ELSEVIER

Polymer 40 (1999) 2993–2999

polymer

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

Taweechai Amornsakchai[a], Budsaporn Sinpatanapan[a], Sauvarop Bualek-Limcharoen[a,*], Wiriya Meesiri[b]

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

Received 23 March 1998; revised 19 May 1998; accepted 24 June 1998

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. © 1999 Elsevier Science Ltd. All rights reserved.

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

---

[*] Corresponding author. Fax: +662-2477050; E-mail: scsbl@mahidol.ac.th

0032-3861/99/$ - see front matter
PII: S0032-3861(98)00524-2

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.

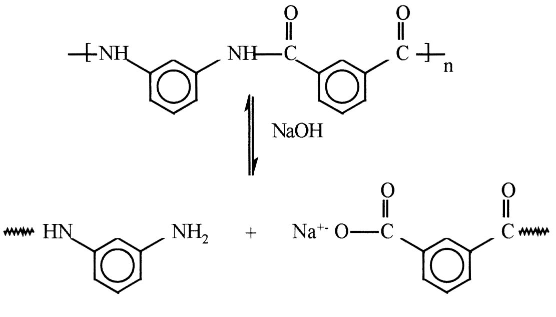

Fig. 1 shows infrared spectra of Conex fibres before and after hydrolysis using DRIFT technique. It can be seen that a new peak appears at 880 cm^{-1} (curve b) after hydrolysis. The peak is associated with the C–H out of plane bending of aromatic ring containing $COO^{-}Na^{+}$ substituent similar to 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 ($\leqslant$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

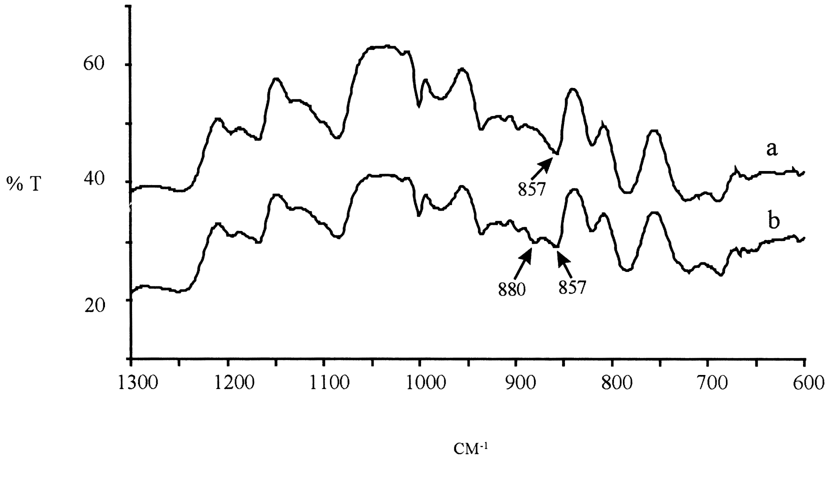

Fig. 1. Infrared spectra of Conex fibres before and after surface hydrolysis.

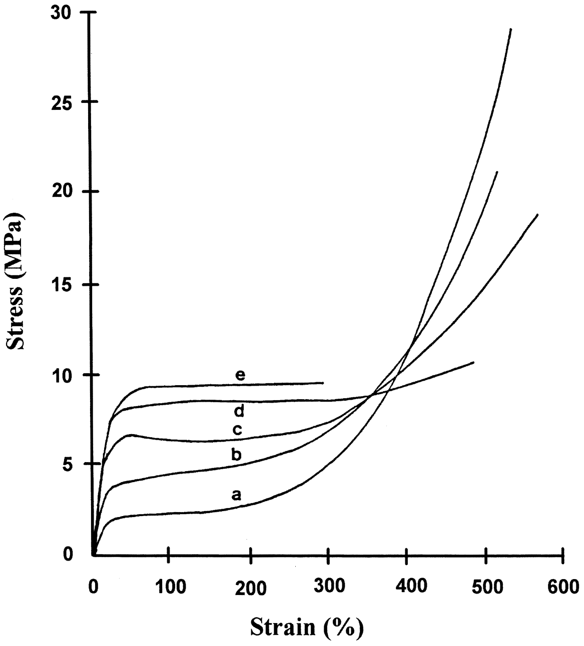

Fig. 2. Stress–strain curves of Conex/SEBS composites at different fibre loading (wt%): (a) 0, (b) 1, (c) 3, (d) 5 and (e) 7.

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

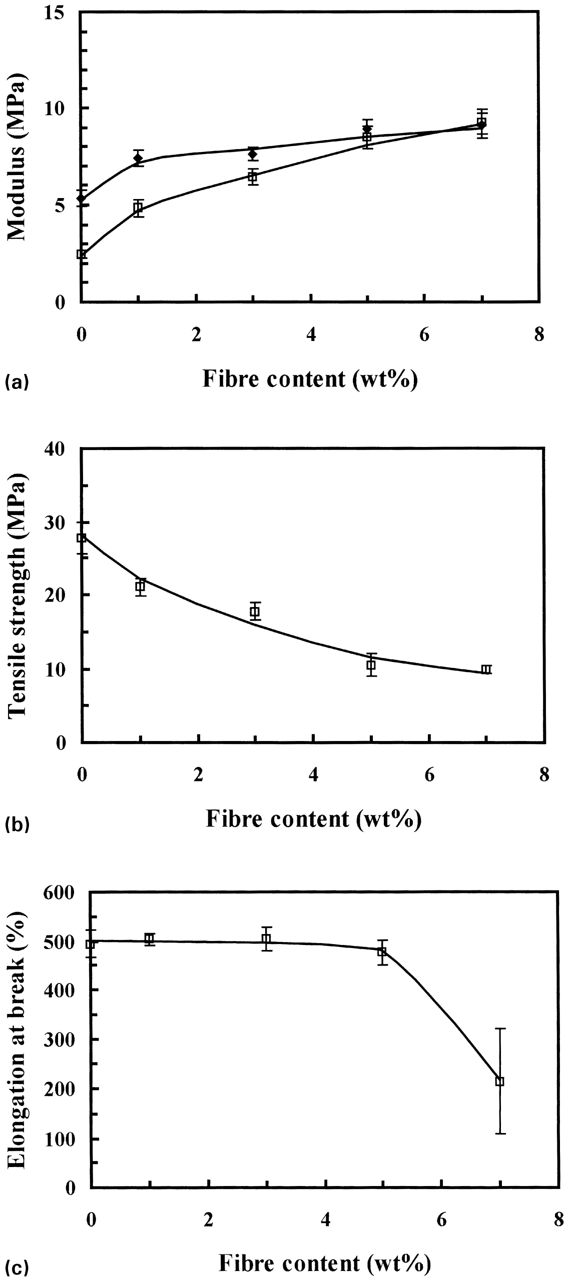

Fig. 3. Tensile properties of untreated aramid fibre/SEBS composite with various fibre loading. (a) Modulus at 100% (☐) and 300% (◆) extensions, (b) tensile strength and (c) elongation at break.

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

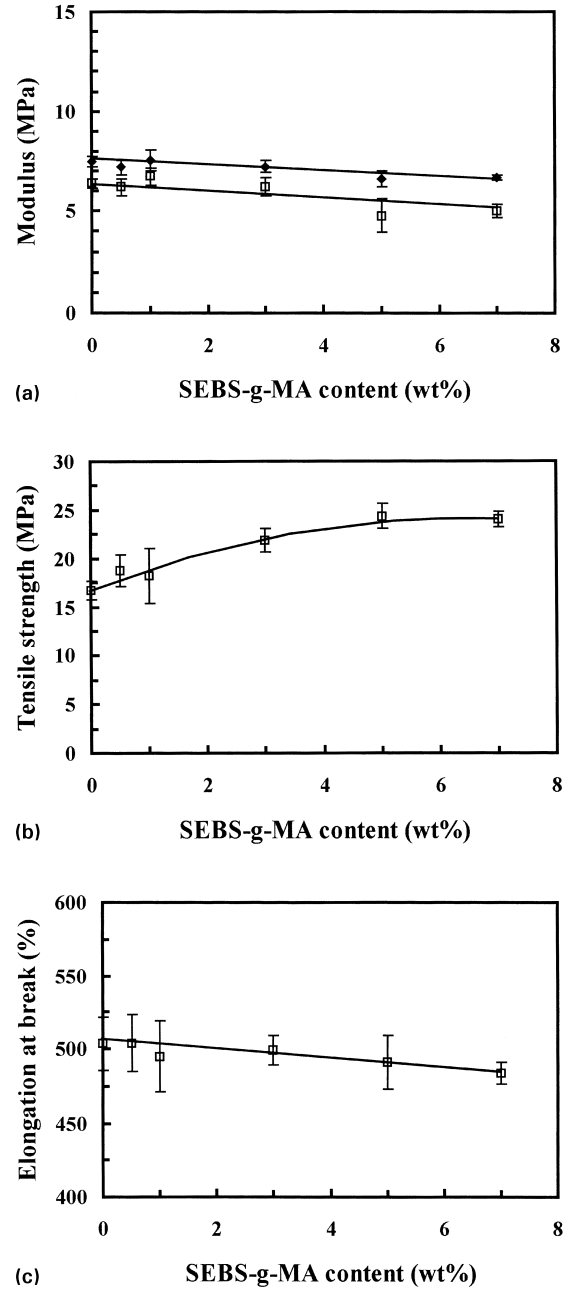

Fig. 4. Tensile properties of treated aramid fibre/SEBS composite with addition of compatibiliser. (a) Modulus at 100% (□) and 300% (♦) extensions, (b) tensile strength and (c) elongation at break.

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.

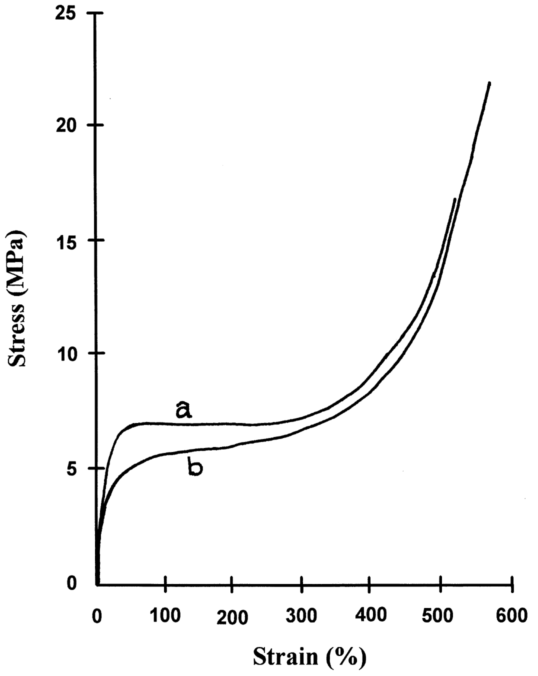

Fig. 5. Stress-strain curves of Conex/SEBS composites with 0 wt% (a), and 3 wt% (b) of MA-g-SEBS.

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

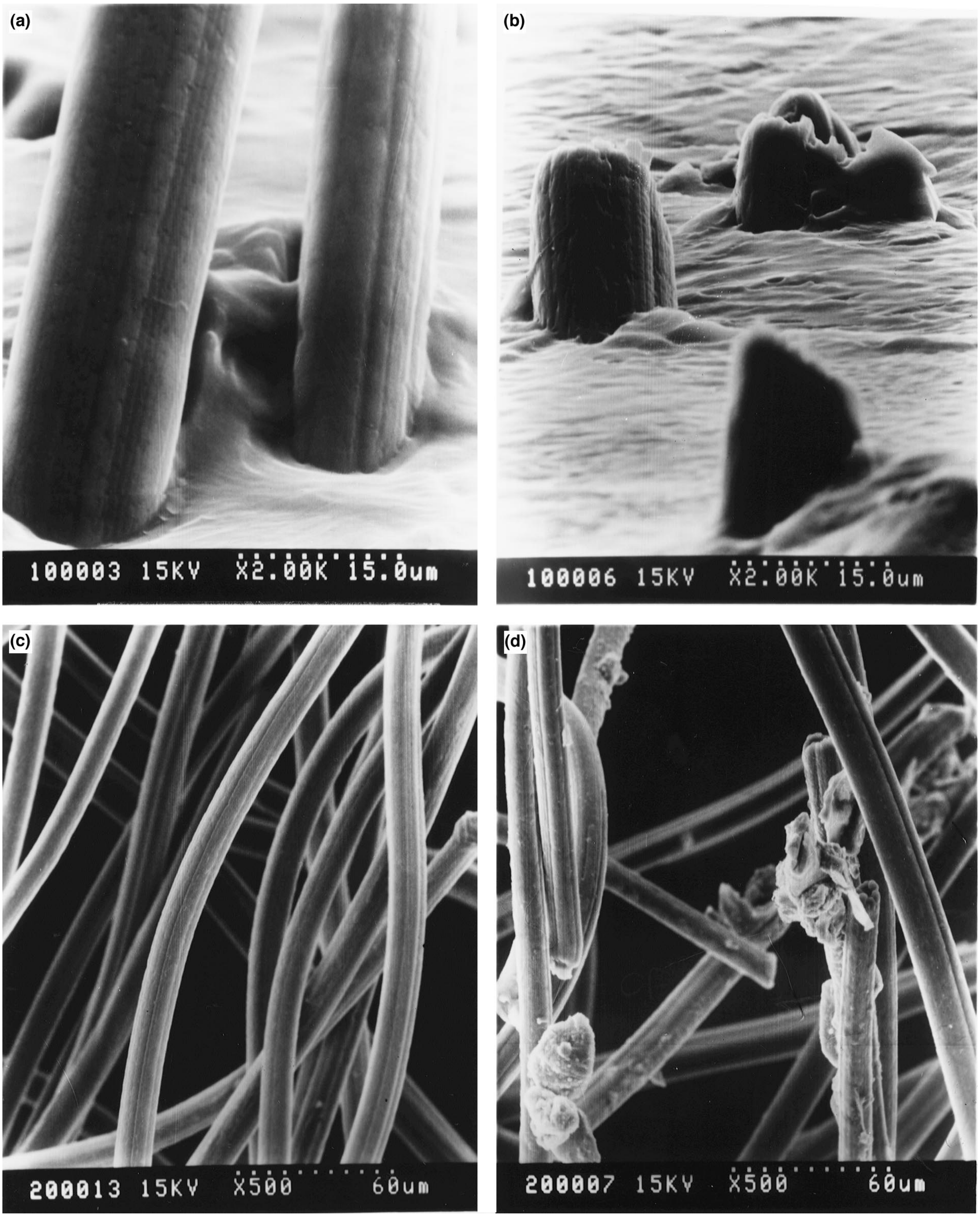

Fig. 6. SEM micrographs of the specimens: (a) fractured surface of the composite without compatibiliser; (b) fractured surface of the composite with 3 wt% MA-g-SEBS; (c) extracted fibres from specimen without compatibiliser; (d) extracted fibres from specimen with 3 wt% of MA-g-SEBS.

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

Support of this work by The Thailand Research Fund is gratefully acknowledged. The authors also would like to thank Shell Chemical Co. for providing SEBS and Teijin Ltd for providing Conex fibre.

References

[1] Foldi AP. In: Vigo TL, Kinzig BJ, editors. Composite applications: the role of matrix, fiber, and interface. New York: VCH Publishers, 1992:133–177.
[2] Foldi AP. Rubber Chem Tech 1976;49:379.
[3] Vaughan D. J Polym Eng Sci 1978;18:167.
[4] Takayanaki M, Kajiyama T, Katayose T. J Appl Polym Sci 1982;27:3903.
[5] Takayanaki M, Katayose T. Polym Eng Sci 1984;24:1047.
[6] Breznick M, Banhaji J, Guttmann H, Marom G. Polym Commun 1987;28:55.
[7] Andreopoulos 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: Wiley; 1994:251–254.
[14] Modic J, Pottick LA. Polym Eng Sci 1993;33:819.
[15] Chatzi EG, Tidrick SL, Koenig JL. J Polym Sci Part B: Polym Phys 1988;26:1585.
[16] Sperling LH. Introduction to physical polymer science, 2nd ed. Singapore: Wiley, 1993:521–522.
[17] Ward IM. Mechanical properties of solid polymers, 2nd ed. Chichester: Wiley, 1983:74.
[18] Edwards SF, Vilgis Th. Polymer 1986;27:483.
[19] Bualek-Limcharoen S, Nakinpong T, Amornsakchai T, Meesiri W. J Sci Soc Thailand 1997;23:101.