PLASMA SURFACE MODIFICATION OF KEVLAR SHORT FIBRES/ABS COMPOSITES

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หัวข้อวิทยานิพนธ์	การปรับปรุงผิวเส้นใยเคฟลาร์ด้วยวิธีพลาสมาเพื่อเตรียมเอบีเอสคอมโพสิต
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บทคัดย่อ

งานวิจัยนี้เป็นการศึกษาเพื่อปรับปรุงสมบัติของพอลิเมอร์คอมโพสิตของ อะคริโลไนไตร์ลบิวทาไดอีน สไตรีน (ABS) เทอร์โมพลาสติก กับเส้นใยเคฟลาร์ชนิดสั้นโดยใช้การปรับปรุงพื้นผิวเส้นใยเคฟลาร์ด้วยวิธีพลาสมาและสารเคมีไอโซไซยาเนต เพื่อเพิ่มการยึดติดระหว่างเส้นใยกับพอลิเมอร์ โดยทำการศึกษาในแนวเปรียบเทียบระหว่างคอมโพสิตที่มีการปรับปรุงและคอมโพสิตที่มิได้ปรับปรุง และศึกษาสมบัติต่างๆ ของคอมโพสิต เช่น สมบัติเชิงกล สมบัติทางความร้อน และสัณฐานวิทยา โดยที่เส้นใยเคฟลาร์และเอบีเอสถูกผสมด้วยเครื่องผสมแบบเปิดชนิดสองลูกกลิ้งและขึ้นรูปโดยการฉีด

จากการทดลองพบว่าคอมโพสิตของเส้นใยเคฟลาร์มีสมบัติเชิงกล และสมบัติทางความร้อนดีขึ้นตามปริมาณเส้นใยที่ใช้ เมื่อทำการปรับปรุงพื้นผิวเส้นใยโดยใช้วิธีการฉายพลาสมาในบรรยากาศออกซิเจน พบว่าการปรับปรุงพื้นผิวเส้นใยโดยใช้กำลัง 30 วัตต์ และความดัน 0.1 ทอรร์เป็นสภาวะที่เหมาะสมที่สุด ส่วนการศึกษาเวลาที่เหมาะสมในการปรับปรุงด้วยพลาสมาในช่วงเวลา 0-15 นาที พบว่าบริเวณพื้นผิวของเส้นใยมีลักษณะไม่เรียบเกิดจากการกัดเซาะเนื่องจากพลาสมา และที่เวลา 3 นาทีให้คอมโพสิตที่มีสมบัติเชิงกลสูงสุด เมื่อปรับปรุงพื้นผิวโดยใช้ไอโซไซยาเนตควบคู่กับการใช้พลาสมาและไม่ใช้พลาสมาที่เวลาต่างๆ พบว่าหลังการปรับปรุงพื้นผิวของเส้นใยมีความขรุขระ อย่างไรก็ตามเวลาที่ใช้ไม่มีผลต่อการปรับปรุงด้วยไอโซไซยาเนตควบคู่กับการใช้พลาสมา สำหรับการปรับปรุงด้วยไอโซไซยาเนตมีผลทำให้สมบัติของคอมโพสิตดีขึ้นยกเว้นค่ามอดุลัสและความทนต่อแรงดึง ส่วนการปรับปรุงด้วยไอโซไซยาเนตควบคู่กับการใช้พลาสมาช่วยทำให้สมบัติของคอมโพสิตดีขึ้น จึงสรุปได้ว่าการปรับปรุงพื้นผิวโดยวิธีพลาสมาและไอโซไซยาเนตมีผลทำให้สมบัติของคอมโพสิตดีขึ้น

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Abstract

This research involved the enhancement of Kevlar short fibres/polyacrylonitrile butadiene styrene (ABS) composites by using plasma treatment in order to improve the fibre-polymer interfacial adhesion. Comparative study of the plasma-treated fibres and untreated composites was carried out. Properties of the composites were characterized including mechanical, thermal, and morphological properties. The Kevlar fibres and the ABS were mixed by two-roll mill and shaped by injection moulding technique.

It was found that mechanical and thermal properties of the composites were improved by increasing the fibre loading. The fibres were treated by plasma in O_2 atmosphere at different discharge power and chamber pressure. The plasma power of 30 w and chamber pressure of 0.1 torr were found to be the optimum conditions. By treated the fibres in various times (0-15 minutes), plasma treatment at 3 minutes yielded the composites with the maximum properties. As the time increased, the fibre surfaces were etched by plasma. The fibres were then treated by isocyanate with and without plasma at different treated times, the fibre surfaces were roughened by treatment, however the treatment time had no effect on the morphology of the fibres. By treated with isocyanate, the modulus and tensile strength of the composites were not improved, however other properties were enhanced. By treated isocyanate with plasma, both mechanical and thermal properties were improved. It can be concluded that properties of the composites were improved by the plasma and isocyanate treatments.

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Benya Sukying

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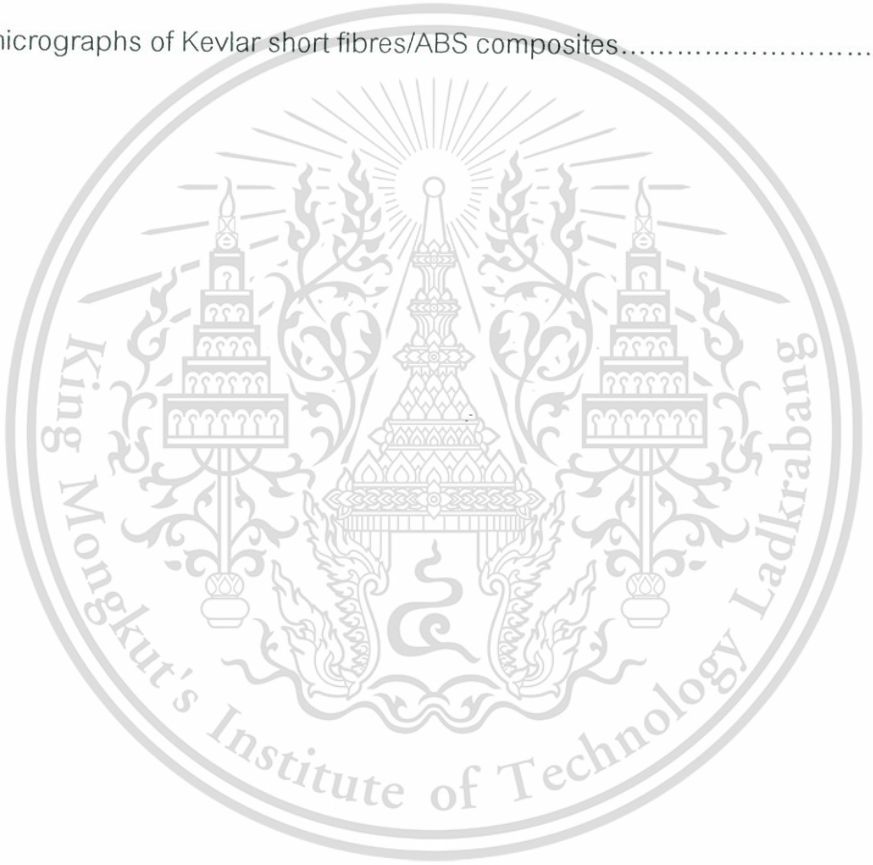


CHAPTER I
INTRODUCTION

1.1 Statement and significance of the problems

Polymer composites have been playing a crucial role in the several industries because of their low densities, high specific strengths and specific moduli. Polymer composites can be used to replace metals and ceramics in several applications. Polymer composites consist of two or more constituents. One of these, the reinforcement, is said to enhance the properties of the other constituent which is known as the matrix. It has been found that physical properties, mechanical properties and performance of polymer composites are generally functions of fibre types, fibre contents, fibre dispersion and fibre-matrix adhesion.

Kevlar aramid fibres have been widely used in the manufacture of advanced composites. The Kevlar fibres are interesting organic fibres due to stiffness, high strength and low density. The fibres are most suitable for uses in rigid reinforced materials and for application where light weight, high strength and stiffness, vibration damping, and resistance to damage, fatigue, and stress rupture are desired. Kevlar fibres possess a highly crystalline microstructure. Although this is responsible for the good tensile strength, it is detrimental for the compressive strength of the fibres which is also reflected in composites reinforced with the Kevlar fibres. The problem of interfacial adhesion was recognized in early work with these fibres. The adhesion between Kevlar fibres and most materials is poor due to the high crystallinity leading to a chemically inactive surface and the relatively smooth of the fibres. In order to improve the interfacial bonding between Kevlar fibre and matrix composites, a variety of fibre surface modification techniques have been developed, i.e., plasma treatment, chemical modification and incorporation of coupling agents. Fibre surface modifications result in improved wettability, surface energy, surface roughness and polar groups on fibre surfaces (1-8).

Plasma treatment offers an important advantage in comparison with other methods, because the plasma process can be controlled easily through the control of a large number of independent parameters. Energy can be transferred from a plasma to a

solid through optical radiation, through a neutral particle flux, and through an ionic particle flux. The energy transferred from the plasma is dissipated within the solid by a variety of chemical and physical processes. These dissipation processes are the origin of the desired surface modification.

1.2 Objectives of this study

1.2.1 To improve adhesion between Kevlar fibres and the matrix by plasma surface treatment.

1.2.2 To study optimum conditions of plasma treatment.

1.2.3 To make the composites that have good properties.

1.3 Scope of this work

1.3.1 To study percentage of the fibres loading on physical properties of the composites.

1.3.2 To find optimum conditions of plasma surface treatment, i.e.,

1.3.2.1 Discharge power

1.3.2.2 Pressure of the reaction chamber

1.3.2.3 Treatment time

1.3.3 To study effects of plasma treatment onto Kevlar fibres on mechanical and morphological properties of the fibres and the composites.

1.3.4 To study effects of treatment by isocyanate onto Kevlar fibres on mechanical and morphological properties of the fibres and the composites.

CHAPTER II

THEORETICAL CONSIDERATION AND LITERATURE REVIEWS

A composite is a material having two or more distinct constituents or phases. The constituent that is continuous and is often but not always, present in the greater quantity in the composite is termed the matrix. Properties of the matrix are improved on incorporating another constituent to produce a composite. A composite may have a ceramic, metallic or polymeric matrix. The second constituent is referred to the reinforcing phase, or reinforcement, as it enhances or reinforces mechanical properties of the matrix (1).

Polymer composites have played an important role in chemical industries. The composites which have been interesting are fibre-reinforced composites. The principle fibres in commercial uses are various types of carbon, glass, and aramid fibres. All these fibres can be incorporated into a matrix either in continuous or discontinuous length. The matrix material may be a thermoplastic or thermoset polymer (2,3).

Composite materials may be classified into several sub-groups, i.e., "basic composite materials", used in automotive, consumer, electronics, and marine applications, "advanced composite materials" used mainly in the aerospace industry and "particulate reinforced composites" for less demanding appliances.

2.1 Fibre-reinforced composites

Fibre-reinforced composites have been important in the fact that these materials can have unusually high strength and stiffness. In fibre-reinforced composites, the performance and properties are generally a function of fibre types, fibre contents, fibre aspect ratios, fibre orientation, fibre dispersion, fibre-matrix adhesion, processing methods, and properties of matrix (4). The fibre-matrix interface is the critical factor that determines properties of composites such as mechanical, dynamic mechanical, and rheological characteristics since the stress transfer occurs at the interface from the

matrix to the fibres. Though the mechanism of stress transfer is not clear yet, it has been postulated that it takes place though shearing at the fibre-matrix interfaces.

The most common reinforcement for polymer matrix composites is glass fibres. The glasses are based on silica (SiO_2) with addition of oxides of calcium, boron, sodium, iron, and aluminum. These glasses are usually amorphous although some crystallisation may occur after prolonged heating at high temperatures. This usually leads to a reduction in strength properties. Typical glass fibres are; E-glass, C-glass, and S-glass. The two types of glass fibres commonly used in the fibre-reinforced plastic industry are E-glass and S-glass. C-glass is used in chemical applications requiring greater corrosion resistance to acids than provided by E-glass. Advantages of glass fibres include low cost, high tensile and impact strength, and high chemical resistance. Disadvantages of glass fibres are relatively low modulus, self-abrasiveness, low fatigue resistance, and poor adhesion to matrix resins (2-3,6).

Carbon fibre composites are ideally suited to applications where strength, stiffness, lower weight, and outstanding fatigue characteristics are critical requirements. Because of its relative high cost, carbon fibre was applied in the advanced structural materials. It was focused in the aircraft/aerospaces, sporting goods, and other applications where costs are of secondary concern relative to performance. They also find applications where high temperature, chemical inertness, and high damping are important (7).

Aramid fibres, first introduced on a commercial basis by DuPont in the early 1960s, and widely used in the manufacture of advance composites now (2). Composite materials obtained from aramid fibre reinforcement give the lightweight, strength and stiffness especially compared to glass fibres. The composite materials are also resistant to fatigue, impact damage, stress rupture, excellent vibration damping, and wear resistance. Aramid fibres are aromatic polyamides. These fibres under trade names Conex® (Teijin), Kevlar® (DuPont), Nomex® (DuPont), and Twaron® (Akzo Nobel) are widely used in the manufacture of advanced composites. The Kevlar fibre is an interesting organic fibre that has stiffness, high strength, and low density (1-8). A number of researchers have used Kevlar fibres for reinforcing polymer materials, such

as polyethylene (9-10), epoxy resin (11-15), polyurethane (16-17), silicon rubber (18), and nylon (19).

However, the adhesion between Kevlar fibres and most materials are poor, due to high crystallinity leading to a chemically inactive and relatively smooth surface of the fibres. In order to improve the interfacial bonding between Kevlar fibres and matrix, a variety of fibre surface modification techniques have been developed. Among these are chemical modification (9,11,20-22), surface graft polymerisation (23-24), and plasma treatment (11-15). Fibre surface modification results in improved wettability, surface energy, surface roughness, and polar groups on the surface. The aramid composites can have unusually high strength and stiffness. In order to evaluate the potential for composites in structural applications, three basic mechanical properties must be known for designing purpose, such as, tensile strength, tensile modulus, and impact strength.

2.1.1 Tensile strength of fibre-reinforced composites (25-26)

For a reasonable engineering estimate of tensile strength of a short-fibre reinforced composite, a modification to the simple rule of mixtures has been effectively used, i.e.,

$$\sigma_c = \sigma_p \phi_p + \sigma_f \phi_f \varepsilon_1 \varepsilon_0 \qquad (2.1)$$

where

σ_c is the tensile strength of the composites

σ_f is the tensile strength of the reinforcing fibres

σ_p is the tensile strength of the polymer

ϕ_p is the volume fraction of the polymer in the composites

ϕ_f is the volume fraction of the fibres in the composites

ε_0 is an efficiency factor related to the orientation of the fibres in the composites

ε_1 is an efficiency factor related to the orientation of load transfer between the fibres and matrix

The values of ε_0 can be different. If the fibres are unidirectionally oriented, ε_0 is 1.0. When they are randomly dispersed in a plane, the value of ε_0 is approximately 0.33. For very small reinforcing fibres, three-dimensional random isotropy is possible, in which case ε_0 is approximately 0.162 (25).

The tensile strength of composites can be greatly affected by such factors as the perfection of packing and alignment of the fibres and by imperfections such as voids. Point of contact between different fibres are points of stress concentration which can be especially damped to transverse strengths. The reason for this decrease in strength are: (1) appreciable lengths near each end of the fibres are ineffective in transmitting load from the matrix to the fibres; (2) the fibres ends act as stress concentrations and therefore as crack initiators; (3) fibres that do not overlap one another appreciably can not contribute to strengthening the composites ; and (4) in general, it is impossible to achieve perfect orientation with short fibres as with continuous fibres.

One of the primary problems using short-fibre reinforced composites is their anisotropy. Different regions of a moulded part have not only different fibre orientation but also different concentrations of fibres. Moreover, the fibre orientations may be varied not only in the in-plane dimension but also within the thickness of the part. Extensional flow gives a high degree of fibre orientation parallel to the direction of flow whereas divergent flow gives fibres oriental perpendicular of the direction of flow. Elongational flow produces a higher degree of orientation than shear flow. In either case, at near the surface of mould or flow channel, fibres orient parallel to the surface. This generally produces a fibre orientation at a surface that is different from the orientation inside a moulded object. Figure 2.1 illustrates some of these phenomena. Fibres with a high aspect ratio tend to become entangled into clusters. This 'logjam' effect tends to give big variations in the concentration of fibres within a moulded object. This poor dispersion of fibres gives poor mechanical properties.

Figure 2.1 Orientation of short fibres in a flowing polymer matrix (26)

In discontinuous-fibre composites the polymer is the only continuous phase. Longitudinal tensile stresses are applied to the fibres though shearing stresses in the matrix. These shearing stresses in the matrix are maximum near the ends of the fibres and gradually decrease to zero away from the ends. The tensile loads in the fibres are zero at the ends and gradually increase to a plateau in the control portion of the fibres. Thus the part of the fibres near the ends carries less load than the middle section. The sum of the length of the fibre on each end required for the tensile load to reach its plateau or maximum value is often called the critical or ineffective fibre length (L_c) since the end portion of the fibres are ineffective in carrying the load. The critical fibre length depends on such factors as the relative moduli of the two phases, the strength of the interfacial bond, the shear strength of the matrix and the tensile strength of the fibre.

In the special case of perfect adhesion, the equation used to establish the critical fibre aspect ratio is;

$$L_c = D\left(\frac{\sigma_f}{\tau_l}\right) \tag{2.2}$$

where

D is the reinforcing fibre diameter

σ_f is the tensile strength of the reinforcing fibre

τ_l is the interfacial strength between the fibre and the matrix.

In some case if $L > L_c$ the tensile strength of the composite is;

$$\sigma_c = \sigma_f \phi_f \left(1 - \frac{L_c}{2L}\right) + \sigma_p \phi_p \tag{2.3}$$

where L is the total length of fibres

The shear strength of the polymer is often used as an estimate of τ_l. The relationship between the shear strength of a polymer and the critical aspect ratio for glass fibre reinforced composites is shown in Figure 2.2.

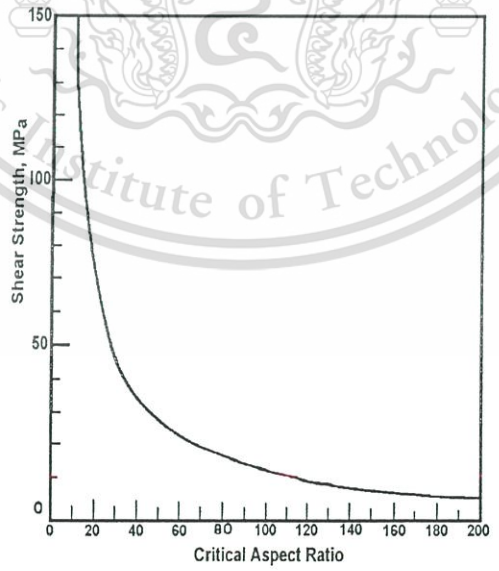


Figure 2.2 Relationship between the shear strength of a polymer and the critical aspect ratio for glass fibre reinforced composites (25).

For many polymer-fibre combinations, the critical aspect ratio is between 15:1 and 30:1. As it might be expected, the interfacial strength is strongly influenced by coupling agent. Coupling agents improve the wetting of thermoplastic polymers to the fibres, because they drive away the moisture that is present on the surface of the fibres. This will improve the strength of the composite.

2.1.2 Modulus (25-26)

Most fibre-filled composites are anisotropic, so that properties are different in different directions. A simplified analysis of composite materials allows the mechanical performance of a composite material to be determined from the properties of its individual components. First, stress (σ), strain (ε), and modulus (E) in an article are defined as;

$$\sigma = F / A \tag{2.4}$$

where F is the applied load and A is the cross-sectional area of the specimen.

$$\varepsilon = \left(\frac{l - l_0}{l_0} \right) \tag{2.5}$$

where l_0 is the original length and l is the length of the specimen after a certain time under a load F, and

$$\mathrm{E} = \frac{\sigma}{\varepsilon} \tag{2.6}$$

In the transverse direction, a tensile force tends to the fibre and the matrix in the same amount. Therefore, for very long fibres, they will assume a predominantly two-dimensional packing arrangement. A relationship similar to that used for the tensile strength of composites can be used to estimate the modulus of the composites (E_l). The modified rule of mixtures equation for modulus enhancement is

$$E_l = E_p \phi_p + E_f \phi_f \quad (2.7)$$

where

E_p is the modulus of the matrix

E_f is the modulus of the fibres

ϕ_p is the volume fraction of the matrix

ϕ_f is the volume fraction of the fibres

The longitudinal Young's modulus (E_T) can be estimated by many equations. The most convenient equation is the Halpin-Tsai equation as modified by Nielsen as;

$$\frac{E_T}{E_p} = \frac{1 + AB\phi_2}{1 + B\psi\phi_2} \quad (2.8)$$

where

$$A = 0.5$$

$$B = \frac{E_f / E_p - 1}{E_f / E_p + A}$$

and

$$\psi = 1 + \left(\frac{1 - \phi_m}{\phi_m^{\,2}} \right) \phi_f$$

The factor ψ takes into account the maximum packing fraction ϕ_m of the fibres. For cubic of fibres, ϕ_m = 0.785, which for hexagonal packing, ϕ_m = 0.907. In general, ϕ_m lies between these limits near the random close packing case where ϕ_f = 0.82. Compared to E_T, E_l is very small. It means fibres are not very effective in increasing the modulus in a direction perpendicular to their lengths.

2.1.3 Impact strength (25-27)

The impact strength of composites is more complex than that of unfilled polymers because of the part played by the fibres and the interface in addition to the polymer. Correlations that correspond to reality may be difficult to establish, and one kind of impact tests may contradict the results of another type of tests. For a material

that to be very tough and to have a high impact strength, in general there must be some mechanisms for spreading the energy to be absorbed throughout as large a volume of material as possible. If the energy is concentrated in a small volume, the material fails in a brittle manner and the impact strength is low.

Fibres give to at least two mechanisms for the dissipation of energy (26);

1. Fibres may pull out of the matrix and dissipate energy by mechanical friction. At the some time the pulling out of the fibres prevents localisation of stress in one area along the fibres.

2. Controlled dewetting of the fibres, as illustrated in Figure 2.3, dissipates energy in the dewetting process, spreads the region of stress concentration throughout a larger region, and tends to step the propagation of the crack.

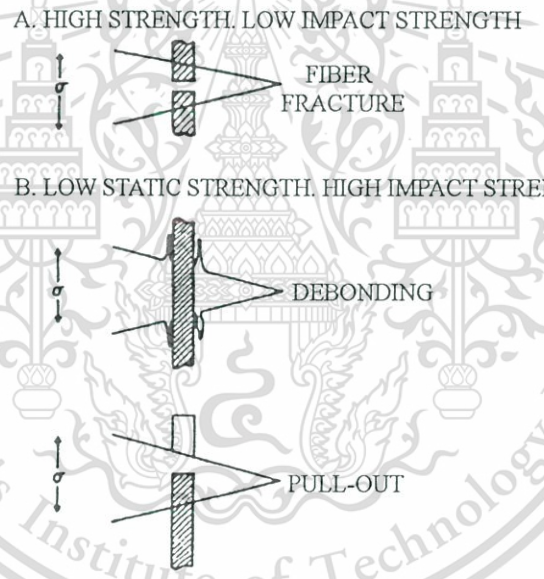


Figure 2.3 Schematic diagram of behavior of fibre-filled composites near the tip of a growing crack. The fibres can (a) fracture; (b) debond or pull out of the matrix (26)

The impact performance of fibre reinforced composites depends on several factors, including the nature of constituents, fibres, matrix, and interface, the construction of geometry of the composites and the test condition. It is useful to device a discussion of impact performance into two categories; impact performance under

relatively low energy impacts, where the composite is damaged but still capable of performing its primary function ; and impact performance under higher energy impacts, where the composites is completely ruptured or penetrated by the striker (27).

One way of representing impact strength is the energy required to fracture a sample in a impact test. This energy is the area under the stress-strain curve that can be represented by the following equation, (25)

$$I = \int \sigma(y)dy \qquad (2.9)$$

where I is the energy absorbed during impact and $\sigma(y)$ is the stress as a function of strain.

Fibres also tend to reduce the impact strength by at least two mechanisms : (1) fibres generally drastically reduce the elongation at break and many reduce the area under the stress-strain curve, and (2) stress concentration occurs at region around fibre ends, area of poor adhesion and regions where fibres contact one another. Thus, depending on the nature of the composite and the type of impact test, fibres can cause the apparent impact strength to either increase or decrease. This complex behavior is in part due to the fact that crack initiator or nucleation as well as crack propagation is important in determining impact strength. Fibres reduce the resistance to crack initiation by acting as stress concentrators, thus causing embrittlement. However, fibres also reduce crack propagation by forcing cracks to go around the fibres or by bridging cracks (26).

If the impact load is applied parallel to the fibres, highest impact strengths are obtained if the adhesion is relatively poor and if the fibres are short so that maximum energy can be dissipated by mechanical friction during the pull-out process and by debonding of the fibres. Very long fibres with good adhesion decrease the impact strength at least for tough matrices largely because of the greatly reduced elongation at break and the reduced plastic flow of the matrix. However, if the load is applied perpendicular to the fibres, good adhesion is required for even moderate impact strength.

2.2 Aramid fibres

Aramid fibres are the types of Nylon of which the molecular structure comprises of linked benzene rings and amide bonds. Aramids are high performance polymeric materials and are noted for their lightness in weight, higher stiffness, good thermal stability, greater damage tolerance, and excellent toughness. Aramid is available in either a straight-chain structure, as shown in Figure 2.4, known as the Kevlar® family, or bent-chain structure known as Nomex® (from Tijin as Conex®), depending on whether the aromatic rings are para- or meta-disubstituted, respectively.

The principle aramid fibre for composite reinforcement for high performance composites used in this work is Kevlar®.

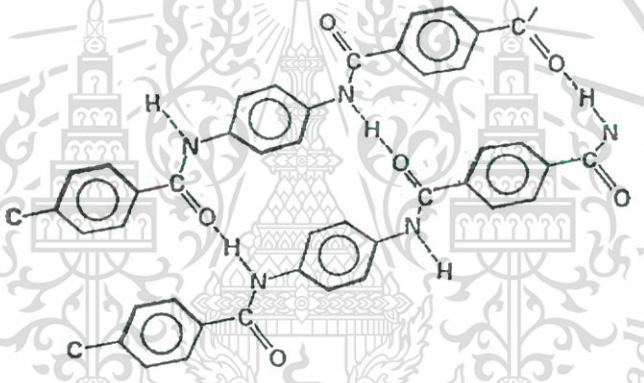


Figure 2.4 Chemical structure of the straight-chain Kevlar showing intermolecular hydrogen bonding (27)

Poly (*p*-phenyleneterephthalamide) fibres (PPTA) are currently commercially available from DuPont as known as Kevlar. The Kevlar fibres with a straight-chain polymer structures, are very stiff and can be proceeded into more than one high stiffness version, depending on the degree of polymer chain alignment introduced (27). Kevlar aramid fibres are available in four forms, i.e., Kevlar, Kevlar-29, Kevlar-49, and Kevlar-149. Kevlar is manufactured specifically for reinforcement of elastomers for tires, hoses, and belts. Kevlar-29 is used in cables, ropes, coated fabrics, tapes, and ballistics. Kevlar-49, which has a strength similar to Kevlar-29 but 50% higher modulus, is principally used as a reinforcement for polymeric organic matrix composites used in

aircraft, aerospace marine, sporting goods, and electrical application. Recently, Kevlar-149 has become commercially available, offering 40% higher modulus and 70% lower moisture absorption than Kevlar-49 (28).

2.2.1 Production methods of Kevlar fibres

The technique of transformation aramids into fibres is solution spinning, i.e., wet, dry or dry jet-wet spinning methods. Wet spinning is one of the processes whereby a solution of polymer has extruded the polymer dope into a non-solvent where the fibre coagulates. The coagulated fibre is then washed to complete the solvent removal and often drawn to achieve the desired fibre properties. The dope temperature and the coagulation temperature are the same.

Kevlar is a synthetic organic fibres comprising of poly *p*-phenylene terephthalamide, which is formed by *p*-phenylene diamine and terephthalic acid.

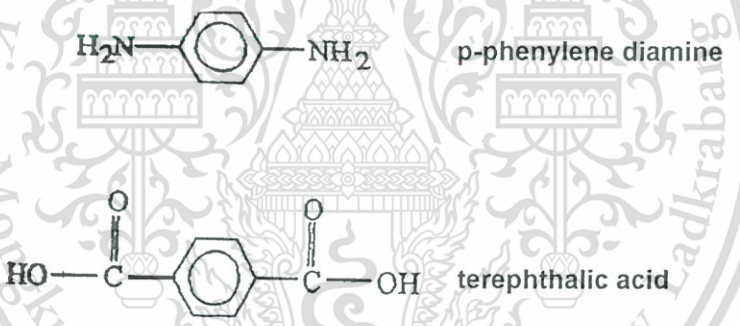


Figure 2.5 Chemical structures of *p*-phenylene diamine and terephthalic acid

The spinning solvent for this fibre is 100% sulphuric acid but the low spinning speeds are needed for good properties, hence the process was uneconomical.

2.2.2 Structure and properties

Kevlar fibres consist of extended-chains, rodlike macromolecule aligned in the fibre direction. The para substitution of benzene rings makes Kevlar rigid molecules with limited flexibility adjacent to the para-substituents of the aryl rings. Furthermore, the C-N bonds of the amide groups have considerable double bond character which severely limits rotation. The restricted rotation contributes to the stiffness of the molecule. Hydrogen bond between the amide groups further enhances the rodlike configuration and morphology of Kevlar.

The supermolecular structure was investigated by Johnson and his co-workers by electron diffraction and dark field electron microscopy (6). They suggested that Kevlar-49 fibres consist of system of H-bonded sheets, regularly pleated along their axes and arranged radially. The angle between adjacent components of the pleats is 170^{0}C. This supermolecular structure leads to a periodic bonding along the fibre axis with periodicities of approximately 250 and 500 nm (28). A schematic representation of the structure is shown in Figure 2.6

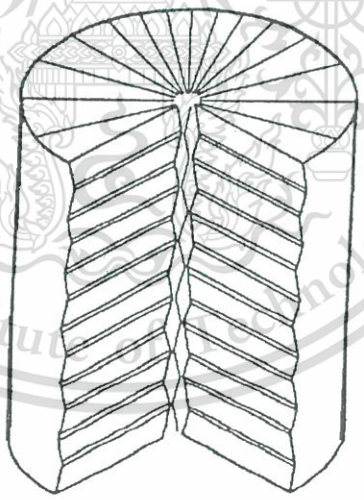


Figure 2.6 Pleated hydrogen-bond sheet in Kevlar-49 (28)

The molecules from rigid planar sheets with the chain-extended molecules hydrogen bonded is shown in Figure 2.7

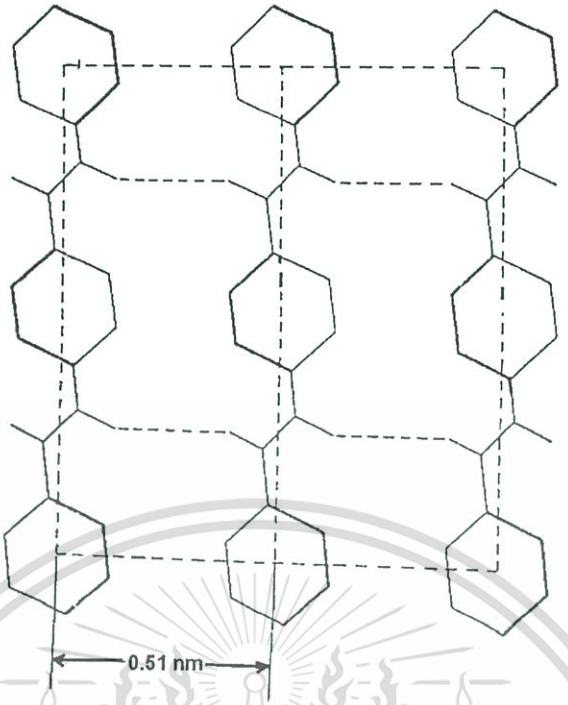


Figure 2.7 Interchain hydrogen bonding of poly *p*-phenylene terephthalamide molecules (6)

Fibres with this structure are likely to have a low longitudinal shear modulus and poor transverse properties. In particular, Kevlar fibres have a very low resistance to axial compressive failure. Aromatic polyamides have remarkably good resistance to temperature, given that they are organic fibres (6).

Aramid's yellow colour is derived from its extended conjugated π-electron system. This also means that the bare fibre is vulnerable to visible light, and deteriorates if exposed to sunlight. For this reason, although the degradation products themselves screen the underlying polymer, Kevlar structures are coated or covered, or buried within another part of the structure. The conjugated π-electron system confers double bond character on most of the chemical bonds in the polymer structure. This in turn gives the aramids their excellent thermal stability. Thermal decomposition does not begin until above 400^0C, a surprisingly high value for an organic polymer. In inert atmosphere decomposition does not occur untill almost 500^0C (27).

Because of their good properties such as high tensile strength, high modulus, low elongation, fire resistance, temperature resistance and solvent resistance. However, the fibres are susceptible to attack by acids and bases, especially by strong acids. The mechanical properties of Kevlar fibres differ from those of other organic fibres but similar to glass fibres and carbon fibres (29). Their stress-strain curves are essentially linear that shown in Figure 2.8

The basis physical and mechanical properties of aramid fibres produced in various countries are specified in Table 2.1

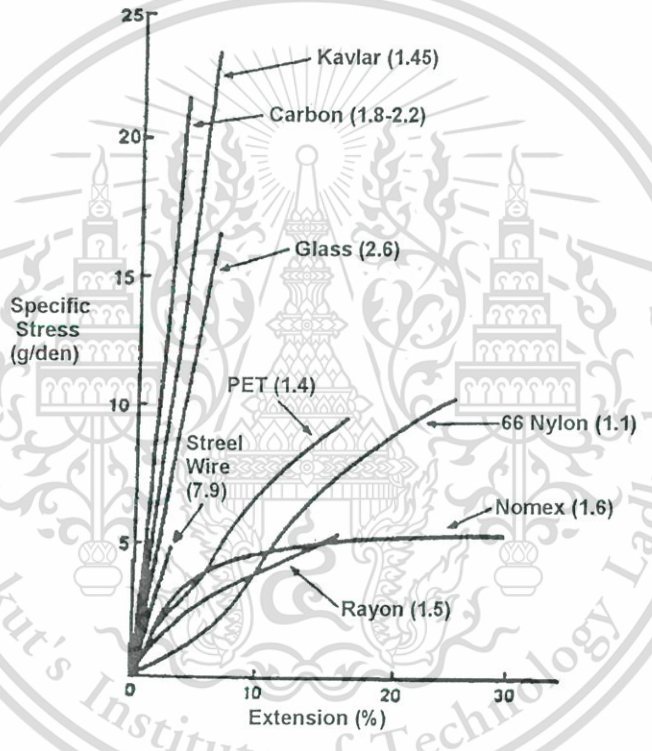


Figure 2.8 The stress-strain curves of fibres (29)

Table 2.1 Physical and mechanical properties of aramid fibres (30)

Property	Kevlar 29	Kevlar 49	Kevlar 149	Kevlar 129(HT)	Twaron 900	Twaron 930	Technora
Density (kgm^{-3})	1440	1440	1470	1440	1440	1450	1390
Yarn strength (N tex^{-1})	2.07	2.07	1.62	2.39	2.0	2.0	2.25
Strength of fibre in epoxy Impregnated strand (GPa)	3.6-3.7	3.6-3.7	3.5	4.3	2.5-3.0	2.5-3.0	3.04
Elongation (%)	3.6	2.5	1.5	3.3	3.7	2.0	4.4
Yarn modulus of elasticity (GPa)	84	125-133	175-185	112	61	125	73.6
Equilibrium moisture absorption (%)	4.3	4.3	1.5	4.3	7.0	3.5	3.0
Oxygen index (%)	28-30	28-30	-	-	29	29	30

This combination of strength, toughness and textile processability makes Kevlar fibres versatile reinforcements for a variety of application composites, yarns, roving, chopped, coated fabrics, and so on. The chopped fibres have 12 μm diameter and 1/4 -1/2 inches in length. The pulp is a highly fibrillated form of the fibres which can be dispersed into many different matrix systems. The fibrillation results in a high surface area of 7 m^2/g to 10 m^2/g and the length about 2 mm. Kevlar pulp is non-brittle, so standard mixing, and dispersion equipment will not affect the fibre size. This fibre enhances the performance of elastomers, thermoplastics and thermoset resins, especially where high-temperature performance is required.

The length of short fibres is 1/4 inch or longer. It is used to manufacture spun yarns, which provide enhanced wear resistance and comfort compared to filament yarns. Their applications generally take advantage of the barrier properties of Kevlar, rather than the tensile and modulus properties. And it is also used to increase thermal insulation and vibration-dampening properties. Other applications include thermoset and thermoplastic resin systems, where Kevlar increases strength and wear resistance over a wide range of temperatures (31).

Although Kevlar aramid fibres have superior advantages in mechanical properties. But when the fibres are used as a reinforcing agent in composite materials, the drawbacks on the use of the fibres in the composites include; low compressive strength that is a direct result of the orientation of the fibres in the longitudinal direction. This directional trade-off arises because of the much weaker lateral or transverse bonding mechanism. The second drawback is the poor wetting characteristic of the

fibres with typical high performance resins such as epoxies or imides. The surface energy associated with the aramid fibres indicates that it is difficult to coat the fibre surfaces with the resin matrices. The final reason that aramid fibres are not used extensively is their cost. Because of the superb strengths and the light weight when they are used in the composite materials, their cost are relatively high. Thus aramid fibres are mostly used in special applications that strength and weight are more concerned than the cost.

2.2.3 Applications (5,32)

The unique combination of properties found in the aramid fibres has led to their uses in a wide variety of commercial applications such as; (5)

1) Aircraft/aerospace : High-modulus aramid fibres are used extensively in aircraft/aerospace applications, primarily because of their light weight, good damage tolerance, high strength, and stiffness. In aircraft the modest compressive strength of the fibre has, so far, limited use mostly to nonstructural and semistructural parts, both interior and exterior, in large and small planes, and helicopters. Other aircraft applications include passenger seats, seaplane floats, and propellers. The major aerospace applications for aramid fibres have been in rocket motor cases and other pressure vessels.

2) Marine : The use of high-modulus organic fibre reinforcement in marine applications offers the advantages of light weight, higher stiffness, good impact, and repeated impact strength, good fatigue resistance and vibration damping. These advantages are typically utilized in canoes, kayaks, offshore racers, sport fishing boats, and patrol boats. Canoe and kayak constructions usually employ fabric reinforcement in polyesters, vinyl ester or epoxy matrix resins.

3) Automotive : Kevlar enables the automotive companies to eliminate the potential environmental and health hazards associated with asbestos. A small amount of Kevlar can serve as a cost effective reinforcing fibres replacement for asbestos and provide higher strength and greater durability. The remarkable strength to weight ratio of Kevlar allows considerable reduction in auto body weight without sacrificing strength. That is why body panels and other made of composites of Kevlar

are used in racing cars. Thus, Kevlar is giving automotive designers the best of both worlds; adding strength and durability to parts while reducing weight to increase fuel efficiency.

4) General industries : Broad industrial uses for Kevlar aramid fibres generally fall into three categories, i.e., (a) mechanical rubber goods such as drive belts, conveyer belts and hoses ; (b) fabrics such as tarpaulins, oil spill recovery booms, mine air ducts and architectural fabrics ; (c) asbestos replacement application including pump packing, brake linings, gaskets, sealants, and plastics or concrete reinforcement.

5) Personal protection ; Several police officers in the United States and undoubtedly many more officers and military personal around the world have been saved from death or injury, because they wear body armor of Kevlar. Designed to stop bullets fired most common handguns, soft body armor of Kevlar is notably lighter in weight than old fashion ballistic apparel. This reduction in weight provides police officers with an effective body armor that is inconspicuous under the uniform and comfortable enough to wear routinely on an everyday basis in all climates.

2.3 Polymer matrices (1,3,6)

The matrix materials in fibre composites are extensive and varied in properties. They may be classified as polymers, metals, or ceramics. The property requirements for a matrix material are different than those for a reinforcement. Since the fibres must serve as the principal load-bearing members in a composite, they must be of high strength and stiffness. With some exceptions, reinforcement fibres are usually of low ductility. In contrast, matrix materials usually have relatively low modulus and strength values and comparable or higher ductility values. The matrix serves to bind the fibres together, and therefore the thermal stability of the composite is determined by that of the matrix. The matrix protects the typically rigid and brittle fibres from abrasion and corrosion. The matrix transmits load in and out of composites, and in some cases, carrier some transverse load. The matrix provides the composite with interlaminar fracture toughness, damage tolerance and impact resistance.

When selecting a particular resin for a specific composite application, service environment parameters such as temperatures, stress, moisture, chemical effects, and possibly radiation dosage must be considered. The processability and the processing history of the matrix must be taken into account, since it directly influences the formation of flow and microstructures in the matrix, residual stress, and the fibres-matrix interface. These factors ultimately determine the properties of a composite (3). The most common matrix materials for composites are polymeric. A simple classification of polymers is given in Figure 2.9. These classes of polymers, i.e, thermosets, thermoplastics, and rubbers, are all important (1).

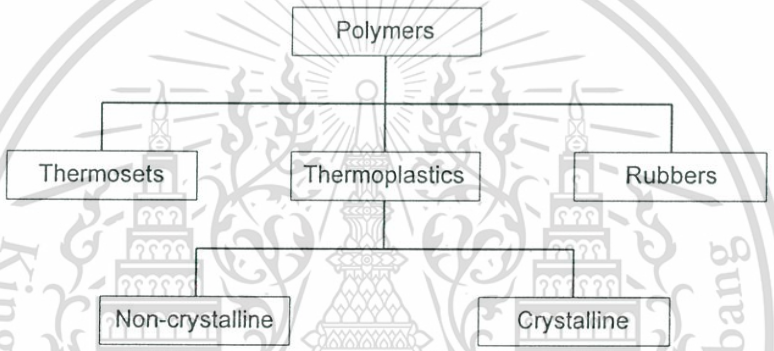


Figure 2.9 Simple classification of the polymers used for matrices in composites (1)

2.3.1 Thermosets

Thermosets are resins which readily crosslink during curing. Curing involves the application of heat and pressure or the addition of a catalyst known as a curing agent or hardener (1). Thermosetting resins are usually isotropic. Their most characteristic property is in response to heat since, unlike thermoplastic, they do not melt on heating. However, they loss their stiffness properties at the heat distortion temperature and this defines an effective upper limit for their uses in structural components (6).

Several important general classes of thermosetting resins are used as composite matrices. These include unsaturated polyesters, vinyl esters, epoxides, phenolics, polyimides, and modified versions of these such as interpenetrating networks. Thermoset matrix materials result in composites that have higher specific tensile strength and stiffness properties than metal matrix composites. Thermosetting resin

composites are also more advanced in fabrication technology and lower in raw material and fabrication costs (3).

2.3.2 Rubbers

Natural rubber is obtained from the latex from the *Hevea Brasiliensis* consisted of over 98% polyisoprene. Polyisoprene exists in two forms, i.e., cis- and trans- forms. The cis form is the main constituent of the natural rubber. Nowadays a wide range of synthetic rubbers are available and dominate the market. A number of synthetic rubbers are derived from butadiene, such as polybutadiene, styrene-butadiene (SBR), and nitrile-butadiene (NBR) and of these the copolymers SBR and NBR are the most importance (1).

2.3.3 Thermoplastics

Thermoplastics readily flow under stress at elevated temperatures, so allowing them to be fabricated into required components, become solid and retain their shapes when cooled to room temperature. These polymers may be repeatedly heated, fabricated and cooled and consequently scrap may be recycled, though there is evidence that this slightly degrades the properties probably because of a reduction in molecular weight (1).

Unlike thermosetting resins, thermoplastics are not crosslinked. They derive their strength and stiffness from the inherent properties of the monomer units and the very high molecular weight. This ensures that in amorphous thermoplastics there is a high concentration of molecular entanglement, which acts like crosslinks. In crystalline materials there is a high degree of molecular order and alignment. Both amorphous and crystalline polymers may have anisotropic properties depending on the conditions during solidification. In amorphous polymer anisotropy is due to molecular alignment which occurs during melt flow in moulding the materials or subsequently during plastic deformation. Similarly, in crystalline polymers, the crystalline lamellar units can develop a preferred orientation due, for example, to nonuniform nucleation at surface or in the flowing melt and preferential growth in some directions because of temperature

gradients in the melt. There is increasing evidence that these effects can have a profound effect on the properties of composite materials (6).

The most important advantage of thermoplastic polymers over thermoset polymers is their high impact strength and fracture resistance, which in turn impact an excellent damage tolerance characteristic to the composite materials. In general, thermoplastic polymers have higher strains-to-failure than thermoset polymers, which may provide a better resistance to matrix microcracking in the composite laminate.

Thermoplastic matrices are normally used with short fibre reinforcement for application in products made by injection moulding. The feed stock is usually in the form of pellets which contain the short fibres, typically 1-3 mm long, intimately mixed and dispersed in the matrix. The common matrix polymers are polypropylene, nylon and polycarbonate. Some typical properties are given in Table 2.2. It is possible to blend two or more polymers to obtain a multi-phase polymer such as acrylonitrile-butadiene-styrene (ABS) which is a terpolymer (1).

Table 2.2 Properties of thermoplastics

	ASTM Test	HDPE	PP	30% GF PP	PVC	ABS	PMMA	50% RH PA6	Dry PA6.6	50% RH PA6-6	33% GF/T*** 50% RH PA6-6	PC	POM	MPPO	PBT	30% GF PBT	40% GF PPS	PSF	PES
Relative price		1.0	1.0	1.6	0.7	1.8	1.8	2.8	2.9	2.9	3.0	3.5	2.5	3.0	3.1	3.1	6.9	12.0	12.0
Young' s modulus (GPa)	D790	0.8	1.5	6.5	3.0	2.1	3.2	1.2	2.8	1.2	5.5	2.3	2.8	2.5	2.5	7.5	11.7	2.7	2.6
Yield/fracture stress (MPa)	D638	28	33	86	55	41	72	41	83	59	110	65	69	55	50	120	134	70	82
Elongation at Break (%)	D638	300	50	4	30	20	4	290	60	300	4	100	40	50	300	3	1	50	40
Notched Izod impact Strength (J/m)	D256	>1300	150	125	70	350	40	75	53	112	140	700	75	200	55	65	75	86	84
Heat distortion Temperature (°C)	D648	<23	<23	148	55	110	95	<23	90	<23	232	140	136	130	55	215	<260	174	203
Limiting oxygen index	D2863	18	18	18	45	19	17	23	28	31	28	25	16	24	20	32	46	30	36
Coefficient of linear Expansion ($10^{-6D}K^{-1}$)	D696	90	110	25	60	96	68	70	81	81	18	70	122	60	70	25	22	54	55
Specific gravity	D792	0.96	0.9	1.12	1.4	1.04	1.18	1.13	1.14	1.14	1.32	1.2	1.42	1.06	1.31	1.62	1.60	1.24	1.37

***GF/T means (glass-filled and rubber toughened)

2.4 Acrylonitrile-Butadiene-Styrene Copolymer

Acrylonitrile-Butadiene-Styrene (ABS) plastics comprise a broad, versatile family of engineering thermoplastic materials offering a balance in rigidity, toughness, processability, cost, and chemical resistance (33-35). ABS plastics are polymerized from the three monomers, i.e., acrylonitrile, butadiene, and styrene (33). Each monomer is an important component. Styrene contributes to processability, rigidity, and strength while acrylonitrile provides surface hardness and chemical resistance. The butadiene rubber contributes toughness, but at the expense of rigidity.

Molecular structure of ABS and its monomer usually have the following structures shown in Figure 2.10. The ratio of comonomers as well as the microstructures of ABS can be controlled to produce a family of copolymers with a broad range of properties. Compositions of commercial ABS materials range from 15 to 30% acrylonitrile, 5 to 30% butadiene, and 45 to 70% styrene.

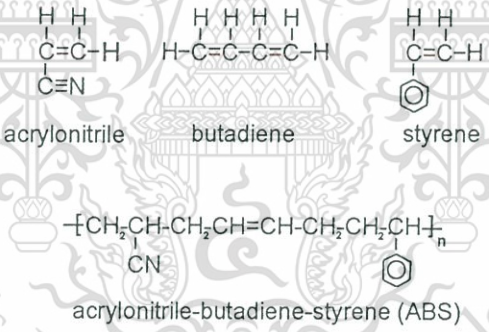


Figure 2.10 The structures of ABS and its monomers

2.4.1 Preparation of ABS

ABS polymers are produced by the free-radical polymerisation of styrene and acrylonitrile in the presence of polybutadiene or butadiene copolymers. Radical attack on the polybutadiene substrate leads to the formation of grafted styrene-acrylonitrile copolymer along with free copolymer (34).

ABS is produced commercially by emulsion, suspension, and bulk polymerisation (33). The emulsion process involves a two-step polymerisation in which a rubber subtract latex is produced and then styrene and acrylonitrile are grafted in a separate latex reduction. The suspension process is a two-part process in which a bulk polymerised prepolymer is made using a linear rubber and styrene and acrylonitrile monomers followed by polymerisation in a suspension reaction. In the bulk process, all polymeri ation reactions are completed in a monomer-polymer medium starting with a linear rubber dissolved in styrene and acrylonitrile monomers. Typically the bulk process produces smaller particles (0.1-1 μm) (34).

2.4.2 Properties of ABS

The degree of freedom permitted through compositional and structural variations makes possible ABS grades with a broad range of strength-to-toughness property balances. The rigid phase provides strength, while toughness is primarily a function of the elastomeric content and the molecular weight of the rigid phase (33). The range of properties typically available for ABS and its alloys are illustrated in Table 2.3.

Table 2.3 Properties of ABS and related products (34)

Properties	ASTM Method	Units	Low Impact	Medium Impact	High Impact	High Resistant	Flame Retardant	Plating	Clear	ABS-PVC	ABS-PC
Izod impact	D256	J/m[a]	105-215	215-375	375-440	120-320	185-280	265-375	134	340-695	370-560
Tensile strength	D638	MPa[b]	41-52	41-47	33-44	41-52	40-50	38-44	43	30-41	45-60
Tensile elongation	D638	%	5-30	15-50	15-70	5-20	5-25	10-30	20-35	25-100	25-80
Tensile modulus	D638	GPa[c]	2.2-2.6	2.1-2.4	1.7-2.1	2.1-2.6	2.1-2.5	2.3-2.6	2.3	2.1-2.3	2.4-2.6
Flexural yield strength	D790	MPa[b]	68-87	68-80	55-68	68-90	69-86	69-80	72	54-73	79-90
Flexural modulus	D790	GPa[c]	2.3-2.6	2.2-2.5	1.8-2.2	2.1-2.8	2.3-2.8	2.3-2.7	2.4	2.1-2.3	2.2-2.6
Rockwell hardness	D785	R	105-110	95-105	88-100	100-112	97-111	103-110	103	95-100	111-120
Heat deflection temp.[d]	D648	°C									
at 1820 kPa[e]			94-11	96-100	98-104	105-121	90-107	95-100	88	70-90	114-121
at 455 kPa[e]			100-108	102-104	103-108	108-127	96-111	99-104	92	77-96	117-124
Coefficient of thermal Expansion	D696	$x10^5$ cm/cm/°C	7.0-8.8	7.8-8.8	9.5-11.0	6.4-9.3	7.0-8.8	6.5-7.0	8.6	7.6-8.5	6.2-7.4
Specific gravity	D792		1.05-1.07	1.04-1.05	1.02-1.04	1.04-1.06	1.20-1.22	1.04-1.06	1.07	1.16-1.20	1.07-1.12

[a] To convert J/m to ft.lb/in., divide by 53.1
[b] To convert MPa to psi, mutiply by 145
[c] To convert GPa to psi, multiply by 145,000
[d] Annealed
[e] To convert kPa ti psi, multiply by 0.145

As seen in Table 2.3, several grades widely ranging in modulus, flow, and tensile strength can be made available, allowing considerable freedom in part designs and fabrication methods while maintaining adequate toughness. The polar character of the nitrile groups from the acrylonitrile component reduces interaction of the polymer with hydrocarbon solvents. Thus, ABS is more resistant to attack by mineral oils, waxes, and related household and commercial materials than high impact polystyrene. Like most polymers, ABS will undergo stress cracking when it is brought into contact with certain chemical agents under stress. The presence of unsaturation in the polybutadiene component increases susceptibility to oxidation, halogenation, sulfonation, etc, by reactive chemical agents such as concentrated nitric acid, sulfuric acid, chlorine, etc.

Thermal oxidation of ABS can induce embrittlement of the rubber and detachment of the graft chains. Under oven-aging conditions, oxidation is diffusion limited, and is restricted to the outer surface of the sample. Antioxidant has been shown to substantially improve oxidative stability. Extended outdoor applications require measures to protect against photooxidative degradation. Increased stability may be achieved by the use of stability additives, pigments, protective coatings, and films.

2.4.3 Applications of ABS

Because of excellent balance of mechanical properties and desirable flow and surface appearance, ABS and ABS blends have numerous uses. Some important applications are listed below (33,35):

2.4.3.1 Appliances

Typical applications include injection moulded housing for blenders, mixers, microwave door, and other kitchen appliances. The largest-volume application for ABS in the appliance market is refrigerator door and tank lines. For this particular application, extrusion grades have been developed for chemical resistance, low-temperature toughness, high surface gloss, and good hot strength for deep-draw thermoforming.

2.4.3.2 Automotive

ABS high heat grades have been developed for instrument panels light housing, pillar post moulding, and other interior trim parts. These applications require a material having high flow, good process stability, and functional part distortion temperatures in the 80-100^{0}C range. ABS is also used by the automotive industry because it can easily be decorated, excellent plate adhesion, low coefficient of expansion, low temperature ductility, and high heat resistance. It is estimated that ABS plating grades account for nearly 65% of the plated plastics used in automotive applications. Typical applications include knobs, light bezels, mirror housing, wheel covers, decorative trim, and grilles.

2.4.3.3 Building and construction

Not long ago, the largest single application for ABS was pipe, fittings, and conduit. Two factors leading to a reduction in ABS use were a depressed building industry and a significant cost differential that favored PVC pipe. This difference has been offset by price increase for PVC and the introduction of ABS foam-core coextrusion technology to provide pipe with lower part density at no sacrifice of required performance properties. Other applications in the building and construction market include roof ventilators, bathtub surrounds, and plated plumbing fixtures.

2.4.3.4 Business machines / Consumer electronics

Application requirements in the business machine and consumer electronics market vary considerably. General-purpose ABS is suitable for applications such as telephones; business machine requires a flame-retardant grade. Typical business machine applications include housing, covers, and consoles. The ease with which ABS can be electroplated or vacuum metallized to meet EMI/RFI (electromagnetic or radio frequency interference) shielding requirements is another important advantage.

2.4.3.5 Other applications

Low-temperature impact resistance and excellent thermoformability is the basis for selection of ABS in such applications as boat hulls, snowmobile shrouds, and camper components. UV protection for these applications is achieved through the

lamination of an acrylic film or a coextruded UV-resistant cap. Other ABS applications include luggage, toys, furniture, and impact modifiers for rigid PVC.

2.4.4 Advantages / disadvantages

ABS has excellent chemical resistance and impact resistant with fairly high strength, combined with good processability and good aesthetics at a reasonable price. For many applications that require higher performance properties than available in polystyrene, PVC, or polypropylene, a "stepping up" to ABS is successful. Conversely, all of the premium properties of metal or higher price plastics are not needed in many of their applications, and significant savings can be realized in "stepping down" to ABS.

2.5 Surface modifications (3,33-35)

The surface properties and the structures are of obvious importance. The chemical structure and thermodynamic state of polymer surface are important factors that determine many of their practical characteristics. Examples of properties affected by polymer surface structure include adhesion, wettability, friction, coatability, permeability, dyeability, and corrosion. Interfacial characteristics of polymer systems control domain size and stability of polymer-polymer dispersions, adhesive strength of laminates and composite materials, cohesive strength of polymer blends, and mechanical properties of adhesive joints.

Polymer surfaces are unique among solid surfaces in that chains near the surface can be mobile and resemble in many aspects a viscous fluid. The degree of this mobility depends on environment of the sample as well as morphology, molecular weight, and glass-transition temperature (T_g) of the polymer (34).

Fibre surface modifications and coatings can be used to control the properties of the fibre-matrix interface, to form an adequate adhesion in polymer matrix composites. Poor bonding will lead to ineffective load transfer from the matrix to the fibres. A strong interfacial bond tends to reduce the fracture toughness of a composite (3). Surface treatments can be divided into surface-modification techniques; surface graft polymerisation, chemical reaction, and plasma modification.

2.5.1 Surface graft polymerisation (34)

Numerous references describe the modification of polymer surfaces by graft polymerisation of a monomer or monomers from active sites generated on solid polymer surfaces. The most common technique is γ-radicals, which generates surface radicals, but thermal, mechanical, photochemical, plasma, and wet chemical methods are also used to introduce sites for initiation. Monomer can be presented in the gas phase, in solution, or as neat liquids. Reactive species can be generated prior to monomer exposure, during contact with monomer, or after the polymer surface has been saturated with monomer, or after the polymer surface has been saturated with monomer and isolated.

2.5.2 Chemical modifications (34)

Polymer surface modifications by organic reactions are employed in which reagents in solution are allowed to react with solid organic polymers at the solution-polymer interface. Most of the reports involved conditions under which the solution interacts strongly with the polymer surface chains. The interface between the solid and the solution is diffused and the reaction can be viewed as a solution reaction. If organic chemistry is used to rationally control polymer surface properties, modification reactions must change only the chemical structure of the surface. The chemical modification of polymers are oxidations especially of polyethylene, reductions of fluoropolymers, sulfonations, dehydrohalogenations, and hydrolysis.

2.5.3 Plasma modification

The modification of the chemical structure, reactivity, and bonding characteristics of polymer surfaces has considerable technological importance in the areas of metallisation, composite fabrication, and biomedical compatibility. Plasma treatment is one type of surface modifications that is commonly used. This can be used to modify the surface of a polymer to improve adhesion or wettability, to provide a diffusion barrier layer, or to minimize degradation of a polymer surface during metallisation.

A plasma is an excited gas which consists of atoms, molecules, ions, free radicals, free electrons, and metastable species. The chemistry of plasma is complex because many different interactions are possible: electron-atom/molecule, electron-metastable atom/molecule, ion-atom/molecule, etc. If the molecular structure of the gas is not particularly simple, the chemistry of the discharge is very complicated and depends on plasma parameters (36).

2.5.3.1 Description of Plasma

Different types of plasma can be created, depending on experimental conditions. The most frequently cited types are thermal plasma, corona or point-plane discharges, and cold plasma.

Thermal plasmas or hot plasmas (36) are obtained by coupling energy into a high pressure gas, normally using dc, ac, radiofrequency (rf), or microwave (mw). In thermal plasmas a temperature of some thousand degrees centigrade is reached by coupling electromagnetic energy into a high-pressure gas under equilibrium condition. One of the effects is the cleavage of many chemical bonds, with formation of very reactive species, which can either form new compounds or interact with surfaces. Typical application of this type of plasma is synthesis of ceramic powders and the deposition of ceramic coatings.

Corona discharge can be sustained at high-pressure gas using the physical fact that close to a conductor with a small radius of curvature, the electric field is much higher than when it is flat. A typical apparatus for corona discharges is shown in Figure 2.11. Thin wires are held at high voltage respect to ground. Films or fibres are rolled around a grounded cylinder and pass through the discharge, where it is expected that their surface will be activated (36). Corona systems are very common in the plastic film industry for the activation of polymer surfaces, mainly to enhance adhesion or printability.

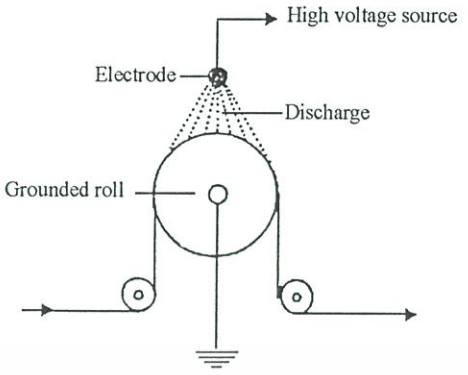


Figure 2.11 Schematic representation of a corona treatment apparatus (36)

Glow discharges or cold plasmas are excited again by dc, ac, rf or mw but operated in gases held at low pressure and temperature. (Figure 2.12) It is easier to control than corona, and it is rather flexible. The main distinction encountered in cold plasma treatments is between etching and deposition. The effect of the treatment is normally evaluated in terms of loss or gain of weight. Whenever energy is introduced in a low pressure gas, the result is the formation of active species for instance, atoms or excited molecules. Active species can hit the surface and possibly interact, which can lead also to some abstraction of material. On the other hand, when a hydrocarbon or fluorocarbon gas is excited, radicals can be formed. The effect is the deposition on the substrate surface of a so-called plasma polymer. This is also an important practical difference between plasma etching and plasma deposition process, namely the treatment time. In fact, the functionalisation of the surface is fast, requiring only seconds, while the formation of a sizable coating needs minutes.

In the case of composite materials, it is a question of modifying in a suitable way the surface of the filler. Depending on its nature and on the required modification, a different approach is required. In any event, the most applications are relative to cold plasma treatments.

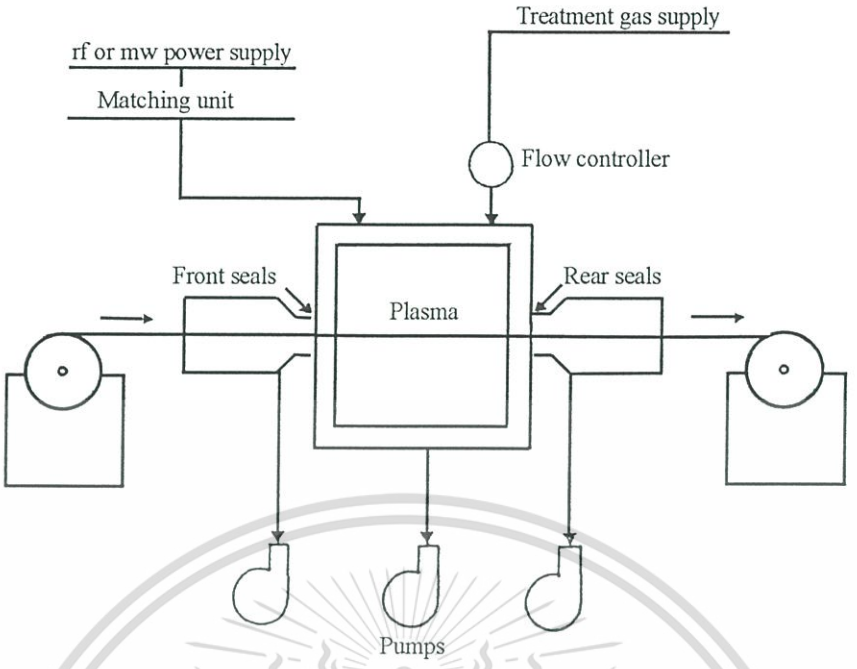
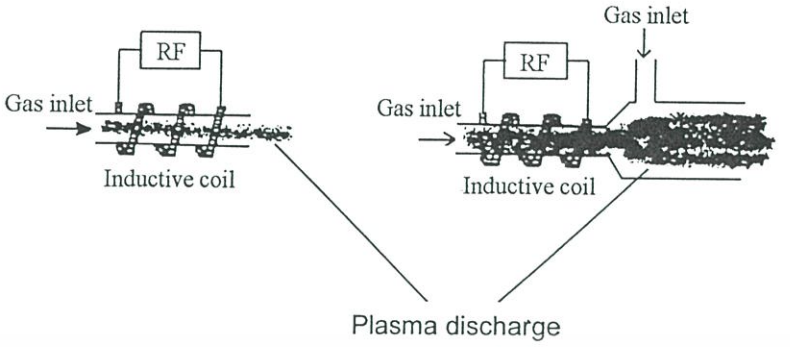


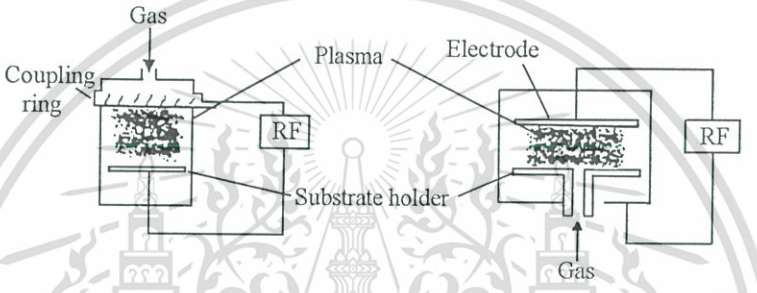
Figure 2.12 Schematic representation of a continuous cold plasma treatment system (36)

2.5.3.2 Equipment

Plasma equipment usually consists of power supply, vacuum system, reactor chamber, matching network, power monitor, and control system. For cold plasma treatment techniques the energy used to create the plasma is direct current (dc), low-frequency (lf), radiofrequency (rf), and microwave (mw). More recently rf and mw plasmas have been widely used. The conventional frequency for rf is 13.56 MHz and it has two divided inductive coupling and capacitive coupling. (Figure 2.13) The frequency for mw is 2.45 GHz and this has more energetic electrons and excited species than rf plasma. The microwave plasma is shown in Figure 2.14. The vacuum system is able to reach the desired pressure, typically in the 0.1-100 Pa range. And the vacuum chamber is metallic, stainless steel or aluminum being flow meters. In applications such as fibre modification, where a continuous system is desirable, more than one chamber can be used.

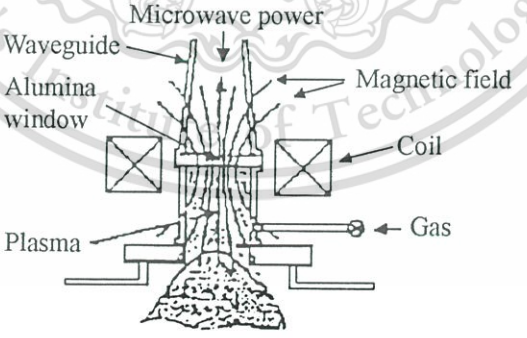


Inductive couping RF plasma reactor



Ductive couping RF plasma reactor

Figure 2.13 Schematic representation of Radio-frequency (RF) plasma



ECR discharge

Figure 2.14 Schematic representation of Microwave plasma

2.5.3.3 The effect from plasma treatment (38)

When a polymer surface is plasma-treated, the major effects can occur including;

(i) Surface cleaning, that is, removal of organic contamination from the surfaces. This is one of the major reasons for improved bonding to plasma-treated surfaces. Oxygen-containing plasmas are capable of removing organic contamination from inorganic and polymeric surfaces, but it is critically important to plasma-clean a polymer for a sufficiently long time to remove all of the surface contamination. Almost all commercial polymer films, and most moulded parts, contain additives or contaminants polymer films, such as oligomers, anti-oxidants, mould release agents, solvents, or anti-block agents, which are oily or wax-like. Most of these are deliberately incorporated into the polymer formulation to improve its properties, and they are designed to "bloom" to the surface and to coat that surface.

(ii) Ablation, or etching, is distinguished from cleaning only by the amount of material that is removed. Ablation is important for the cleaning of badly contaminated surfaces, for the removed of weak boundary layers and increase the surface area. Some ablations of reinforcing fibres tend to improve composite properties, but the fibres must not be significantly reduced in diameter by over treatment because thinner fibres will be weaker.

(iii) Crosslink or branching of near-surface molecules, which can improve the heat resistance and bond strength of the surface by forming a very cohesive skin. It occurs in polymer surfaces exposed to noble gas plasma (e.g. He or Ar), which is effective at creating free radicals but do not add new chemical functionalities from the gas phase. Ion bombardment or vacuum ultraviolet photons can break C-C or C-H bonds, and the free radicals resulting under these conditions can only react with other surface radicals or with other chains-transfer reactions; therefore, they tend to be very stable. If the polymer chain is flexible, or if the radical can migrate along it, this can give rise to recombination, unsaturation, branching or crosslinking.

(iv) Ion implantation the plasma may cause foreign atoms to be implanted in the surface regions of the substrate and these atoms may either aid adhesion. Ion implantation may also be used to achieve an interphase region of properties intermediate between those of the substrate and adhesive.

(v) Modification of surface-chemical structure, which can occur during plasma treatment itself, and upon re-exposed of the treated part to air, at which time residual free radicals can react with atmospheric oxygen or water vapour.

2.5.4 Surface treatments of aramid fibres

Aramid fibres are widely used in the manufacture of advance composites. This has been due to major advances in composite mechanical properties that have resulted from the use of the stiffness, high fracture strain, and low-density reinforcing fibres (11). Kevlar aramid fibres are very useful as a reinforcing fibre for polymer composites, because of the excellent thermal and mechanical properties of the fibres. However, the adhesion between the fibres and most matrices is poor, due to their chemical inertness and smooth surface which prevent chemicals as well as mechanical bonding. Several modifications of the Kevlar fibres have been attempted to improve the adhesion, including grafting, substitution reactions of hydrogen in amide groups, hydrolysis of amide groups, and the formation of oxygen functionalities by plasma treatments. Physical and chemical modifications of the fibre surfaces can be enhanced experimentally by plasma treatment. The modification of surface will facilitate chemical bonding between the fibres and the matrix.

2.6 Literature reviews

Aramid is poor in terms of the interfacial adhesion between the fibres and a polymer matrix, although the surface properties are key factors governing the performance of the composites. Therefore, many surface modifications have been attempted on aramid fibres to improve their adhesion to polymer matrices such as flame treatments, plasma treatments, X-ray and γ-ray treatments, and chemical treatments.

Wu and Tesoro (20) incorporated amine functional groups into aramid fibre surfaces by bromination followed by ammonolysis and also by nitration followed by reduction. The presence of amine groups on the aramid fibre provides remarkably improved peel strength and apparent interlaminar shear strength in epoxy laminates, suggesting a significant role of covalent bonding in improving the adhesion in aramid-epoxy composites.

Takayanagi *et al.* (9) modified the surface of poly (*p*-phenylene terephtalamide) fibres to polyethylene and ionomer by the polymer reaction via the metalation reaction in a solution of sodium methysulfinylcarbanion in dimethyl sulfoxide. The mechanical properties of polyethylene composites were improved with the surface-modified PPTA fibres by octadecyl groups. In the case of ionomer composites, the mechanical properties of the composite of ionomer and PPTA fibres with the surface modified by carboxymethyl groups were remarkably improved.

Mercx and Lemstra (22) studied a chemical method for the surface modification of Kevlar fibres with oxalylchloride. The adhesion to epoxy resins, as measured by multifilament pull-out tests, was markedly improved (by up to 70 %) by this treatment. However, the fibre properties were not affected.

Yu *et al.* (19) studied the interfacial adhesion of Kevlar fibres and nylon. Various chemical treatments were performed on the fibres, i.e., surface hydrolysis, succinyl chloride reactions, and suberoyl chloride reactions. These were shown to affect significantly the mechanical properties, depending on the treatment of the fibre. The fibre-matrix adhesion could be improved by the use of appropriate chemical treatments of the fibres.

Takayanagi *et al.* (39, 40) reported that the reagent prepared by the reaction of sodium hydride with dimethyl sulfoxide (DMSO), giving a solution of sodium methylsulfinylcarbanion in DMSO, dissolved poly (*p*-phenylene terephthalamide , PPTA) in inert gas atmosphere. The polyanion of metalated PPTA dissolved in DMSO was able to react with various aliphatic and arylalkyl halides, giving N-substituted PPTA, that increased their solubilities but decreased their thermal stabilities compared with nonsubstituted PPTA.

Inagaki *et al.* (18) investigated the surface modification of poly(*p*-phenylene terephthalamide, PPTA) film with 2-aminoethanethiol (AET) to adhere to silicon rubber. The X-ray photoelectron spectroscopy (XPS) analyses showed that the AET treatment generated oxygen functionalities at the surface of the PPTA film. The C(O)O moiety at the PPTA film surface might be a key factor for the adhesion with silicon rubber. The concentration of the C(O)O moiety at the film surface for the AET-treated PPTA film was 21% higher than that for the original PPTA film.

Kim *et al.* (24) studied the graft copolymerisation of Ɛ-caprolactam onto the Kevlar-49 fibre surface by anionic polymerisation on the N-metalated Kevlar-49 fibre surface with the metalation reaction in a solution of sodium methylsulfinylcarbanion in DMSO. Graft yield significantly increased with increasing metalation time, NaH concentration, and monomer concentration. The grafted Kevlar fibre reinforced Nylon 6 composite film exhibited mechanical properties superior to those of the original Kevlar fibre reinforced composite film. The higher thermal and mechanical properties were due to the effect of higher interfacial interaction between the grafted Kevlar fibre and matrix.

Wang *et al.* (10) used oxygen plasma treatment to modify the surface structure of Kevlar fibres. The reactive sites, namely, -COOH, -OH and possibly $-NH_2$ occured on the surface, were used to anchor catalysts for ethylene polymerisation. The composites reinforced by catalytically grafted Kevlar fibre exhibited higher tensile strength both parallel and transverse to the fibres. The improved interfacial adhesion was attributed to the interfacial chemical bonding established by catalytic grafting.

Wu, Sheu and Shyu ·(11) modified surface of Kevlar-49 fibres by NH_3-, O_2- and H_2O- plasma etching and chlorosulfonation and subsequent reaction with some reagents to improve the adhesion to epoxy resin. Interlaminar shear strength (ILSS) and T-peel strength between the fibre and epoxy resin were remarkedly improved by plasma treatment and chlorosulfonic. But when the fibre was treated at higher concentrations of chlorosulfonic acid or longer reaction times, ILSS and T-peel strength would decrease.

Sheu and Shyu (12-14) modified Kevlar-49 fibres surface and Kevlar-149 by NH_3, O_2 and H_2O plasmas to improve the adhesion to epoxy resin. After treatments the results showed that the interfacial shear strength (IFSS) of both fibers in epoxy resin systems were remarkably improved by these plasma treatments and the treatment time. In Kevlar-149 fibre surfaces, changes in surface topography of fibres were quite pronounced. The results showed that the etching abilities of gas plasma were dependent on the type of gas used for plasma treatment. The surface compositions of plasma-treated fibres were highly dependent on the type of gas used and treatment time.

Yamada *et al.* (41) studied plasma-graft polymerisation of glycidyl methacrylate and acrylamide onto a surface of Kevlar fibre. The degree of grafting was increased with increasing polymerization time and the pull-out force increased with increasing degree of grafting. The covalent bonds formed between the graft polymer and the matrix resin resulted in an increment of pull-out force.

Inagaki *et al.* (42) investigated the plasma graft copolymerisation of glycidyl methacrylate (GMA) onto PPTA film to improve adhesion between the PPTA film and epoxy adhesives. The adhesion strength was improved 2.7 times by the graft copolymerization and the failure from the adhesive joint occurs in the epoxy adhesive layer rather at the interface between the PPTA film and the epoxy adhesive layer.

Guo *et al.* (43) studied mechanical properties of the PET short fibre-Hytrel TPE composites after treated with isocyanate in toluene solution. The results showed excellent interface adhesion for the PET fibre-Hytrel system. The stress-strain curve of the composite showed a similar tensile behavior, with higher values, to that for the matrix elastomer when fibres loading was less than 5 vol%.

CHAPTER III

EXPERIMENTAL DETAILS

3.1 Materials

3.1.1 Reinforceing fibres

Poly (*p*-phenylene terephthalamide) (PPTA, Kevlar-49) short fibres were provided by E.I. Du Pont de Nemours & Co. Inc., with density of 1.44 g/cm^3, specific surface area of 7-10 m^2/g, moisture regain of 6%, decomposition temperature of 427-480^{0}C, the fibre diameter is approximately 12 μm, and the fibre length is approximately 7 mm.

3.1.2 Polymer matrix

Injection-grade acrylonitrile-butadiene-styrene (ABS) (MH-1) was obtained from TPI Co., Ltd., with melt flow index of 18 g/10 min at 220^{0}C using 10 kg piston-weight, and processing temperature of 200-250^{0}C.

3.1.3 Other chemicals

Other chemicals were used in this research, being shown in Table 3.1

Table 3.1 Grades and supplier for chemicals used in the experiment

Materials	Suppliers / Grades
Isocyanate (phenyl isocyanate; C_7H_5NO)	Fluka / analytical grade
Toluene	CARLO ERBA / Analytical grade
Acetone	Mallinckrodt Baker / Analytical grade

3.2 Instruments

List of instruments were shown in Table 3.2

Table 3.2 List of instruments and their manufactures

Instruments	Manufacturers
Two-roll mill	Lab Tech
Injection Moulding Machine	Cosmo ; TTI-220/80 HITECH
Granulator	BASCO
Plasma tester	SAMCO Model BP-1
Tensile testing machine	LLOYD ; 30 kN
Izod Impact Resistance	YASUDA
Rockwell Hardness	YASUDA
Scanning Electron Microscope	Hitachi ; s-2500
Atomic Force Microscope	TopoMetrix ; TMX 2000
Heat Distortion Tester	YASUDA
Vacuum Oven	Hot pack
Blender	National

3.3 Flow chart of the experiments

As shown in Figure 3.1 was the flow chart of the experiments

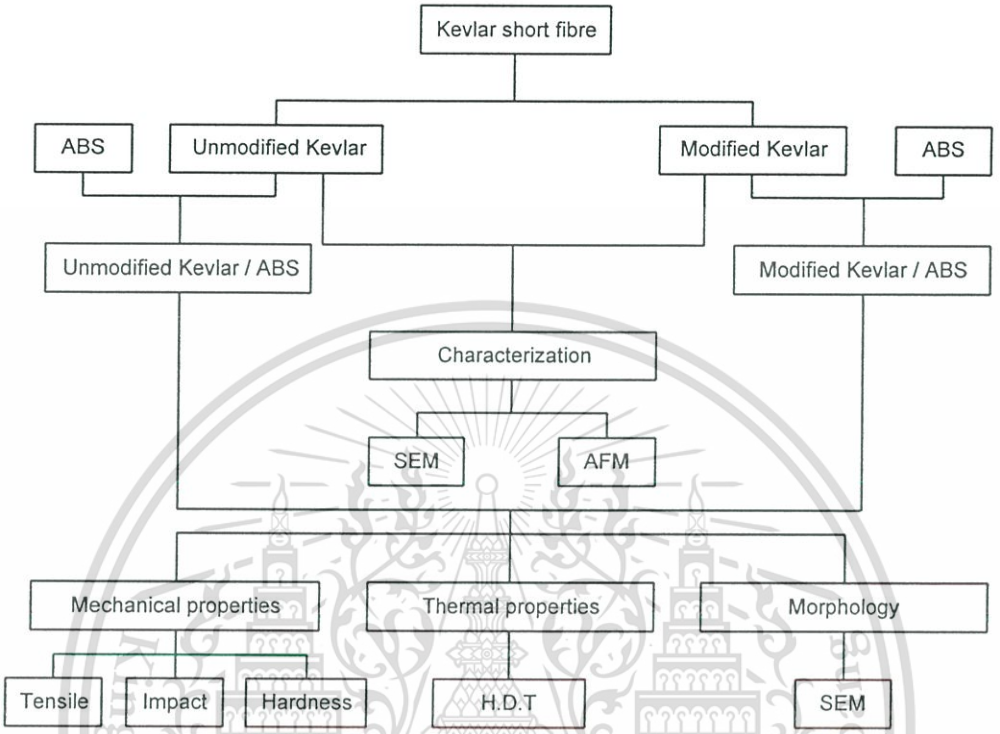


Figure 3.1 Flow chart of the experiments

3.4 Preparation of Kevlar short fibres

3.4.1 Untreated Kevlar short fibres

Kevlar-49 (short fibre) was prepared by washing the fibres with distilled water and acetone to remove impurities such as lubricants then dried in vacuum oven at 50^{0}C for 48 h and kept in desiccator before use. This Kevlar short fibre was used in studying the effects of mixing conditions, effects of fibre loading on the properties of the composites, and comparison of treated plasma fibres and dipped fibres in isocyanate 5% wt solution.

3.4.2 Plasma treatment of Kevlar short fibres

Kevlar obtained from the untreated fibres in the previous section was treated with plasma in SAMCO Model BP-1 bell jar plasma reactor (as shown in Figure 3.2). The gas used for the plasma treatments was oxygen. The chamber was first evacuated to a pressure lower than ~8 mtorr before the plasma gas was introduced. After three times purging with oxygen gas, the chamber pressure was treated at 30-100 W of radio frequency (rf, 13.65 MHz) plasma power for 1-15 min treatment time. After the plasma treatment, the samples were left there for 10 min (post-treatment) to allow for the decay of residual surface radicals.

This Kevlar short fibre was used to study the effect of time in plasma treatment on the composites, and the reaction between active functional groups on treated Kevlar short surface with isocyanate. Then, the surface morphology was observed by using the scanning electron microscope (SEM).

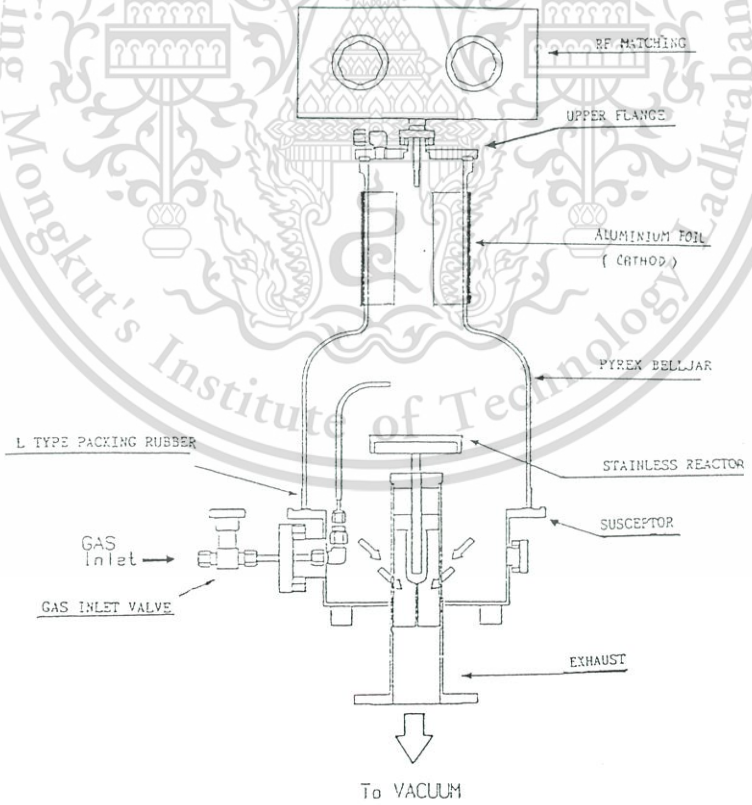


Figure 3.2 Schematic representation of plasma tester

3.4.3 Treatment of Kevlar short fibres with isocyanate

Kevlar was treated with 5% wt isocyanate in toluene solution. The fibres were treated by two methods. In the first method, Kevlar was dipped in 5% wt isocyanate solution for 30 sec and 10 min, then washed several times with toluene. The fibres were dried in a vacuum oven at 115^0 C for 3 h and kept in desiccator. In the second one, Kevlar was treated with plasma and then followed by isocyanate. The surface morphology was observed by using SEM.

3.5 Characterisation of Kevlar short fibres

3.5.1 Scanning electron microscopy (SEM)

SEM was used to observe the surface morphology of Kevlar short fibre before and after modification. The sample was Palladium-coated with Hitachi E 102 ion sputter and then viewed under Hitachi s2500 scanning electron microscope that operated at 15 kV.

3.5.2 Atomic force microscopy (AFM)

Surface topography of Kevlar fibres before and after modification were investigated extensively by atomic force microscope (AFM). The sample need not electrically conducting and sample preparation is relatively simple. It is also possible to obtain surface information similar to that provided by scanning electron microscopy (SEM), but better sensitivity to surface corrugation. The digitized image data of AFM have more advantages than images of SEM because they can be analyzed easily by surface analysis software to measure surface roughness and its fractal dimension. The range of magnification covers that for the optical microscope (microns) to that for the electron microscope (Angstroms). The AFM records forces between the apex of a tip and atoms in a sample as the tip is scanned over the surface of the sample. The AFM system is shown in Figure 3.3.

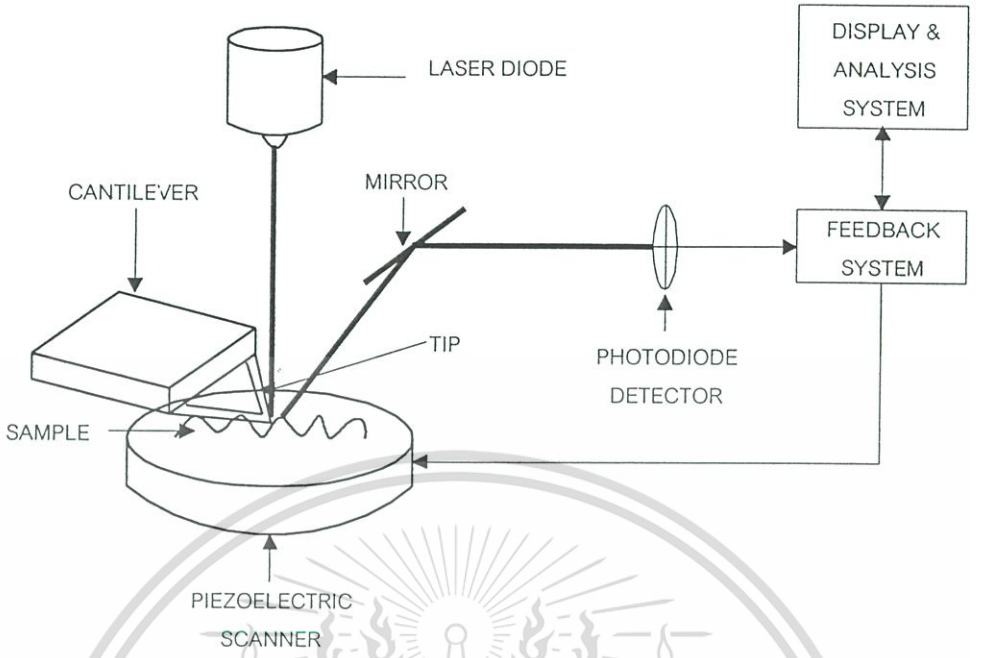


Figure 3.3 Schematic diagram of the AFM system

The AFM system consists of a sample positioning system and electronic control unit, microcomputer with a super VGA color monitor, an optical microscope connected to a monochrome monitor, and a vibration isolation system in a fully integrated system. Since vibrations cause unwanted motions of the probe tip relative to the sample, they yield a substantial decrease in resolution. Therefore a vibration isolation system is crucial for AFM studies.

The initial tip-approach to the sample was facilitated by an optical microscope which provided a 45° view of tip and sample with magnification from 100x to 300x. The tip can be made of a small fractured diamond fragment attached to the cantilever spring or an integrated silicon nitride (Si_3N_4) tip. The scanner in this study is the 70-micron scanner. The mode of operation is constant force mode. In this mode, the force on the cantilever is fixed while the sample is scanned. The voltage applied to the vertical piezoelectric translator to maintain a constant cantilever deflection (force) provides the image signal. The constant force mode requires high responsiveness of the feedback electronics, so, it is used to scan large areas (typically larger than 100 A° x100 A°) and large surface features.

After the tip-approach was performed successfully, the line scan mode was selected in order to diagnose the feedback response to the surface features. In this mode, the scanner moves the probe repeatedly over the first scan line to test the reproducibility of the scans. The PID (Proportional, Integral, and derivative) feedback control values and scan speed can be adjusted to give a good feedback loop to respond to the surface features indicated by overlapping lines seen in the voltage and current traces. The force used at the cantilever was set as light as possible so as to not damage the sample, but heavy enough so that surface features were accurately scanned. The scan rate was controlled to be 2 Hz for low magnification images. A resolution of 300x300 data points per image was used to collect the data.

3.5.2.1 Area. roughness

There are two surface roughness parameters which are frequently used, i.e., average roughness (R_a) and root-mean-square roughness (RMS). The R_a is the arithmetic mean of the absolute values of departures of the roughness profile from the mean line. For N measurements of height Z, R_a can be written as :

$$R_a = \frac{1}{N}\sum_{i=1}^{N}\left|Z_i - \bar{Z}\right| \qquad (3.1)$$

The root-mean-square roughness is the standard deviation of the height measurement which can be written as:

$$R_{ms} = \sqrt{\frac{1}{N}\sum_{i=1}^{N}\left\langle Z_i - \bar{Z}\right\rangle^2} \qquad (3.2)$$

In this study, the R_a and RMS were calculated from digitized image data using the TopoMetrix surface Analysis Software. First, each images was flattened by using second order leveling to reduce the effect of fibre curvature on the roughness measurement. Then, AFM images for 5 μm x 5 μm scanning areas were used to study the roughness of each fibre surface.

measurement. Then, AFM images for 5 μm x 5 μm scanning areas were used to study the roughness of each fibre surface.

3.5.2.2 Area measurement

In area measurement, values for projected area and the surface area were calculated. Projected area was defined as the X scan range multiplied by the Y scan range. Surface area was the calculated area including X, Y, and Z data.

3.6 Preparation of Kevlar short fibres/ABS composites

3.6.1 Pre-opening of Kevlar short fibres

Kevlar short fibre was pre-opened using a blender (National) with interior blades turning at a high rate of revolution for about 10 seconds before charging into the two-roll mill.

3.6.2 Mixing procedure

In the mixing procedures, acrylonitrile butadiene styrene (ABS) was put into the two-roll mill set at 210 ^{0}C for 1 min to form band. Then, Kevlar short fibres were placed into rolls and mixed continuously for 10 min.

3.6.3 Variation of fibre loading

Loading of untreated Kevlar short fibre was varied at 0,1,3,5,7 and 10 parts per hundred parts of ABS.

3.7 Specimen preparation by injection moulding

The composites obtained from the two-roll mill were pelletized using Basco granulator. Tensile and impact specimens were prepared using Injection moulding machine. The tensile and impact moulds used were in accordance with ASTM D 638 M, and ASTM D 256, respectively.

Conditions of injection moulding were studied by varying from 190 to 230 ^{0}C in the system of pure ABS.

3.8 Characterization of composites

3.8.1 Tensile testing

The tensile bar of size 10 mm wide x 2.50 mm thick x 151 mm long (as shown in Figure 3.4) was tested on a tensile testing machine (LLOYD: 30 kN). Twelve specimens were tested at maximum load cell of 30 kN, crosshead speed of 5 mm/min and gauge length of 50 mm.

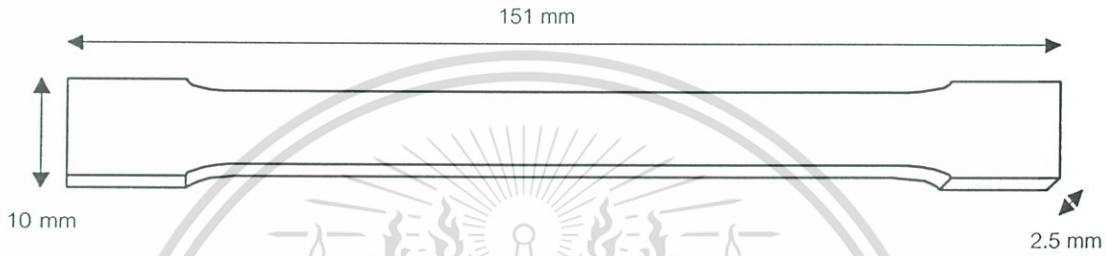


Figure 3.4 Dimensions of the tensile specimen.

3.8.1.1 Tensile strength

From tensile testing, tensile strength was calculated by the equation (3.4),

$$\sigma = F / A \tag{3.4}$$

where σ = tensile strength (MPa or N/mm^2)

F = force at yield or at break (N)

A = initial cross-sectional area of the test specimen (mm^2)

3.8.1.2 Modulus at 3 % strain

Modulus at 3 % strain could be calculated by the equation (3.5),

$$E = \frac{(F / A)}{(3/100)} \tag{3.5}$$

where E = modulus at 3 % strain (MPa)

F = load at 3 % strain (N)

A = initial cross-section area of the test speciman (mm^2)

3.8.1.3 Elongation at break

The Elongation at break (EB) was obtained from the equation (3.6),

$$EB = \frac{(l - l_0)}{l_0} \times 100 \tag{3.6}$$

where EB = elongation at break (%)

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

l_0 = the initial gauge length, which set at 50 mm (mm)

The standard deviation (sd) and mean value ($\bar{x}$) were calculated from equations (3.7 and 3.8)

$$\bar{x} = \frac{\sum x_i}{n} \tag{3.7}$$

and

$$sd = \sqrt{\frac{\sum (x_i - \bar{x})^2}{n}} \tag{3.8}$$

where x_i = values of properties of each sample

n = number of observation

3.8.2 Impact testing

Notched izod impact strengths of ten speciments of impact bars were measured on Yasuda pendulum type impact following ASTM D256. The impact strength (IS) of each specimen could be calculated from the equation (3.9),

$$IS = W / A \tag{3.9}$$

where IS : impact strength (kJ/m^2)

W : loss energy

3.8.3 Rockwell hardness testing

The hardness value was measured from Rockwell hardness tester in Rockwell R (Yasuda), following ASTM D785. The sample had a thickness of 6 mm (1/4in) cut from a moulding or sheet or a pile-up of several pieces of same thickness. Mean values of ten specimens were determined.

3.8.4 Heat distortion temperature (HDT)

The sample was cut from a moulding by using the punching machine. Figure 3.5 shows dimensions of sample, according to ASTM D648. The sample bar of size is 4.00 ± 0.2 mm wide x 10.00 ± 0.2 mm thick x 127 mm long. Three specimens were tested under a load of 66 psi (0.45 MPa), and the temperature raised at 2^{0}C/min.

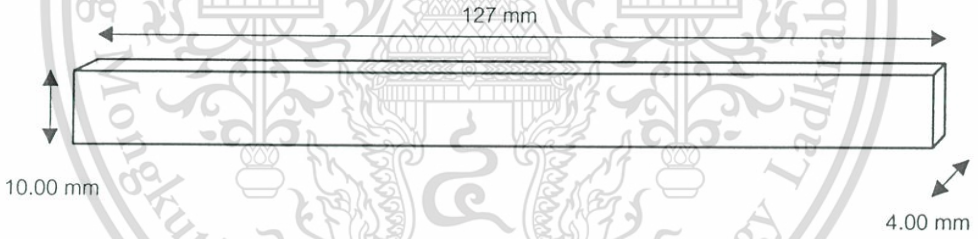


Figure 3.5 Dimensions of HDT specimen

3.8.5 Scanning electron microscopy (SEM)

The fractured surface of fibre reinforced composites was prepared by freezing the specimen in liquid nitrogen for 10 min and breaking rapidly above the surface of liquid nitrogen. A thin layer of palladium was coated on the fractured surface of the specimen to prevent charging on the surface. SEM (Hitachi S-2500) was used to observe the fracture at the accelerating voltage of 15 kV.

The SEM micrographs of different types of composites were compared in order to investigate whether the improvement of adhesion at the interface could be achieved.

CHAPTER IV
RESULTS AND DISCUSSION

In this study, the results and discussion would be presented into three parts. First part involved the effect of plasma treatment on surface morphology of Kevlar short fibres. The second part was about the study of modified Kevlar short fibres surface by plasma treatment on tensile properties and surface morphology of Kevlar short fibres/ABS composites. The last part involved the effect of treatment by isocyanate on the mechanical properties and surface morphology of composites.

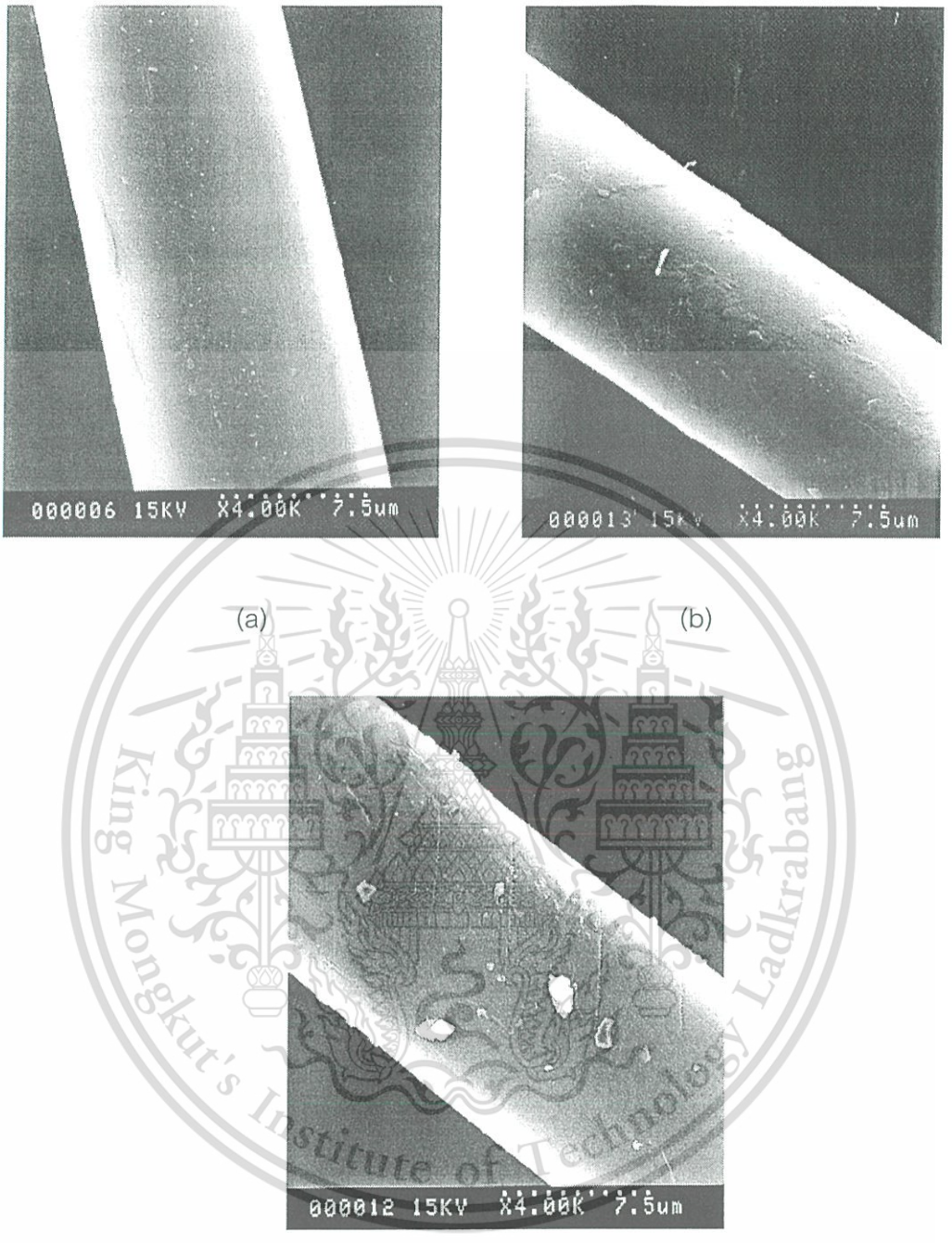
4.1 Surface modification of Kevlar short fibres by plasma treatment

The problem in a preparation of Kevlar-reinforced polymer composite is a poor interfacial adhesion between Kevlar and the polymer matrix. Modification of the fibre surface by plasma treatment would be expected to enhance the number of reactive groups on the surface and roughen the Kevlar surface. This would result in increasing bonding, chemically and/or physically, between Kevlar and the matrix. This part would concern the plasma treatment of fibre surface and its effects on morphology.

4.1.1 Effect of discharge power and pressure

Effect of discharge power and pressure were investigated in order to find the optimum discharge power and pressure of plasma reaction chamber for treating the fibres before studying other effects. Morphology of Kevlar short fibres was investigated and used as a criteria to obtain the optimum values. Surface morphology of Kevlar short fibres treated with the oxygen plasma was examined by scanning electron microscope (SEM) and atomic force microscope (AFM).

SEM micrographs of treated Kevlar short fibres were shown in Figures 4.1 and 4.2. Figure 4.1 showed the effect of the discharge power whereas Figure 4.2 showed the effect of pressure on Kevlar short fibres.



(a) (b)

(c)

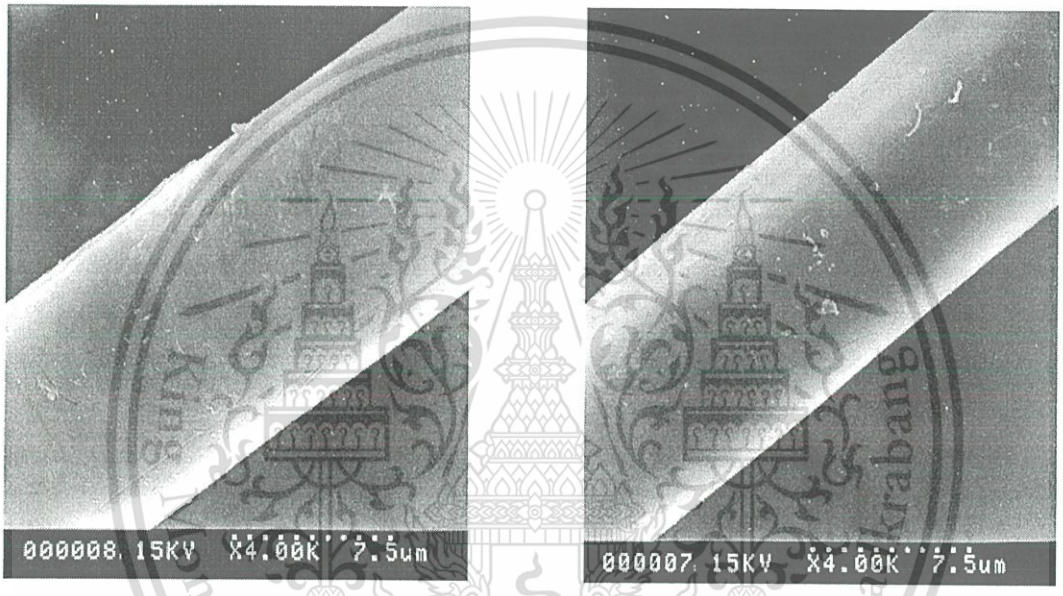
Figure 4.1 SEM micrographs of Kevlar short fibre surfaces :

a) treated by O_2 plasma at 30 w, pressure 0.2 torr for 5 min

b) treated by O_2 plasma at 60 w, pressure 0.2 torr for 5 min

c) treated by O_2 plasma at 100 w, pressure 0.2 torr for 5 min

Figure 4.1 shows the effect of discharge powers in plasma treatment on the surfaces of Kevlar short fibres. It can be seen that the surface roughness of treated fibres was increased with increasing the discharge power. As observed from SEM micrographs, there are considerable differences in etching abilities among different discharge powers. The surface of treated fibres at the power 100 w showed some particle-like structures (Figure 4.1c) which were evidences of more etching effect and more homogeneous roughness than the others (Figures 4.1a, 4.1b).



(a) (b)

Figure 4.2 SEM micrographs of Kevlar short fibre surfaces :

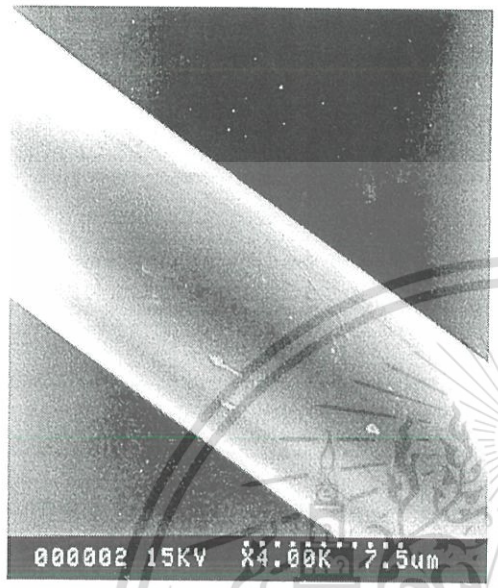
a) treated by O_2 plasma at 30 w, pressure 0.1 torr for 5 min

b) treated by O_2 plasma at 30 w, pressure 0.2 torr for 5 min

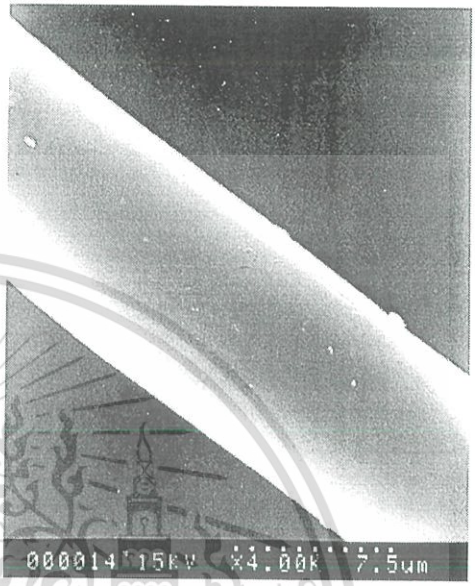
In order to study the effect of the plasma treatment chamber, the Kevlar fibres were treated at different pressures, i.e., 0.1 torr and 0.2 torr. It was found that the pressure had small effect on the fibre surfaces as shown in Figures 4.2a, 4.2b. From the results, it can be concluded that the optimal conditions for plasma treatment of Kevlar short fibres were discharge power of 30 w and chamber pressure of 0.1 torr.

4.1.2 Effect of plasma treatment on surface morphology of Kevlar short fibres.

The effect of the treatment time on the surface morphology of treated fibres was investigated by using SEM as shown in Figures 4.3a-4.3i.

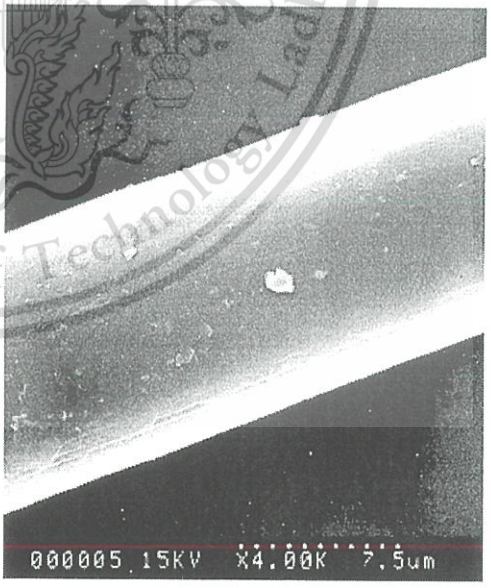


(a)

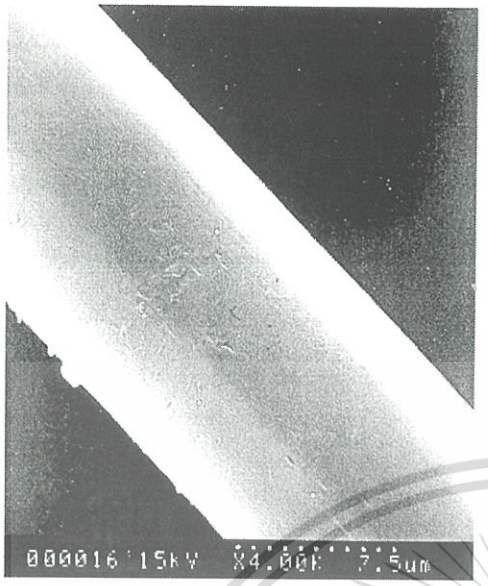


(b)

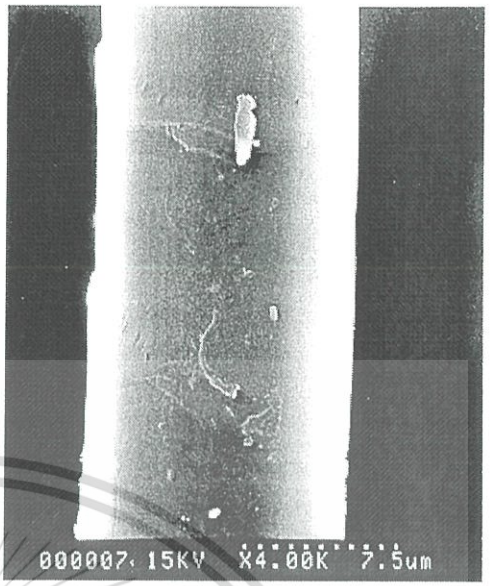
(c)



(d)

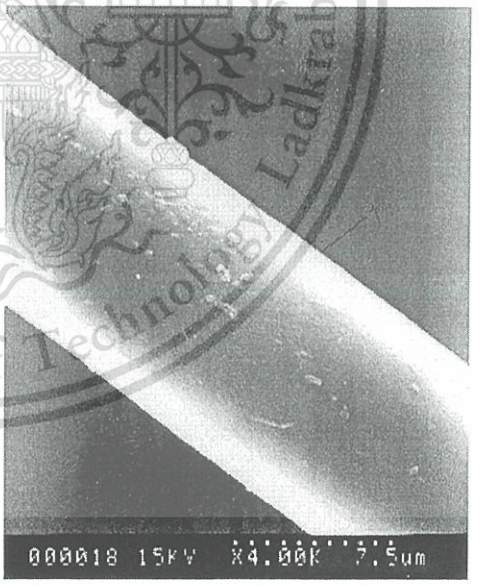


(e)

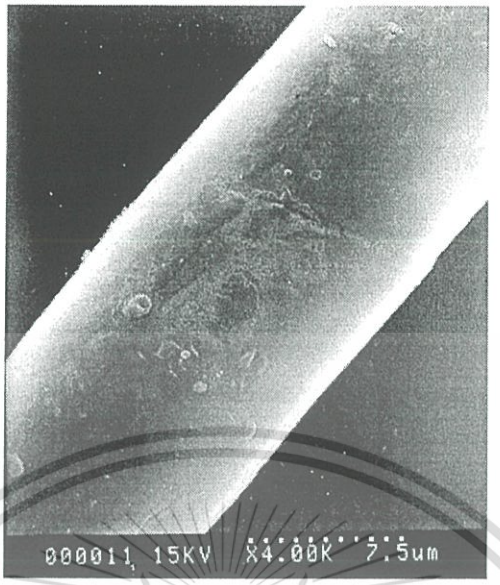


(f)

(g)



(h)



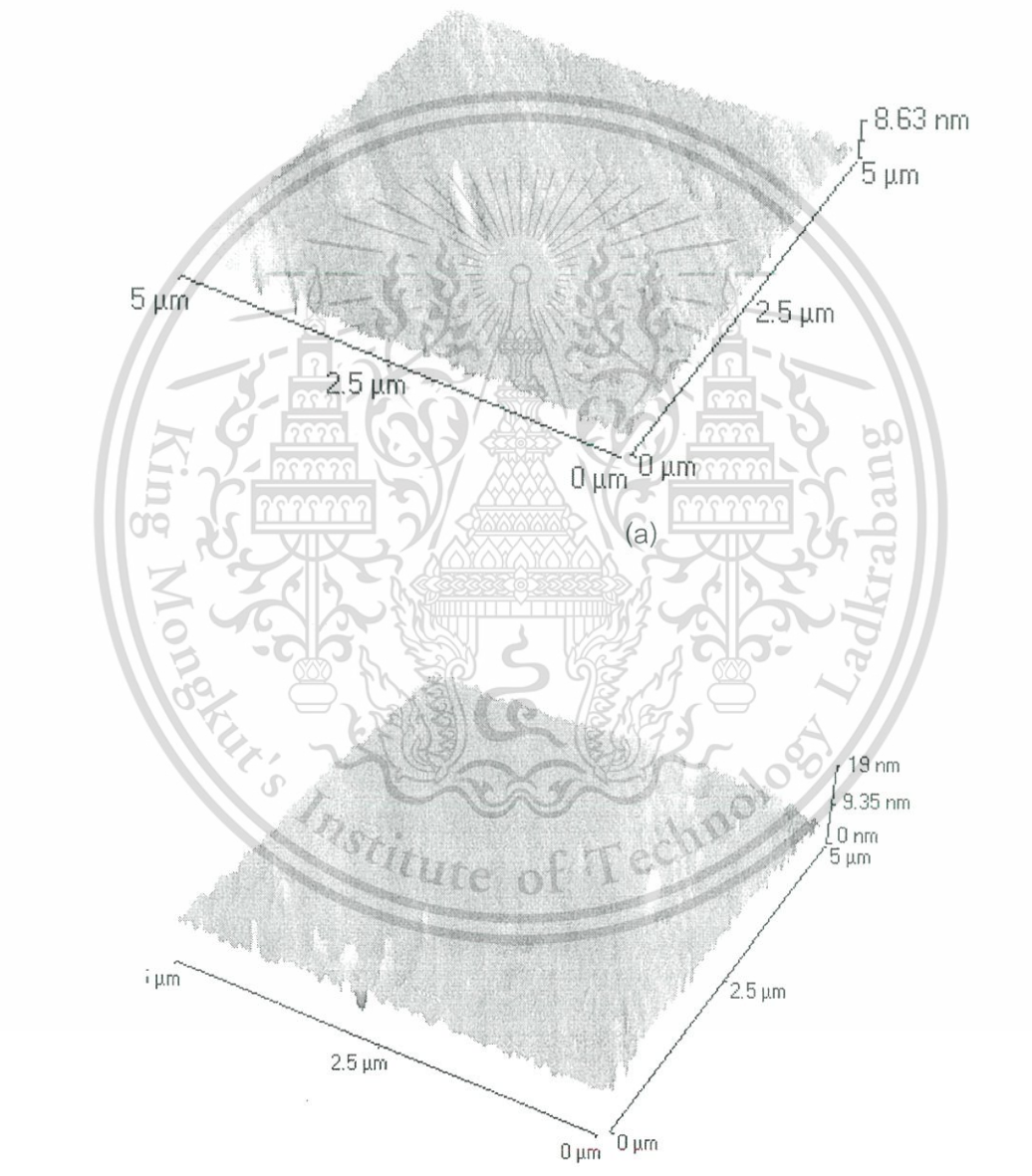
(i)

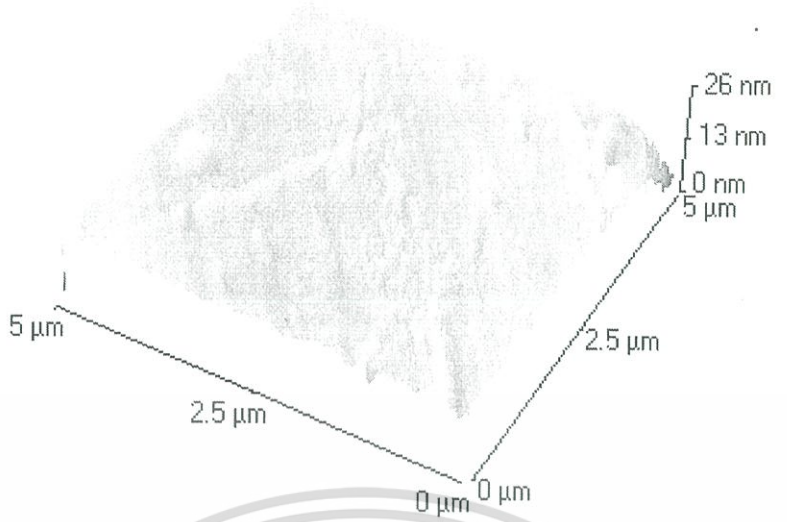
Figure 4.3 SEM micrographs of treated Kevlar short fibres at different times for a) 0 min b) 1 min c) 2 min d) 3 min e) 4 min f) 5 min g) 7 min h) 10 min i) 15 min

Comparison of the surfaces of untreated Kevlar short fibres (Figure 4.3a) with those of plasma treated fibres at different times (Figures 4.3b-4.3i) shows that the surface roughness of treated fibres was increased with increasing time. It was revealed that the surface of controlled fibres was quite smooth, as shown in Figure 4.3a. After the treatment for 1-2 minutes, there was a little change on the surface (Figures 4.3b-4.3c). However, at longer treatment times (Figures 4.3d-4.3i), the fibre surfaces were etched and had a number of particle-like structures that were clearly visible on the fibre surfaces. The change in morphology resulted from the bombardment of the fibre surfaces with high-energy species (e.g. ion, neutral and metastable particles) in the plasma environment. During these processes, the structure of the fibres skin was etched out and some of the fragments would be precipitated on the fibre surfaces. In the treatment time of 15 minutes it was shown some continuous grooves, ridges and several

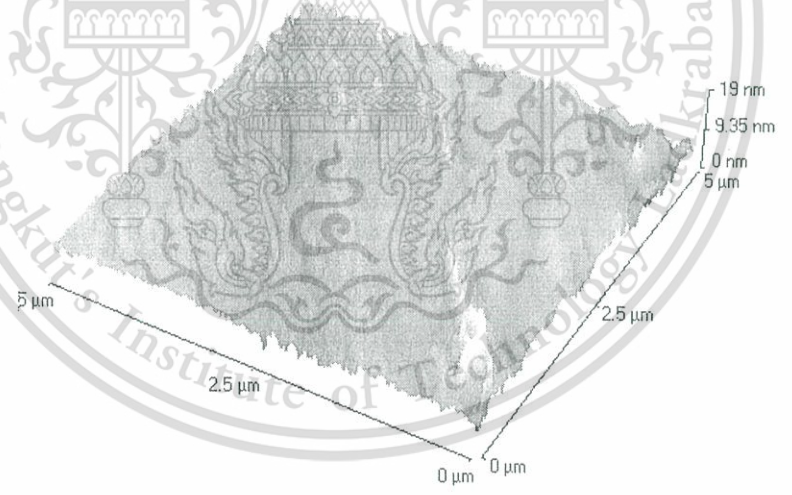
periodic structures along the fibres direction, as seen in Figure 4.3i. Similar results were reported by sheu *et al.* (12). They investigated the surface of Kevlar fibres after treated with plasma. It was found that after treatment in O_2 plasma at 30 w for 10 minutes, a number of particle-like structures were obviously seen on in the fibre surfaces.

In order to evaluate the surface roughness, topographies of the plasma treated the surface of Kevlar short fibres were studied by AFM (Figures 4.4a-4.4i).

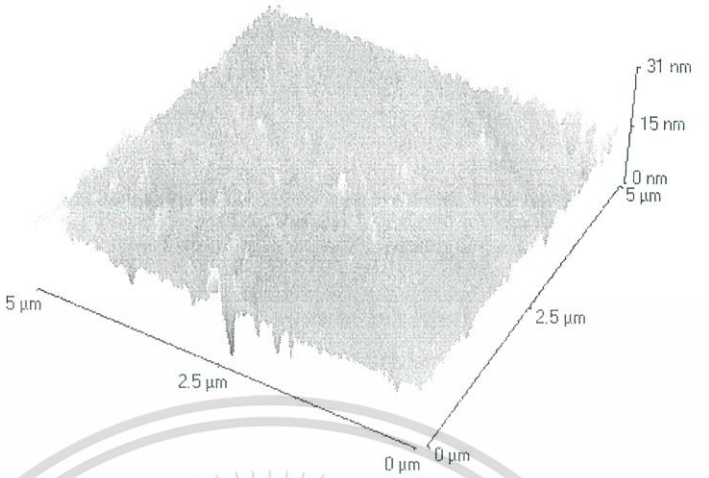




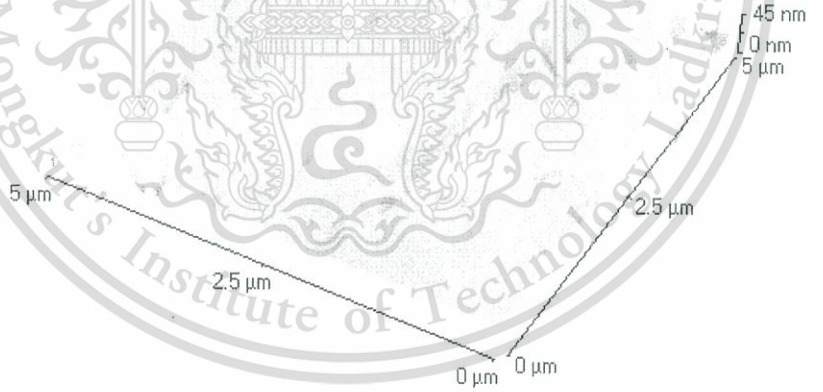
(c)



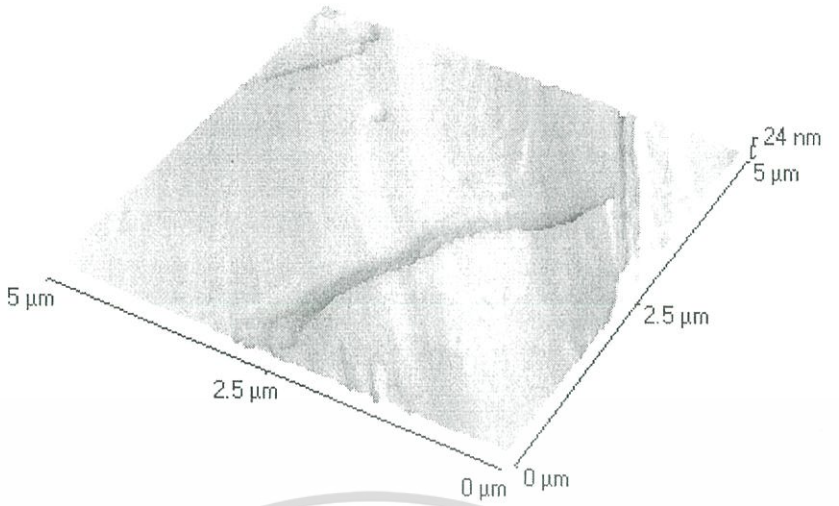
(d)



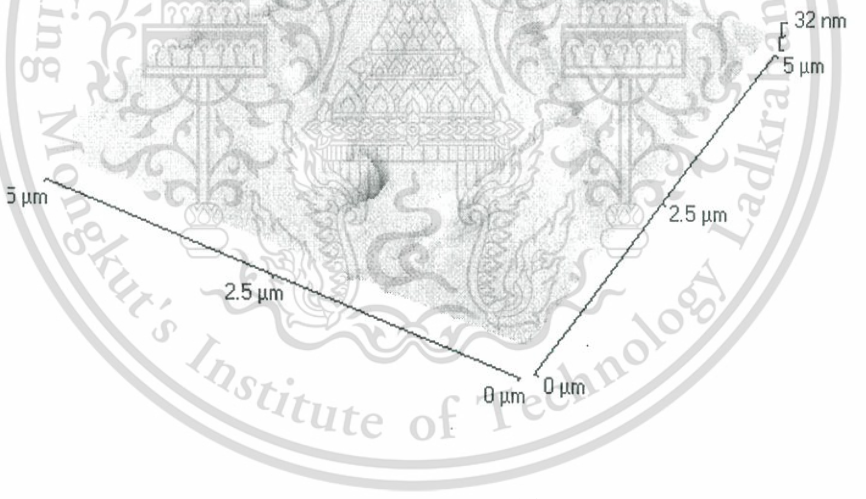
(e)



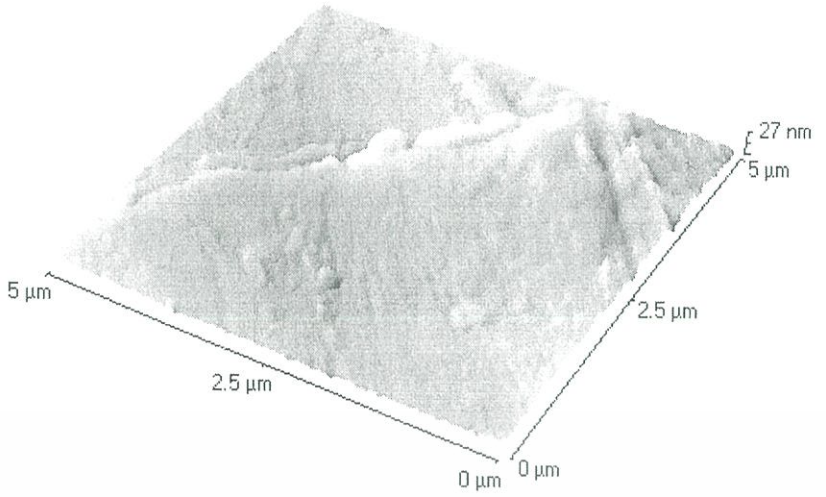
(f)



(g)



(h)



(i)

Figure 4.4 AFM images of Kevlar short fibre surfaces treated with plasma at different times for a) 0 min b) 1 min c) 2 min d) 3 min e) 4 min f) 5 min g) 7 min h) 10 min i) 15 min

The results from AFM images were similar to those of SEM micrographs. It was found that the surface roughness of the treated fibres was increased with increasing time. From the AFM results, arithmetic means of the area roughness and surface areas were calculated as shown in Table 4.1.

Table 4.1 Surface roughness of Kevlar short fibres treated with oxygen plasma at 30w

Treatment time (minutes)	Area roughness (nm)		Surface area (μm^2)
	R_a	R_{ms}	
0	0.57	0.76	25.20
1	0.73	1.04	25.52
2	0.99	1.35	25.51
3	0.99	1.47	25.74
4	1.16	1.59	25.62
5	1.11	1.75	25.24
7	1.81	2.40	25.22
10	1.07	1.71	25.22
15	1.87	2.59	25.24

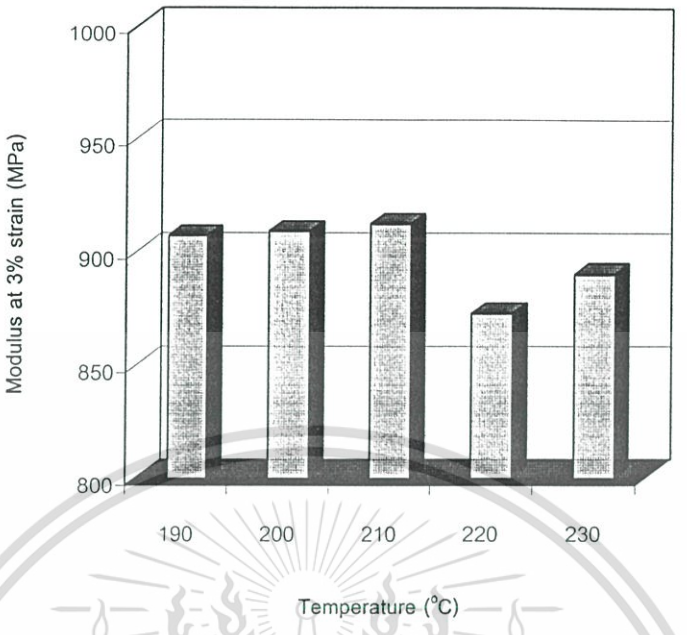
As seen in Table 4.1, average roughness (R_a), root-mean-square roughness (R_{ms}), and surface roughness had a trend to increase as the treatment time increased. The results from AFM study confirmed that the plasma treatment caused the increase in the surface roughness of the fibres.

4.2 Study of the effect of surface treatment by plasma on mechanical properties of Kevlar short fibres/ABS composites

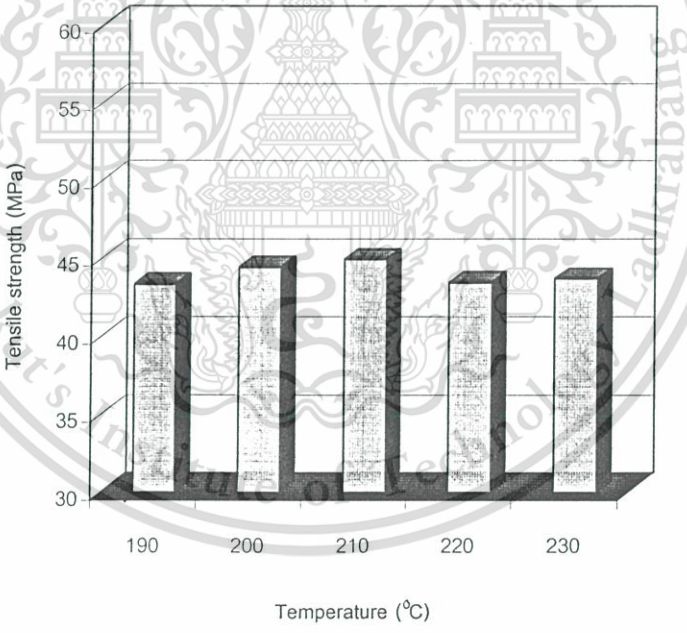
The interfacial adhesion of Kevlar short fibres and the matrix could be improved by plasma treatment. The effect of injection temperature, loading of fibre and its effect of treatment of the fibre on tensile properties and surface morphology of Kevlar short fibres/ABS composites were investigated.

4.2.1 Effect of injection temperatures on mechanical properties of the ABS

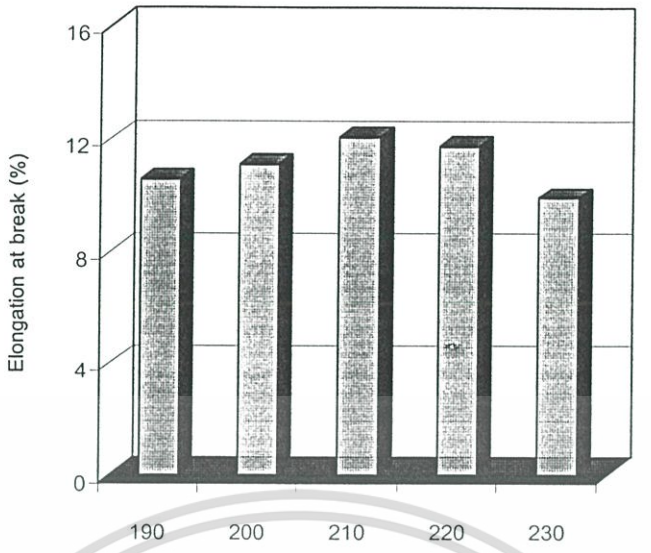
Injection moulding technique was used to prepare the samples for tensile and impact tests. Injection temperatures of the injection moulding machine were varied in the range of 190 to 230 ^{0}C. The tensile properties of ABS were measured and chosen to use as the criteria to obtain the optimum shaping condition. Figures 4.5a-4.5d show the effect of injection temperature on modulus at 3 % strain, tensile strength, elongation at break and impact strength of ABS, respectively.



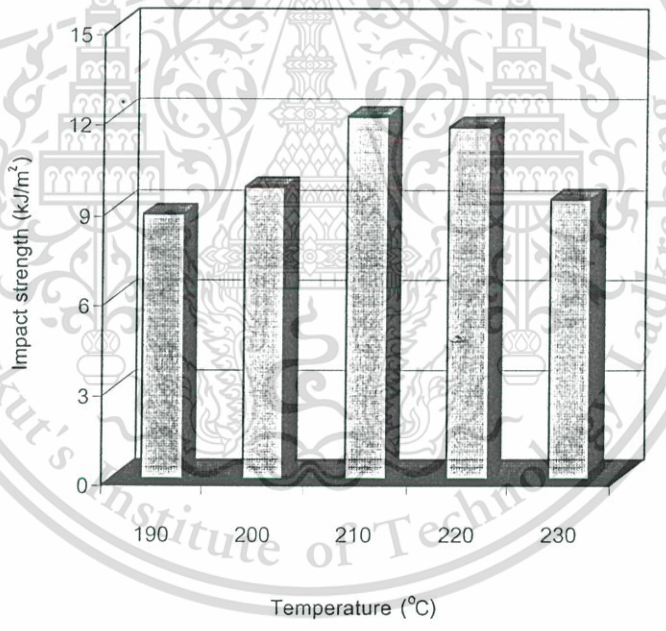
(a)



(b)



(c)



(d)

Figure 4.5 Effect of injection moulding temperatures on mechanical properties of ABS a) modulus at 3 % strain b) tensile strength c) elongation at break d) impact strength

It can be seen that the injection moulding temperature of 210^{0}C seemed to yield ABS with the optimum tensile properties. It was found that the samples had dark brown colour when the injection temperature was higher than 230^{0}C. It was the result of degradation of ABS matrix.

4.2.2 Effect of Kevlar short fibres loading on mechanical properties of the composites

The fibre loading is an important factor on properties of the composites since it has the effect on the dispersion of short fibres in the ABS matrix. In this study, all composites were prepared at the temperature of 210^{0}C, and mixing time of 10 minutes. The loading of Kevlar short fibres was varied from 0 to 10 parts per hundred ratios (phr) of the ABS, in order to study the effect of fibre loading on tensile properties of Kevlar short fibres/ABS composite. Figure 4.6 shows the stress-strain curves of Kevlar short fibres/ABS composites with fibre loading varied from 0 to 10 phr.

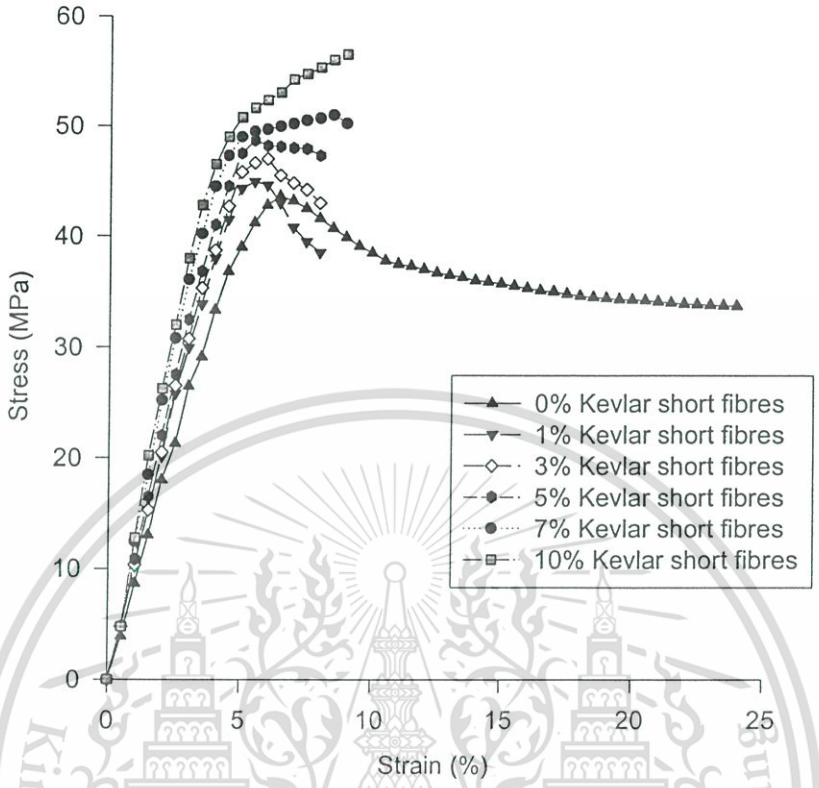
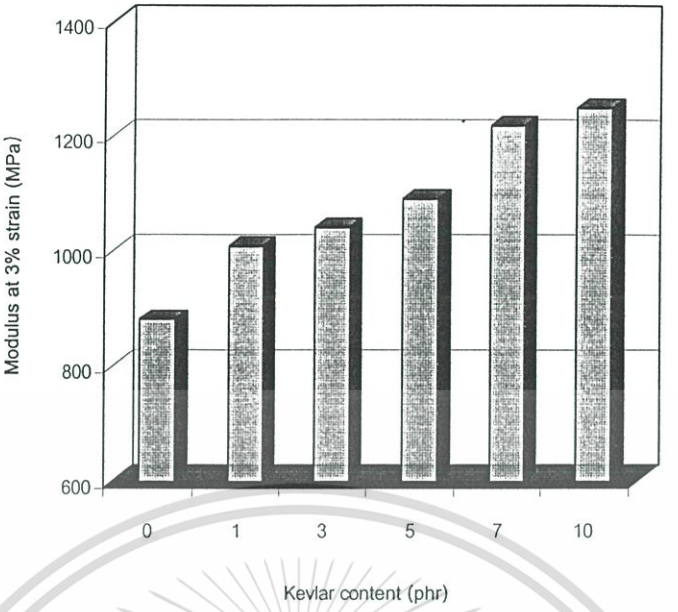


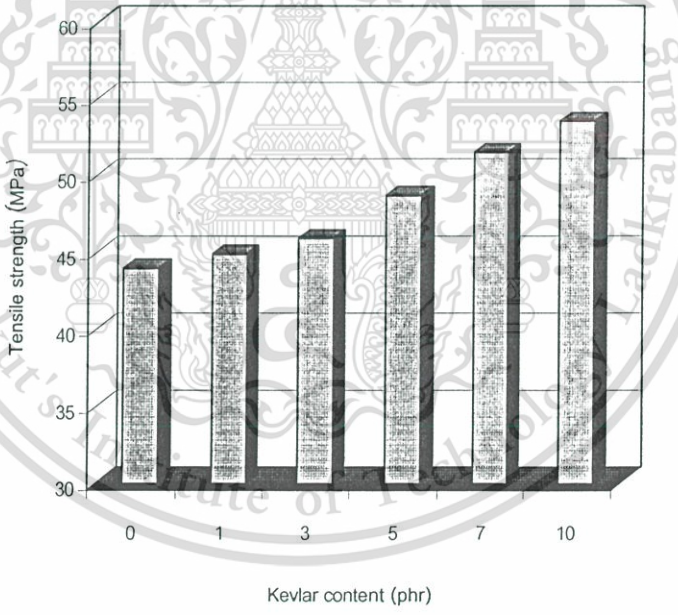
Figure 4.6 Stress-strain curves of untreated Kevlar short fibres/ABS composites of various Kevlar loading

Figure 4.6 shows that pure ABS has the lowest tensile modulus. When the kevlar short fibre was incorporated, the modulus was increased because of the stiffness of Kevlar fibres. It showed higher modulus of the composite with more addition of Kevlar short fibres.

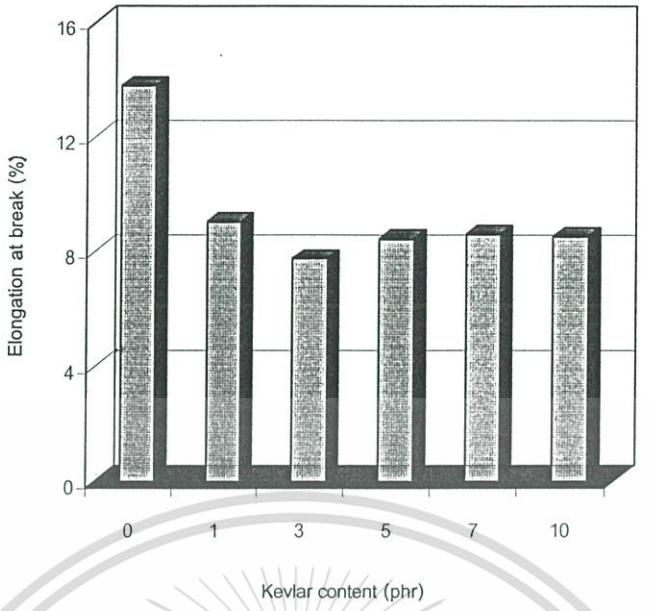
Figures 4.7a-4.7f show the effect of the Kevlar short fibres loading on modulus at 3 % strain, tensile strength, elongation at break, impact strength, Rockwell hardness and heat distortion temperature of the ABS composites, respectively.



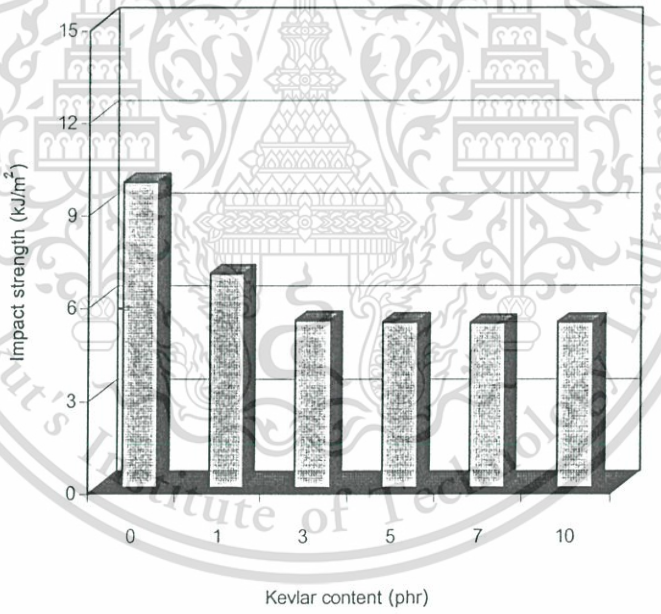
(a)



(b)



(c)



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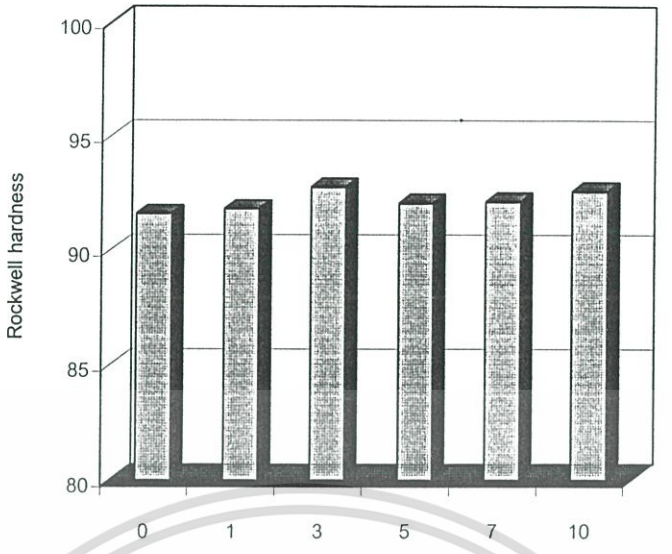

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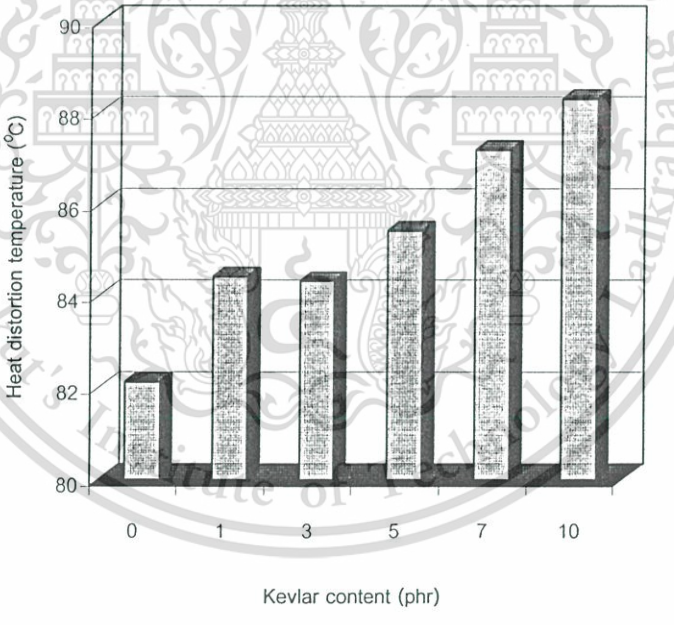


(f)

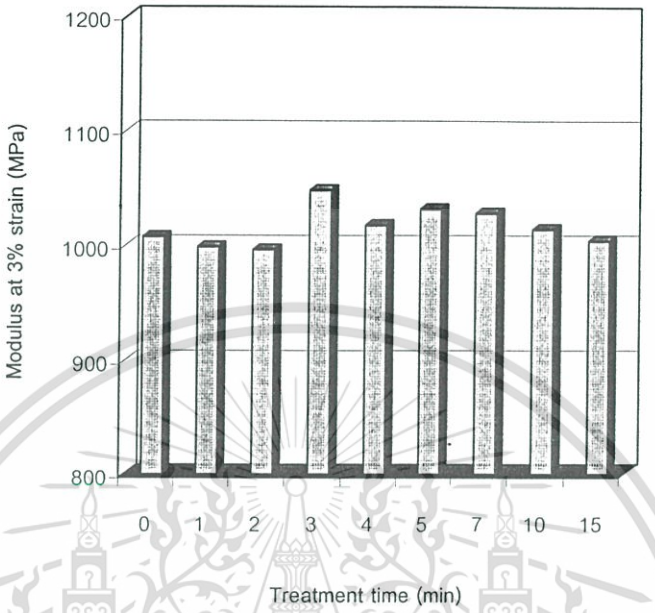
Figure 4.7 Effect of Kevlar short fibres loading on mechanical properties of composites a) modulus at 3% strain b) tensile strength c) elongation at break d) impact strength e) Rockwell hardness f) heat distortion temperature

Figure 4.7a shows that the modulus at 3% strain of the composites was increased with the addition of Kevlar short fibres since the stretching of ABS matrix was controlled by the high modulus fibres at the initial deformation. In Figure 4.7b, tensile strength was found to increase with short fibres content in the same manner as the modulus. From these results, it could be explained that Kevlar short fibres had much more strength than ABS since the fibres acted as a reinforcing material for the composites due to large surface area of the short form. Figure 4.7c shows the result of elongation at break as it decreased with increasing Kevlar short fibres content. The drop of elongation at break is due to the poor adhesion between fibre and the matrix. The effect of fibre loading on impact strength of the composite was shown in Figure 4.7d. Addition of Kevlar short fibres decreased the toughness of the composites. It had believed that there are two mechanisms by which the fibres can reduce the impact strength of the composites, i.e., 1) fibres tend to reduce the elongation at break and may reduce the area under the stress-strain curve and 2) stress concentrations may occur at regions around fibre ends, areas of poor adhesion and regions where fibre contact one another. The result of Rockwell hardness shows in Figure 4.7e, which did not exhibit any significant change for varying the loading of fibre. Figure 4.7f shows the effect of loading on heat distortion temperature (HDT) of untreated Kevlar short fibres/ABS composites. The result was found that the HDT was increased with the addition of Kevlar short fibres because of good thermal stability of the Kevlar.

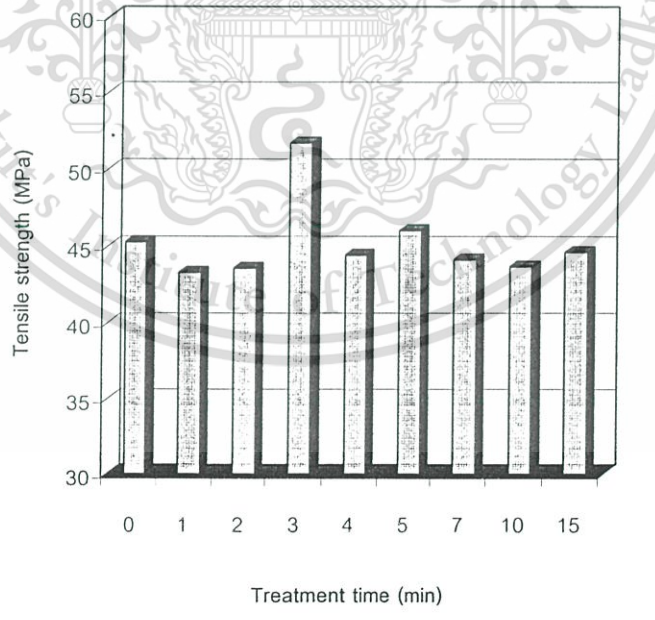
4.2.3 Mechanical properties of treated Kevlar short fibres/ABS composites at various treatment times

In order to improve the fibre-matrix interfacial adhesion, plasma treatment of Kevlar short fibre was used in this study. It would be expected that the treatment of the fibre surfaces would enhance the mechanical properties of the composites due to the increase of the surface roughness and surface functionalities by plasma treatment. In this study, all composites were prepared at fibre loading of 3 phr of the ABS. As studied in the previous section, the optimum plasma treatment condition was used in this experiment, i.e., discharge power of 30 w and chamber pressure of 0.1 torr. The effect

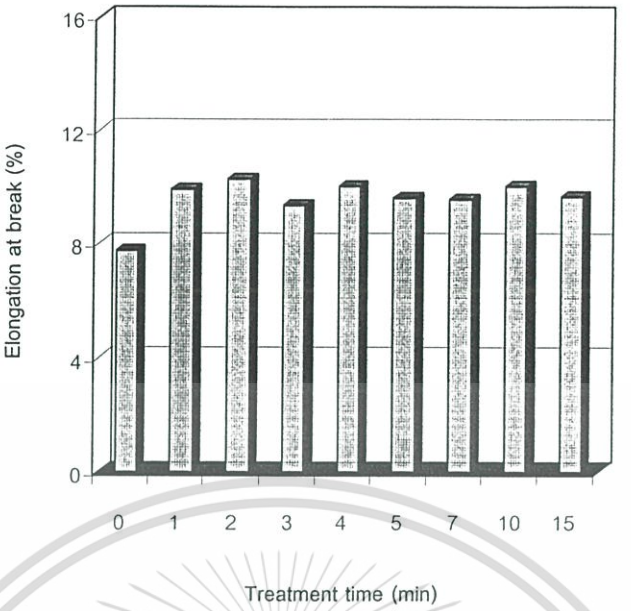
of treatment times on mechanical properties of the composites was investigated (Figures 4.8a-4.8f).



(a)



(b)



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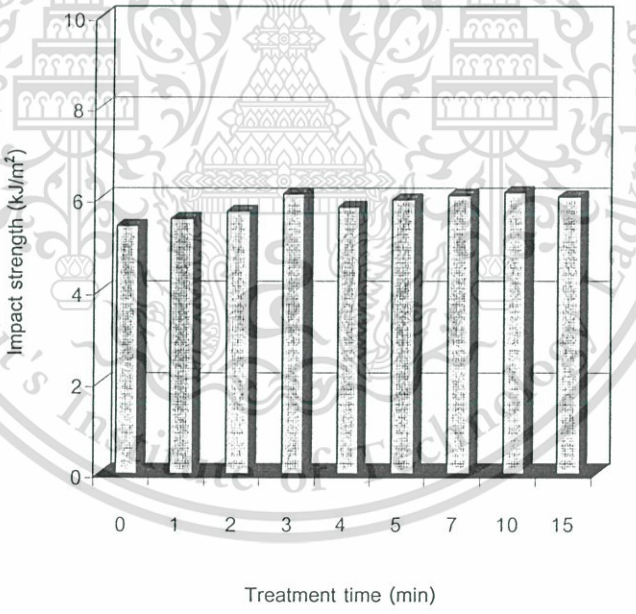
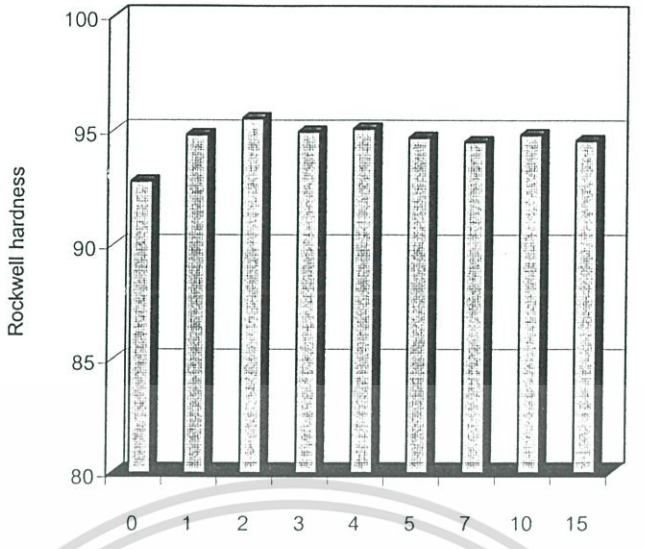
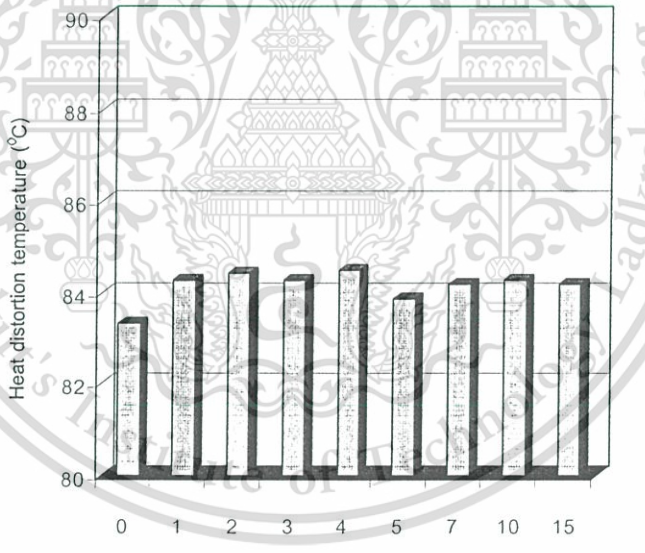


(d)



(e)



(f)

Figure 4.8 Effect of treatment times on mechanical properties of composites a) modulus at 3% strain b) tensile strength c) elongation at break d) impact strength e) Rockwell hardness f) heat distortion temperature

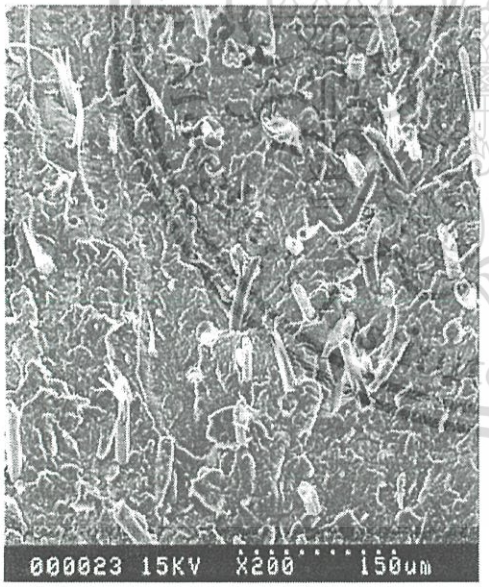
The effect of the plasma treatment time on the modulus of the composites was shown in Figure 4.8a. It can be seen that there was a little difference in the modulus between the untreated and plasma treated composites. In treatment time of 1-2 minutes, there was no effect on modulus at 3% strain of the composites. The maximum strength of the composite was optimized when treated at 3 minutes and then decreased as the treatment time increased. The tensile strength of composites was shown in Figure 4.8b. The result was similar to that of the modulus at 3% strain. The composite reinforced with treated Kevlar short fibres at 3 minutes showed higher tensile strength than that obtained from the untreated fibres. The increase in tensile strength might be due to the improvement of interfacial adhesion between the Kevlar fibres and ABS. It was likely to believe that the treated Kevlar short had higher surface roughness than the untreated one generating the mechanical bonding and therefore the properties were improved. The decrease in tensile strength was significant when the fibre was treated at long reaction time. It was found that the over treatment time can cause the fibre surfaces to be etched vigorously and the decrease in fibre strength. The result was similar to the results obtained by Wu *et.al* (21). Figure 4.8c shows the effect of treatment time on elongation at break of the composites. After treatment, elongation at break was higher than that of the untreated one. The result of impact strength of the composites was shown in Figure 4.8d. It can be seen that the impact strengths of the treated composites were higher than those of the untreated composites. The treatment time showed a small effect on the impact strength. The results of Rockwell hardness and HDT were shown in Figures 4.8e and 4.8f. After treatment the values of those properties were improved, however, the treatment times had no effect on both properties.

4.2.4 Morphology of fractured Kevlar short fibres/ABS composites

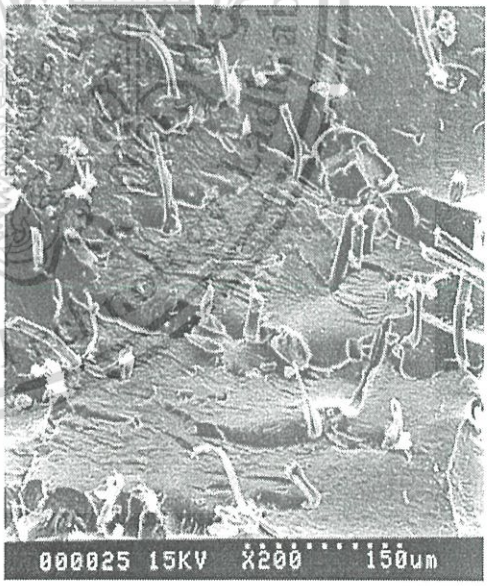
The interfacial adhesion between the fibre and ABS was investigated by SEM in order to observe the effect of plasma treatment of Kevlar fibres. The SEM micrographs of fractured Kevlar short fibres/ABS composites were shown in Figures 4.9a-4.9i and 4.10a-4.10i at magnifications of x200 and x2200, respectively.

(a)

(b)



(c)



(d)

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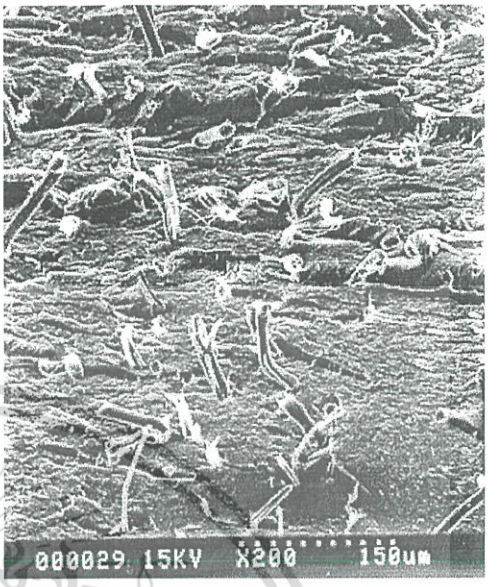
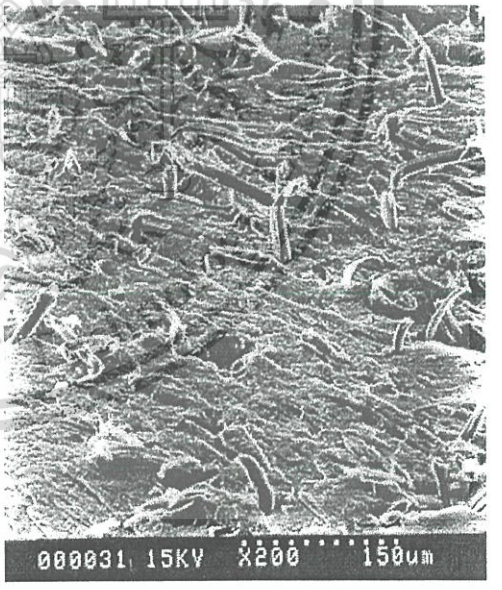


(f)

(g)

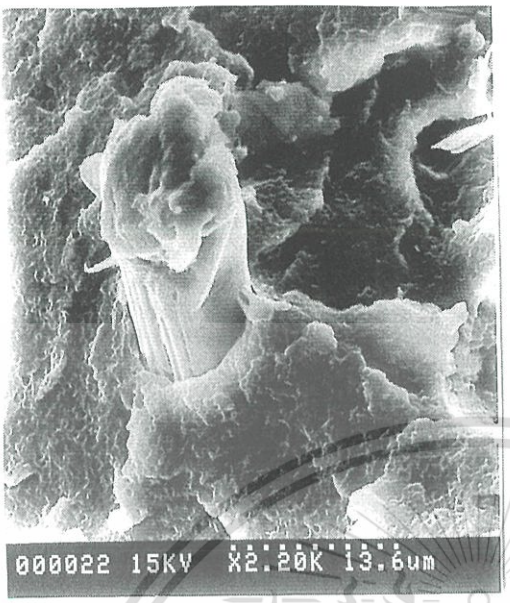


(h)

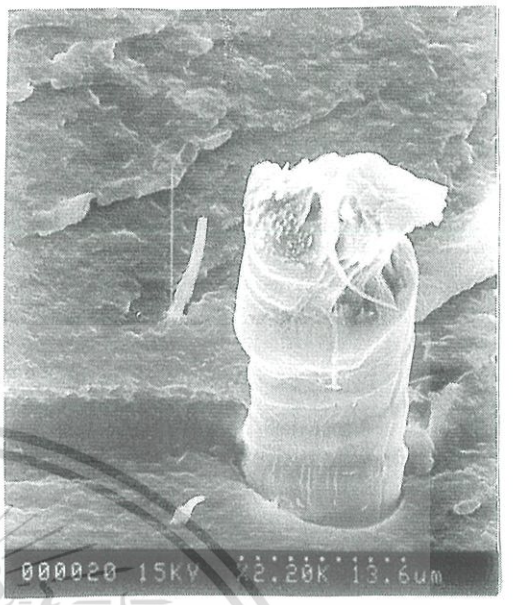
(i)

Figure 4.9 SEM micrographs of fractured surface of 3% Kevlar short fibres/ABS composites: a) 0 min b) 1 min c) 2 min d) 3 min e) 4 min f) 5 min g) 7 min h) 10 min i) 15 min

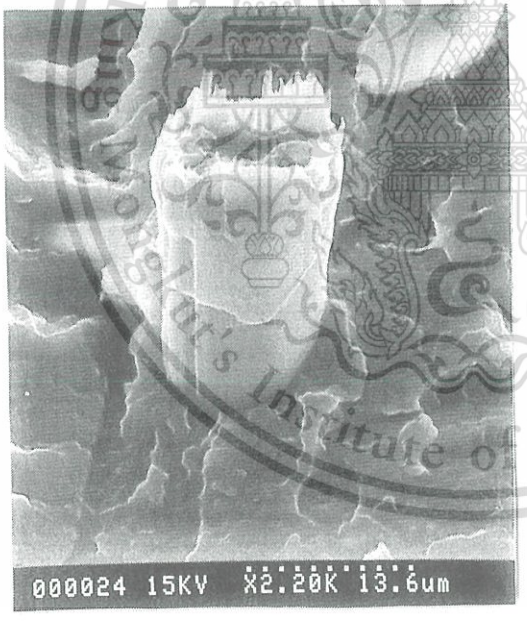
The factured surface of the untreated Kevlar composites (Figure 4.9a) showed long pull-out fibres and a number of holes, which indicate the poor interfacial adhesion between the fibres and the matrix. On the other hand, the fractured surfaces of the treated Kevlar composites (Figures 4.9b-4.9i) showed more fibre breakage than fibre pull-out. This evidence confirms that the plasma treatment of fibre can improve the fibre-matrix adhesion at the interface. Clearer pictures can be seen in Figures 4.10a-4.10i at the magnification of x2200.



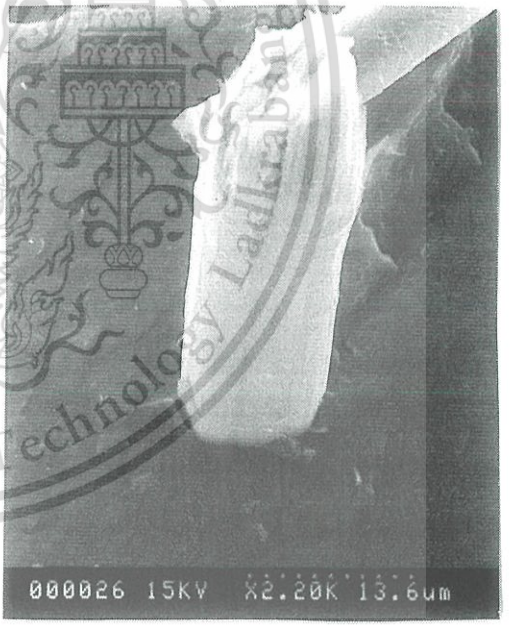
(a)



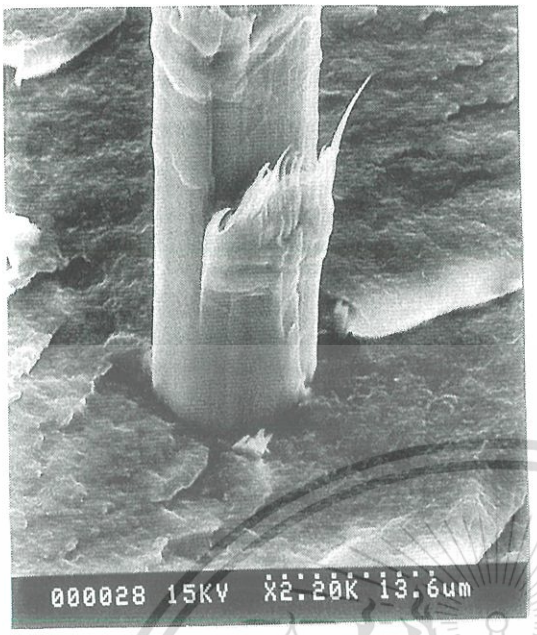
(b)



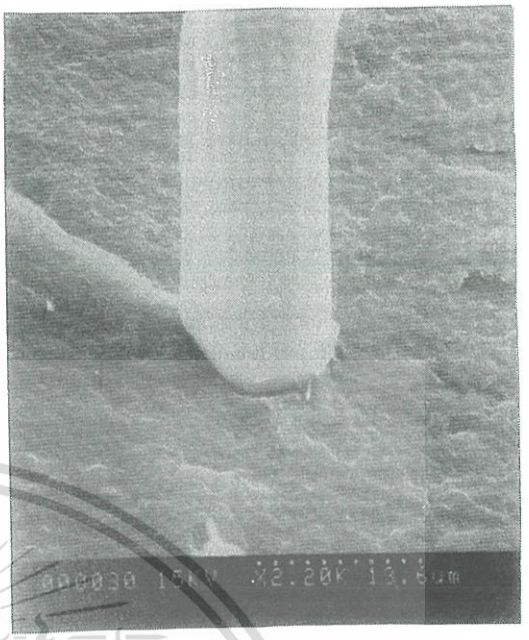
(c)



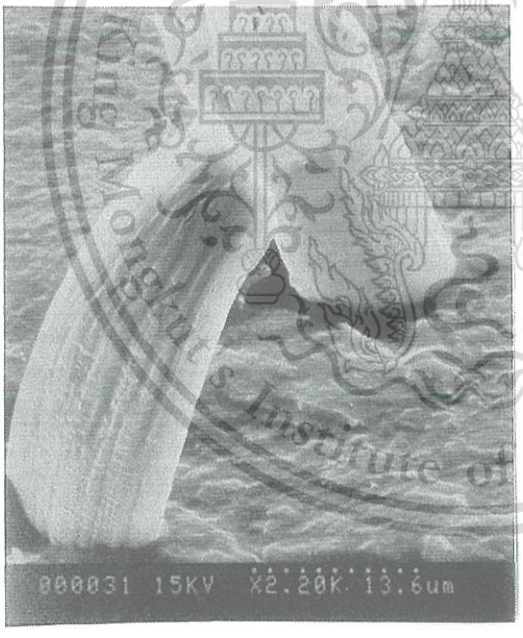
(d)



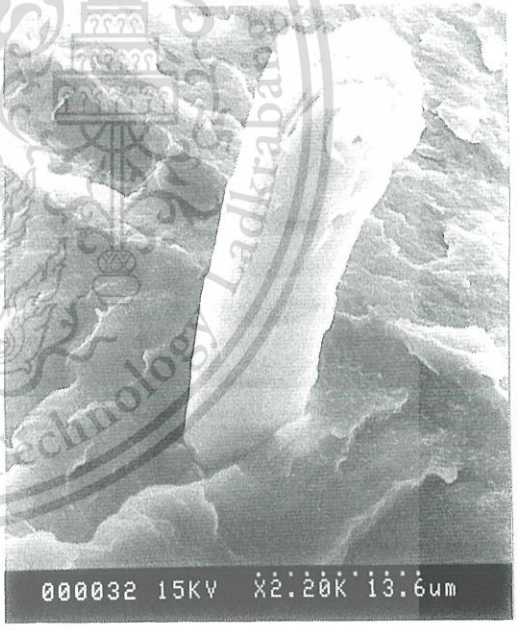
(e)



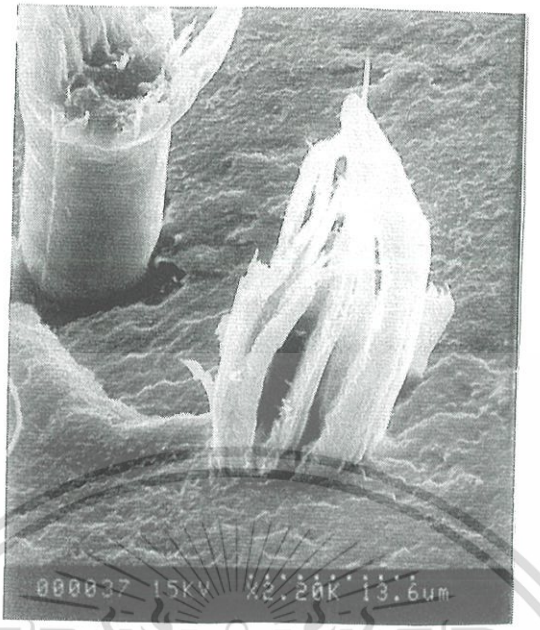
(f)



(g)



(h)



(i)

Figure 4.10 SEM micrographs of fractured surface of 3% Kevlar short fibres/ABS Composites: a) 0 min b) 1 min c) 2 min d) 3 min e) 4 min f) 5 min g) 7 min h) 10 min i) 15 min

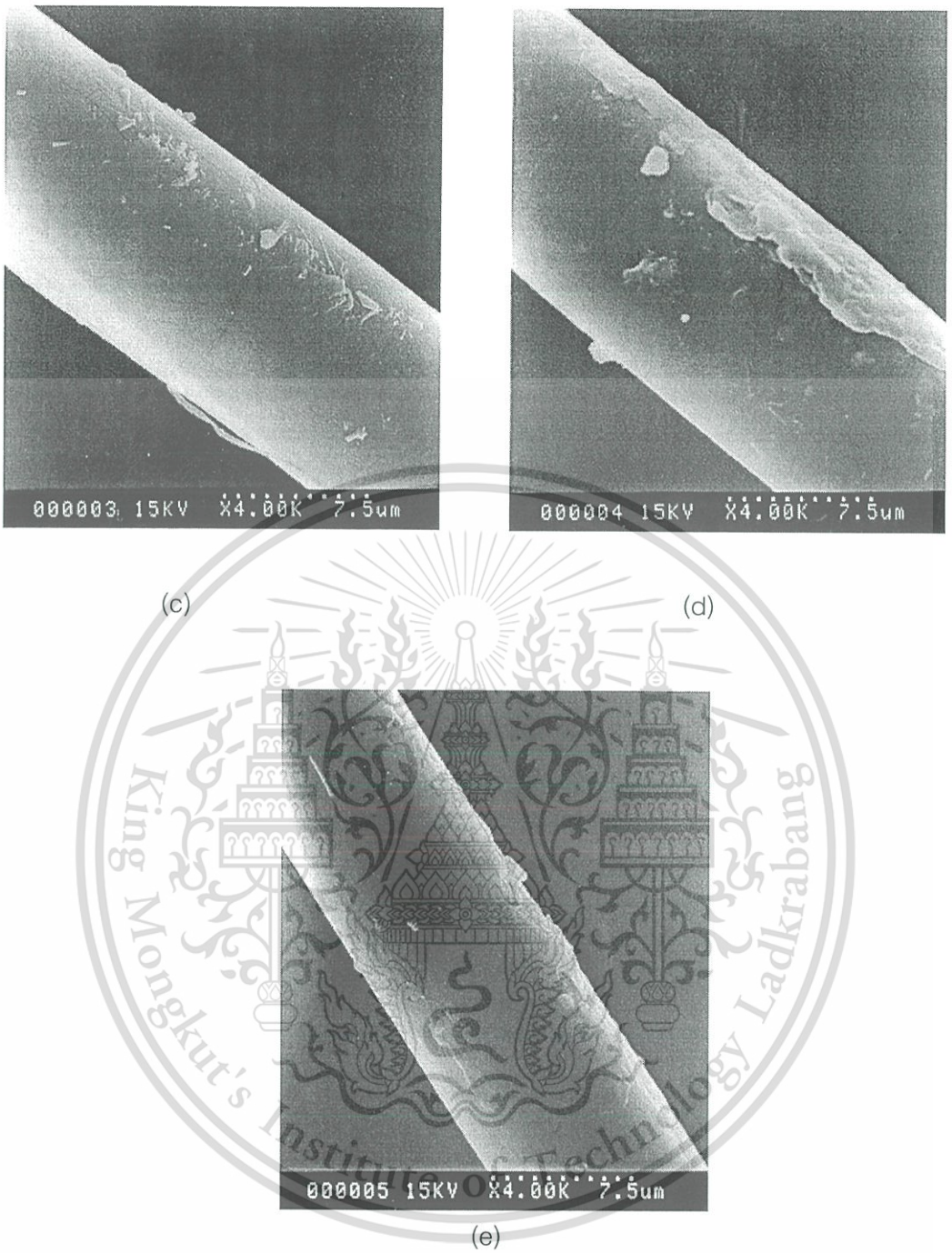
Figure 4.10 showed adhesion between the fibre and the matrix. It was found that no gap at the base of the treated fibres as shown in the case of untreated fibres. This indicated that the adhesion between the fibre and the matrix had been improved by the plasma treatment.

4.3 Study of the effect of surface treatment by isocyanate on mechanical properties of Kevlar short fibres/ABS composites

4.3.1 Effect of the treatment by isocyanate on surface morphology of Kevlar Short fibres

SEM technique was used to characterize the surface of the Kevlar fibres after treating with isocyanate. The SEM micrographs of Kevlar short fibres were shown in Figures 4.11a-4.11e.

(a) (b)



(c) (d)

(e)

Figure 4.11 SEM micrographs of Kevlar short fibres

a) untreated

b) treated by isocyanate for 30 sec

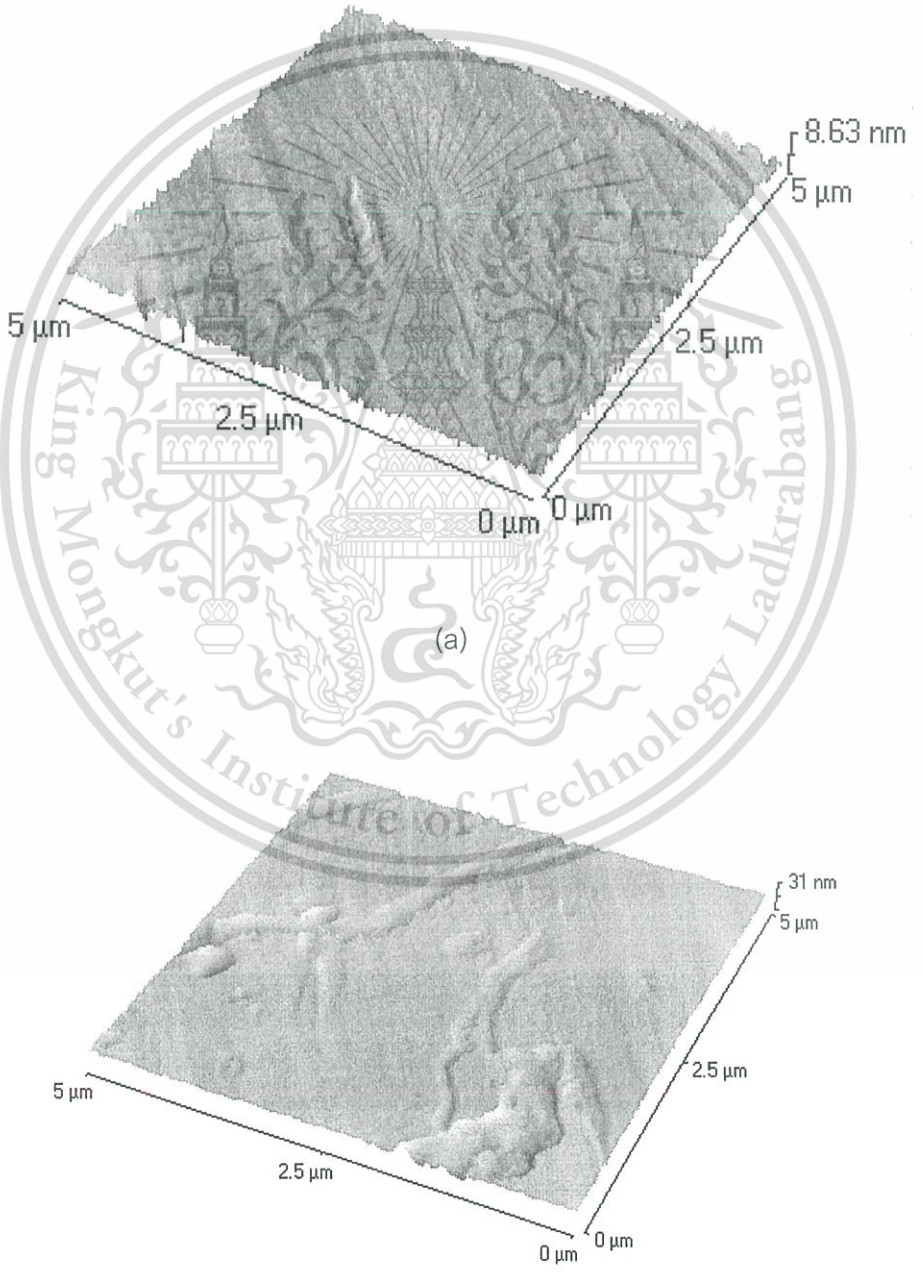
c) treated by isocyanate for 10 min

d) treated by plasma + treated by isocyanate for 30 sec

e) treated by plasma + treated by isocyanate for 10 min

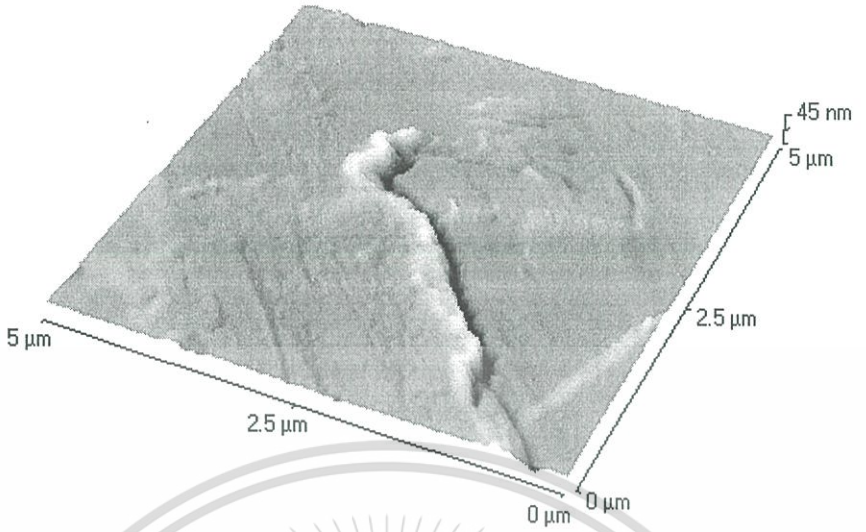
Figures 4.11a-4.11e show that after the treatment there were some particles and films on the surface of the fibres. However the treatment time by isocyanate has no effect on the fibres because isocyanate is one of reactive chemicals that have high activity to react with other substances.

AFM technique was used to characterize the surface of the Kevlar fibres after treating with isocyanate. The AFM images of Kevlar short fibres were shown in Figures 4.12a-4.12e.

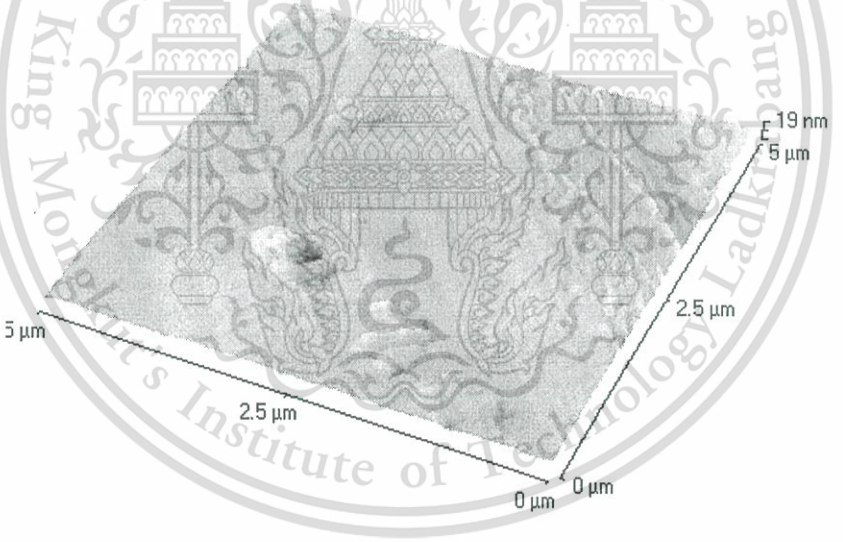


(a)

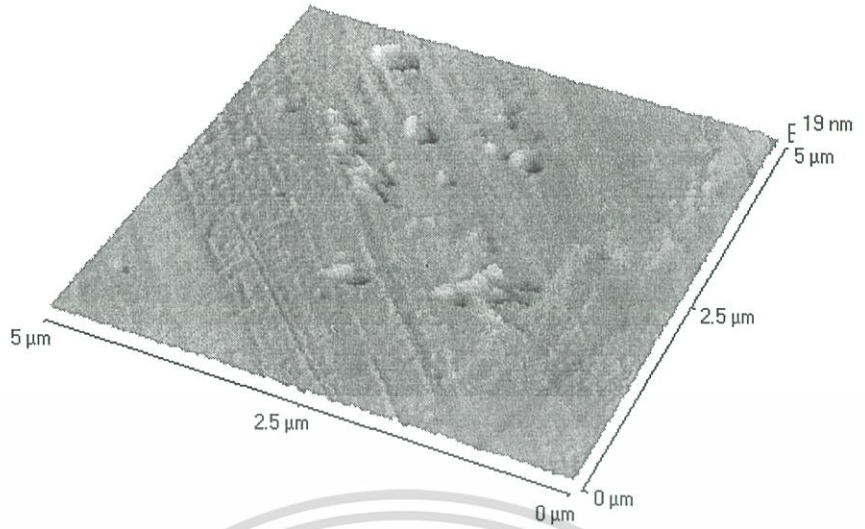
(b)



(c)



(d)



(e)

Figure 4.12 AFM images of Kevlar short fibres

a) untreated

b) treated by isocyanate for 30 sec

c) treated by isocyanate for 10 min

d) treated by plasma +treated by isocyanate for 30 sec

e) treated by plasma + treated by isocyanate for 10 min

The results from AFM studies (Figures 4.12a-4.12e) were similar to those of SEM micrographs. It was found that after the treatment there were some particles and films on the surface of the fibres. From the AFM results, an arithmetic mean of the area roughness and area measurement were calculated as shown in Table 4.2.

Table 4.2 Surface roughness of Kevlar short fibres treated by isocyanate

Sample	Area roughness (nm)		Surface area (μm^2)
	R_a	R_{ms}	
Untreated	0.5731	0.7634	25.20
Untreated + dip isocyanate 30 sec	1.2234	1.9462	25.53
Untreated + dip isocyanate10 min	1.5464	2.9273	25.55
Treated plasma+ dip isocyanate 30 sec	0.8059	1.1507	25.21
Treated plasma+ dip isocyanate 10 min	0.8135	1.2117	25.41

From Table 4.2, the results showed that after treated by isocyanate the average roughness (R_a), root-mean-square roughness(R_{ms}), and surface area were increased. However the treatment time by isocyanate has no effect on the fibres. From this study, in comparison of treatment by isocyanate together with and without plasma, it was found that the treatment of isocyanate without plasma yielded the fibres with more roughness than that of isocyanate with plasma.

4.3.2 Study of mechanical properties of Kevlar short fibres/ABS composites treated by isocyanate

In this study, treatment of isocyanate together with and without plasma were carried out on Kevlar short fibre surfaces. The mechanical properties of both composites were investigated. The stress-strain curves of untreated and treated Kevlar short fibres/ABS composites were shown in Figure 4.13.

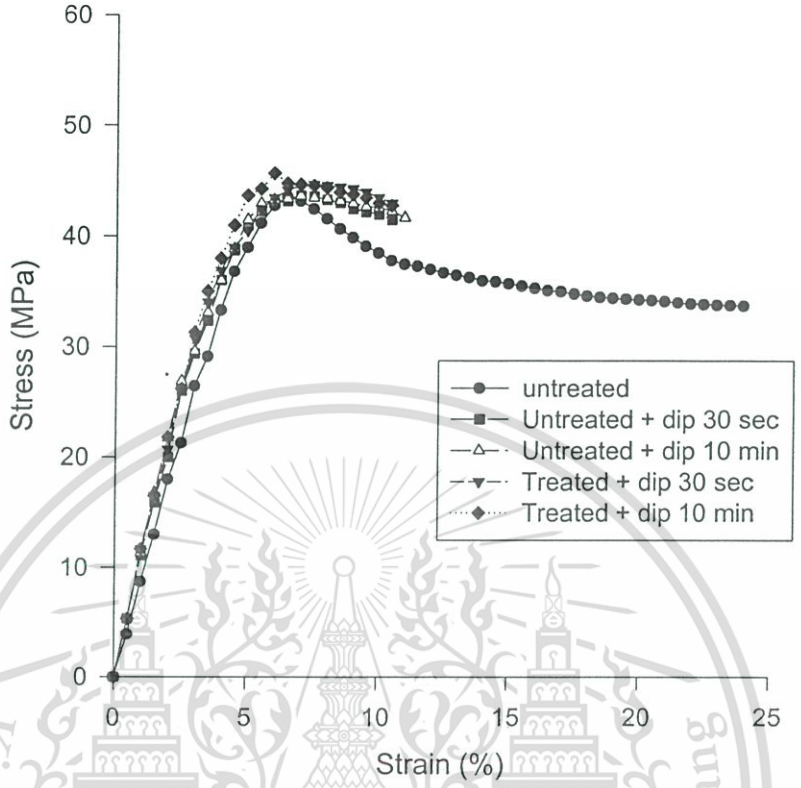
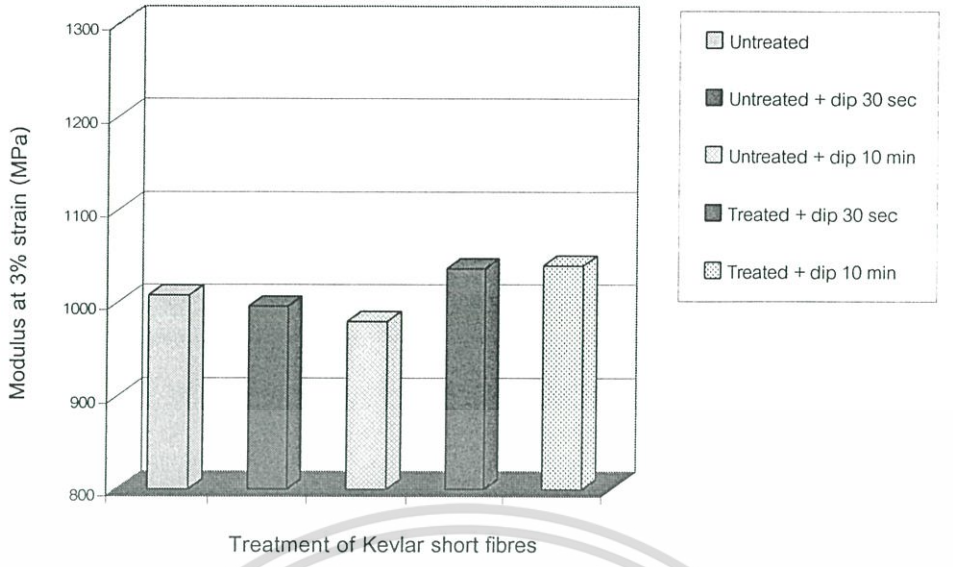


Figure 4.13 Stress-strain curves of treated Kevlar short fibres/ABS composites

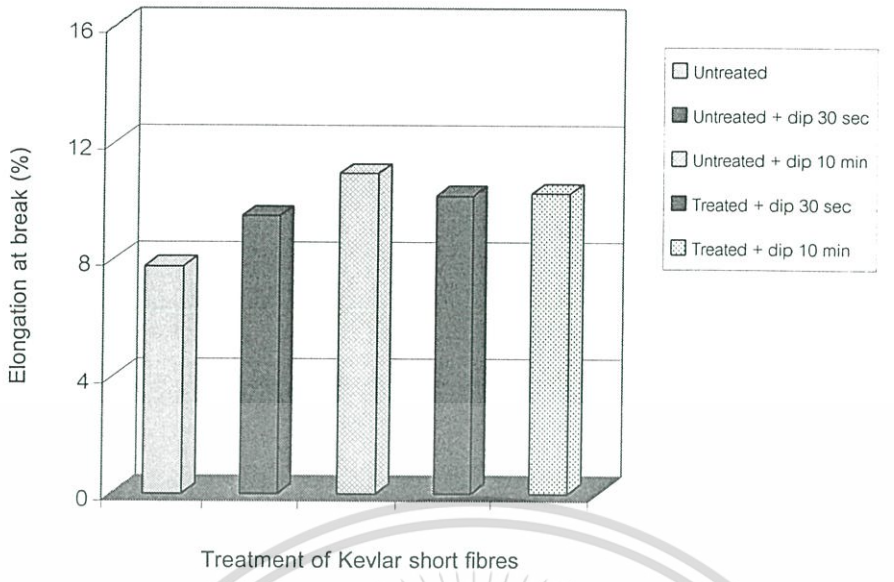
The result from Figure 4.13 showed that the treated of Kevlar composites had higher moduli than the untreated Kevlar composites

Figures 4.14a-4.14f show the effect of the treatment on modulus at 3 % strain, tensile strength, elongation at break, impact strength, Rockwell hardness and heat distortion temperature of the composites, respectively.

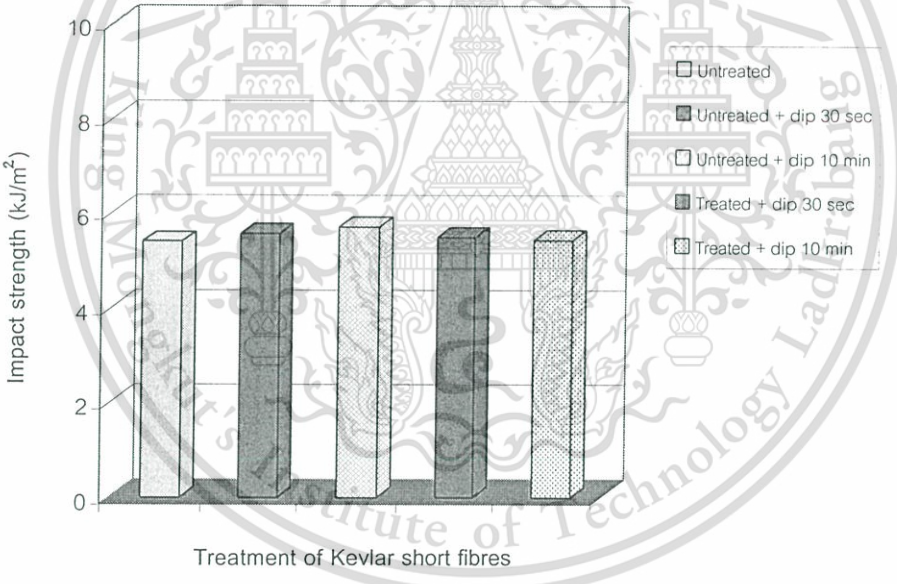


(a)

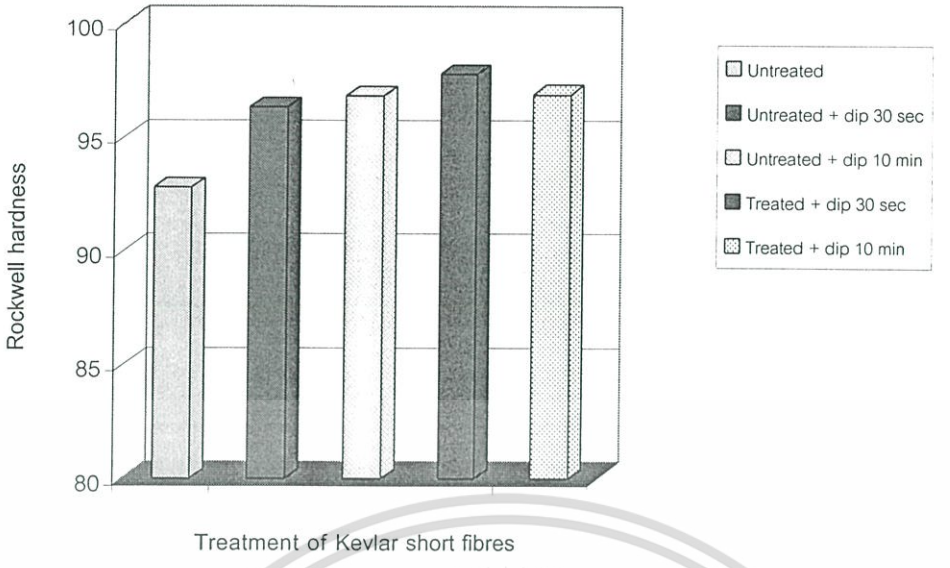
(b)



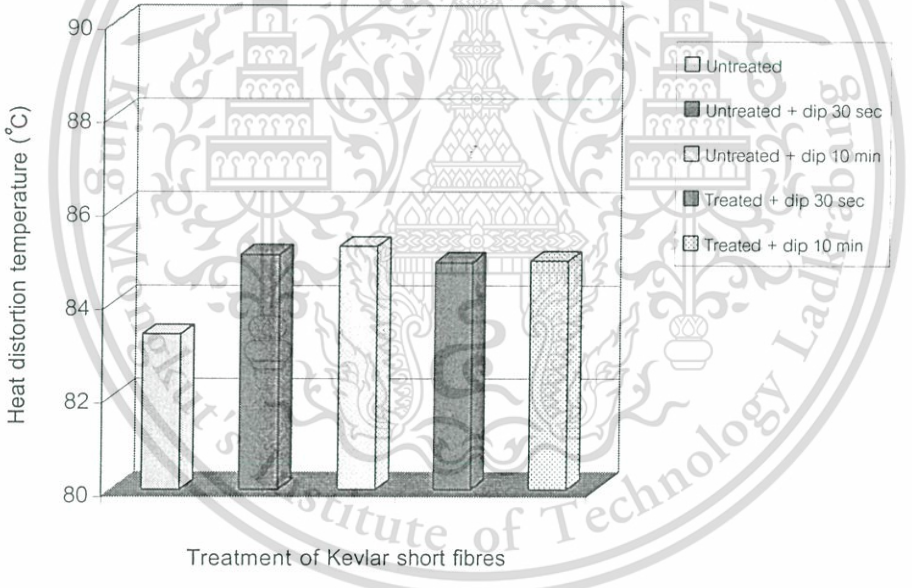
(c)



(d)



(e)



(f)

Figure 4.14 Effect of the treatment on mechanical properties of composite
a) modulus at 3% strain b) tensile strength c) elongation at break
d) impact strength e) Rockwell hardness f) heat distortion temperature

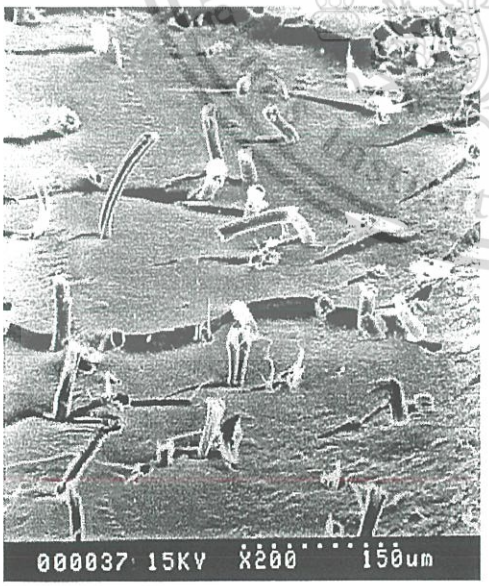
From the results presented in Figure 4.14 , it appears that the fibre treatment by plasma followed by isocyanate would affect in some mechanical properties of the composites. The modulus at 3% strain of Kevlar treated by isocyanate was not different compared to untreated composites. However the modulus of fibres treated by plasma and followed by isocyanate was increased (Figure 4.14a). The composites of both treatments showed same tensile strength that obtained from untreated Kevlar (Figure 4.14b). The elongation at break of composites was shown in Figure 4.14c. It can be seen that after the treatment, elongation at break was increased. The increased modulus, tensile and elongation of composites showed that the adhesion between fibres and the matrix was improved by treated with plasma for 3 min and followed by isocyanate. Figure 4.14d shows the impact strength of composites. The small improvement was seen in both treatment. The Rockwell hardness and heat distortion temperature of composites show in Figures 4.14e and 4.14f. It can be seen clearly that both properties were increased after treated by isocyanate and treated by plasma and followed by isocyanate.

4.3.3 SEM micrograph of Kevlar short fibres/ABS composite treated by isocyanate

The fractured surfaces of Kevlar short fibres/ABS composites were studied by SEM. The SEM micrographs of Kevlar short fibres/ABS composites were shown in Figures 4.15a-4.15e and 4.16a-4.16e at magnification of x200 and x2200, respectively.

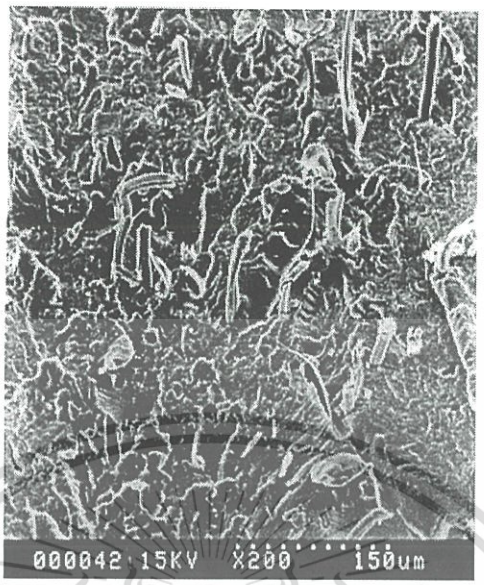
(a)

(b)



(c)

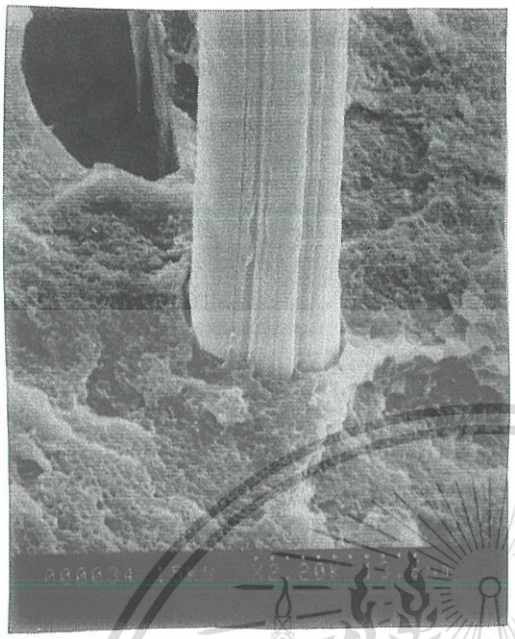
(d)



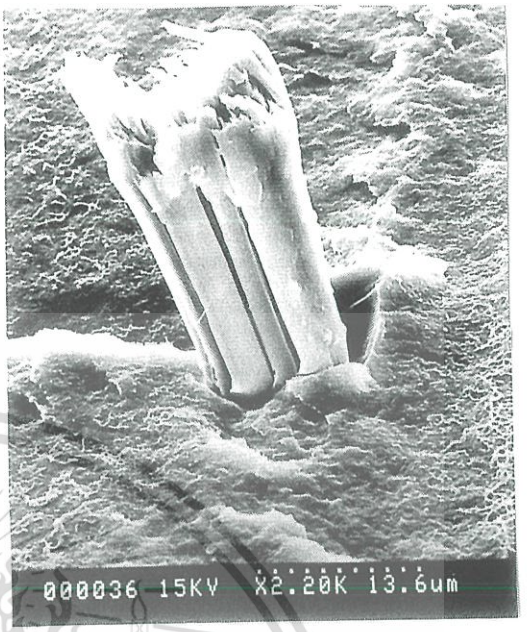
(e)

Figure 4.15 SEM micregraphs of Kevlar short fibres/ABS composites
a) untreated
b) treated by isocyanate for 30 sec
c) treated by isocyanate for 10 min
d) treated by plasma +treated by isocyanate for 30 sec
e) treated by plasma + treated by isocyanate for 10 min

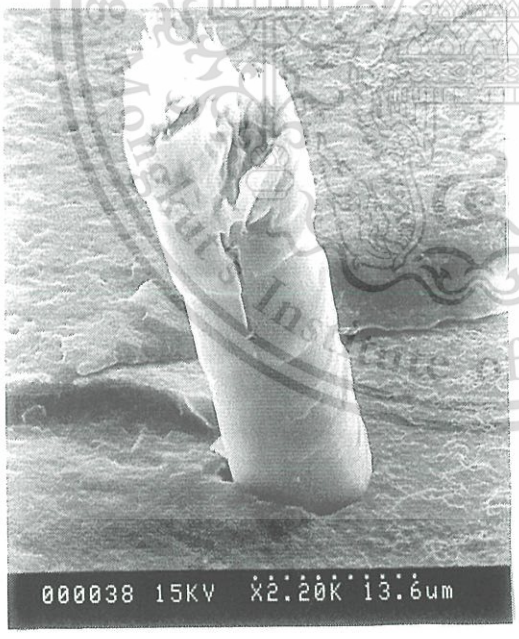
Form Figures 4.15a-4.15e, it can be seen that fractured surfaces of the composites treated by isocyanate and treated by plasma then followed by isocyanate showed short pull-out fibres than untreated Kevlar fibres. However, the treatment times of treated by isocyanate had no effect on the fibres. The treatment with and without plasma had a little effect on the composites. Clearer pictures can be seen in Figures 4.16a-4.16e at magnification x 2200.



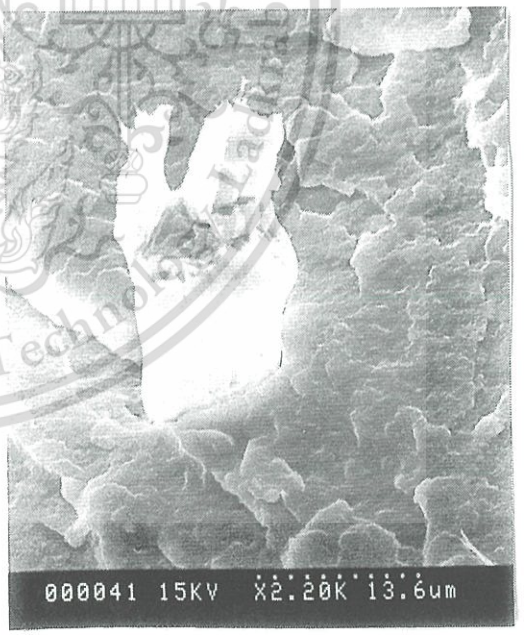
(a)



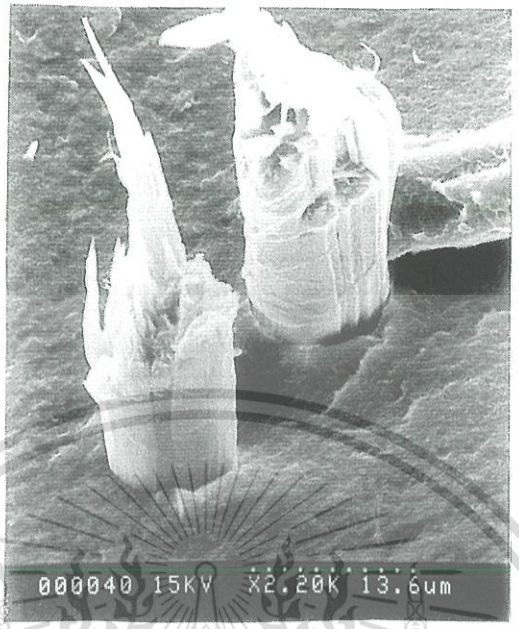
(b)



(b)



(d)



(e)

Figure 4.16 SEM micregraphs of Kevlar short fibres/ABS composites
a) untreated
b) treated by isocyanate for 30 sec
c) treated by isocyanate for 10 min
d) treated by plasma +treated by isocyanate for 30 sec
e) treated by plasma + treated by isocyanate for 10 min

From Figures 4.16a-4.16e, it can be seen that after treated by isocyanate with and without plasma had no change on the fibres. However the surface of the fibre in the untreated Kevlar composites (4.16a) was smoother than that of treated Kevlar composites (4.16b-4.16e).

CHAPTER V

CONCLUSION AND SUGGESTION

Part I : Surface modification of Kevlar short fibres by plasma treatment

In this study, the effect of plasma treatment on Kevlar short fibre surfaces was investigated. Both plasma and isocyanate treatment generate surface roughness on the fibres which in-turn improve the interfacial adhesion between the Kevlar short fibres and the matrix.

Part II : Study of the effect of surface treatment by plasma treatment on mechanical properties of Kevlar short fibres/ABS composites

Attempts had been made to improve the adhesion between Kevlar fibres and ABS matrix by modifying the fibre surfaces using plasma treatment. The following conclusions could be drawn:

1. Incorporation of Kevlar short fibres into ABS matrix could improve mechanical properties of the composite due to the outstanding mechanical properties of the fibres.

2. Modulus at 3% strain, tensile strength and HDT were increased, elongation at break and impact strength were decreased and no significant change of hardness is observed, as the loading of Kevlar fibre was increased.

3. Surface treatment of Kevlar short fibres by plasma treatment led to an improvement of the mechanical properties of composites.

4. The fractured surfaces of the composites with the untreated Kevlar showed higher proportion of fibre pull-out from the matrix than that of composites with treated Kevlar. This might be due to the mechanical interlocking between the fibre and the matrix through roughening of the fibre surfaces might also help improving interfacial adhesion. It can be concluded that the improvement of mechanical properties of the treated Kevlar/ABS composites is due to the physical force arised from the surface roughness.

Part III : Study of the effect of surface treatment by isocyanate on mechanical properties of Kevlar short fibres/ABS composites

In this study, surface treatment by isocyanate was carried out to modify Kevlar fibre surfaces in order to improve the adhesion between the fibres and ABS matrix. The following conclusions could be drawn:

1. By treated the fibres with isocyanate but without plasma, the modulus and tensile strength of the composites were not improved. However elongation, impact strength, and HDT were enhanced. By treated the fibres with isocyanate together with plasma, both mechanical and thermal properties of composites were improved.

2. Fractured surfaces of both treated composites revealed better interfacial adhesion between the fibres and the matrix than that of the untreated composites.

Suggestions for further work

1. The effect of conditions in plasma treatment should be investigated in more details such as flow rate, gas.

2. Other fibres to reinforce the matrix by plasma treatment to improve the adhesion between fibres and the matrix should be investigated such as Conex fibre.

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APPENDICES

APPENDIX A

Condition of Injection molding machine for preparing tensile and impact specimens.

TEMPERATURE PROGRAMMING

NOZZLE	TEMP.	210
ZONE 1	TEMP.	200
ZONE 2	TEMP.	195

TIME PROGRAMMING

DIE CLS/OPN	TIME	60	MELTING	TIME	120
SID-COR ACT	TIME	0	DECOMPRS	TIME	2
1ST STG. INJ.	TIME	20	COOLING	TIMR	200
2ND STG. INJ.	TIME	15	EJECTOR	COUNT	2
3RD STG. INJ.	TIME	10	SCW.FEW.	TIME	0
EJE.FWD.DLY	TIME	0	SCW.BWD.	TIME1	0
MEL.FWD.DLY	TIME	0	SCW.BWD	TIME2	0
EJE.BKD.DLY	TIME	0	ALARM	TIME	500

PROGRAMMING FLOW SPEED

RAPID CLS.	SPD.	40	1ST STG. INJ.	SPD.	40
HIGH CLS.	SPD.	25	2ND STG. INJ.	SPD.	25
CLAMPING	SPD.	15	3RD STG. INJ.	SPD.	25
DIE OPN.	SLW.1	10	MELTING	SPD.	35
RAPID OPN.	SPD.	25	DECOMP.	SPD.	30
DIE OPN.	SLW.	15	EJECTOR	SPD.	20
PLUNGER	SPD.	20	SCREW-IN	SPD.	0
DIE ADJ.	SPD.	25	DIE CHANGE	SPD.	50

PRESSURE PROGRAMMING

DIE CLS.	PRESR.	25	MELTIN	PRESR.	80
CLS. LOW	PRESR.	30	DECOMP.	PRESR.	70
CLS. HI	PRESR.	50	PLUNGER	PRESR.	35
DIE OPN.	PRESR.	30	EJECTOR	PRESR.	30
1^{ST} INJ.	PRESR.	60	SCW.-IN	PRESR.	10
2^{ND} INJ.	PRESR.	55	DIE ADJ.	PRESR.	50
3^{RD} INJ.	PRESR.	50			

APPENDIX B

Tables of mechanical properties of Kevlar short fibres / ABS composites

Table B.1 Effect of Injection temperature on mechanical properties of composites

Properties / Temperature	Modulus at 3% strain (MPa)		Tensile strength (MPa)		Elongation at break (%)		Impact strength (kJ/m^2)	
	Mean	SD	Mean	SD	Mean	SD	Mean	SD
190^{0}C	907.03	12.77	43.36	0.61	10.58	2.64	8.83	0.11
200^{0}C	908.72	15.61	44.43	0.71	11.08	1.98	9.72	2.81
210^{0}C	912.39	16.69	44.92	0.66	12.06	2.89	12.04	1.02
220^{0}C	872.92	25.09	43.45	1.0	11.76	3.3	11.71	0.49
230^{0}C	890.16	22.37	43.68	0.7	9.91	0.62	9.31	0.63

Table B.2 Effect of Kevlar short fibres loading on mechanical properties of composites

Properties	Modulus at 3% strain (MPa)		Tensile strength (MPa)		Elongation at break (%)		Impact strength (kJ/m^2)		Rockwell Hardness (Rockwell R)		HDT (°C)	
Kevlar content (%)	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD
0	880.81	21.18	43.99	1.03	13.78	3.13	9.87	0.36	91.6	1.41	82.13	0.51
1	1008.19	35.92	44.89	1.26	9.03	1.09	6.92	0.35	91.81	1.75	84.43	0.23
3	1041.08	13.69	45.89	0.76	7.74	0.40	5.40	0.24	92.77	1.20	84.33	0.55
5	1090.0	17.21	48.68	1.15	8.43	0.65	5.36	0.16	92.07	1.01	85.43	0.15
7	1217.6	12.27	51.46	0.73	8.59	0.45	5.32	0.26	92.15	1.57	87.2	0.2
10	1249.0	22.38	53.5	1.48	8.52	0.59	5.34	0.15	92.59	1.56	88.3	0.4

Table B.3 Effect of treatment times on mechanical properties of composites

Properties	Modulus at 3%strain (MPa)		Tensile strength (MPa)		Elongation at break (%)		Impact strength (kJ/m^2)		Rockwell Hardness (Rockwell R)		HDT (°C)	
Treatment time (min)	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD
0	1008.1	13.7	45.29	0.76	7.75	0.4	5.4	0.24	92.77	1.2	83.33	0.56
1	998.5	10.68	43.25	1.19	9.91	1.21	5.58	0.26	94.79	1.86	84.27	0.7
2	996.47	9.10	43.57	0.98	10.23	1.56	5.71	0.39	95.53	2.38	84.43	0.15
3	1048.67	20.6	51.74	1.59	9.32	0.82	6.10	0.14	94.91	0.65	84.27	0.21
4	1018.14	28.67	44.4	1.10	9.99	1.27	5.81	0.29	95.07	2.65	84.5	0.17
5	1031.64	15.4	46.0	1.50	9.57	0.42	5.97	0.20	94.67	1.73	83.87	0.44
7	1028.42	20.87	44.13	0.75	9.53	0.87	6.07	0.16	94.48	2.33	84.17	0.06
10	1013.8	19.43	43.64	1.15	9.97	0.90	6.13	0.26	94.81	2.03	84.27	0.21
15	1003.89	20.93	44.59	0.73	9.64	0.87	6.05	0.18	94.56	1.0	84.17	0.21

Table B.4 Effect of the treatment by isocyanate on mechanical properties of composites

Properties / Sample	Modulus at 3%strain (MPa)		Tensile strength (MPa)		Elongation at break (%)		Impact strength (kJ/m^2)		Rockwell Hardness (Rockwell R)		HDT (°C)	
	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD
Untreated	1008.1	13.7	45.29	0.76	7.75	0.4	5.4	0.24	92.77	1.2	83.33	0.56
Untreated+ dip isocyanate 30 sec	995.92	28.48	43.44	0.71	9.49	0.82	5.57	0.15	96.31	2.36	85.03	0.65
Untreated+ dip isocyanate 10 min	980.28	21.84	43.76	0.58	10.95	0.57	5.71	0.22	96.81	2.34	85.2	0.1
Treated plasma+ dip isocyanate 30 sec	1036.53	29.34	44.81	0.93	10.18	0.87	5.48	0.25	97.76	2.07	84.87	0.38
Treated plasma+ dip isocyanate10 min	1039.28	30.46	44.59	0.65	10.26	0.51	5.43	0.21	96.87	1.99	84.9	0.1

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