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รายชื่อผู้ทำงานในโครงการวิจัย ทุนเมธีวิจัยอาวุโส-สกว เสาวรภย์ บัวเล็ก-ลิ้มเจริญ

ชื่อ-นามสกุล	ตำแหน่งวิชาการ		ต้นสังกัด			ตำแหน่งในโครงการ	สถานภาพปัจจุบัน
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6 ชาคริต สิริสิงห	อาจารย์	ผู้ช่วยศาสตราจารย์	เคมี	วิทยาศาสตร์	มหิดล	ผู้ร่วมวิจัย	
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8 ธีรวุฒิ นคินพงษ์			เคมี	วิทยาศาสตร์	มหิดล	นักศึกษาปริญญาโท	บริษัท TPI
9 วรพงษ์ ชวลิตอัมพร			เคมี	วิทยาศาสตร์	มหิดล	นักศึกษาปริญญาโท	โรงเรียนศรีวิกรม์
10 จรีรัตน์ สำราญ			เคมี	วิทยาศาสตร์	มหิดล	นักศึกษาปริญญาโท	มหาวิทยาลัยสงขลานครินทร์, ปัตตานี
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12 อนงค์นุช จันทรัตน์เจริญ			เคมี	วิทยาศาสตร์	มหิดล	นักศึกษาปริญญาโท	บริษัท Bang Trading
13 บรรจบ วันโน			เคมี	วิทยาศาสตร์	มหิดล	นักศึกษาปริญญาโท	มหาวิทยาลัยมหาสารคาม
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18 ภัควดี สุขอนันต์			เคมี	วิทยาศาสตร์	มหิดล	นักศึกษาปริญญาเอก	

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KEVLAR PULP-THERMOPLASTIC ELASTOMER COMPOSITES: MORPHOLOGY AND MECHANICAL PROPERTIES

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ABSTRACT

Reinforcement of Styrene (Ethylene Butylene) Styrene thermoplastic elastomer (SEBS) with Kevlar pulp was investigated. Surface treatment of the fibre was carried out by alkali hydrolysis in order to increase the number of reactive groups. Maleic anhydride-grafted-SEBS was used as a compatibiliser. The composites were prepared by a one step process in an internal mixer. Mechanical properties of the composites were assessed using a tensile testing machine. The results suggested that as the loading of Kevlar pulp increased, tensile modulus increased but tensile strength and elongation at break decreased. The fracture surface of the composites observed under Scanning Electron Microscope (SEM) revealed fibre pull-out in the composite without compatibiliser and more fibre breakage were observed in the samples containing compatibiliser. Quantitative analysis of the adsorbed elastomer on the fibre surface using gravimetric, diffuse reflectance FTIR (DRIFT) techniques and observation of SEM micrographs of extracted pulp showed that in the presence of compatibiliser, a large amount of elastomer was adsorbed. However, SEBS-g-MA showed no remarkable effect on the tensile properties of the composites and this might be due to uneven adsorption of rubber particles.

INTRODUCTION

The excellent thermal and mechanical properties of poly (*p*-phenylene terephthalamide) (aramid) fibre make it a good candidate as reinforcement fibre in polymer composites. The main problem due to poor adhesion between the fibre and a polymer matrix, however, does exist and continues to pose a challenge to researchers. Vaughan[1] applied various commercial coupling agents and obtained some improvement on adhesion. Other efforts to modify the fibre by dispersion of fibre in an ionomer matrix seemed to be very effective[2,3]. Marom *et al.*[4] proposed a surface treatment technique using bromine water which led to surface roughening and resulted in improvement of interlaminar shear strength. Andreopoulos[5] used various compounds to promote adhesion of Kevlar fibre and pulp with unsaturated polyester. Treatment of fibre with methacryloyl chloride resulted in considerably high tensile strength compared to that of composites incorporating untreated fibre. Wang *et al.*[6] prepared plasma treated aramid fibre-polyethylene composites. The reactive groups such as -COOH, -OH, $-NH_2$ were generated on the aramid fibre surface using oxygen plasma. These groups were used to chemically anchor Ziegler-Natta catalyst to the fibre surface, which was then followed by ethylene polymerisation on the surface. This type of composites exhibit higher tensile strength both in parallel and transverse to the fibre direction. Yu *et al.*[7] studied nylon/Kevlar composites and found that Kevlar could be used to reinforce nylon. The effect of various surface treatment methods, *e.g.* hydrolysis and hydrolysis followed by chemical grafting with acid chloride, were also studied. It was found that the mechanical properties of the composite could be improved by appropriate fibre treatment.

Recently, short-fibre reinforced elastomers have increasingly attracted more attentions by several researchers.[8-12] Reinforcements for such system mainly involved using conventional fibres like poly (ethylene terephthalate) (PET) and nylon. Consequently, the use of Kevlar fibre as a reinforcement in thermoplastics have become an interesting application of this high performance fibre.

The present work involved the studies of Kevlar pulp reinforced styrene (ethylene butylene) styrene (SEBS) thermoplastic elastomer. SEBS represented a model thermoplastic elastomer matrix to be reinforced by an organic fibre. From a molecular structure point of view, the two components are quite incompatible. Kevlar is a highly hydrogen-bonded polyamide while SEBS containing olefinic and styrenic blocks is relatively nonpolar. In order to obtain compatibility, chemical bonding was introduced by partially hydrolysing the amide bonds on Kevlar fibre surface followed by the addition of SEBS-grafted-maleic anhydride (SEBS-g-MA), a compatibiliser for this system. The formation of imide groups from the reaction of maleic anhydride and amine end groups on the fibre surface was expected[13]. This should be able to improve the adhesion of fibres and rubber matrix

EXPERIMENTAL

Materials

Styrene-(ethylene-co-butylene)-styrene (SEBS) triblock copolymer (Kraton G1652, Mn ≈ 83,700) and Maleated SEBS (Kraton FG1901x, Mn ≈ 85,000) were provided by Shell Chemical Co. Poly(*p*-Phenylene Terephthalamide) pulp (Kevlar 49) was provided by E.I. Du Pont .

Hydrolysis of Kevlar 49 pulp

Kevlar 49 pulp was first washed with acetone and distilled water in order to remove the possible surface impurities such as lubricating agents and dried in vacuum oven at 50°C . Ten grams of Kevlar pulp was dispersed in 400 ml 10 wt% aqueous NaOH solution at ambient temperature for 20 minutes. Following the hydrolysis, Kevlar 49 pulp was throughly washed with distilled water and toluene, dried in vacuum oven at 50°C for 48 hours and kept in desiccator.

Spectroscopic characterisation

Diffuse Reflectance Infrared Fourier Transform (DRIFT) spectrometer (Perkin Elmer FTIR 2000) was used to characterise the surface of Kevlar 49 pulp. Two hundred scans at a resolution 4 cm^{-1} and throughout the range 4,000-600 cm^{-1} were usually required to obtain a decent spectrum.

Preparation of SEBS/Kevlar 49 pulp composites

Pulp was first opened by using a Moulinex blender for half a minute, then it was put in the internal mixer, Haake Rheocord 90, together with SEBS and compatibiliser. Samples weight 50 grams of various Kevlar pulp/SEBS composites were blended at 165°C, rotor speed 90 rpm for 10 minutes and passed through a two-roll mill twice. The composites were collected promptly and kept in a desiccator in order to mininize moisture adsorption.

Loading of Kevlar pulp was varied from 0 - 10% by weight. The effect of compatibiliser was studied in a composite of 3wt% of Kevlar in SEBS. The amount of SEBS-g-MA varied from 0 - 10% by weight was added to the composites using the same mixing condition.

Extraction of the composites

A known weight of the composite was extracted in Soxhlet apparatus using toluene as a solvent for 72 hours. The sample was then dried in a vacuum oven at 50°C. The amount of the bound rubber can be calculated by gravimetric method. The extracted pulp was also characterised by DRIFT and SEM.

Mechanical properties of the composites

Kevlar 49 pulp/SEBS composites were compression moulded at 180°C for 10 minutes under a pressure of 15 MPa and quenched with cold water. After conditioned for at least 24 hours, tensile specimens were cut with dumbell-shape die of size 115 x 6 x 1 mm parallel and transverse to the direction passing through the two-roll mill. Testing was carried out on an Instron testing machine model 4301 in accordance with ASTM D638 at a cross head speed of 500 mm/min with a full scale load cell at 100 kg.

Scanning electron microscopy (SEM)

Observation of fibre surface and fracture surfaces of the composite were performed on Hitachi S2500. A thin layer of palladium was coated by Hitachi E102 ion sputter on the specimen to prevent charging on the surface. SEM was operated at 15 kV.

Fracture surface of the composites was prepared by freezing the composite in liquid nitrogen for 5 minutes and then broken rapidly above the surface of liquid nitrogen.

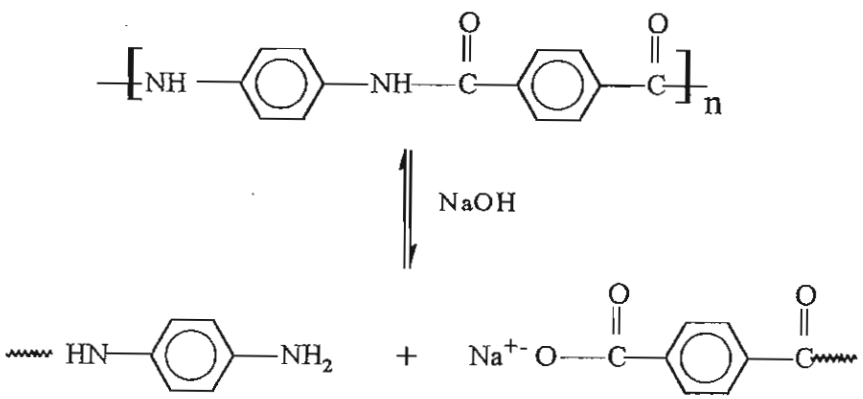
Optical microscopy

Orientation and fibre length in the composite were observed under an optical microscope (Nikon 70562). The sample was prepared by melt-press between slide glasses. The fibre aspect ratio (length to diameter ratio) was evaluated from the photographs taken at various points.

RESULTS AND DISCUSSION

Hydrolysis of Kevlar surface

It is generally known that Kevlar aramid is poly (*p*-phenylene terephthalamide) or PPTA. In this study, Kevlar pulp was partially hydrolysed on the surface by using 10% NaOH for 20 minutes to create more -NH_2 and -COOH end groups as indicated in the following reaction.



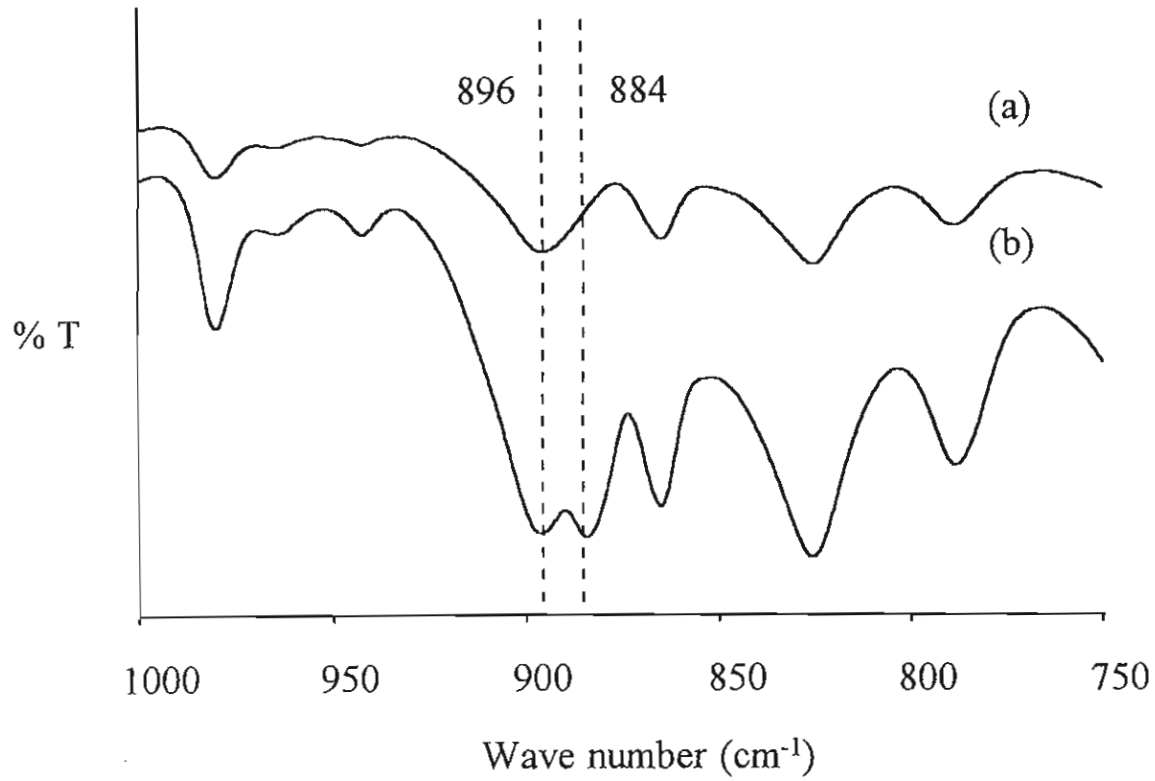


Fig.1. Infrared spectra of Kevlar surface (a) before and (b) after hydrolysis (without washing with water).

Fig.2. Optical micrograph of Kevlar pulp/SEBS composite pressed between slide glasses.

Figure 1 shows infrared spectra of Kevlar pulp before and after hydrolysis using DRIFT technique. It can be seen that a new peak appears at 884 cm^{-1}. The peak is associated with the C-H out of plane bending of aromatic ring next to $-COO^-Na^+$ substituent as reported by Chatzi[14-15]. The pulp was throughly washed with distilled water, followed by toluene and dried to constant weight at 50°C under vacuum. The resulting pulp had a pale yellow colour. At this stage the 884 cm^{-1} peak disappeared. This can be explained by the fact that washing the pulp with distilled water would change $-COO^-Na^+$ to -COOH. It was found that the washing step was very important. If care was not taken the resulting pulp would turn dark yellow to brown after storage for a few days. Blending of this dark colour pulp with SEBS elastomer gave rise to a composite with very poor tensile properties.

Optical microscopic observation

Figure 2 shows the optical micrograph of the thin layer of the composite SEBS/Kevlar pulp. Two features of fibre can be seen, namely, long fibres and small fibrils which split from the long one, since pulp is a highly fibrilated form of fibre. According to the compressive force applied on the slide glasses the direction of orientation of these small fibrils are therfore perpendicular to the long ones. The similar orientation behaviour should also be found in the compression moulded specimen prepared for the tensile measurement. It should be noted here that the measurement of tensile properties of the specimens prepared in this experiment and cut in the direction parallel and perpendicular to the direction of passing through the two-roll mill were found to be approximately the same. This should be due to the biaxial orientation of these two types of fibre.

The average length of fibre before and after mixing was about 1.8 mm and 0.5 mm, respectively. Distribution of the aspect ratio of fibres after mixing evaluated from optical micrographs is shown in Figure 3. It can be seen that most of the fibre has aspect ratio of 22-38.

Mechanical properties

Fibre reinforced composites generally exhibit anisotropic properties. Mechanical properties in the machine direction are normally higher than those measured in the transverse direction (cross-machine direction). Our preliminary results showed that the mechanical properties in the two directions were not much different. This is probably due to biaxial orientation of the fibre and fibril as discussed above. However, the results to be followed are measured in the machine direction.

Stress-strain behaviour of SEBS/Kevlar pulp composites is shown in Figure 4. SEBS exhibits a typical characteristic of rubber with strain hardening effect at very high strain. This effect leads to a very high ultimate tensile strength. Addition of Kevlar up to 5% did not affect the shape of the curves to a great extent, ie. the composites still show strain hardening effect. Beyond 5 % of Kevlar, the composites failed at strain below the point which strain hardening effect was observed. The reinforcement effect of Kevlar can be clearly seen in all samples. However, the composites broke at relatively low strain when more Kevlar was added. This is probably due to debonding of the Kevlar from SEBS as indicated by whitening of the samples. Such debonding would leave certain imperfection on SEBS surface and cause premature failure. The other reason for premature failure would be due to poor dispersion of Kevlar pulp at high loading.

Tensile properties of Kevlar reinforced SEBS are shown in Figure 5. It can be seen that as the Kevlar loading is increased the tensile strength of the composite decreases. Modulus at

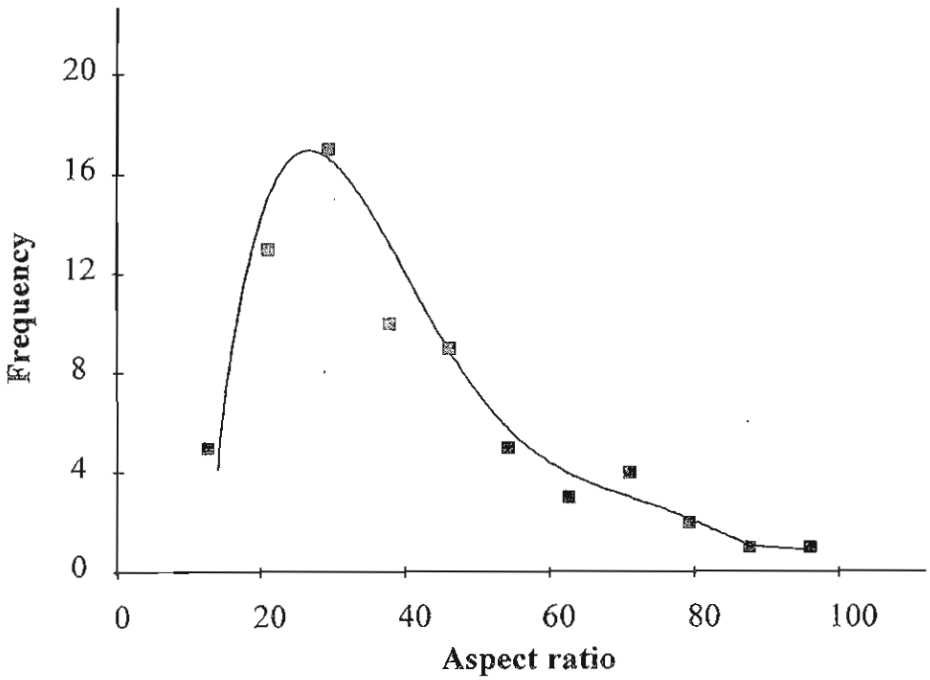


Fig.3. Distribution of aspect ratio of fibre after mixing.

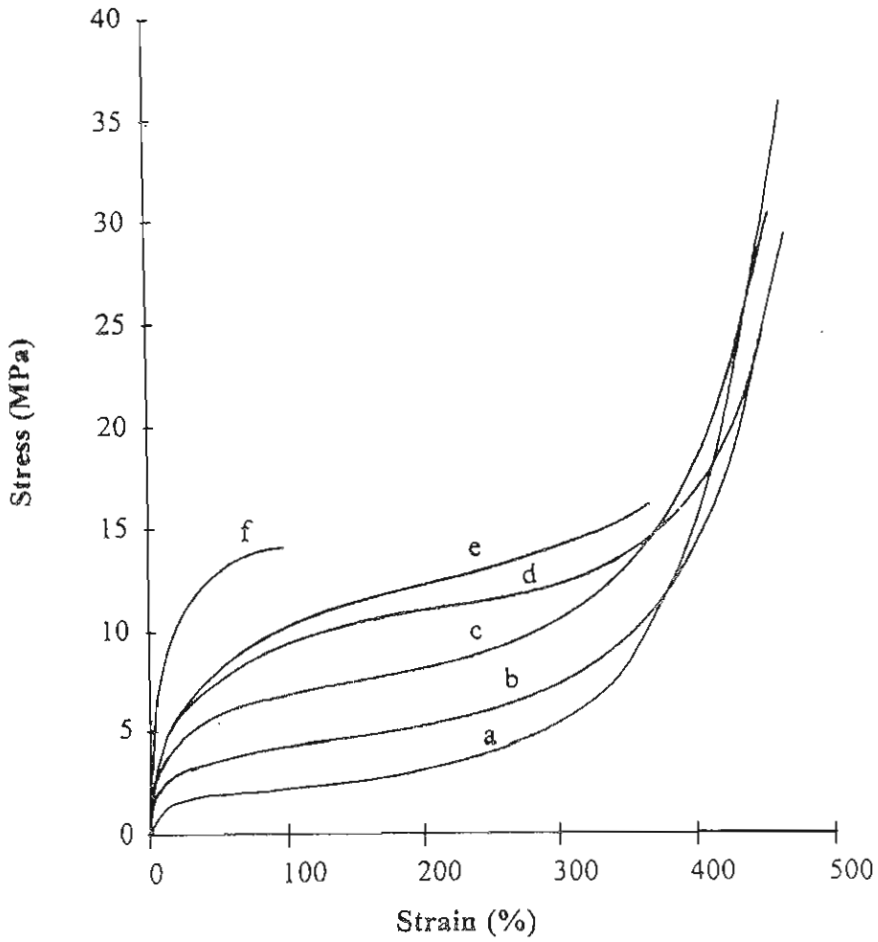


Fig.4. Stress-strain curves of Kevlar pulp/SEBS composites at fibre loading (wt%) a = 0, b = 1, c = 3, d = 5, e = 7 and f = 10.

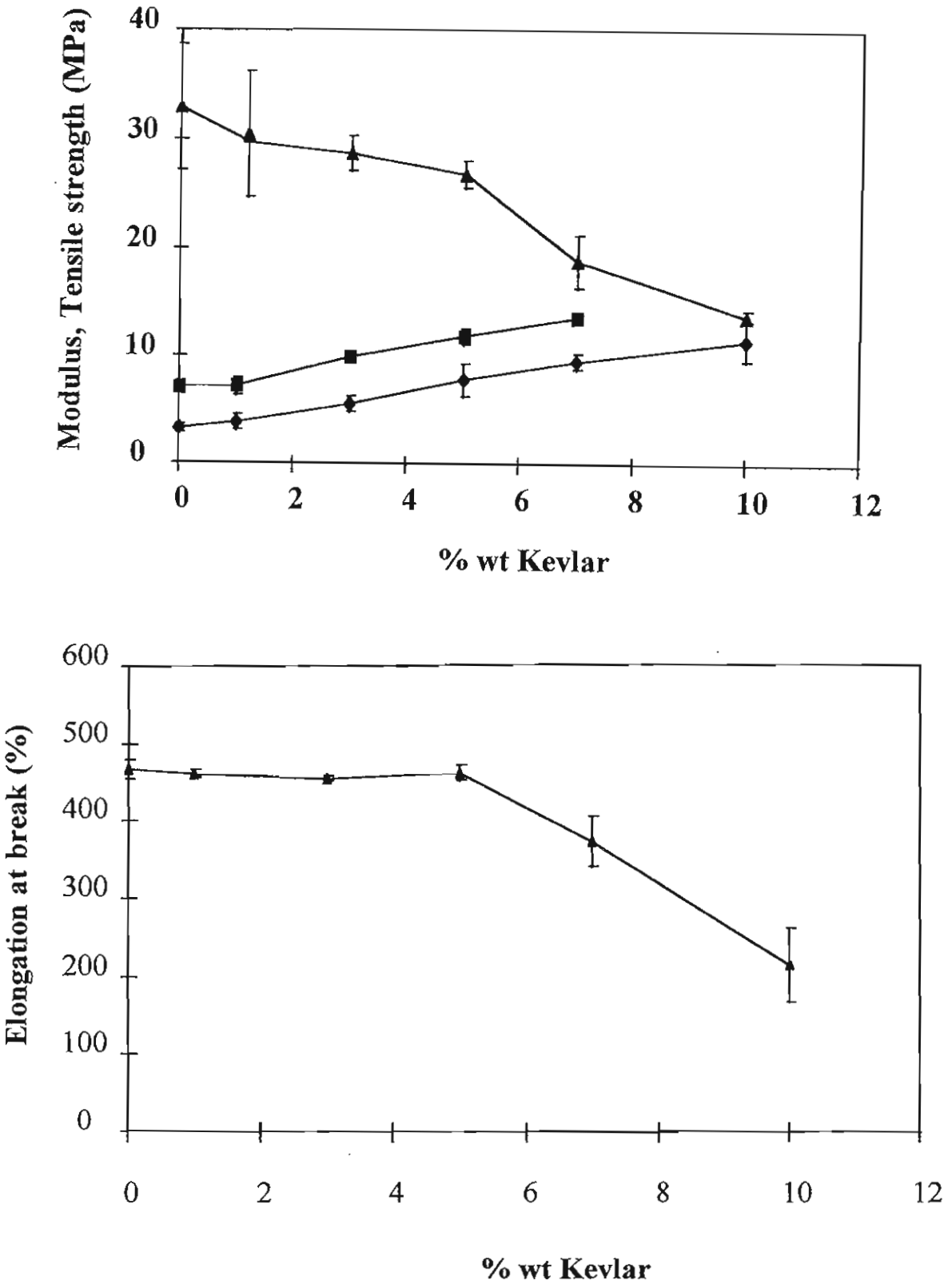


Fig.5. Shows a) Modulus at 100% (◆), 300% (■) and Tensile strength (▲) and b) Elongation at break of Untreated Kevlar/SEBS composite.

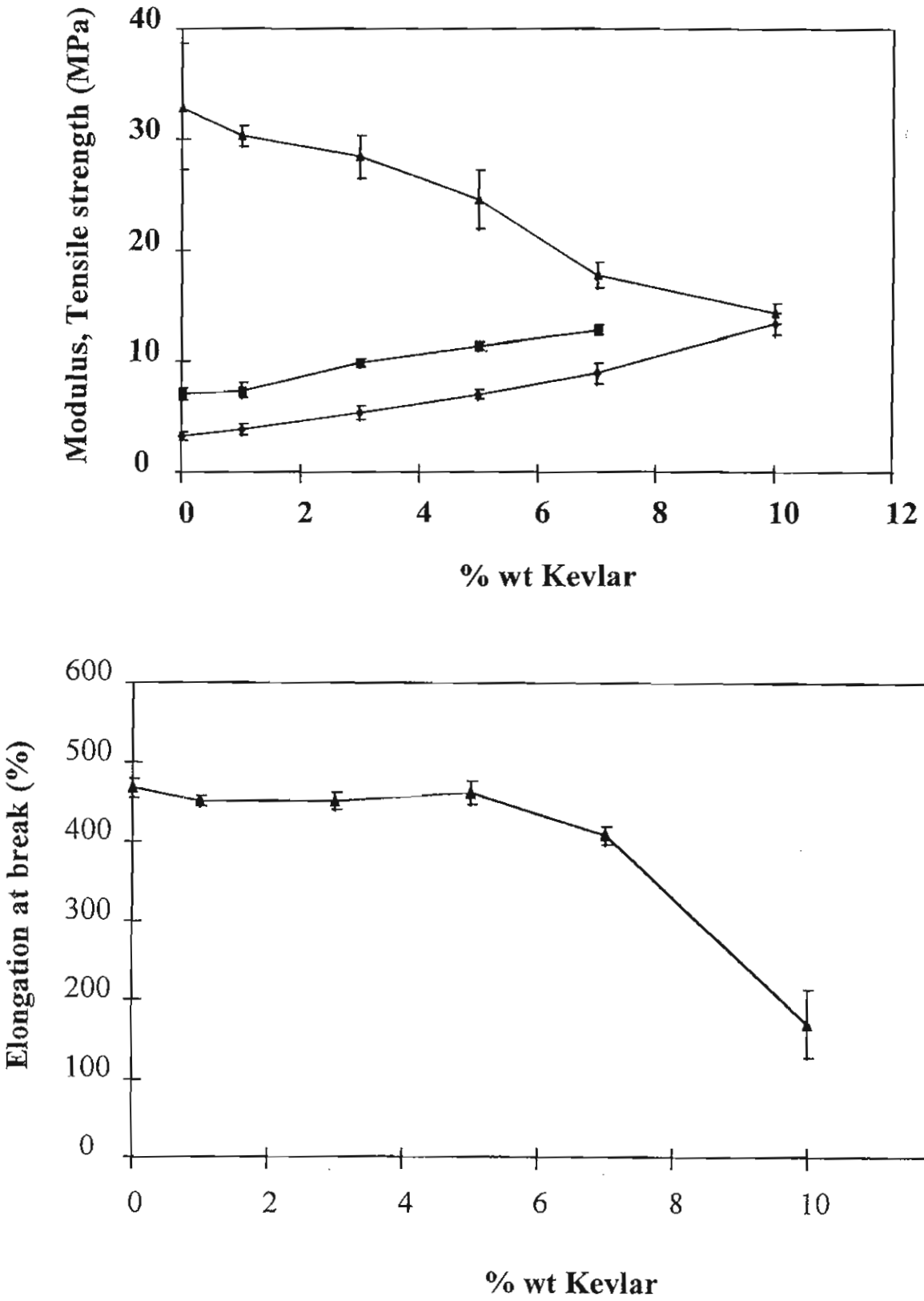


Fig.6. Shows a) Modulus at 100% (◆), 300% (■) and Tensile strength (▲) and b) Elongation at break of Treated Kevlar/SEBS composite.

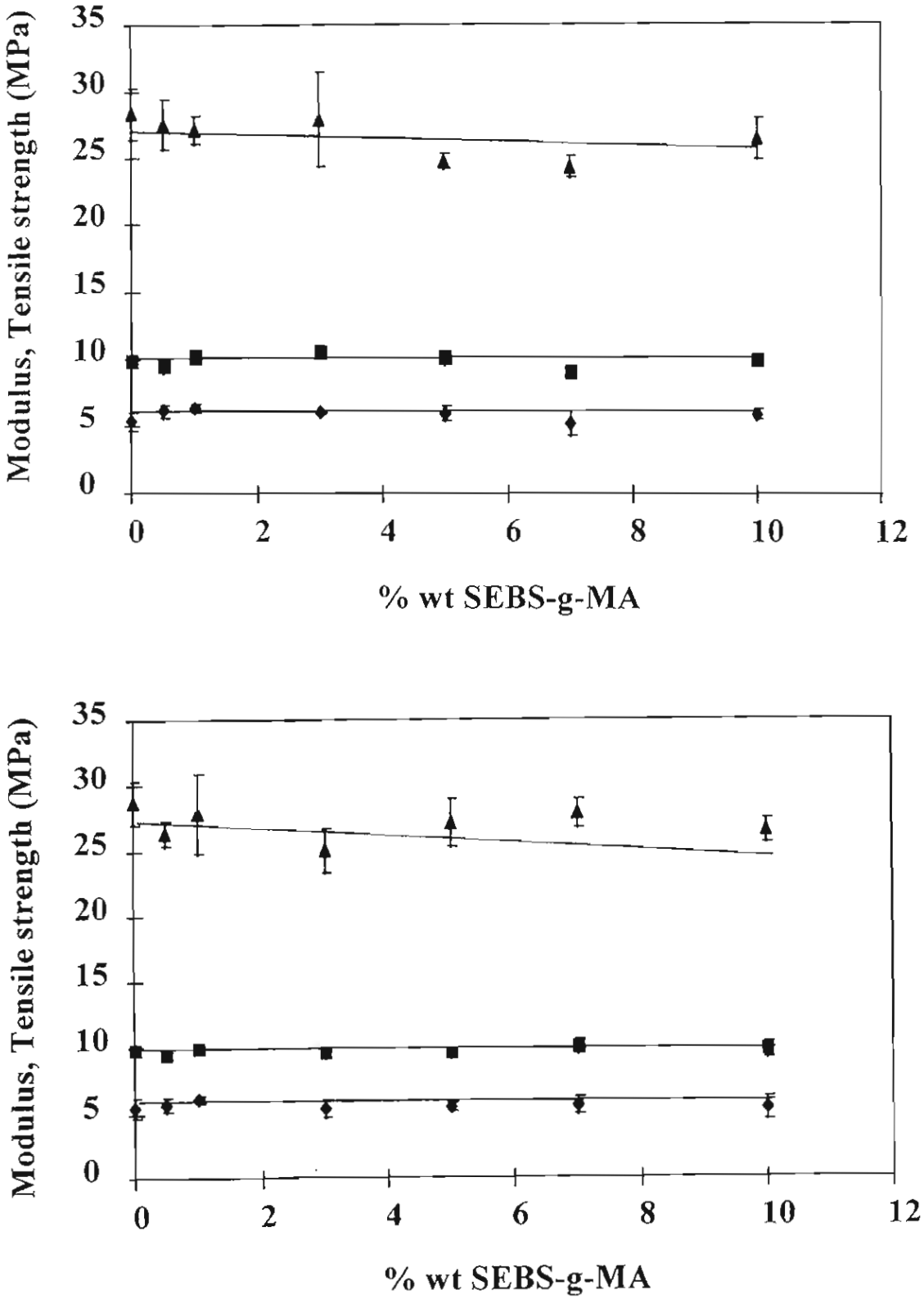


Fig.7. Shows effect of SEBS-g-MA on modulus at 100% (◆), 300% (■) and Tensile strength (▲) of (a) Untreated Kevlar/SEBS composite and (b) Treated Kevlar/SEBS composite.

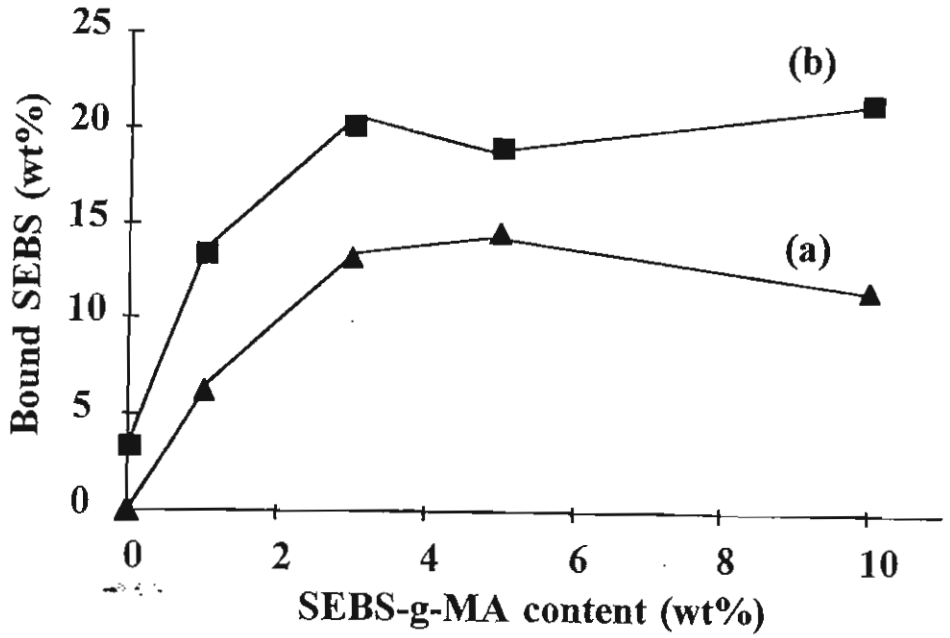


Fig.8. Bound SEBS (wt%) on extracted Kevlar pulp (a = as received, b = treated) obtained from composites containing various SEBS-g-MA contents.

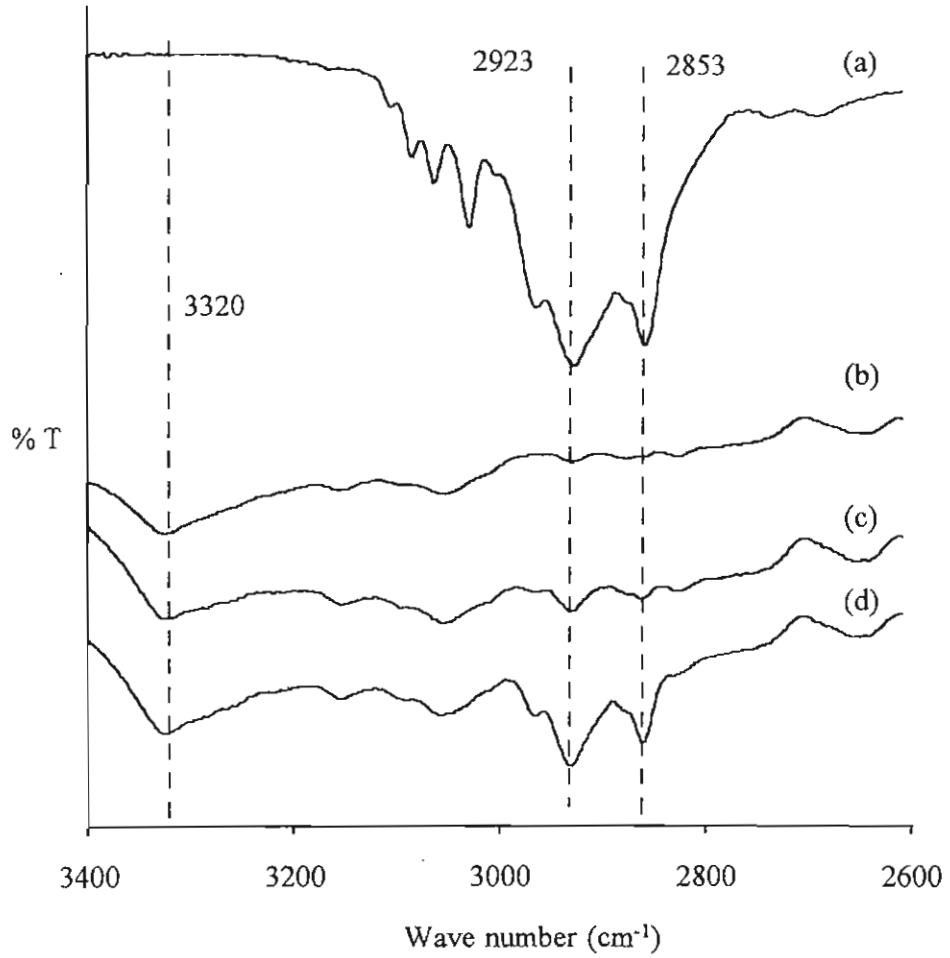
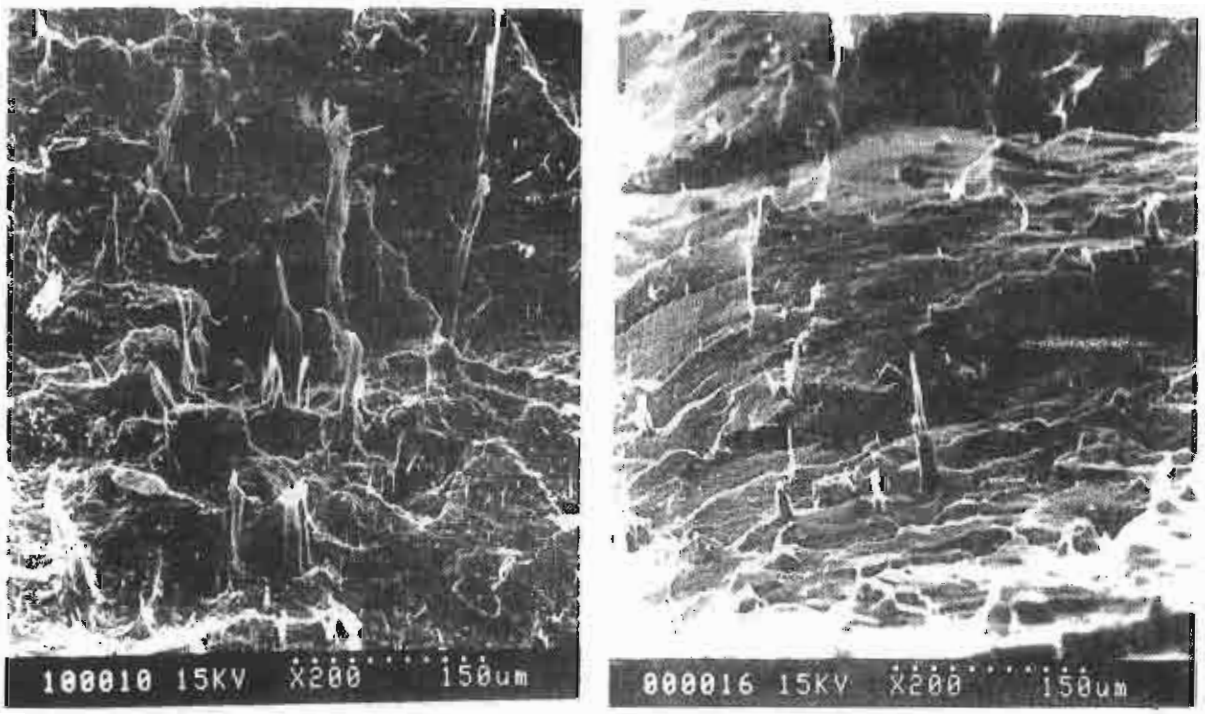
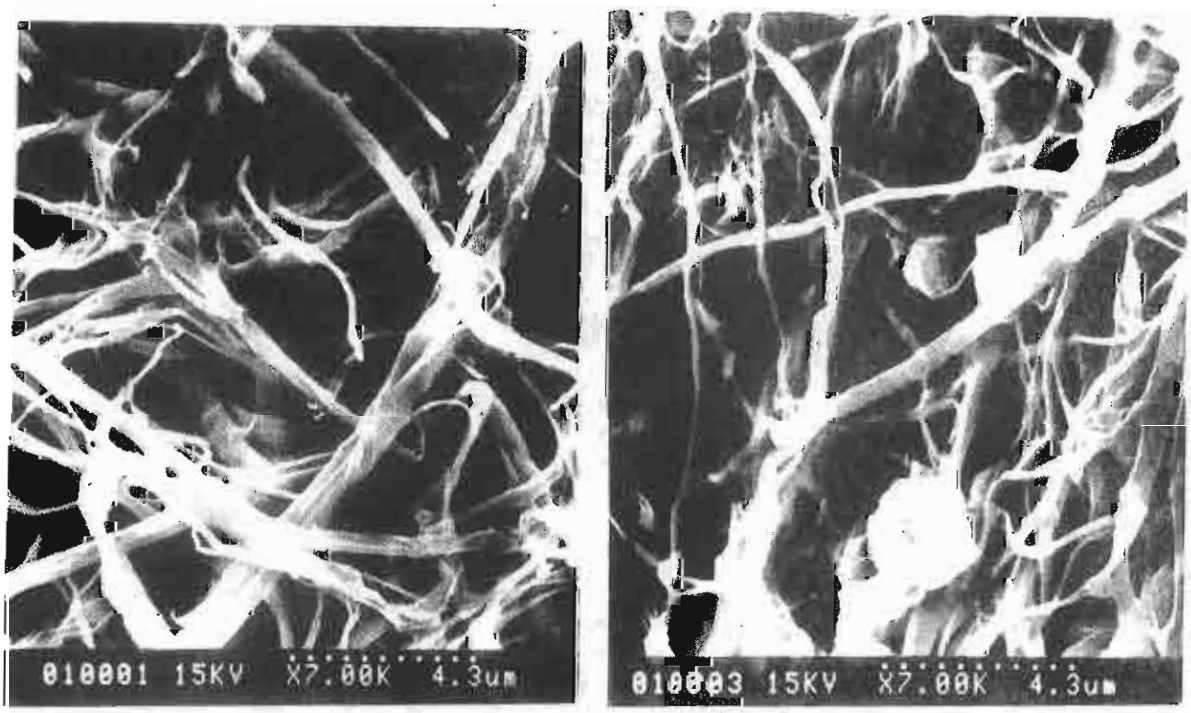


Fig.9. Spectra of extracted samples of (a) SEBS pure, (b) Kevlar, (c) Kevlar/SEBS (3/97) and (d) Kevlar/SEBS-g-MA/ SEBS (3/1/96).



a b

Fig.10. SEM micrographs of
(a) Kevlar/SEBS (3/97).
(b) Kevlar/SEBS-g-MA/SEBS (3/1/96).



a b

Fig.11. SEM micrographs of extracted pulp from
(a) composite without SEBS-g-MA.
(b) composite with 1 wt% SEBS-g-MA.

100 and 300%, on the other hand, increases with increasing Kevlar loading. Elongation at break of the composite was found to drop slightly when Kevlar loading was increased. Beyond 10% Kevlar the elongation at break drops sharply. This was found to coincide with the observation of poorly dispersed Kevlar in SEBS.

An increase in modulus at both 100 and 300% was as expected when pulp of very high modulus like Kevlar was incorporated into SEBS elastomer matrix. A monotonic decrease in tensile strength with pulp loading was due to the fact that SEBS could be strain hardened at very high strain. Incorporation of Kevlar pulp could reduce such effect and/or impart weak points, which, at relatively low strain, may induce cracks.

Hydrolysis of Kevlar surface was found to have negligible effect on mechanical properties of the composites, as can be seen from Figures 6a and 6b. This indicates that only slight modification, either chemically or physically, had been done.

Effect of compatibiliser, SEBS-g-MA, on a composite containing 3% wt. Kevlar can be seen from Figures 7a and 7b. Two sets of Kevlar were studied, i.e. as received Kevlar and surface hydrolysed Kevlar. It was found that surface hydrolysed Kevlar resulted in a composite with approximately the same mechanical properties as that of untreated Kevlar.

In order to determine how SEBS was adsorbed on Kevlar surface the blends were subjected to extraction with toluene. Since SEBS can be dissolved in toluene at room temperature, it should be completely leached out after extraction for 72 hours at boiling temperature of toluene. Solvent extraction of the composite shows that the amount of bound (unextractable) rubber increases as SEBS-g-MA was added, as can be seen in Figure 8 from gravimetric measurement. Curves (a) and (b) are results from untreated and treated Kevlar, respectively. This figure clearly shows the effect of hydrolysis on the efficiency of adsorption. This suggests that SEBS-g-MA reacted with active group on the surface of Kevlar. The amount of bound rubber calculated base on the weight of fibre is, however, less than the amount of added SEBS-g-MA. The rest of SEBS-g-MA (unreacted) is likely to disperse in SEBS matrix and could weaken the composite if phase-separation occurs.

Figure 9a shows Infrared spectra (DRIFT) of pure SEBS in the range 2600-3400 cm^{-1}. Peaks at 2923 and 2853 cm^{-1} correspond to asymmetric and symmetric stretchings, respectively, of the $-CH_2-$ groups from ethylene block of SEBS. Figure 9b displays Infrared spectrum of as-received Kevlar pulp in the same region. It can be seen that there is a peak at 3320 cm^{-1} which corresponds to intermolecular hydrogen bonding in Kevlar. The Infrared spectra of the extracted pulp from specimens without and with SEBS-g-MA, shown in Figures 9c and 9d, respectively, display both typical peaks of SEBS and Kevlar. The ratio of the peak at two positions clearly shows the higher percentage of SEBS on the Kevlar surface as SEBS-g-MA was added.

Solvent extraction and spectroscopic evidences clearly suggest that the compatibiliser, SEBS-g-MA, reacted with Kevlar. The tensile strength of the blends are, however, not improved. Ishihara *et al.*[16]. reported that, for poly(ethylene terephthalate)-hydrogenated styrene-isoprene-styrene triblock copolymer (PET-SIPS) composite, treatment of PET fibre improved tensile strength in the fibre direction significantly. Tensile strength in the transverse direction was, however, not affected.

Morphology

Fracture surfaces of composites with and without compatibiliser are shown in Figures 10a and 10b, respectively. Detailed investigation of the photographs reveals very much different

fracture characteristics betweeen the two systems. Composite with compatibiliser, Figure 10b, exhibits mostly fibre breakage, whereas composite without compatibiliser exhibits both fibre pull out and fibre breakage (Figure 10a). Fibre pull out in the latter case seems to dominate. This evidence confirms that the compatibiliser, SEBS-g-MA, improves the adhesion between fibre and matrix.

Figures 11a and 11b are SEM micrographs taken from extracted fibre from the composites without and with compatibiliser, respectively. No adsorption of rubber can be seen in the first case whereas a few rubber particles adsorbed on fibre surface in the latter one. These particles of rubber might cause voids between the fibre surface and the rubber matrix, which led to poor contact at the interface, and hence no improvement of mechanical properties could be obtained even though larger amount of bound rubber on the fibre surface was found.

CONCLUSIONS

The above results can lead to the following conclusions:

1. Creation of reactive groups on Kevlar pulp by surface hydrolysis in this work does not lead to deterioration of its mechanical properties.

2. Moduli at 100 and 300% of the composites increase, tensile strength slightly decreases, and there is no significant change of elongation at break, as the loading of Kevlar is increased upto 5 wt%. However, beyond 10%wt of Kevlar loading, the dispersion is poor, and as a result tensile strength and the elongation at break drop sharply.

3. From gravimetric measurement and DRIFT technique, it is found that higher amount of SEBS adhered at the surface of Kevlar pulp as SEBS-g-MA is added.

4. In the presence of compatibiliser, SEM micrograph of fracture surface of the composite shows fibre breakage and the micrograph of extracted pulp shows adsorption of rubber particles on pulp surface, which are evidences of improvement of fibre-matrix adsorption.

5. Tensile strength of the composite containing SEBS-g-MA is, however, not improved. This might be due to uneven adsorption of rubber particles which probably cause some voids at the interface giving rise to the weak points.

ACKNOWLEDGEMENTS

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บทคัดย่อ

งานวิจัยนี้เป็นการศึกษาการเสริมแรงยางเทอร์โมพลาสติกสไตรีนเอทธิลีนบิวธิลีนสไตรีน (SEBS) ด้วยเยื่อเคฟล่าร์(Kevlar pulp) ซึ่งปรับปรุงผิวเพื่อเพิ่มหมู่ที่ไวต่อการทำปฏิกิริยาด้วยวิธีไฮโดรไลซ์ด้วยเบส และใช้ SEBS ที่มีหมู่มาเลอิกแอนไฮดรายด์ต่อด้านข้าง (maleic anhydride grafted SEBS) เป็นสารช่วยผสม การผสมคอมพอสิทนี้ทำโดยใช้เครื่องผสมภายในโดยวิธีขั้นตอนเดียว แล้วนำไปวัดสมบัติการทนต่อแรงดึง พบว่าเมื่อเพิ่มปริมาณของเยื่อเคฟล่าร์ทำให้ค่ามอดูลัสของยางผสมนี้สูงขึ้นมาก แต่ค่าความทนต่อแรงดึงที่จุดขาดและความยาวที่จุดขาดลดลง ได้ใช้เทคนิค scanning electron microscopy (SEM) ศึกษาผิวของคอมพอสิทโดยการหักชิ้นงานในไนโตรเจนเหลว พบว่าเส้นใยมีลักษณะแบบหลุดออกจากเมทริกซ์เป็นส่วนใหญ่ แต่เมื่อมีสารช่วยผสมลักษณะของเส้นใยจะเป็นแบบขาดมากขึ้น และจากการสกัดเส้นใยจากคอมพอสิทแล้ววิเคราะห์ผิวโดยใช้อินฟราเรดสเปคโตรสโคปีและ SEM รวมทั้งโดยการชั่งน้ำหนัก พบว่ามียางเกาะที่ผิวของเส้นใยมากขึ้นเมื่อมีสารช่วยผสม อย่างไรก็ตาม จากการวัดสมบัติการทนต่อแรงดึงของคอมพอสิท พบว่าไม่เพิ่มขึ้น ซึ่งอาจเกิดจากการเกาะที่ไม่สม่ำเสมอ

Research Article

Aramid Fibres-Thermoplastic Elastomer (SEBS) Composites: Effect of Maleic Anhydride Grafted Compatibiliser on Mechanical Properties

Teeravut Nakinpong*, Budsaporn Sinpatanapan*, Wiriya Meesiri**, Taweechai Amornsakchai*, Sauvarop Bualek-Limcharoen*

Composites of styrene (ethylene butylene) styrene (SEBS) thermoplastic elastomer containing short aramid fibres were studied. Three types of fibres which include Kevlar, Conex and Technora, were used. Firstly, the fibres were used as-received. It was found that for all types of fibres, the modulus at 100% strain increased with increasing fibre content and there was no different between the type of loaded fibres. For modulus at 300% strain, a similar trend was still seen with Kevlar-SEBS exhibits approximately 50% higher moduli than those of Conex- and Technora-SEBS composites. Tensile strength of Kevlar-SEBS composites increased slightly with increasing fibre content and dropped off above 5%. Tensile strengths of Conex- and Technora-SEBS composites, however, decreased with increasing fibre content and were lower than that of Kevlar-SEBS composites at all compositions. Secondly, an attempt was made to improve the interfacial adhesion between fibres and matrix by modifying the fibre the surface using alkali hydrolysis to increase the number of active end groups on fibre surface. These active end groups could then react with anhydride grafted SEBS (SEBS-g-MA) which was used as a compatibiliser. It was found that surface hydrolysis and compatibiliser has little effect on moduli at 100 and 300% strain of the composites. Tensile strength of compatibilised Kevlar and Technora-SEBS decreased slightly with increasing the content of SEBS-g-MA. However, significant enhancement of tensile strength was observed for compatibilised Conex-SEBS composites. This result indicates improvement of the interfacial adhesion between fibre and the matrix.

Key words: aramid, composite, thermoplastic elastomer, fibre reinforcement

INTRODUCTION

Polymer composites using aramid fibres as reinforcement exhibit excellent thermal and mechanical properties. However, problems due to poor adhesion between the fibre and polymer matrix still remain to be solved. Researchers have used different techniques to obtain desired properties. Vaughan[1] applied various commercial coupling agents to composite mixtures and obtained improved adhesion. Other techniques involving modification of fibre reinforcement by dispersion in an ionomer matrix seemed to be very effective.[2,3] Marom *et al.*[4] proposed a technique using bromine water to roughen fibre surface which resulted in improved interlaminar shear strength. Andreopoulos[5] used methacryloyl chloride, an adhesion-promoting compound, to treat Kevlar fibre in an unsaturated polyester matrix and obtained higher tensile strength than the composite without such compound. In another surface modification technique, Wang *et al.*[6] prepared plasma-treated aramid fibre/polyethylene composites. Oxygen plasma was used to generate reactive groups such as -COOH, -OH, -NH_2 on the fibre surface. The reactive groups were used to chemically anchor Ziegler-Natta catalyst which in turn effected polymerization of polyethylene on the fibre surface. Yu *et al.*[7] reported works on nylon/Kevlar composites using various fibre surface treatment methods including hydrolysis, and hydrolysis followed by acid chloride grafting. The composites exhibited better mechanical properties compared to composites with unmodified fibre.

Short-fibre reinforced elastomer has attracted several researching groups.[8-11] Reinforcement used in these works involved conventional fibres like poly(ethylene terephthalate) (PET), and nylon. It is, therefore, quite logical to include such high-performance fibre like aramid in this type of composite.

In the present work, Styrene (Ethylene Butylene) Styrene (SEBS) represented a model thermoplastic elastomer to be reinforced by organic aramid fibres. Our work on composites containing Kevlar[12] and Conex[13] have been reported elsewhere. In this paper, another type of aramid fibre, Technora, will be reported in comparison with the previous results. On a molecular level, these fibres and SEBS are quite incompatible. The incompatibility arises from the relatively non-polar olefinic and styrenic blocks in SEBS and the highly polar hydrogen-bonded amide groups in aramid fibres. To improve compatibility, partial hydrolysis of fibre surface, followed by the addition of maleic anhydride grafted SEBS (SEBS-g-MA), a compatibiliser for this system, were carried out. The treatment should introduce chemical bonding due to the reaction of maleic anhydride and amine groups on the fibre surface, similar to that reported by Modic *et al.*[14] The resulted composites were expected to exhibit improved adhesion between the components and thus provide better mechanical properties.

EXPERIMENTAL

Materials

The materials used in this study are summarized in Table 1. Properties of the fibres are shown in Table 2.[15] Molecular structures of the three aramid fibres are given below.

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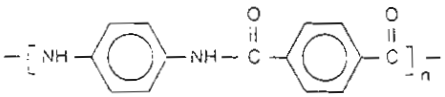
Table 1 Materials used for this study.

Materials (Commercial designation)	Specification	Manufacturer
Styrene (Ethylene Butylene) Styrene Thermoplastic Elastomer (SEBS, Kraton G 1652)	29% styrene Mw S-block = 7,200 Mw EB-block = 37,500	Shell Chemical Co.
SEBS grafted with maleic anhydride (SEBS-g-MA, Kraton FG 1901x)	29% styrene 1.84 wt% MA	Shell Chemical Co.
Poly-*p*-phenylene terephthalamide (Kevlar)	pulp	DuPont Co.
Poly-*m*-phenylene isophthalamide (Conex)	short fibre	Teijin Ltd.
Poly-*p*-phenylene-3,4'-oxydiphenylene terephthalamide (Technora)	short fibre	Teijin Ltd.

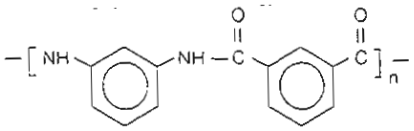
Table 2 Properties of aramid fibres.[15]

Properties	Kevlar	Conex	Technora
Modulus (GPa)	24 - 25	8 - 10	20 - 21
Tensile strength (GPa)	1.8 - 2.1	0.5 - 0.6	3.0 - 3.2
Elongation at break (%)	3 - 4	35 - 45	5 - 7
Specific gravity	1.44	1.38	1.39
Fibre diameter (μm)	13	15	12
Fibre length (mm)	2	3	3

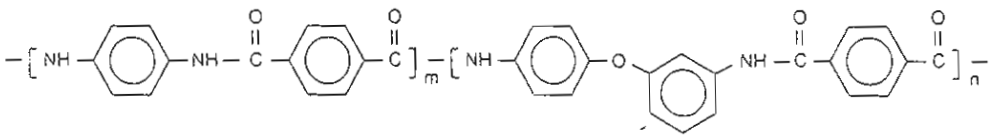
Kevlar



Conex



Technora



Hydrolysis of Aramid Fibre

The as-received aramid fibre was washed with distilled water, followed by acetone, and dried in a vacuum oven at 50°C for 24 h. Hydrolysis was carried out by dispersing about 10 grams of fibre in 400 ml of 10% sodium hydroxide aqueous solution at ambient temperature for 20 min. After hydrolysis, the fibre was thoroughly washed with distilled water, followed by toluene, and dried in a vacuum oven at 50°C for 48 h. The dried fibre was stored in a desiccator prior to use.

FTIR Characterisation

An FTIR spectrometer with a DRIFT attachment (Diffuse Reflectance Infrared Fourier Transform spectrometer, Perkin Elmer PE 2000) was used to probe the surface of fibre before and after hydrolysis. Each spectrum was obtained from 200 scans at 4 cm^{-1} resolution.

Preparation of Composites

Various compositions of aramid fibre/SEBS composite were prepared. The dried fibre was first pre-opened in a Moulinex blender for a few seconds, followed by blending for 0.5 min in an internal mixer (Haake Rheocord 90) with a rotor speed of 90 rpm at 175°C. The compatibiliser was then added and blended for another 0.5 min, and finally, SEBS was blended in for 9 min. The 50-gram batch composite was passed through a two-roll mill twice to obtain fibre orientation. The composite sheet was kept in a desiccator at room temperature for 24 h.

The effect of mixing condition on tensile properties of Kevlar-SEBS composites was investigated by Nakinpong.[16] The rotor speed at 90 rpm was found to give composites with the best tensile properties and mixing temperature within the range from 165 to185°C showed no effect on tensile properties.

Extraction of Composites

Extraction of composite specimen was carried out using a Soxhlet apparatus and toluene as a solvent. After extraction for 72 h, the sample was dried in a vacuum oven at 50°C for 24 h. The bound rubber on the extracted fibre was determined by DRIFT.

Mechanical Properties of Composites

The composite sheet was compression moulded at 185°C for 10 min under a pressure of 15 MPa, into a 1-mm thick sheet, followed by conditioning at room temperature for at least 24 h. Tensile specimen was die cut at the size of 115x6 mm with the long dimension parallel to the machine direction (direction passing through the two-roll mill). Testing was performed on an Instron testing machine model 4301, in accordance with ASTM D638 at a cross head speed of 500 mm/min with a full scale load cell at 100kg.

RESULTS AND DISCUSSION

Hydrolysis of Aramid Fibre Surface

Aramid fibres were partially hydrolysed to create more $-NH_2$ and -COOH end groups on the surface. Figure 1a, b and c show DRIFT spectra of untreated and treated Kevlar, Technora and Conex fibres, respectively. The peak at 880-884 cm^{-1} is due to C-H out-of-plane bending of the aromatic ring adjacent to $-COO^-Na^+$ as reported by Chatzi.[17] After washing with distilled water, followed by toluene, and dried, the peak disappeared, apparently due to the change from $-COO^-Na^+$ to -COOH. Without this washing step, sodium hydroxide would further hydrolyse to amide bonds on the fibre surface, resulting in a dark brown colour and reduced tensile properties of the composite.

Mechanical Properties of Composites

1. As-received fibres

Tensile properties of the aramid fibre/SEBS composites are shown in Figure 2. It is evident that for all composites Modulus at 100% (M100) increases linearly with increasing the amount of fibre loading and there is virtually no effect of fibre types on M100. An increase in M100 with fibre loading is due to incorporation of high modulus fibre in soft matrix. The fact that all type of fibres resulted in the same M100 would suggest that there is a saturation in M100 of the composites, regardless the mechanical properties and geometry of the reinforcing fibre. Similar effect of fibre loading are seen for Modulus at 300% (M300). In this case, however, Kevlar composites exhibit significantly higher M300 than Conex and Technora composites. Again, no difference was found between M300 of Conex and Technora composites. It appears that at this high strain (300%) stress transfer to Kevlar is greater than that to Conex and Technora. This would suggest that reinforcing element in pulp geometry is better than short cylindrical fibre.

Tensile strength of the composites are shown in Figure 2 (c). It can be seen that, for Kevlar composites, addition of fibre upto 5% slightly decreases the tensile strength of the composites. At higher fibre loading tensile strength drops sharply. This was found to coincide with the observation of poorly dispersed fibre in the matrix. For Conex and Technora composites, it can be seen that tensile strength linearly decreases with increasing fibre content. This can be understood as a debonding of fibre-matrix interface at very high strain which

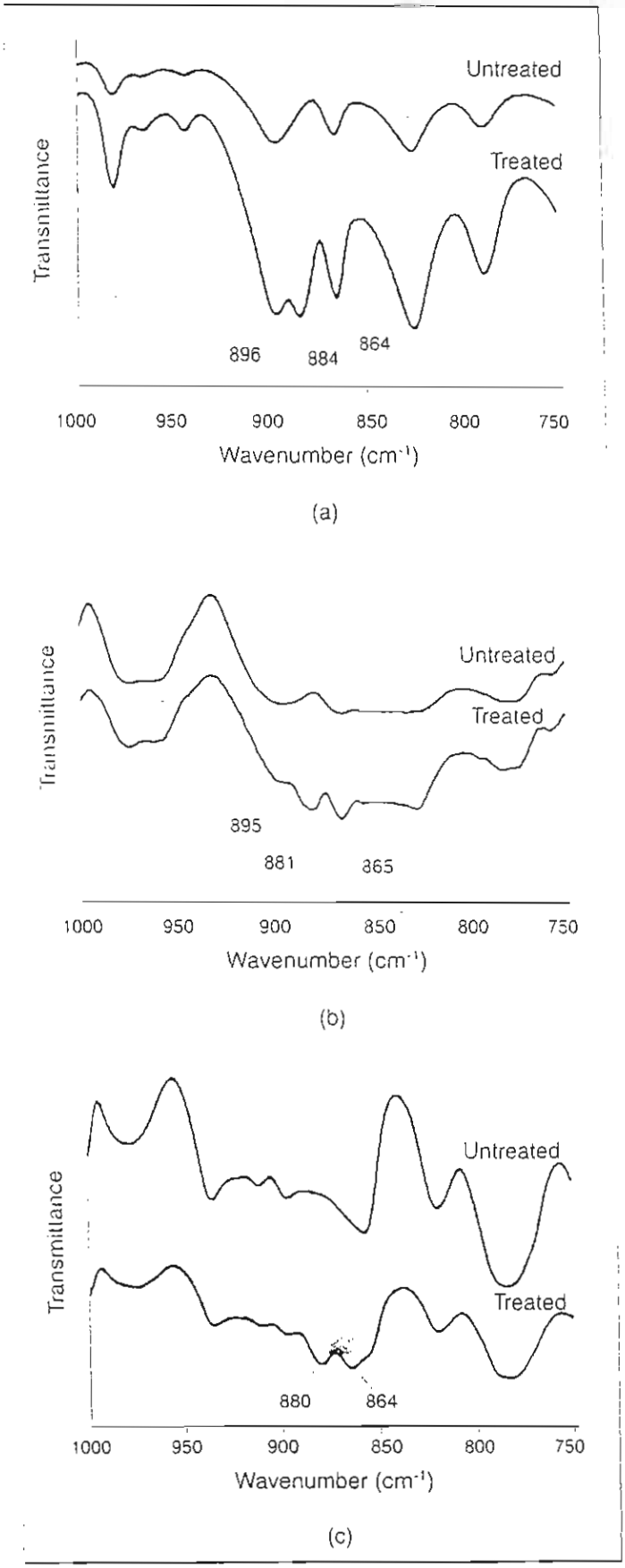


Fig. 1 Infrared spectra of untreated (as-received) and treated (surface hydrolysed) aramid fibres (a) Kevlar (b) Technora (c) Conex

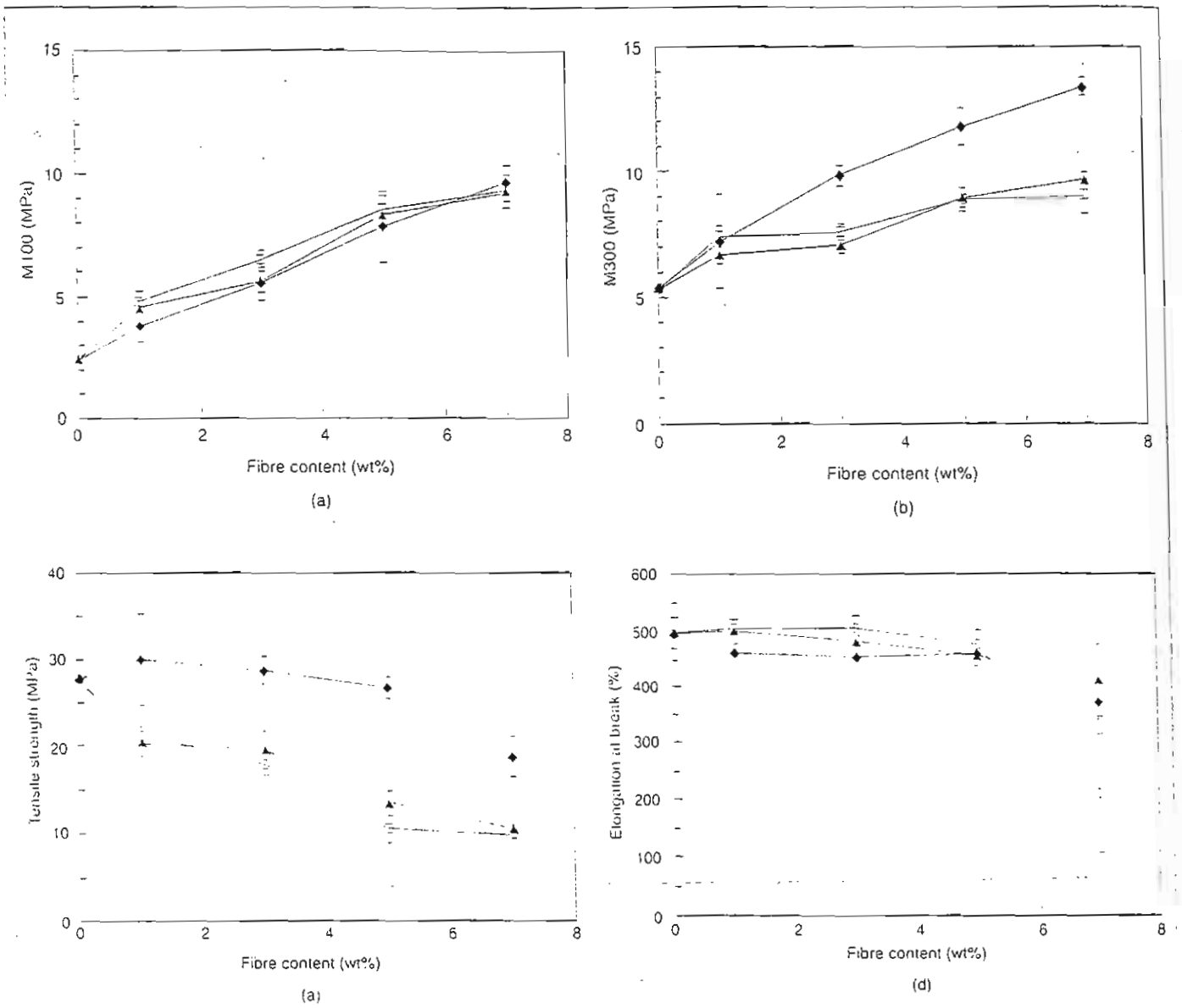


Fig. 2 Tensile properties of untreated aramid fibre/SEBS composite with various fibre loading (◆ : Kevlar, □ : Conex, ▲ : Technora) (a) Modulus at 100%, (b) Modulus at 300%, (c) Tensile strength, and (d) Elongation at break.

could be seen as specimen whitening. The specimens will therefore be weaken.

Elongation at break of all types of composites is virtually unchanged by increasing of fibre loading up to 5%. However, above 5% fibre content, elongation at break drops sharply. This is due to severe weakening of the interface debonding and poor dispersion of fibre at the high fibre content.

The results reported above were obtained from measurements of the specimens cut parallel to the machine direction (direction passing through the two-roll mill). In the case of Kevlar pulp-SEBS composite, tensile properties measured in the directions parallel and perpendicular to the machine direction were found to be approximately the same due to the biaxial orientation of the main fibre and the spitted small fibril as reported elsewhere.[12] The effect of fibre orientation was observed, however, in the case of composites with Conex and Technora short fibres. The properties of specimen measured in the direction perpendicular to the machine direction were about 10% less than those in the machine direction.

2. Surface-hydrolysed fibres

Surface hydrolysis of aramid fibre was carried out to increase the number of reactive end groups. These end groups could then react with SEBS-g-MA compatibiliser and modify surface properties of the fibres closer towards that of SEBS matrix.

Tensile properties of the composites containing 3% of treated fibres and compatibiliser are shown in Figure 3. It can be seen that compatibiliser content only slightly affects the properties of Kevlar and Technora composites. However, for Conex composites, it is clearly seen that the compatibiliser greatly improves the tensile strength of the composite. Tensile strength was found to increase with increasing compatibiliser content and approaching that of Kevlar composites at 5%. This

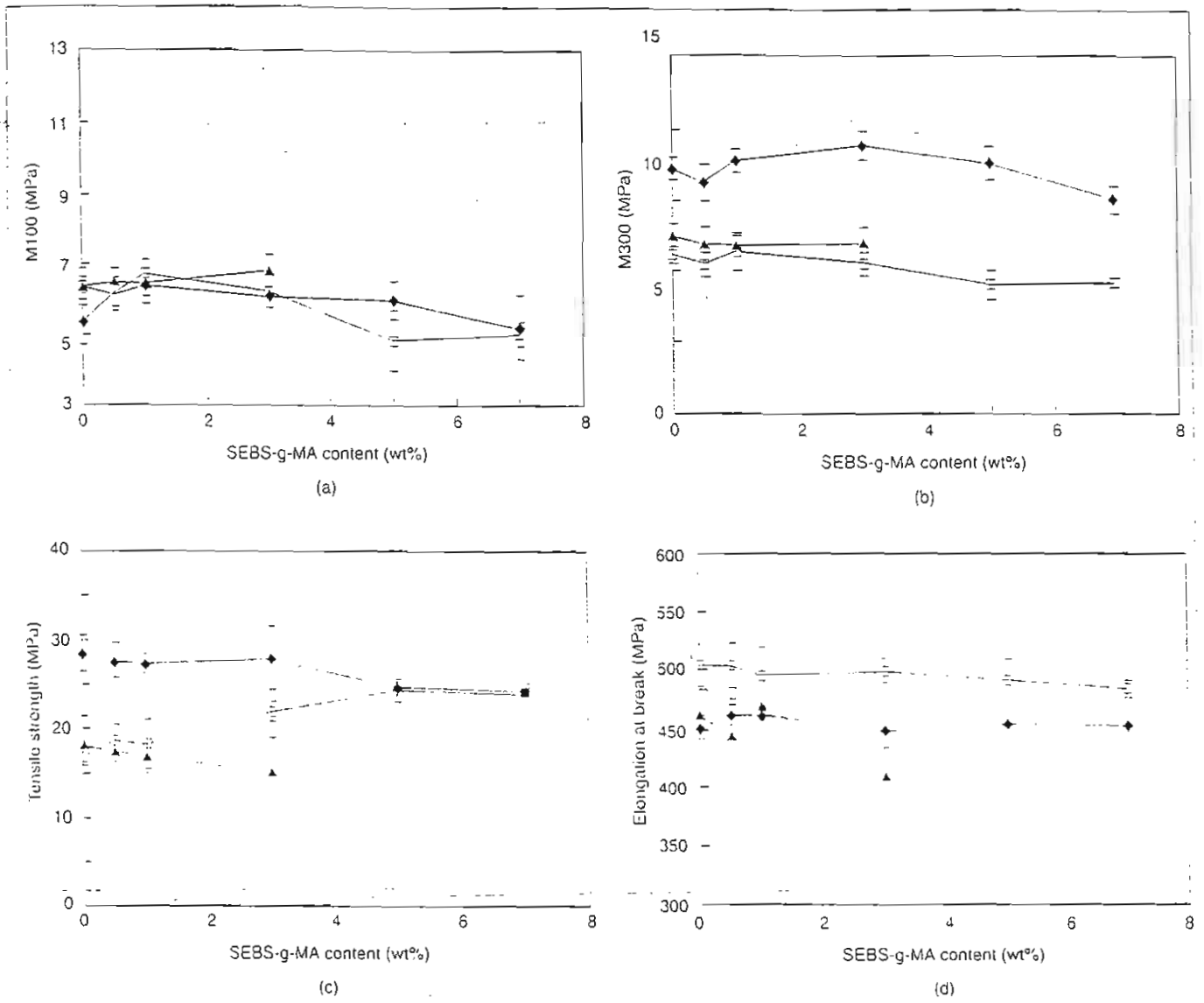


Fig. 3 Tensile properties of treated aramid fibre/SEBS composite with various compatibiliser contents (◆ : Kevlar, □ : Conex, ▲ : Technora) (a) Modulus at 100%, (b) Modulus at 300%, (c) Tensile strength, (d) Elongation at break.

is the evidence of the improvement of interfacial adhesion through the interaction of MA group and the reactive NH_2 end group of Conex. No improvement of tensile strength is found in the case of Kevlar pulp. It might be due to fibrillation of pulp during processing which peeled-off the treated surface. However, no improvement of tensile strength is observed in the case of Technora, though it is in the form of short fibre as Conex. This might be due to poor dispersion of Technora in SEBS matrix. This can be seen in the drop of elongation at break and large error bar (see Fig. 3d) at 3 wt% fibre loading. Poorer dispersion of Technora compared to Conex might be due to its larger fibre aspect ratio (length to diameter ratio) and hence fibres are curled and entangled to a greater extent.

Analysis of extracted fibres

FTIR spectra of Kevlar fibres extracted from the composites containing different concentration of compatibiliser, SEBS-g-MA, are shown in Fig. 4. The peaks at 2923 and 2853 cm^{-1} correspond to anti-symmetric and symmetric C-H stretching, respectively[18], of CH_2 group in the ethylene block of SEBS. Curve 4a is the infrared spectrum of extracted Kevlar pulp from the composite without compatibiliser, showing the typical peak at 3320 cm^{-1} which corresponds to N-H stretching in Kevlar. These spectra clearly demonstrate the increasing of bound SEBS on the fibre surface with increasing amount of compatibiliser, SEBS-g-MA. This clearly suggests the presence of the chemical bonding between the NH_2 group on aramid fibre and the maleic anhydride group on SEBS-g-MA. Similary, bound SEBS on extracted Conex and Technora fibres was also observed. The above finding suggests that chemical interaction between compatibiliser and fibre may or may not result in improvement of mechanical properties.

CONCLUSIONS

Reinforcement of SEBS thermoplastic elastomer with aramid fibres at low strain can be achieved without any

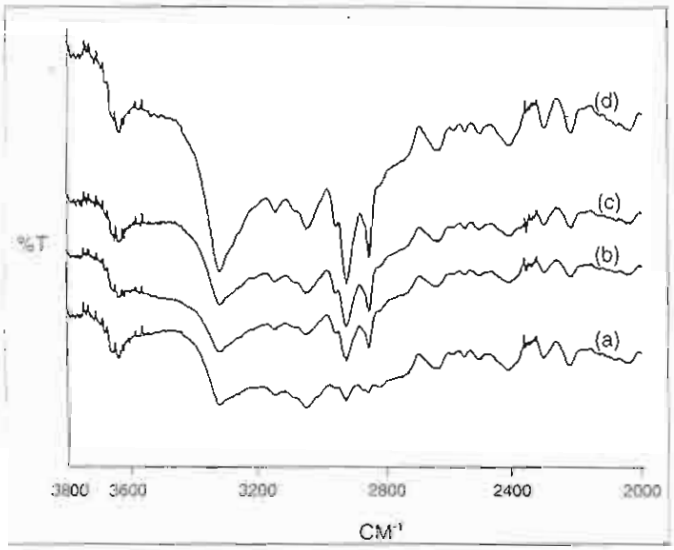


Fig. 4 DRIFT spectra of extracted Kevlar/SEBS composite containing various SEBS-g-MA (a) 0 wt% (b) 1 wt% (c) 3 wt% (d) 10 wt%.

compatibilisers. It appears that geometry of the fibre has greater effect on mechanical properties of the composites than the mechanical properties of the fibres. At the same fibre content, pulp was found to be more effective in reinforcing than short fibre.

Alkaline hydrolysis of fibre surface in conjuction with reactive compatibiliser was found to be effective on certain type of aramid fibre, i.e. Conex. No improvement was achieved for Kevlar and Technora composites despite surface modification had been achieved.

ACKNOWLEDGEMENTS

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Effect of Compatibilizers on Mechanical Properties and Morphology of In-Situ Composite Film of Thermotropic Liquid Crystalline Polymer/Polypropylene

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An *in-situ* composite film of a thermotropic liquid crystalline polymer (LC3000)/polypropylene (TLCP/PP) was produced using the extrusion cast film technique. The compatibilizing effect of thermoplastic elastomers, styrene-ethylene butylene-styrene (SEBS), maleic anhydride grafted SEBS (MA-SEBS), and maleic anhydride grafted polypropylene (MA-PP) on the mechanical properties and morphology of the TLCP/PP composite films was investigated. It was found that SEBS provided a higher value of tensile modulus than MA-SEBS, which in turn was higher than MA-PP, despite the expected stronger interaction between the MA chain and TLCP. The observation of the morphology under optical and scanning electron microscopes suggested that all three compatibilizers helped improve the dispersion of the TLCP fibers and increased the fiber aspect ratio to a different extent. The fractured surface of the specimens showed more fiber breakage than pull-out when a compatibilizer was added, which suggested the improvement of interfacial adhesion. The surface roughness of fibers with an added elastomeric compatibilizer may also provide mechanical interlocking at the interface. It is suggested that the increase in the viscosity ratio of TLCP/PP due to the added elastomeric compatibilizer, SEBS and MA-SEBS, compared with the thermoplastic compatibilizer, MA-PP, is more effective in improving the composite mechanical properties.

INTRODUCTION

The modification of polymers through the blending of a thermotropic liquid crystalline polymer (TLCP) with thermoplastics (TP) providing superior rheological and mechanical properties of the composite has drawn considerable attention (1–4). The processing of an incompatible TLCP/TP blend under an elongational flow condition is known to produce an oriented TLCP-fiber phase. Hence, the term "in-situ composite" was coined (5) for this type of polyblend, which means self-reinforcement due to the fibers formed during processing.

Blends of Hoechst Celanese Vectra A900 TLCP and SEBS (styrene-ethylene butylene-styrene) thermoplastic elastomer were intensively studied by De Boer *et al.* (6–8). They reported the formation of TLCP fibers in an almost pure shear flow condition, which contradicted previous works suggesting that the fibers only form in an elongational flow condition.

In-situ composites produced mostly by fiber spinning and injection molding have a higher modulus than sheet or film (9) because of a fibrillar structure that can be obtained more effectively by elongational force in the spinning process. *In-situ* composite film has only recently gained much interest for applications such as high-strength balloons (10). However, the main problem in the TLCP blend system in such an application has been due to the high degree of anisotropy of the mechanical properties, i.e., the properties along the machine direction (MD) are different from those along the transverse direction (TD). Chinsirikul *et al.* (11) attempted to reduce the anisotropy

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using a counter-rotating die in film extrusion. Another approach to improve the properties was investigated by Datta *et al.* (12) through the addition of a compatibilizer. In their work, a blend of polypropylene (PP) and TLCP (Vectra A) with a maleic anhydride-grafted polypropylene (MA-PP) added as a compatibilizer was produced as an extruded strand and injection-molded sheet. An increase of about 25% in modulus was found in injected tensile bars containing about 30% TLCP. A similar investigation by O'Donnell (13) using MA-PP as a compatibilizer in a PP/Rodrun LC3000 (70/30 weight ratio) system also reported about a 30% increase in the modulus of the blend. It was concluded that the added compatibilizer helped produce more finely dispersed TLCP fibrils and consequently improved the tensile strength and modulus.

The objective of the present work is to improve the mechanical properties of *in-situ* composite film based on TLCP/PP using block and grafted copolymers as compatibilizers at various concentrations. Cast films were characterized in morphological and mechanical aspects.

EXPERIMENTAL

Materials

The thermoplastic polymer matrix used in this study was an injection grade polypropylene (PP6331) with a melt flow rate (MFR) of 12g/10 min (230°C, 2.16 kg load). A thermotropic liquid crystalline polymer was a copolyester comprising 60 mol% of p-hydroxybenzoic acid and 40 mol% of poly(ethylene terephthalate) (Rodrun LC3000) purchased from the Unitika Company. The crystal-nematic and nematic-isotropic transitions of LC3000 are 220°C and 280°C, respectively. A triblock thermoplastic elastomer of styrene ethylene butylene styrene (SEBS, styrene/rubber ratio 29/71, Kraton G-1652) and maleic anhydride-grafted SEBS (Kraton FG1901X, containing 1.8 wt% maleic anhydride) was provided by Shell Chemical Co. Maleic anhydride-grafted polypropylene (MA-PP), containing about 0.1 wt% maleic anhydride, was provided by the Mitsubishi Co.. The materials were vacuum dried at 60°C for 12 h before use.

Blending

Melt blending of PP and 10 wt% TLCP was performed using a co-rotating twin screw extruder (PRISM TSE-16TC) with a screw diameter of 16 mm, L/D = 25, intermeshing, at an extrusion rate of 150 rpm. The processing temperature profile was 180/220/220/225/225°C (14), representing temperatures at the hopper zone, the three barrel zones, and the heating zone in the die head, respectively. The strand exiting the extruder was immediately quenched in a water bath and subsequently was pelletized.

Extrusion Film Casting

TLCP/PP blend pellets were extruded using a 16-mm mini-extruder (Randcastle RCP-0625) equipped with a cast film line. The temperature profile was 190/220/230/240°C for the hopper zone, two barrel zones, and slit-die, respectively. The screw speed was 70 rpm. The gap of the die lip was adjusted at 0.65 mm and the width fixed at 152 mm. Extruded film was drawn downward as a molten blend exiting the die outlet and then quenched on a water-cooled roll. The draw ratio (slit width-to-film thickness ratio) was controlled by adjusting the take-off speed. The highest draw ratio used in this experiment was about 33. The film thickness was varied from 20 to 70 μm.

Mechanical Testing

Tensile testing was conducted using an Instron mechanical tester (Model 4301) with a grip length of 25 mm, a crosshead speed of 50 mm/min, and a full-scale load of 10N. Tensile properties of the dumbbell-shaped specimens (70 mm × 4 mm) were measured in the flow (machine) and transverse directions (ASTM D412). Data were taken and averaged from at least ten specimens for each blending system.

Impact testing was performed using a pneumatic driving impact tester Radmana ITR-2000 at a constant temperature and humidity (ASTM D3763). The test films were about 70 μm thick. The results are averaged values of at least ten measurements for each blending system.

Morphology

The distribution of TLCP fibrils in the PP matrix was directly observed under an optical microscope at a magnification of 100–400 times. In order to inspect the size and shape of the fibers more clearly, composite films were extracted in boiling xylene and the remaining fibers were dried before observation. The observation of the fractured surface of the composite films was performed using a scanning electron microscope (SEM, Hitachi S2500) operated at 15 kV. Fractured surfaces were prepared by fracturing the composite film in liquid nitrogen. Palladium film was coated on the specimens using a Hitachi E102 ion sputtering coater.

Order Parameter

The order parameter or orientation function (S) (15-17) defined as the degree of alignment of liquid crystal molecules with a preferred direction, was determined from the infrared dichroic ratio, $R = A_{\parallel}/A_{\perp}$, where $A_{\parallel}$ and $A_{\perp}$ are absorbance values for plane polarized light with the electric vector parallel and perpendicular to the preferred direction, respectively. For a band whose transition moment is parallel to the major molecular axis, $S = (R - 1)/(R + 2)$. The IR absorption spectra of composite films about 25 μm thick were recorded using a Perkin-Elmer FTIR (System 2000) with an aluminum wire-grid polarizer placed between the sample and the light source. The polarization directions of the polarizer were adjusted parallel and perpendicular to the machine direction of the film. Each spectrum was collected in a

transmission mode at a resolution of 4 cm^{-1} and 25 scans. An area under the peak at 1601.5 cm^{-1}, (C-C stretching vibration of para-substituted benzene ring of p-hydroxybenzoic acid) corresponding to the parallel transition moment was used to determine the order parameter of the TLCP.

RESULTS AND DISCUSSION

Mechanical Properties

Young's moduli of TLCP/PP/compatibilizer films with varied amounts of compatibilizer are shown in *Fig. 1*. Young's moduli of pure polypropylene film produced under the same processing conditions (not shown) were also determined and compared: 616 ± 66 MPa and 586 ± 44 MPa in machine direction (MD) and transverse direction (TD), respectively. The film evidently exhibited a slight anisotropy in its moduli. The addition of 10 wt% TLCP resulted in an increase in the modulus in MD by almost twice as much. The modulus in TD, however, increased slightly. It is evident that the composite film exhibited a high degree of anisotropy due to the preferred fiber orientation in the composite film. The effect of a compatibilizer on the film modulus, especially in MD, varies by different extents depending on the type and amount of compatibilizer. SEBS improved the film modulus in MD to the greatest extent with a peak value at 3 wt% SEBS. The improvement was about 46% over that without the compatibilizer (1,592 MPa vs. 1,091 MPa). The modulus decreases with an increasing SEBS content above 3 wt%. However, at 8 wt% SEBS the modulus is still slightly higher than without SEBS. Films with added MA-SEBS exhibited a similar effect as those with SEBS but to a lesser extent. A peak in modulus was found at 1.5 wt% MA-SEBS with a 21% improvement over that with no compatibilizer. On the other hand, MA-PP did not appear to have a significant effect on the film modulus.

The effect of a compatibilizer on the film modulus in TD is less pronounced than that found in MD. It appears that Young's modulus in TD was not significantly affected by the type and content of the compatibilizer, with an exception of an improvement of about 28% for film with 1.5 wt% SEBS.

The yield stress of composite films will now be discussed. *Figure 2* shows the yield stress of composite films containing various amounts of compatibilizer. For comparison, yield stress values of pure PP film were 20.2 ± 1.4 and 15.4 ± 1.5 in MD and TD, respectively (not shown in the *Figure*). The composite films were found to have a slightly higher yield stress than PP in both directions. A slight improvement of the yield stress in MD was found in the composite film with SEBS. In other cases, it was found that yield stress in both MD and TD decreases with an increasing amount of compatibilizer. In all cases, the yield stress in MD is higher than that in TD.

From the mechanical results presented above, it is rather surprising that such a soft elastomer such as SEBS improved the modulus of the composite films more than MA-SEBS, which in turn improved it more than MA-PP. This contradicts the expectation that the presence of a reactive MA group in the latter two compatibilizers could form a chemical or hydrogen bond with TLCP, which consequently, should improve the interfacial adhesion between the two phases. Such bonding between an MA group, and TLCP domains was probably formed during processing as previously

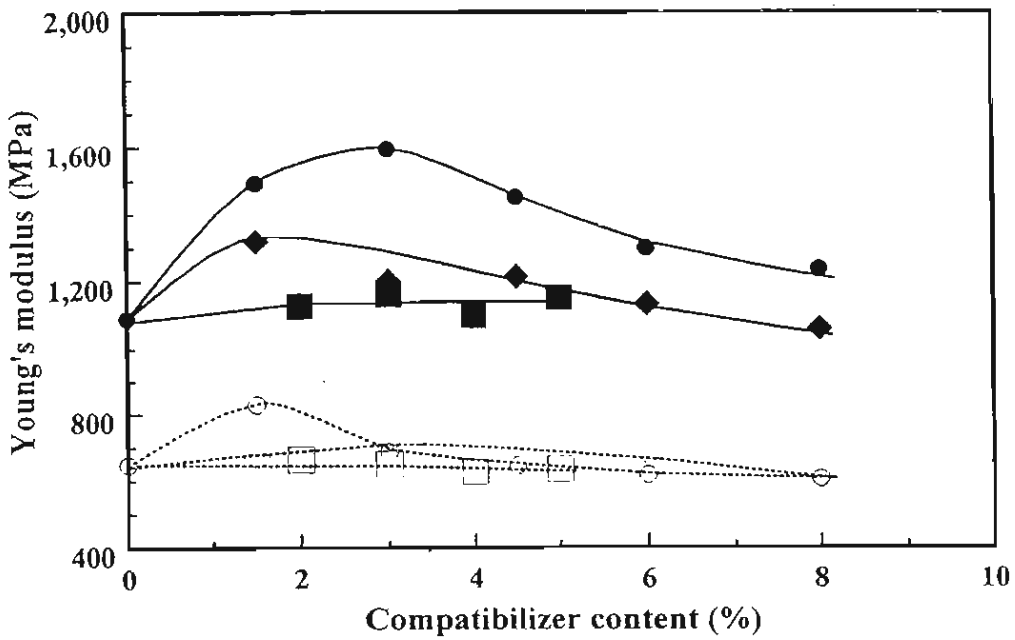

Fig. 1. Effect of compatibilizers on Young's Modulus of TLCP/PP composite films. (●, ○: SEBS; ◆, ❖: MA-SEBS and (■, □: MA-PP. MD: filled and TD: unfilled.)

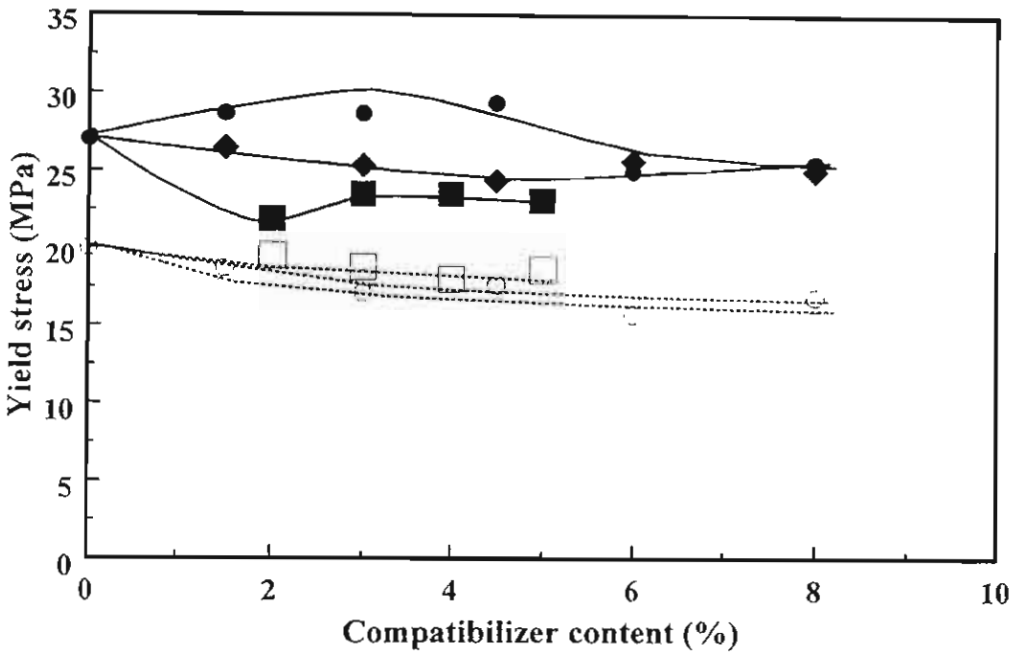

Fig. 2. Effect of compatibilizers on yield stress of TLCP/PP composite films. ●, ○: SEBS; ◆, ❖: MA-SEBS and ■, □: MA-PP. MD: filled and TD: unfilled.)

reported by O'Donnell (13) and Seo (18). However, this kind of bonding may retard the extension of the TLCP fibers by elongational flow. Hence, using MA-SEBS may give rise to thicker TLCP fibers (lower fiber aspect ratio) than those obtained in the case of SEBS. Since the modulus is measured at low strain, the difference in modulus would indicate a difference in the structure of the composite film, i.e., the size and aspect ratio of fiber formed in the film. The better properties of composite with the elastomeric compatibilizer may be due to the effect of a compatibilizer on the viscosity of the system. In order to support this assumption we measured the melt flow rate (MFR) (using 2.16 kg force at 230°C) of these blend systems. It was found that MFR reduces from 19.5g/10 min for the composite without a compatibilizer to 12.5, 13.2, and 17.6g/10 min for the blends containing 3 wt% SEBS, 1.5 wt% MA-SEBS, and 3 wt% MA-PP, respectively. A further addition of the compatibilizers showed no further significant change in MFR (see *Fig. 3*). The results reveal that SEBS and MA-SEBS increase the viscosity of the blend to a much greater extent than MA-PP, and hence, aid the formation of TLCP fibers. The effect of the viscosity ratio of LC3000/PP blends on their morphology was investigated by Heino *et al.*(14). They reported that the most fibrous structure was achieved when the viscosity ratio ranged from about 0.5 to 1. At the lower viscosity ratio the fiber structure was coarser, while at viscosity ratio above unity, the TLCP domains tended to be spherical. Similarly, in our work, the addition of SEBS to the TLCP/PP blend may affect the matrix viscosity to help form the fibrous structure of TLCP. The evidence from the morphology study will be discussed later.

A drop in the Young's modulus of the composite film at a high SEBS content will now be discussed. Since SEBS is a triblock copolymer with a styrene block at both ends and an ethylene/butylene block in the middle, it would be expected that the two ends containing aromatic rings would be compatible with the TLCP phase, while the rubbery EB block would be compatible with the PP matrix. Accordingly, SEBS should be present at the interface to promote interfacial adhesion and to help disperse the TLCP phase. At a high content, however, the amount of compatibilizer at the interface is likely to exceed the saturation limit (critical micelle concentration) and phase separation of the compatibilizer may take place (19, 20), resulting in an overall decrease in the properties of the blend. A further increase in the SEBS content lowers the Young's modulus of the composite due to the soft nature of the added rubber. However, even at 8 wt% SEBS, the composite film still shows a higher modulus than the film without a compatibilzer. This lowering effect at a high SEBS concentration was in agreement with the decrease in the shear modulus of PP on blending with SEBS (no reinforcing fibers), as reported by Gupta *et al.* (21).

The addition of MA-PP to the composite film shows only a slight increase in the modulus in MD. Although it is likely that the compatibilizer helps disperse the TLCP phase, it appears to be less effective than MA-SEBS. This may be due the lower concentration of the MA-group in MA-PP than in MA-SEBS and because MA-PP does not affect the viscosity of the blend (see *Fig. 3*).

Morphology

Figure 4 shows optical micrographs of composite films with: a) no compatibilizer, b) 3 wt% SEBS, c) 1.5 wt%

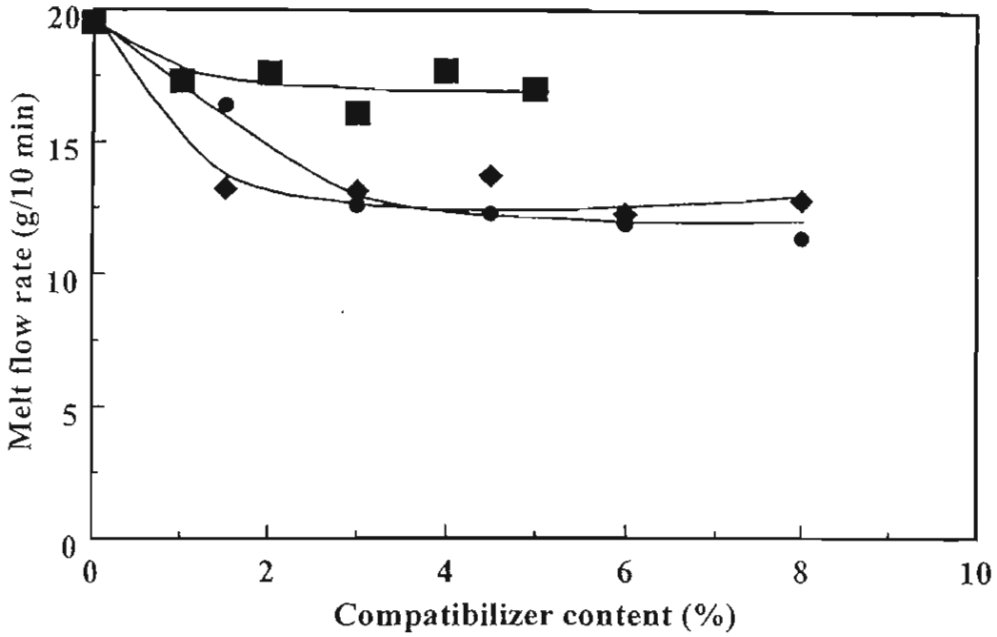

Fig. 3. Effect of compatibilizers on melt flow index of TLCP/PP blend. ●: SEBS; ◆: MA-SEBS and ■: MA-PP.

MA-SEBS, and d) 3 wt% MA-PP. At these concentrations of compatibilizer, a maximum value of tensile modulus is observed in each system. It is evident that the number of fibers per unit area as well as the aspect ratio of the TLCP fiber increase with the addition of a compatibilizer. The incorporation of a compatibilizer results in a more finely dispersed TLCP phase, and hence, more fibers are formed under shear and elongational forces. The addition of a compatibilizer, therefore, has a similar effect to increasing the fiber loading, giving rise to

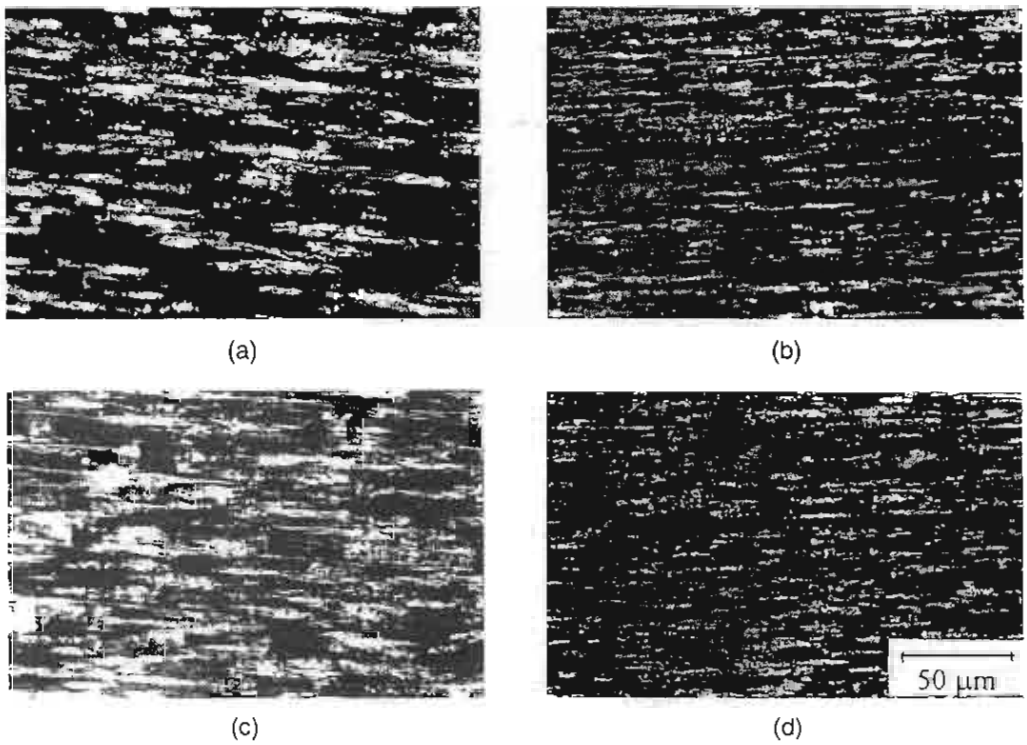

Fig. 4. Optical micrographs of in-situ composite films containing (a) no compatibilizer (b) 3 wt% SEBS (c) 1.5 wt% MA-SEBS and (d) 3 wt% MA-PP.

the enhancement of the modulus. This is in good agreement with the results reported by O'Donnell (13). In addition to the difference in shape of the dispersed TLCP fibers, the birefringence characterizing the frozen nematic phase of TLCP domains also differs. Without a compatibilizer, the TLCP phase exhibits a birefringence less homogeneous than that of the systems containing a compatibilizer, suggesting a better molecular orientation of the TLCP domains in the latter case. The result is supported by the increase in the order parameter of the TLCP phase, to be discussed later. To study the size and shape of fibers more clearly, composite films were extracted using boiling xylene, a good solvent for PP but a nonsolvent for TLCP. *Figure 5* shows photomicrographs of TLCP fibers extracted from films, taken at the same magnification. Fibers extracted from films containing compatibilizers (*Figs. 5b-d*) appear to be thinner and longer than those obtained from films with no compatibilizer (*Fig. 5a*). Among the three compatibilizers, SEBS yields the thinnest, and hence, the highest fiber aspect ratio, resulting in the highest Young's modulus discussed above.

Figure 6 shows SEM micrographs of the fractured surface of composite blends, broken along the direction normal to the flow direction. The film with no compatibilizer (*Fig. 6a*) shows a number of TLCP-fiber pull-outs with a smooth surface, suggesting a poor fiber-matrix interfacial adhesion. In the case of a composite with a SEBS compatibilizer (*Fig. 6b*), different features are observed: fiber breakage, fiber surface roughness, and fiber-tip bending. Similar features are also observed in the case of using an MA-SEBS compatibilizer (*Fig. 6c*). However, in the presence of MA-PP (*Fig. 6d*), the fiber surface is rather smooth with spike fiber tips and less fiber pull-out than in *Fig. 6a*, suggesting a better adhesion in the compatibilized composite. The appearance of fiber surface roughness in composites with an elastomeric compatibilizer may arise from an uneven extension of the TLCP phase caused by non-uniform friction due to the elastomer partly adhering at the interface. Such surface roughness was recently reported by Seo (22) for the ternary blend systems, nylon/TLCP/MA-EPDM, and PBT/TLCP/MA-EPDM. Though with higher viscosity of TLCP than the matrix, fibrillation of TLCP could be obtained at a low shear rate. Seo proposed the mechanism for the existing surface roughness: That it is a result of the relaxation of the elastomer surrounding the elongated TLCP phase.

Order Parameter

For thin film specimens, it is rather simple to determine the molecular orientation from the anisotropy of the absorption spectra (dichroism), especially in the infrared region. Since the selected peak used to measure the dichroic ratio belongs to the benzene ring in the TLCP molecule, the calculated order parameter,

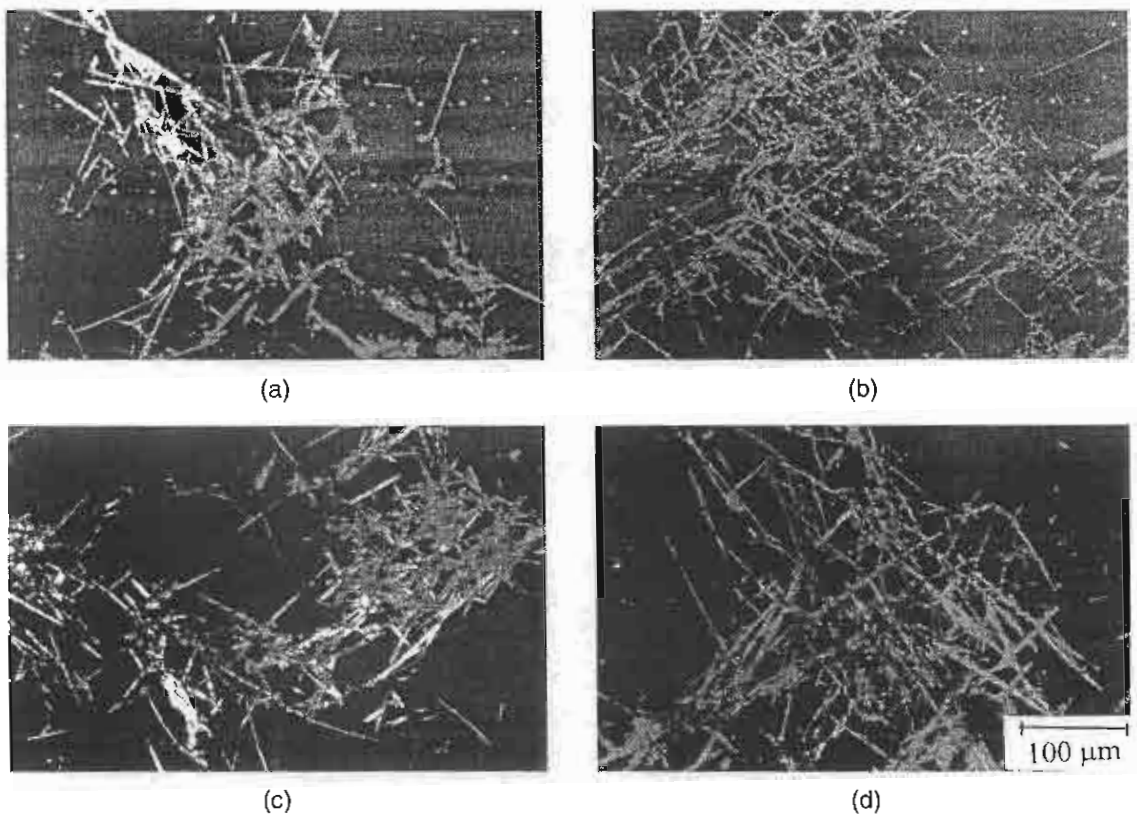

Fig. 5. Extracted TLCP fibers obtained from composite films containing (a) no compatibilizer (b) 3 wt% SEBS (c) 1.5 wt% MA-SEBS and (d) 3 wt% MA-PP.

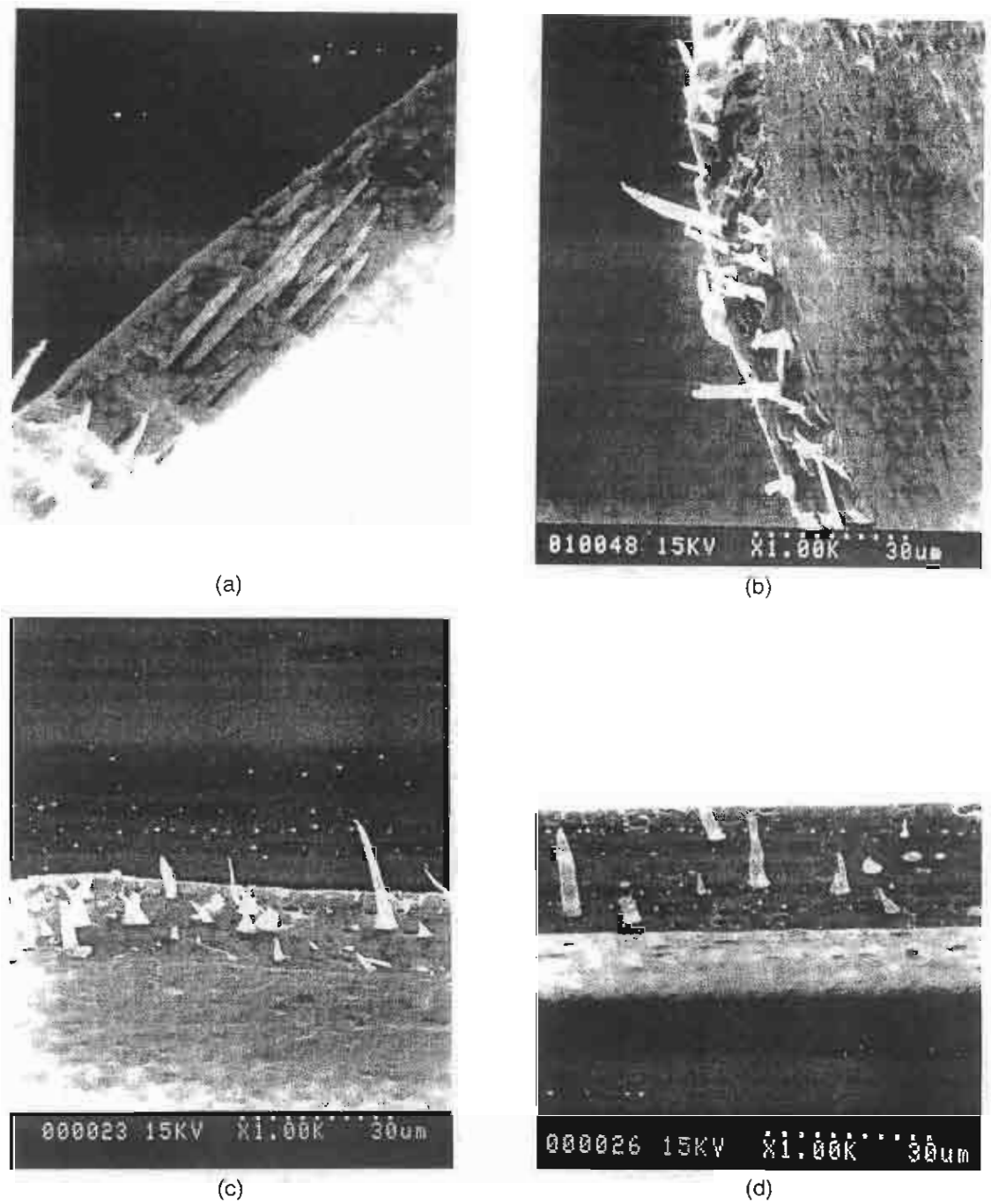

Fig. 6. SEM micrographs of fractured surface of composites film containing (a) no compatibilizer (b) 3 wt% SEBS (c) 1.5 wt% MA-SEBS and (d) 3 wt% MA-PP.

therefore, represents only the order in the TLCP phase. The order parameter of TLCP in the composite films containing compatibilizers is shown in *Fig. 7*. The films with about 1.5 wt% SEBS and with 1.5 wt% MA-SEBS have an increase of order parameter in the TLCP phase from about 0.5 to 0.6 and are roughly unchanged beyond this value. In the case of MA-PP, the less pronounced increase in order parameter is observed. This is in good agreement with the increase in modulus of the composite films at a low percentage of compatibilizer. Better molecular orientation in the TLCP phase translates to better mechanical properties of TLCP (16, 23), and hence, to a better composite.

Impact Strength

Results obtained from the impact testing of TLCP/PP composites without and with compatibilizers are illustrated in *Fig. 8*. Break energy in J/m is plotted

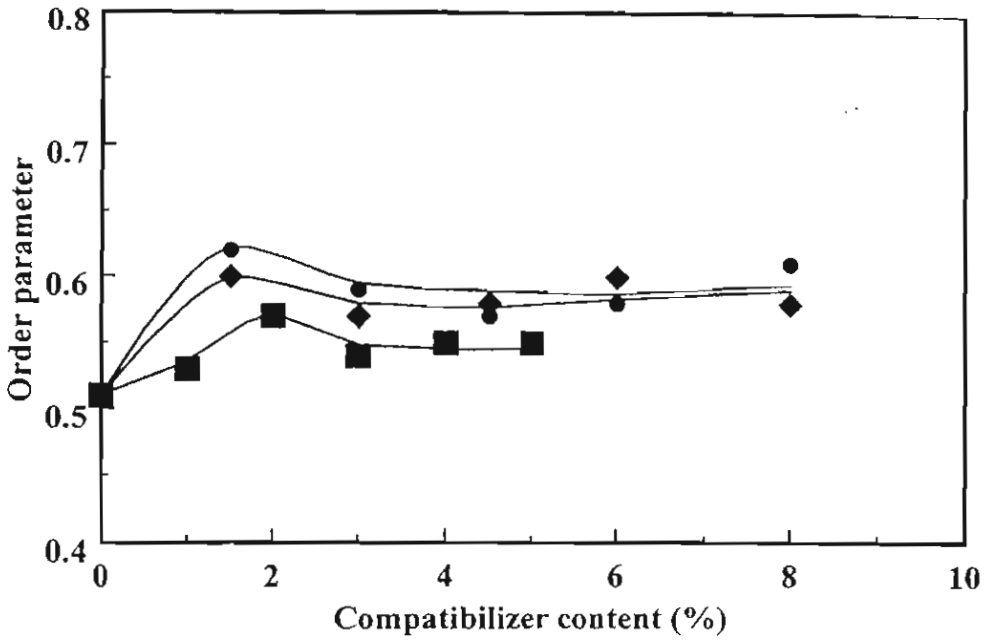

Fig. 7. Order parameter of TLCP phase in TLCP/PP composite films containing ●: SEBS; ◆: MA-SEBS and ■: MA-PP.

against the concentration of compatibilizer in percentage by weight. The composite without a compatibilizer has a very low impact strength (318 J/m) compared with that of pure PP (1,840 J/m). The results suggest poor interfacial adhesion between TLCP and the matrix, which is always a problem with *in-situ* composites. This results show an improvement of impact strength when an elastomeric compatibilizer was added. At a low level of compatibilizer concentration, e.g., up to about 5 wt% SEBS and MA-SEBS, the impact property improves slightly with an increasing amount of compatibilizer. With an 8 wt% compatibilizer, the impact strength increases steeply to about 1,300 J/m, approximately a four-fold increase. A sim-

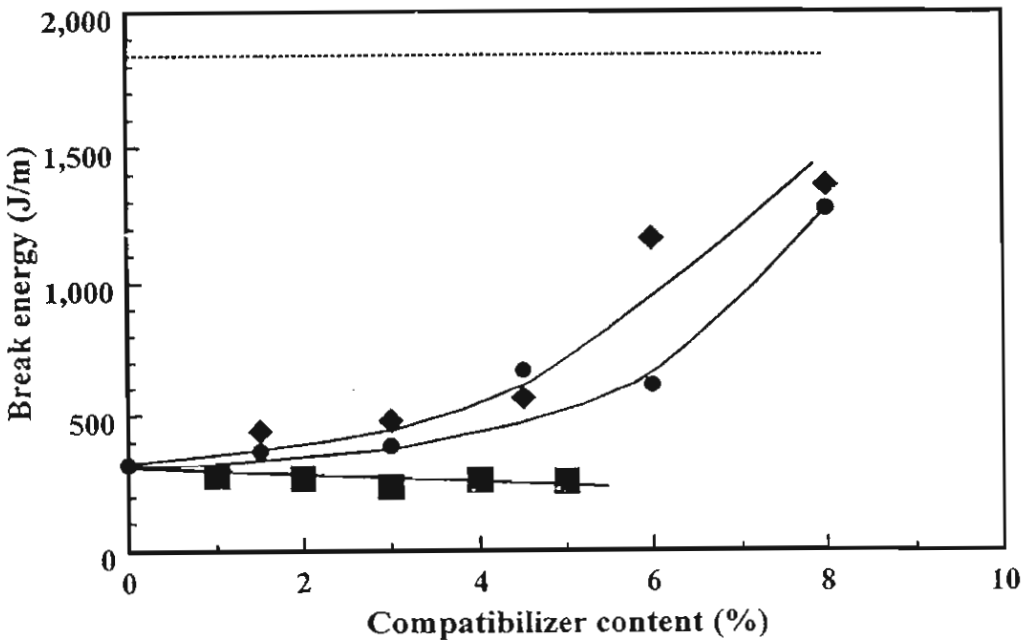

Fig. 8. Effect of compatibilizers of impact strength of TLCP/PP composite films ●: SEBS; ◆: MA-SEBS and ■: MA-PP; dotted line pure PP. Size of error bar is not bigger than twice the size of the symbol.

ilar result was observed by Gupta *et al.* (21, 24) and Setz *et al.* (25) for a PP/SEBS system with no fiber reinforcement. It is concluded that the addition of elastomeric compatibilizers not only improves the tensile modulus but also the impact strength of the composites. This large improvement of impact property at a high concentration of the elastomer may be due to its action as an impact modifier, the mechanism of which was explained in the established rubber-toughening theory (26). Evidently, MA-PP does not show any effect on the impact strength of the composite, since it is a thermoplastic in nature and is unable to absorb impact energy like the rubbery SEBS and MA-SEBS can.

CONCLUSIONS

All three compatibilizers used in this study, namely, SEBS, MA-SEBS, and MA-PP, were found to improve the dispersion and interfacial adhesion of the TLCP phase (Rodrun LC3000) and PP matrix, giving rise to the enhancement of the tensile modulus. In this study, thermoplastic elastomers, SEBS and MA-SEBS, were found to be more effective as compatibilizers than MA-PP. The addition of an elastomeric compatibilizer ehanced the viscosity of the system as evident in the decrease in its melt flow rate, which in turn affected the elongational flow of the dispersed phase to form thinner (and hence, higher aspect ratio) TLCP fibers. Surprisingly, SEBS was found to be a much more effective compatibilizer than MA-SEBS, despite the presence of an MA reactive group that could have improved the interfacial adhesion in the latter. An additional advantage of using an elastomeric compatibilizer is that it could also improve the impact strength of the *in-situ* composite due to its action as an impact modifier.

ACKNOWLEDGMENT

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Composite of aramid fibre (poly-*m*-phenylene isophthalamide)-thermoplastic elastomers (SEBS): enhancement of tensile properties by maleated-SEBS compatibiliser

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Abstract

Aramid fibre, poly-*m*-phenylene isophthalamide (Teijin-Conex), was used to reinforce thermoplastic elastomer, styrene (ethylene butylene) styrene (SEBS). It was found that the moduli at 100 and 300% elongation of the composite increased linearly with increasing fibre loading. On the other hand, tensile strength of the composites decreased as the fibre content was increased. Improvement of interfacial adhesion was carried out by, first, slightly hydrolysing the fibre with sodium hydroxide solution to increase the number of reactive amino end groups and then mixing with the matrix and compatibiliser, maleic anhydride grafted SEBS (MA-g-SEBS), at various concentrations. Tensile strength of the compatibilised composite was found to increase and then level-off at 5 wt% compatibiliser. Fractured surface of composite containing compatibiliser showed more fibre breakage than the uncompatibilised one. Examination of the extracted fibre revealed that some fraction of rubber was chemically bonded to the fibre surface. These results suggest good compatibilising performance of MA-g-SEBS for the system studied.

Keywords: Poly-*m*-phenylene isophthalamide; SEBS; Composites

1. Introduction

Short fibre reinforced rubber has now received much attention. The main advantage is that it allows greater speed and flexibility in processing as compared with continuous fibre [1]. A high degree of low strain reinforcement can also be achieved at relatively low content of fibre as compared with particulate fillers. Various systems of short fibre reinforced rubbers have been studied. The fibre studied includes Rayon, polyvinyl alcohol, Nylon, *p*-aramid (Kevlar), *m*-aramid (Nomex), polyester and glass fibres [2]. The nature of the fibre determines the interfacial interaction between fibre and matrix and also the strength of the composites. To achieve maximum reinforcement, strong fibre with good interaction with matrix rubber will be needed. As far as mechanical properties are concerned, aramid fibres (Kevlar for example) are good candidates. There is, however, a problem of poor interfacial adhesion between the fibre and a matrix. Various methods have been used to modify the surface of aramid fibre, Kevlar in particular. These include coupling agents [3], ionomer matrix, [4–5] chemical treatments [6–8] and plasma treatment [9–12]. One of the simple chemical treatment techniques reported in the literature is surface hydrolysis [10,13]. The technique allows simple and easy preparation of Kevlar with an increased number of active amino groups on its surface. These functional groups can then be employed in further reaction with other chemicals e.g. reactive or functionalised compatibilisers. The level of achievement depends to a great extent on the matrix studied.

In this paper, a system of poly-*m*-phenylene isophthalamide (Conex) short fibre reinforced styrene (ethylene butylene) styrene (SEBS) thermoplastic elastomer was studied. Thermoplastic elastomer was chosen as a matrix to ease composite preparation and avoid the need for curing used in a conventional rubber system. Conex fibre was first used as-received. In the second part, surface hydrolysis of the

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fibre in conjunction with the use of reactive compatibiliser, MA-g-SEBS, was studied.

2. Experimental

2.1. Materials

The materials used in this study were styrene (ethylene butylene) styrene (SEBS, Kraton G 1652), which consisted of 29% styrene with $\bar{M}_w$ S-block = 7200, $\bar{M}_w$ EB-block = 37 500 and maleic anhydride grafted SEBS (MA-g-SEBS, Kraton FG 1901x), which consisted of 29% styrene and contained 1.84 wt% MA. These two thermoplastic elastomers were kindly provided by Shell.

Aramid short fibre, poly-*m*-phenylene isophthalamide (Teijin-Conex) with average length of 3 mm (aspect ratio, i.e. length to diameter ratio is about 200–250) was kindly provided by Teijin Ltd. These materials were dried at 50°C for at least 24 h in a vacuum oven to remove sorbed water before processing.

2.2. Treatment of aramid fibre

Aramid fibres used in this experiment are classified as untreated and treated fibres. As-received fibre was first washed with acetone and distilled water in order to remove the possible surface impurities, such as oil or lubricant, and dried in a vacuum oven. This is called untreated fibre. Then untreated fibre was dispersed in 10 wt% sodium hydroxide solution for 20 min at the ambient temperature. Following the hydrolysis, fibre was thoroughly washed with distilled water to remove excess sodium hydroxide, then washed with toluene, and dried at 50°C in vacuum oven. This will be called treated or hydrolysed fibre. Partial hydrolysis of the aramid fibre with alkaline solution was performed in order to create more chemical reactive $-NH_2$ end groups on the fibre surface, which should enhance the probability to react with the compatibiliser containing maleic anhydride group [14].

2.3. Preparation of composites

Sample weight 50 g of aramid fibre/SEBS at a specified weight ratio was mixed in an internal mixer (Haake Rheocord 90) at 175°C, rotor speed of 90 rpm, for 10 min. In order to obtain better dispersion, dried fibre was first pre-opened in a Moulinex blender for a few seconds then put in the internal mixer and the rotor was operated for half a minute. Thereafter, the compatibiliser was added and blended for half a minute, and finally SEBS was placed and blended further for 9 min. After that, the composite was discharged and passed through a two-roll mill once to obtain a flat sheet then kept in a desiccator at room temperature for 24 h in order to minimize moisture adsorption. The amount of added compatibiliser was 0, 1, 3, 5 and 7 wt% to the composite with the fixed amount of fibre at 3 wt%.

2.4. Characterisation

2.4.1. Mechanical properties

The aramid fibre/SEBS composite was compression moulded into 1-mm thick sheet at 185°C for 10 min and subsequently quenched with water. After being conditioned for at least 24 h, dumbbell-shape tensile specimens were cut with a cutting die of size 115 × 6 mm, parallel to the machine direction (direction passing through the two-roll mill). Testing was performed on an Instron testing machine model 4301 in accordance with ASTM D638 at a cross head speed of 500 mm/min with a full scale load cell at 100 kg. All the values were averages of at least five measurements.

2.4.2. Spectroscopic characterisation

An Infrared Fourier Transform Spectrometer attached with Diffuse Reflectance unit (DRIFT, Perkin Elmer PE 2000) was used to characterise the surface of the fibre before and after surface treatment. The infrared spectrum throughout the range of 4000–600 cm^{-1} was obtained by performing 200 scans at a resolution of 4 cm^{-1}.

2.5. Extraction of composite

The composite was extracted to remove SEBS in a soxhlet apparatus using toluene as a solvent for 72 h. The extracted fibre was collected, dried in a vacuum oven at 50°C and observed under SEM. The aspect ratio of the extracted fibre was measured with the optical microscope and was found to be in the range of 30–80.

2.6. Morphology

The morphology of the fibre surface and fractured surface of the composite was observed under a Scanning Electron Microscope (Hitachi S2500). A thin layer of palladium was coated with Hitachi E102 ion sputter on the specimen to prevent charging on the surface. SEM was operated at 15 kV. The fractured surface of the composites was prepared by freezing the composite in liquid nitrogen and then breaking rapidly above the surface of liquid nitrogen.

3. Results and discussion

3.1. Hydrolysis of aramid fibre surface

In this study, aramid fibre was partially hydrolysed on the surface in order to create more $-NH_2$ and $-COOH$ end

groups, as shown in the following reaction.

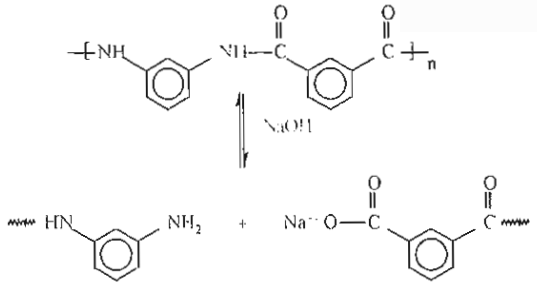

Fig. 1 shows infrared spectra of Conex fibres before and after hydrolysis using DRIFT technique. It can be seen that a new peak appears at 880 cm^{-1} (curve b) after hydrolysis. The peak is associated with the C–H out of plane bending of aromatic ring containing $COO^- Na^+$ substituent similar to that reported by Chatzi et al. [15] for Kevlar fibre. The surface hydrolysis was therefore considered successful.

3.2. Mechanical properties of composites

Stress–strain curves of untreated Conex fibre reinforced SEBS composites with various amounts of fibre content are illustrated in Fig. 2. Most of the curves exhibit similar stress–strain behaviour. For convenience in the discussion, the stress–strain curve will be divided roughly into three regions. In the first region, stress increases linearly with strain. Beyond a certain strain, depending on fibre content, the stress starts to level-off and then, in the third region, rises up sharply. The pronounced rising up of stress in the third region is known as self-reinforcing effect or strain-hardening effect [16–18]. This is a typical behaviour, and often an advantage, of a few elastomers such as natural rubber, styrene butadiene styrene (SBS) rubber and *cis*-polybutadiene.

Pure SEBS (curve a) shows stress–strain curves with all regions. The stress in the first and second regions is lowest among the others. On the other hand, stress in the third region reached a maximum value of almost 30 MPa. Addition of Conex fibre increases the stress in the first and second regions in all specimens. At Conex content up to 3%, the stress–strain behaviour does not significantly change, i.e., the curves still have three regions with strain-hardening effect. At the fibre content of 5 and 7% no more strain-hardening effect is observed. The composites broke at lower strain when higher content of fibre is added.

Fig. 3 shows the tensile properties of untreated Conex composite. It can be seen that tensile moduli at 100 and 300% extension increased with increasing fibre loading but the tensile strength decreased. Elongation at break of the composite was virtually unchanged up to 5 wt% of fibre loading then dropped sharply as the fibre content was further increased.

An enhancement in modulus at both 100 and 300% extension is as expected when fibre of very high modulus is incorporated into the elastomer matrix. At low strain (≤100%) a significant improvement can be clearly seen. Modulus at 100% strain increases almost four-fold when 7 wt% of Conex was incorporated. The level of improvement, however, decreases with increasing strain.

For untreated Conex/SEBS system, the adhesion between fibre and matrix is poor (as will be seen in the next section) and will de-bond at low strain. Therefore, the main mechanism of stress transfer is friction. Upon further straining, voiding at the ends of fibre will be created and crack initiation will start before strain-hardening takes place. Increasing fibre content will increase the number of voids and hence the probability of failure will be higher.

Modification of interfacial interaction was carried out by surface hydrolysis and use of a reactive compatibiliser. The effect of surface hydrolysis alone on mechanical properties of the composites was not found to be significant. Therefore, only surface hydrolysis in conjunction with the compatibiliser will be considered. Effects of MA-g-SEBS on tensile properties of the composite are illustrated in Fig. 4. There is no significant change of modulus at 300% extension as the

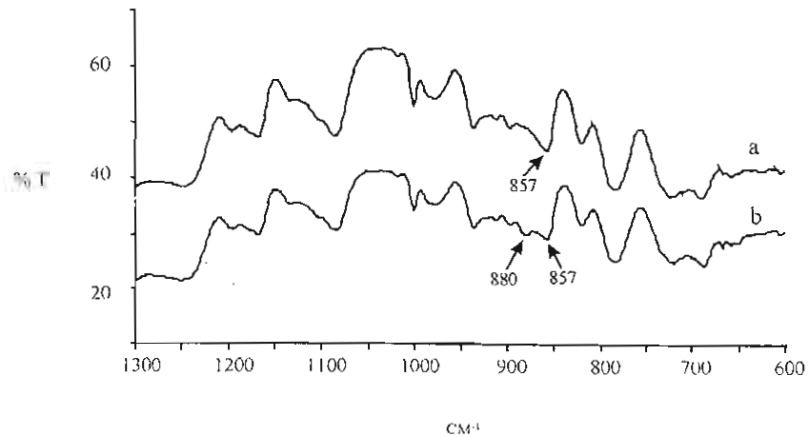

Fig. 1. Infrared spectra of Conex fibres before and after surface hydrolysis.

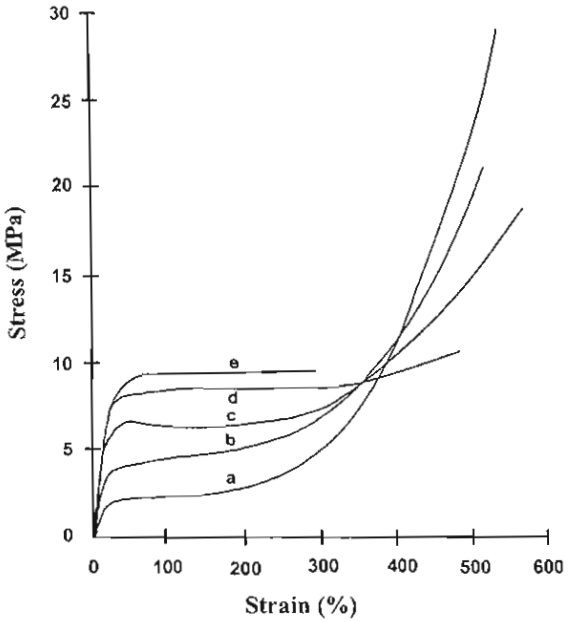

Fig. 2. Stress–strain curves of Conex/SEBS composites at different fibre loading (wt%): (a) 0, (b) 1, (c) 3, (d) 5 and (e) 7.

amount of MA-g-SEBS is increased, whereas the modulus at 100% elongation is slightly decreased when MA-g-SEBS is higher than 3%. No effect of compatibiliser on the elongation at break was observed. A significant improvement in tensile strength with the addition of MA-g-SEBS can be seen in Fig. 4(b). Tensile strength was found to level off at 5 wt% of MA-g-SEBS. The improvement is about 45% over that without MA-g-SEBS. This shows that MA-g-SEBS improves the interfacial adhesion between the fibre and the matrix. Further evidence regarding improved interfacial adhesion will be shown in the next section.

In order to understand the effect of added MA-g-SEBS, the stress–strain curve of the composites will be considered. Fig. 5 shows the stress–strain curves of composites (3 wt% Conex) without and with 3 wt% MA-g-SEBS. It can be seen that the addition of MA-g-SEBS reduced stress in the low strain region. As strain is increased, the tensile stress of the composite with MA-g-SEBS approached that of the composite without MA-g-SEBS. The composite without MA-g-SEBS failed at lower strain, and hence lower tensile strength. From these results, it is postulated that the softer MA-g-SEBS stays preferentially at the matrix–fibre interface (supporting evidence will be shown in the morphology section). Stress transfer through this softer layer will therefore be reduced. At high strain, however, the strain-hardening effect in this type of material comes into play and increases stress transfer. The fact that the composite with MA-g-SEBS failed at higher strain would suggest that interfacial bonding between the matrix and fibre is better. In other words, interfacial de-bonding in the composite with MA-g-SEBS started at higher strain than that in the composite without MA-g-SEBS. As a consequence, an

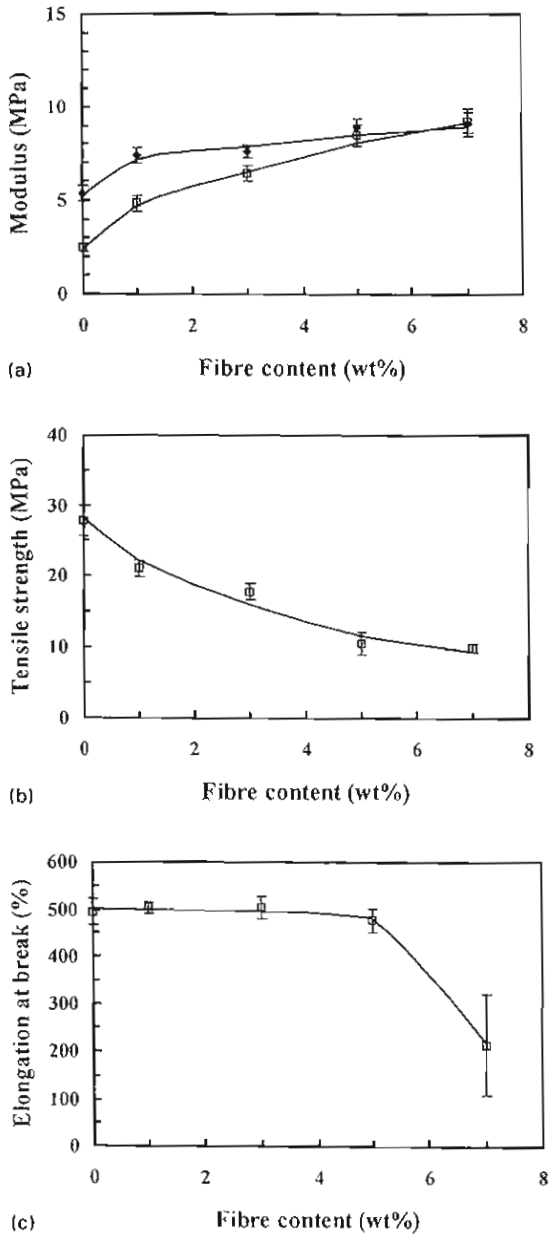

Fig. 3. Tensile properties of untreated aramid fibre/SEBS composite with various fibre loading. (a) Modulus at 100% (□) and 300% (◆) extensions, (b) tensile strength and (c) elongation at break.

improvement in tensile strength was observed in the composite with MA-g-SEBS.

3.3. Morphology

SEM micrographs (at × 2000 magnification) of fractured surface of 3 wt% Conex/SEBS composites without compatibiliser and with 3 wt% MA-g-SEBS are shown in Fig. 6(a) and (b), respectively. Without compatibiliser, fibre pull-out is observed, which indicates poor adhesion at the interface. However, fibre breakage is observed when MA-g-SEBS is added and adhesion of rubber at the base of

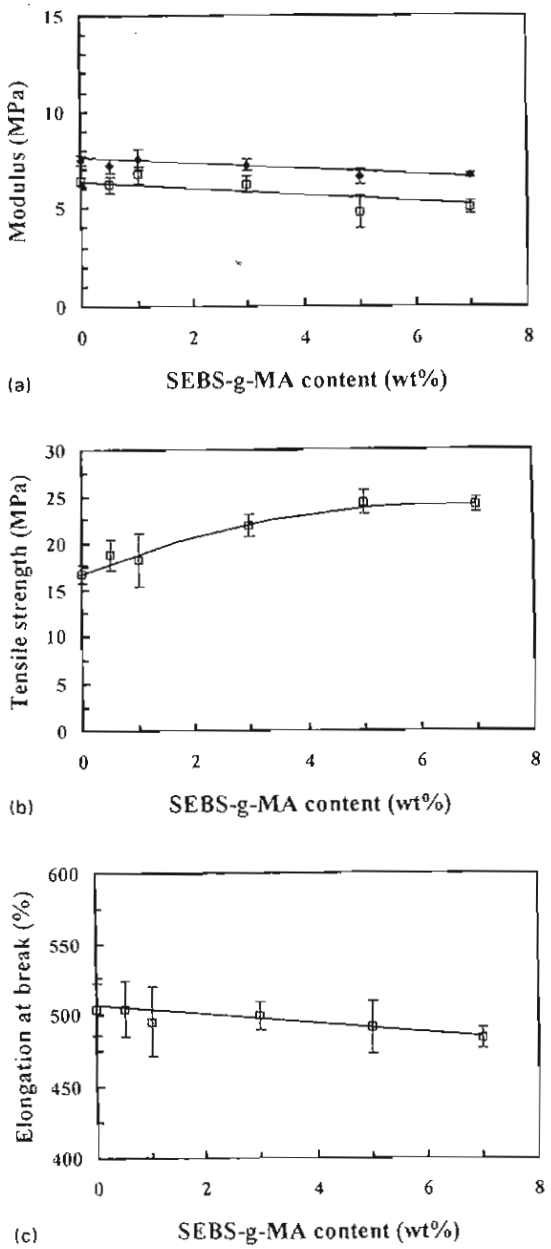

Fig. 4. Tensile properties of treated aramid fibre/SEBS composite with addition of compatibiliser. (a) Modulus at 100% (□) and 300% (♦) extensions, (b) tensile strength and (c) elongation at break.

fibres is observed which suggests the improvement of interfacial adhesion.

SEM micrographs (at ×500 magnification) of solvent extracted fibres from the composites without and with compatibiliser (3 wt% MA-g-SEBS) are presented in Fig. 6(c) and (d), respectively. In the case of the composite without MA-g-SEBS, very clean fibre was obtained after extraction. On the other hand, for the composite with MA-g-SEBS, the extracted fibre showed a rough and irregular surface and also lumps of unextractable rubber.

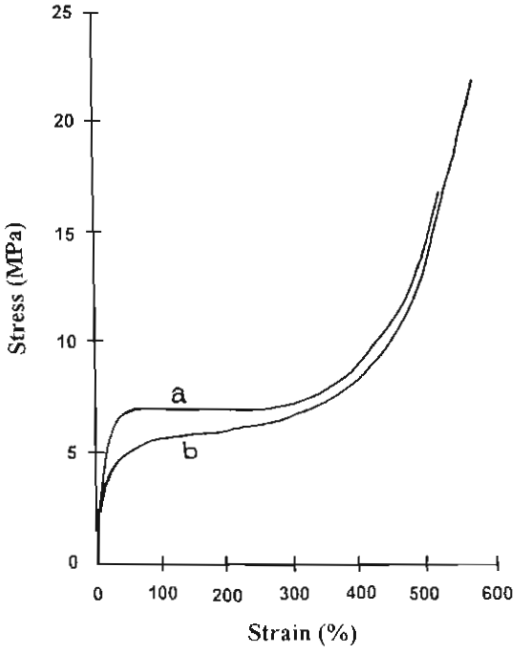

Fig. 5. Stress-strain curves of Conex/SEBS composites with 0 wt% (a), and 3 wt% (b) of MA-g-SEBS.

It is clear, from the above results, that in a system with MA-g-SEBS there are some fractions of rubber which can not be extracted. It is likely that this rubber is chemically bonded to the fibre surface and results in surface irregularity as seen above. This would suggest that MA-g-SEBS reacts with reactive end groups, i.e. $-NH_2$, on the surface of partially hydrolysed Conex fibre and hence the tensile strength of the compatibilised composite is improved.

4. Conclusion

Reinforcement of SEBS thermoplastic elastomer with Conex fibres at low strain can be achieved without any compatibiliser. Modulus of thermoplastic elastomer was enhanced to more than 100% at the fibre content as low as 3 wt%. The strain-hardening effect was found to decrease with increasing fibre loading.

Alkaline hydrolysis of fibre surface in conjunction with reactive compatibiliser, MA-g-SEBS, was found to be effective since this resulted in improvement of the tensile strength. SEM micrographs of the fractured surface revealed a high proportion of fibre breakage. The extracted fibres show patches of unextractable rubber on the surface which is taken as additional evidence for improvement of the bonding at the interface. The results observed in this work suggested good compatibilising effect of MA-g-SEBS for Conex short fibre/SEBS composite. Compared with our previous study on the properties of Kevlar pulp/SEBS system using a similar procedure [19], no improvement was

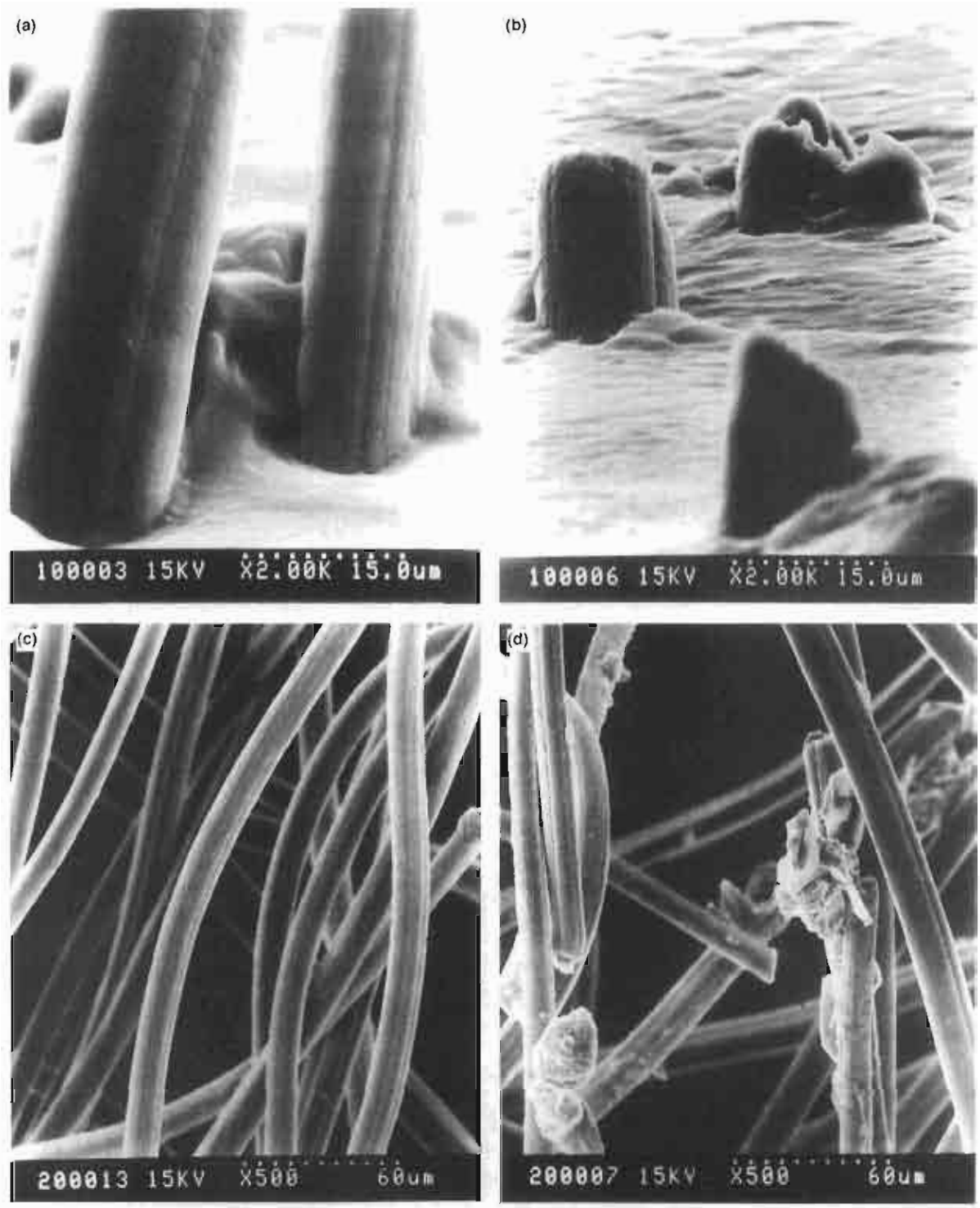

Fig. 6. SEM micrographs of the specimens: (a) fractured surface of the composite without compatibiliser; (b) fractured surface of the composite with 3 wt% MA-g-SEBS; (c) extracted fibres from specimen without compatibiliser; (d) extracted fibres from specimen with 3 wt% of MA-g-SEBS.

observed when MA-g-SEBS was added. In that case, it might be due to fibrillation of pulp during processing, causing the treated surface to peel-off, hence, no improvement of adhesion at the interface can be achieved.

Acknowledgements

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thank Shell Chemical Co. for providing SEBS and Teijin Ltd for providing Conex fibre.

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Kevlar reinforcement of polyolefin-based thermoplastic elastomer

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Abstract

Composite systems of Kevlar, poly(*p*-phenylene terephthalamide), and Santoprene, a polyolefin-based thermoplastic elastomer, were studied. Kevlar pulp was used as-received in one system, and modified in the other. The as-received Kevlar pulp was found to reinforce Santoprene to a certain degree. It was found that with increasing amount of Kevlar in the composite, low-strain modulus and tensile strength increased, while the elongation at break decreased sharply. To improve mechanical properties of the composite, hydrolysis of Kevlar pulp surface was employed in conjunction with maleic anhydride-grafted-polypropylene (MA-g-PP), a reactive compatibiliser. It was found that the treated Kevlar pulp greatly improved the low-strain modulus, tensile strength, and elongation at break of the composite. Dynamic mechanical analysis showed that the storage modulus of the Kevlar/MA-g-PP/Santoprene composite was significantly higher than the as-received Kevlar composite. A slight increase in transition temperatures of polypropylene matrix was also observed. As a result of the fact that low-strain modulus and tensile strength of the composite were improved when hydrolysed Kevlar pulp and MA-g-PP were used, it is suggested that such a combination might have increased the interfacial adhesion of the fibre and the matrix, and effective fibre volume fraction, resulting in a better distribution of stress along the reinforcing fibre.

Keywords: Kevlar composite; Santoprene; Polyolefin

1. Introduction

Fibre-reinforced rubber composites have widely been in use for some time, because of their good mechanical properties. Most systems employed continuous fibres because of the vastly improved properties of the composites [1]. Recently, interests have turned to short-fibre reinforced rubbers because of the greater speed and flexibility in processing inherent in these systems. In comparison with particulate-filler composites, a short-fibre reinforced system possesses a high degree of low-strain reinforcement even at relatively low-fibre content. Various studies on short-fibre systems include Rayon, poly(vinyl alcohol), Nylon, *p*-aramid (Kevlar), *m*-aramid (Nomex), polyester, and glass fibres [2]. The degree of reinforcement greatly depends on the nature of the system. The chemical structures of both the fibre and the matrix determine the extent of the interfacial adhesion, and thus the strength of the composites. In order to achieve maximum reinforcement, strong fibre with good compatibility with the matrix is required. As far as mechanical properties are concerned, aramid fibres (e.g. Kevlar) are good candidates as a reinforcement. Although these fibres are not very compatible with the matrix being used, attempts were made to tackle the problem of poor interfacial adhesion in their composites. Various methods include the incorporation of coupling agents [3], the use of ionomer matrix [4,5], chemical [6–8], and plasma treatments [9–12] of the fibre surface. Hydrolysis was reportedly one of chemical treatment techniques, allowing simple and easy modification of Kevlar surface [10,13]. Such treatment increased a number of active amine end groups on the surface, providing functional groups for further reaction with, e.g. a reactive or functionalized compatibiliser.

This article describes a composite system composed of Kevlar pulp, poly(*p*-phenylene terephthalamide), and Santoprene, a polyolefin-based thermoplastic elastomer. The thermoplastic elastomer is used as matrix because of its ease of preparation, with no need of curing, normally used in conventional rubber systems. A hydrolysis of Kevlar pulp, followed by reaction with a reactive compatibiliser are employed.

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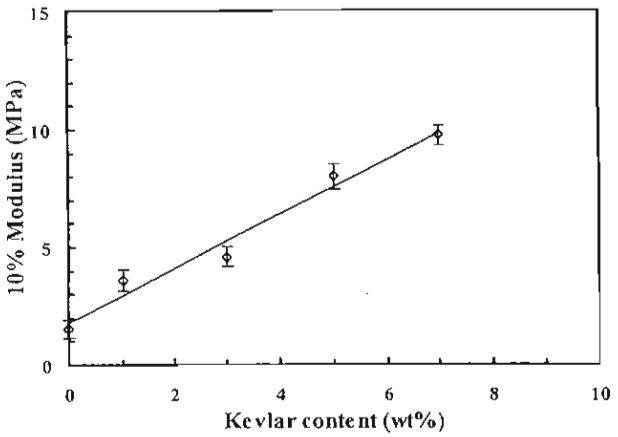


Fig. 1. Modulus at 10% strain of untreated Kevlar/Santoprene composites at various Kevlar content.

2. Experimental

2.1. Materials

The matrix is Santoprene thermoplastic elastomer grade 691-73W175 from Advance Elastomer Systems. The elastomer contains PP 18 wt.%, and EPDM 82 wt.%. Reinforced fibres were Kevlar-49 pulp and short fibre from DuPont. The compatibiliser, maleic anhydride-grafted-polypropylene (MA-g-PP, trade name POLYBOND 3150) was provided by Uniroyal Chemical Co. The compatibiliser contains 0.5 wt.% maleic anhydride and has a melt flow rate of 50 g/10 min.

2.2. Composites preparation

The composites were prepared by melt blending in a miniature internal mixer (Haake Rheocord 90) at a temperature of 165°C and a rotor speed of 90 rpm for 10 min. Kevlar pulp (or short fibre) was pre-opened using a Grinder

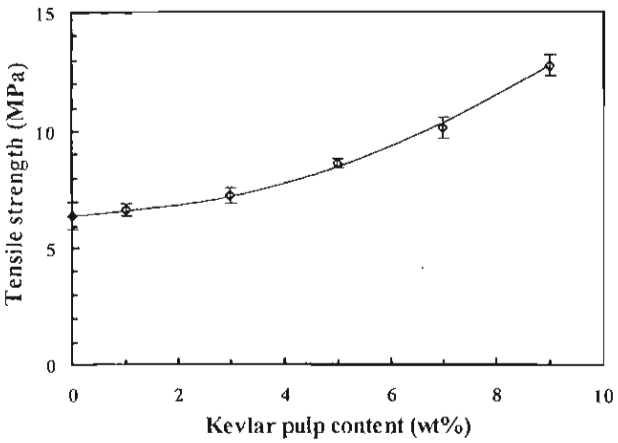


Fig. 2. Tensile strength of untreated Kevlar/Santoprene composites at various Kevlar content.

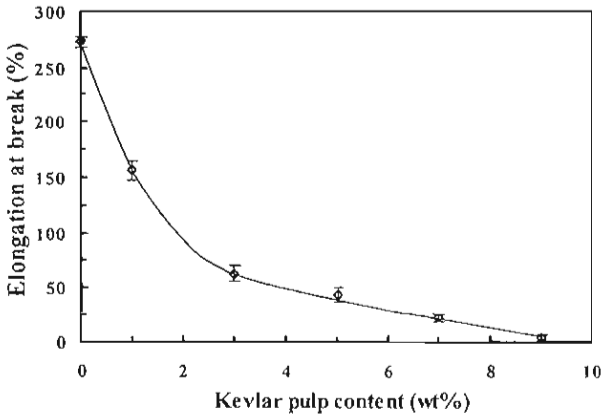


Fig. 3. Elongation at break of untreated Kevlar/Santoprene composites at various Kevlar content.

(Moulinex) with interior blades turning at a high rate of revolution for about 10 s before charging into the mixer. After that the mixture was passed through a two-roll mill once to obtain a flat sheet. The composite sheets were kept in a desiccator in order to minimize moisture adsorption.

2.3. Testing and characterizations

Composite sheets were compression moulded into sheets of 1 mm thickness. The moulding condition was 180°C under a pressure of 15 MPa for 10 min. Later, the mould was transferred to a water cooled press machine. The moulded sheets were kept in a desiccator for at least 24 h.

Dumb-bell-shaped samples were punched out (using Die C-ASTM D412-92) from the moulded sheets in the two-roll mill direction. Tensile properties were measured using an Instron 4301 tensile tester with a crosshead speed of 500 mm/min and a full scale load cell of 100 kg in accordance with ASTM D638. Dynamic properties were measured on Polymer Laboratories DMTA Mk II in bending mode at a frequency of 10 Hz. The sample length was 5 mm and peak to peak displacement was 64 μm. Measurements were carried out from −120°C to 120°C at a scan rate of 5°C/min.

Fracture surfaces of the composites were prepared by freezing the sample in liquid N_2 and breaking it rapidly. The samples were then coated with palladium (Hitachi E102 ion sputter) and observed under scanning electron microscope (SEM) (Hitachi S-2500) using an accelerating voltage of 15 kV.

3. Results and discussion

3.1. Untreated Kevlar pulp composites

Tensile properties of Kevlar/Santoprene composite with varying amount of Kevlar are shown in Figs. 1–3. As the composites with high Kevlar content failed at low elongation, the low-strain modulus was determined and reported

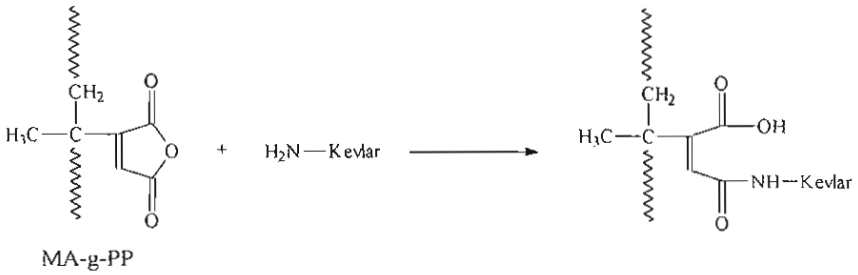


Fig. 4. Reaction between MA-g-PP and the amine group on the Kevlar surface.

here. Fig. 1 shows that stress at 10% extension (10% modulus) increases linearly with Kevlar content. The improvement is slightly above 1 MPa per 1 wt.% Kevlar added. The 10% modulus at 9 wt.% Kevlar could not be obtained as the composite failed before reaching the 10% extension.

Tensile strength as a function of Kevlar loading is shown in Fig. 2. The tensile strength of the composite increases slightly up to 3 wt.% Kevlar, and then more steeply approaches a value of 13 MPa at 9 wt.% Kevlar, an improvement of almost 100%. In this particular system, a minimum value of tensile strength at low-fibre content, or dilution effect [14], was not observed. Although the tensile strength improves significantly, the composite with high Kevlar content lost the extensibility property of the rubber matrix. Fig. 3 shows that elongation at break decreases sharply with increasing Kevlar content at low value, drops off more slowly at higher value, and reaches zero at about 9 wt.% Kevlar.

The aforementioned results suggest that the addition of Kevlar pulp significantly improved the properties of Santoprene, i.e. the modulus and tensile strength increased with increasing Kevlar content. However, the low extensibility at high Kevlar content may be a limiting factor that reduces the usability of the composite. These results, therefore, demonstrated that for a short-fibre reinforced composite, the mechanical properties are very much system dependent. Different results were reported in our previous study on Kevlar pulp/SEBS system in which tensile modulus increased, but tensile strength decreased with increasing Kevlar content [15]. Similar results were also reported in other systems [16–18].

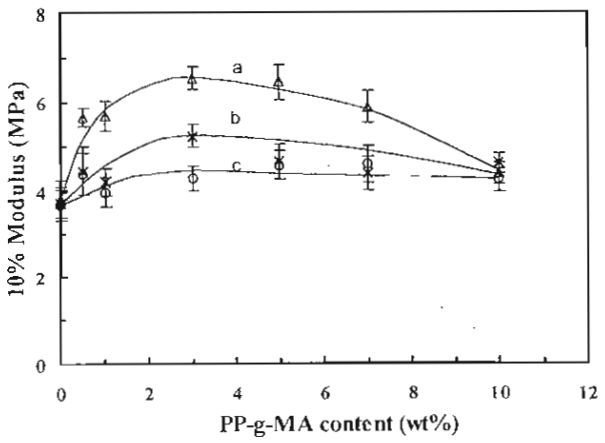


Fig. 5. Modulus at 10% strain of various Kevlar/Santoprene composites: (a) hydrolysed Kevlar/MA-g-PP/Santoprene (△), (b) hydrolysed Kevlar/PP/Santoprene (×), (c) untreated Kevlar/MA-g-PP/Santoprene (○).

3.2. Hydrolysed Kevlar pulp composites

To further our study, a composite system containing 3 wt.% Kevlar was chosen, because of the moderate improvement in modulus and tensile strength over the unreinforced matrix, and also because of the relatively high extensibility of the composite. In our system using Santoprene, a polypropylene-based matrix, MA-g-PP is used as a compatibiliser. The compatibiliser was incorporated in Kevlar pulp by first hydrolysing the fibre surface [10,13,15], introducing amine groups, which then react to form covalent bonds with MA groups of the compatibiliser added (Fig. 4), thus maximizing the compatibiliser efficiency. To compare the two systems, a third system containing hydrolysed Kevlar/polypropylene (PP)/Santoprene was investigated.

Fig. 5 shows curves of 10% modulus as a function of compatibiliser (MA-g-PP or PP) content. Curve a is the hydrolysed Kevlar/MA-g-PP/Santoprene composite with 3 wt.% Kevlar showing a maximum value at about 3 wt.% MA-g-PP, an improvement of about 50% over the untreated Kevlar/MA-g-PP/Santoprene system (curve c). The results of hydrolysed Kevlar/PP/Santoprene composite is shown in curve b, where modulus was only slightly improved.

Fig. 6 shows curves of tensile strength as a function of compatibiliser content. The hydrolysed Kevlar/MA-g-PP/Santoprene composite (curve a) shows the highest value of about 30% improvement at about 1 wt.% MA-g-PP, which levels off at higher MA-g-PP content. The addition of MA-g-PP and PP to the untreated and hydrolysed Kevlar composites, respectively, had no effect on tensile strength (curves b and c).

Fig. 7 shows curves of elongation at break (%EB) as a function of compatibiliser content. The hydrolysed Kevlar/MA-g-PP/Santoprene composite (curve a) shows an increase in %EB with increasing MA-g-PP content. At 3 wt.% MA-g-PP, where a maximum in 10% modulus was

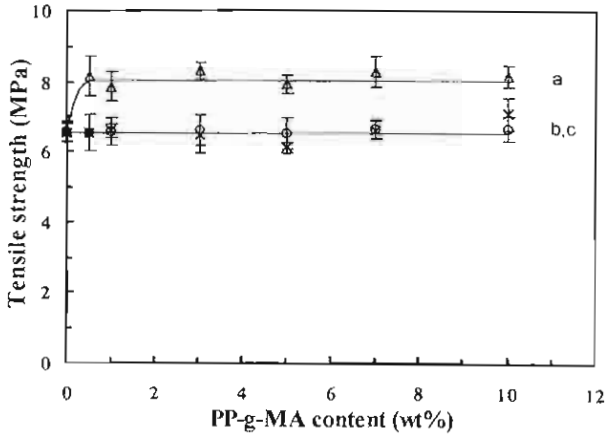


Fig. 6. Tensile strength of various Kevlar/Santoprene composites; (a) hydrolysed Kevlar/MA-g-PP/Santoprene (△), (b) hydrolysed Kevlar/PP/Santoprene (×), (c) untreated Kevlar/MA-g-PP/Santoprene (○).

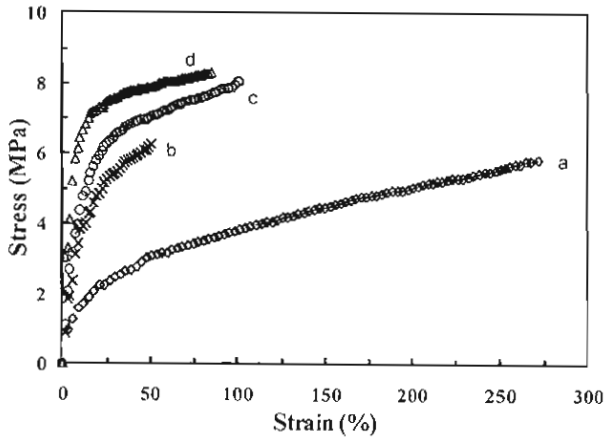


Fig. 8. Stress–strain curves of various Kevlar/Santoprene composites: (a) Santoprene, (b) 3 wt.% untreated Kevlar/Santoprene, (c) 3 wt.% hydrolysed Kevlar/3 wt.% PP/Santoprene, (d) 3 wt.% hydrolysed Kevlar/3 wt/% MA-g-PP/Santoprene.

obtained, an improvement in %EB is about 30% over that of the other two systems. The systems of untreated Kevlar/MA-g-PP/Santoprene and hydrolysed Kevlar/PP/Santoprene show no change in %EB.

From the results of these three composite systems shown in Figs. 5–7, it can be concluded that the presence of both the MA group on polypropylene chain and the amine groups on Kevlar surface are essential for the improvement of the mechanical properties.

Mechanical properties of Kevlar/Santoprene composite systems are summarized as stress–strain curves in Fig. 8. Santoprene with no reinforcement shows the highest strain at break as expected (curve a). The addition of 3 wt.% of Kevlar (untreated) to Santoprene caused a steep rise of stress and a break at a very low strain (about 50%) as shown in curve b. The 3 wt.% hydrolysed Kevlar/3 wt.% PP/Santoprene system shows an even steeper rise in stress and a break at higher strain (about 100%EB) shown in

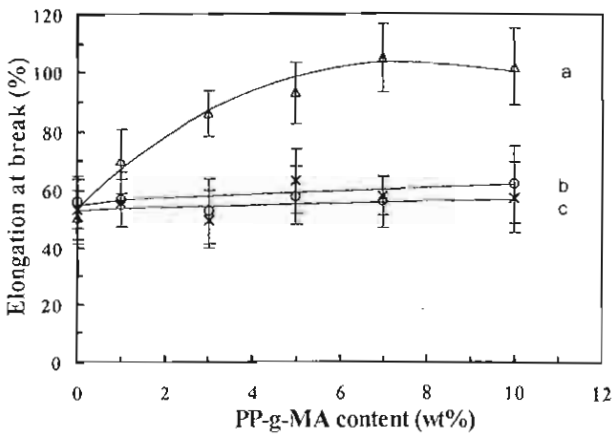
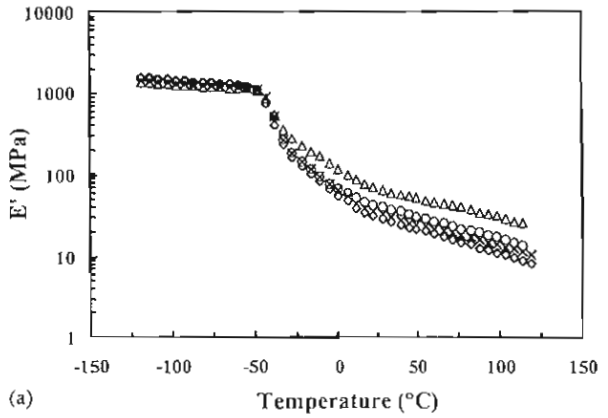


Fig. 7. Elongation at break of various Kevlar/Santoprene composites; (a) hydrolysed Kevlar/MA-g-PP/Santoprene (△), (b) hydrolysed Kevlar/PP/Santoprene (×), (c) untreated Kevlar/MA-g-PP/Santoprene (○).



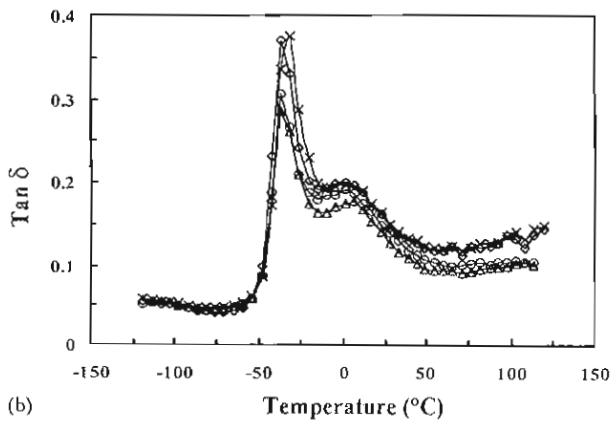
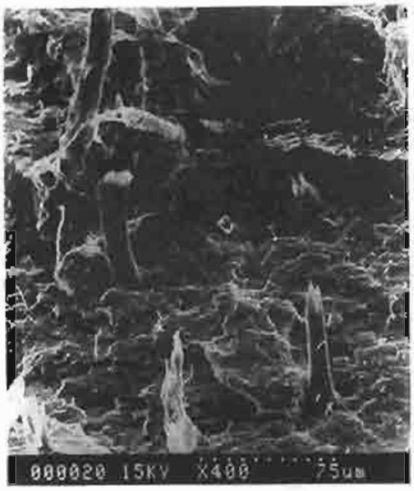
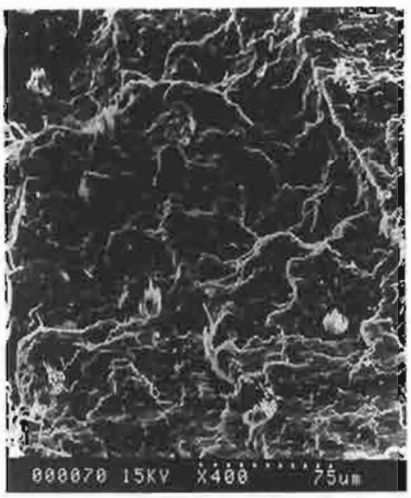


Fig. 9. (a) Storage modulus (E') and (b) tan δ of various Kevlar/Santoprene composites: 3 wt.% hydrolysed Kevlar/3 wt/% MA-g-PP/Santoprene (△), 3 wt.% untreated Kevlar/Santoprene (×), 3 wt.% hydrolysed Kevlar/3 wt.% PP/Santoprene (○), Santoprene (◇).



(a)



(b)

Fig. 10. SEM micrographs of fractured surfaces of (a) 3 wt.% untreated Kevlar/Santoprene composite and (b) 3 wt.% hydrolysed Kevlar/3 wt.% MA-g-PP/Santoprene composite.

curve c. The steepest rise and maximum value in stress (breaks at about 80% EB) found in the 3 wt.% hydrolysed Kevlar/3 wt.% Ma-g-PP/Santoprene system are shown in curve d. The results suggest that bonding through the reaction of MA groups grafted on PP with amine groups on Kevlar surface is the main factor improving the mechanical properties of Kevlar/Santoprene system.

In order to gain further information regarding the effect of MA-g-PP on interfacial adhesion of the composite, dynamic tests at various temperatures were conducted and summarized in Fig. 9. Storage modulus as a function of temperature is shown in Fig. 9(a). All materials have about the same values of storage modulus from −120°C to −50°C, but start to decay off at different rates from this point up to the end temperature of 120°C. It is shown that the hydrolysed Kevlar/MA-g-PP/Santoprene composite has the highest storage modulus over the whole temperature range, while the other two composite systems show relatively same values and Santoprene (control) shows the lowest value.

Fig. 9(b) shows curves of tan δ vs. temperature for Santoprene and all composites under study. The peaks at about −40°C are associated with the glass transitions of the EPDM part, and those at about 0°C with the PP part of Santoprene. It is shown that the PP peak shifts slightly to higher temperature and decreases to lower height in hydrolysed Kevlar/MA-g-PP/Santoprene system. The results suggest that PP chains are constrained by the compatibiliser as reported earlier [4]. Such a constraint is likely to occur at Kevlar/Santoprene interface, leading to better transfer of stress from the PP chains to the reinforcing Kevlar and resulting in the improvement of both the dynamic and tensile moduli. In other words, better stress transfer increases the effective fibre volume fraction and leads to composites with higher moduli.

Fig. 10 shows SEM micrographs of fractured surfaces of untreated Kevlar/Santoprene (Fig. 10(a)) and hydrolysed Kevlar/MA-g-PP/Santoprene (Fig. 10(b)). The untreated Kevlar composite shows a number of fibre pull-outs, while the hydrolysed Kevlar/MA-g-PP/Santoprene composite shows a rather smooth surface with no evidence of fibre pull-out. It appears that only the fractured fibres are seen. The results suggest an improved interfacial adhesion provided by the latter system.

Bonding of MA-g-PP and the amine group on Kevlar surface could not be directly investigated. An attempt was made to study what may remain on the Kevlar surface after solvent extraction of the elastomer matrix. However, a difficulty was encountered as the elastomer matrix did not dissolve in any available solvents because of the cross-linked EPDM part in Santoprene.

4. Conclusion

A system of Kevlar/Santoprene composite was studied. It was found that Kevlar pulp with no treatment can be used to reinforce Santoprene. However, the use of hydrolysed Kevlar and a small amount of MA-g-PP, a reactive compatibiliser, can significantly improve the modulus, tensile strength, and elongation at break of the composite. The results suggest the reaction between the MA groups on MA-g-PP, and the free amine groups on the hydrolysed surface of Kevlar, thus modifying the highly polar surface of Kevlar into a non-polar polypropylene surface. The non-polar modified fibre is expected to be miscible and be able to co-crystallize with polypropylene-containing Santoprene matrix, leading to a better stress transfer from the matrix to the reinforcing fibre.

4.6

Improvement of Interfacial Adhesion of Poly(*m*-phenylene isophthalamide) Short Fiber–Thermoplastic Elastomer (SEBS) Composites by N-Alkylation on Fiber Surface

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ABSTRACT: A composite of short-fiber, poly(*m*-phenylene isophthalamide), and thermoplastic elastomer styrene (ethylene–butylene) styrene (SEBS), was investigated. The fiber surface was modified by N-alkylation (heptylation and dodecylation) to improve their compatibility with a less polar SEBS matrix. Observation of fiber-surface morphology by SEM revealed surface roughness after N-alkylation. Nearly complete coating of the polymer matrix on the fiber was observed on a fractured surface of the composite, which is evidence for the improvement of fiber–matrix adhesion. It was found that the modulus of the composites grew with increasing fiber loading to approximately the same extent for both unmodified and modified fiber composites. Tensile strength of the modified fiber composites was found to improve significantly over that of the unmodified fiber composite. This suggests that the presence of the alkyl group on the fiber surface is responsible for an improvement of interfacial adhesion. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 74: 000–000, 1999

Key words: short-fiber composite; aramid; poly(*m*-phenylene isophthalamide) thermoplastic elastomer; SEBS

INTRODUCTION

Aramid short fibers such as poly(*p*-phenylene terephthalamide) (under the trade name of Kevlar by Du Pont Co.) and poly(*m*-phenylene isophthalamide) (under the trade name of Nomex by Du Pont Co. or the trade name of Conex by Teijin Co. Ltd.) are important as reinforcing fibers for plastics and elastomers due to their high strength, good thermal stability, sufficient flexibility, and light weight. However, the problem of fiber dispersion in the matrix often arises due to inertness of the fiber surface and the agglomeration of fibers due to hydrogen bonding. In order to overcome this problem, chemical or physical bonding between the fiber and the matrix is usually introduced through the addition of a suitable coupling agent[1–2] or chemical modification of the fiber surface.[3–6] Plasma treatment has also been used to create a functional group on Kevlar and hence to provide bonding with the matrix.[7–10]

One chemical method used to modify the surface of aramid fiber is the metalation reaction of the fiber surface to form polyanions, which is then followed by reaction with some functional groups or the grafting of suitable polymer segments.[11–15]

Short-fiber reinforced thermoplastic elastomers have recently gained much attention due to their attractive properties.[16–17] The advantages of thermoplastic elastomers are ease and economy in processing, high strength, and rigid-

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ity and recyclability, but some of their disadvantages are low thermal and low-dimensional stability at elevated temperatures. Incorporation of short fibers with high thermal stability and high strength, such as aramid fibers, in order to enhance dimensional stability is therefore interesting. We have investigated a system of poly(*m*-phenylene isophthalamide) (Conex) short-fiber reinforced styrene (ethylene–butylene) styrene (SEBS) thermoplastic elastomer composite. An improvement of interfacial adhesion of this composite system by partial hydrolysis on the fiber surface and the addition of a reactive compatibilizer, maleic anhydride–grafted SEBS, was reported.[18] In this study another method of surface treatment was carried out by N-alkylation to reduce the interaction through hydrogen bonding between fibers and to reduce the polarity of the highly polar surface. The alkyl groups on the fiber surface are expected to be compatible with the EB block in the SEBS matrix, which should facilitate the enhancement of interfacial adhesion and therefore will result in the improvement of tensile properties of the composite.

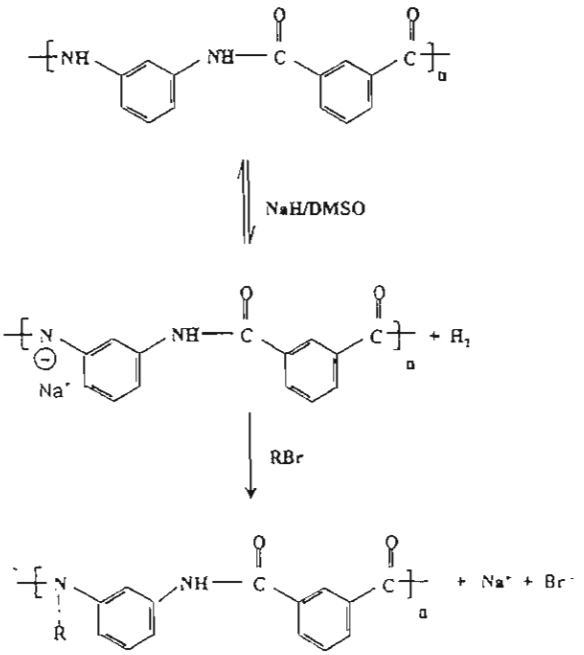


Figure 1 N-alkylation reaction on poly(*m*-phenylene isophthalamide) (Conex) short fiber.

EXPERIMENTAL

Materials

Materials used in this study were a styrene (ethylene–butylene) styrene block copolymer (SEBS, Kraton G1652), provided by Shell chemical Co. Ltd., with 29% styrene content as thermoplastic elastomer matrix, and poly(*m*-phenylene isophthalamide), Teijin-Conex, provided by Teijin Co. Ltd. in the form of short fibers with an approximate length of 3 mm and a diameter of 12–15 μm. The fibers were first washed with acetone, followed by distilled water to remove possible contamination, and they were then dried at 5°C to a constant weight in a vacuum oven. Anhydrous dimethyl sulfoxide (DMSO) and alkyl bromides were used as received. Sodium hydride (60% suspension in paraffin oil) was washed three times with dried hexane before use.

Surface Modification of Conex Fiber by N-alkylation

The technique used for N-alkylation of Conex fibers was similar to that reported earlier by Takayanagi et. al.[11] The reaction scheme is presented in Figure 1. Since only slight modification on the fiber surface is needed, a small amount of the reagents and short reaction times were employed. In the first step, i.e. a metalation reaction, about 1,000 mL of anhydrous DMSO and 0.05 mol of purified NaH were reacted for 40 min at 70°C in a nitrogen atmosphere. After cooling to 30°C, 30 g of fiber were added into the reactor and stirred mechanically for 10 min. At this stage, the skin color of the fiber changed from off-white to pale yellow. Then about 0.25 mol of heptyl bromide was added and stirred for a further 3 h. The reaction was stopped by transferring the fibers into a large quantity of distilled water. The products were washed with acetone and water several times and dried at 60°C to a constant weight in a vacuum oven. For dodecylation, only 0.025 mol of NaH was used; otherwise the resulting fibers became hard and stuck together, and hence were difficult to disperse in the matrix.

The alkyl group on the fiber surface was characterized by Fourier transform infrared (FTIR) spectroscopy recorded on a Perkin-Elmer PE2000 spectrometer using diffuse reflectance accessory (DRIFT). Two hundred scans at a resolution of 2 cm^{-1} were performed to obtain a good spectrum.

Preparation of Composites

The composites were prepared by a melt blending technique, using a laboratory-size internal mixer (Haake Rheomix 90) at the set temperature of 175°C at a rotor speed of 90 rpm. To obtain good

dispersion, the fiber was first preopened in a Moulinex blender for a few seconds, then put in the mixing chamber in which the rotor was operated for 30 sec before the SEBS was added. After mixing for 10 min, the composite was discharged from the mixer and immediately rolled into a single sheet using a small laboratory two-roll mill. The composite sheet was then compression molded into a sheet 2 mm thick under a pressure of 15 MPa at 180°C for 10 min. The molded sheets were kept in a desiccator for 24 h prior to tensile measurement.

Fiber loading was varied from 0 to 7% by weight. We studied low-fiber content composites so as to maintain an important property of elastomers—their high percentage of extension. Another reason for studying such composites is that at low-fiber concentration, there is less of a problem of fiber agglomeration, so we can evaluate the results by focusing only on the effect of adhesion at the interface.

Measurement of Tensile Properties

The composite sheets were cut into dumbbell-shaped specimens with a cutting die of size 115 × 6 mm, parallel to the direction passing through the two-roll mill. According to ASTM D638, tensile properties were measured using an Instron 4301 tensile tester with a cross-head speed of 500 mm min^{-1} and a full-scale load cell of 100 kg. All values presented were averages of at least five measurements.

Morphology Study

A scanning electron microscope (SEM, Hitachi S-2500) was utilized to characterize the surface morphology of Conex short fibers before and after modification, as well as the fractured surface of composites. The fractured surfaces of the composites were prepared by freezing the sample in liquid N_2 and breaking it rapidly. The samples were then coated with palladium (Hitachi E102 ion sputter) and observed using an accelerating voltage of 15 kV.

RESULTS AND DISCUSSION

N-Alkylation of Conex Fiber Surface

In this study, the aramid (Conex) fiber surface was modified by a deprotonation reaction with NaH in DMSO, followed by N-alkylation.

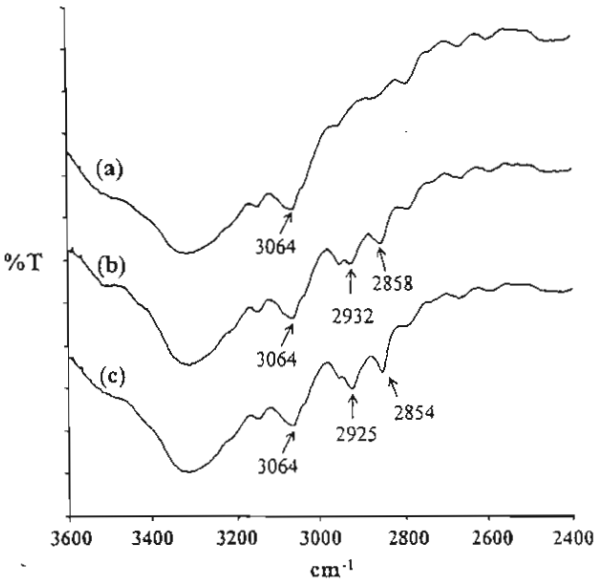


Figure 2 Infrared spectra (DRIFT) of (a) unmodified, (b) heptylated, and (c) dodecylated Conex fibers.

Infrared spectra of unmodified, heptylated, and dodecylated Conex fibers are presented in Figure 2 as curves a, b, and c, respectively. The C—H F2 stretching vibration peaks at 2,858 and 2,932 cm^{-1} are of the heptyl group, the peaks at 2,854 and 2,925 cm^{-1} are of the dodecyl group, and the N—H stretching peak appears in all spectra at 3,064 cm^{-1}. Therefore, the partial N-alkylation on the fiber surface is considered successful.

SEM micrographs demonstrating surface morphology of the fibers before and after modification are shown in Figure 3. The surface of controlled F3 fiber (unmodified) shown in Figure 3(a) is relatively smooth. Figure 3(b) shows the fiber taken from the reaction just after deprotonation for 10 min, that is, without alkyl groups on the surface, still shows a relatively smooth surface. It is seen that the ionization step does not affect the appearance of the fiber surface. In contrast, heptylated and dodecylated fibers exhibit high surface roughness, as shown in Figures 3(c,d), respectively. Takayanagi et al.[11] reported that deprotonated and N-heptylated Kevlar were soluble in DMSO. In our case, the Conex fiber surface was only partially deprotonated and then N-alkylated. During the alkylation reaction time of 3 h, some parts of modified fiber surface might be swollen in DMSO. When the reaction had been terminated with distilled water, the swollen parts might redeposit on the fiber surface and hence might cause the surface roughness as seen in Figure 3(c,d). Apart from the expected compatibility of the alkyl group and the EB block in the SEBS

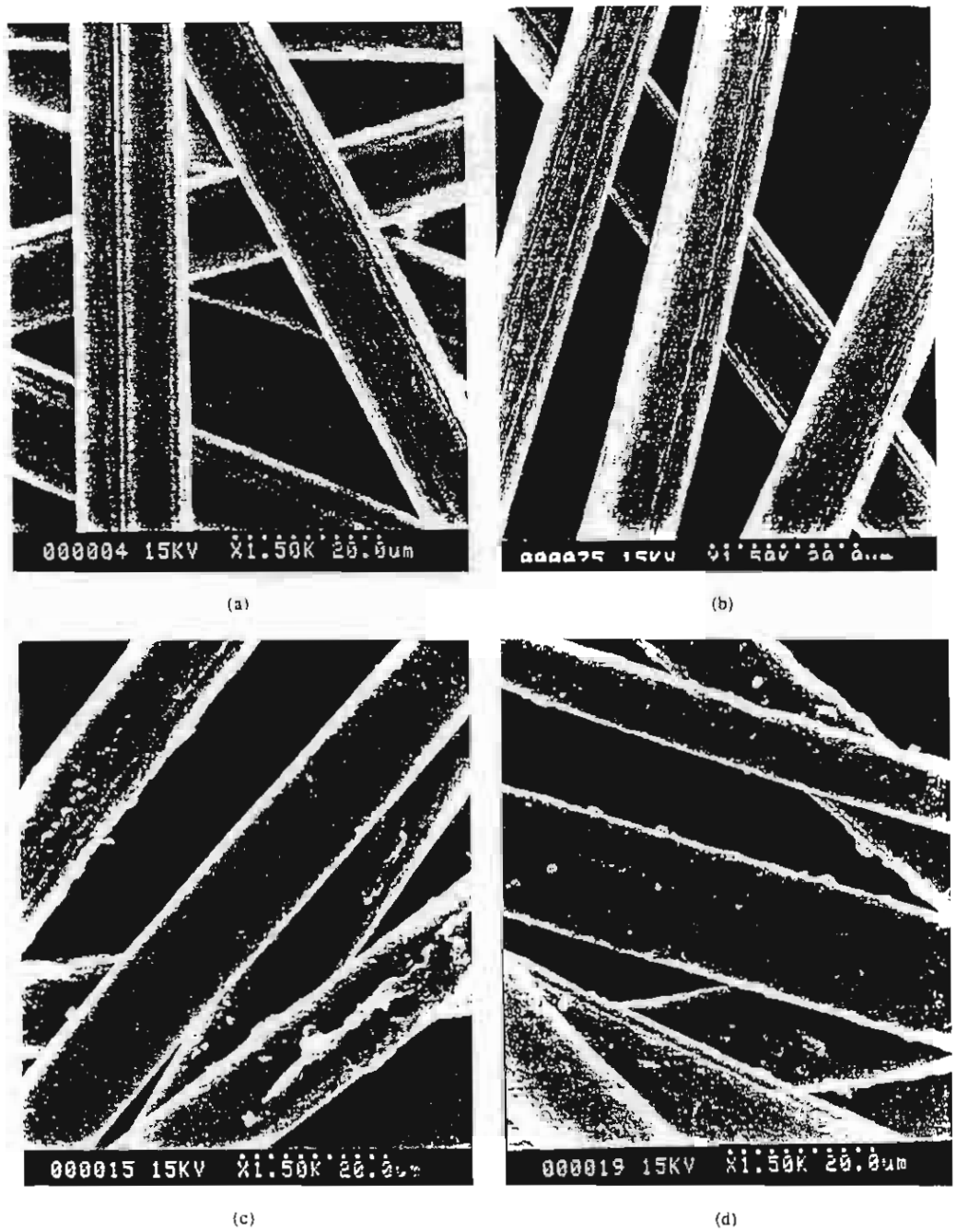


Figure 3 SEM micrographs of various Conex fibers (a) unmodified, (b) deprotonated, (c) heptylated, and (d) dodecylated Conex fiber.

matrix, this surface roughness of the alkylated Conex fibers will, in theory, also enhance the interfacial bonding between the fibers and polymer matrix via a physical interlocking or a friction mechanism.

Mechanical Properties of Composites

Plots of tensile properties of the composites containing unmodified and alkylated fibers—i.e., 100% modulus, 300% modulus, tensile strength, and elongation at break as a function of fiber loading—are shown in Figures 4–7, respectively. F7 The values of modulus at 100% and 300% extensions (Figs. 4 and 5, respectively) increase almost linearly with fiber loading at approximately the same extent for composites filled with unmodified and modified fibers. The increase in modulus of the composites with an increasing amount of fiber

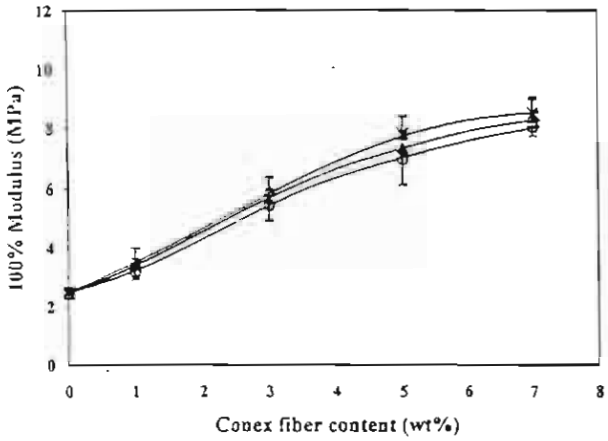


Figure 4 Tensile modulus at 100% strain versus fiber content of composites with (a) unmodified (Δ), (b) hetylated (X), and (c) dodecylated (O) Conex fibers.

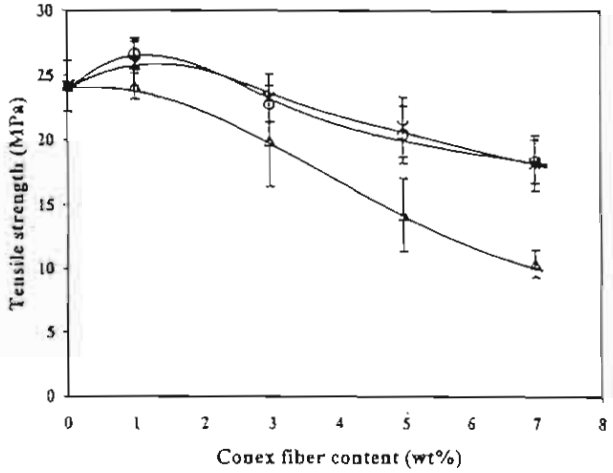


Figure 6 Tensile strength versus fiber content of composites containing (a) unmodified (Δ), (b) hetylated (X), and (c) dodecylated (O) Conex fibers.

is mainly a result of the modulus of Conex fibers, which is far greater than that of SEBS. The higher the fiber loading is, the larger the volume fraction of high-modulus phase and thus the greater will be the bulk modulus of the composites. It can be seen that the tensile modulus is not affected significantly by N-alkylation at low-fiber loading. A slight improvement in 300% modulus is observed at 7 wt % fiber loading. Tensile strength is decreased, however, with increasing fiber loading due to the dilution effect of the matrix (see Fig. 6). However, the tensile strength of N-alkylated Conex composites is significantly higher than that of the composite filled with the unmodified fiber, particularly at high-fiber loading. At 7 wt % fiber loading, tensile strength of N-alkylated fiber-filled composites (18 MPa) is about 80% higher than that of the composite with unmodified fiber (10 MPa). On the other hand, elongation at break, shown in Figure 7, is only slightly decreased with increasing fiber loading. A slight increase of elongation at break is observed for N-alkylated fiber-filled composites, particularly at higher fiber content. No effect of the length of the alkyl groups on tensile properties of the composites can be noticed. The remarkable enhancement in tensile strength might be due to an increase in interfacial adhesion between fiber and polymer matrix via improvement of the com-

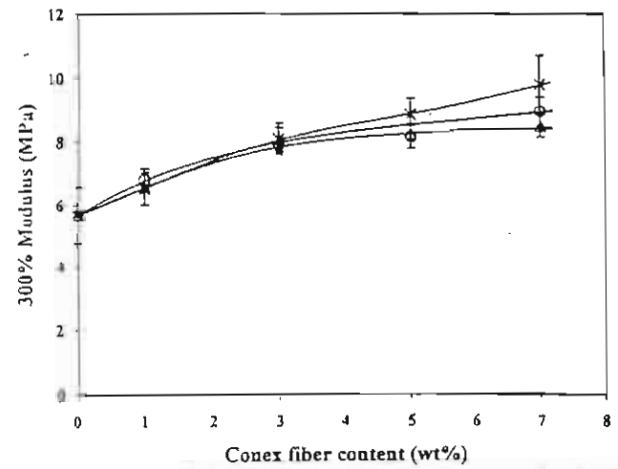


Figure 5 Tensile modulus at 300% strain versus fiber content of composites containing (a) unmodified (Δ), (b) hetylated (X), and (c) dodecylated (O) Conex fibers.

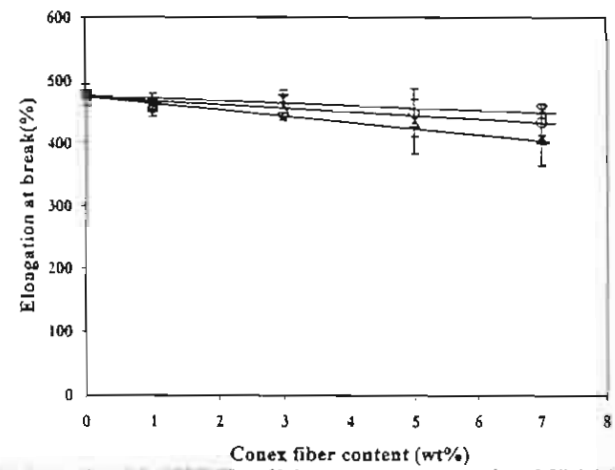


Figure 7 Elongation at break versus fiber content of composites containing (a) unmodified (Δ), (b) hetylated (X), and (c) dodecylated (O) Conex fibers.

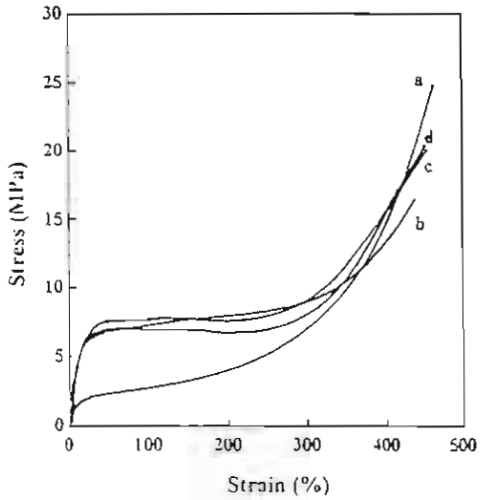


Figure 8 Stress–strain behavior of (a) neat SEBS, (b) 5 wt % unmodified Conex–SEBS, (c) 5 wt % heptylated Conex–SEBS and (d) 5 wt % dodecylated Conex–SEBS composites.

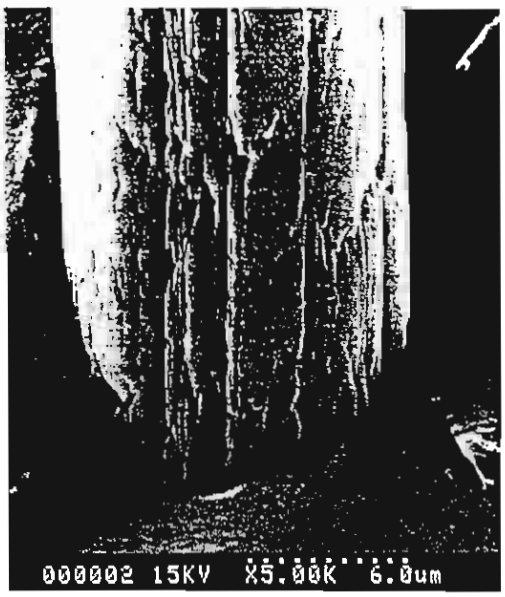
patibility between the alkyl group on the fiber surface and the EB block in SEBS matrix. In other words, the alkyl groups could assist the wetting of the fiber by the matrix. In addition, the bonded clumps on the surface could help enlarge the contact area between the fibers and the polymer matrix and hence enhance their interfacial bond strength. The evidence for improvement of adhesion at the interface can be clearly seen in SEM micrographs of fractured surfaces illustrated in the next section.

For comparison, the stress–strain behavior of unfilled SEBS and composites containing 5 wt % of unmodified and modified fibers is illustrated in Figure 8. It can be seen clearly that the unfilled SEBS (curve a) possesses the lowest tensile modulus at low strain and shows a strain-hardening effect (strain crystallization) at high strain. The thermoplastic elastomer SEBS exhibits similar behavior as a conventional strain crystallizing rubber due to the strong intermolecular interaction between the chains in the hard phase.[17] Obviously, the strain hardening of SEBS decreases, causing tensile strength to decrease, as 5 wt % of unmodified fiber is added (curve b). This is due to the dilution effect of the matrix, and the high-stress concentration at the fiber ends destroys adhesion at the interface. As heptylated and dodecylated fibers are incorporated (curves c and d), strain crystallization increases again, this is, tensile strength becomes higher than that of the composite with unmodified fiber. Since the stress–strain curves rise steeply near the break point, the elongation at break is therefore not much affected.

Morphology of Composites

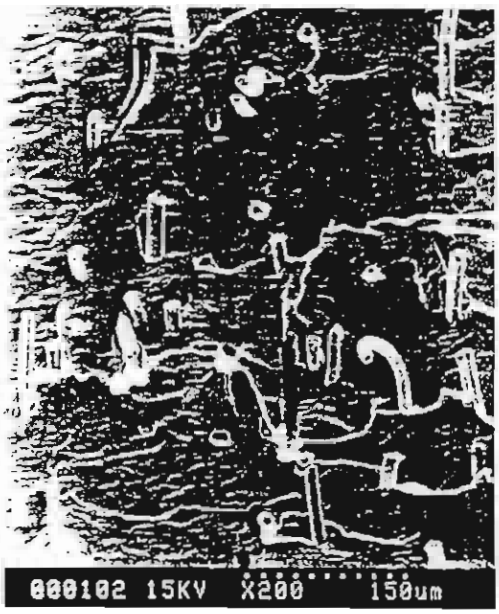
To obtain more information on the effect of fiber surface, the composites were studied using SEM. The micrographs of fractured surfaces of compos-

(a)



(b)

Figure 9 SEM micrographs of fractured surface of unmodified Conex composite at magifications of (a) ×200 and (b) ×5,000.



(a)

(b)

Figure 10 SEM micrographs of fractured surface of heptylated Conex composite at magifications of (a) ×200 and (b) ×5,000.

ites filled with unmodified and alkylated Conex fibers are shown in Figures 9(a)–11(a) at magnification ×200 and in Figures 9(b)–11(b) at magnification ×5,000. Evidently, long fiber pullout is seen on the fractured surface of unmodified Conex–SEBS composite [Fig. 9(a)], indicating poor interfacial adhesion between fiber surface and polymer matrix. Magnification of this specimen at ×5,000, shown in Figure 9(b), indicates a number of grooves and cracks on the fiber surface. By contrast, the composites filled with heptylated and dodecylated short fibers, presented in Figures 10(a) and 11(a), respectively, show fiber breakage rather than pullout phenomena, which are evi-

(a)

(b)

Figure 11 SEM micrographs of fractured surface of dodecylated Conex composite at magifications of (a) ×200 and (b) ×5,000.

dent in that the N-alkylation of the Conex fibers improves interfacial adhesion between Conex fiber and SEBS matrix. Clearer evidence of strong interfacial adhesion can be seen from micrographs at higher magnification power shown in Figures 10(b) and 11(b). In these figures, the surface of the fibers is coated by SEBS layer, thus no grooves and cracks can be observed. Also at the proximal end of the fiber that is buried in the matrix, there is good sticking between the matrix and the fiber. This evidence clearly supported the conclusion that the interaction force responsible for adhering the fiber to the matrix is the purely physical force acting through the alkyl groups since no chemical bonding between the fiber and the matrix is expected. The resulting improvement of interfacial adhesion is supported by a significant increase in tensile strength of the modified fiber-filled composites as discussed in the previous section.

Since the fibers were modified by using two successive steps—deprotonation followed by N-alkylation—we had to find out which step was more effective. To do this, deprotonated fibers were prepared by stopping the reaction in the first step with distilled water. The fibers obtained at this stage are shown in Figure 3(b). The other procedures used for preparation of the composites were the same as those described in the experimental sections. Tensile properties of deprotonated Conex–SEBS composites were measured (data not shown here). Modulus and elongation at break were found to be about the same as those of unmodified fiber. However, the tensile strength was found to be slightly higher than that of the unmodified Conex–SEBS system but lower than that of the alkylated Conex–SEBS system. These results ensured that the presence of the alkyl group was essential for the improvement of the composite properties.

Since the results from tensile measurements and the morphology shown in SEM micrographs are in good agreement, it can be concluded that the application of the N-alkylation process described to Conex fibers can significantly enhance the interfacial adhesion between the fibers and SEBS, and thus the mechanical properties of these Conex short-fiber-filled SEBS composites.

CONCLUSIONS

The partial N-alkylation onto short-fiber surface of poly(*m*-phenylene isophthalamide (Conex) was carried out by a metalation reaction with NaH in DMSO solution followed by the addition of alkyl bromide (heptyl and dodecyl). The presence of alkyl groups on the fiber surface was detected by FTIR DRIFT technique. Original and modified fibers were melt-blended with thermoplastic elastomer styrene (ethylene–butylene) styrene (SEBS). Tensile properties of compression-molded specimens were measured. The morphology of the modified fibers and the fractured surfaces of the composites were investigated using SEM. The results obtained were as follows:

1. N-Alkylated Conex fibers show characteristic C—H stretching of alkyl groups in the DRIFT spectra. The result reveals that the fiber surface is successfully modified.
2. By comparison with the unmodified Conex short fibers, the alkylated fibers enhance tensile strength of the composites, probably due to the improvement in interfacial adhesion between the fibers and the SEBS matrix. This result is evident by SEM micrographs of fractured surface, which show nearly complete coating of matrix on the fiber surface.
3. From the systems studied, no difference has been observed from the effect of the length of the alkyl groups, i.e. 7- and 12-carbon atoms on the fiber surface, on tensile properties of the composites.

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