Polymer 40 (1999) 6437–6442

Kevlar reinforcement of polyolefin-based thermoplastic elastomer

Sunan Saikrasun[a], Taweechai Amornsakchai[a], Chakrit Sirisinha[a], Wiriya Meesiri[b], Sauvarop Bualek-Limcharoen[a,*]

[a]*Department of Chemistry, Faculty of Science, Mahidol University, Rama 6 Road, Bangkok 10400, Thailand*
[b]*Directorate of Armament, Royal Thai Air Force, Bangkok, Thailand*

Received 11 August 1998; accepted 24 November 1998

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. © 1999 Elsevier Science Ltd. All rights reserved.

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.

---

* Corresponding author. Fax: 00662 2477050.
E-mail address: scsbl@mahidol.ac.th (S. Bualek-Limcharoen)

PII: S0032-3861(98)00853-2

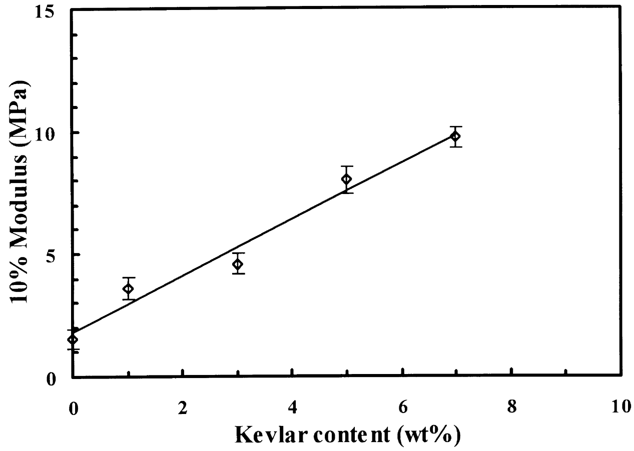

Fig. 1. Modulus at 10% strain of untreated Kevlar/Santoprene composites at various Kevlar content.

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 (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.

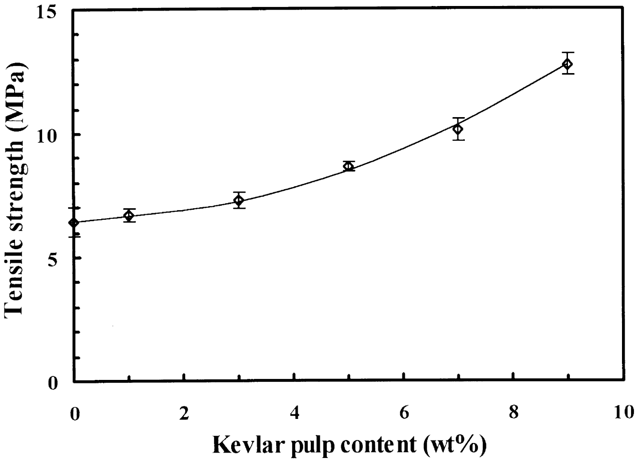

Fig. 2. Tensile strength of untreated Kevlar/Santoprene composites at various Kevlar content.

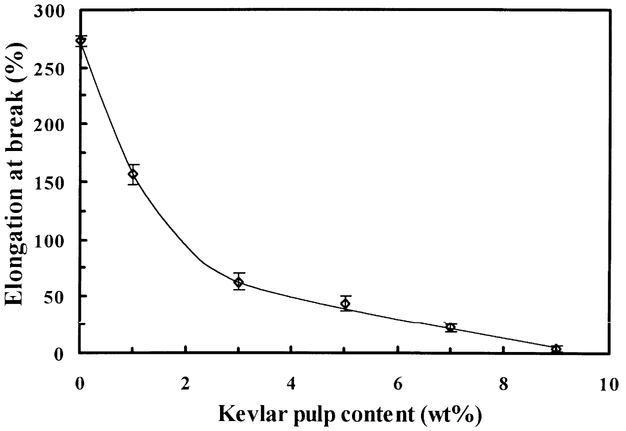

Fig. 3. Elongation at break of untreated Kevlar/Santoprene composites at various Kevlar content.

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

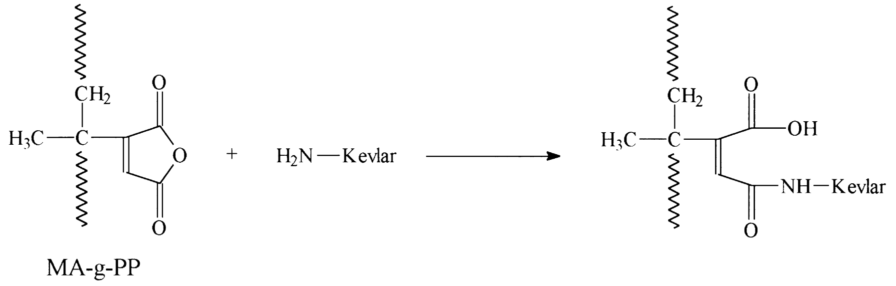

Fig. 4. Reaction between MA-g-PP and the amine group on the Kevlar surface.

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].

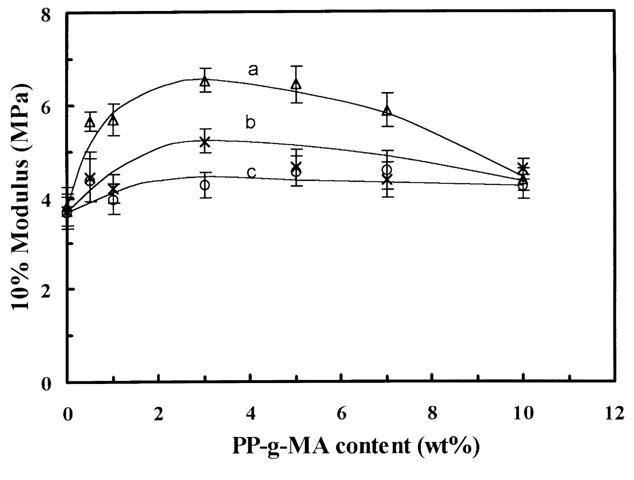

Fig. 5. Modulus at 10% strain of various Kevlar/Santoprene composites; (a) hydrolysed Kevlar/MA-g-PP/Santoprene (△), (b) hydrolysed Kevlar/PP/Santoprene (×), (c) untreated Kevlar/MA-g-PP/Santoprene (○).

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

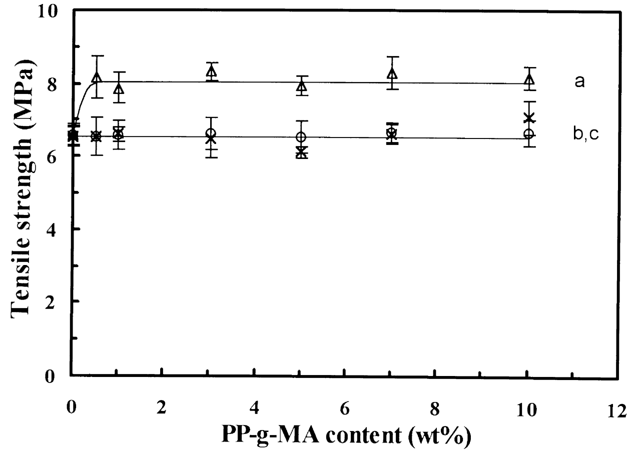

Fig. 6. Tensile strength of various Kevlar/Santoprene composites; (a) hydrolysed Kevlar/MA-g-PP/Santoprene (△), (b) hydrolysed Kevlar/PP/Santoprene (×), (c) untreated Kevlar/MA-g-PP/Santoprene (○).

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

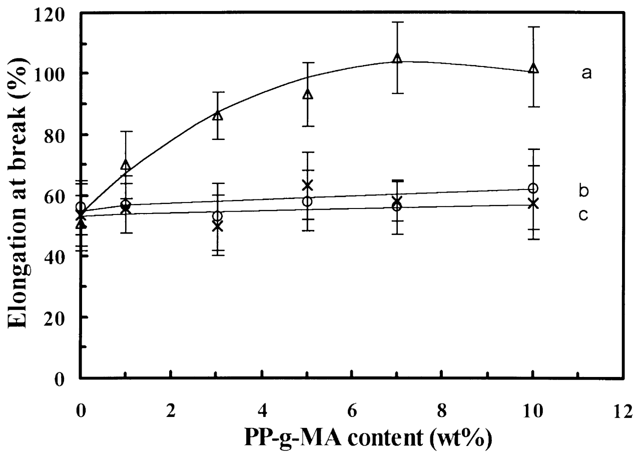

Fig. 7. Elongation at break of various Kevlar/Santoprene composites; (a) hydrolysed Kevlar/MA-g-PP/Santoprene (△), (b) hydrolysed Kevlar/PP/Santoprene (×), (c) untreated Kevlar/MA-g-PP/Santoprene (○).

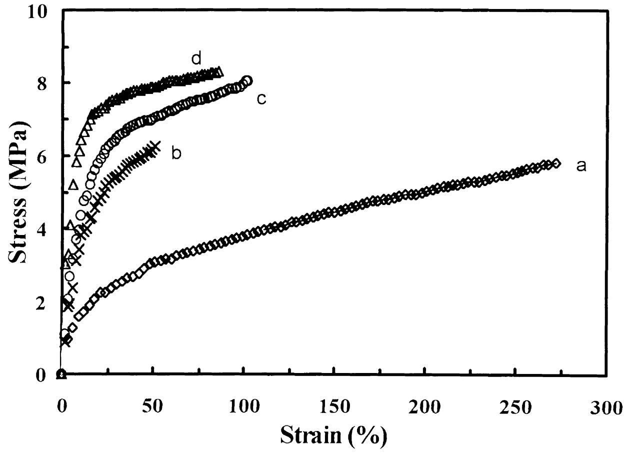

Fig. 8. Stress–strain curves of various Kevlar/Santoprene composites; (a) Santoprene, (b) 3 wt.% untreated Kevlar/Santoprene, (c) 3 wt.% hydrolysed Kevlar/3 wt.% PP/Santoprene, (d) 3 wt.% hydrolysed Kevlar/3 wt/% MA-g-PP/Santoprene.

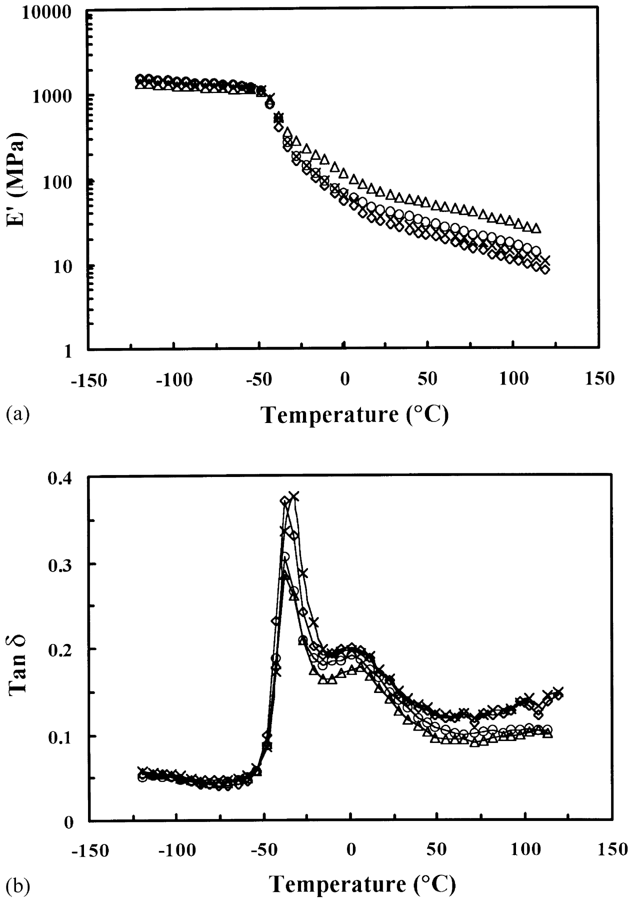

Fig. 9. (a) Storage modulus (E′) and (b) tan δ of various Kevlar/Santoprene composites; 3 wt.% hydrolysed Kevlar/3 wt/% MA-g-PP/Santoprene (△), 3 wt.% untreated Kevlar/Santoprene (×), 3 wt.% hydrolysed Kevlar/3 wt.% PP/Santoprene (○), Santoprene (◇).

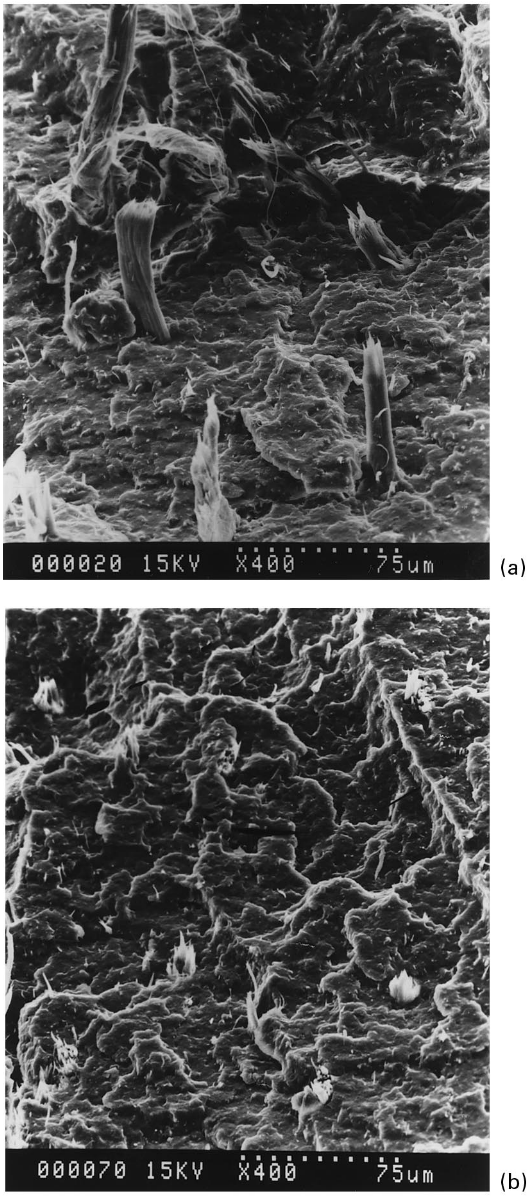

Fig. 10. SEM micrographs of fractured surfaces of (a) 3 wt.% untreated Kevlar/Santoprene composite and (b) 3 wt.% hydrolysed Kevlar/3 wt.% MA-g-PP/Santoprene composite.

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.

Acknowledgements

Support of this work by The Thailand Research Fund is gratefully acknowledged. The authors also would like to thank Uniroyal Chemical Co. for providing MA-g-PP and Du Pont for providing Kevlar pulp.

References

[1] Foldi AP. In: Vigo TL, Kinzig BJ, editors. Composite applications: the role of matrix, fibre, and interface, New York: VCH publishers, 1992. p. 133–177.

[2] Foldi AP. Rubber Chem Technol 1976;49:379.

[3] Vaughan D. Polym Eng Sci 1978;18:167.

[4] Takayanagi M, Kajiyama T, Katayose T. J Appl Polym Sci 1982;27:3903.

[5] Takayanagi M, Katayose T. Polym Eng Sci 1984;24:1047.

[6] Breznick M, Banhaji J, Guttmann H, Marom G. Polym Commun 1987;28:55.

[7] Andrepoulos AG. J Appl Polym Sci 1989;38:1053.

[8] Tarantili PA, Andreopoulos AG. J Appl Polym Sci 1997;65:267.

[9] Wang Q, Kaliaguine S, Ait-Kadi A. J Appl Polym Sci 1993;48:121.

[10] Yu Z, Ait-Kadi A, Brisson J. Polym Eng Sci 1991;31:1222.

[11] Sheu GS, Shyu SS. J Adhesion Sci Technol 1994;8:1027.

[12] Brown JR, Mathys Z. J Mater Sci 1997;32:2599.

[13] Garbassi F, Morra M, Occhiello E. Polymer surfaces: from physics to technology. Chichester: John Wiley and Sons, 1994. p. 251–254.

[14] Coran AY, Boustany K, Hamed P. Rubber Chem Technol 1974;47:396.

[15] Bualek-Limcharoen S, Nakinpong T, Amornsakchai T, Meesiri W. J Sci Soc Thailand 1997;23:101.

[16] Foldi AP. Paper presented at the ACS Rubber Division Meeting, New York, 1986.

[17] Foldi AP. Paper presented at the International Rubber Conference, Sydney, Australia, 1988.

[18] Amornsakchai T, Sinpatanapan B, Bualek-Limcharoen S, Meesiri W. Polymer, in press.