

Localized Compatibilization in Immiscible Blends of Thermoplastic Polyurethane and Ethylene-Octylene Copolymer

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ABSTRACT: To prepare thermoplastic polyurethane (TPU)/ethylene-octylene copolymer (POE) blends, which are thermodynamically immiscible, maleated POE and aminated POE were incorporated as compatibilizers. Effect of addition of the compatibilizers and their contents on morphology, coalescence, and mechanical properties of TPU/POE blends were investigated. The microstructural observation revealed that the compatibilizers are located at the interface in the blends, forming a stable interfacial layer. As a result, the dispersed phase particle size was

greatly reduced and tensile properties of the blends were significantly improved. POE-NH₂ provides the blends with higher compatibility than POE-MA. The interfacial interaction offered by the compatibilizers was found to be a function of the amount of the reactive groups grafted onto POE. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 105: 1309–1315, 2007

Key words: blends; compatibilization; morphology; interfaces; polyurethanes

INTRODUCTION

In recent years, blends of thermoplastic polyurethane (TPU) and polyolefin (PO) have been investigated for their academic interests and commercial importance.^{1–5} TPU, with properties from those of a high performance elastomer to those of a tough thermoplastic, is extensively used because of its superior physical properties and versatility in chemical structures. Blending TPU with PO is generally based on the following two goals. First, PO is added into TPU to reduce the latter's cost and to improve its thermal stability, mechanical properties (e.g., modulus, strength, and hardness) and processing performance. Second, TPU is blended with PO to improve PO's properties including impact strength, adhesion, and paintability.

For making packing vessels and blow films, compatibilized blends of TPU and polypropylene (PP)^{1–3,6,7} or polyethylene (PE)^{2,4,8} have been produced. In the case of artificial leathers, however, the above TPU/PP and TPU/PE blends are not qualified because the higher crystallinity of the polyolefins would lead to reduced pliability of the blends. In this context, mixing ethylene-octylene copolymer (POE) with TPU might be a solution as the former has rather low crystallinity and tiny crystallites and is thus able to provide the blends with balanced performance. To the authors' knowledge, TPU/POE blends have not yet been reported. Similar to TPU/PP or TPU/PE, TPU/POE is thermodynamically immiscible. Therefore, blending TPU and POE might lead to multiphase morphologies and deteriorated mechanical properties,^{9,10} as compared to those of the individual components.

In general, the dispersed phases in an immiscible blend would become larger during processing or annealing, accompanied by broader size distribution.^{3,11,12} So far, it is known that two counteracting factors control morphology evolution when polymer blends are compounded^{2,13,14}: (i) deformation and breakup of the dispersed phases, and (ii) coalescence of the dispersed phases. A great deal of work has been done concerning droplet breakup (e.g. Ref. 13) and coalescence mechanism and kinetics (e.g. Ref. 5).

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The compatibilizer has a significant effect on coalescence in polymer blends. Being located between the phases, the compatibilizer can work either by reducing interfacial tension¹⁵ or by steric suppression of coalescence.¹⁶

In the current work, TPU/POE blends were produced with the aid of the compatibilizers that were prepared by grafting reactive groups onto POE and are able to react with urethane linkages of TPU. The influence of compatibilizers on the morphology, coalescence, and mechanical properties of the blends was clarified, with the objective of establishing the knowledge framework for adding new members to the family of TPU based blends.

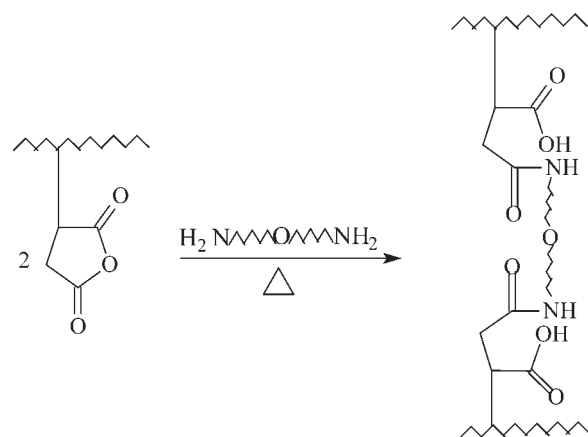
EXPERIMENTAL

Materials

The polymers used in this work are polyester thermoplastic polyurethane elastomer (TPU, S85A, BASF, Germany) and ethylene-octylene copolymer (POE, 8130, Dow Chemical, USA). The thermoplastic polyurethane (Shore hardness: 85A) is a block copolymer consisting of hard segments and polyester soft segments. The ethylene-octylene copolymer has a MFR (190/21.6) of about 13 g/910 min, preferentially employed for blow molding.

Preparation of POE-based compatibilizers

Grafting of POE with maleic anhydride (MA), POE-MA, was conducted by using a co-rotating intermeshing twin-screw extruder with a screw configuration adapted for grafting. POE granules and 1.2 wt % MA were fed to the extruder set at 200°C. The grafted content of MA is 0.8 wt %, as determined by quantitative



Scheme 1 Reaction process of POE-MA and end amino-group polyether.

infrared spectroscopy using the adsorption band at 1790 cm⁻¹. To systematically study the effect of grafting percentage, a series of POE-MA with different grafting percentages were synthesized in terms of solution copolymerization following the procedures described in Ref. 17.

Aminated POE (denoted by POE-NH₂) was also prepared with the aforesaid twin-screw extruder approach. A mixture of POE-MA and 0.6 wt % end amino-group polyether was melt compounded at 200°C. The reaction process is illustrated in the following scheme.

Preparation of TPU blends

Prior to blending, TPU was dried at least for 3 h in vacuum at 100°C. The blends were extruded at 200°C by a co-rotating intermeshing twin-screw extruder with a screw configuration adapted for blending. The main processing parameters are: 80 rpm

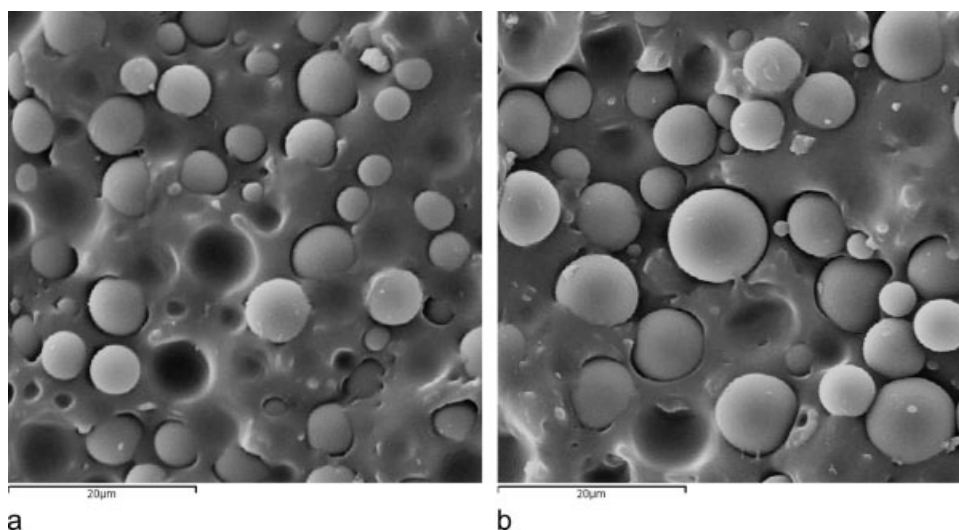


Figure 1 SEM micrographs of cryo-fracture surface of (a) TPU/POE (80/20) and (b) TPU/POE (70/30) blends.

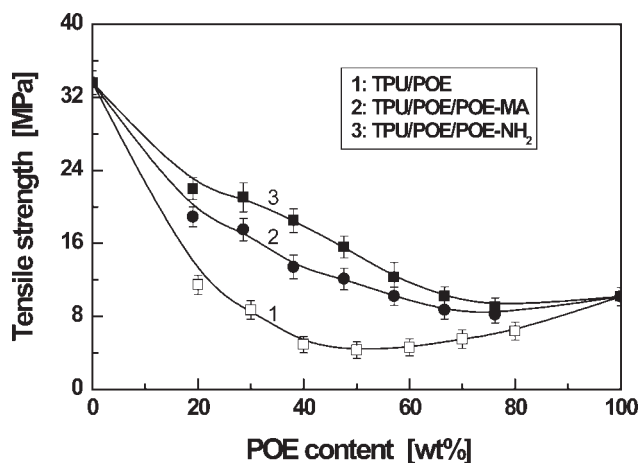


Figure 2 Tensile strength of TPU/POE blends as a function of POE content. For the blends containing POE based compatibilizers, the amount of the compatibilizers is 5 wt %.

(screw speed), 10 kg/h (output), and 50 s (residence time).

Tensile specimens were prepared by injection molding at 170°C. The mold temperature was preset at 40°C.

Characterization

Scanning electron microscopy (SEM) observation was performed with a Philips XL-30 FEG instrument under an accelerating voltage of 10 kV. The polymer blends were cry-fractured in liquid nitrogen, and then the fracture surface was coated with platinum 10 Å thick for SEM examination. The SEM micrographs were then used to analyze the POE particle size and shape, size distribution. The analysis was carried out using a computerized image analyzer

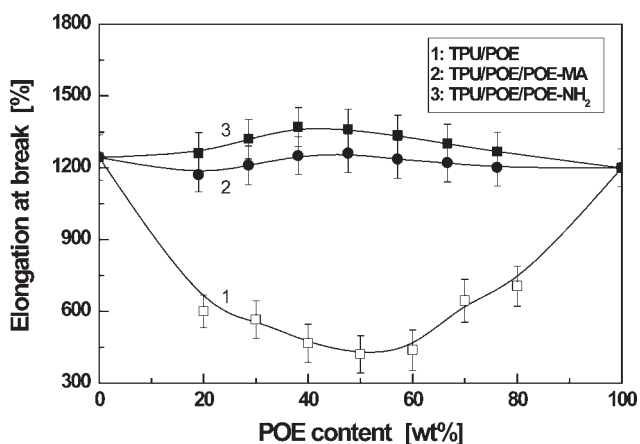


Figure 3 Elongation at break of TPU/POE blends as a function of POE content. For the blends containing POE based compatibilizers, the amount of the compatibilizers is 5 wt %.

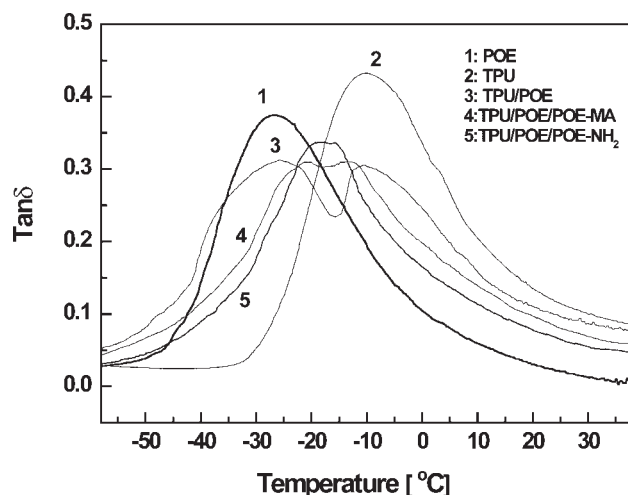


Figure 4 Temperature dependence of loss factor, $\tan \delta$, of TPU, POE, TPU/POE (50/50), TPU/POE/POE-MA (50/50/5), and TPU/POE/POE-NH₂ (50/50/5) blends.

with Image-Pro Plus software. Typically, 80–100 particles and several fields of view were measured.

The samples for transmission electron microscopy (TEM) observation were cryo-microtomed. The slices were stained in RuO₄ vapor for 20 min in advance. The TEM machine was a JEM-100CX II (Japan Electron) working at an acceleration voltage of 100 kV.

The tensile tests were carried out at room temperature under a loading speed of 200 mm/min by using a Hounsfield H10KS universal testing machine. Eight specimens were used for each result. A TA-DMA2980 instrument was employed to conduct dynamic mechanical analysis of the materials in parallel plate mode at a frequency of 10 Hz and a heating rate of 5°C/min under N₂.

RESULTS AND DISCUSSIONS

TPU/POE blends without compatibilizers

TPU is a polar polymer, while POE is nonpolar. They exhibit distinct differences in polarity and surface free energy. Consequently, the high interfacial free energy has to result in negligible interaction at the interface in the blends of TPU and POE. The fractographs in Figure 1 show that the cracks mainly propagate along the phase boundaries, and POE particles exhibit smooth surface. No signs of interfacial adhesion are observed either on the dispersed POE particles or in the holes left by detachment of POE. Besides, size distribution of the POE particles in TPU is rather broad. These results coincide with the characteristics of immiscible polyblends described in the introductory part.

From Figure 1(a,b), it is seen that the size of POE particles becomes coarser when the TPU/POE ratio is decreased from 80/20 to 70/30. The POE particle

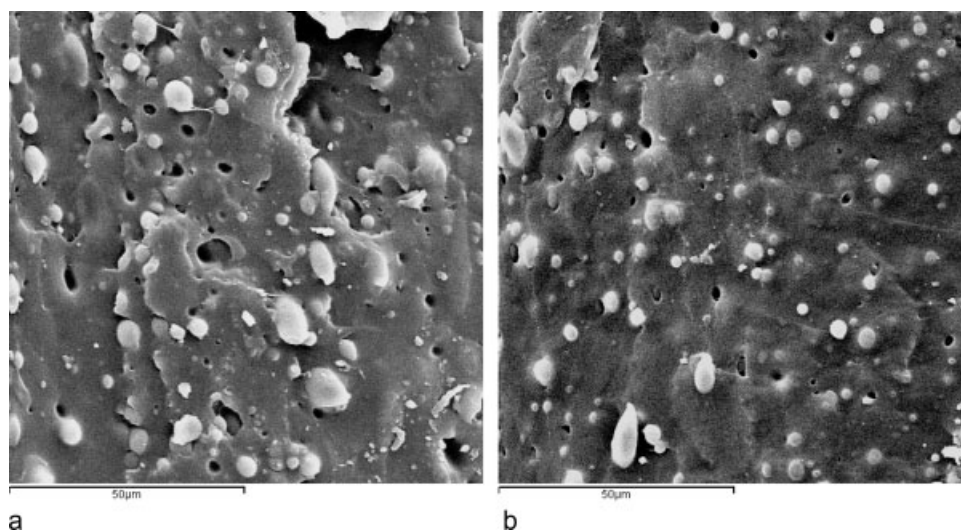


Figure 5 SEM micrographs of the cryo-fracture surface of (a) TPU/POE/POE-MA (80/20/5) and (b) TPU/POE/POE-NH₂ (80/20/5) blends.

size reduced to 3.7 μm (TPU/POE 80/20) from 5.4 μm (TPU/POE 70/30). Coalescence of the dispersed phases should account for this, which has been observed in the blends of TPU/PP and TPU/PE.^{2,18}

Figures 2 and 3 illustrate the tensile properties of TPU/POE blends as a function of POE content. As expected, the uncompatibilized blends of TPU and POE have significantly lower tensile strength and elongation at break than the values of neat TPU and POE, showing U-shaped dependence on blending composition typically for immiscible blends. Pötschke et al. suggested that the decrement of mechanical properties of immiscible polymer blends is related to the morphology.¹⁰ A blend having finer dispersibility would show less reduction in properties. According to this rule and the SEM micrographs in Figure 1, tensile strength of TPU/POE (80/20) blend should be higher than that of TPU/POE (70/30) blend. Evidently, the estimation fits the experimental data in Figure 2. To demonstrate the immiscibility of the blends from another angle, temperature dependence of loss factor, $\tan\delta$, of TPU, POE and TPU/POE (50/50), TPU/POE/POE-MA (50/50/5) and TPU/POE/POE-NH₂ (50/50/5) blends was measured around their glass transition temperatures (Fig. 4). Generally for an immiscible blend, two damping peaks corresponding to the glass transition temperatures of individual polymers should appear on its $\tan\delta$ curve. According to this criterion, it is known that the blends of TPU and POE are indeed immiscible. Two damping peaks of TPU/POE/POE-MA (50/50/5) blend become closer compared with those of TPU/POE (50/50) blend. However, TPU/POE/POE-NH₂ (50/50/5) only shows a broad damping peak, this indicates that POE-NH₂ provides the blends with higher compatibility than POE-MA.

Effect of compatibilizers on morphology and properties of TPU/POE blends

It is worth noting that the morphology of TPU/POE blends is greatly changed when suitable compatibilizers are incorporated (Fig. 5). Surface of POE particles in the blends containing POE-MA or POE-NH₂ becomes rather rough, implying that interfacial adhesion has been built up due to the addition of the compatibilizers. Moreover, The POE particle size reduced to 1.20 μm (TPU/POE/POE-NH₂ 80/20/5) from 1.35 μm (TPU/POE/POE-MA 80/20/5); this indicates that TPU/POE/POE-NH₂ (80/20/5) blend shows remarkable reduction in particle size of the dispersed POE as compared to TPU/POE/POE-MA (80/20/5) blend. The difference in compatibilization efficiency of the two compatibilizers might result from the difference in their ability to form a stable interphase between TPU and POE. In general, the interphase should hinder coalescence by immobilizing the interface.¹⁹ To reach the target, the compatibilizer must be located at the interface and have sufficient interactions with the blend components to resist being removed from the droplets during their collision. Clearly, the above results demonstrate that the two compatibilizers are efficacious.

To further look into the details of the microstructure, the blends were also examined by TEM (Fig. 6). The compatibilizers POE-MA or POE-NH₂ only produced a little contrast when stained with RuO₄. Nevertheless, it is obvious that the majority of the compatibilizers is situated at the interface [Fig. 6(b,c)], and no compatibilizer micelles are perceived. For the uncompatibilized blend, the POE particles have smooth boundaries [Fig. 6(a)]. On the other hand, Figure 6(b) indicates that POE-MA has not

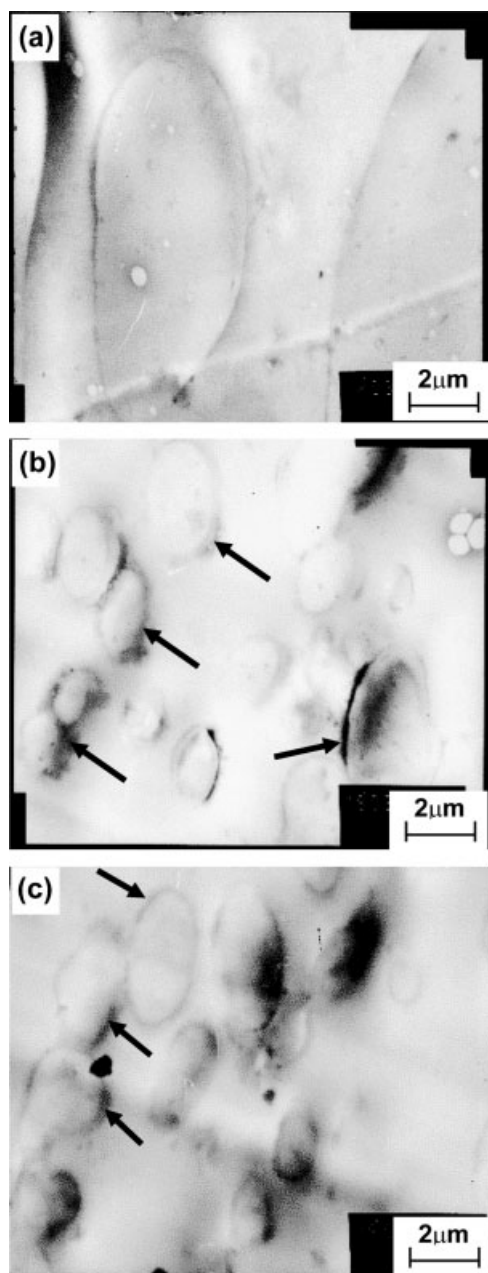


Figure 6 TEM micrographs of (a) TPU/POE (80/20), (b) TPU/POE/POE-MA (80/20/5) and (c) TPU/POE/POE-NH₂ (80/20/5) blends. The arrows indicate the compatibilizer at the interfaces.

homogeneously covered POE particles because of its relatively poor interaction at the interface as compared with the case of POE-NH₂ [Fig. 6(c)]. The TEM images of the interfacial layer agree well with the aforesaid morphological observation given by SEM. POE-NH₂ exhibits strong interfacial interaction between TPU and POE, indicating much reduced interfacial tension between TPU and POE phases. On the basis of the above the study, the compatibil-

TABLE I
Effect of Grafted Content of MA on POE on Tensile Properties of TPU/POE/POE-MA (80/20/5) Blend

Grafting percentage of MA (wt %)	σ (MPa)	ε (%)
0.4	15.3	780
0.7	18.8	1080
1.0	19.6	1160
2.2	21.2	1245
4.0	22.4	1290
6.7	22.9	1307
8.3	23.3	1338
9.2	22.7	1240
10.6	21.5	1032
11.1	20.4	986

ity of POE-MA and POE-NH₂ in the blend TPU/POE is ranked as: POE-NH₂ > POE-MA.

Effect of POE-MA and POE-NH₂ on tensile properties of TPU/POE blends is shown in Figures 2 and 3. As a result of the improved compatibility of the blends, both tensile strength and elongation at break of the blends are increased. The blends compatibilized with POE-MA or POE-NH₂ display much larger ultimate elongations (>1200%). Considering that the blends containing POE-NH₂ have gained more remarkable improvement in the tensile performance than those with POE-MA, it is known that POE-NH₂ provides the blends with higher compatibility than POE-MA. It should be attributed to the higher reactivity of amine functional groups with urethane linkages,^{6,20} which leads to generation of substantial copolymers of TPU and POE at the interface; that is, covalent bonding is more effectively established between TPU and POE in the blends when POE-NH₂ is used.

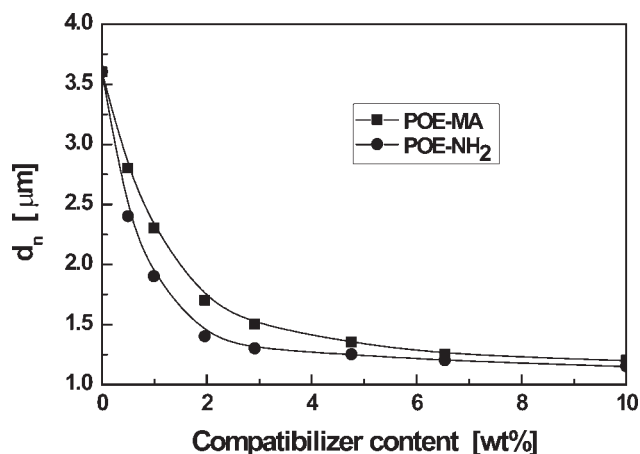


Figure 7 Number-average particle diameters, d_n , of POE in TPU/POE (80/20) blends with different contents of the compatibilizers.

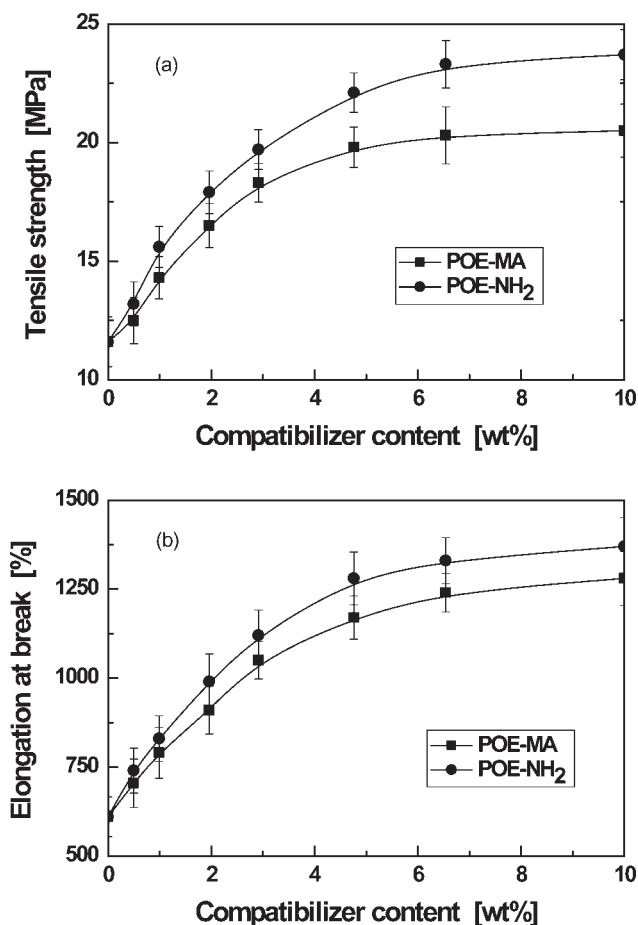


Figure 8 Tensile strength (a) and elongation at break (b) of TPU/POE (80/20) blends as a function of content of the compatibilizers.

Effect of grafting percentage of POE-based compatibilizer on tensile properties of TPU/POE blends

The above study has demonstrated efficiency of the POE based compatibilizers in improving mechanical properties of TPU/POE blends. Since the reactive groups grafted onto POE play the leading role, it is necessary to examine effect of the amount of the grafted reactive groups. As shown in Table I, by increasing the grafting percentage of MA on POE backbone, tensile strength and elongation at break increase and then, when the grafting percentage exceeds 8.3 wt %, decrease. In general, an increase in amount of the grafted reactive groups on the compatibilizer molecules benefits the interfacial interaction. The improvement in the mechanical properties is thought to be due to (i) the effect of the compatibilizer on particle size and stabilization of the particles against coalescence, and (ii) the increased stress transfer efficiency that involves more POE phases in the deformation as well. With respect to the decline trend of mechanical performance at higher grafting percentage, the following factors might take the

responsibility: (i) POE-MA compatibilizer with greater amount of grafted MA might lower the compatibility between POE-MA and POE, and (ii) POE-MA with higher MA content might form micelles, resulting in incomplete surface coverage of POE particles. The formation of compatibilizer micelles in polymer blends has been reported by Wallheinke et al.²¹

Effect of compatibilizer content on morphology and properties of TPU/POE blends

If suppression of coalescence is a steric effect of the interfacial layer generated by the compatibilizer, the compatibilizer content in the blend should be high enough to at least partially coat the dispersed particles. To verify this issue, the influence of the compatibilizer content on the particle size of POE and the mechanical properties of the blends were studied.

Quantitative analysis of the SEM micrographs shows that the addition of about 1 wt % POE-MA or POE-NH₂ leads to significant reduction of the particle size of POE compared to the unmodified blend (Fig. 7). It means that coarsening of the morphology can be greatly suppressed with small amount of the compatibilizers, and greater amount of the compatibilizers can completely suppress coalescence of the dispersed phase. These results are consistent with the conclusions of Horák et al.,²² who found that 2.5% of a copolymer compatibilizer is sufficient to coat the surface of the dispersed phase in the blend of high-impact polystyrene (PS) and PP. Also, Macosko et al.²³ reported that as little as 1% copolymer is sufficient for particle size reduction.

Accordingly, tensile strength and elongation at break of the TPU/POE blends increase with a rise in the compatibilizers' loading (Fig. 8). It is in agreement with the result revealed by Figure 7. Therefore, the improvement in the mechanical properties should be attributed to the effects of the compatibilizers, which hinder coalescence of the dispersed POE phase and induce an easier fracture of the particles after compatibilization.

CONCLUSIONS

To improve morphology stability of the immiscible TPU/POE blends against coalescence, home-made maleated POE and aminated POE compatibilizers were added. Microstructural observation indicates that the compatibilizers are located at the interface between the blending components. The size of the dispersed phase in the blends is greatly reduced by incorporation of small amount of the compatibilizers as expected. Tensile strength and elongation at break of the blends are improved accordingly.

POE-NH₂ provides the blends with higher compatibility than POE-MA because of the higher reactivity of the amine groups with urethane linkages.

Amount of the reactive groups grafted onto POE is a key factor controlling the effectiveness of the compatibilizers. With a rise in the grafting percentage of POE-MA, tensile properties of TPU/POE/POE-MA blends increase first and then decrease. There is an optimum grafting percentage of the reactive groups attached to the compatibilizer, which offers the highest compatibility.

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