

Synergetic Effect of Polyamide 1212 and Diisocyanate on Performance Improving of Thermoplastic Polyurethane via Melt Compounding

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ABSTRACT: To improve the heat resistance of thermoplastic polyurethane (TPU), in the melt blending process polyamide 1212 (PA1212) and trace amount of 4, 4'-diphenylmethane diisocyanate (MDI) were used as modifier and reactive solubilizer, respectively. Compared with pure TPU, the combinatorial addition of PA1212 and MDI resulted in remarkable improvement of mechanical, thermal, environmental, and aging properties of the TPU matrix. The reactive MDI contributes to the better interfacial

adhesion between TPU and PA1212, and the dispersed PA1212 particles act as fillers as well as crosslinking points in the TPU/PA1212/MDI ternary blend. It was revealed that the synergetic effect of PA1212 and MDI is responsible for the enhanced performance of modified TPU. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 125: 1077–1083, 2012

Key words: thermoplastic polyurethane; polyamide 1212; diisocyanate; melt compounding

INTRODUCTION

Thermoplastic polyurethane (TPUs) elastomers are now widely used because of their unique properties, such as the high tensile strength, high elongation at break, good wear and tear resistance, low temperature elasticity, etc. However, the intrinsic poor heat resistance of TPU strongly jeopardizes those excellent properties as the service temperature of the material exceeds 80°C.¹ It has been found that TPU-based products can be used for several days in the temperature range of 80–100°C, but only a few hours above 120°C, the mechanical properties emerges significant decrease.^{1–3} Therefore, the instability at high temperature limits the applications of TPU. To improve the service temperature of TPU, some heat-resistant chemicals have been tried to incorporate into TPU by chemical and physical approaches. In the process of chemical modification, the reactive additives are structurally introduced via backbone modification or copolymerization into TPU macromolecular chains; whereas in the process of physical modification approach, the additives are mechani-

cally blended with TPU. The latter one is usually considered as a more flexible and inexpensive method. For example, TPU can be modified by inorganic fillers or other polymers through melt compounding to improve its heat resistance and processability. Many kinds of polymers have been tried to blend with TPUs, among which polyamide is an alternative modifier. Polyamides have some superior advantages, including superior resistance to chemicals, high temperature stability, and structural similarity to TPUs. By blending TPU with polyamides,^{4–9} intermolecular hydrogen bonds can be formed between amide groups of polyamide and urethane groups or ester/ether groups of TPU, thus improving the compatibility of the blends. Among these studies, TPU is mostly employed as an impact modifier of polyamides, namely, polyamide is considered as the matrix and TPU only plays the role of additive. In our previous work,¹⁰ polyamide 1212 (PA1212) was used as TPU modifier, and it was found that TPU and PA1212 is partially miscible, and with the addition of a small amount of PA1212, the thermal and mechanical properties of TPU are obviously improved.

Diisocyanate with two NCO reactive groups is feasible to react with chemicals possessing active hydrogen, so it is usually used as a polymer modification reagent. Grafting 4, 4'-diphenylmethane diisocyanate (MDI) through allophanate bonds onto the urethane groups of TPU can modify the thermomechanical properties of TPU matrix. Some researchers^{11–14} reported the effect of diisocyanate on the

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TABLE I
The Compositions of TPU/PA1212/MDI Compounds

Item	TPU/PA1212/MDI									
Content(wt/wt)	100/0/0	99/0/1	95/5/0	94/5/1	90/10/0	89/10/1	80/20/0	60/40/0	0/99/1	0/100/0

performance of TPU, though the grafted TPU tends to form crosslinked structure, thus limiting further processing of the materials. MDI was also used as the reactive solubilizer for PA/TPU blends to improve the compatibility between PA6 and TPU, and enhanced mechanical properties were achieved.^{15,16}

In this work, PA1212 with a high melt flow rate was selected to blend with polyether-based TPU, and trace amount of MDI was introduced into the blend as a reactive solubilizer. The main aim is to investigate whether the reaction of MDI with TPU and PA1212 during the melt compounding process can improve the compatibility between the two components and consequently influence the mechanical and physical properties of TPU. The morphology, mechanical properties, as well as thermal aging behaviors of the TPU-based blends were systematically investigated.

EXPERIMENTAL

Materials

The TPU used is a product of Noveon Inc. (Belgium), which is a polyether-based TPU (Estane 58315) with the melt flow rate of 16.5 g/10 min (210°C, 2.16 kg). FTIR and NMR analysis showed that the soft segment is based on polytetramethylene glycol, and the hard segment (38 wt %) is based on MDI and 1,4-butanediol. The average molecular weights determined by gel permeation chromatography (Waters 1515 pump/2414 detector/THF eluant) were $M_n = 53,800$ and $M_w = 106,000$ (referred to polystyrene calibration standard).

The PA1212 was kindly provided by Zibo Guangtong Chemical Co., Ltd. (China) with the melt flow rate of 31.2 g/10 min (210°C, 2.16 kg), which was synthesized by condensation polymerization of dodecanedioic acid and dodecanedioic amine.

MDI was obtained from Yantai Wanhua Polyurethane Co., Ltd. (China), with the purity $\geq 99.6\%$ and melting temperature of 38°C. MDI was kept at -7°C to prevent dimer formation before use.

Samples preparation

Before melt compounding, the TPU and PA1212 pellets were dried at 85°C in a vacuum oven for 12 hr, and then introduced (with or without MDI) into a twin-screw hopper. A HAAKE twin-screw extruder with an aspect ratio of 40 and barrel diameter of 30

mm was used. The processing temperature was set in the range of 180–200°C and the rotating speed of the extruder was controlled at 35 rpm. The extrudates were cooled in a water bath and were pelletized for further processing and characterization. The weight ratios of TPU/PA1212/MDI ternary blends are listed in Table I. If no other information is pointed out, the pure TPU and PA1212 refer to the extruded TPU and PA1212 under the same processing condition.

Mechanical testing

An Instron 3365 universal tensile tester was used to determine the mechanical properties of the materials. The crosshead speed was set at 200 mm/min. For mechanical testing, the sample plates with the thickness of 1 mm were obtained by a LP-S-50 compression molder, and then cut into dumbbell specimens according to ASTM-D-638-2003 (Type IV). The average value of at least five tests was reported.

Rheological measurements

A capillary rheometer (Rosand RH7, Malvern Instruments, Ltd., UK) with an aspect ratio of 32 and capillary die of 1 mm was used to measure the rheological property under steady shear mode of all pure components and blends. The die entry angle was 180°. The test was conducted at 200°C in the frequency range of 20–8000 rad/s. Before testing, the samples were dried at 85°C in a vacuum oven for 12 h to remove the moisture.

Scanning electron microscopy

A field-emission scanning electron microscope (SEM, JSM-6700F, JEOL) was used to observe the morphology of the cross section of the extruded samples. The samples were cryogenically fractured in liquid nitrogen, and the cross section was gold-sputtered in vacuum before SEM observation. PA1212 particles were obtained by dissolving the blends in dimethyl formamide and then filtering under low pressure membrane to get rid of the TPU ingredient. Sections of the dried membrane were cut out and gold-sputtered in vacuum for SEM observation.

Vicat softening temperature measurements

Vicat softening temperature (VST) of the samples was measured according to the ISO 306 standard on

a 10XRW-300 tester (Hebei Chengde Testing Machine Co., Ltd., China). The sample dimension was $10 \times 10 \times 5 \text{ mm}^3$. A force of 10 N was applied for each specimen and the temperature was increased at a heating rate of 50°C/h . The VST value for each sample was averaged over three parallel tests.

Environmental and aging testing

The experiments were performed in a hot air circulating oven, inside which the temperature was kept at 70°C . First, three flasks were placed in the oven [one empty, one filled with plenty of water, one filled up with fuel (30 vol % toluene + 70 vol % isooctane)], then the dumbbell specimens were placed in the flasks, and finally two of the flasks with water and fuel were stuffed with plug to prevent liquid evaporation. The mechanical properties of the samples were tested at 1, 2, and 4 weeks after aging. The results reported were the average value of five specimens.

RESULTS AND DISCUSSION

Intermolecular interaction and rheological behavior in TPU/PA1212/MDI blends

TPU and PA all have active hydrogen atoms. In the melt extrusion process at 200°C , a small amount of MDI was introduced as reactive solubilizer, which can react with active hydrogens of both TPU and PA to decrease the interfacial adhesion. Lapprand et al. studied the reactions of isocyanates with urethanes by the combination of $^1\text{H-NMR}$, $^{13}\text{C-NMR}$ and MALDI-TOF.¹⁷ Rached et al. synthesized PA12-*b*-PDMS-*b*-PA12 triblock copolymers and confirmed its chemical structure by $^1\text{H-NMR}$ spectroscopy.¹⁸ PDMS macroinitiator was obtained by an original synthesis scheme involving the reaction of MDI with silanol groups. This macroinitiator was then used for the anionic polymerization of lauryl lactam at high temperature. Brauer et al. found an insoluble and inseparable polyurethane residue on the PA6 fracture surface in PA6/TPU/MDI blends.¹⁵ The results of ATR-FTIR spectroscopy showed the formation of chemical bonding between PA6 and TPU. Based on the above literatures, a reaction mechanism among MDI, TPU, and PA1212 is proposed (Fig. 1). MDI seizes the active hydrogen of urethane units and forms allophanate bonds, resulting in the formation of crosslinking networks [Fig. 1(a)]. MDI also can react with the active hydrogen atoms of amide groups in PA1212 to form acylurea bond, then form a crosslinking network [Fig. 1(b)]. Therefore, with the addition of MDI in TPU/PA1212 blends, a crosslinking structure can be formed between TPU and PA1212 molecules, and thus improving the compatibility between the two components.

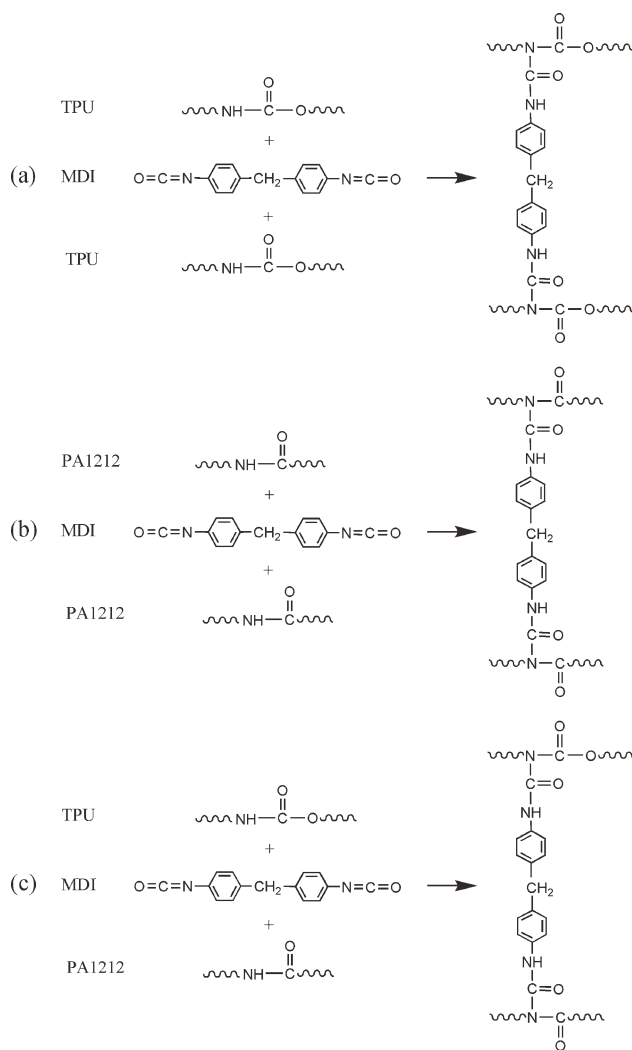


Figure 1 The interactions among the three components: (a) the reaction between MDI and TPU; (b) the reaction between MDI and PA1212; (c) the reaction of MDI with TPU and PA1212.

On the other hand, according to the results of $^1\text{H-NMR}$ and GPC, the average number of urethane bonds per TPU chain is about 170. With the addition of 1 wt % MDI, the molar ratio of isocyanate group to the urethane group is 0.025. Therefore, it is estimated that average 40 urethane bonds have a chance to react with one NCO group to form allophanate, resulting in the formation of weak crosslinking network. Therefore, the modified TPU can still be regarded as a thermoplastic material.

Capillary rheological test is a convenient method for determining the viscosity properties of polymers. Slight crosslinking in the TPU/PA1212/MDI blends will lead to the increase of viscosity. Figure 2 presents the effect of MDI on the shear viscosity of TPU, PA1212, TPU/PA1212 blends. The shear viscosity of PA1212, especially TPU, increases significantly with the addition of 1 wt % MDI. The further addition of MDI in TPU/PA1212 blends results in an obvious

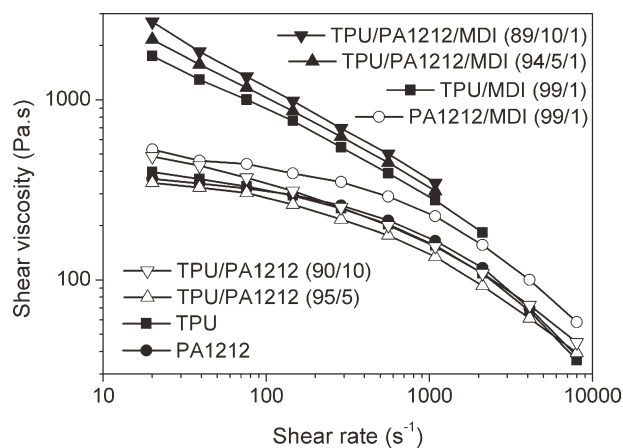


Figure 2 Effect of MDI on shear viscosity of TPU, PA1212, and their blends at 200°C.

increase of the viscosity. The above results imply that a certain degree of crosslinking structure with the addition of MDI exists in the TPU/PA1212 blends.

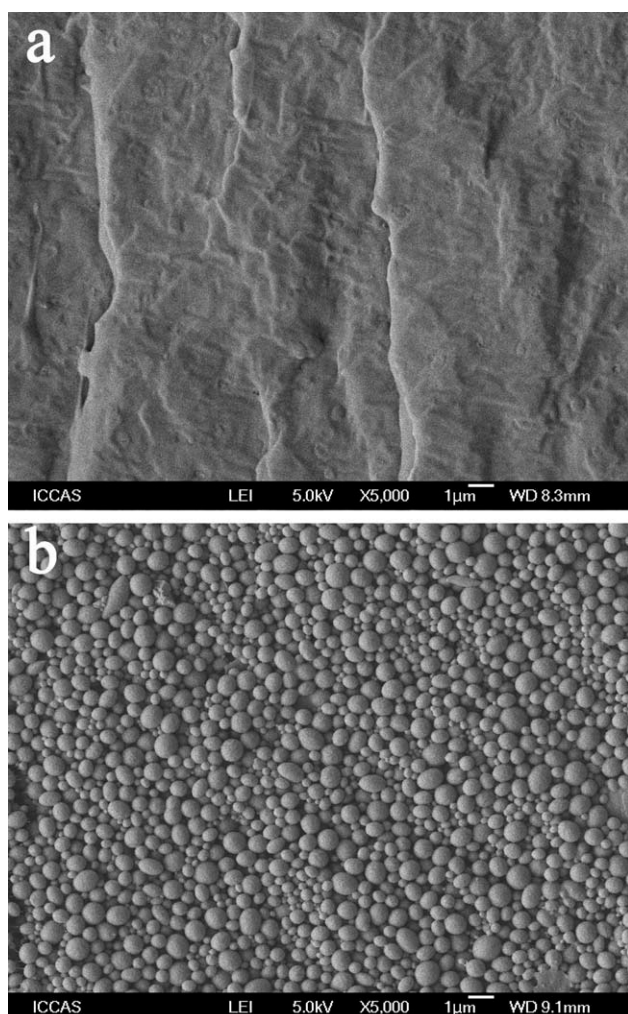


Figure 3 SEM micrographs of TPU/PA1212 (90/10) blend: (a) cryogenically fractured surface of the extruded sample; (b) PA1212 particles separated from the blends.

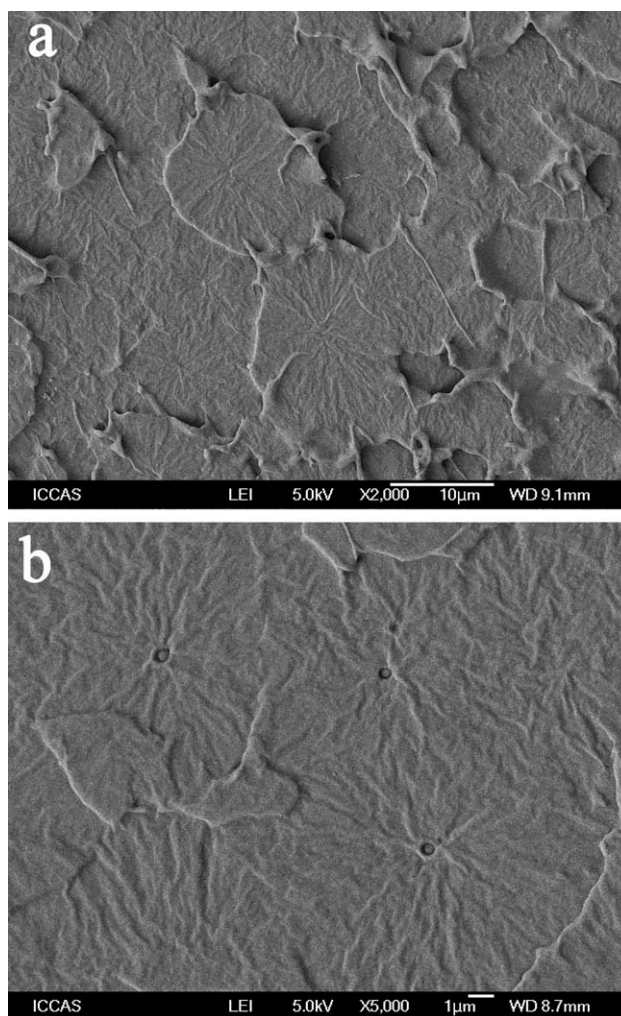


Figure 4 SEM micrographs of samples obtained by extruding: (a) TPU/PA1212/MDI (94/5/1); (b) TPU/PA1212/MDI (89/10/1).

Morphological investigation

The mechanical properties of polymer blends are not only determined by the chemical structure of different components and compositions, but also correlated with the morphology. Figures 3-6 shows the SEM photographs of different TPU/PA1212/MDI blends. For TPU/PA1212, it was observed that PA1212 is well dispersed in the TPU matrix and the boundary between the two phases is blurred [Fig. 3(a)], indicating that TPU is compatible with PA1212. SEM observation showed that the PA1212 particles are spherulitic/ellipsoidal-shaped with diameter of ~ 500 nm [Fig. 3(b)]. With the addition of 1 wt % MDI, the dispersed phase of PA1212 in TPU/PA1212/MDI (94/5/1, 89/10/1) blends could not be observed by SEM [Figs. 4(a,b)]. To characterize the phase morphology in these blending systems, the PA1212 particles were separated by repeated centrifugation, leaching, and filtration processes. Figure 5 showed that most PA1212 particles are of spherical/ellipsoidal shape with a

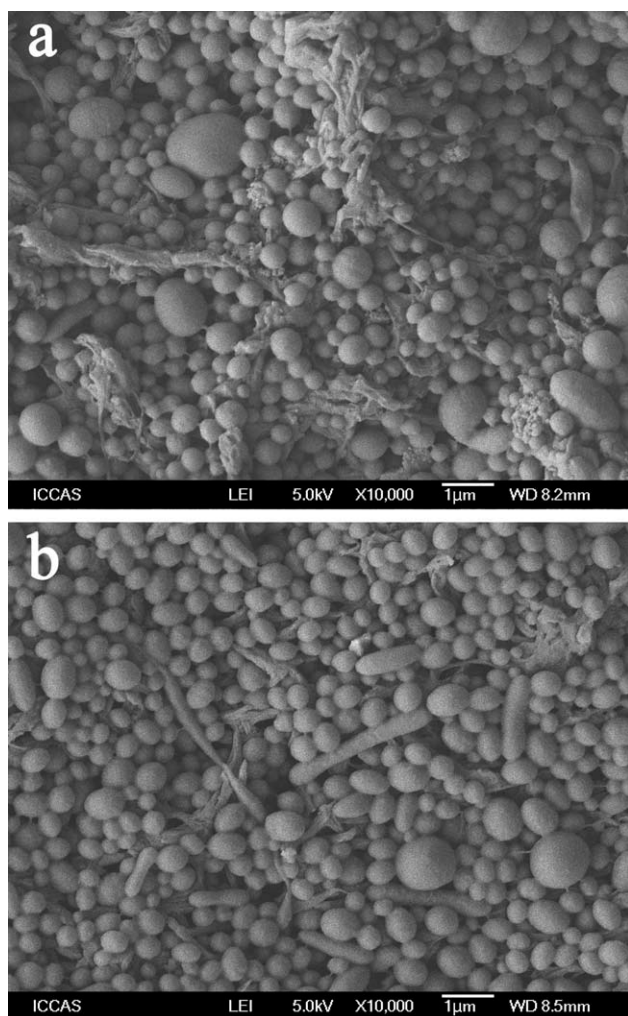


Figure 5 SEM micrographs of PA1212 particles separated from (a) TPU/PA1212/MDI (94/5/1) and (b) TPU/PA1212/MDI (89/10/1).

small fraction of rod-like shape. The diameter of the spherical particle is about 500 nm, whereas the length of the rod-like particle is $\sim 10\text{--}30\ \mu\text{m}$ and the diameter is similar to the spherical particle. It is worth to note that some PA1212 particles stick together (Fig. 6), implying the existence of chemical interactions among TPU, PA1212, and MDI, which results in partially crosslinked structure and viscosity increasing.

Mechanical and thermal-stable testing

Tensile strength

Slight crosslinking imparts great influence on the performance of polymer materials. As early as in 1961, Mobay Company produced the slightly cross-linked TPU elastomer Texin with excellent performance.¹⁹ The effect of PA1212 and MDI on the mechanical properties of TPU is shown in Figure 7. It is observed that the tensile strength of TPU is slightly improved with the addition of 5 or 10 wt %

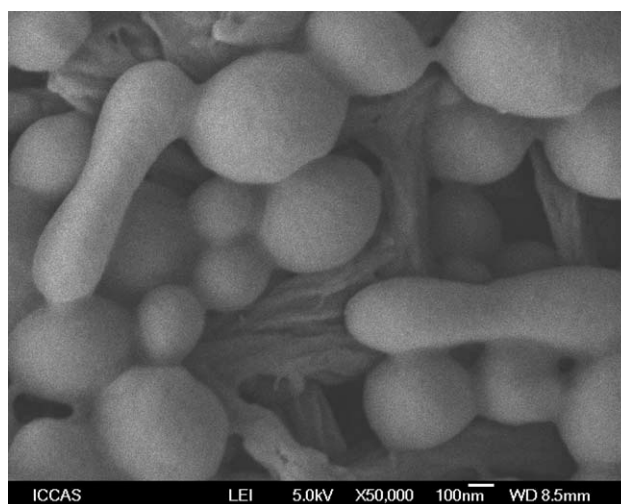


Figure 6 The magnified SEM micrograph of PA1212 particles separated from TPU/PA1212/MDI (89/10/1).

PA1212. With further increasing PA1212 content, i.e., exceeding 20 wt %, the tensile strength of the blends is smaller than that of pure TPU. The results are

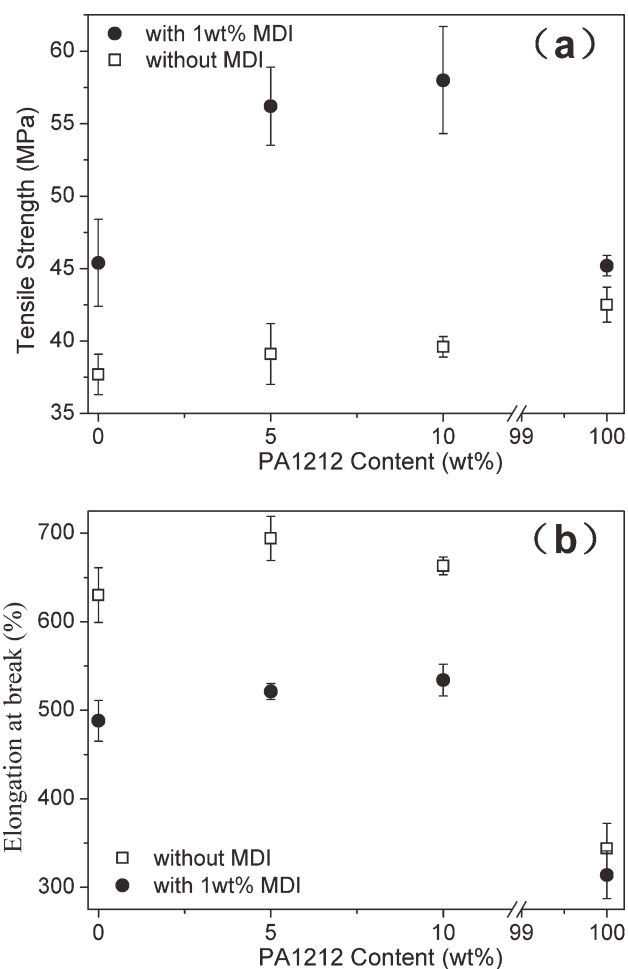


Figure 7 Effect of PA1212 with or without MDI on mechanical properties of TPU: (a) tensile strength; (b) elongation at break.

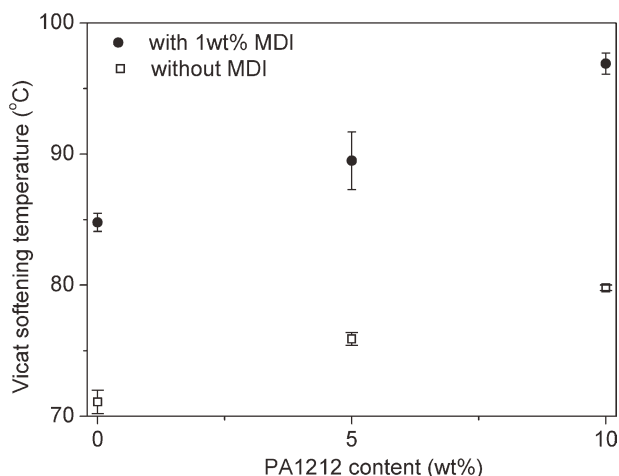


Figure 8 Effect of PA1212 and MDI on the VST of TPU.

similar with the early report.¹⁰ Compared with pure TPU, the tensile strength of TPU/MDI (99/1) increases by 20%, reaching 45.4 MPa. The addition of MDI further increases the tensile strength of TPU/PA1212. For blends, the tensile strengths of TPU/PA1212/MDI (94/5/1) and TPU/PA1212/MDI (89/10/1) reaches 56.2 and 58 MPa, respectively, much higher than that of pure TPU (37.7 MPa) and TPU/PA1212 blends (39 MPa). It should be pointed out that the elongation at break of TPU/PA1212/MDI (94/5/1) and TPU/PA1212/MDI (89/10/1) is still large enough (above 520%), which can meet the practical applications. According to the aforementioned reaction mechanism, when a small amount of MDI is introduced into TPU/PA1212 blends, part of MDI function groups can react with the active hydrogens of both TPU and PA1212, forming a weak crosslinked structure to link TPU and PA1212 molecules, improving the tensile strength and decreasing the elongation at break of the TPU/PA1212 blends.

It is generally recognized that the excellent mechanical properties of TPU are attributed to the microphase separation between the hard segments and the soft segments. By adding a small amount of PA1212 in TPU, PA1212 forms spherical particles with a size of hundreds of nanometers, which play the role of strengthening filler. With adding trace amount of MDI in TPU, TPU reacts with MDI to form slightly crosslinked structure. For TPU/PA1212/MDI blends, the TPU matrix increases the interfacial adhesion due to the reaction of MDI with TPU and PA1212, resulting in the formation of a small fraction of rod-like particles as well as spherical particles with a size of hundreds of nanometers. The results resemble to use nanoparticles and microfibers to strengthen the vulcanized rubber. Therefore, it is a synergetic effect of PA1212 and MDI to improve the tensile strength of TPU.

Vicat softening temperature

The VST is an important parameter to evaluate the thermal deformation resistance of thermoplastic materials. The higher the VST, the better thermal deformation resistance the material has. TPU exhibits relatively low heat resistance, and 80°C represents the maximum service temperature for most TPUs. Figure 8 illustrates the effect of PA1212 and MDI on the VST of TPU. It can be seen that the VST increases linearly from 71 to 80°C with the increase of PA1212 content. The further addition of MDI in TPU/PA1212 blends results in further increase of the VST. The VST of TPU/PA1212 (90/10) is 80°C, while the VST of TPU/PA1212/MDI (89/10/1) reaches as high as 97°C, 26°C higher than that of pure TPU. These results confirm the synergetic effect of PA1212 and MDI on the significant improvement of the VST of TPU. Therefore, the addition of PA1212 and MDI enhances the heat resistance of TPU, and expands its application temperature range.

Environmental and aging properties

TPU, as a widely used polymer materials, usually contacts with various environmental media. There are usually three important environmental effects for polyurethane elastomers: heat effect, hydrolytic stability, and fluid resistance. The tensile strength variation of pure TPU and TPU/PA1212/MDI (94/5/1) blends in different environmental media is shown in Figure 9. Because the maximum surface temperature is ~70°C in the natural environment, 70°C is chosen as the aging experiment temperature. It was found that the tensile strength of TPU changed a little after 4 weeks aging in 70°C air, indicating TPU can still be used after long-term storage

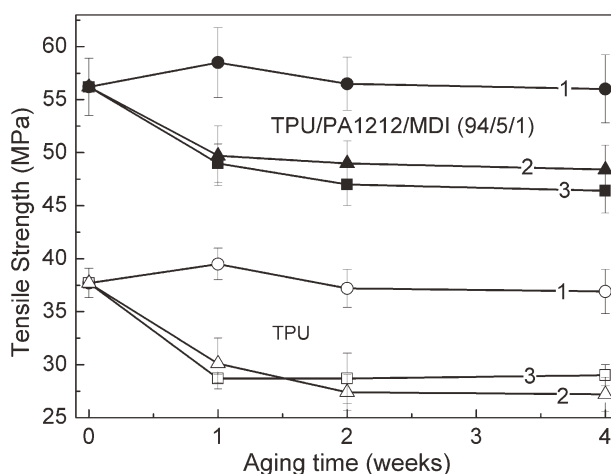


Figure 9 The variation of tensile strengths of TPU and TPU/PA1212/MDI (94/5/1) compound with accelerating aging in different media. (1) 70°C air; (2) 70°C water; (3) 70°C fuel.

in the natural environment. In 70°C hot water, however, the tensile strength of pure TPU was reduced to 77% of its initial value after 4 weeks immersion. The tensile strength of pure TPU, after 4 weeks' immersion in 70°C fuel, is reduced to 72% of its initial value. For TPU/PA1212/MDI (94/5/1) blend, the initial tensile strength is much higher than that of pure TPU. Furthermore, the blends also have excellent tensile strength after 4 weeks' immersion in different environmental media at 70°C, and the remaining tensile strength of the blend is still much higher than the initial tensile strength of pure TPU. The above results prove that the resistance of TPU to different environmental media is greatly improved with the addition of PA1212 and MDI.

According to Mark triangle theorem, the heat resistant of polymers can be improved through changing three kinds of structural factors: increasing the rigidity of the polymer chain, improving the crystallinity, and forming crosslinking structure. In the present work, first, the rigidity of TPU was increased due to the presence of spherical and rod-like particles of PA1212; second, a slightly crosslinked structure was formed due to the reaction of MDI with PA1212 and TPU. So, the above two factors can explain the increase of the heat resistance of TPU-based blends.

CONCLUSIONS

In this work, a high melt flow rate PA1212 was selected to blend with polyether-based TPU, and a trace amount of MDI was introduced as the reactive solubilizer during melt compounding. The reactive MDI results in better interfacial adhesion between TPU and PA1212. The PA1212 particles act as fillers as well as crosslinking points in TPU/PA1212/MDI blend. The tensile strength of TPU is enhanced by 50%, reaching 50 MPa, whereas the elongation at break remains at a relatively high level (>500%).

The thermal stability, heat resistance, and resistance to environmental media are all improved significantly. The synergetic effect of PA1212 and MDI is responsible for the high performance of TPU-based blends.

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