

Dynamic Rheological and Morphological Study of the Compatibility of Thermoplastic Polyurethane/Ethylene–Octene Copolymer Blends

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ABSTRACT: Two grafted ethylene–octene copolymers [POEs; i.e., POE-g-maleic anhydride (MAH) and aminated POE (denoted by POE-g-NH₂)] were used as compatibilizers in immiscible blends of thermoplastic polyurethane (TPU) and POE. The effects of the compatibilizers on the dynamic rheological properties and morphologies of the TPU/POE blends were investigated. The characteristic rheological behaviors of the blends indicated that the strong interactions between the two phases were due to the compatibilization. Microstructural observation confirmed that the com-

patibilizers were located at the interface in the blends and formed a stable interfacial layer and smaller dispersed phase particle size. Compared with POE-g-MAH, POE-g-NH₂ exhibited a better compatibilization effect in the TPU/POE blends. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 109: 3452–3457, 2008

Key words: blends; morphology; phase behavior; polyurethanes; rheology

INTRODUCTION

The design and synthesis of the new polymers for specific applications are time-consuming and expensive processes. Therefore, polymer blending is an efficient method because it offers an extraordinary rich range of new materials with enhanced characteristics with regard to chemical or mechanical performance. Correspondingly, the study of binary polymer blends has significantly increased during the past few years because of the important implications for both science and technology.^{1–4}

Thermoplastic polyurethane (TPU), with properties covered from a high performance elastomer to tough thermoplastic, has been extensively used because of its superior physical properties (e.g., high tensile strength, abrasion and tear resistance, oil and solvent resistance, low temperature flexibility, paintability) and high versatility in chemical structures.^{5,6} Therefore, TPU is an excellent candidate for polymer

blending.^{7,8} In recent years, blends of TPU and polyolefins (POs), such as polyethylene (PE)⁹ and polypropylene (PP),^{10–12} have been investigated for technological, economical, and environmental reasons. Blending TPU with a PO is generally based on the following two goals. First, a PO is added to TPU to reduce the latter's cost and to improve its thermal stability, mechanical properties (e.g., modulus, strength, hardness), and processing performance. Second, TPU is blended with a PO to improve the PO's properties, including impact strength, adhesion, and paintability.^{13,14} However, finding suitable compatibilizers for such an extremely immiscible system has always been a great challenge. Recently, Lu et al.¹⁵ found a simple method to prepare primary and secondary amine functional PPs.

However, TPU/PP and TPU/PE blends are not qualified for many applications, such as artificial leathers, because of the high crystallization capacity of the POs, which leads to reduced pliability of the blends. The newest members of the PE family, ethylene–octene copolymers (POEs), are produced by metallocene technology,¹⁶ which is considered to be one of the most significant achievements in polymer history in the past 20 years.^{17–19} Therefore, mixing POE with TPU might be a solution because the former has a rather low crystallinity and tiny crystallites and is, thus, able to provide the blends with balanced performance.

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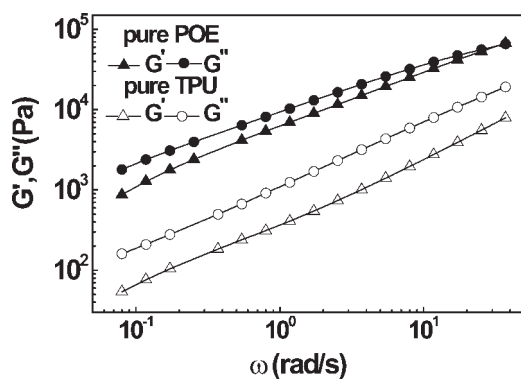


Figure 1 Relationships of G' , G'' , and ω for the pure components, TPU and POE, at 200°C.

With the objective of establishing a knowledge framework for adding new members to the family of TPU-based blends, we investigated the compatibility of TPU/POE blend systems mainly by dynamic rheological and morphological methods in this study, which plays an important role in the investigation of TPU/POE blends for their future applications.

EXPERIMENTAL

Materials

TPU (Elastollan S85A, Shore A hardness = 85A, melt flow index = 3 dg/min) was provided by BASF (Germany).

POE with an octene content of 39% (Engage 8150) was supplied by Dupont-Dow (U.S.A) (specific gravity = 0.868 g/cm³, melt flow index = 0.5 dg/min).

Maleic anhydride (MAH; number-average molecular weight = 98.02 g/mol), purchased from Qifeng Chemical Reagent Factory (Shandong, China), was recrystallized twice with CHCl₃.

Dicumyl peroxide, obtained from Gaoqiao Chemical Reagent Co. (Shanghai, China), was also purified with absolute alcohol before use.

The diamine, Jeffamine D2000, was provided by Huntsman U.S.A.

All of the raw materials were dried at 80°C in a vacuum oven overnight before processing.

Sample preparation

POE-g-MAH was synthesized in our laboratory with a corotating intermeshing twin-screw extruder with a screw configuration adapted for grafting. POE granules and 1.2 wt % MAH were fed to the extruder, which was set at 200°C. The grafting ratio of MAH was about 1 wt %, as determined by quantitative infrared spectroscopy with the adsorption band at 1790 cm⁻¹. In addition, aminated POE-g-NH₂ (POE-g-MAH/diamine = 1 : 1.5 by the molar ratio of

MAH to diamine) was prepared with the aforementioned twin-screw extruder approach in our laboratory.

All of the blends examined were prepared in an instrumented batch mixer (HBI System 90, Haake U.S.A) with two counterrotating roller blades at 190°C and 60 rpm for 5 min. Sheets 2 mm thick were prepared by compression molding at 165°C under 10 MPa of pressure.

Measurements

The rheological tests were conducted at 200°C on an ARES/RFS advanced rheometric expansion system (TA Instruments, U.S.A) with parallel plate geometry 25 mm in diameter.

A field emission scanning electron microscope (JEOL JSM-6330F, Hitachi, Japan) was used to observe the morphologies of the samples. Before the examination, the samples were cryofractured in liquid nitrogen, and then, the fracture surfaces were coated with a very thin layer of gold.

RESULTS AND DISCUSSION

TPU/POE binary blends

As described in our previous publication,²⁰ the TPU/POE binary blends exhibited two glass-transition temperatures (i.e., -10 and -25°C) in the dynamic mechanical analysis, which implied that TPU and POE were thermodynamically immiscible. The dynamic rheological method was applied to further study these blend systems in this study. Figure 1 gives the frequency dependence of the dynamic storage modulus (G') and dynamic loss modulus (G'') for the pure TPU and POE at 200°C. It is clear, for both TPU and POE, that G'' was always higher than G' , which suggested that disentanglement processes were faster than entanglement processes for the molecular chains so that blends always

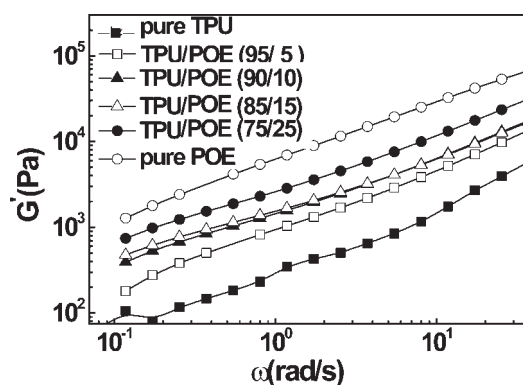


Figure 2 G' as a function of frequency for the TPU/POE binary blends with different compositions at 200°C.

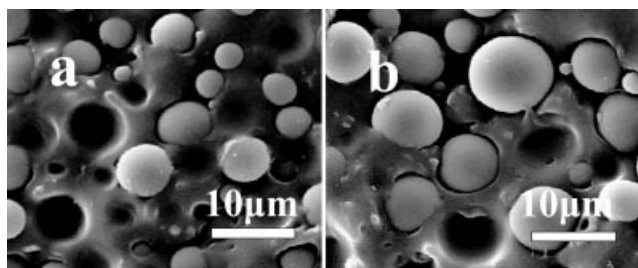


Figure 3 SEM micrographs of the cryofracture surfaces of the (a) 80/20 and (b) 70/30 binary blends.

exhibited a predominantly viscous behavior over the whole frequency range studied.

Because G'' is not sensitive to droplet deformation, we focus our discussion on G' . Figure 2 shows G' of the TPU/POE blends as a function of frequency. Compared with pure POE, pure TPU had rheological complex behavior, which was due to the phase separation of the soft and hard segments, as discussed by Kapnitos et al.²¹ In the measured region, G' of POE was higher than that of TPU. The G' values of the blends had an intermediate value between the pure TPU and POE in all compositions. The appearance of shoulders in Figure 2 for the TPU/POE

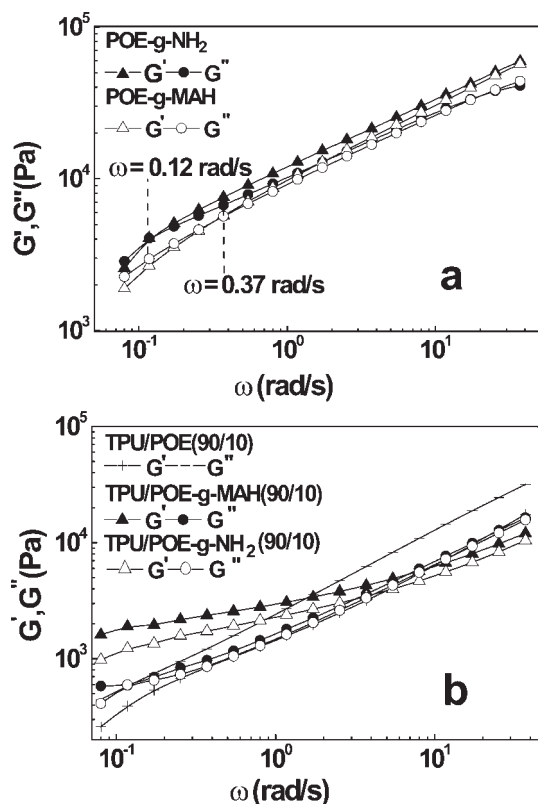
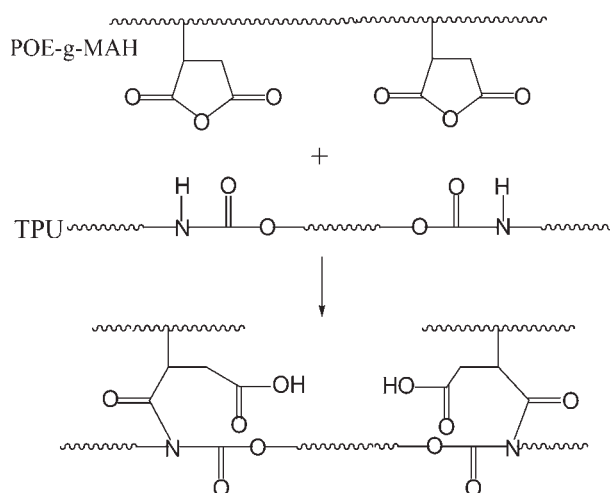


Figure 4 Relationship of G' , G'' , and ω for (a) POE-g-MAH and POE-g-NH₂ and (b) the 90/10 TPU/POE, 90/10 TPU/POE-g-MAH, and 90/10 TPU/POE-g-NH₂ binary blends at 200°C.

blends at low frequency was attributed to the dispersed particle's deformability.²²

Scanning electron microscopy (SEM) micrographs of the fractured surface of the TPU/POE binary blends are shown in Figure 3. The TPU phase was the continuous phase in the blends because the POE phase was less than 50 wt %. The blend with 20 wt % POE showed large discrete domains of POE dispersed in the TPU matrix. It was clear that the TPU/POE binary blends exhibited poor interfacial adhesion because of poor interaction, and immiscibility was evident from the many round holes around the dispersed POE phase. In the 70/30 TPU/POE binary blends [see Fig. 3(b)], the size of the dispersed POE phase increased remarkably, which suggested that

Scheme A :



Scheme B :

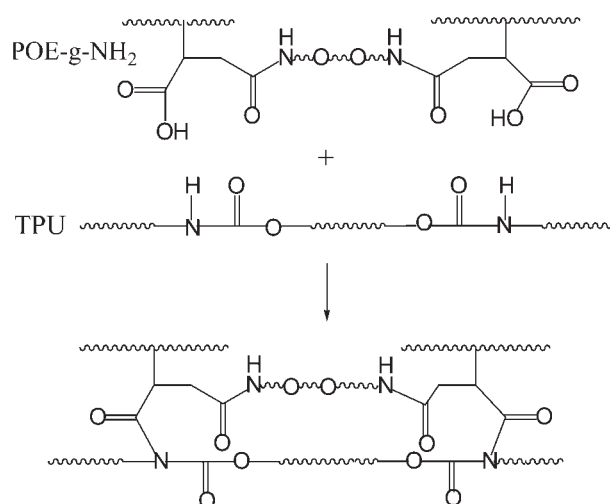


Figure 5 Interfacial chemical reactions in the (Scheme A) TPU/POE-g-MAH and (Scheme B) TPU/POE-g-NH₂ binary blends.

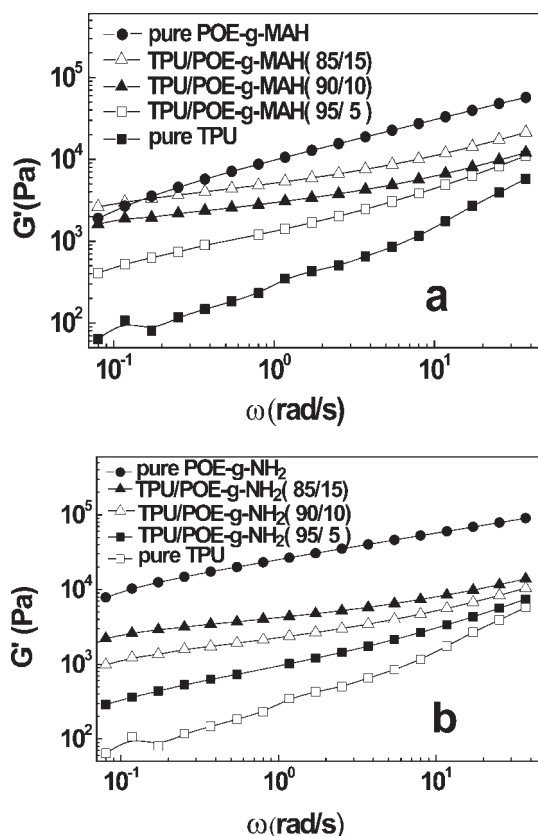


Figure 6 Plots of G' with ω for the (a) TPU/POE-g-MAH and (b) TPU/POE-g-NH₂ binary blends with different compositions at 200°C.

there was coalescence between the dispersed particles as the concentration of POE increased before the phase inversion occurred. Similar results have also been reported in TPU/PP and TPU/PE blends.^{23,24}

TPU/POE-g-MAH and TPU/POE-g-NH₂ binary blends

To improve the interaction between TPU and POE, it was necessary to modify one of components in this binary blend, POE. In contrast to Figure 1, Figure 4(a) shows distinct differences between the pure and grafted POEs (i.e., POE-g-MAH and POE-g-NH₂). For pure POE, G' was always lower than G'' through the entire frequency range examined. However, both POE-g-NH₂ and POE-g-MAH showed a crossover between G' and G'' , which indicated that G'' was higher at low frequencies, but G' was higher than G'' at higher frequencies. This result was ascribed to the fact that the interaction of molecular chains of the grafted POE was much stronger than that of pure POE. However, the crossover frequency (ω_c) of POE-g-NH₂ (0.12) was lower than that of POE-g-MAH (0.37), which was because of the higher crosslinking of molecular chains in POE-g-NH₂. As shown in Fig-

ure 4(b), the crossovers between G' and G'' in the TPU/POE-g-NH₂ and TPU/POE-g-MAH blends implied that the decreasing interlayer slip was due to the effect of entanglement, which was caused by the formation of interchain chemical bonds (see Fig. 5).

The relationships of G' and ω (frequency) for the TPU/POE-g-MAH and TPU/POE-g-NH₂ binary blends at 200°C are given in Figure 6. It could be that as the content of grafted POE (i.e., POE-g-MAH and TPU/POE-g-NH₂) increased, the plateau became much more obvious, which was attributed to the restricted mobility of molecular chains. This result was in good agreement with the results showed in Figure 4.

TPU/POE/POE-g-MAH and TPU/POE/POE-g-NH₂ ternary blends

To compare the compatibilization of the different compatibilizers (i.e., POE-g-MAH and POE-g-NH₂) in the TPU/POE blends, the relationships between G' and G'' for the TPU/POE/compatibilizer ternary blends with various compatibilizer contents were also investigated (in Fig. 7). As shown in Figure 7,

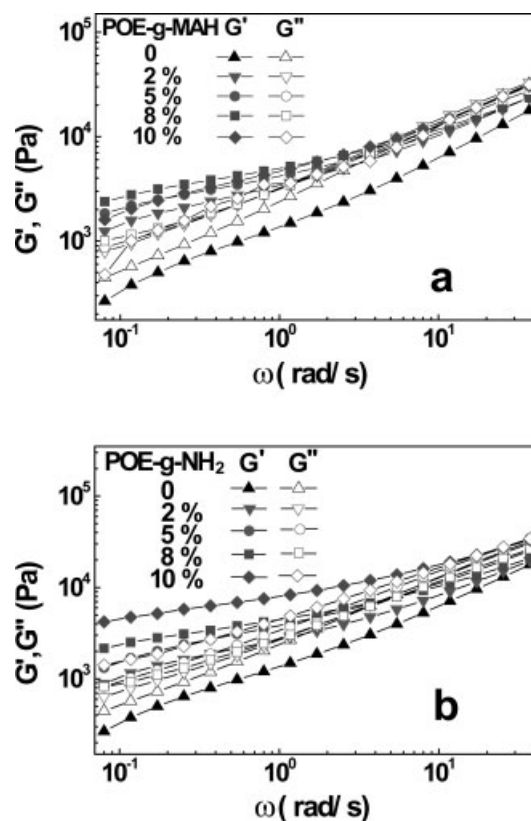


Figure 7 Relationship between G' and G'' for the (a) TPU/POE/POE-g-MAH ternary blends with different POE-g-MAH contents and (b) TPU/POE/POE-g-NH₂ ternary blends with different POE-g-NH₂ contents at 200°C.

there existed a crossover between G' and G'' for each of the ternary blends. The crossover parameters, ω_c and the crossover modulus (G_c ; $G' = G''$), are listed in Table I. As expected, both ω_c and G_c increased with increasing amount of compatibilizer. This phenomenon could be explained by two factors: (1) the reaction of anhydride groups with amino groups on TPU, the hydrogen bond formed in the blends, and (2) the substantial compatibility between the grafted POE chain and the POE phase. Therefore, the compatibilizers located at the interface between the matrix and the dispersed phase so that the degree of compatibility of the blend components increased, which allowed high deformations by the flow stress that led to particle breakage. This was also proven in our previous study.²⁰

The crossover parameters of TPU/POE/POE-g-NH₂ were much greater than those of TPU/POE/POE-g-MAH as the concentration of compatibilizers reached 10 wt %, which implied that the interfaces in the TPU/POE/POE-g-MAH blends were much weaker and lacked sufficient adhesion.

To verify the previous results, SEM micrographs of the cryofracture surfaces of the TPU/POE blends with 10 wt % compatibilizers are shown in Figure 8. In comparison with Figure 3(a), smaller dispersed phase particles and coarser surfaces were clearly observed in both the TPU/POE/POE-g-MAH and TPU/POE/POE-g-NH₂ ternary blends. This implied that the compatibilizer located at the interface between matrix and that the dispersed phase increased the interfacial thickness and adhesion, which showed a remarkable compatibilization effect as a result of the suppression of coalescence and also a reduction in the interfacial tension.^{25,26} Compared with TPU/POE/POE-g-MAH, the TPU/POE/POE-g-NH₂ ternary blends displayed significantly finer morphologies, that is, a much reduced particle size of the dispersed phase. In addition, the particle size distribution was narrow, which also indicated a lower interfacial energy due to the fast interfacial reactions between amine and urethane linkages. Accordingly, POE-g-NH₂ showed a better effect of compatibilization in the TPU/POE blends. A similar result was reported by Lu et al.¹² in PP/TPU blends.

TABLE I
Crossover Parameters of the TPU/POE Blends with Different Compatibilizers

Compatibilizer content (wt %)	POE-g-MAH		POE-g-NH ₂	
	ω_c (rad/s)	G_c	ω_c (rad/s)	G_c
2	1.17	3620.16	1.17	2872
5	2.52	5803.26	1.72	4714.18
8	5.45	8863.73	5.45	7859.04
10	11.74	14795	17.23	22640

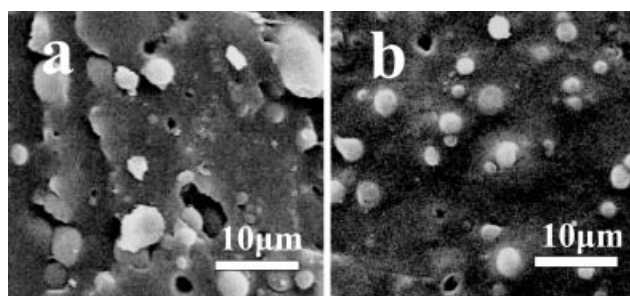


Figure 8 SEM micrographs of the cryofracture surfaces of 80/20 TPU/POE with 10 wt % (a) POE-g-MAH and (b) POE-g-NH₂ ternary blends.

CONCLUSIONS

To improve the compatibility of immiscible TPU/POE blends, two grafted POEs (i.e., POE-g-MAH and POE-g-NH₂) were used as compatibilizers in this study.

Several characteristic rheological behaviors were observed. TPU/POE-g-MAH and TPU/POE-g-NH₂ binary blends exhibited a crossover between G' and G'' . With increasing content of grafted POEs, the plateau in the plots of G' with ω became much more obvious. For the TPU/POE/POE-g-MAH and TPU/POE/POE-g-NH₂ ternary blends, both ω_c and G_c increased with increasing amount of compatibilizers. These results were due to stronger interaction between the dispersed phase and matrix phase, which was confirmed by SEM micrographs. The size of the dispersed phase in the blends could be greatly reduced by the incorporation of the compatibilizers.

Compared with POE-g-MAH, POE-g-NH₂ provided blends with higher compatibility because of its higher reactivity of the amine groups with urethane linkages.

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