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.

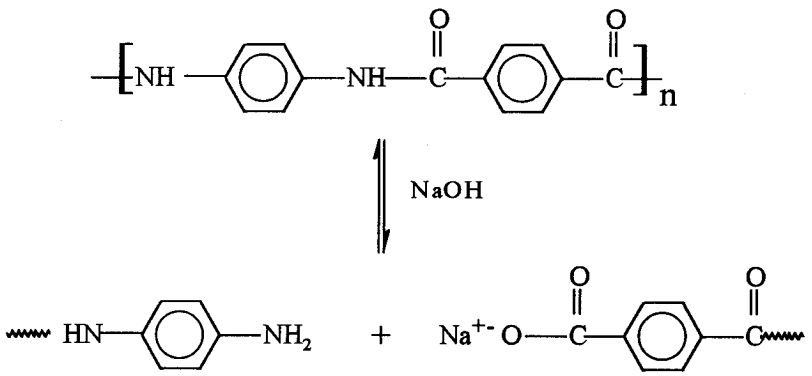
Optical microscopy

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.



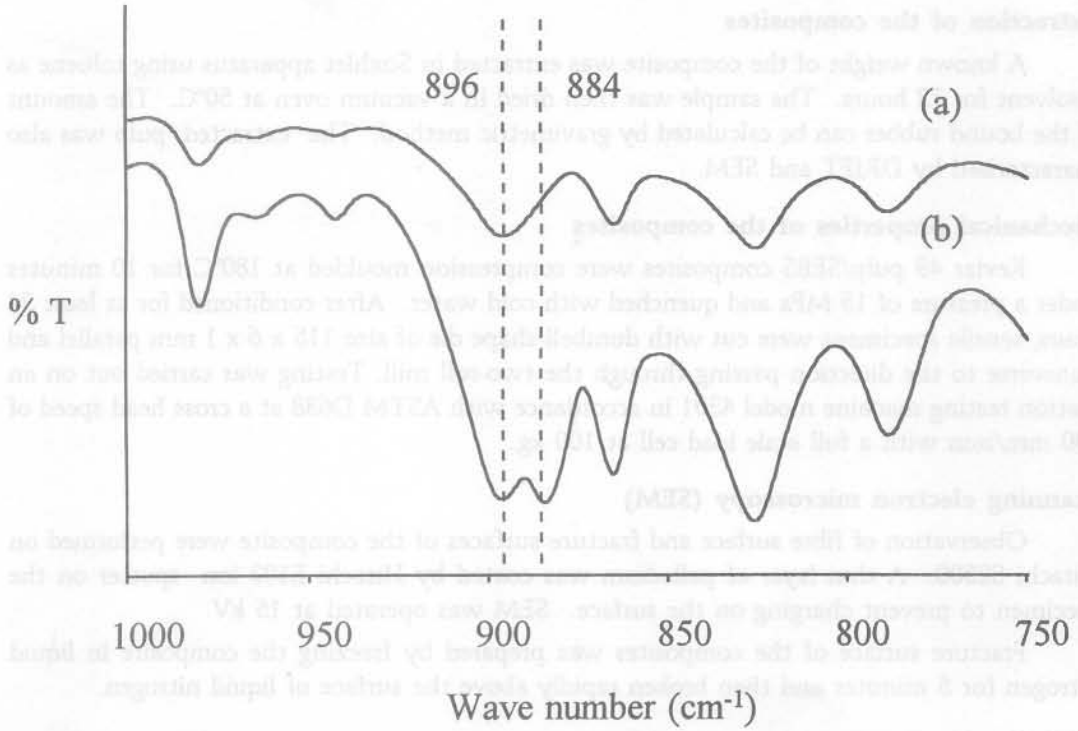


Fig.1. Infrared spectra of Kevlar surface (a) before and (b) after hydrolysis (without washing with water).

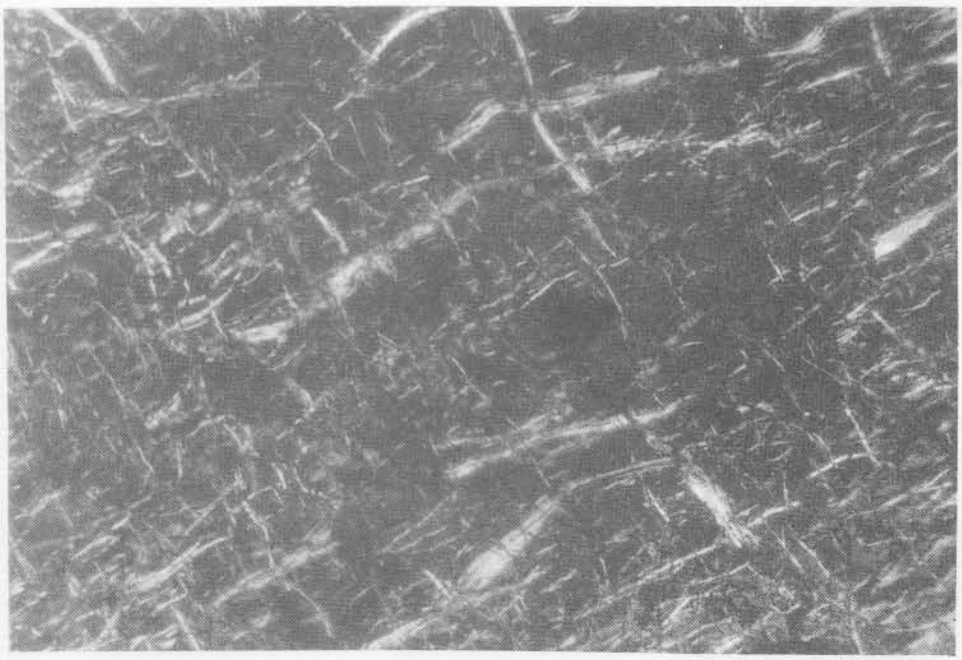


Fig.2. Optical micrograph of Kevlar pulp/SEBS composite pressed between slide glasses.

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

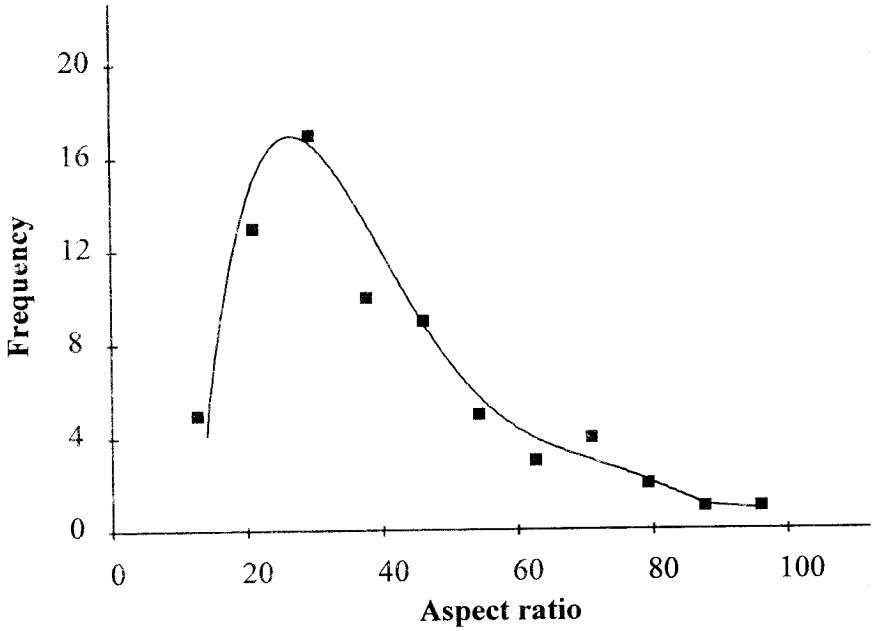


Fig.3. Distribution of aspect ratio of fibre after mixing.

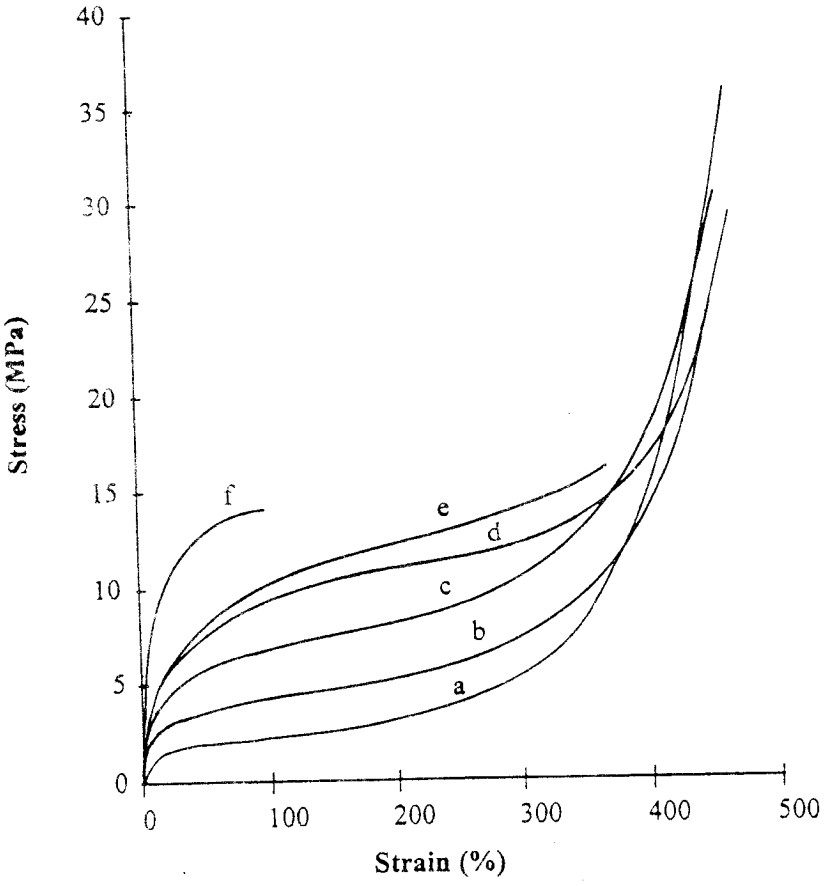
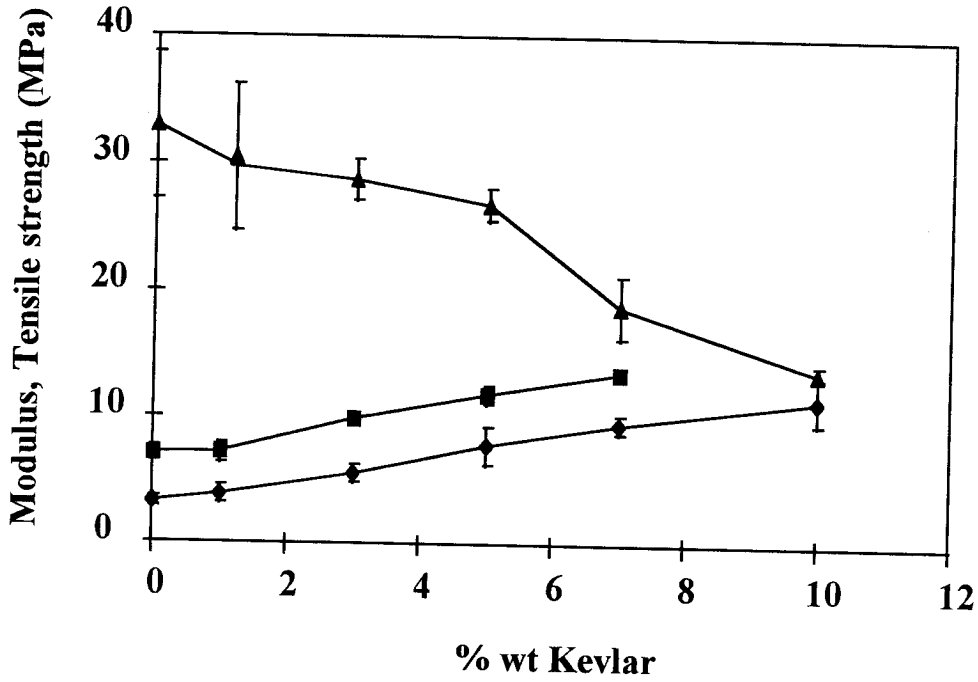


Fig.4. Stress-strain curves of Kevlar pulp/SEBS composites at fibre loading (wt%) a = 0, b = 1, c = 3, d = 5, e = 7 and f = 10.



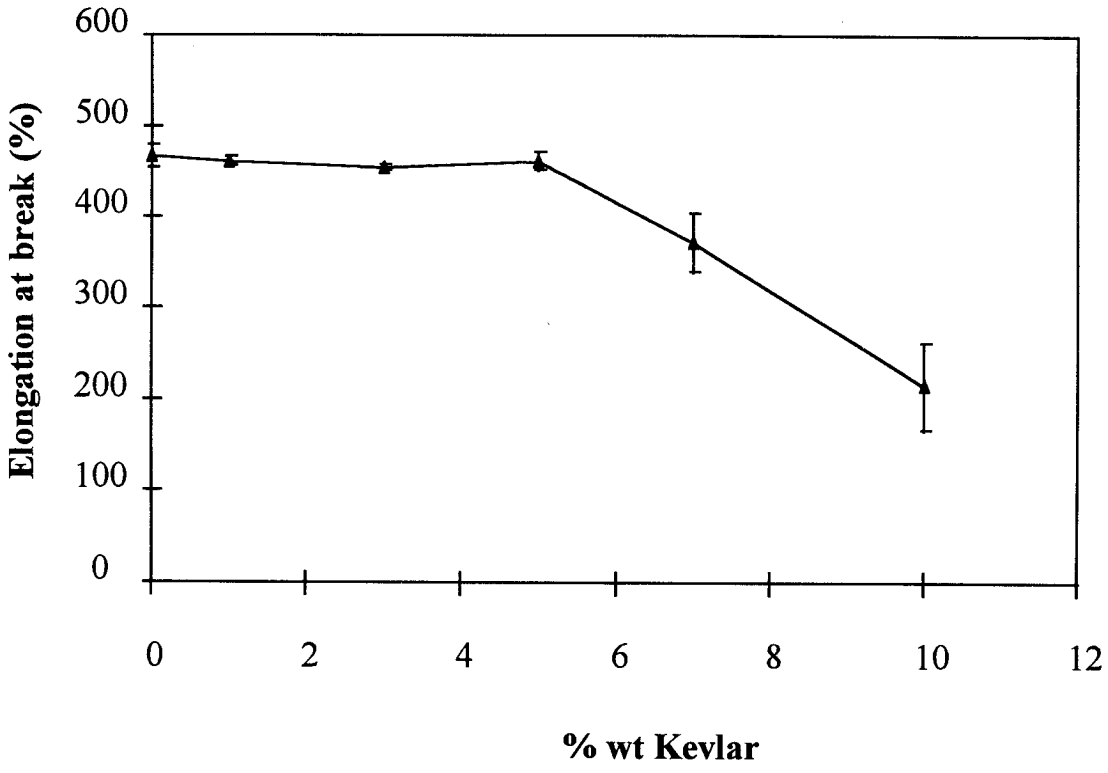


Fig.5. Shows a) Modulus at 100% (◆), 300% (■) and Tensile strength (▲) and b) Elongation at break of Untreated Kevlar/SEBS composite.

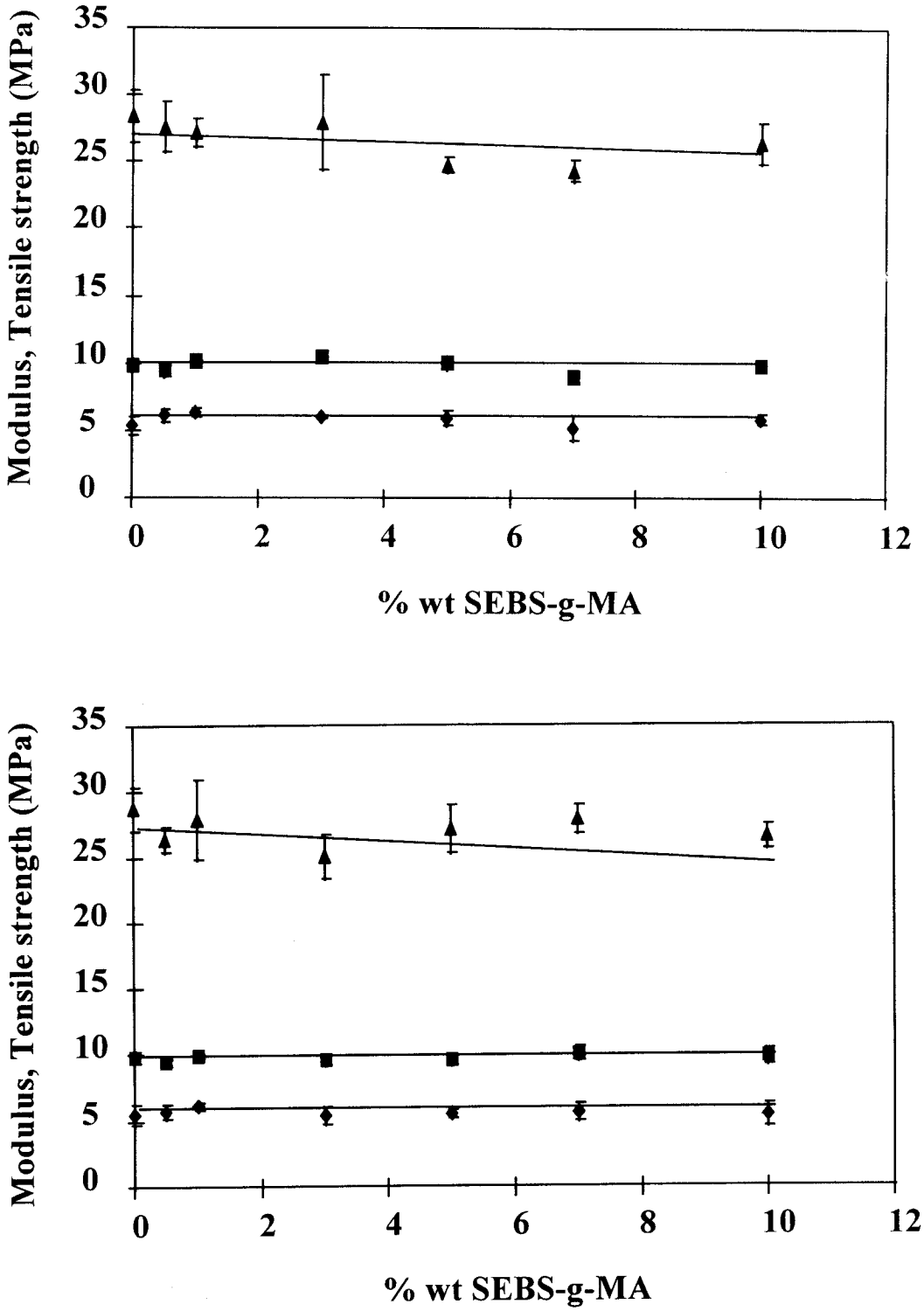


Fig.7. Shows effect of SEBS-g-MA on modulus at 100% (◆), 300% (■) and Tensile strength (▲) of (a) Untreated Kevlar/SEBS composite and (b) Treated Kevlar/SEBS composite.

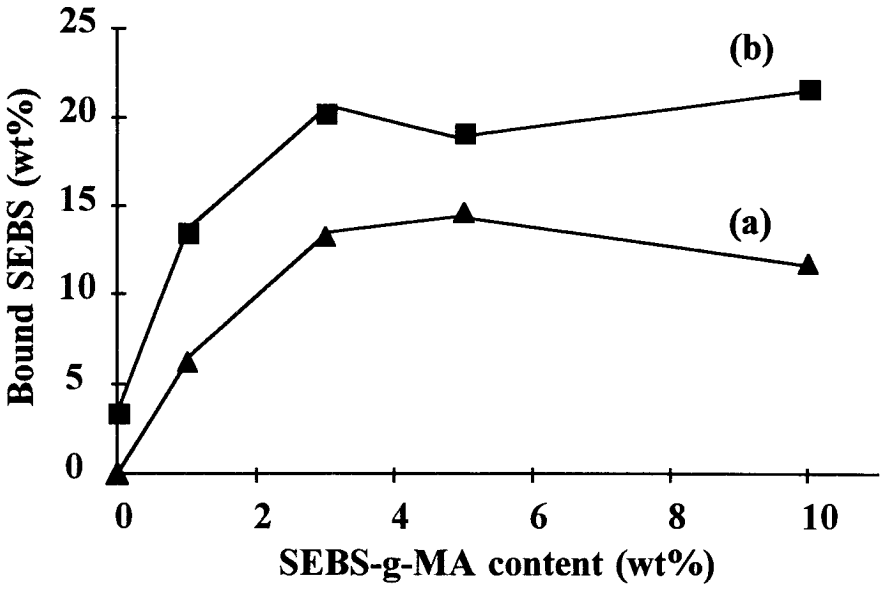


Fig.8. Bound SEBS (wt%) on extracted Kevlar pulp (a = as received, b = treated) obtained from composites containing various SEBS-g-MA contents.

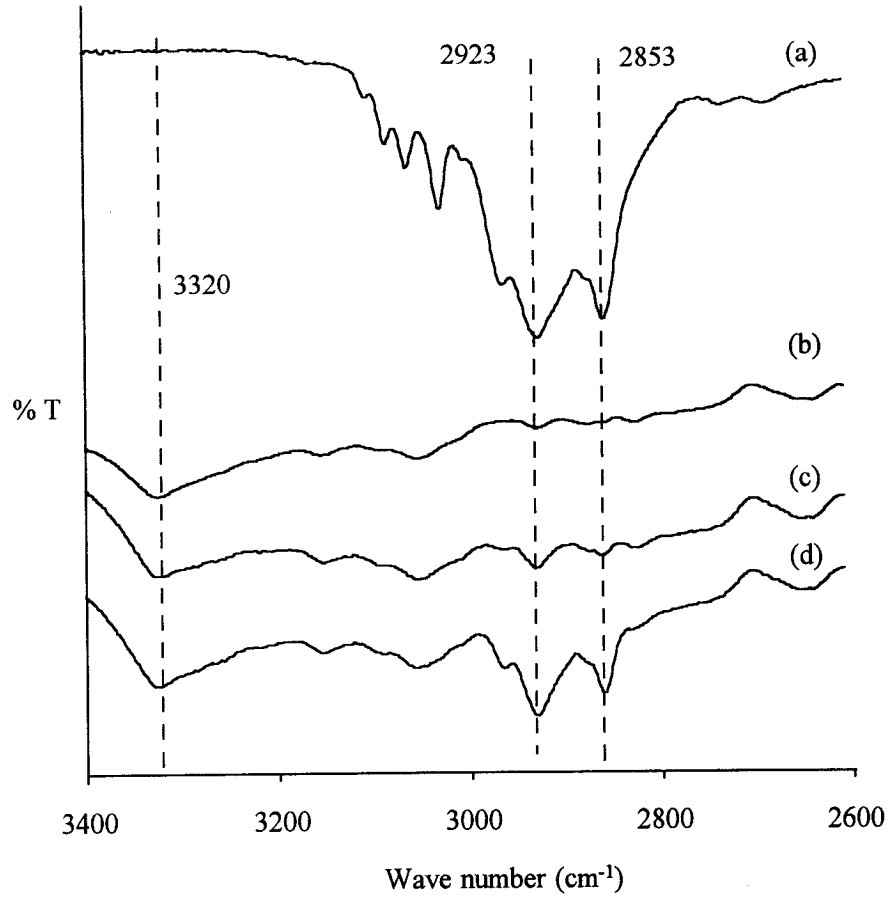
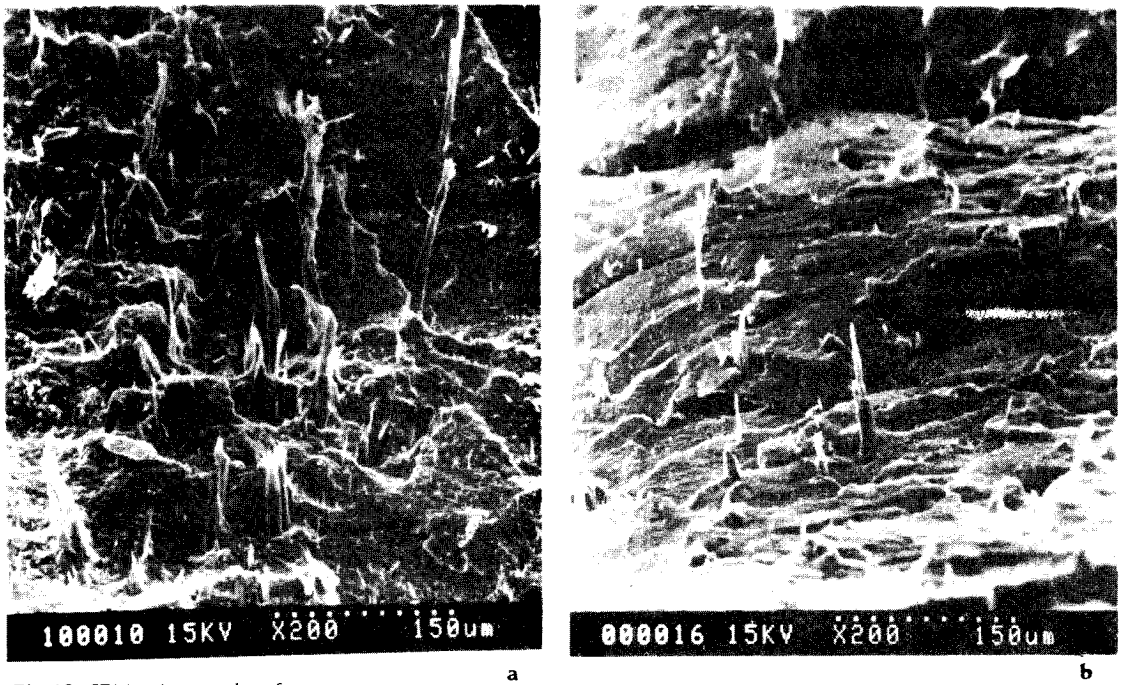
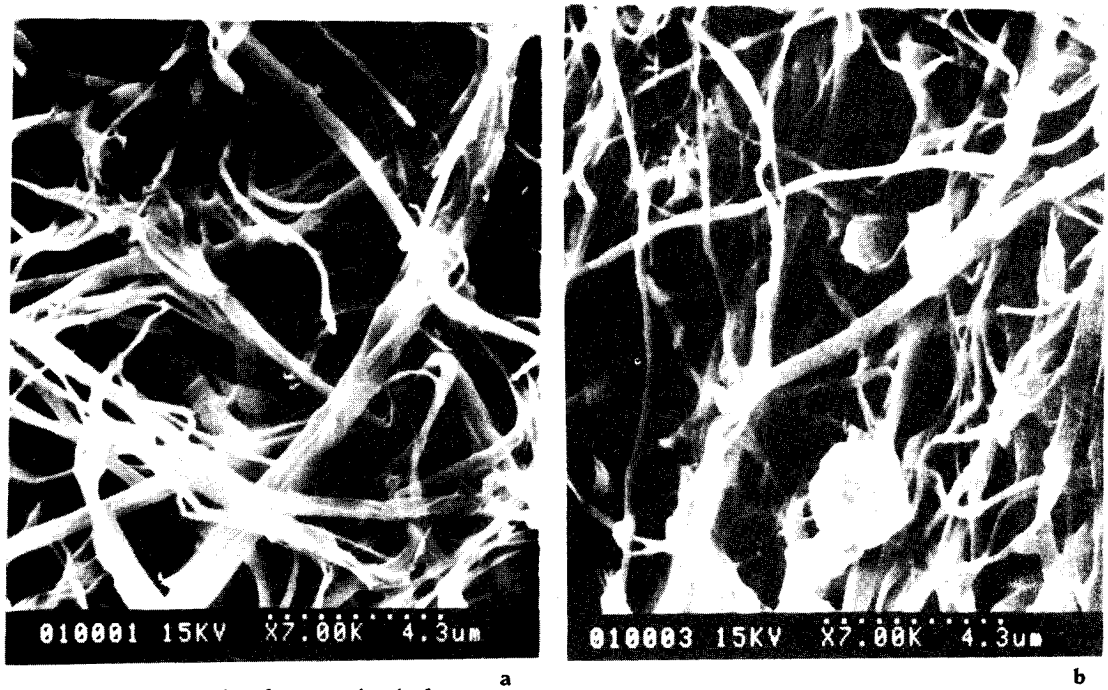


Fig.9. Spectra of extracted samples of (a) SEBS pure, (b) Kevlar, (c) Kevlar/SEBS (3/97) and (d) Kevlar/SEBS-g-MA/ SEBS (3/1/96).



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.

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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