbed NR. The scrubbing of NR surface increased roughness, led to increase in surface interaction between chlorinated NR and NBR, hence the peel strength can increase. Moreover, the scrubbing of NR surface can remove some antiherend matters such as dust, greases, weak boundary layer etc. [41]

5.2 Effect of chlorination time of NR surface

5.2.1 Infrared spectroscopy

As mentioned in chapter 1 that chlorination of NR could be achieved by chlorine substitution onto NR backbone structure. Degree of chlorination could affect the peel strength of NR//NBR bonding. The degree of chlorination could be determined both qualitatively and quantitatively *via* several techniques.

ATR-FTIR under single bounce reflection gave satisfactory result qualitatively. It was noticed that chlorination modified NR surface, the longer was the chlorination time the stiffer was the NR surface. ATR-FTIR by using Ge crystals was employed previously. The obtained data were hugely scattered. NR surface stiffness was expected to be the cause of this scattered result which limited the contact between NR surface and crystals.

Figure 5.2 shows the results of ATR spectrum of chlorinated NR surface for various chlorination times. Absorbance bands at 650, 730 and 910 cm^{-1} show the presence of chlorine. They are susceptible even through the short chlorination time for 1 minute. The peak at 650 cm^{-1} is associated with C-Cl bond stretching. It clearly shows that chlorine was introduced into rubber molecule. The intensity of absorbance peak at 830 cm^{-1}, attributed to the =CH out of plane deformation, decreased with chlorination time. This indicates that the electron rich C=C bond on the rubber molecule was also attacked by chlorine.

The absorbance peak at 910 cm^{-1} is attributed to Cl stretching adjacent to C=C (Cl-C=C) and slightly shifts to higher wave number at chlorination times increase or higher chlorine population [30]. While the peaks at 725 cm^{-1} is due to multiple chlorine stretching substitutions at H atom (Cl-Cl-H) and the peak at 1410 cm^{-1} is indicated to chlorine atom influenced side chain CH_2 bending.

Table 5.2 FTIR-ATR absorbance peaks and bond types for chlorinated NR surface

Functional group	Mode	Wavenumber (cm^{-1})
Cl—Cl—H	Cl stretching	725
Cl—C=C	olefinic Cl stretching	910
-CH_2—Cl	Cl-influenced sidechain CH_2 bend	1410

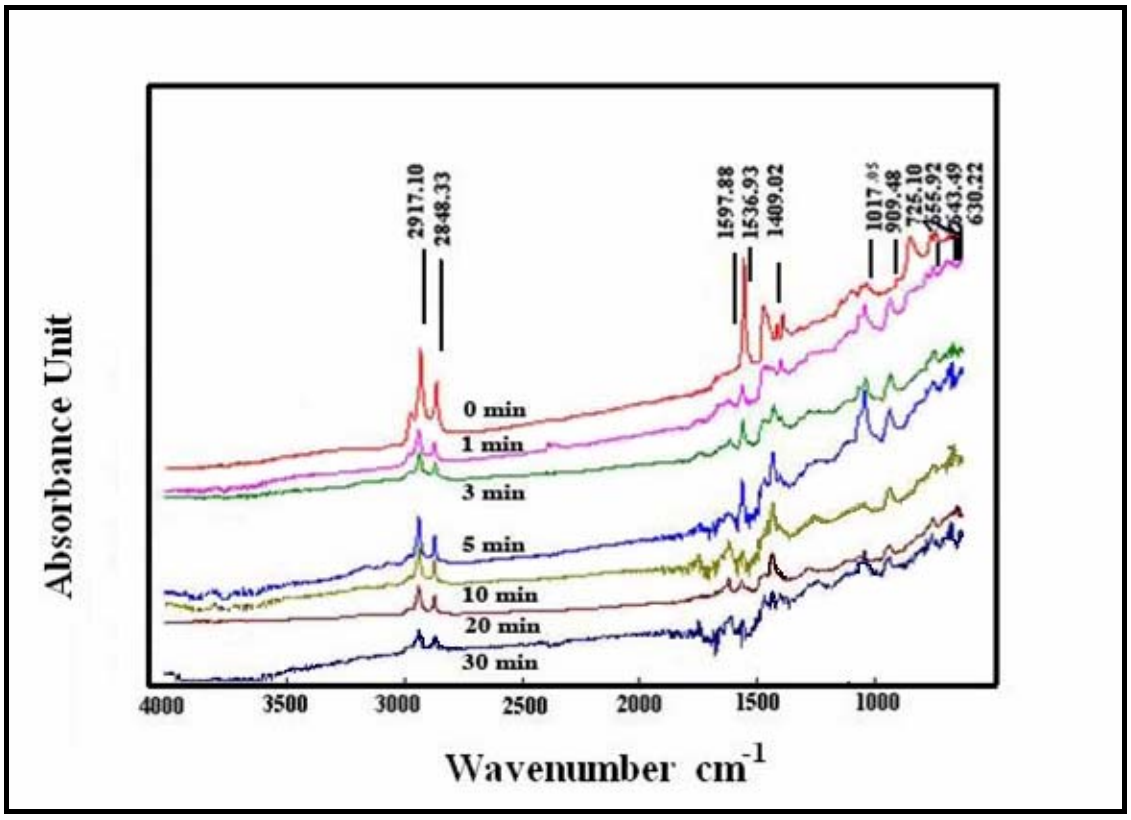

Figure 5.1 FTIR-ATR spectra of chlorinated NR at 0, 1, 3, 5, 10, 20, 30 minutes of chlorination time

5.2.2 Contact angle measurement

After chlorination for various chlorination times, the specimens were stored in desiccators in order to remove and prevent adsorption of humidity on the chlorinated NR surfaces. Contact angle was measured and collected from 10 areas on specimen surface. The results of various chlorination times are shown in Table 5.3

Table 5.3 Contact angles of chlorinated NR surfaces at 0, 0.5, 1, 5, 10, 20 and 30 minutes of chlorination time

Chlorination time (min)	Contact angles (^{o})	SD
0	98.05	±0.97
0.5	89.75	±1.49
1	81.25	±2.28
5	86.05	±4.35
10	88.40	±1.85
20	90.21	±0.48
30	89.85	±1.05

From Table 5.3, it was found that contact angle showed rapid decrease at early stage (from 0 to 1 min). After that, the contact angles increased and finally stabilize after 20 min. The plot of contact angles versus chlorination times is shown in Figure 5.2. Decreasing of contact angles indicated a gradual change in surface hydrophilicity. Lower contact angle indicated higher polarity of chlorinated NR surface. However, it is rather surprising that contact angle value after 1 min slightly increased from 5-30 minutes.

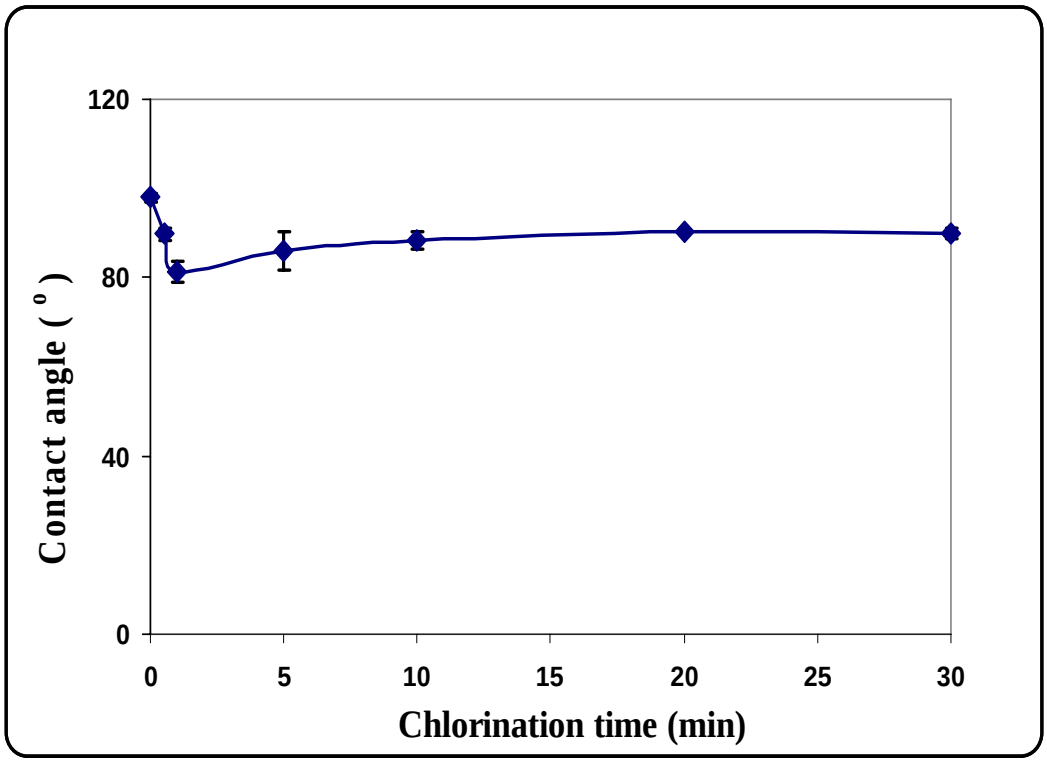

Figure 5.2 The effect of chlorination time of NR surface on contact angles

The reason of the lowest contact angle at 1 min of chlorination time may be because of the suitable chlorination on NR surface. Increasing chlorination time above 1 min could lead to more cracking (surface roughing) [30] and more migration of wax and other components in NR compounded sheet which are the hydrophobic ingredients. Therefore, the contact angles increased again after the chlorination time of 1 minute.

5.2.3 X-ray absorption spectroscopy (XAS)

X-ray absorption near-edge spectroscopy (XANES) is one mode of XAS that was used to determine the density of chlorine on the chlorinated NR surface resulted from chlorination treatment. It is a specific and highly precise technique for determining such element via absorption ratio of photon intensity. Chlorine atom was found to absorb photon energy around 2828 eV. Degree of chlorination depends on amount of chlorine absorption energy due to chlorine replaced hydrogen and then

bond to carbons backbone of NR chain. The photon energy corresponds to C-Cl bond of NR surface.

To calculate the amount of chlorine, it is necessary to create a calibration curve by using a known chlorinated compound. In this study, chloranil ($C_6Cl_4(=O)_2$ or 2,3,5,6-Tetrachloro-p-benzoquinone) [59-60] was used as standard compound for creating a correlation between amount of chlorine and photon absorption. The calibration curve is displayed in Figure 5.3.

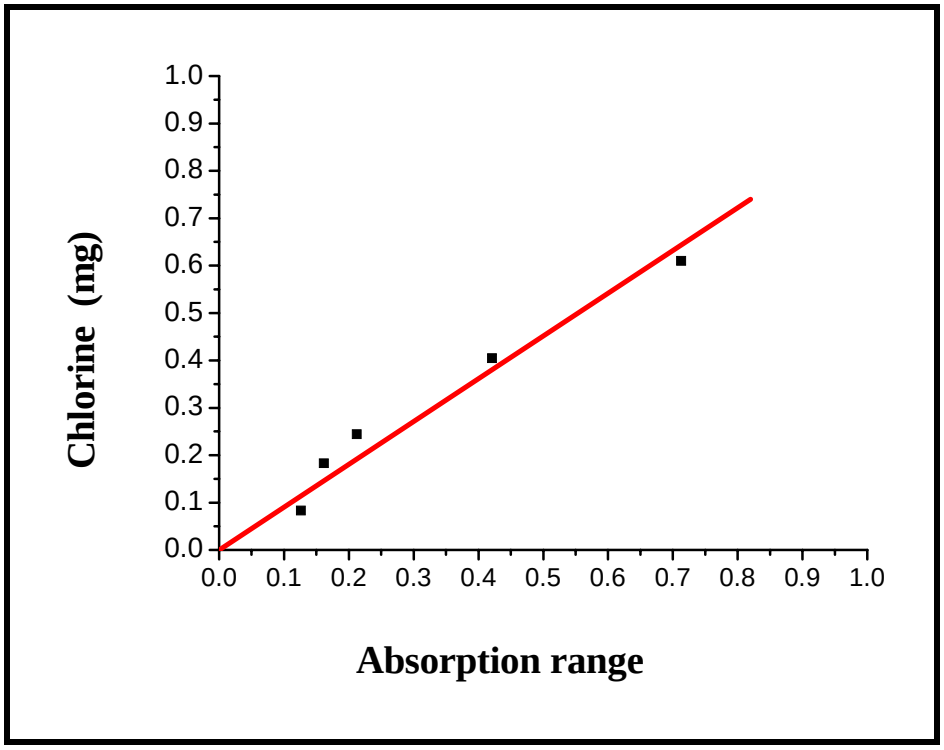

Figure 5.3 Plot of calibration curve between chlorine in chloranil and absorption range.

Data for calibration curve were obtained from using chloranil (powder) diluted by activated carbons (powder) and performed XANES measurements that are corresponding number of chlorine atoms. The chlorine population on NR surfaces was reported in Table 5.4 and the plot of chlorine population and chlorination time was shown in Figure 5.4.

Chlorine population or degree of chlorination can be determined. A slope of calibration curve was found to be the straighten line. The absorption of photon intensity for each chlorination time could be calculated following equation 5.1.

$$y = ax \qquad \text{Equation 5.1}$$

y = chlorine content in chloranil
x = absorption range
a = slope of the curve

Table 5.4 Chlorine content on NR surface with different chlorination times by XANES

Chlorination time (min)	**Sample thickness (± 20 microns)**	**Chlorine content (mg/mm^2)**
0	130	0.00000
0.5	220	0.04748
1	220	0.05668
5	220	0.09652
10	180	0.11491
20	160	0.10572
30	170	0.11798

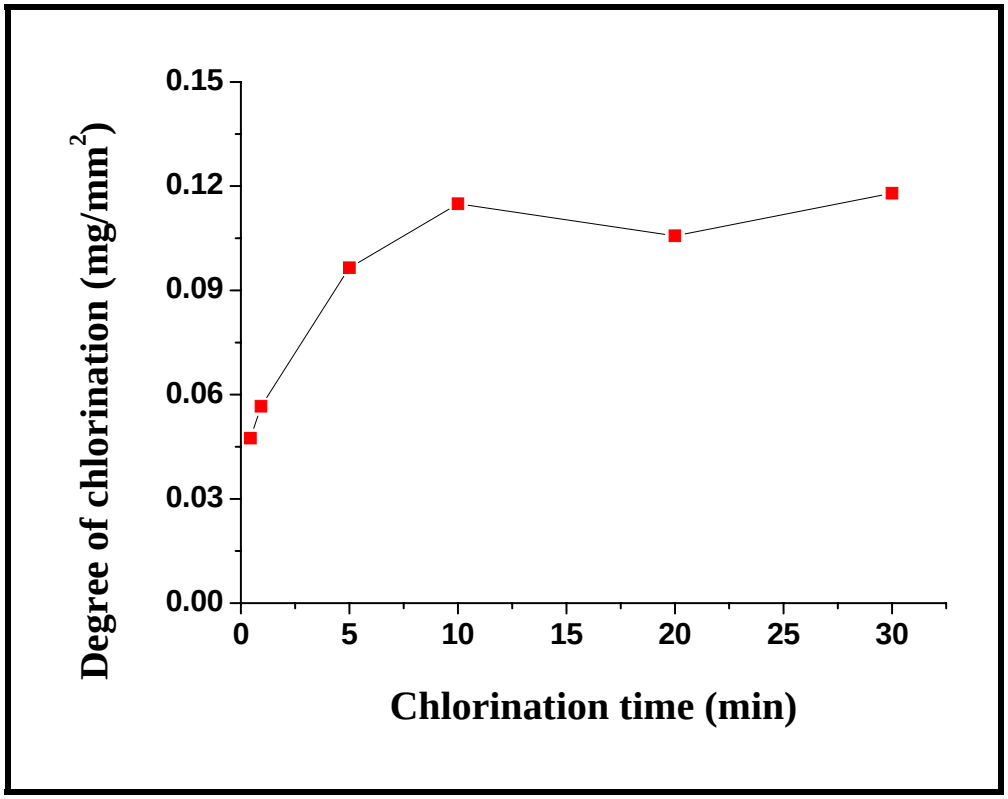

Figure 5.4 Degree of chlorination on chlorinated NR surfaces at different chlorination times

In order to determine the chlorine content on NR surface that is calculated by using equation 5.2

$$[Cl] = [a \times A] / b \qquad \text{Equation 5. 2}$$

Where [Cl] = chlorine population
a = slope of calibration curve
A = absorption range of sample
b = 20 mm^2 of absorbed sample area

Plot of the degree of chlorination versus chlorination time is shown in the Figure 5.4. It was found that chlorine population increased with increasing

chlorination time. The amount of chlorine on NR surface seems to be saturated after 10 minutes.

From the results of contact angle measurement and XAS, it was found that the surface energy or wettability on chlorinated NR surface were independence on degree of chlorination.

5.2.4 AFM investigation

AFM is recent technique for surface characterization of materials. Its principle is to detect interaction between surface and device probe while scanning or mapping on a surface. The obtained results related to surface properties such as magnetic field, electro-conductivity, electrostatic, stiffness, modulus, adhesion, morphology etc. AFM was aimed to characterize the properties change of NR surface due to chlorination. Surface topology, stiffness and adhesion of NR after chlorination for various times will be discussed in this part.

5.2.4.1 Topology of chlorinated NR surface

The nature of surface is important for understanding the mechanism of adhesion and some surface properties [2]. AFM could be used to observe surface roughness of materials in micro- and nanoscale. NR vulcanizate is generally very rough surface, due to surface relaxation after vulcanization. In vulcanization, NR compound was covered between PMMA sheets during pressing, in order to control surface roughness. Topological profiles of chlorinated NR were exhibited in Figure.5.5

Roughness was determined on the surface area of 50 x 50 μm^2 before being flatten.

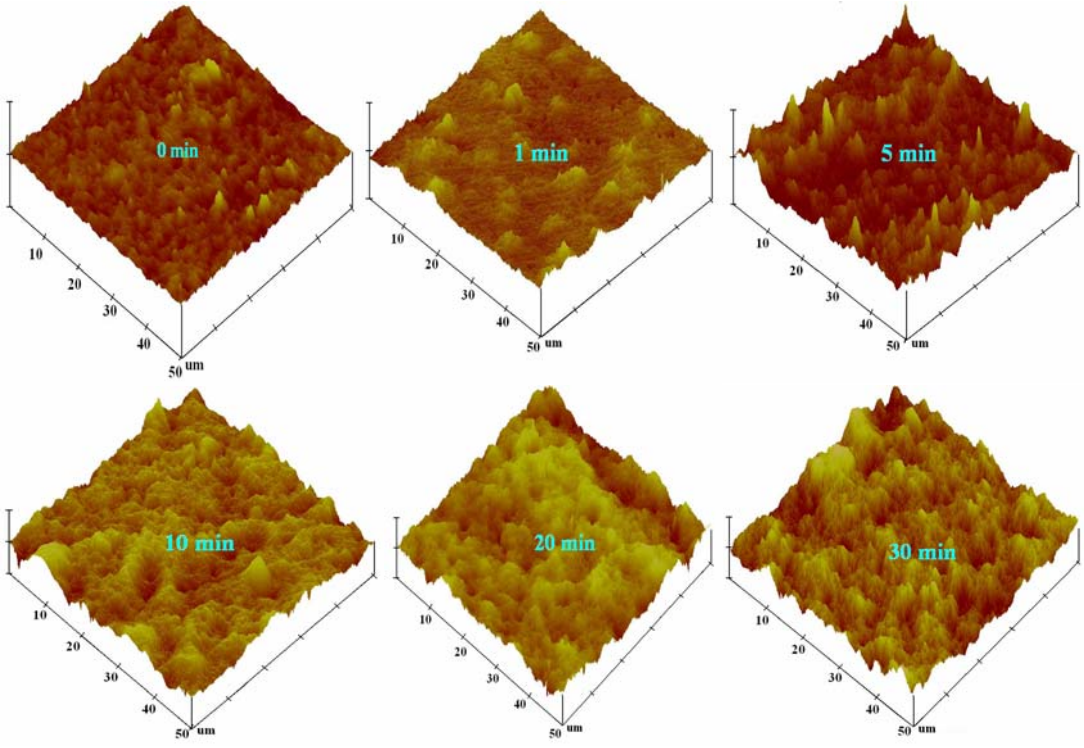

Figure 5.5 Surface morphology and roughness of chlorinated NR surfaces by AFM

The mean roughness (R_a) could be analyzed on their image topology. It was derived from equation 5.3 [43]

$$R_a = \frac{\sum_{i=1}^{N} \left| Z_i - Z_{cp} \right|}{N} \qquad \text{Equation 5.3}$$

Where R_a = The Mean Roughness represents the arithmetic average of the derivations from the center plane.

Z_i = The current of vertical coordinate value.

Z_{cp} = The vertical coordinate value of the center plane.

Table 5.5 Mean Roughness (R_a) 50x50 μm^2 of chlorinated NR surface at various chlorination times.

Chlorination time (min)	R_a (nm)
0	33.81
1	72.08
5	95.05
10	110.00
20	144.90
30	145.41

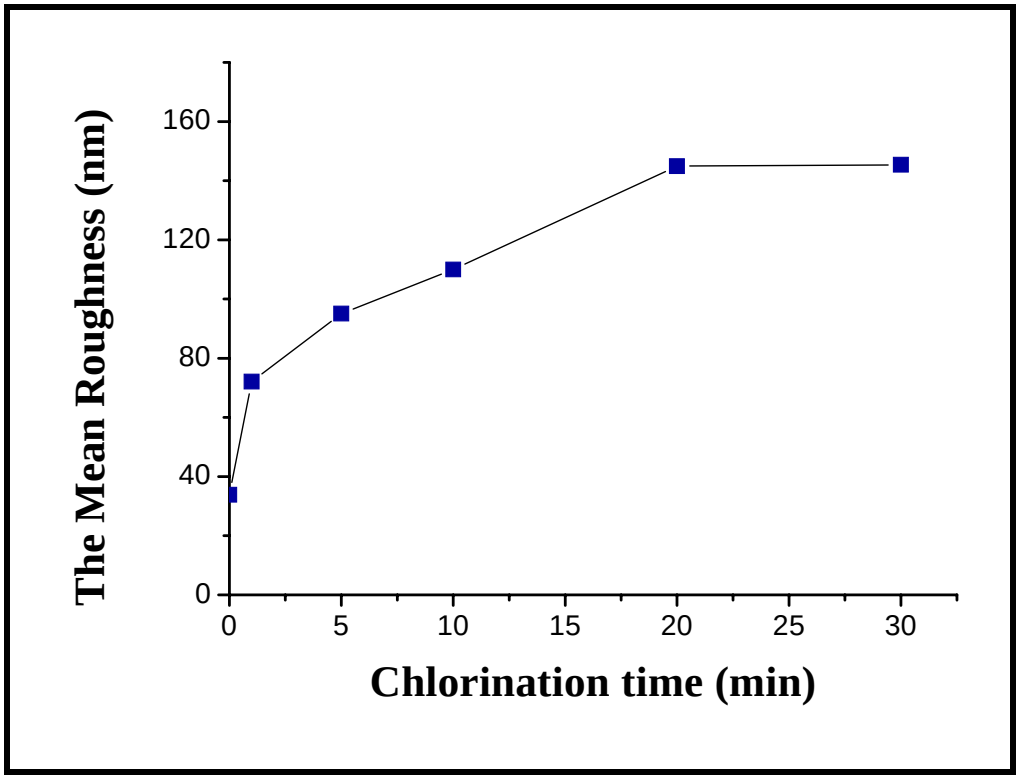

Figure 5.6 The mean roughness (R_a) at different chlorination times.

Figure 5.6 and Table 5.5 show average roughness of chlorinated NR surface for different chlorination time under scanning area of 50x50 μm^2.

It was found that after chlorination, roughness of NR surface increased gradually. Chlorination of NR gave stiffer surface. The treated surfaces could be cracked resulting in higher roughness. Similar observation was reported in previous works [30]. Moreover the substitution of chlorine might reduce mobility of treated NR surface, hence surface cracking was occurred.

5.2.4.2 Surface stiffness and adhesion

Chlorination of NR surface could modify various properties. Stiffness (hardness) and adhesion were also investigated. Force-distance measurement was performed by using AFM contact mode. Surface stiffness was tested on extending line while adhesion was observed on retracting line. The spring constant of cantilever used in this study was 0.15 N/m. The surface stiffness was calculated as following

$$\text{Relative surface stiffness} = \frac{S_C}{S_T} \qquad \text{Equation 5.4}$$

Where S_C = slope of retracting tip on control untreated sample

S_T = slope of retracting tip on chlorinated sample

According to the plot in Figure 5.7, the stiffness slightly decreased from 1 to 5 minutes of chlorination time, then increased from 5 to 20 minutes. Beyond 20 minutes the stiffness seemed to be unchanged. Nevertheless longer chlorination time exhibited the tendency to give higher surface stiffness.

Table 5.6 The relative surface stiffness of chlorinated NR surfaces for 0, 1, 5, 10, 20, 30 minutes of chlorination time obtained from force-distance measurement in AFM contact mode

Chlorination time (mins)	Relative slope	Relative stiffness
0	0.95	1
1	0.86	0.91
5	0.80	0.84
10	1.10	1.16
20	1.56	1.64
30	1.59	1.67

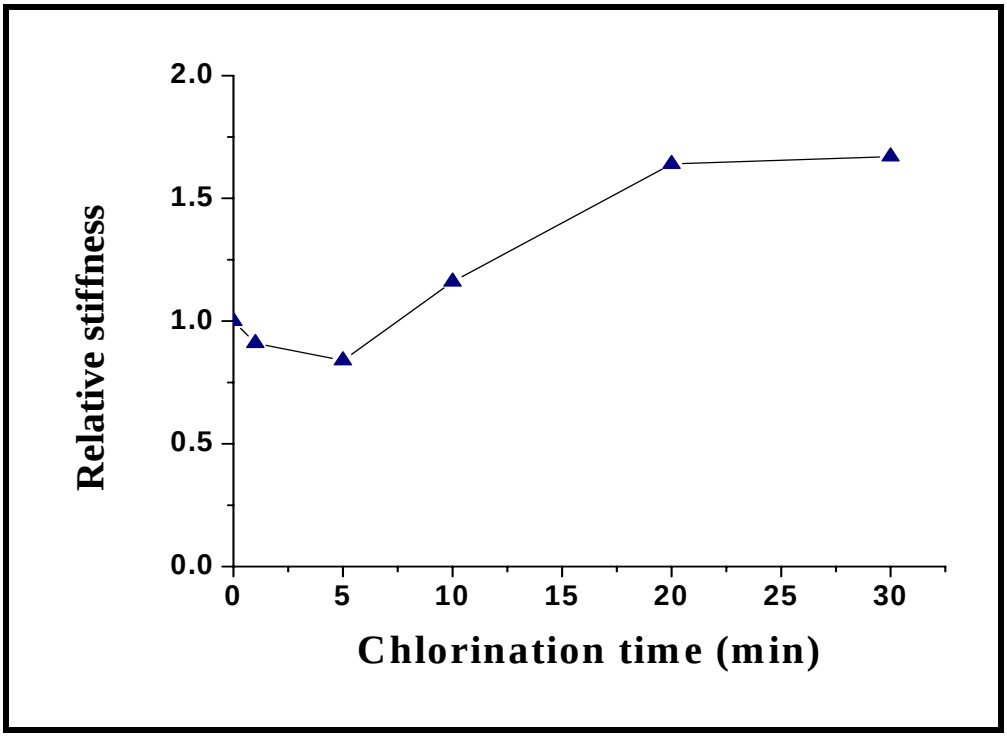

Figure 5.7 Relative slope of chlorinated NR surfaces at 0, 1, 5, 10, 20, 30 minutes of chlorination time obtained from AFM contact mode.

On retracting tip off the surface, adhesion force between tip and surface was determined. Adhesion force can be determined following Hook's law [43] on adhesion hysteresis loop multiplied by the spring constant of cantilever. The retracting lines of chlorinated NR surface of different chlorination time are illustrated in Figure 5.8.

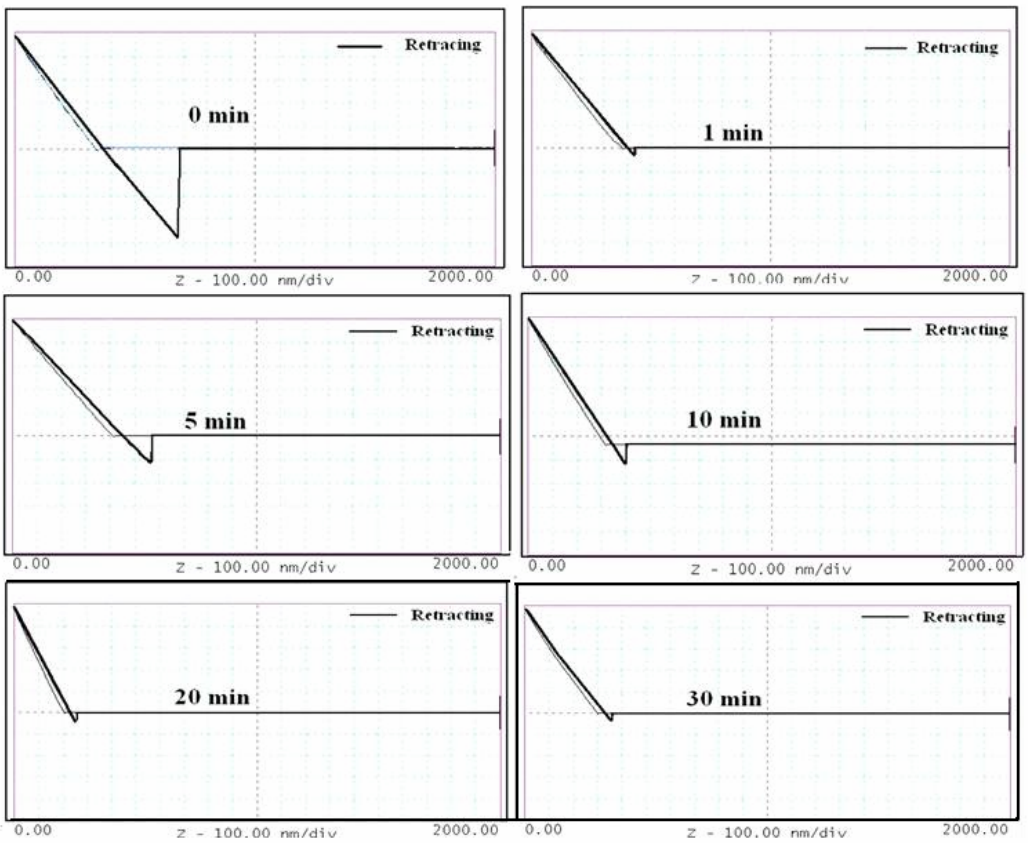

Figure 5.8 Force calibration plot of chlorinated NR at 0, 1, 5, 10, 20, 30 minutes of chlorination time by AFM in contact mode

From Figure 5.8 it seems that adhesion hysteresis loop reduced with chlorination time. This could be related to the stiffness of the treated surface. The molecular interaction force of tip-Cl and tip-C showed less effect on the adhesion (cantilever tip of contact mode is made of silicon nitride, Si_3N_4).

Table 5.7 Adhesion force of chlorinated NR surface at 0, 1, 5, 10, 20, 30 mins of chlorination time, obtained by force distance measurement in AFM contact mode

Chlorination time (mins)	Adhesion force (nN)
0	35.56
1	3.04
5	9.47
10	8.27
20	6.79
30	4.63

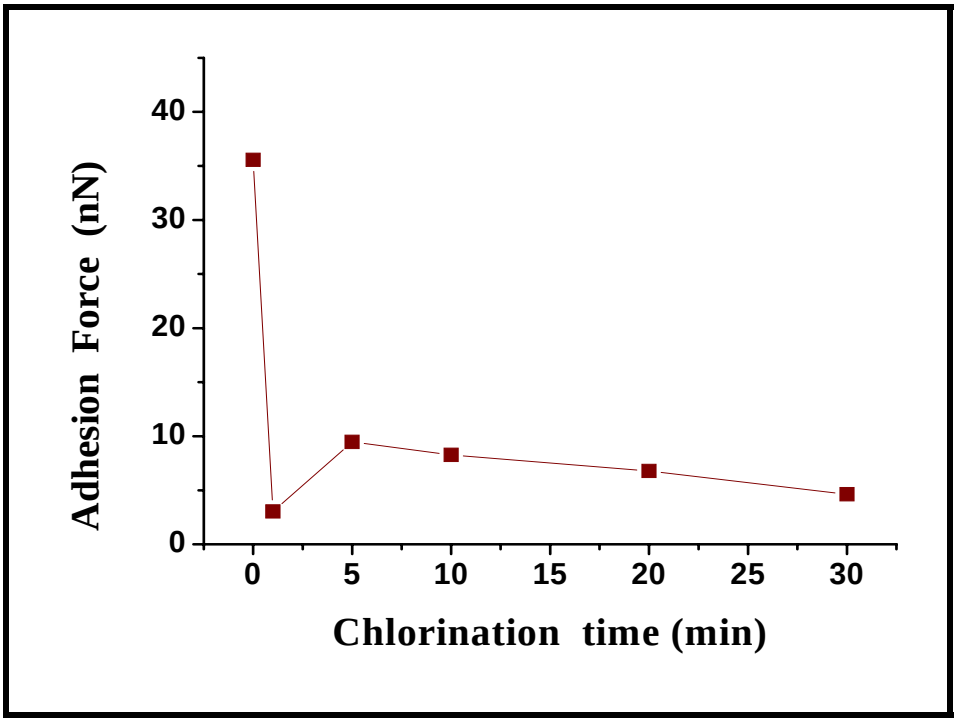

Figure 5.9 Adhesion force of treated NR surface at 0, 1, 5, 10, 20, 30 minutes of chlorination time by force distance measurement in AFM contact mode

Figure 5.9 shows the adhesion force between contact tip and chlorinated NR surfaces. According to these results, the adhesion force rapidly decreased as the chlorination time increased from 0 to 1 minute. Afterward, the adhesion force hardly changed with the chlorination time. This study could be claimed that chlorination of NR surface decreased the tackiness of surface and increased the stiffness of NR surface.

5.2.5 Peel strength of chlorinated NR// NBR

As discussed previously, chlorination of NR resulted in surface modification of NR surface properties. The main objective of the work is to improve the adhesion. Peel test is used to report the bond strength between them. The effect of chlorination time of NR surface on peel strength, and correlation of the peel strength and other properties were studied and discussed here.

The specimens were prepared and described earlier in Section 4.3 and 5.1 (surface of NR sheets were scrubbed by sand paper no. 80). Chlorinated NR sheets were laminated and cured to NBR sheets. The peel strength obtained from different chlorination time of NR is tabulated and plotted in Table 5.8 and Figure 5.10, respectively.

Table 5.8 Peel strength of chlorinated NR//NBR for various chlorination times

Chlorination time (min)	Peel strength of Cl-NR// NBR
0	1742 (±192)
1	15859 (±1200)
5	11540 (±1755)
10	11933 (±196)
20	6235 (±763)
30	8842 (±681)

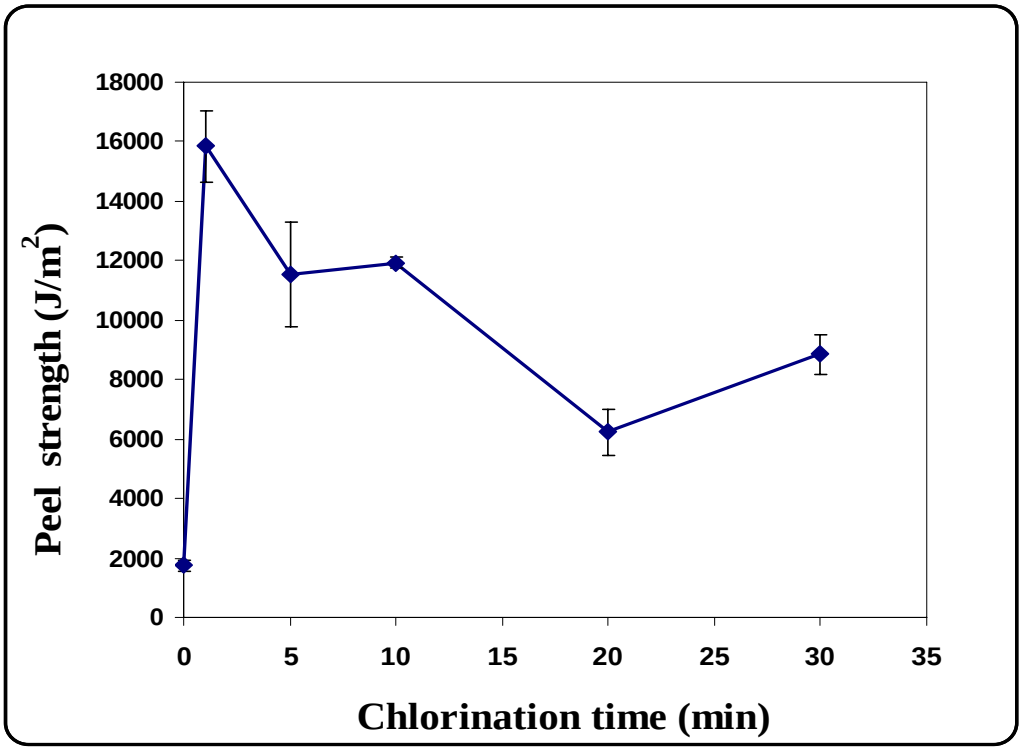

Figure 5.10 The effect of chlorination time on peel strength of chlorinated NR bonded to NBR

It was found that chlorination time of 1 min showed the highest peel strength although the standard deviation are quite scattering values compared with other chlorination times. The peel strength is a surface property that is governed by several parameters, e.g. surface hardness, interfacial miscibility. Chlorination solution was prepared by dissolving of sodium hypochlorite in diluted hydrochloric acid. The NR surface was hardened. The surface hardness was detected by force distance measurement resulting in relative slope of extending line. The higher relative slope, the stiffer of treated NR surface (see Section 5.2.4.2). On the contrary, the degree of chlorination investigated by XAS did not increase as function of chlorination time. That means the observed peel strength is not related to amount of chlorine atom only but other properties such as surface hardness, roughness, adhesion and polarity play an combination role on the peel strength of chlorinated NR//NBR.

The peel strength might be discussed to closely relate with surface tensile strength. The surface tensile strength can promote peel strength as well [44]. The

tensile strength of a vulcanizate rubber is highest when its hardness is optimized [45]. On the other hand, the maximum peel strength is found at 1 minute of chlorination time and tends to decrease afterwards. That is optimized for getting the excellent peel strength, and surface hardness is still suitable for the peel strength.

5.2.6 Chemical interaction between chlorinated NR // NBR

During the vulcanization process, cyanide group in NBR can be hydrolyzed to amides and acids in NBR structure [46]. Therefore, the concentration of reactive species in NBR was increased as shown in Figure 5.11.

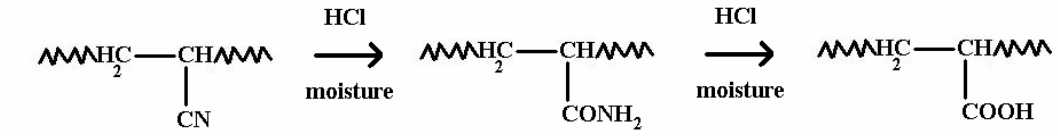

Figure 5.11 Hydrolysis of cyanide group in NBR [46].

From Figure 5.11, all of allyl chloride in chlorinated NR can react with amide and carboxylated groups in NBR chains favors the self-crosslinking as shown in Figures 5.12 and 5.13

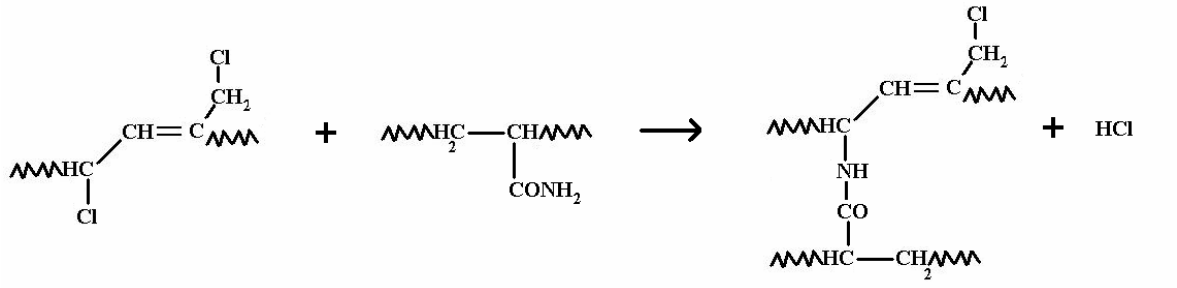

Figure 5.12 Self-crosslinking of primary amides in NBR and allyl chlorides of chlorinated NR.

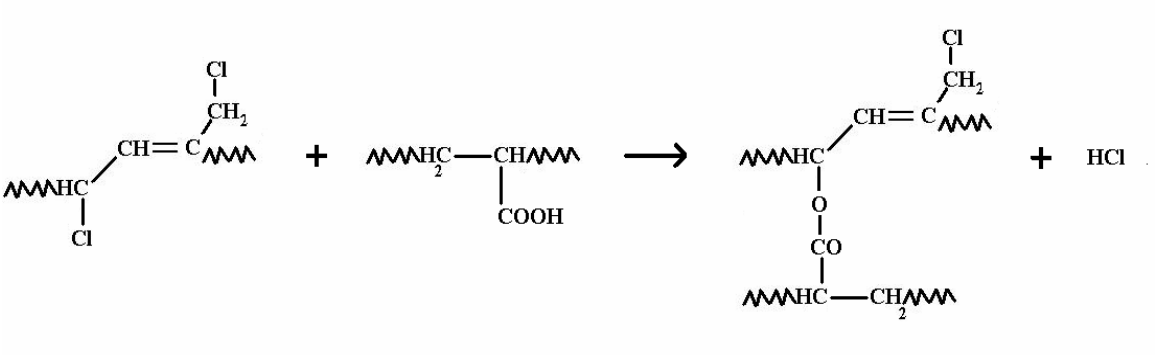

Figure 5.13 Self-crosslinking of carboxylated group in NBR and allyl chlorides of chlorinated NR.

5.2.7 Mechanism of failure of chlorinated NR// NBR

To study the mechanism of peeling, NBR was compounded by using silica as filler and NR was mixed with carbon black in order to make the different color in both rubbers. After peeling, the separated surfaces were examined. On the NR surface no white color compound represented NBR was observed. On the other hand black color representing the compounded NR was found on the NBR surface. This can be considered that the cohesive failure mechanism occurred by the weak layer of chlorinated NR was broken and moved to adhere on the NBR surface. This result according to Figure 5.14 shows the separated surfaces which NR was broken and stuck onto NBR layer.

Figure 5.14 Evidence of the chlorinated rubber bonded with silica filled in NBR specimen after T-peel test. Chlorinated NR surface was attached to Si-NBR side**.**

5.2.8 Peel strength of identical rubbers

The peel strength of same rubbers can be used to justify the mechanism of failure either adhesive or cohesive failure. In some cases the combination of both mechanisms are found in peel test. Moreover, this can indicate cohesive failure in specific layer [47, 54].

The peel strength of NR//NR and NBR//NBR was determined under similar condition as for the study of NR//NBR peel strength. For NR//NR, only carbon black filled sheets were studied, while NBR//NBR the peel strength of pair NBR sheets compounded with silica (Si-NBR//Si-NBR) and carbon black (CB-NBR//CB-NBR) were reported. The comparison of the peel strengths for identical rubbers was presented in Table 5.9 and Figure 5.15.

Table 5.9 The peel strength of the identical rubbers

Peel strength (J/m^2)		
CB-NR//CB-NR	**CB-NBR//CB-NBR**	**Si-NBR//Si-NBR**
22976 (±743)	29838 (±969)	27239 (±865)

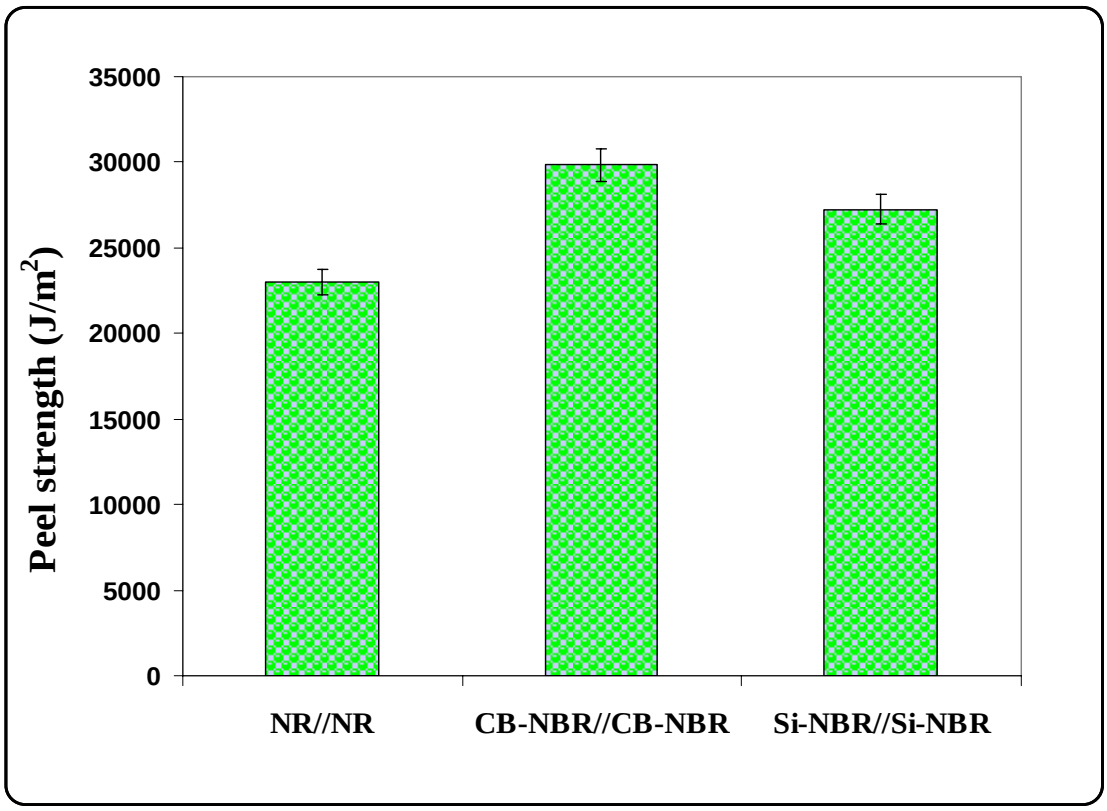

Figure 5.15 The peel strength of the same rubbers of NR//NR, CB-NBR//CB-NBR, Si-NBR// Si-NBR.

This test was done in order to study the peel strength of the same rubbers. The failure mechanism found was certainly cohesive type. The peel strengths in this case relates directly to the bulk strength of rubber itself. CB-NBR//CB-NBR shows highest peel strength followed by Si-NBR// Si-NBR and CB-NR//CB-NR respectively. Nevertheless, all surfaces were not modified by chlorination. This might be the reason

that the peel strength of unmodified rubber with cohesive failure exhibits better peel strength than that of chlorinated surface one.

5.3 Effect of extent of cure on peel strength

In this section, the effect of cured extent of NR compounding affected on peel strength of NR//NBR laminates was studied. Before chlorination, the cure extent of NR was determined by varying time in mould during vulcanized process that was assumed by using MDR measurement.

5.3.1 Uncured NR// CB-NBR and uncured NR// Si-NBR

In previous study, chlorination of NR surface was performed on cured NR. It would be interesting to study the bonding between chlorinated NR and silica-filled NBR when chlorination was effected on uncured NR surface. The bond strengths by peel test are shown in Table 5.10

Table 5.10 Comparison of peel strength of chlorinated uncured NR//CB-NBR and Si-NBR

Chlorination time (min)	Peel strength (J/m^2) of Cl- uncure NR// NBR	
	CB-NBR	Si-NBR
0	933 (±159)	860 (±17)
1	6783 (±1052)	10945 (±470)
3	5897 (±347)	8371 (±885)
6	5681 (±867)	6413 (±785)
10	4723 (±302)	6053 (±1264)
15	5825 (±1302)	8241 (±523)
60	4748 (±852)	6822 (±855)

Table 5.10 shows the peel strength of chlorinated uncured NR bonded with CB-NBR and Si-NBR. It was found that the peel strength was maximized at 1 min of chlorination time for both cases. Moreover, the peel strength of NR//Si-NBR is higher than that of NR//CB-NBR. This effect is caused by the combination of the interaction of silica-chlorine atoms and optimized surface stiffness of NR treated surface. In this case, the chlorine appearance on NR surface from chlorination method is not affected by the lamination step.

Figure 5.16 shows the comparison of peel strength between chlorinated uncured NR//CB-NBR and chlorinated uncured NR//Si-NBR. It was found that the interfacial strength of chlorinated uncured NR//Si-NBR were higher than those of uncured NR//CB-NBR. Moreover, it is considered that NR//CB-NBR does not show great variation in peel strength after 1 minute of chlorination as NR//Si-NBR does. This is due to the interaction of silica – chlorine is greater than that of carbon black – chlorine.

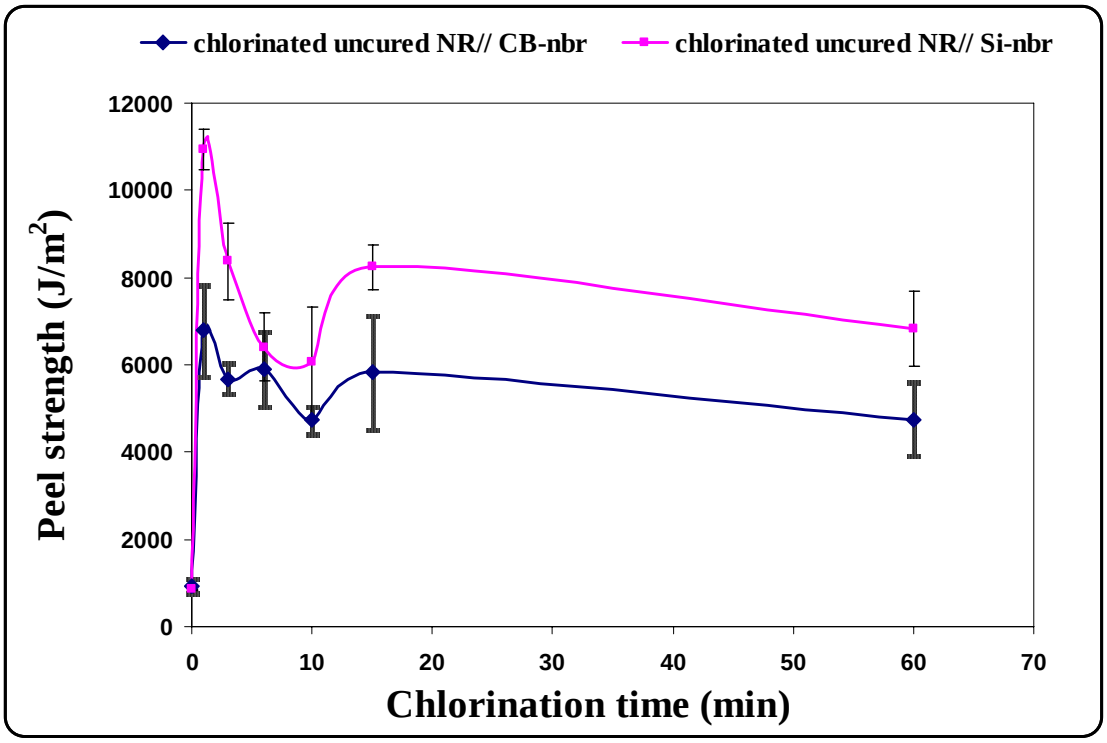

Figure 5.16 The effect of the different fillers in NBR bonded chlorinated uncured NR on peel strength.

From Figure 5.10 and Figure 5.16 could be compared and discussed. Figure 5.10 is shown the effect of chlorinated cured NR bonded CB-NBR on peel strength whereas Figure 5.16 is shown the effect of chlorinated uncured NR laminated with both types of filler in NBR. It was found that the peel strength of chlorinated uncured NR bonded with CB filled NBR gave the lower peel strength than the chlorinated cured NR bonded with CB filled NBR. These results might be scrubbing on cured NR surface. From Table 5.1, Scrubbing of NR surface can increase the peel strengths of NR//NBR because of increasing in surface roughness.

5.3.2 The effect of precuring of NR on Peel strength

Uncured NR sheets at different degree of crosslinking were chlorinated. In the chlorination step, chlorine atoms appear on the NR surface. During pressing together with NBR layer, NR surface might be deformed resulting in decrease in interaction between chlorine functional group and NBR surface. Crosslinking of NR was aimed to fix chlorinated NR surface and increase the interaction to NBR layer. The peel strengths of NR//NBR at various percentages of precuring of NR prior to chlorination are presented in Table 5.11 and Figure 5.17

The degree of precuring was investigated by using MDR measurement. 10 and 100 percent of precuring *for example* were determined in similar way as curing, T_{10} and T_{100} respectively. After precuring, the specimens were chlorinated for 1 minute, and then pressed together with CB-NBR and Si-NBR.

Table 5.11 The effect of cured time of NR before chlorination on peel strength of Cl-NR// CB-NBR and Cl-NR// Si-NBR

Cure time of NR	Peel strength (J/m^2) of Cl- NR// NBR	
	CB-NBR	Si-NBR
t_0	3464(±720)	9573(±332)
t_{10}	3649(±881)	10321(±1704)
t_{25}	3374(±929)	15736(±435)
t_{50}	4197(±596)	8888(±644)
t_{70}	4628(±920)	22929(±2440)
t_{100}	5696(±428)	11364(±1501)

From Table 5.11, it can be seen that the peel strength of chlorinated NR bonded with CB-NBR and Si-NBR increased with increasing percentage of precuring. While NR//Si-NBR the value of peel strength is rather fluctuated but shows the trend to increase with percentage of precuring. On comparing (see Figure 5.17) the effect of filler type in NBR compound, silica filled NBR gave higher peel strength than those of carbon black filled NBR.

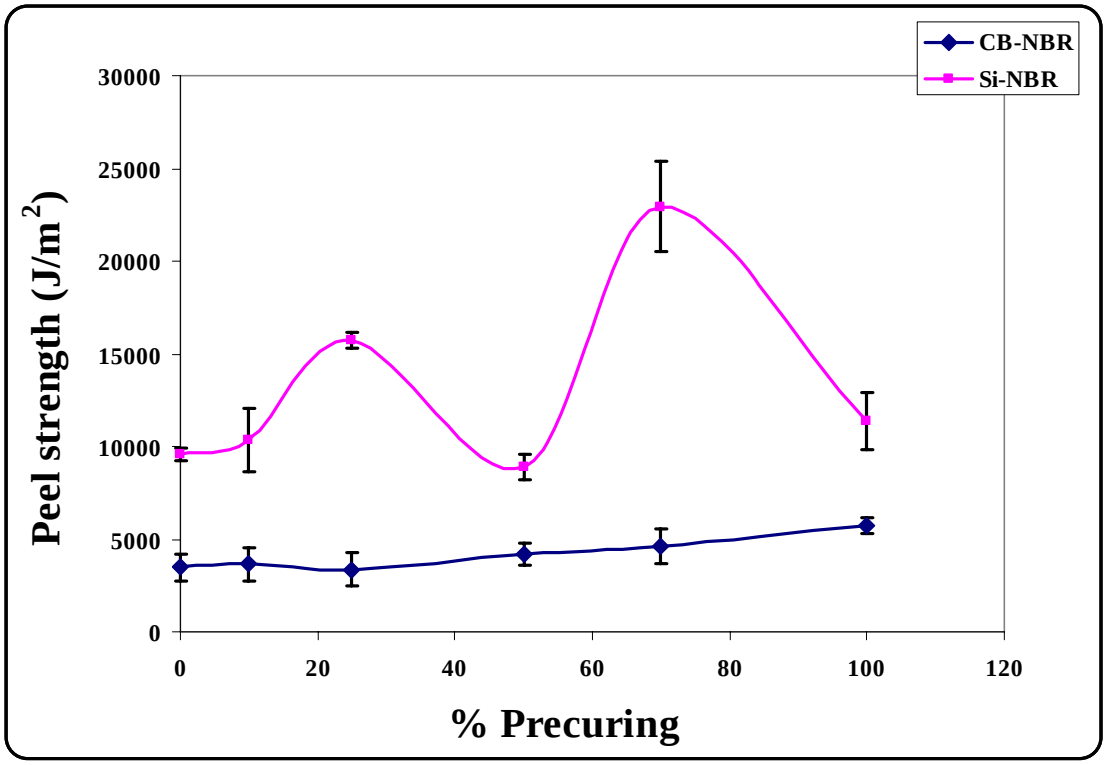

Figure 5.17 Comparison of peel strength between chlorinated NR// CB-NBR and chlorinated NR//Si-NBR by vary cured time of NR

5.4 Effect of compounding on peel strength

This section reports studies of the effects of filler type in NBR compound, cured- and uncured NR prior to chlorination, the effect of precuring of NR and effect of carbon black loading in NR compound on peel strength of NR//NBR. The results are shown and discussed below.

5.4.1 Effect of carbon black and silica in NBR compound

NBR compounds were prepared by using carbon black and silica as fillers. Generally carbon black is used to reinforce the rubber than silica. The effect of reinforcement by carbon black is known to give higher strength than that of silica [48].

As NR was chlorinated at the surface, silica in Si-NBR was expected to express any interactions between silica and chlorinated NR. The peel strength was used for evaluation of bond strength. The results in these studies are given in the Tables 5.10, 5.11, 5.12 and Figures 5.16, 5.17, 5.18.

Table 5.12 Comparison of peel strength between the specimens of chlorinated cured NR bonded with carbon black filled in NBR and chlorinated cured NR bonded with silica filler filled in NBR.

Chlorination time (min)	Peel strength (J/m^2) of Cl-NR//filled-NBR	
	CB-NBR	Si-NBR
0	1742 (±192)	1579 (±306)
1	15859 (±1200)	15958 (±1618)
5	11540 (±1755)	15415 (±1393)
10	11933 (±196)	12821 (±840)
20	6235 (±763)	8458 (±510)
30	8842 (±681)	12040 (±15)

Figures 5.16 and 5.18 show the peel strengths of filled NBR bonded to chlorinated cured NR and uncured NBR at 0, 1, 5, 10, 20, 30 minutes of chlorination. The fillers in NBR in this work were carbon black N-330 and silica Hi-sil® 233-s. Figures 5.16, 5.17, 5.18 show peel strength results of the chlorinated cured NR bonded with CB-NBR and Si-NBR, chlorinated uncured NR bond with CB-NBR and Si-NBR and the effect of cured time of NR before chlorination and bonding with CB-NBR and Si-NBR afterward, respectively. It was found that all the peel strengths of either chlorinated cured or uncured NR bonded with silica filled in NBR are higher than either chlorinated cured or uncured bonded with carbon black filled in NBR.

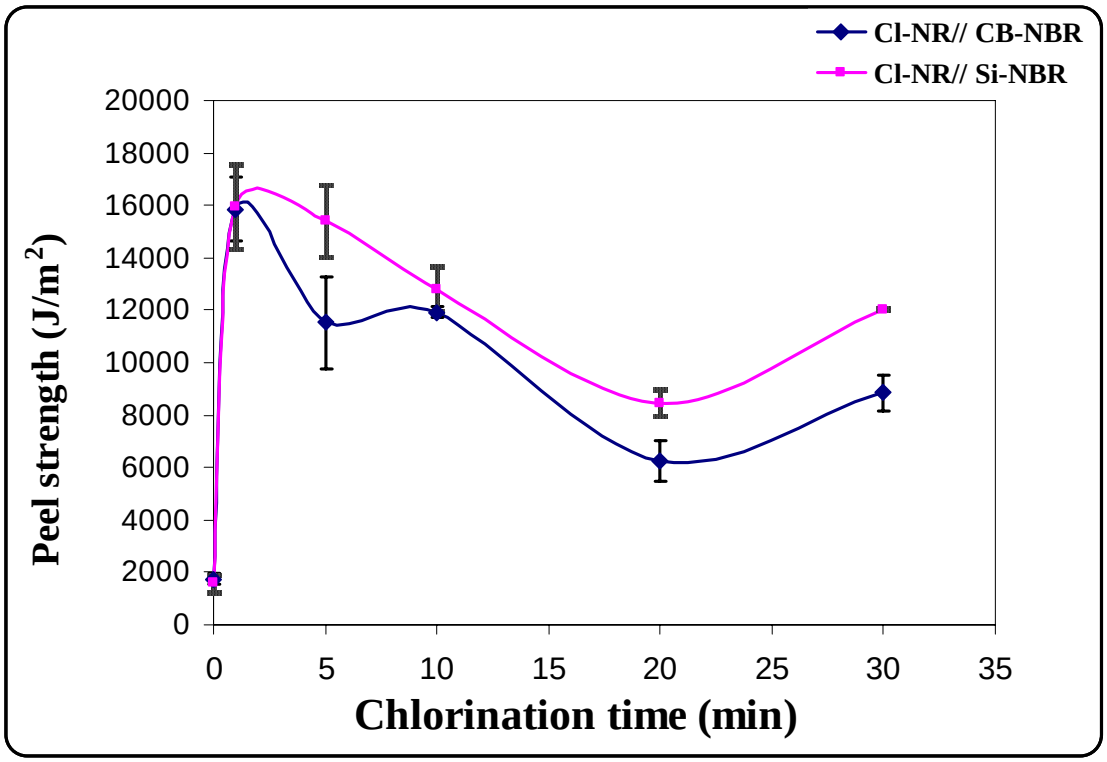

Figure 5.18 Peel strength of chlorinated NR and filled NBR at 0, 1, 5, 10, 20, 30 minutes of chlorination time of NR surfaces.

NR//Si-NBR shows higher peel strength than that of NR//CB-NBR. This effect could be attributed to some interaction of silica and chlorinated NR and/or reinforcing effect in NBR compound. The interaction of silica and chlorinated NR is proposed as shown in Figure 5.17

The interfacial failure of bonding between chlorinated NR and filled NBR occurred at the chlorinated NR side that was attached to filled NBR side in every condition. For example are shown in the figure 5.14 (Section 5.2.7).

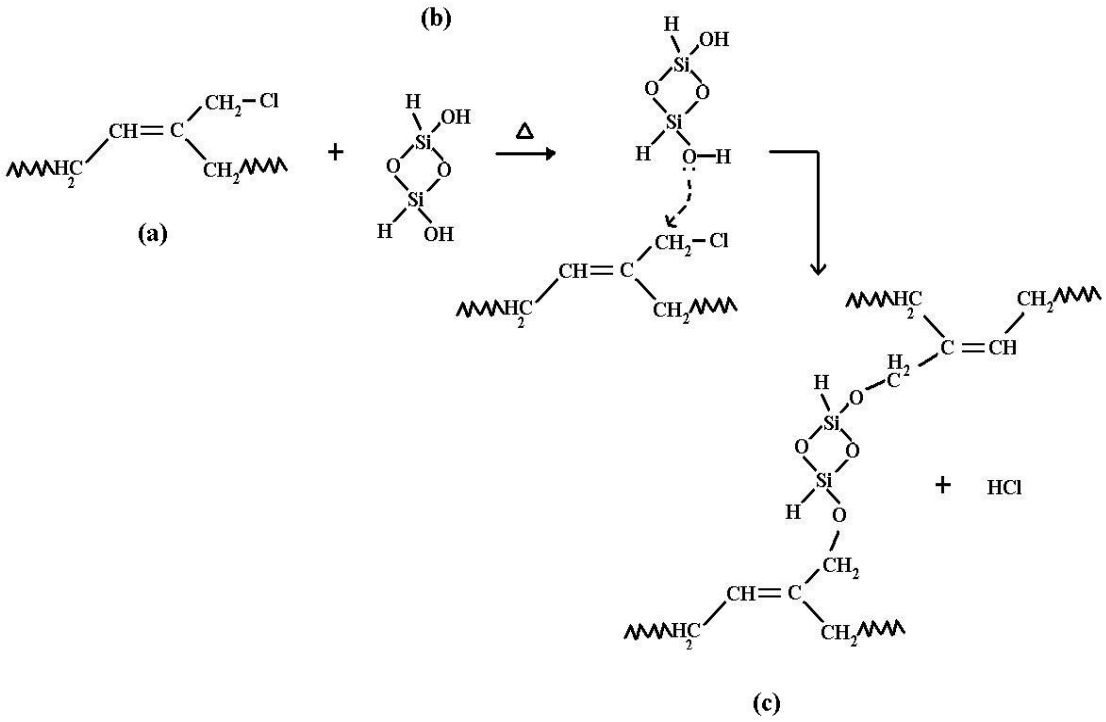

Figure 5.19 Schema of a proposed mechanism for the chlorinated NR-silica interaction [49]

According to the earlier reports [50, 51, 52] on the study of polymer-filler and filler-filler interaction. It might be another reason to explain the peel strengths of chlorinated NR//Si-NBR were higher than CB-NBR one. It has been found that the silica and carbon black show different components in surface energy and also difference in the specific interaction. In this regard, it is apparently that the specific surface energy and specific interaction of silica filler is higher than those of carbon black, which give rise to stronger polymer-filler interaction especially for NBR which is high polar elastomers. In NBR structure has the highly polar CN-group whereas silicas were much higher interaction than carbon blacks. Therefore, the higher peel strengths of chlorinated NR//Si-NBR could be due to the interaction between the CN-groups and the silanol-groups via dipole-dipole polar interaction as well as hydrogen bonding including the interaction between Cl-groups and silanol-groups. Because of during T-peel test, the interfacial fracture between Cl-NR and Si-NBR were shown in adhesive and cohesive failure where as the adhesive failure of Cl-NR//CB-NBR was

occurred. This means that the great difference in polymer-filler interactions between silica and carbon black will be, in the case of silica, greatly augmented in NBR.

Therefore, the higher in surface energy and polymer-filler interaction of silica filled NBR have more effect to the adhesion strength between chlorinated NR and filled-NBR. From all of the results reported, it could be concluded that silica filled NBR showed stronger bonding to surface chlorinated NR than carbon black fill NBR

Table 5.13 Characteristics of carbon black N330 and Silica Hi-Sil® 233-S

	Carbon Black N-330	Silica Hi-Sil® 233-S
Surface area:		
* CTAB m^2/g	84.0	–
† BET (N_2), m^2/g	110.0	150.0
‡ DBPA (24M4), $cm^3/100g$	105.0	190.0

***** CTAB (Cetyltrimethyl ammonium bromide) = Carbon black absorb this aqueous solution for surface area determination [61]**.**

† BET (Brunaver, Emmett, and Teller) using the nitrogen isotherm determined the particle size and specific surface area [62].

‡ DBPA (Dibutyl phthalate absorption) is structure measurement by determining the total volume of the air spaces between aggregates per unit weight of particles by measuring the volume of a liquid (DBP) require to fill the void.

The characteristics of specific surface area of carbon black and silica are shown in Table 5.13. It was found that the surface area of silica Hi-Sil® 233-S is greater than carbon black N-330. Therefore, the chlorine groups on NR surface could be interacted with silanol-groups of silica more than carbon black filled NBR. This means that the greater peel strengths of Cl-NR and Si-NBR bond.

5.4.2 The effect of carbon black loading in NR on Peel strength

As we have studied that the adhesion of NR//NBR can increase via chlorination of NR surface. The precuring of NR before chlorination also proves the increase in the peel strength. That might be the presence of chlorine on NR surface. This section aims to study the effect NR compound viscosity by varying the carbon black loading. The higher NR viscosity tends to more stabilize the NR surface. In other word, high viscosity gives less surface deformation during bonding with NBR. The amount of carbon black at 40, 60, 80, 100 phr were used in NR compounding. The viscosity of compounds was evaluated by using Mooney viscometer, and the values are presented in Table 5.14.

Table 5.14 Mooney viscometer test of different carbon black loading in NR

CB loading in NR (phr)	Mooney viscosity [MS(1+4)]
40	19
60	38
80	Not measurable
100	Not measurable

Table 5.15 and Figure 5.20 present the peel strength of NR//NBR with various carbon black loading in NR. The peel strength was increased with carbon black content up to 80 phr and decrease afterward. This increment could be attributed to two factors. Firstly the higher viscosity NR causes the surface to be more stable leading to more interaction of chlorine-NBR. Secondly, the higher loading of carbon black could results in the greater bulk strength of NR layer. Noteworthy, the peel strength of the laminate containing 100 phr of CB filled NBR decreased. This might be due to the fact that the specimen is too stiff causing in less energy dissipation during peeling. In addition, poor carbon black dispersion might results in defect on NR surface.

Table 5.15 The peel strength of chlorinated uncured NR bonded with carbon black filled in NBR by vary carbon black loading in NR compounds

Carbon black loading in NR (phr)	Peel strength (J/m^2) of Cl-uncured NR// CB-NBR
40	10836(±175)
60	20421(±150)
80	21132(±1829)
100	14230(±3469)

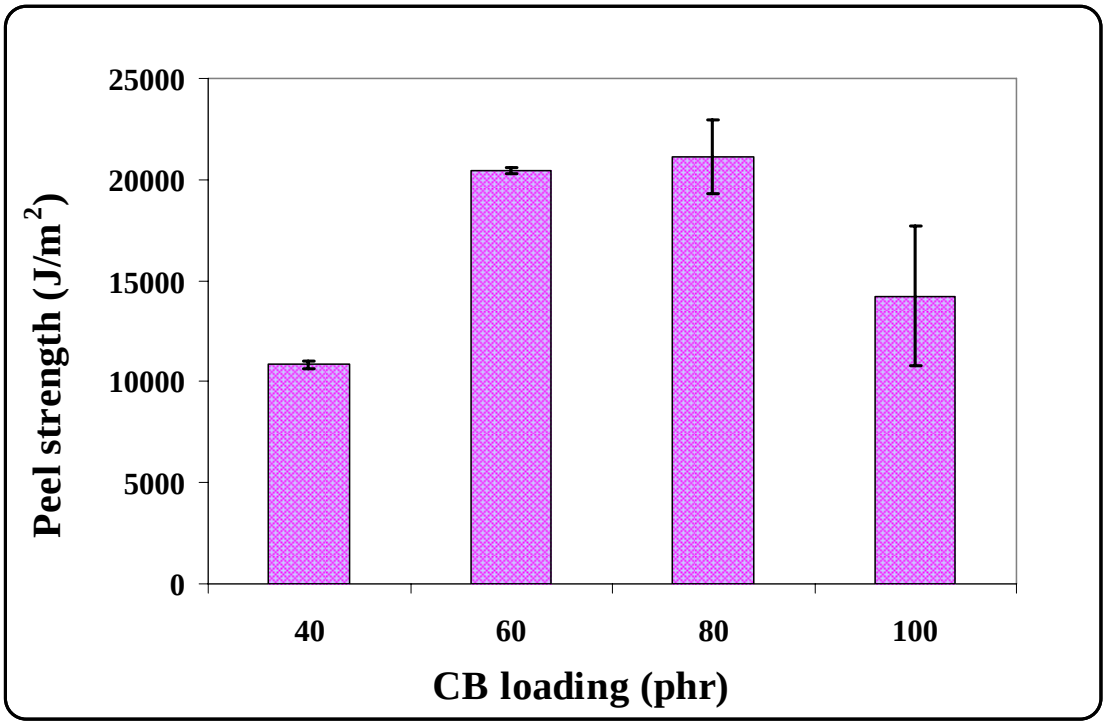

Figure 5.20 The effect of carbon black loading in NR compound on the peel strength.

5.4 Stability of chlorinated NR and NBR bonding

The objective of this part of study was to assess the stability of bonding between NR and NBR. This might relate to the service life of NR//NBR lamination products for several kinds of treatment. The specimens in this part were chlorinated for 1 minute, and then laminated to NBR layer on curing. The changes in peel strength of before and after treatment were reported as relative peel strength. The peel strength of control sample was about 12000 J/m^2 and used for comparison with treated sample. The stability under heat, ozone, storage, and flex treatments are presented and discussed

5.4.1 Heat treatment

From Figure 5.21, it was found that the relative peel strength of chlorinated NR bonded to carbon black filled NBR slightly decreased comparing to control sample. That means could not be affected significantly by heat at 100^0C for 2 days. It was surprising that the relative peel strength was slightly decreased because NR was not heat resistance material. Heat could generally reduce the bulk strength of NR and that governed consequently the peel strength.

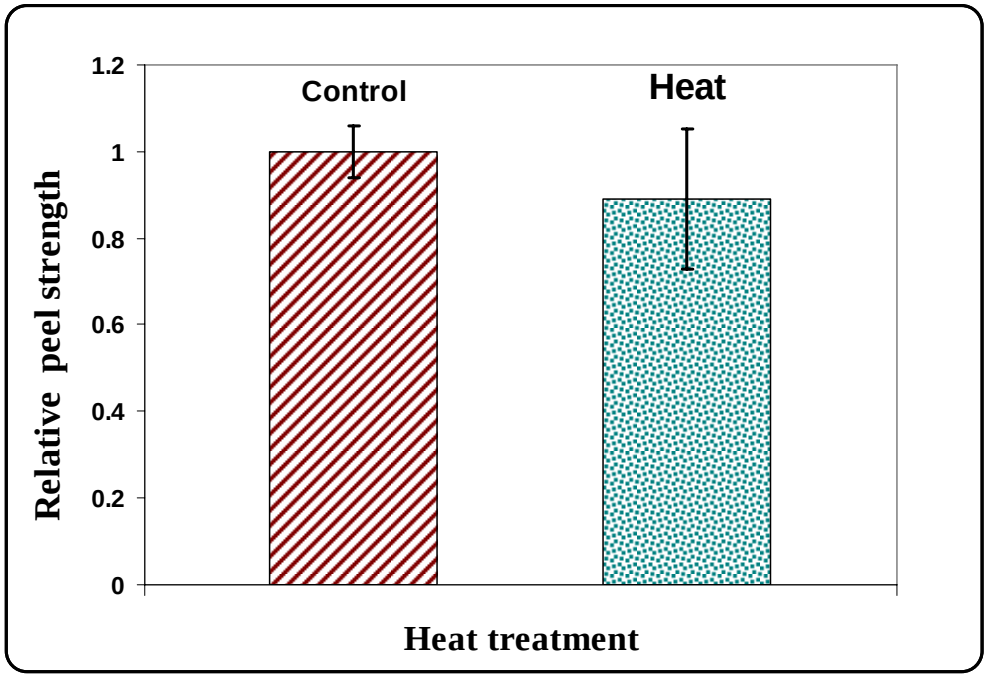

Figure 5.21 The relative peel strength of chlorinated NR bonded to carbon black filled NBR, after placing in hot air oven for 2 days compared with untreated specimen.

5.4.2 Storage time

The objective of this work was the observation of stability of chlorinated cured NR bonded with carbon black filled in NBR by storage the chlorinated cured NR sheets of one minute of chlorination time in two systems. The series of chlorinated cured NR sheets were kept in opened air and closed air systems for 1, 2, 3, 4 weeks respectively. Afterward, these specimens were bonded with carbon black filled NBR.

The results of peel strengths of those series were reported as relative peel strength as shown in Figure 5.22.

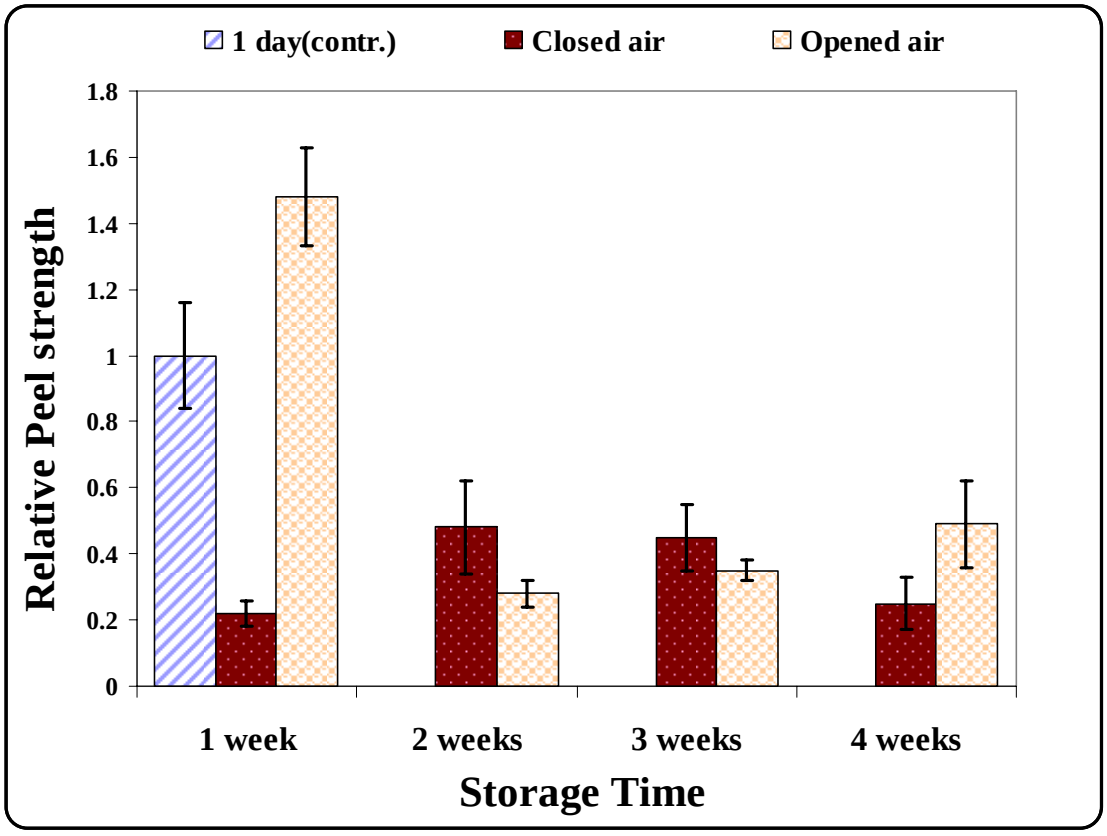

Figure 5.22 The relative peel strength of chlorinated cured NR bonded with carbon black filled NBR. The chlorinated cured NR sheets were kept at 1, 2, 3, 4, weeks before pressing with carbon black filled NBR sheets.

It was found that the relative peel strength of the most specimens decreased after keeping for several weeks. The remained peel strength was less than a half of the control except the storage for a week in opened air. It can be concluded that the storing of chlorinated NR before pressing effected significantly on the peel strength of NR//NBR bonding. The decrement of peel strength might be caused by air borne contamination, chlorine functional rearrangement, for example. It was noted that 1 week storing in opened air showed very good peel strength.

5.4.3 Ozone treatment

The Figure 5.23 shows the results of the relative peel strength of the bonded specimens after ozone treatment compare with untreated ozone specimens. Both types of filler (carbon black and silica) in NBR were studied. After exposure for 3 days in ozone chamber, the relative peel strength found decreased slightly. It seems that NR//NBR laminate was rather stable against the ozone treatment.

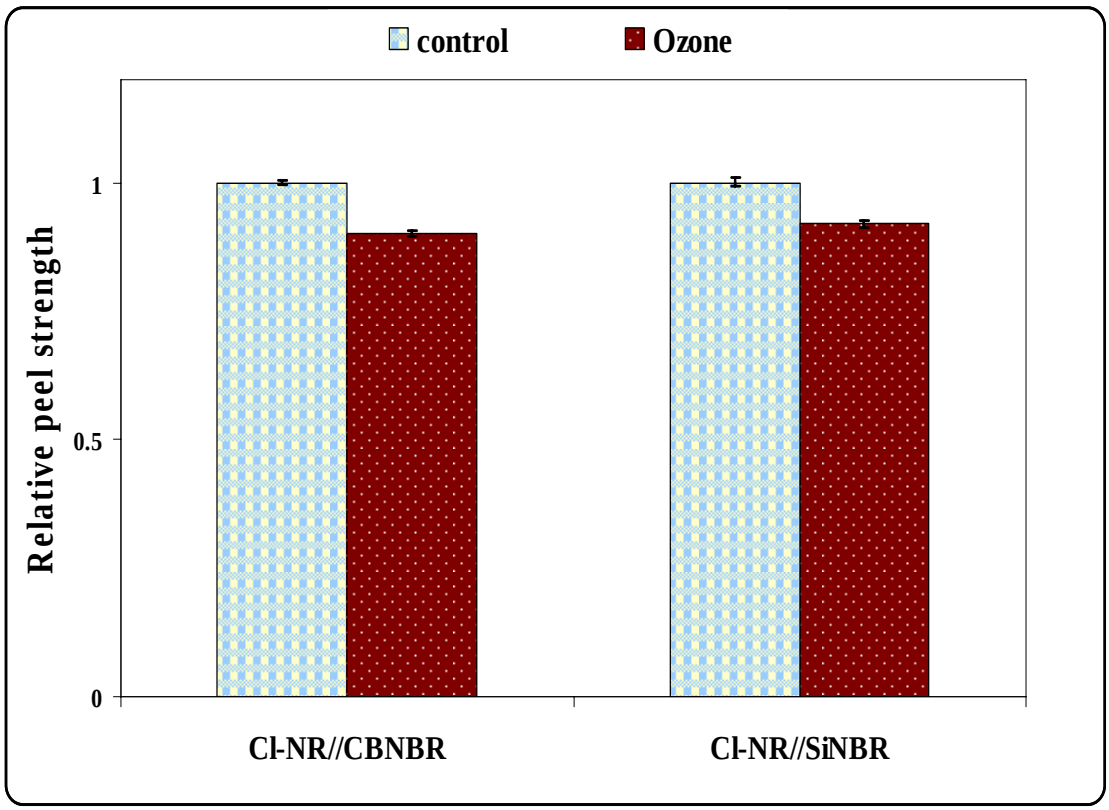

Figure 5.23 The relative peel strength of NR//CB-NBR, and NR//Si-NBR, after exposure in ozone chamber for 3 days.

It was noticed that ozone treatment might not affect the bonding resulting in small decrease in relative peel strength. This is because ozone can not attack directly to bonding interfacial.

5.4.4 Flex resistance

Figure 5.24 shows the changes in relative peel strength of various NR//NBR laminates as a function of cycle time in dynamic flex experiment. It was found that the peel strength of all specimens decreased after dynamic flex treatment. NR laminated with carbon black filled NBR seems to retain the stability better than silica filled NBR. It was also noted that chlorinated cured NR//CB-NBR was stabilize excellently under 1000 and 2500 cycles, taking into account the unchanged in relative peel strength. The lowest relative peel strength was observed from the chlorinated uncured NR//Si-NBR laminate under 5000 cycles. This could be attributed to the different structure of silica and carbon black. The carbon black structure was known to contribute to flex treatment. The results of this study are shown as below.

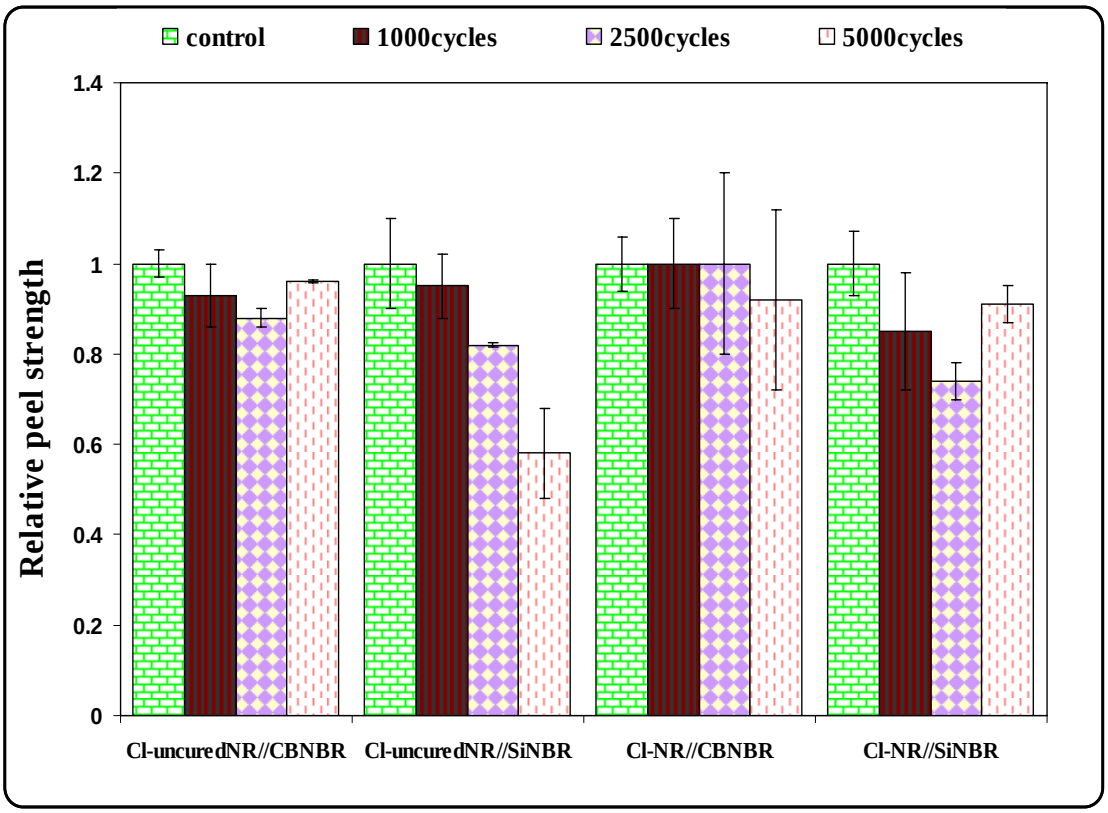

Figure 5.24 The relative peel strength of chlorinated cured and uncured NR bonded with carbon black and silica filled NBR, after flex experiment compared to control samples. The flex cycles were 1000, 2500, and 5000 cycles.

From the above results, it could be concluded that the bonding strength of both chlorinated cured and uncured bonded with silica as filler in NBR give the lower adhesion after dynamic flex test. That represented the weaker bonding at the interfacial surfaces of two rubbers when compared with the specimens of both cured and uncured bonded with carbon black filled NBR.

CHAPTER 6
CONCLUSIONS

This work mainly focuses on the method of chlorination on NR surface and adhesion improvement of chlorinated NR to NBR. After the study, the appropriate conclusions could be drawn as following:

1. The degree of chlorine substitution on NR surface increased gradually from 0 up to 30 minute of chlorination time. The optimum substitution of chlorine was found at 10 minute and longer treatment time. The surface investigation by AFM exhibited that the local hardness and roughness tended to increase as function of chlorination time. On the contrary, the adhesion between AFM tip and chlorinated NR surface showed the tendency to be reduced with chlorination time.

2 The bond strength of Cl-NR// NBR showed the maximum peel strength at 1 minute of chlorination time when the chlorination time was longer than 1 minute, the peel strength tended to decrease, even though the degree of chlorination was increased. It could be considered that the peel strength was not only governed by the degree of chlorine substitution. Other parameters i.e. surface roughness and stiffness might play an important role on peel strength. Increasing the surface roughness could promote the physical interfacial interaction whereas the higher stiffness might reduce the energy dissipation during the peel test.

3. The effect of NR surface viscosity modified by carbon black loading and precuring of NR compound showed the increase in peel strength. Carbon black loading and precuring of NR compound were introduced in order to modify the viscosity of NR vulcanizate. The higher NR viscosity, the greater stability NR surface. The peel strength of t_{100} NR bonded to NBR showed maximum peel strength. While at 80 phr carbon black loading in NR met the highest peel strength.

4. For the effect of filler type in NBR, silica filled NBR showed higher peel strength than that of carbon black filled NBR even lower amount of silica in NBR compound. The peel strength of NR// Si-NBR might be promoted by the interaction of Cl-group on NR surface and silanol group of silica.

5. The stability of bond strength of NR// NBR tested by heat, flex and ozone treatment did not change significantly. On the contrary, the storage of chlorinated NR before pressing together with NBR revealed enormously the decrease in peel strength of NR// NBR bonding.

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APPENDIX

Appendix A

The calculation of available chlorine in sodium hypochlorite solution

A Summary of test method (ASTM D 2022)

The sample is added to an acidified solution of potassium iodide and the released iodine is titrated with standard sodium thiosulfate solution to the usual starch end point.

A.1 Standardization of titrant $Na_2S_2O_3$

Standard sodium thiosulfate solution ($Na_2S_2O_3$) was titrated with Potassium iodate (KIO_3) to determine the concentration of solution.

No.	o.1 N of KIO_3	$Na_2S_2O_3$ (mL)
1	50 ml	48.80
2	50 ml	48.85
Avg.		48.825

Thus;

Concentration of $Na_2S_2O_3$ = 0.1024 N

A.2 Iodometric Titration

The sodium hypochlorite solution (NaOCl) was titrated with known concentration of $Na_2S_2O_3$ solution.

No.	NaOCl (mL)	$Na_2S_2O_3$ (mL)
1	5 ml	105.30
2	5 ml	106.40
Avg.		105.85

From ASTM D 2022, calculate the sodium hypochlorite content as follows:

Sodium hypochlorite (NaOCl), weigth % = [(AN x 0.03722)/VS] x 100

Where:

A = $Na_2S_2O_3$ solution required for titration of the sample, mL

N = normality of the $Na_2S_2O_3$ solution,

V = original sample in aliquot used, mL

S = specific gravity of the sample

Thus;

% NaOCl = [(AN x 0.03722)/ VS] x 100

= [(105.85 x 0.1024 x 0.03722)/ 5x1.1] x 100

= 7.34 %

Therefore, the concentration of sodium hypochlorite solution in a bottle is 7.34%.

Appendix B

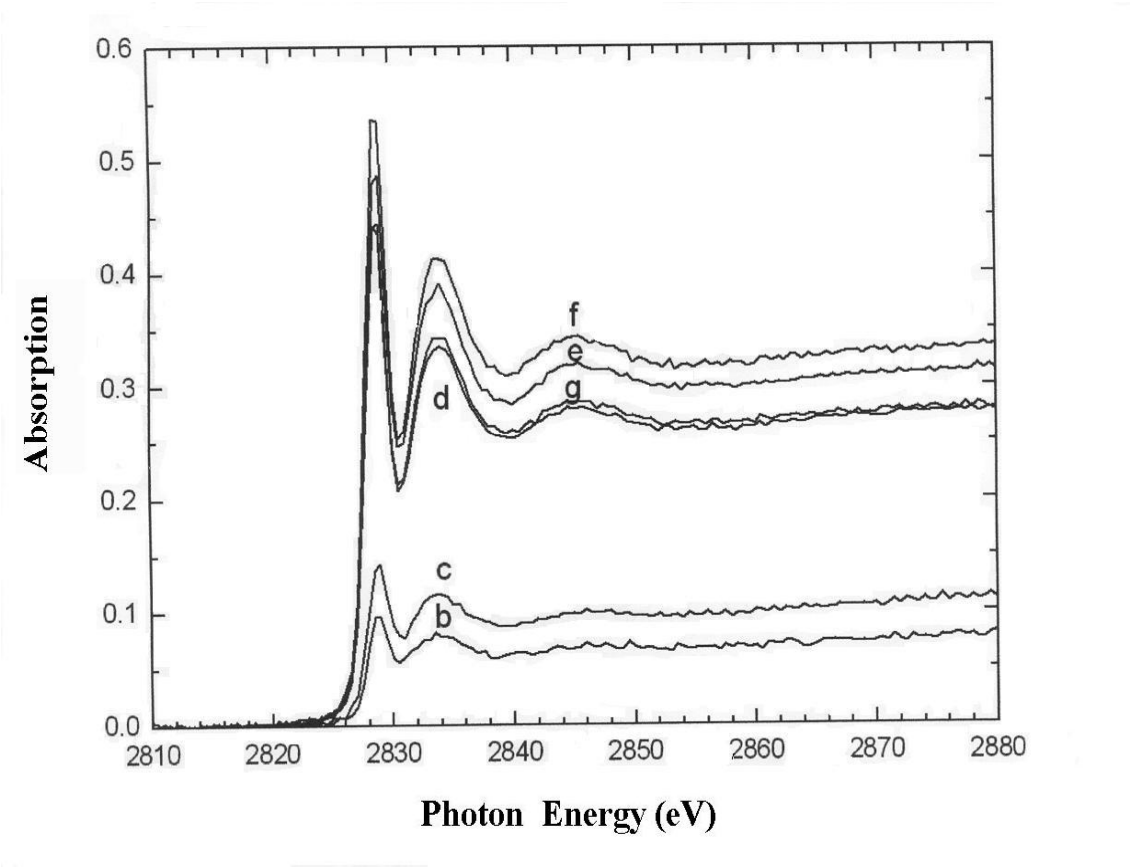

Figure B1 Chlorine K-edge XANES spectra of chlorinated NR samples at different chlorination time. (b) 0.5 min, (c) 1 min, (d) 5 min, (e) 10 min, (f) 20 min, and (g) 30 min.

Appendix C

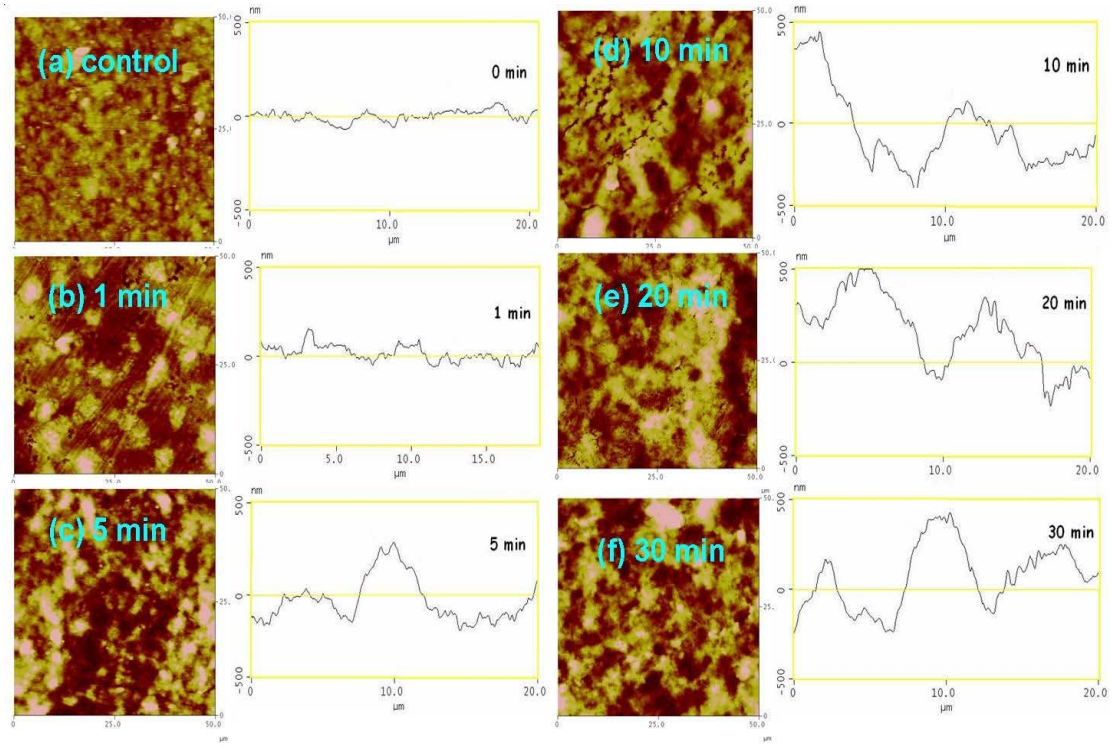

Figure C1 The 2D topology and roughness images of unchlorinated and chlorinated NR at different times by using Atomic Force Microscopy (AFM).

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