MORPHOLOGY AND MECHANICAL PROPERTIES OF COMPATIBILISED POLYPROPYLENE/VULCANISED RUBBER BLENDS

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ABSTRACT

Blends of polypropylene with vulcanised rubber obtained from the buffing process in sports shoe sole manufacture has been investigated. Two types of vulcanised rubber were used, midsole (M, vulcanised EVA foam) and outsole (O, vulcanised rubber blend of NR, SBR and BR). Styrene-ethylene-buthylene-styrene (SEBS) and maleic anhydride grafted styrene-ethylene-buthylene-styrene (SEBS-g-MA) were used as compatibilisers. It was observed that both SEBS and SEBS-g-MA enhanced the impact strength of the blends. The morphology of the blend observed by means of scanning electron microscopy (SEM) and optical microscopy showed the reduction of rubber dust into small rubber particle size of the compound with addition of SEBS and SEBS-g-MA up to 10 phr.

INTRODUCTION

Polymer blends play an important role in the modern polymer industry not only for the development of new materials but also for practical recycling purposes.[1,2,3] Most polymer blends are incompatible, and the final performance of a polymer blend is determined by the polymer compatibility and the phase morphology. Blends of PP and rubber have been extensively studied, since a wide range of properties can be obtained by selecting properly their compositions in the blends.[4,5,6] It was generally considered that PP and rubber are incompatible despite their similar non-polar structure. Thus, the addition of small amounts of compatibiliser has been attempted for PP/rubber blends in order to enhance the miscibility between the two components. Generally, there are two methods of compatibilisation: physical compatibilisation and chemical compatibilisation. The former technique utilizes a pre-made block or graft copolymer whose constituent component is compatible with each component in the blend. Compatibilisation may lower the interfacial tension between the two phases, reduce the physical size of the domains, stabilize the morphology, and provide for better adhesion between the phases. While the chemical compatibilisation technique is based on chemical reaction induced during blending process.

The focus of this work is the investigation of the impact properties of polypropylene/vulcanised rubber blends in the presence of styrene-ethylene-buthylene-styrene (SEBS) and maleic anhydride grafted styrene-ethylene-buthylene-styrene (SEBS-g-MA) as compatibilisers. The vulcanised rubbers used were recycled rubber from sport shoe sole manufacturer in Thailand. The morphological changes occurred as a result of the use of compatibilisers were also investigated as well as the effect of concentration of compatibiliser on the morphology of the blend.

Experimental

Commercial polypropylene (PP) used in this study was injection grade 6331 from HMC Co., Ltd.,Thailand. Two types of vulcanised rubber were scrap rubber dusts from sport shoe manufacture, midsole (M,vulcanised EVA foam) and outsole(O, vulcanised rubber blend of NR, BR and SBR) supplied by Piyavat Rubber Industry Co., Ltd, Thailand. Styrene ethylene butylene styrene (SEBS) and maleic anhydride grafted styrene ethylene butylene styrene (SEBS-g-MA) from Shell Chemical Co., Ltd. were used as compatibilisers.

Formulation

The compound formulations in this study consisted of 75 % PP, 25 % scrap rubber dust, 1 phr Ultranox 626 (GE Speciality Chemicals) and compatibiliser at various additions, from 0 to 10 phr.

Masterbatch preparation

Masterbatches containing polypropylene, scrap rubber dust and compatibiliser, were prepared with an Internal mixer (Chang Tong 1655) by using the ratio of composition of were 30:50:20 % by weight respectively. All of the ingredients were mixed by tumble mixer to give a random distribution before compounding in the mixer. The mixer speed was 70 rpm and mixing time was 20 min. The mixed materials were sheeted on a 2-roll mill then granulated with a granulator.

Compounding

Polypropylene, scrap rubber dust, masterbatch and antioxidant were mixed by tumble mixer to give a random distribution before compounding in a single screw extruder (Betol 3225J(screw diameter 32 mm), UK; L/D = 25:1) connected with a SD-CTM (self driven cavity transfer mixer, Iddon(screw diameter 30 mm), UK). The temperature profile of the single screw extruder was 190/200/210/220/220°C and the temperature profile of the SD-CTM was 220/220°C. The screw speed of the single screw extruder and SD-CTM were 35 and 60 rpm respectively. The extrudate was cooled in a water bath and the extrudate was granulated by a granulator.

Charpy notched impact strength testing

Impact strength testing was conducted using an impact tester (Zwick). Notched specimen was tested with 2.7 joules pendulum. The average value and the standard deviation of the impact properties were calculated using at least twenty samples.

Tensile testing

Tensile testing was conducted using an Instron mechanical tester (model 4301), with grip length of 50 mm, crosshead speed of 50 mm min^{-1} and a full scale load of 100 kg. Tensile properties of the dumbbell-shaped specimen were measured according to ISO 527 type B. For each specimen, the average value and standard deviation of the tensile properties were calculated using at least twenty samples.

Particle size and particle size distribution

The particle size and size distribution of scrap rubber dust in compound were determined by using an optical microscope. A thin section was produced by using a microtome apparatus (Polycut). The thin section thickness was controlled to be 3-5 μm. The particle size and particle size distribution of the scrap rubber dust were evaluated by a 10X objective lens of the microscope connected to an image analyser (Omminet 4, Buehler, U.S.A.).

Morphology

The morphology of the compound was studied with a scanning electron microscope (SEM). The specimen was obtained from the broken part of the impact bar after testing. The sample was mounted on SEM stubs then sputter coated with palladium. The morphology of the compound was observed by scanning electron microscope (SEM, Hitachi S-2500) at 15 KV accelerated voltage.

RESULTS AND DISCUSSION

Effect of type and amount of compatibilisers on impact strength of PP/vulcanised rubber blend

Generally the impact property of a thermoplastic is often increased by the addition of a rubbery phase. The rubber phase helps in toughening the matrix polymer. It is noteworthy here that the rubber particle size is one of the factors in controlling the rubber toughening of plastics.[7,8,9] According to numerous studies of rubber toughening, the optimum particle size of the rubbery phase should be somewhere in the range of a micron. However, the toughening effect is also dependent on the nature of the base polymer matrix. For example, in the case of pseudoductile polymers in general the optimum rubber particle size has been reported to be about 0.1-0.5 μm. By contrast for a brittle polymer such as polystyrene it has been reported to be 1-3 μm.[10] In this study, the vulcanised rubber dust incorporated in a thermoplastic matrix was most likely acting as a filler and adhesion between the rubber dust and the matrix polymer is crucial for the improvement of mechanical properties of such a composite.

It can be seen in Figure 1 that the Charpy notched impact strengths of both PP/midsole and PP/outsole compounds compatibilised by SEBS and SEBS-g-MA significantly increase with increased SEBS and SEBS-g-MA loading. This may be explained that SEBS would be used as a compatibiliser for the PP blends as the EB (ethylene butylene) middle block copolymer would be compatible with PP one phase and the non-polar component in midsole the other phase . In the case of PP and outsole, which is the vulcanised rubber blends of NR, SBR and BR, the SEBS would be compatible with PP and outsole by the polybutylene middle-block and the polystyrene end block segments respectively. Therefore the compounds compatibilised with SEBS and SEBS-g-MA gave good impact strength because of good compatibility between each of the phases. Especially at 10 phr of compatibiliser loading the Charpy notched impact strength increased approximately 90% for PP/midsole/SEBS compound, 70% for PP/midsole/SEBS-g-MA compound, 63% PP/outsole/SEBS compound, and 86% for PP/outsole/SEBS-g-MA compound.

Tensile mechanical properties of compatibilised PP/vulcanised rubber blends

Generally, the tensile properties of the PP modified by addition of rubber decreased because of the incompatibility of the phase in the compound. Addition of compatibiliser into the PP/rubber blend could improve compatibility between the two phases.[11] Figure 2(a-b) and Figure 3(a-b) showed the tensile yield strength and elongation at break of PP modified by addition of 25% scrap rubber dust and different loading of SEBS and SEBS-g-MA compatibiliser. It can be seen that an increase in elongation at break was achieved for all the compatibilised compounds, especially with 10 phr SEBS and 10 phr SEBS-g-MA. This is due to sufficient adhesion between the matrix phase and dispersed phase hence efficient stress transfer from the matrix to the dispersed phase occurred resulting in an increase of elongation at break. The tensile yield strength shown in Figure 2 presumably decreased due to the plasticizing effect of PP.

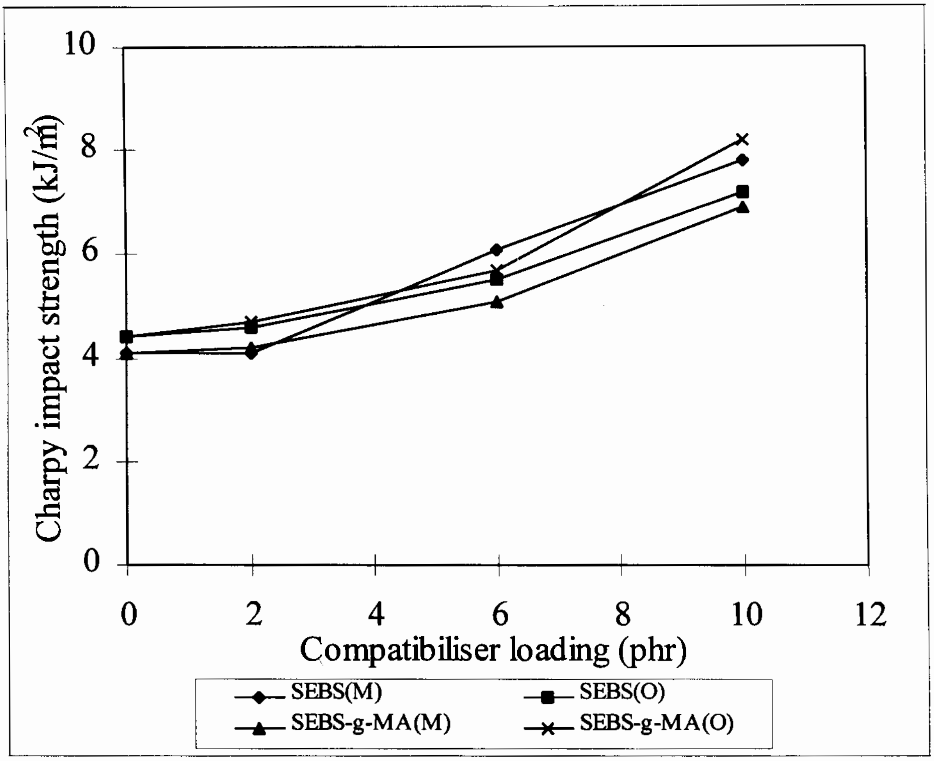
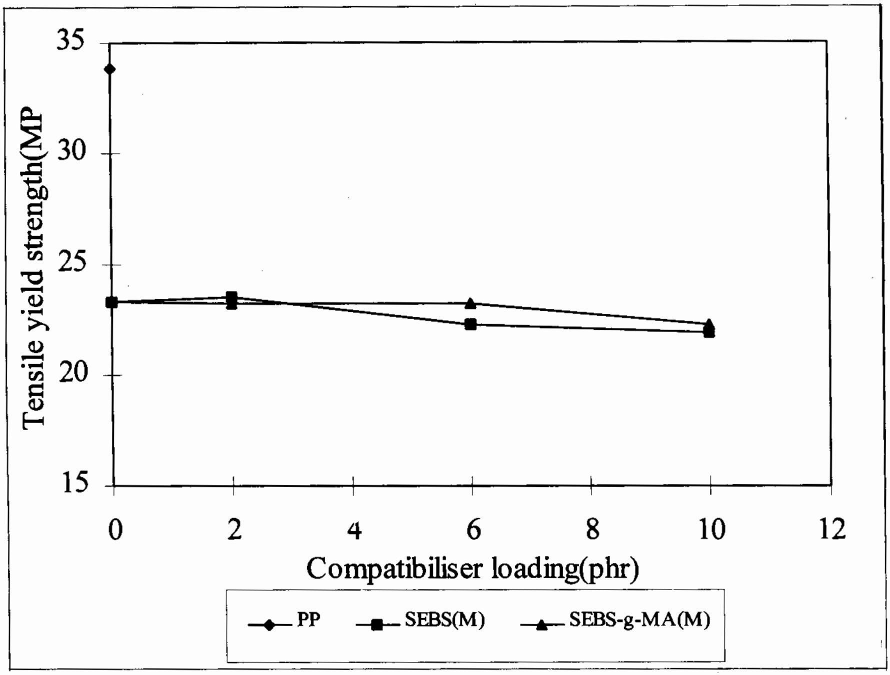


Fig.1 Effect of compatibiliser type and compatibiliser loading on Charpy notched impact strength of PP/vulcanised rubber blend.

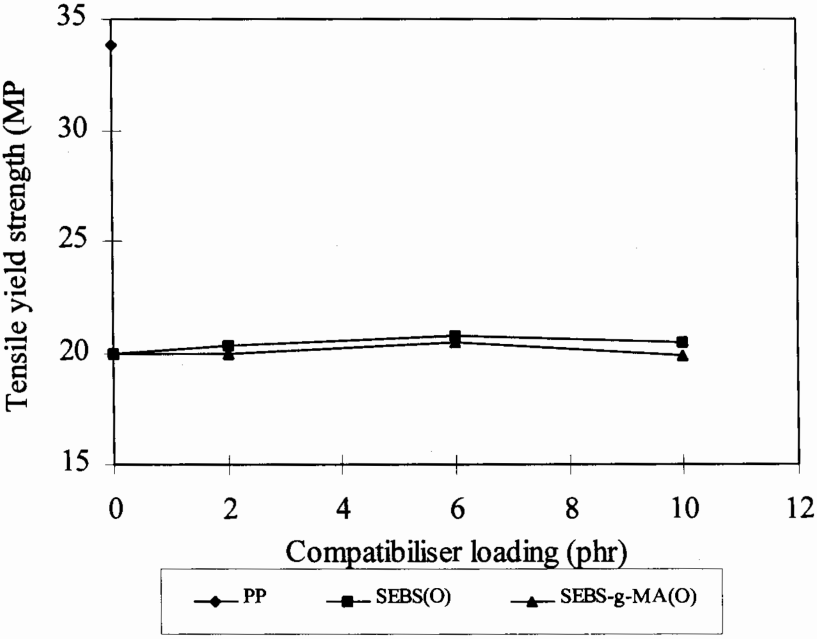
Figure 4 shows a typical stress-strain curve of the compatibilised PP/midsole compound. The differences in failure behaviour are obvious, with the incorporation of midsole, 25 % wt, the plastic deformation is inhibited, the compound failed at a lower elongation and the yield behaviour was not observed. This was due to poor adhesion between the PP matrix and the dispersed phase. In general, the elongation at break of rubber filled thermoplastic increases if there is sufficient adhesion between the matrix and the rubber.[12] An interesting observation in this study is the high increase in elongation at break and slight decrease in tensile strength and modulus for the compound containing 10 phr SEBS. This may be due to the increase of ductility in the compound which may have been due to two reasons. First, the overall crystallinity of the compound decreased. Second, it is thought to be because the midsole dust had better compatibility with PP when SEBS was used and hence slow crack growth occurred dissipating energy in the plastic deformation region.

Effect of compatibiliser on morphology of PP/vulcanised rubber blends

The particle size and particle size distribution of the vulcanised rubber dust in PP blends were analysed by optical microscopy. It can be seen in Table1 and 2 that addition of compatibiliser both SEBS and SEBS-g-MA into PP/M and PP/O give smaller particle size of the rubber dust than in the uncompatibilised compounds. The mean diameter of dust particle size in the PP/M/10 phr SEBS and SEBS-g-MA compound were 5.5 microns and 5.7 microns. Charpy notched impact strengths of 7.8 kJ/m^2 and 6.9 kJ/m^2 were obtained respectively. Whereas the mean diameter of dust particle sizes in the PP/M compound was 8.6 microns and



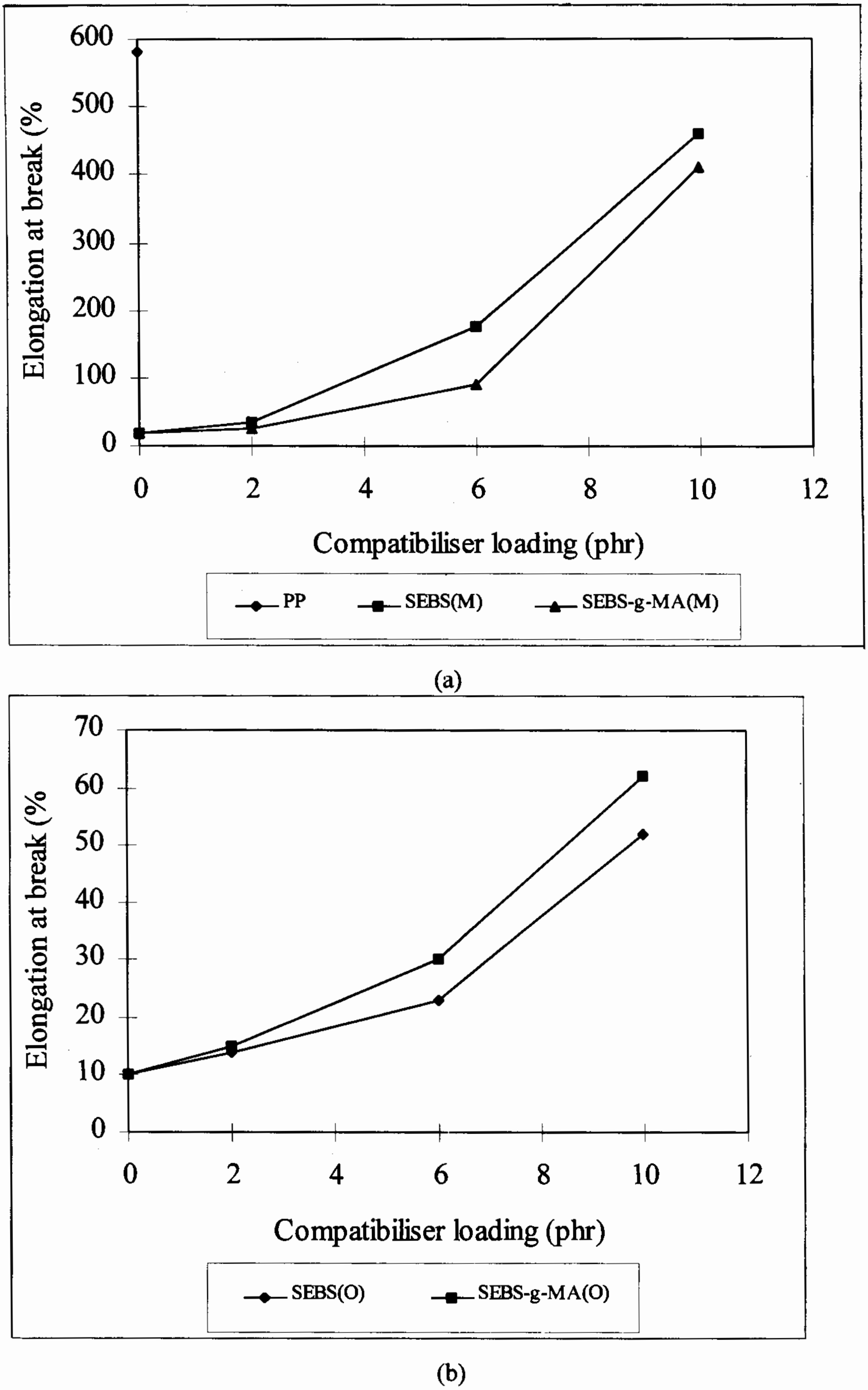
(a)



(b)

Fig.2 Effect of compatibiliser on the tensile yield strength of PP/vulcanised rubber blend

(a) PP/midsole (b) PP/outsole



(a)

(b)

Fig.3 Effect of compatibiliser on the elongation at break of the PP/vulcanised rubber blend
(a) PP/midsole (b) PP/outsole

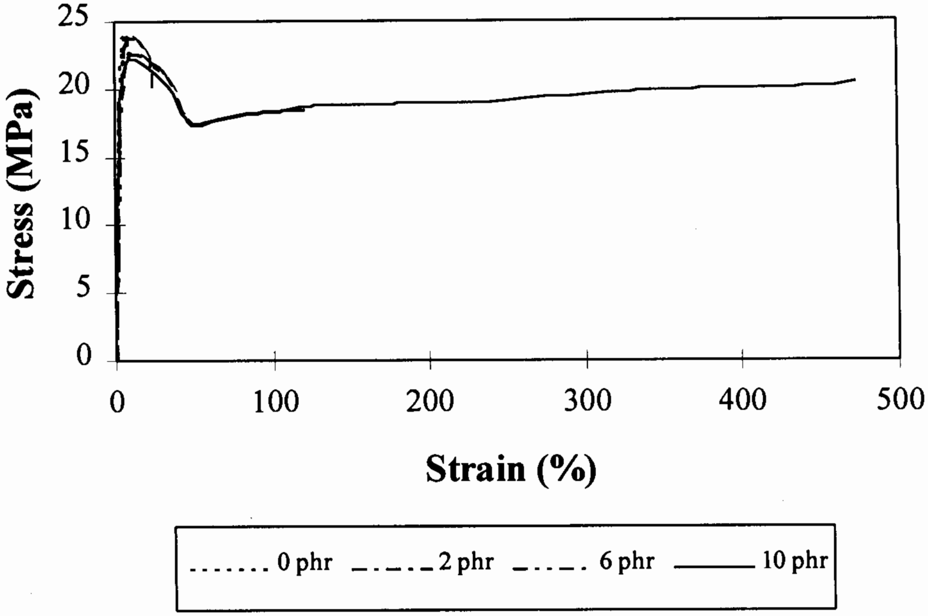


Fig.4 Typical stress-strain curve of compatibilised PP/M/SEBS at different SEBS loading

the Charpy notched impact strength was 4.1 kJ/m^2 . The mean diameters of the dust particle sizes in the PP/O/10 phr SEBS and SEBS-g-MA compounds were 5.9 microns and 5.4 microns. Charpy notched impact strengths of 7.2 kJ/m^2 and 8.2 kJ/m^2 were obtained respectively. Whereas the mean diameter and range of dust particle sizes in the PP/O compound was 8.6 microns and the Charpy notched impact strength was 4.4 kJ/m^2 . The results also show the diameter decreased as the concentration of compatibiliser increased. Therefore, it can be concluded that the impact strength was inversely proportional to the size of rubber particles and that smaller particles resulted in higher impact strengths.

The morphology of the compatibilised compounds of PP/midsole and PP/outsole were investigated to evaluate the effect of compatibiliser content on morphology. The SEM micrographs of fractured surface from impact testing of compatibilised compounds with SEBS and SEBS-g-MA are shown in Figure 5-8. At low magnification, it can be seen that the uncompatibilised compounds of both PP/midsole and PP/outsole have larger rubber particles but with addition of the SEBS and SEBS-g-MA at various loadings the particle size of rubber or dispersed phase decreased significantly. At 6 and 10 phr loading of SEBS and SEBS-g-MA, smaller dust particle size occurred and was dispersed in the matrix, approximately 1 μm particle diameter. At these concentrations of compatibiliser especially when the compounds were compatibilised with SEBS-g-MA, there existed two shapes of particle rubber, one is smaller and spherical particle and the other platelet shaped. It can be expected that the small spherical particles are SEBS or SEBS-g-MA and the platelet shapes are the scrap rubber dust particles.

The SEBS and SEBS-g-MA appear to function both as impact modifiers and as compatibilisers for PP/vulcanised rubber dust compounds. The SEBS and SEBS-g-MA content in the compound is expected to be a key variable affecting the toughness of PP/scrap dust compounds. An increase in the SEBS or SEBS-g-MA content might be expected to have a two-fold effect. First, it will increase the volume fraction of rubber dispersed in the PP, which

Table 1 Particle size and particle size distribution of dust in the PP/midsole and PP/outsole compound compatibilised with SEBS-g-MA.

SEBS-g-MA (phr)	Midsole			Outsole		
	mean diameter (μm)	SD	range (μm)	mean diameter (μm)	SD	range (μm)
0	8.6	15.12	1.2-190.5	8.7	14.22	1.2-170.0
2	6.8	12.17	1.2-185.5	7.0	12.43	1.2-172.9
6	6.1	7.71	1.2-115.9	5.7	9.77	1.2-172.4
10	5.7	6.70	1.2-83.1	5.4	7.80	1.2-106.8

Table 2 Particle size and particle size distribution of dust in the PP/midsole and PP/outsole compound compatibilised with SEBS.

SEBS-g-MA (phr)	Midsole			Outsole		
	mean diameter (μm)	SD	range (μm)	mean diameter (μm)	SD	range (μm)
0	8.6	15.12	1.2-190.5	8.7	14.22	1.2-170.0
2	6.5	9.20	1.2-122.7	6.9	8.98	1.2-117.3
6	5.7	8.95	1.2-137.3	6.5	9.32	1.2-121.5
10	5.5	7.66	1.2-94.5	5.9	10.24	1.2-118.3

greatly affects the toughness of this phase. Second, it will reduce the interfacial tension between the phases, preventing coalescence between minor phase particles and improving the adhesion between the phases, which in turn should contribute to an improved dispersion of the rubber dust phase.

The SEM micrographs of impact specimen fracture surface of the compounds compatibilised with 10 phr of SEBS and SEBS-g-MA both in PP/midsole and PP/outsole are shown in Figure 9. It can be observed that elastic deformation occurred at the interface between PP matrix and vulcanised rubber dust particles forming fibrils(see arrow on micrograph). A well-developed fibrillar feature resembles a craze-like deformation structure. The observation of fibrils can explain the improvement in toughness of the compound as previously reported.[13]

From the improved impact strength values observed for the compatibilised compound with SEBS and SEBS-g-MA, it can be deduced that the impact values improved because of the good compatibility of the components at the interface of polypropylene/ rubber dust compound. At the same time, the average dimensions of the dispersed phase was observed to have decreased, and interfacial adhesion between the polypropylene and rubber dust was indicated to be improved, due to the formation of fibrillar texture between the phases shown on the SEM micrograph.

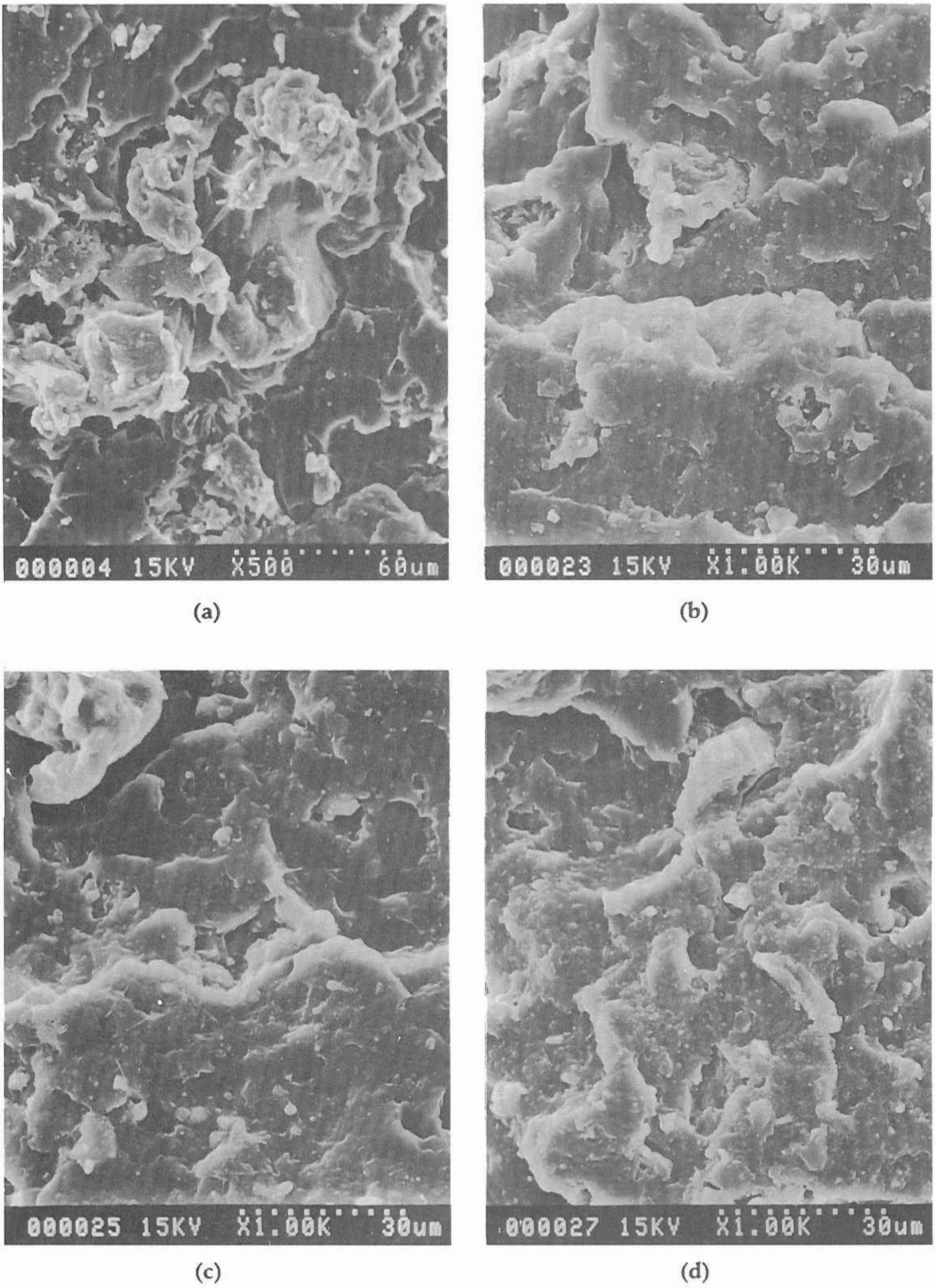
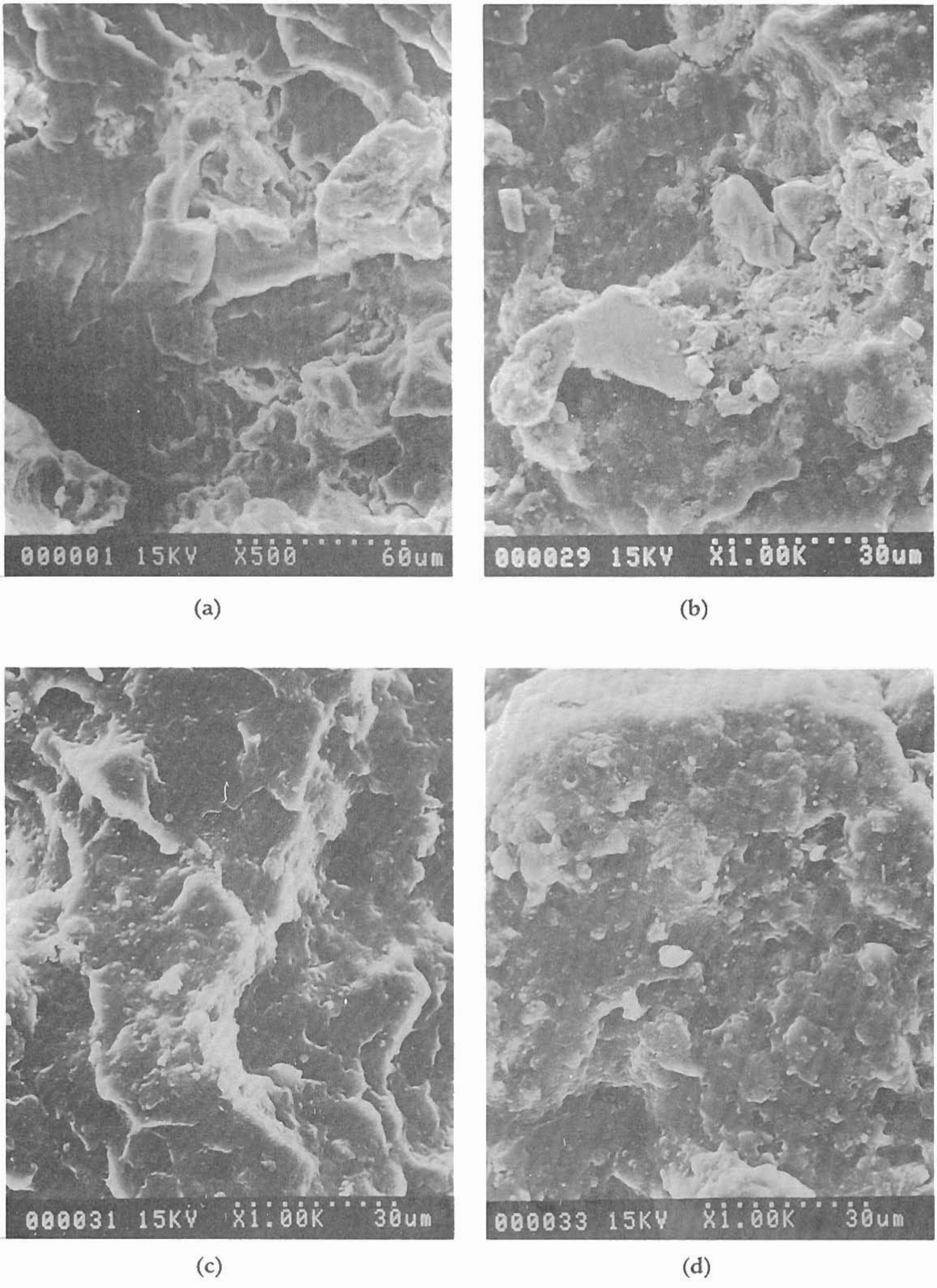


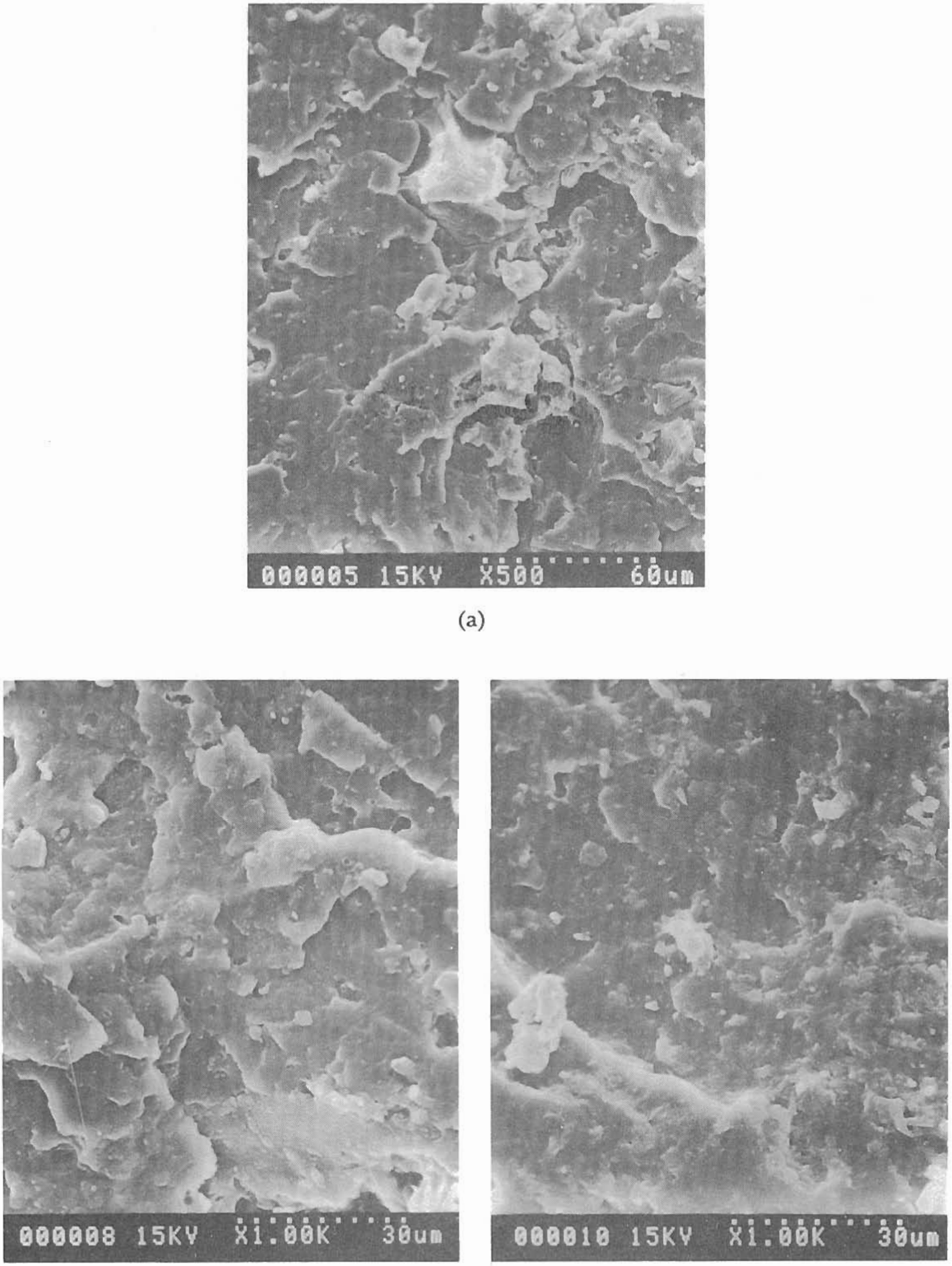
Fig.5 SEM micrographs of PP/Midsole/SEBS-g-MA compound at various SEBS-g-MA loading
(a) 0 phr (b) 2 phr (c) 6 phr (d) 10 phr



(a) (b)

(c) (d)

Fig.6 SEM micrographs of PP/Outsole/SEBS-g-MA compound at various SEBS-g-MA loading
(a) 0 phr (b) 2 phr (c) 6 phr (d) 10 phr



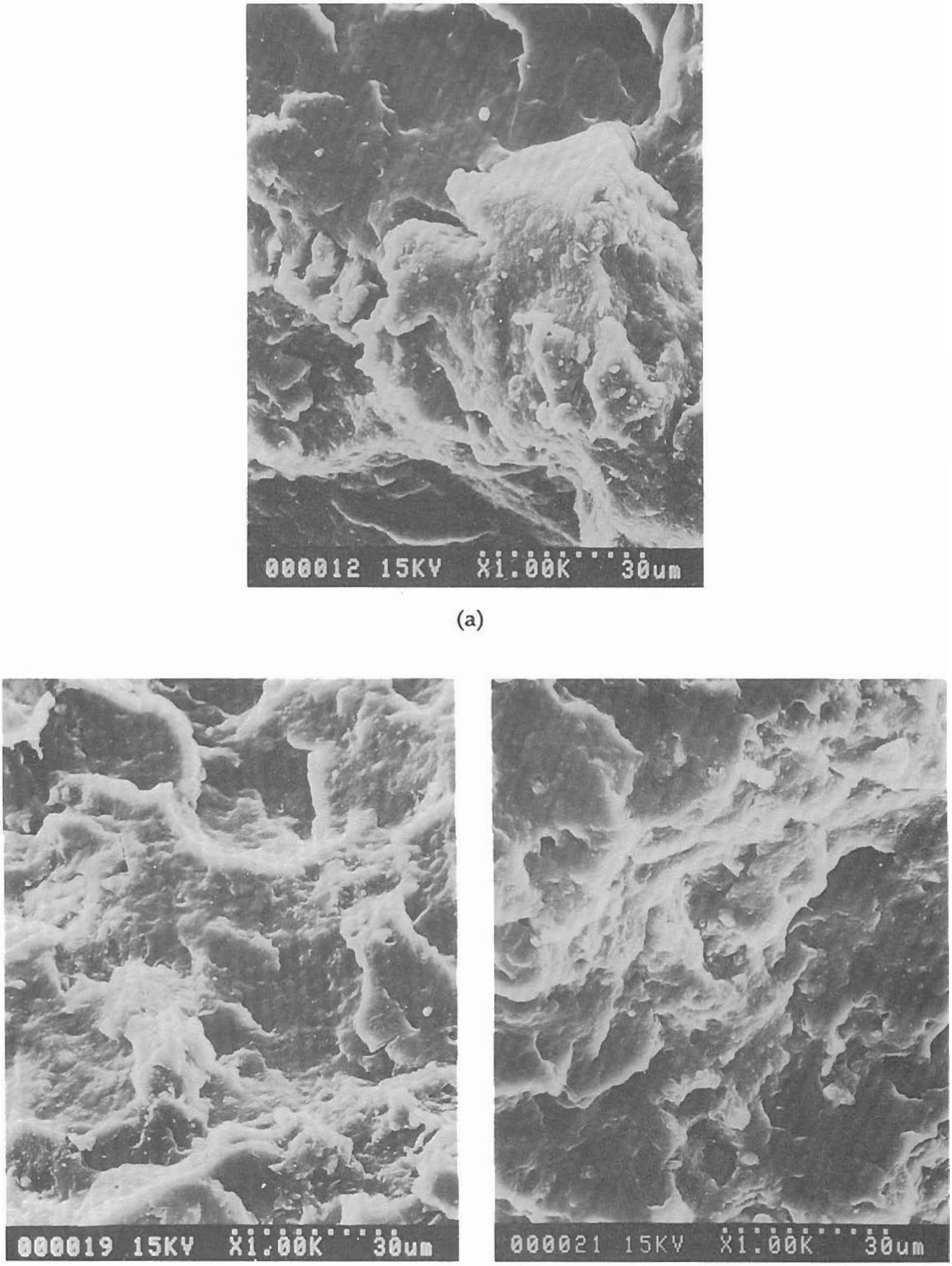
(a)

(b)

(c)

Fig.7 SEM micrographs of PP/Midsole/SEBS compound at various SEBS loading

(a) 2 phr (b) 4 phr (c) 10 phr

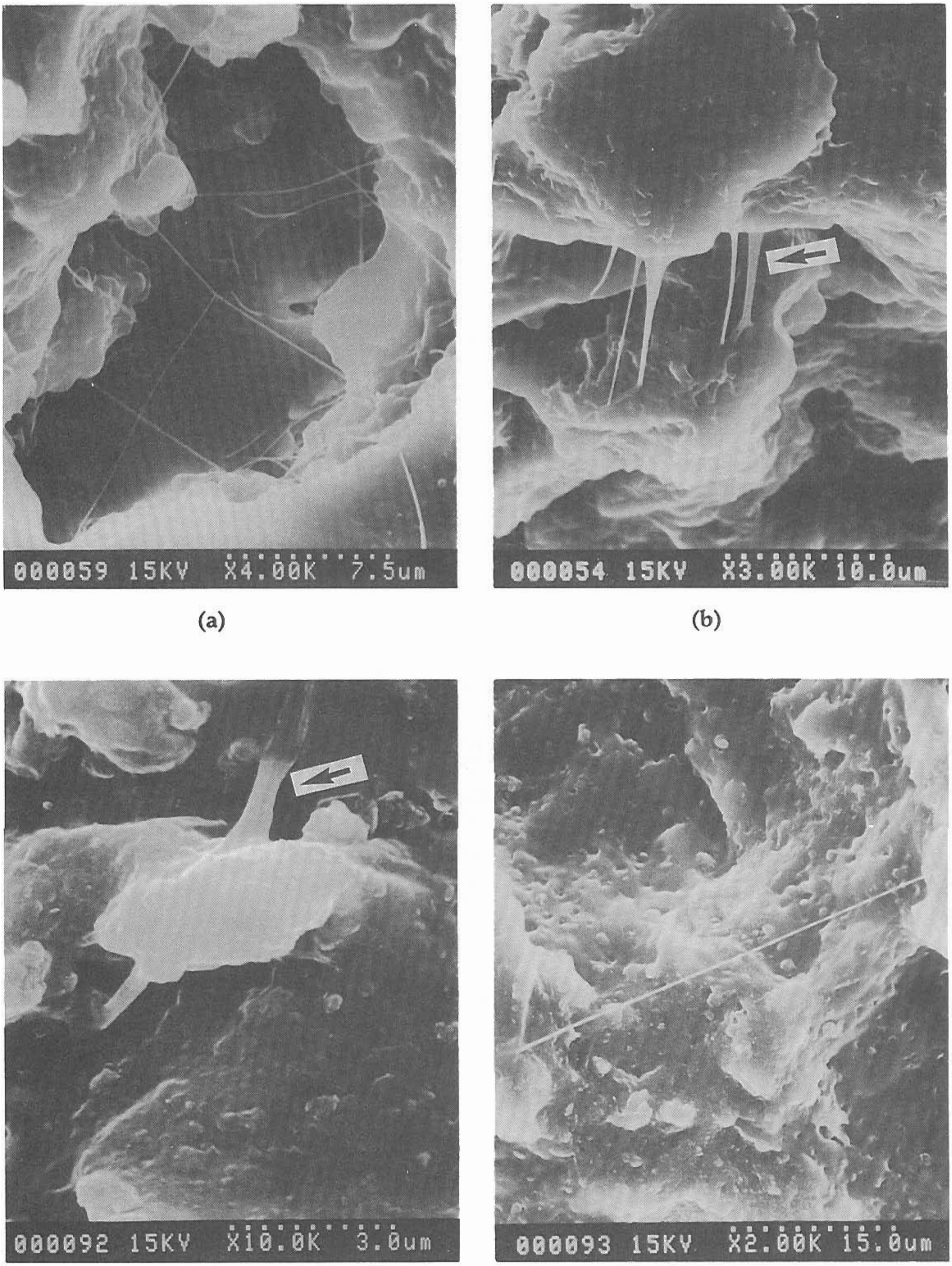


(a)

(b)

(c)

Fig.8 SEM micrographs of PP/Outsole/SEBS compound at various SEBS loading
(a) 2 phr (b) 6 phr (c) 10 phr



(a) (b)

(c) (d)

Fig.9 SEM micrographs of impact fracture surfaces of compatibilised compound of PP/rubber dust (10 phr compatibiliser)
(a) Midsole/SEBS (b) Outsole/SEBS (c) Midsole/SEBS-g-MA (d) Outsole/SEBS-g-MA

CONCLUSIONS

From the SEM micrographs together with optical microscopy observations, the addition of SEBS and SEBS-g-MA compatibilisers to PP/vulcanised rubber compounds have been shown to increase the adhesion between the matrix and the dispersed phase. The compatibilised compounds exhibited a much finer dispersion of the minor phase in the matrix PP, resulting in enhancement of impact properties of the compounds. The application of SEBS and SEBS-g-MA as compatibilisers for both PP/midsole and PP/outsole compounds was shown to be very effective. The improvement of impact strength was approximately 90% for PP/midsole/SEBS compounds, 70% for PP/midsole/SEBS-g-MA compounds, 63% PP/outsole/SEBS compounds, and 86% for PP/outsole/SEBS-g-MA compounds.

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