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Compatibilization of polystyrene and low density polyethylene blends by a two-step crosslinking process

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A new method has been developed to compatibilize the blends of polystyrene (PS) and polyethylene (PE). Polyethylene is first crosslinked partially by using a small amount of dicumyl peroxide (DCP) in a mixer at 165°C. Then the crosslinked PE is melt-blended with PS for another 5 min. Finally, a styrene–butadiene–styrene block copolymer (SBS) is added to the melt and mixed for another 5 min. We refer to this special procedure as the two-step crosslinking process. During the final mixing step of this process, the residual free radicals in the PE react with SBS. The crosslinking that occurs between PE and SBS has a significant impact on the mechanical properties of the blends including the impact strength, the tensile modulus, and the elongation-at-break. Scanning electron microscopy (SEM) results indicate that the interfacial adhesion is increased significantly, even though the domain sizes have not changed significantly in comparison with the non-crosslinked system. Transmission electron microscopy (TEM) results indicate that a thin SBS interfacial layer fully encapsulates the PE particles. This method could also be applied to other blend systems containing at least one component and a compatibilizer that are crosslinkable. © 1998 Elsevier Science Ltd. All rights reserved

(Keywords: polystyrene; polyethylene blends; two-step crosslinking process)

INTRODUCTION

Compatibilization of polystyrene and polyethylene blends has been the subject of considerable research and development efforts in recent decades[1–23]. Both PE and PS are the most commonly used polymers. However, when blended together, the resulting materials have poor mechanical properties. Therefore, it is highly desirable to develop new cost-effective ways of generating PS/PE compatible blends with improved mechanical properties. One of the most frequently used methods to compatibilize these blends is the incorporation of a copolymer such as a block copolymer of polystyrene and polyethylene (PS-*b*-PE) or a graft copolymer such as polystyrene-*g*-polyethylene (PS-*g*-PE) as a compatibilizer[1–12]. The beneficial effects of the compatibilizer on the morphological and mechanical behaviour of the blends have been well demonstrated. A small amount of the compatibilizer reduces the particle size, stabilizes the phase morphology against coalescence, and increases the interfacial adhesion. The effects of the molecular weight, the composition, and the molecular structure of the copolymer on the blend miscibility or compatibilization have also been extensively studied[3–7]. However, the costs of synthesizing these tailor-made compatibilizers make this route commercially unattractive. In addition, the weak interaction between PE and SBS results in only moderate improvement in the tensile properties and impact strength. Another popular approach is to introduce reactive groups onto each of the two polymers to be blended[13,14]. These functionalized polymers may form the required compatibilizer during a subsequent reactive extrusion. However, this approach also requires separate processes to produce the functionalized polymers. An alternative to this approach is the use of peroxide-initiated functionalization leading to grafting or crosslinking reactions[15–17], but this method proved to have limited success because of the difficulties in achieving the optimal conditions with minimal levels of intra-species crosslinking of PS and PE and chain degradation.

Recently, a new method has been developed in our laboratory to compatibilize PS/PE blends. Polyethylene is first crosslinked partially in the melt at high temperatures by using a small amount of DCP. Then the crosslinked polyethylene is melt-mixed with PS and SBS. Through the careful control of the processing parameters and procedures, the residual free radicals in PE will react with the butadiene component of SBS at the interface. This reaction will enhance the adhesion between the PS and PE phases, leading to significant improvement of the mechanical properties of the blends. We believe that this process could also be applied to other polymer blend systems that have one of the components and the compatibilizer able to be crosslinked by a curing agent. The objective of this work is to investigate the morphology and mechanical properties of PS/PE blends compatibilized by this method.

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EXPERIMENTAL

Materials

Polystyrene (PS 666 from Asahi Chemical Co. Ltd), low-density polyethylene (LDPE 2F4B from Shanghai Petrochemical Co.), styrene–butadiene–styrene block copolymer (SBS 791 from Yueyang Petrochemical Co.), and dicumyl peroxide (from Shanghai Chemical Supply Co.) were used in this study. All materials were commercially available and used without further purification. The composition of the blend was fixed at a weight ratio of 80/20 (PS/PE). The SBS and DCP contents were varied from 5 to 15 wt%, and from 0.01 to 0.1 wt%, respectively, based on the total weight of PS and LDPE.

Sample preparation

Mixing was performed using a Haake Rheocord mixer 9000. The process temperature was set at 165°C and the roller blades were operated at 30 rpm. LDPE and DCP were introduced into the preheated mixing chamber through a chute. After 5 min of mixing, the mixture was taken out and palletized. This material was then blended with PS at 165°C. After 5 min of mixing, SBS was added to the melt and further mixed for another 5 min. We refer to this special procedure as the two-step crosslinking process.

Mechanical tests

Test specimens for tensile and impact measurements were prepared by a small injection moulding machine (Morgan Press) at processing temperatures of 210–230°C. Standard specimens (ASTM D638) were used for tensile measurements and rectangular-shape specimens (ASTM D256) were used for impact tests. Tensile testing was performed with an Instron tester (Model 5567), at a cross head speed of 20 mm/min. Notched impact strength was determined by the Izod method with a Tinius Olsen impact tester (Model 92T).

Characterization

The fracture surface morphology of the notched impact specimens was studied with a JEOL JSM-6300 scanning electron microscope (SEM). The transmission electron microscopy study was performed with a JEOL JEM 100 CXII transmission electron microscope at an acceleration voltage of 100 kV. The specimens were prepared with an ultra-cryomicrotome (Leica) and the thin sections were stained with RuO_4.

RESULTS AND DISCUSSION

Process selection

Table 1 gives a summary of the mechanical properties of PS/PE blends prepared by various processing methods. In all samples the PE to PS weight ratio was 1:4. 10 wt% of SBS and 0.05 wt% of DCP were used (the wt% is calculated with respect to the total weight of PS and PE). The impact strength, tensile strength, and elongation-at-break of the PS/PE blend are 13.8 J/m, 22.4 MPa, and 5%, respectively. Addition of SBS as the compatibilizer increases the impact strength and the elongation-at-break of the blend (PS/PE/SBS) to 28.1 J/m and 12%, respectively. The mechanical properties of this blend even with the compatibilizer are not much better than PS, probably because of the weak interaction between the PE and the butadiene component of SBS.

In order to illustrate the uniqueness of the two-step crosslinking procedure, a PE/PS (20/80) blend containing 10 wt% of SBS was prepared by mixing PE, PS, SBS and 0.05 wt% of DCP in the mixer at 165°C for 15 min. The mechanical properties of this blend (PS + PE + SBS + DCP) are shown in *Table 1*. Its impact strength, tensile strength, and elongation-at-break are 14.7 J/m, 23.2 MPa, and 7.8%, respectively. Clearly these values are much lower than those of the blends prepared by the other crosslinking processes. The reason is that during the single-crosslinking step, crosslinking occurs mainly in the butadiene component of SBS and inter-crosslinking between PE and the butadiene component is minimal, leading to weak interfacial adhesion.

The blends (PS + PE + DCP/SBS, PE + DCP/PS + SBS, and PE + DCP/PS/SBS) were prepared by first crosslinking PE with DCP, then followed by various mixing sequences. The (PS + PE + DCP/SBS) blend was prepared by mixing PS, PE and DCP together at 165°C for 10 min, then SBS was added to the mixer and further mixed for another 5 min. The (PE + DCP/PS + SBS) blend was prepared by first mixing PE and DCP for 5 min and then PS and SBS were added into the mixer and mixed again for another 10 min. In the preparation of PE + DCP/PS/SBS, the DCP was first dispersed in the PE phase. The addition of PS alone did not cause any significant crosslinking reaction between PS and PE, but resulted in a good dispersion of PE in the PS matrix. Upon the final addition of SBS to the melt, the residual free radicals in PE would react mostly with SBS upon mixing. The SBS then acts as a strong coupling agent between the PE and PS phases by crosslinking the butadiene component with the PE phase and intermixing the styrene component with the PS matrix. From the results shown in *Table 1*, the blend PE + DCP/PS/SBS is clearly the best and its impact strength is much better than some commercial grades of high-impact PS (HIPS).

Effect of SBS and DCP concentrations

Figures 1–3 show the mechanical properties of the

Table 1 The effects of different processing methods on the mechanical properties of the PS/PE blends

Blend sample	Impact strength (J/m)	Tensile strength at break (MPa)	Elongation-at-break (%)
PS	22	42	2
PS/PE	13.8	22.4	5
PS/PE/SBS	28.1	26.7	12
PS + PE + SBS + DCP[a]	14.6	23.2	8
PS + PE + DCP/SBS[b]	50.6	29.5	26
PE + DCP/PS + SBS[c]	40.7	26.8	23
PE + DCP/PS/SBS[d]	115.7	35	42
HIPS[e]	80–133		

[a] All the components were mixed together. [b] PS, PE and DCP were mixed first and then SBS was added. [c] PE was mixed with DCP and then PS and SBS were added together. [d] PE and DCP were mixed and then PS was added and mixed for 5 min, and finally SBS was added. [e] (18).

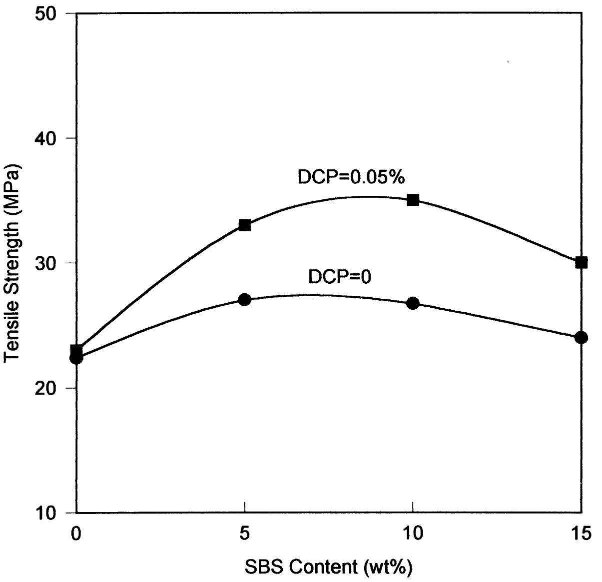

Figure 1 The tensile strength of the non-crosslinked PS/PE blends and the PE/PS blends prepared by the two-step crosslinking process as a function of SBS concentration

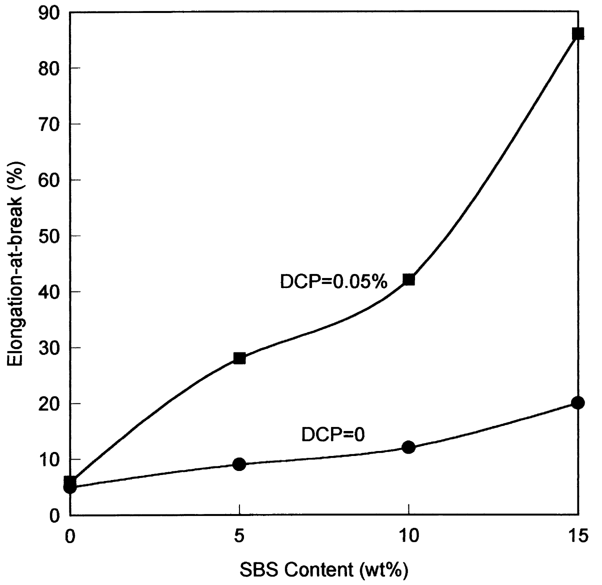

Figure 2 The elongation-at-break of the non-crosslinked PS/PE blends and the PE/PS blends prepared by the two-step crosslinking process as a function of SBS concentration

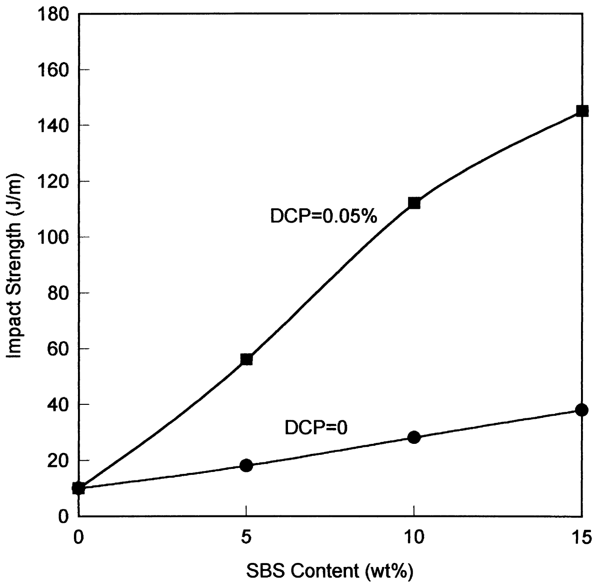

Figure 3 The impact strength of the non-crosslinked PS/PE blends and the PE/PS blends prepared by the two-step crosslinking process as a function of SBS concentration

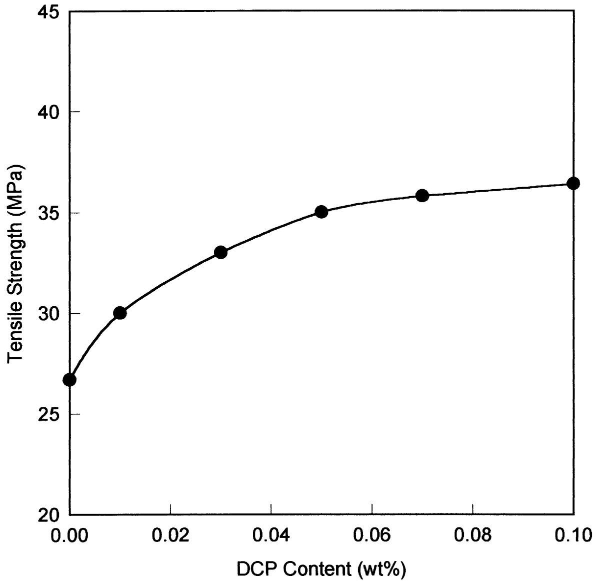

Figure 4 The tensile strength of the PE/PS blends with 10 wt% SBS prepared by the two-step crosslinking process as a function of DCP concentration

non-crosslinked PE/PS and the PE/PS blends prepared by the two-step crosslinking process with the SBS content varying from 0 to 15 wt%. For the non-crosslinked PE/PS blends, the addition of SBS only shows a slight improvement in the mechanical properties. These results indicate that in this system SBS is not an effective compatibilizer, as is well demonstrated in the literature[4–7]. The results shown in *Figures 1–3* also indicate that the mechanical properties of the blends (using 0.05 wt% DCP) prepared by the two-step crosslinking process are significantly enhanced. In particular the impact strength and the elongation-at-break increase dramatically when the concentration of SBS increases. The significant increase in the impact strength and the elongation-at-break is attributed to the crosslinking between PE and SBS. It is well recognized that strong interfacial adhesion in a multiphase-structure blend gives rise to an increase of impact strength[24]. The tensile strength of the blends also increases as a function of the SBS concentration up to 10 wt% of SBS and then decreases on further increases of the SBS concentration. This is consistent with the fact that a large amount of SBS at the interface of PE and PS will undoubtedly reduce the tensile strength of the blends.

Figures 4–6 show the effects of the DCP content on the mechanical properties of the blend containing 10 wt% SBS. Both impact and tensile strengths increase as the DCP concentration increases. However, the increase is relatively small when the concentration of DCP is more than 0.05 wt%. In addition, the elongation-at-break reaches a maximum at 0.05 wt% of DCP as it is well known that any

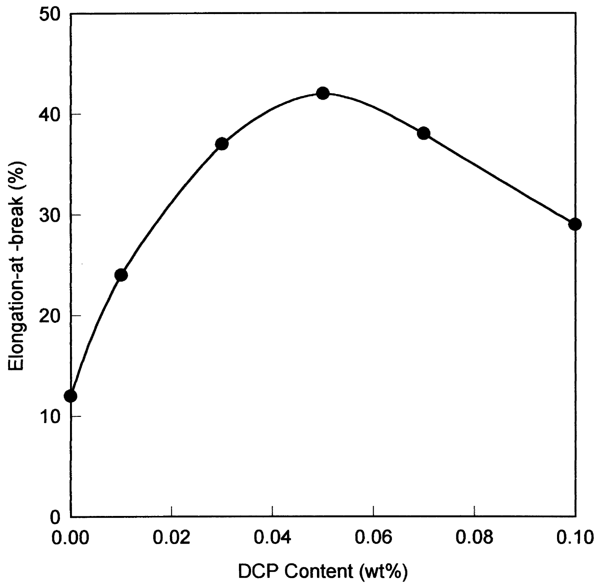

Figure 5 The elongation-at-break of the PE/PS blends with 10 wt% SBS prepared by the two-step crosslinking process as a function of DCP concentration

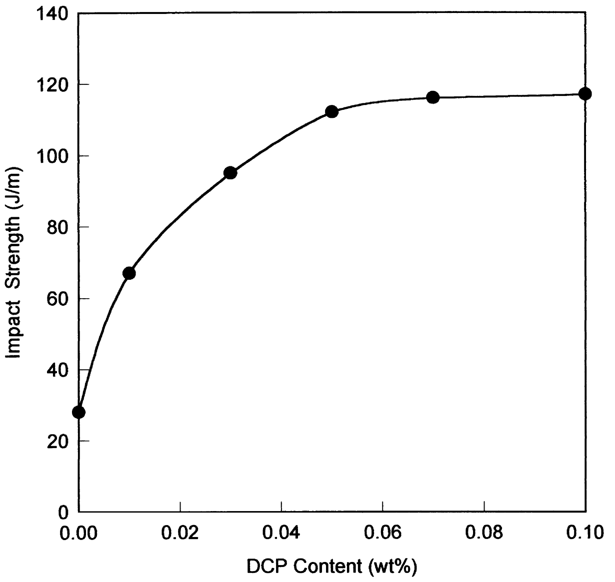

Figure 6 The impact strength of the PE/PS blends with 10 wt% SBS prepared by the two-step crosslinking process as a function of DCP concentration

excess degree of crosslinking will reduce the elongation-at-break of a polymer. From these results, we can conclude that 0.05 wt% of DCP is the optimal concentration for this blend.

Figure 7a displays a TEM micrograph of the PE/PS blend with 10 wt% of SBS. It can be easily identified in the TEM micrographs that PE is the discrete phase and PS is the matrix. The dark areas at the interface between the PE and PS as shown in *Figure 7* represent SBS. Although SBS segregates at the interface, only slight improvement in impact strength, tensile properties, and elongation-at-break is observed because the interaction between the polybutadiene block and polyethylene is weak. *Figure 7b* shows the TEM micrograph for the blend containing 10 wt% of SBS prepared by the two-step crosslinking process. The presence of SBS at the interface of PE and PS is confirmed and the domain sizes of PE are slightly reduced, as the viscosity of PE increases as a result of crosslinking (cf. *Table 2*). However, the materials produced by the two-step crosslinking procedure have much improved physical properties which are attributed to the crosslinking between PE and the butadiene component of SBS.

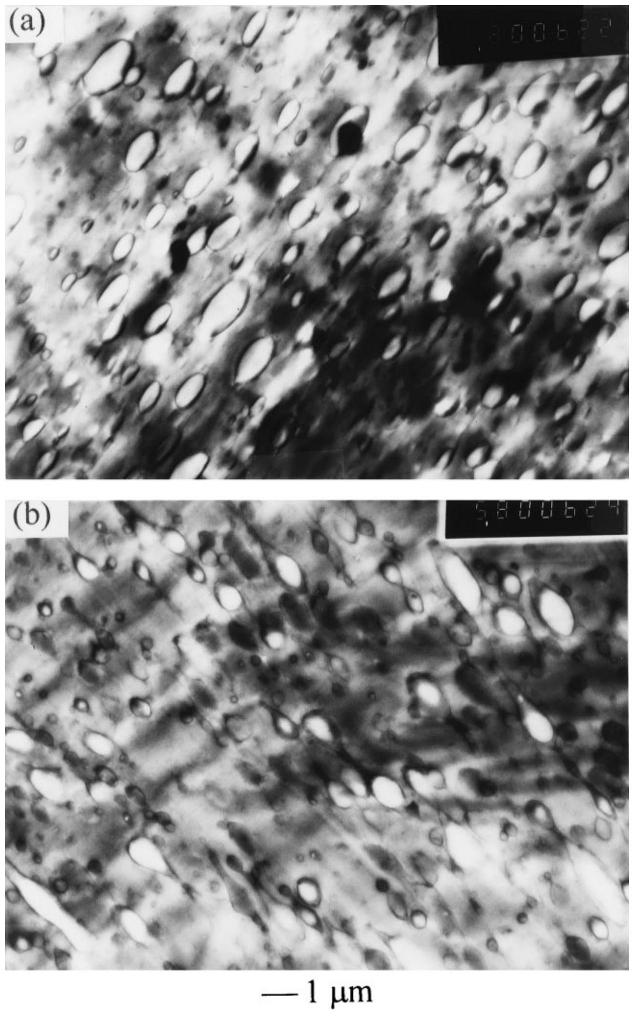

Figure 7 (a)TEM micrograph for PS/PE (80/20) blend with 10 wt% of SBS as the compatibilizer. (b) TEM micrograph for PS/PE (80/20) blend with 10 wt% of SBS as the compatibilizer prepared by the two-step crosslinking procedure

Table 2 The torque values for LDPE, PS and SBS at 150°C and 30 rpm

	LDPE	PS	SBS
Torque, N m	0.74 (1.22)[a]	1.33	1.75

[a] The torque value at 5 min after addition of 0.25 wt% of DCP.

Figure 8 shows SEM micrographs of the non-crosslinked and crosslinked PE/PS blends with and without SBS. *Figure 8a* and *b* are micrographs for uncrosslinked PE/PS and crosslinked PE/PS blends (without SBS), respectively. The detachment of the PE phase from the PS matrix is observed and there is no indication of adhesion between these two polymers. The morphology is typical of that of incompatible blends. However, different shapes of the PE phase are observed—a mixture of elongated and spherical PE particles is seen in *Figure 8a,* while only spherical PE particles are observed in *Figure 8b*. This may be due to the fact that crosslinking has rendered PE more difficult to

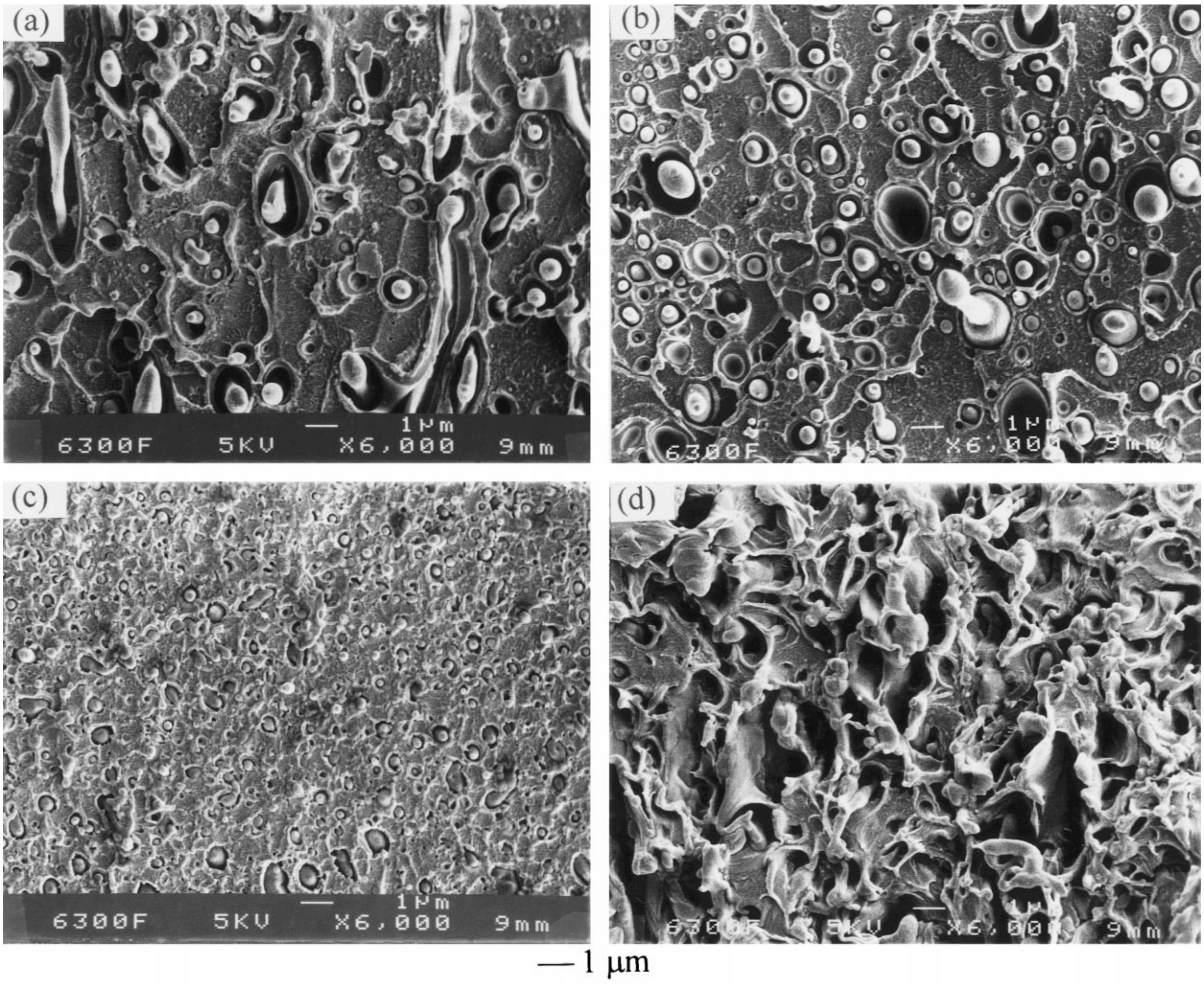

Figure 8 (a) Fracture surface of a non-crosslinked PE/PS blend without SBS. (b) Fracture surface of a crosslinked PE/PS blend. (c) Fracture surface of a non-crosslinked PE/PS blend with 10 wt% of SBS. (d) Fracture surface of a PE/PS blend with 10 wt% of SBS prepared by the two-step crosslinking process

deform during the high shear injection moulding process[16,25]. When 10 wt% of SBS is added to the uncrosslinked PE/PS blend, a finer dispersion of the PE phase is observed in *Figure 8c*. This finer dispersion of the PE phase in the matrix brings about only slight improvement in the mechanical properties due to the weak interaction between PE and SBS. However, when the blend was prepared by the two-step crosslinking procedure with 10 wt% of SBS, a substantially different morphology was observed, as shown in *Figure 8d*. This micrograph, which displays strong plastic deformation of the matrix, accompanied by high shear deformation of PE particles, is a strong indication of the improved adhesion at the interface between the PE and PS phases. This behaviour is attributed to the crosslinking between the PE and the butadiene component of the SBS.

CONCLUSION

This two-step crosslinking procedure has been shown to be a very effective method to compatibilize PE/PS blend with SBS as the coupling agent between PE and PS. Significant improvements in impact strength, elongation-at-break, and tensile strength were observed with the blends prepared by this process. Crosslinking between PE and SBS is identified as the key factor that causes the improvement. This method could also be applied to other blend systems containing at least one component and a compatibilizer that are crosslinkable.

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