Morphology and Mechanical Properties of Blends of Thermoplastic Polyurethane and Polyolefins

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ABSTRACT: Polyolefins (PO) were melt mixed with thermoplastic polyurethane (TPU) in a 20 : 80 weight ratio with or without compatibilizer containing 0.5 wt % of maleic anhydride. Effects of component viscosities on morphology and on mechanical properties of the blend were studied by scanning electron microscope (SEM), tensile property analysis, and dynamic mechanical analysis (DMA). It was found that the disperse particle size of compatibilizer-free blends decreased with the decreasing viscosity ratio of the disperse phase to TPU. The efficiency of the compatibilizer in reducing the particle size varied with viscosity ratios of the disperse phase to compatibilizer. However, the particle size did not decrease with the decreasing viscosity ratio monotonically. With lower viscosity ratio, addition of 5 wt % compatibilizer resulted in a greater reduction of particle size and less loss in the tensile properties as compared to the TPU matrix. For the polyethene (PE) that has the lowest viscosity value among all the POs, its size in the blend was stabilized with the addition of compatibilizer and no compatibilization was detected by DMA and by tensile property analysis. The mobility of the disperse phase and compatibilizer and the dispersion competition between them seemed important. © 2005 Wiley Periodicals, Inc. J Appl Polym Sci 99: 875–883, 2006

Key words: polyurethanes; polyolefins; viscosity; morphology; mechanical properties

INTRODUCTION

The blending of immiscible polymers is an economically attractive approach to the development of new materials since it combines the desirable properties of more than one polymer. It is well-known that the multiphase morphology has a considerable influence on the mechanical properties of the blend. The dispersity in melt-mixed immiscible blends is dependent upon material parameters such as viscosity and polarity ratios.[1–2]

Blends of TPU and PO are highly incompatible because of large differences in polarities and high interfacial tensions between them. This compatibilizer-free immiscible polymer system was commonly used to determine the influence of the viscosity ratio on the blend morphology, the morphology stability, and the mechanical properties. Petra Potschke[3] reported that the viscosity ratio of PO to TPU could be correlated directly to the blend morphology obtained under similar blending conditions. TPU/PE blends showed a lower dispersity than TPU/PP blends, due to higher viscosity ratios η_d/η_m (η_d is the viscosity of the disperse phase and η_m is the viscosity of the matrix) of

the former, which resulted in a greater reduction in tensile strength of the TPU/PE blend than that of TPU/PP blend at the same disperse phase content. At similar viscosity ratios, the blends with polyether-based TPU had a finer dispersed morphology than blends with polyester-based TPU because of lower surface free energy of the polyether soft segments than that of the polyester soft segments. Coalescence was also studied by Katrin Wallheinke,[4] in the immiscible system of TPU and POs. As the interfacial tensions of the two polyolefins with TPU were shown to be very similar, the polyethylene is much more viscous and elastic than the polypropylene, leading to higher viscosity and elasticity ratios with TPU. The particle sizes in the TPU/PE blend are larger, and coalescence is much more pronounced than in TPU/PP.

Since most immiscible blends are thermodynamically unstable, the copolymer must be added to stabilize the morphology. This process of stabilizing polymer blends is commonly called compatibilization. Effect of rheology of the copolymer on morphology development of the blends in extensional flow conditions was studied by several research groups.[5,6]

Macosko[7] studied PMMA melt mixing with polystyrene (PS) of symmetric P(s-b-MMA) diblock copolymer in a 30 : 70 weight ratio and found that lowering the molecular weight of PMMA phase from 43,000 to 11,000 resulted in marked decrease of particle size

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TABLE I
Characteristics of the Polymers

Denotation	Material	Tensile strength (MPa)	Viscosity ratio[a]	
			$\eta_{PO}/\eta_{PE\text{-}g\text{-}MA}$	η_{PO}/η_{TPU}
TPU	Thermoplastic polyurethane[b]	20.06		
PE 1	LD 1I 50A	7.5	0.09	0.92
PE 2	LD 605	10.5	0.13	2.16
PE 3	LD 1I 2A	15.0	0.30	2.60
PP	PP 1700 Homopolymer	38.0	0.54	3.31
PE-g-MA	Compatibilizer fusabond 493D			

[a] Determined at 150/s at 170°C.
[b] Based on polyetherdiol polyolefins (POs).

from 700 to 60 nm. These variables were discussed in terms of mobility of the block copolymer that is expected to increase significantly as the homopolymer molecular weight decreases due to faster diffusion. Compatibilized blends of TPU and polyolefins have been investigated for technological, economical, and environmental reasons. PO's functionalized with common functionalities including anhydride,[8,9] acid,[10] primary amine, and secondary amine.[11,12] Wallheinke[10] studied the effect of addition of ethylenic copolymers (EC) with different acrylic acid contents on the morphology and coalescence of TPU and polypropylene (PP) blends. Addition of 5 wt % EC 4 (4% acrylic acid) led to complete stabilization of granule morphology. EC 20 (20% acrylic acid) showed a similar stabilizing effect, with the mean particle diameters larger than that of EC 4. This was ascribed to the different rheological properties of the EC, because the viscosity of EC 4 is much higher than that of EC 20, but the interfacial tension difference of the two copolymers was not taken into account. Anhydride functional PO has been the most frequently used compatibilizer. Although some compatibility with TPU, including finer morphology and improved mechanical properties, has been reported, no reaction was detected between the functional group and the urethane linkage or free isocyanate group from thermal degradation of TPU.[13] The dependence of the surface tension on temperature as measured by pendant drop analysis was reported by Katrin Wallheinke; the surface tension of PP was close to that of PE.[4]

To the best of our knowledge, there are few publications in the literature thus far using TPU/PO/anhydride functional PO to deal with the dependence of the morphology on the viscosity ratio between the disperse phase and compatibilizer at a similar interfacial tension. In this work, the effect of the viscosity ratio of the disperse phase to compatibilizer phase on morphology in mixing and in coalescence as well as dependence of morphology of blends on its mechanical properties were investigated.

EXPERIMENTAL

Materials and characterizations

The thermoplastic polyurethane elastomer (TPU) JM-80 employed in this work consisting of hard segments and polyether soft segments is provided by ChengYu Elastomer Co. (Tianjin, China).

The POs used in this research are commercially available products from Yanshan Petrochemical Co. (Beijing, China). Some characteristic data are listed in Table I.

Ethylenic copolymer with maleic anhydride (PE-g-MA) obtained from Dupont, China, was used as compatibilizing agent.

Rheological measurements were carried out with a high-pressure capillary rheometer (HKV), Rheograph 2003 (Gottfert). The capillary had a diameter of 1 mm, and a length-to-diameter ratio of 30. The viscosity functions of the polymers were measured at the processing temperature of TPU (170°C) and corrected with the Rabinowitsch-Weissenberg correction. Oscillatory shear measurements were carried out at 170°C, with plate-plate (25 mm diameter) configuration and a gap of 2 mm by use of a Rheometrics Mechanical Spectrometer (RMS 800). The TPU for measurement was dried at 100°C for 3 h. The viscosity ratios of the blend components were determined at 150/s by division of the viscosities of the dispersed phase (PO) by that of the PE-g-MA copolymer and by that of TPU.

Processing

Before processing, the thermoplastic polyurethane was dried at 100°C in vacuum for 3 h.

Pellets of TPU and each of the POs and PE-g-MA at different weight ratios were blended on an instrumented batch mixer (SK-160). The polymers were blended in counter-rotating roller blades at 170°C for 10 min. The screw configuration was adapted for the blend system TPU/PO. Unless otherwise stated, the composition of the blend was TPU/PO = 80/20 in weight ratio.

Morphology

The surface morphology of the cryogenically fractured samples as extruded was observed with a LEO 438VP scanning electron microscope (SEM). The fracture surface of the TPU/PO blends with or without compatibilizer addition was prepared by dipping the sample in liquid nitrogen. Before the examination, the surfaces were coated with a thin layer of gold so as to improve the conductivity and prevent charging.

The stability of the morphology against coalescence in quiescent melt was determined by annealing of granules in a metal bath at 170°C, a temperature similar to the value of processing. The annealing time began with the dipping of the specimen in the metal bath. The specimens were quenched in ice-water after annealing so as to freeze the morphology.

Mechanical properties

All blend samples containing POs for mechanical property measurements were prepared by pressing in a mold on a hot-press at 170°C and 10 MPa for 4 min and subsequently on a cold-press at room temperature for another 4 min.

The tensile strength test was carried out at room temperature and the tensile strength standard was evaluated according to GB 528–92 on a JWL-2500N tester at a speed of 500 mm/min. The dumbbell specimens (25 × 2 × 4 mm^3) were cut from the samples. Mechanical test results are obtained based on three specimens.

Dynamic mechanical properties

The dynamic mechanical behavior of the blends was studied using an advanced rheometric expansion system in the oscillation mode at a frequency of 1 Hz and a strain rate of 0.5–0.7% in N_2 atmosphere. The temperature range used was from −120°C to 120°C. The dimension of the samples cut from compression-molded specimens was about 2 mm of thickness and 12 mm of width. Before the measurements, the samples were precooled at –130°C for 5 min. The heating rate was 5°C/min, and the measurement interval was 15 s.

RESULTS AND DISCUSSION

Properties of the blend components and the unmodified blends

The rheological behavior of the blend components is shown in Figure 1. The viscosity functions of all the blend components have a similar form, leading to a constant viscosity ratio between the blend components over the whole range of the shear rate. The POs studied in this experiment show a higher viscosity
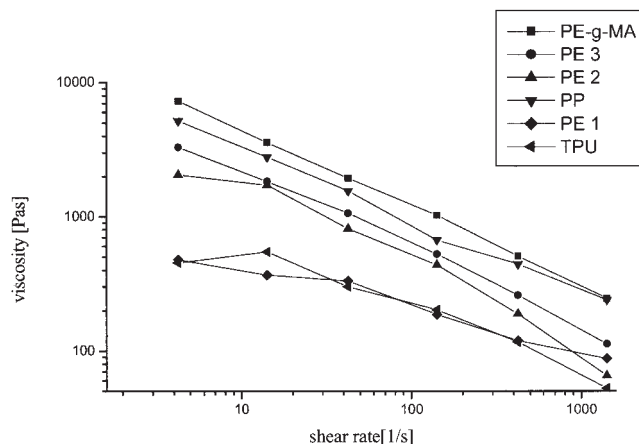

Figure 1 Viscosity functions of the blend components and the copolymer.

than that of TPU except PE 1 that exhibits a viscosity value close to that of TPU. PE-g-MA shows the highest viscosity among all blends component studied. The viscosity ratios of one of POs to PE-g-MA and the viscosity ratios of one of POs to TPU at a shear rate of 150/s are listed in Table I.

TPU elastomer and POs exhibit distinct differences in polarity and surface free energy.[14] Because of the resulting high interfacial free energy, only slight interactions in the interface between these two components in the blend can be expected. SEM photographs of the unmodified blend shown in Figure 2 indicate that the fracture passes mainly along the phase boundaries. The large spherical domains of the dispersed PO phase and the smooth interface between POs and TPU matrix indicate that a poor interfacial adhesion exists between the two phases.

The SEM images shown in Figure 2 also give some implication of the relationship between particle size and viscosity ratio. An increasing viscosity ratio of PO to TPU results in a rise in the number-average mean particle diameter and a broadening of the particle size distribution. The PE 1 that has the lowest viscosity value among all the POs results in a fine dispersion of it within the TPU matrix. PE 2, PE 3, and PP that have higher viscosity ratios, lead to larger particles of blends with TPU. This result was also proved by Potschke[3] and by Wallheinke.[4]

Compatibilizing effects of PE-g-MA for blends of tpu and different POs

Morphology

Shown in Figure 3 is the SEM image of the cryogenically fractured surface of the TPU/PO 80/20 (wt/wt) blends with 5 wt % PE-g-MA.

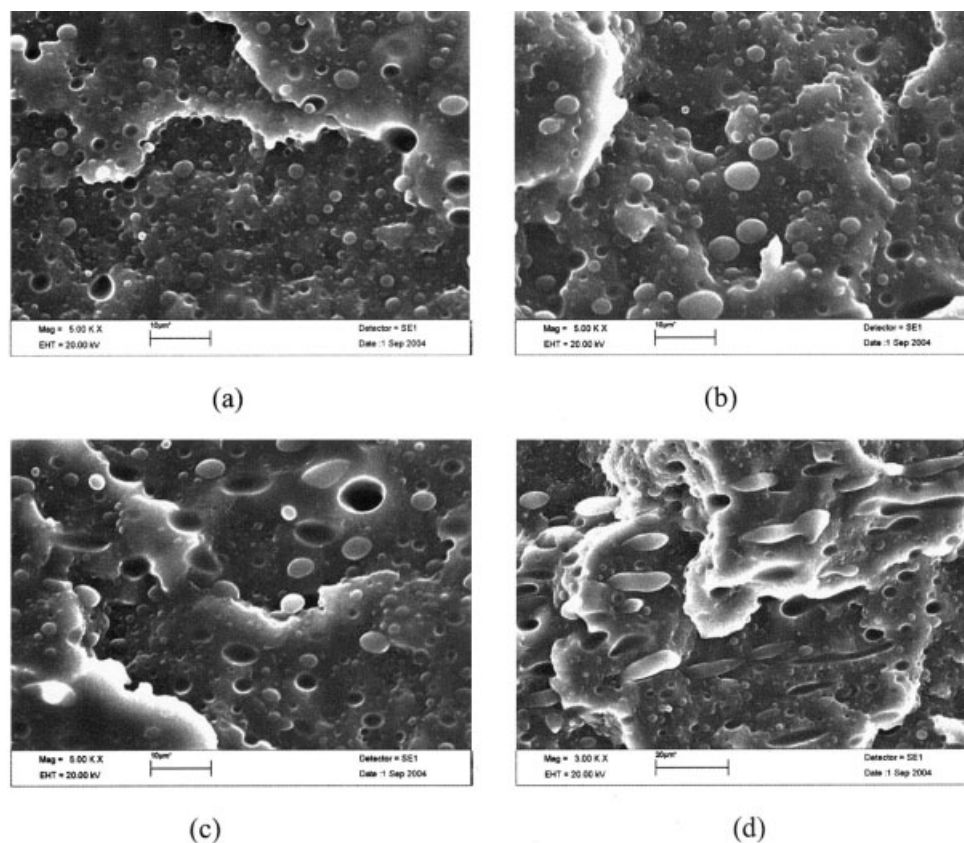When 5 wt % of the PE-g-MA was added, the blends for PE 2, PE 3, and PP display significantly finer mor-

Figure 2 SEM micrographs of cryofractures of TPU/PO/PE-g-MA = 80/20/0 blends with different POs (a) PE 1; (b) PE 2; (c) PE 3; and (d) PP.

phology and reduced particle size of the dispersed phase. Moreover, the interface between the TPU and POs phases became rough as compared with that of the compatibilizer-free blends. This indicates that the PE-g-MA block copolymer acts as an effective compatibilizer.

The efficiency of the copolymer in reducing the particle size varies with blends. With decreasing viscosity ratio of PO to PE-g-MA from PP to PE 3 and further to PE 2, much finer domain size can be clearly observed from Figure 3. The particle size of PE 2 was reduced so remarkably that most of the particles were hardly observed from the cryofractured specimen. However, the particle size of the dispersed phase did not decrease monotonically with the decrease of viscosity ratio. The addition of compatibilizer showed little influence on the particle size of PE 1, leading to larger particles of PE 1 than that of PE 2 with PE-g-MA, though the morphology of compatibilizer-free blends for PE 1 was much finer. And, no compatibilization was detected by the DMA (Fig. 7) and the tensile property analysis (Fig. 6). It can be deduced that little compatibilizer exists at the interface.

The deformation of uncompatibilized droplets due to extensional flow depends both on the capillary number Ca ($Ca = R\eta_m\acute{Y}/a$) and on the viscosity ratio p

($p = \eta_d/\eta_m$, where η_d is the viscosity of the droplet phase, η_m and $\acute{Y}$ are the viscosity of the matrix and deformation rate of the matrix, and a and R are the interfacial tension and characteristic size of the droplets, respectively. It is generally accepted that deformation increases with increasing Ca or with decreasing p.[15] If Ca exceeds a critical value Ca_{cr} (p), uncompatibilized drops will break up. A compatibilizer of course affects deformation and break up by reducing the interfacial tension. However, the view that effects of compatibilization are entirely attributable to a decrease in interfacial tension has been challenged by several observations.[5,6,16,17]

Because blends studied in this work were composed of high-molecular weight commercial polymers, high elasticity, and shear thinning nature of blend components make the quantitative analysis of the result very complicated. This research seeks to clarify the effects of compatibilzer addition on the immiscible blends by using simple model blends as described below.

The phenomena involved are easily understood by considering a droplet in purely extensional flow. In this case, the bulk flow in and around the extended drop convects the copolymer toward the end of droplets[18,19] [Fig. 4(b)]. If the copolymer accumulation at the tips is pronounced, the surface tension is locally
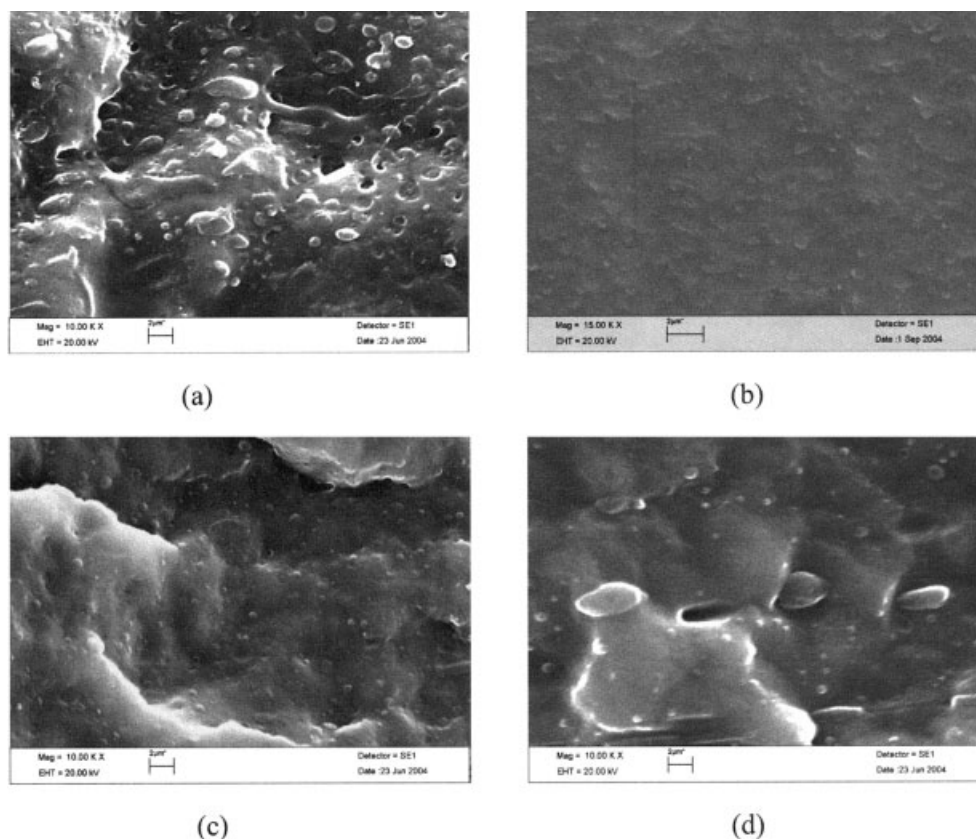
Figure 3 SEM micrographs of cryofractures of TPU/PO/PE-*g*-MA = 80/20/5 blends with different POs. (a)PE 1; (b)PE 2; (c)PE 3; and (d)PP.

reduced. The tip stretches to attain higher curvature, and the droplets become more seriously deformed. If the surface concentration gradients are small, tip-stretching is suppressed.[20]

There is a difference among these POs in the rate of dispersion into the matrix because of the different viscosity values of them. Thus, it is reasonable to presume that there is a dispersion competition between the POs and the compatibilizer. When the PP particles are stretching into the matrix, most of the copolymer have broken up and reached its surface.
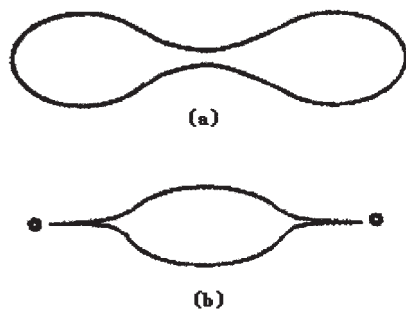

Figure 4 Modes of drop breakup in extensional flow. (a) Simple breakup by waist-thinning that occurs when $Ca > Ca_r$. (b)Tip-streaming that requires a minimum of surfactant.

The reduced flow within the droplet leads to a decreased mobility of the PE-*g*-MA copolymer at the interface. This results in slight nonuniformity in copolymer concentration, and the large particles induced by simple breaking-up mode can be observed. With decreasing viscosity ratio from PP to PE 3 and further to PE 2, the increased mobility of the copolymer at the interface leads to larger concentration gradient of copolymer coverage during flow. As a result, all the droplets break up in tip-steaming mode. For the blend with PE 1, when the PE 1 is stretching into the matrix, the PE-*g*-MA could not disperse into the matrix in time, most of the PE-*g*-MA copolymer might be trapped into the PE 1 particles and TPU matrix, resultantly, little PE-*g*-MA copolymer could exist at the interface.

Coalescence in quiescent melt

Shown in Figure 5 is SEM photographs of cryofractures of these blends after annealing at 170°C for 30 min. One finds that the PE-*g*-MA copolymer shows different stabilizing effect on the blends. Nearly, all of the PE 1 particles and part of the PP particles coalesce to particles about 10 μm. In the blend with PP, a small fraction of particles maintains the particle size close to
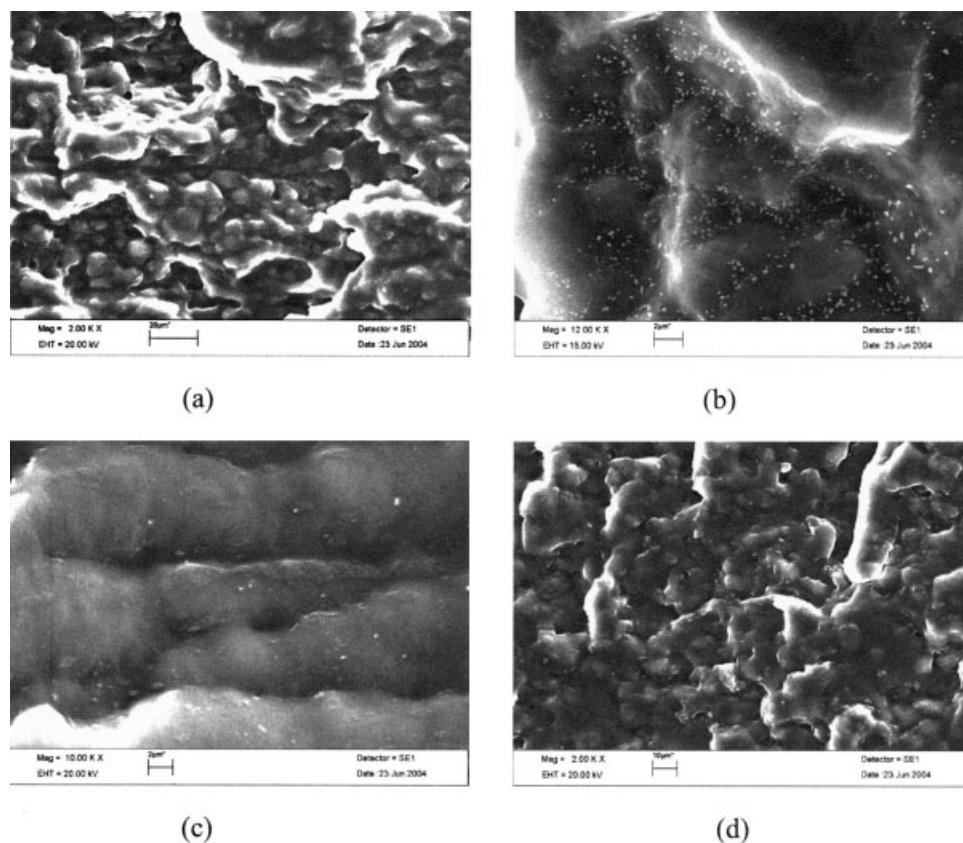
Figure 5 SEM micrographs of cryofractures of TPU/PO/PE-g-MA = 80/20/5 blends after annealing for 30 min (a) PE 1; (b) PE 2; (c) PE 3; and (d)PP.

the original one, and the PE 3 particles also coalesce to form larger and irregular domains. In contrast, the compatibilizer leads to best stabilization of the granule morphology of the TPU/PE 2 blend.

It is well-known that in Newtonian systems coalescence is suppressed by steric hindrance of the surfactant located at the interface between the two liquid components.[21] A similar mechanism has been proposed by Sundararaj[1] for polymer blends with a compatibilizer that forms an interphase between the blend components. According to the mechanism, the particles approach each other and only a thin film of matrix polymer remains at the interface. Coalescence of the two drops can only take place when the matrix polymer between them is removed. The rate of draining of the thin polymer depends on its mobility. If the film thickness becomes smaller than the critical distance for film rupture, instability in the film leads to its rupture and one single particle is formed. To be able to immobilize the interface, the compatibilizer must be located at the interface. Additionally, it must have sufficient interactions with the blend components to resist against being removed from in between the droplets during their collision. Two particles that are in close contact are coalescing. The newly formed particle gets close to a neighboring particle because of

the increase of its diameter after reshaping to a sphere. As one coalescence event causes the next one, the process is similar to a chain reaction and continues until the interparticle distances become too long for coalescence.[4] The shifting of T_g of the blends with PP, PE 3, PE 2, and PE 1 containing 5 wt % PE-g-MA copolymer were detected by DMA (Fig. 7), and it can be deduced that the surface of the droplets, except the PE 1, was surrounded by a stable layer of PE-g-MA copolymer. So, the blend with PE 1 shows the most pronounced coalescence. For the blends with other three POs, the coalescence is suppressed to some extent by steric hindrance of the PE-g-MA. From PP to PE 3, and further to PE 2, the increasing coalescence is caused by the higher probability of collision of the large particles generated during melt-mixing.

Mechanical properties

The phase morphology and the interfacial adhesion between component polymers influence the tensile properties of polymer blends. Because the morphology of two phases that lack of adhesion between the component polymers may lead to premature failure and reduced tensile strength. The composition depen-
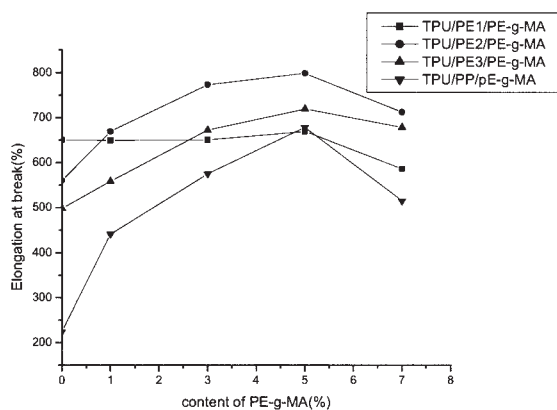
(a)
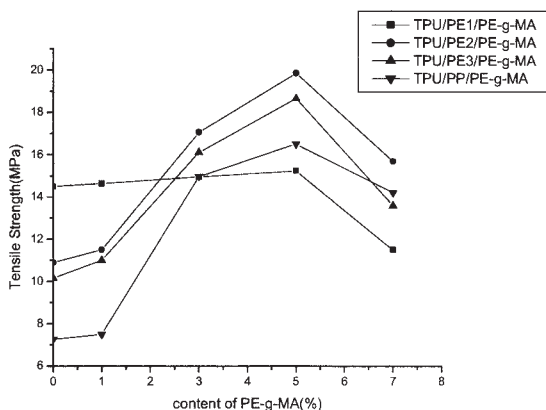
(b)

Figure 6 Elongation at break and tensile strength *versus* PE-*g*-MA content. (a) Elongation at break and (b) Tensile strength.

dence of interconnected interfacial tensile properties and elongation at break are shown in Figure 6.

Tensile strength of TPU is 20.05 MPa, and its elongation at break is 800%. If TPU is simply blended with POs, the tensile strengths of the uncompatibilized TPU/PE 1, TPU/PE 2, TPU/PE 3, and TPU/PP blends decrease to 14.6, 10.9, 10.2 and 7.3 MPa, respectively. The elongation at break decrease to 650, 560, 498, and 224% accordingly. The mechanical behaviors of different POs are listed in Table I. It can be deduced that the tensile strength of the blends has no direct relation to that of the POs themselves. When the block copolymer PE-*g*-MA was added, the properties of the blends, except for PE 1, are enhanced; this phenomenon can be attributed to the compatibilizing effect of PE-*g*-MA. For the blends with four different kinds of POs, about 5 wt % of added compatibilizer addition was sufficient to achieve optimal in mechanical properties. With a compatibilizer content higher than 5 wt %, the tensile

properties decrease, hence excess PE-*g*-MA is not beneficial to the blends. The phenomenon that the tensile property decreases with increasing PE-*g*-MA also appeared in other compatibilized blends.[22,23,24]

The resulting multiphase morphology has a considerable effect on the mechanical properties of the blend. The blends of the same amount of PE-*g*-MA with different POs show different mechanical properties as shown in Figure 6. For PE 2 that has the finest morphology results hardly in loss in the tensile properties as compared with the TPU matrix. In contrast, for other blends, the reduction in the tensile strength and the elongation at break are observed. The tensile properties of the blend with PE 1 have little change at the copolymer content lower than 5 wt %.

Dynamic mechanical properties

DMA spectra of TPU and its blends with or without 5 wt % PE-*g*-MA addition are shown in Figure 7. Glass transition temperatures are determined as the temperature at the maximum of tan δ. We consider that under the conditions studied, this method gives the most reliable and reproducible results. The curve of tan δ *versus* temperature for TPU exhibits a relaxation peak, which is similar to that has been reported in other literature.[25] The relaxation peak is attributed to the soft segment transition from the glassy to the viscoelastic state. The curve of tan δ against temperature of binary TPU/PE-*g*-MA blend exhibits only one broad relaxation peak. The presence of PE-*g*-MA leads to a slight shift of the relaxation peak to high temperature, which is attributed to the compatibility of TPU and PE-*g*-MA. The compatibilizer also leads to little change of *G'*, as shown in Figure 7(a).

DMA spectra of pure TPU/PO blends and the TPU/PO containing 5 wt % PE-*g*-MA blends are shown in Figures 7(b–e). The compatibilized blends of PP, PE 3, and PE 2 exhibit a single broad tan δ peak at higher temperature than that of blends without compatibilizer. The appearance of a single broad peak and the shifting of T_g of the blends to higher temperature can be ascribed to the presence of better adhesion between the phases caused by modified interface in compatibilized blends. The tan δ of the blend with PE 1 shows no change at the original position in the dynamic mechanical spectra, suggesting that the blend was incompatible. It can be inferred that little compatibilizer exists at the interface between the TPU and PE 1 phases and most of them might be trapped in PE 1 particles and TPU matrix.

CONCLUSIONS

POs were melt-mixed into TPU matrix in 20 : 80 weight ratio, with or without PE-*g*-MA. For the blends without copolymer, the particle size of disperse phase
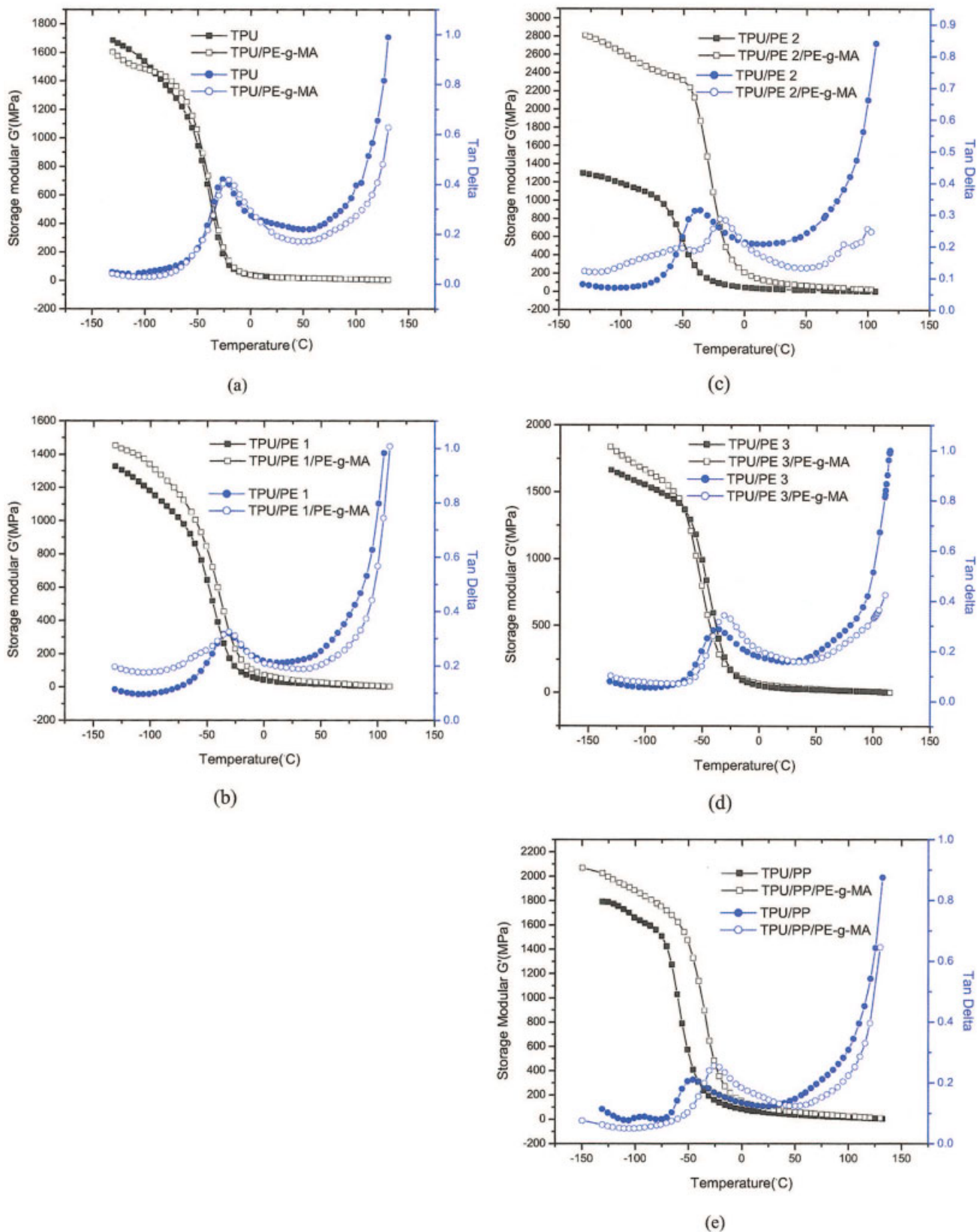
Dynamic Mechanical Properties

Figure 7 Dependence of storage modular and tan δ on the temperature of TPU/PO blends (a) TPU, (b) TPU/PE 1, (c) TPU/PE 2, (d)TPU/PE 3, and (e)TPU/PP. [Color figure can be viewed in the online issue, which is available at www. interscience.wiley.com.]

decreased with the decreasing viscosity ratio of PO to that of TPU. To improve the compatibility of the blends, 5 wt % of PE-*g*-MA copolymer was added. The best morphology was achieved in the blend with PE 2, which has the most suitable rheological property for breaking up in tip-streaming mode. And, the best morphology resulted in no loss in tensile properties as compared with the TPU matrix. Unlike the other POs used, the particle size of PE 1, which has the lowest viscosity value among all the POs, was stabilized with the addition of PE-*g*-MA, and no compatibilization was detected by DMA and by tensile property analysis. It seems reasonable to presume that there is a dispersion competition between the compatibilizer and the dispersion phase.

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