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Compatibilized Blends of Thermoplastic Polyurethane (TPU) and Polypropylene

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Summary: Compatibilized blends of thermoplastic polyurethane (TPU) and polypropylene (PP) were developed using amine (primary or secondary) functionalized PP's (PP-g-NH_2 or PP-g-NHR). The strategy of reactive compatibilization is based on fast reactions between amine functional groups and urethane linkages or traces of free isocyanates released by thermal degradation of TPU. Excellent compatibilization between TPU and PP was confirmed by rheological, morphological, and mechanical properties. Much finer domain size, higher interfacial adhesion, and more stable morphologies were clearly observed by scanning electron microscopy. Significant improvements in the overall mechanical properties (tensile, tear, abrasion) imply significantly more reaction between TPU and PP phases in the two TPU/PP blends containing PP-g-NH_2 or PP-g-NHR than a TPU/PP blend using PP-g-MA as a compatibilizing agent.

Keywords: amine functionalized polypropylene; blends; maleated polypropylene; reactive compatibilization; thermoplastic polyurethane (TPU)

Introduction

Thermoplastic polyurethane (TPU) and polyolefin (PO) blends have been investigated for their academic interest and commercial importance.[1-5] On one hand, PO is added into TPU to reduce TPU's cost and improve TPU's thermal stability, mechanical properties (e.g. modulus, strength, hardness), and processing performance. On the other hand, TPU is blended with PO to improve PO's properties (e.g. impact strength, adhesion, paintability). However, finding suitable compatibilizers for such an extremely immiscible system has been a great challenge. PO's functionalized (graft or random copolymers) with common functionalities including anhydride,[2,3,6] acid,[6,7] and acrylate[8,9] have been blended with TPU. While morphology and mechanical properties were reported, negligible reactions are expected between these functional groups and the urethane linkage (carbamate -NHCOO-). Also, reactions are quite limited between those functional groups and traces of free isocyanate released from thermal degradation of TPU.[10] Stutz[6] found negligible reactive coupling in TPU blends with acrylic acid and

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maleic anhydride functional polymers (polyethylene and polystyrene). He attributed the negligible reaction to interfacial segregation, i.e. preference of the less polar soft segment of polyurethane for the interface. However, sufficiently fast interfacial reactions between highly reactive functional groups may overcome interfacial segregation. In a previous study of model urethane reactions,[10] both primary and secondary amine functionalities were found to be highly reactive toward urethane linkages at melt processing temperatures. Recently we have found a simple method to prepare primary and secondary amine functional polypropylenes (PP).[11]

In this work, compatible TPU/PP blends were developed using amine functional PP's as compatibilizers. Their compatibilization effects on the final blends were investigated by rheological, morphological, and mechanical measurements. The results were compared with two control blends: (1) a TPU/PP blend without any compatibilizer; (2) a TPU/PP blend containing a maleated PP (PP-g-MA) as the compatibilizing agent.

Experimental

Both TPU (Avalon 70AE, Shore hardness: 70A) and PP (13M11, random copolymer) were provided by Huntsman. The maleated PP (PP-g-MA, Fusabond MZ-109D) was obtained from DuPont. The anhydride graft content is 0.55 wt.% according to the supplier. The primary and secondary amine functional PP's (PP-g-NH_2: PP-g-MA/hexamethylenediamine, 1:1.5 by molar ratio of MA to diamine; PP-g-NHR, PP-g-MA/N-hexylethylenediamine, 1:1 by molar ratio of MA to diamine) were prepared according to the method we have developed.[11] All the raw materials were dried at 80 °C in a vacuum oven overnight before processing.

Melt blending of TPU, PP, and the functional PP's (PP-g-X, X = MA, NHR, or NH_2) was performed on a 16-mm co-rotating twin-screw extruder (Prism 16TSC, L/D = 25) at 200 °C and 70 rpm. The screw configuration contains two kneading sections and has been shown effective for melt blending.[12,13] Pellets of the three components were dry-blended before loading. The melt was continuously extruded into a strand through a 10 mm long and 2 mm diameter circular die. Blend compositions and torque and pressure readings during extrusion are listed in Table 1.

Dynamic shear viscosity of each of the blends was obtained using a dynamic stress rheometer (SR-200, Rheometric Scientific) with 25-mm parallel-plates and a 1-mm gap over a frequency range of 500 to 0.1 rad·s^{-1}. The temperature was controlled by forced convection of nitrogen to avoid oxidative degradation. Samples for the dynamic tests were compression-molded at 170 °C under a pressure of 0.55 MPa to round disks. Steady shear viscosity of each of the TPU blends was acquired on a capillary rheometer (RH2200, Rosand) with a circular capillary die ($L/D = 30$, 180° entrance angle). No corrections were applied to the data and only apparent viscosities were reported.

The TPU blends were cryo-fractured in liquid nitrogen, stained in RuO_4 vapor for 20 min, and coated with 20 Å platinum. Both secondary electron images for topology and backscattered electron images for phase contrast were taken on a scanning electron microscope (S-800, Hitachi) with an accelerating voltage of 10 kV. The interfacial area per unit volume was estimated from backscattered micrographs using a 2D digital image processing method,[14] which calculates interface perimeter/area from the number of pixels along the interface. Only one single image was analyzed, thus the interfacial area per volume values have uncertainties of about 15% particularly those with low interfacial area since cryo-fracturing may expose non-random surfaces.

Tensile specimen (ASTM D412 Type 1) were prepared by injection molding at 170 °C. The mold temperature was 40 °C. The tensile test (5500R, Instron) was run at room temperature with a loading speed of 200 mm/min. The testing standard used for PP is ASTM D638 (Type IV) with a speed of 50 mm/min. Abrasion resistance was evaluated according to DIN 53516 on a Zwick abrasion tester. Tear strength was measured according to DIN 53515 on an Instron 5500R tester at a speed of 500 mm/min. Mechanical test results are based on 3 specimens.

Results and Discussion

The torque and die pressure drop during extrusion are recorded (in Table 1). The values of TPU/PP and TPU/PP/PP-g-MA are close to each other because addition of PP-g-MA has two counterbalancing effects: lower blend viscosity; higher polarity in the PP phase. When the amine functional PP (PP-g-NH_2 or PP-g-NHR) is added into TPU/PP blends, both blending torque and pressure at the die entrance are noticeably higher, which gives a clear sign of interfacial reaction between amine (primary or secondary) functional groups on the PP and urethane linkages or traces of free isocyanates in the TPU.

Table 1. Torque and pressure during extrusion and melt viscosity.

Blend component	Weight ratio	Torque (N-m)	Pressure at die (psi)	Viscosity (Pa-s), 190°C	
				0.05 rad/s	10^3 s^{-1}
TPU/PP	70/30	8.4	288	1650	133
TPU/PP/PP-g-MA	70/25/5	8.7	265	2120	178
TPU/PP/PP-g-NHR	70/25/5	9.5	414	2200	231
TPU/PP/PP-g-NH_2	70/25/5	10.8	464	3240	221

Figure 1 shows shear viscosities of each of the blends at two temperatures (170 °C and 190 °C) as a function of steady shear rate or dynamic frequency. The values at 0.05 rad/s and 10^3 s^{-1} and 190 °C are listed in Table 1. The dynamic and steady shear viscosities of each blend follow the Cox-Merz rule. The viscosity ranking in general agrees with that of torques on the extruder: TPU/PP/PP-g-NH_2 > TPU/PP/PP-g-NHR > TPU/PP/PP-g-MA > TPU/PP. However, viscosity differences are relatively small. It's interesting to observe that the uncompatibilized TPU/PP blend has significantly lower viscosity than others at 190 °C and high shear rates. The abrupt viscosity drop is probably caused by interfacial slip between TPU and PP phases in this highly immiscible blend.[15] The interfacial tension between the soft segments of a poly(ester urethane) and PP was reported to be 8.2 mN/m and that between the hard segments of polyurethane and PP was 13.9 mN/m.[16] The TPU/PP/PP-g-NH_2 blend shows viscosity rising at low dynamic frequency indicating a yield stress, which is also seen in PP-g-NH_2 itself due to a lightly crosslinked structure caused by the primary amine functional groups.[11]

Scanning electron micrographs of each of the blends upon extrusion and after injection molding into a mold plaque are illustrated in Figure 2 and Figure 3, respectively. Since topology is represented by secondary electron images and phase contrast can be best viewed in backscattered electron images, combination of the two enables a more comprehensive understanding of the blend morphology. The unsaturated phenyl rings of the TPU can be selectively stained with RuO_4. Therefore, TPU phase displays in white and PP in black in the backscattered electron images. Amount of interface in each of the blends, in terms of perimeter of the interface divided by the area of the SEM image (i.e. interfacial area per unit volume for a random cut) is listed in Table 2.

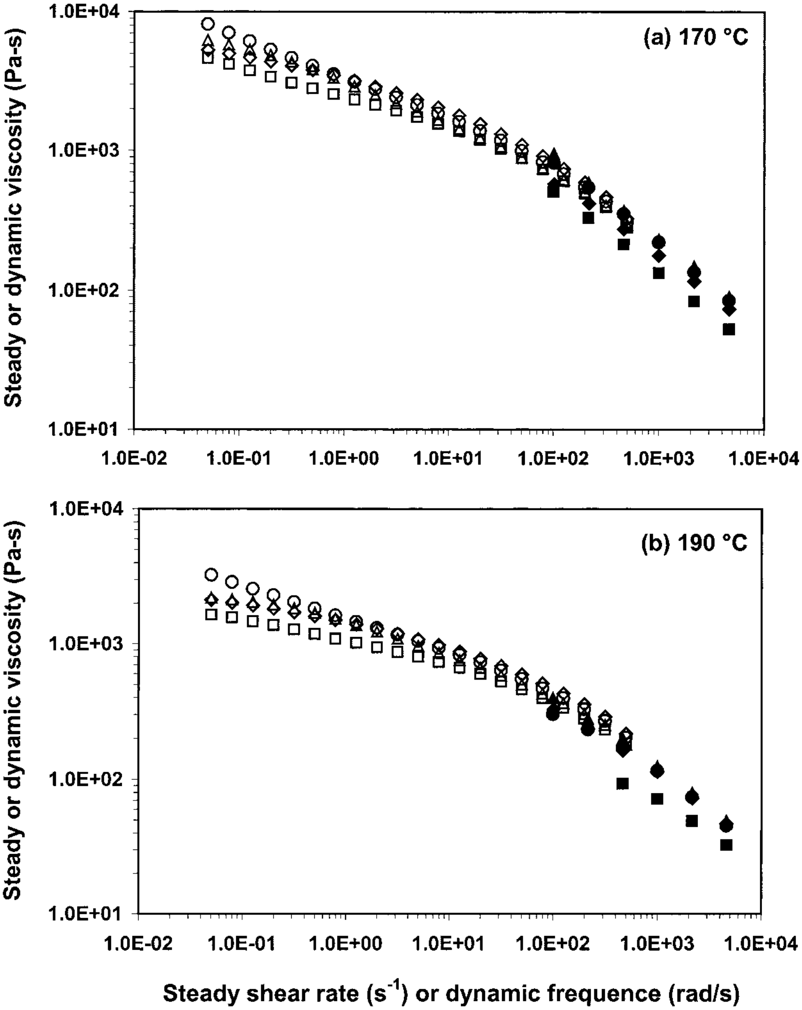
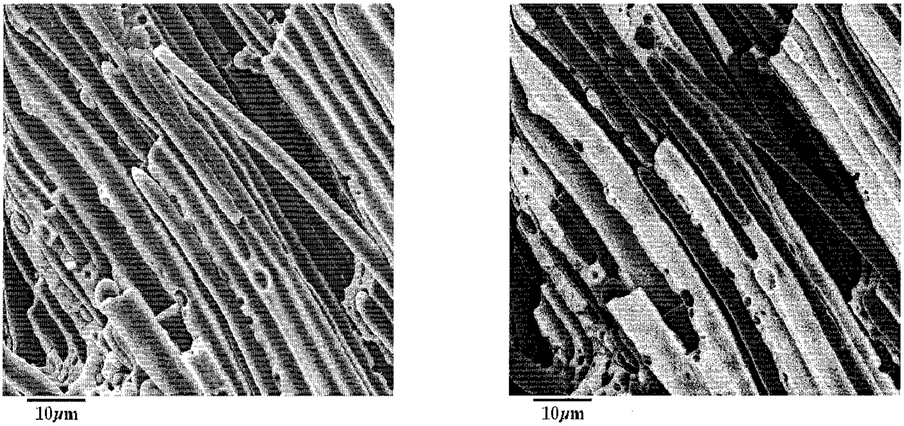
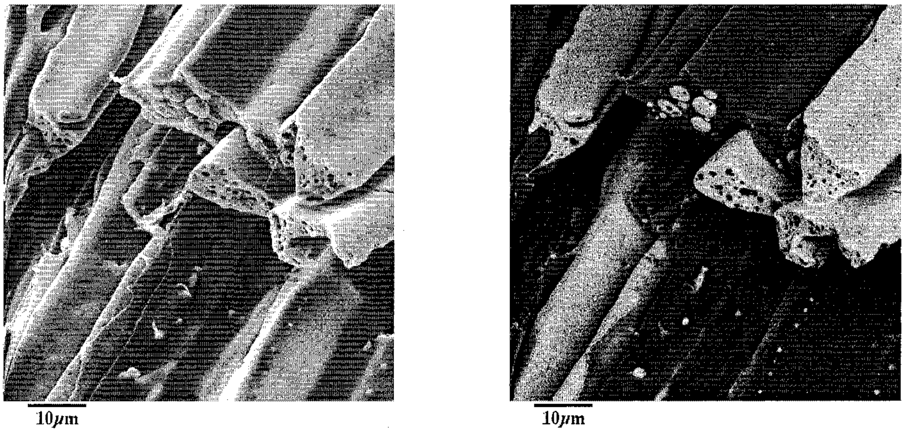


Figure 1. Master curve of viscosity vs. shear rate for different TPU/PP blends at 170 °C (a) and 190 °C (b): TPU/PP: steady (■), dynamic (□); TPU/PP/PP-g-MA: steady (◆), dynamic (◇); TPU/PP/PP-g-NHR: steady (▲), dynamic (△); TPU/PP/PP-g-NH_2: steady (●), dynamic (○). The data from capillary measurement were apparent values without corrections.

In the extrudate of the uncompatibilized TPU/PP blend (Figure 2a), both TPU and PP form long fibers that are well aligned along the flow direction with an aspect ratio greater than 20. The interface is very sharp due to the high interfacial tension. Interfacial failure during the cryo-fracturing (e.g. debonding, pull-out) is obvious. In addition, the morphology is unstable against processing and annealing. After the injection molding, fibers of the same material coalesce to form much larger laminar domains (Figure 3a). The amount of interface (in Table 2) is reduced 75% to a very low level (0.1 μm^{-1}) during coalescence.



(a)



(b)

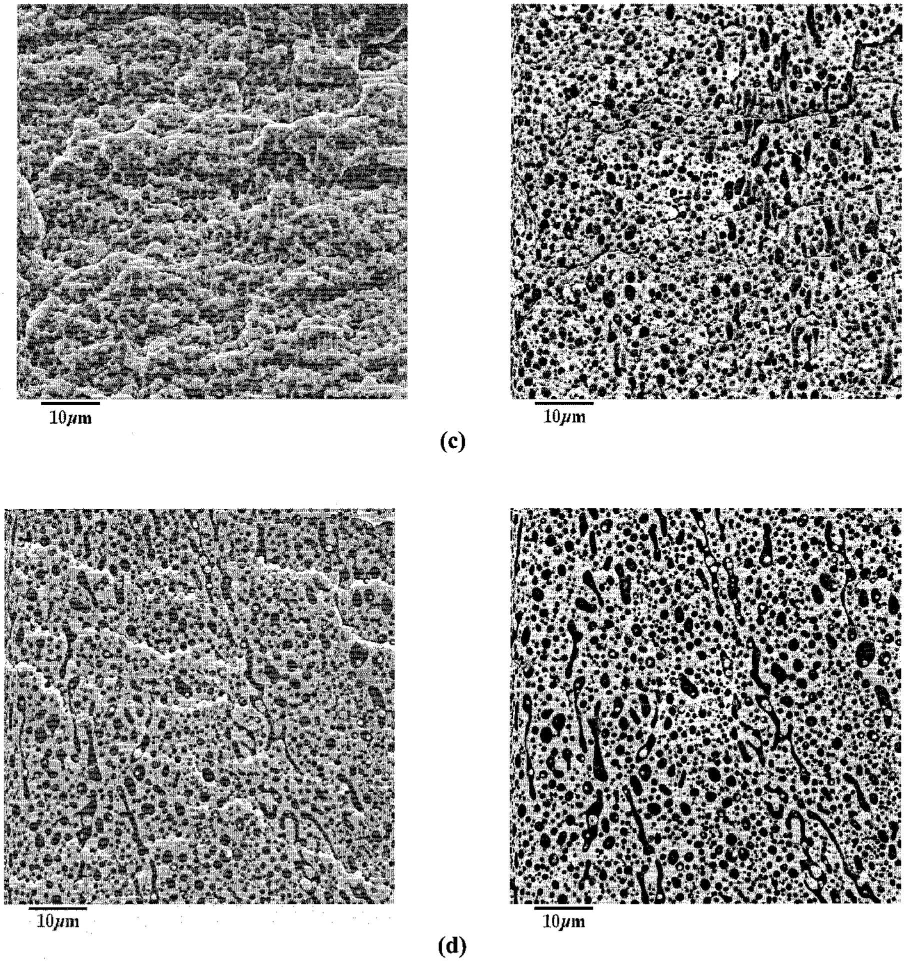
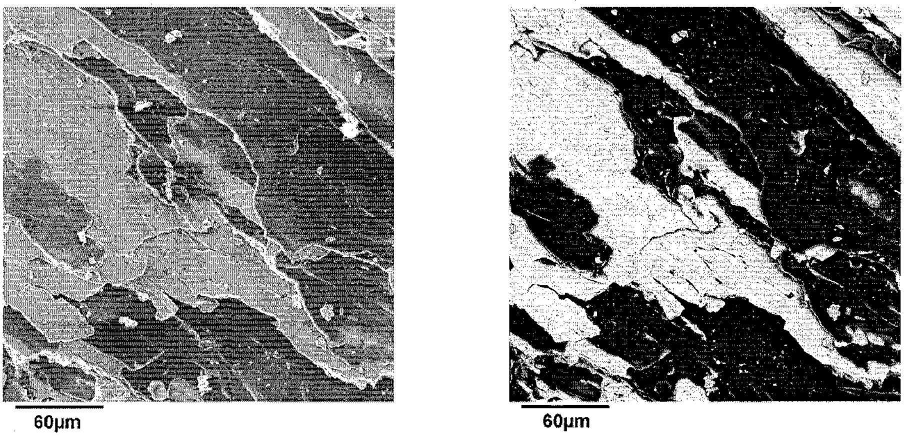
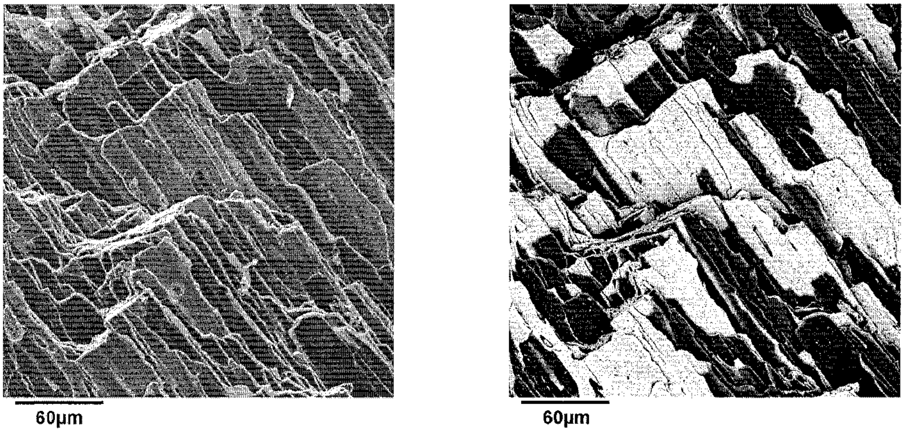


Figure 2. Scanning electron micrographs of different TPU/PP blends upon extrusion. Both secondary electron images for topology (left) and backscattered electron images for phase contrast (right; note: TPU, white; PP, black) are presented. (a) TPU/PP; (b) TPU/PP/PP-g-MA; (c) TPU/PP/PP-g-NHR; (d) TPU/PP/PP-g-NH_2.

Replacing 5 wt.% nonfunctional PP with PP-g-MA, the morphology upon extrusion becomes more laminar (Figure 2b). The morphology change from the uncompatibilized TPU/PP blend is mainly attributed to the reduced viscosity by adding the low-molecular-weight maleated PP. The interface is still sharp and delamination between layers can be clearly observed. Moreover, the domain size is still very large, as reflected in the interfacial area per unit volume (0.1 μm^{-1}). Nonetheless, the blend maintains a similar structure (Figure 3b) after the injection molding and the domain size decreases a little with more interface (0.2 μm^{-1}) probably generated by the high shear.



(a)



(b)

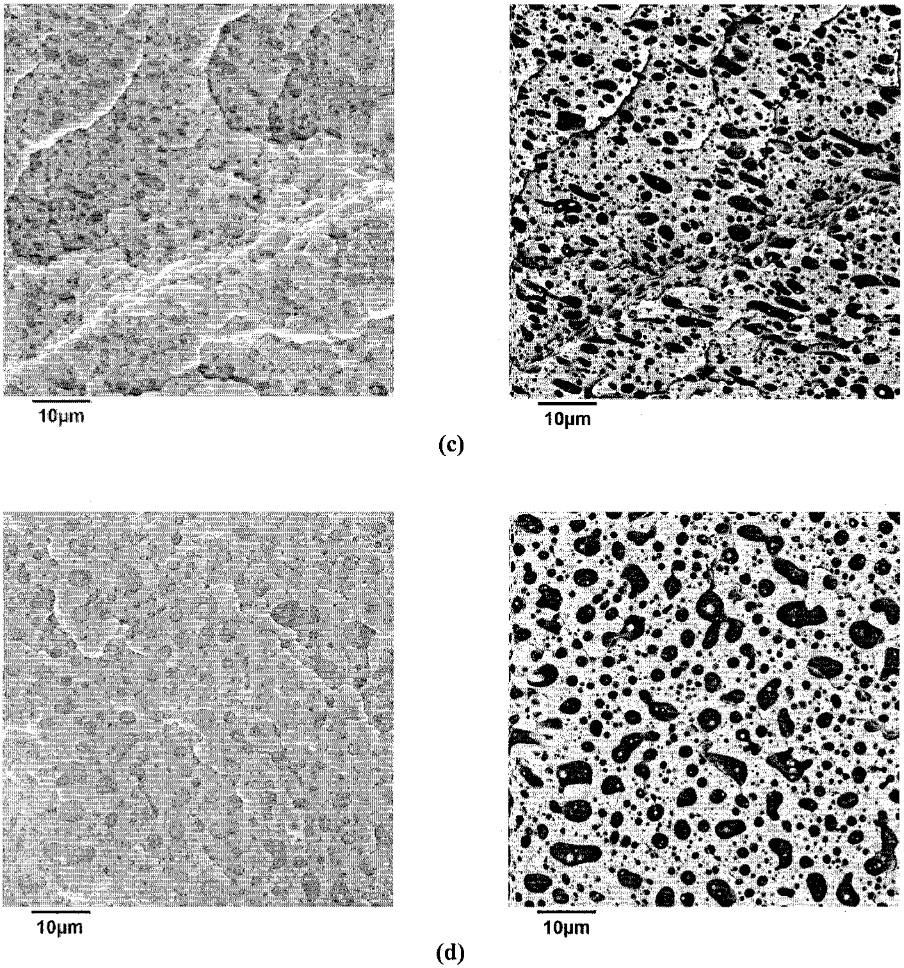


Figure 3. Scanning electron micrographs of different TPU/PP blends after injection molding. Both secondary electron images for topology (left) and backscattered electron images for phase contrast (right; note: TPU, white; PP, black) are presented. (a) TPU/PP; (b) TPU/PP/PP-g-MA; (c) TPU/PP/PP-g-NHR; (d) TPU/PP/PP-g-NH_2.

When 5 wt.% amine (primary and secondary) functional PP is added into the TPU/PP blend, the PP phase becomes particulate (Figures 2c and 2d). The interfacial areas are accordingly much larger (cf. Table 2) compared with the two previous blends. This is probably due to reduced interfacial tension and inhibition of coalescence caused by the reactively generated compatibilizers, i.e. TPU-b-PP block copolymers. All the PP particles on the cryo-fractured surface were broken trans-granularly, i.e. through the particle and no pull-out can be found, indicating the interfacial adhesion between the two phases is very strong. Both amine functional PP blends exhibit excellent morphological stability under a high shear rate during the injection molding. The particles coarsen slightly, i.e. less amount of interface (cf. Table 2). Particle size is somewhat smaller and morphological stability appears to be higher in the TPU/PP/PP-g-NHR blend than in the TPU/PP/PP-g-NH_2 in the micrographs both upon extrusion and after injection molding (Figures 3c and 3d, Table 2). Nonetheless, morphology differences are relatively small between the two amine functional PP blends.

Figure 4 illustrates the stress-stain curves of different TPU/PP blends, as well as TPU and PP homopolymers. The results of all the mechanical (tensile, tear, and abrasion) tests are summarized in Table 2. It's clearly seen that both elastic modulus and tensile strength are significantly higher after adding 30% PP into TPU. However, the uncompatibilized TPU/PP blend yields at 12% and breaks at a very low elongation. The tensile strength is only 5MPa. The TPU/PP/PP-g-MA blend shows considerable improvement with modulus, tensile strength, and elongation at break increased by 66%, 100%, and 220%, respectively. However, other mechanical properties such as tear strength and abrasion resistance are worse. Both TPU/PP/PP-g-NHR and TPU/PP/PP-g-NH_2 blends display higher moduli and much greater toughness. They show quite similar stress-strain behavior. The tensile strengths, close to those of TPU and PP homopolymers, are four times that of the uncompatibilized TPU/PP and twice that of the TPU/PP/PP-g-MA blend. The ultimate elongations, close to that of TPU homopolymer as well, have similar percentage increases. Meanwhile, the tear and abrasion resistance are also enhanced with higher tear strength and less mass loss upon abrasion. These significant improvements in the overall mechanical properties are due to finer morphology, and stronger interfacial adhesion between TPU and PP phases, all produced by the compatibilizers generated by interfacial reactions.

It is important to note that the amine modified PP's were used in relatively small amounts, 16% of the total PP. We have also found that half of that amount still works well.

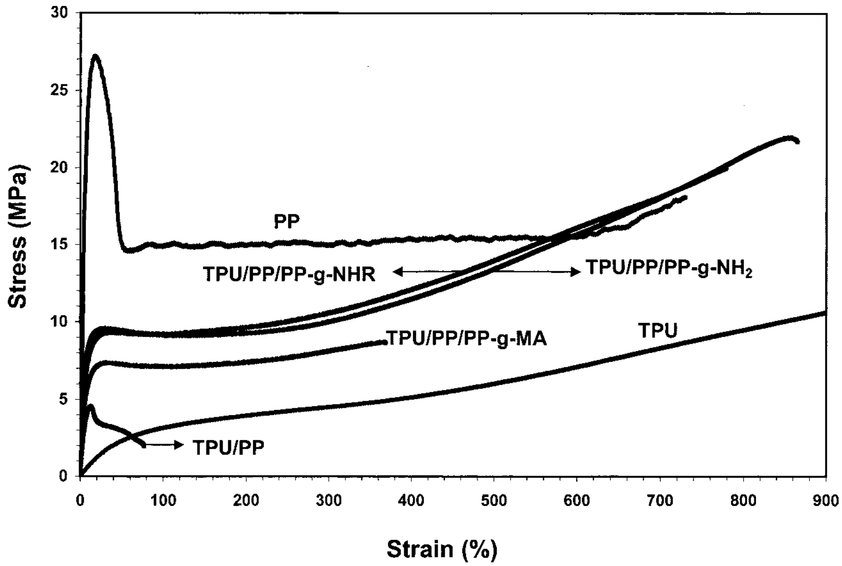


Figure 4. Tensile stress-strain results for different TPU/PP blends and TPU and PP homopolymers. The testing standard for PP is ASTM D638 (Type IV).

Table 2. Morphological and mechanical properties of different TPU/PP blends and TPU and PP homopolymers.

Blend component	Modulus (MPa)	Tensile strength (MPa)	Elongation at break (%)	Tear strength (N/mm)	Abrasion (mg loss)	Amount of interface (μm^{-1})	
						Upon extrusion	After injection molding
TPU*	(6.7)	23	825	65	42	-	
PP	490**	28**	730**	-	-	-	
TPU/PP	82	5	150	33	276	0.4	0.1
TPU/PP/PP-g-MA	136	10	480	25	318	0.1	0.2
TPU/PP/PP-g-NHR	172	20	800	38	173	1.6	1.5
TPU/PP/PP-g-NH_2	225	21	860	39	202	1.5	1.1

* Data provided by the supplier

** ASTM D638

Conclusion

Compatibilized TPU/PP blends can be produced by adding relatively small amount (~10%) of amine (primary and secondary) functional PP's (PP-g-NH_2 and PP-g-NHR). This compatibilization is the result of fast interfacial reactions between amine functional groups and urethane linkages or trace of free isocyanates released by thermal degradation of TPU. Much finer PP domains, better interfacial adhesion, and greater morphological stability were clearly observed. Mechanical properties (tensile, tear, abrasion) wee significantly improved in the two TPU/PP blends containing PP-g-NH_2 or PP-g-NHR compared to the uncompatibilized one, as well as the TPU/PP blend using PP-g-MA as a compatibilizing agent.

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