

Impact Modification of Polyacetal by Thermoplastic Elastomer Polyurethane

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ABSTRACT: The main goal of this study was impact modification of polyacetal [polyoxymethylene (POM)] with thermoplastic elastomer polyurethane (TPU). We modified the impact strength of POM 10-fold. The mechanical properties, thermal behavior, and morphology of POM/TPU blends consisting of 5 to 50% of TPU were studied. It was found that the best impact modification of the blends was at 15% concentration of TPU and the maximum elongation at break was at 30% concentration of TPU. The impact strength of POM/TPU blends can be improved by using diphenylmethane diisocyanate (MDI) as compatibilizer. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 84: 2573–2582, 2002

Key words: blends; polyacetal; polyurethane; impact modification; thermal behavior; mechanical properties

INTRODUCTION

Polyacetal is a rigid and crystalline polymer, used as an engineering plastic. It has good mechanical, thermal, chemical, and electrical properties.¹ Polyacetals, such as polyamides, are characterized by tough behavior but are notch sensitive. They have good resistance to crack initiation, but poor resistance to crack propagation.² The impact strength of POM can be improved by incorporation of a dispersed rubber phase by reaction blending. The rubber particles dispersed in the rigid matrix stop craze growth, which can lead to the formation of failure cracks during impact, and at the same time, the particles act as a stress concentrator, forming a barrier to the extension of crazing. Polyacetals are usually toughened by incorporation of an elastomer such as thermoplastic elastomer polyurethane (TPU).^{3–5} The TPU can

be ether or ester base and it should have a glass-transition temperature (T_g) lower than -15°C and an inherent viscosity greater than 0.7.⁶ The mechanical properties, crystallinity, and effect of melt flow index of polyacetal and polyurethane base on ester or ether were previously investigated,^{3,4} the results of which studies found that the tensile strength, modulus, and crystallinity de-

Table I Compositions of POM/TPU Blends

Code	POM/TPU wt %/wt %	MDI (phr)
A0	100/0	0
A5	95/5	0
A10	90/10	0
A15	85/15	0
A20	80/20	0
A30	70/30	0
A50	50/50	0
C1	85/15	0.5
C2	85/15	1
C3	85/15	2
C4	85/15	3
C5	85/15	4

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Table II Physical and Mechanical Properties of the POM/TPU Blends

Code	Composition	Properties				
		Impact Strength (J/m)	Elongation at Break (%)	Modulus (MPa)	Tensile Strength (MPa)	MFI (g/min)
A0	100/0	26	12	1230	53	26
A5	95/5	45	17	1102	47	23
A10	90/10	65	28	989	44	18
A15	85/15	98	40	847	38	14
A20	80/20	82	98	792	36	13
A30	70/30	74	226	696	33	16
A50	50/50	63	73	351	19	19
C1	85/15	126	25	865	40	9.5
C2	85/15	153	31	886	43	7
C3	85/15	191	42	905	45	3
C4	85/15	257	57	920	49	1.2
C5	85/15	174	35	882	43	4.1

creased by increasing the TPU content. The elongation was maximum at 25 wt % of TPU content. These investigators also reported that for impact improvement, TPU base on ether was better than TPU base on ester. Mitsubishi Co.⁷⁻⁹ used polyhydric alcohol with polyisocyanate for improving the mechanical properties of POM/TPU blends. Palanivelu et al.¹⁰ reported that by increasing TPU content in POM/TPU blends the impact strength increased continuously. Kumar et al.¹¹⁻¹³ also reported on their investigations of POM/TPU blends.

In this study we used an ester base of TPU and applied diphenylmethane diisocyanate (MDI) as modifier. We achieved good improvement of impact strength in low-content TPU in POM/TPU

blends. The morphology of the blends was investigated by SEM and their miscibility by using dynamic mechanical thermal analysis (DMTA) and FTIR.

EXPERIMENTAL

Materials

The elastomer used in this study was polyurethane thermoplastic elastomer, Skytane-S180A (Shore A 82; ester base) obtained from Sunkyong Industries, Korea. Polyoxymethylene or polyacetal [Lucel N109-02 (copolymer)] was obtained from LG Chemical Co., Korea. Diphenylmethane

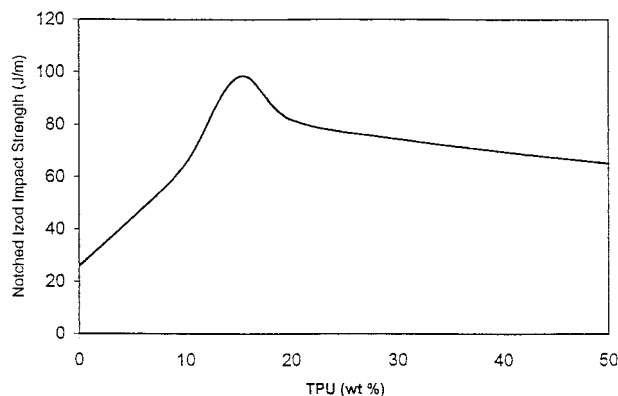


Figure 1 Effect of TPU content on notched Izod impact strength of POM/TPU blends.

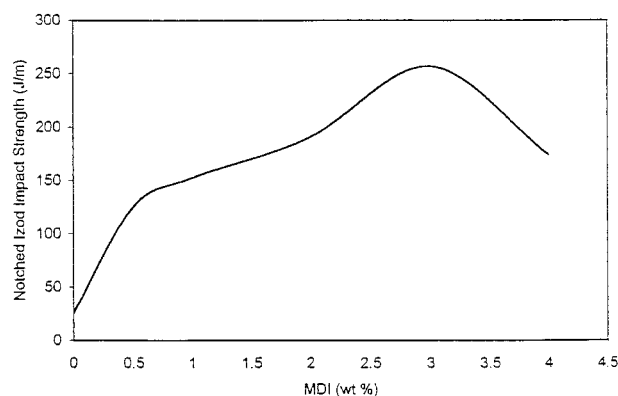
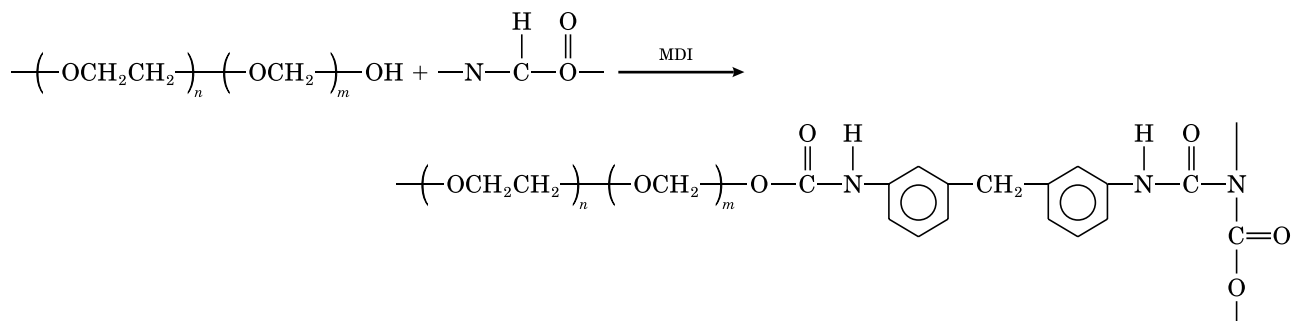


Figure 2 Effect of MDI content on notched Izod impact strength of POM/TPU : 85/15 Blends.



Scheme 1 Compatibilizing effect of MDI.

diisocyanate (MDI) was obtained from Merck (Darmstadt, Germany).

Blend Preparation

The POM/TPU blends were prepared by melt-mixing in a Haake Buchler (Germany) Rheomix 750 internal mixer (300 cm³) at 220°C and 60 rpm for 6 min. The compositions of the blends are listed in Table I.

Mechanical Characterization

The compression-molding technique was used to provide suitable samples for routine tensile testing. At least three and typically five replicate samples were tested for tensile data. Tensile bars conformed to ASTM D-638, using 75 × 5

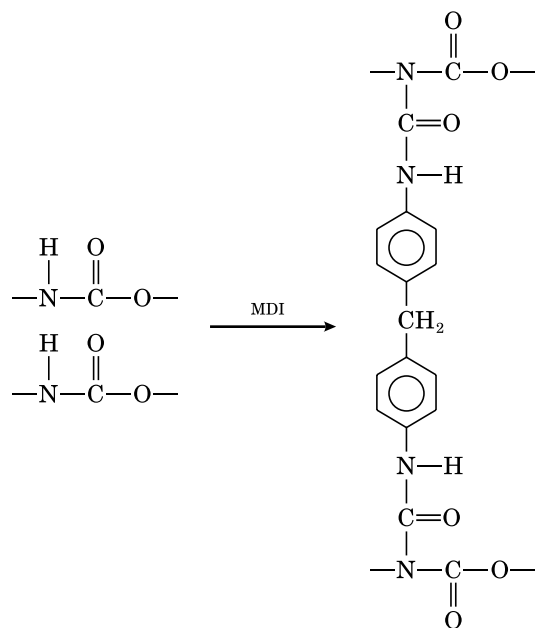
× 0.8-mm tensile samples, and were strained using a crosshead speed of 50 mm/min in an Instron 6025 Universal testing machine.

The hardness of the blends was measured according to ASTM D-2240 and "D" on the Durameter scale instrument was selected.

Impact bars conforming to ASTM D-256 were used to measure the notched Izod impact strength using a Zwick 5102 pendulum impact testing machine at room temperature. The average values of at least five tests are reported.

Melt flow indexes (MFI) of the samples were performed according to ASTM D-1238 by employing a Daven Port Type MFI10.

FTIR spectra of thin films of the samples were obtained by using Bruker IFS48 FTIR (Bruker Instruments, Billerica, MA).



Scheme 2 Crosslinking effect of MDI.

Thermal Behavior

Dynamic mechanical properties of the samples were performed using 30 × 10 × 1-mm compression-molded test pieces and employing a PL-DMTA system equipped with liquid nitrogen cool-

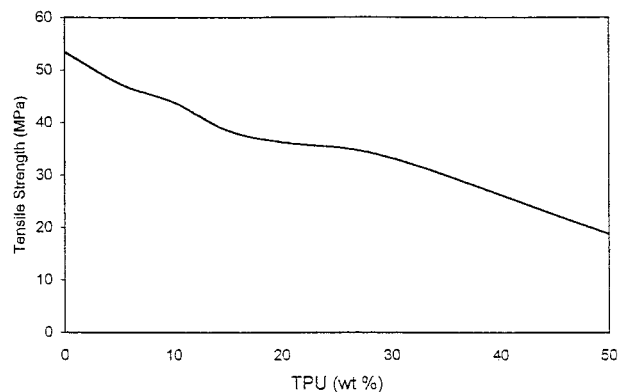


Figure 3 Effect of TPU content on tensile strength of POM/TPU blends.

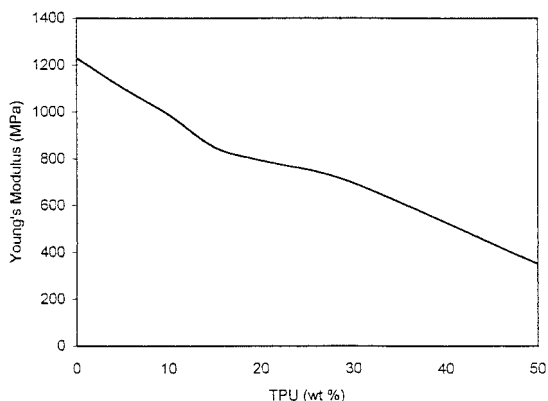


Figure 4 Effect of TPU content on Young's modulus of POM/TPU blends.

ing facilities, which allowed completion of testing over the temperature range at 1 Hz and 10°C/min. The TGA of the samples was measured using DSC-TGA PL.STA625 at 10°C/min.

Morphology Observations

The notched Izod fracture surfaces of the samples at room temperature were sputtered with gold in vacuum and studied by using SEM with a Cambridge Stereoscan S360 (Cambridge Biotech, Rockville, MD).

RESULTS AND DISCUSSION

Mechanical Properties

In POM/TPU blends POM is the matrix and TPU is the dispersed phase. The toughness of the POM depends on concentration, particle size, and par-

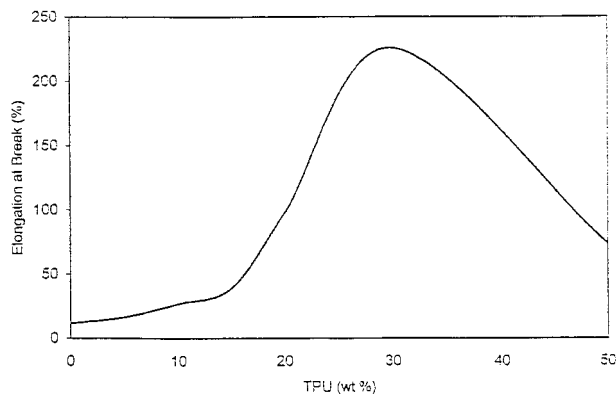


Figure 5 Effect of TPU content on elongation at break of POM/TPU blends.

Table III Effect of MDI on Tensile Strength, Modulus, and Elongation at Break of POM/TPU : 85/15 Blends

MDI (%)	Tensile Strength (MPa)	Modulus (MPa)	Elongation at Break (%)
0.5	40	865	24
1	42	885	31
2	45	903	42
3	50	919	57
4	42	881	35

ticle size distribution of the TPU and compatibility of the POM and TPU. Table II shows the impact strength, elongation at break, tensile strength, and MFI of the blends. Figure 1 shows that by increasing the amount of TPU, the impact strength increases (up to 15%) and then decreases, a result that can be attributed to the small particle size of the TPU and better compatibility at this concentration. By increasing the amount of TPU the coalescence of the TPU particles occurs and impact strength decreases. The toughening of the blends at low TPU content can be attributed to multiple crazing, shear yielding, and cavitation mechanisms.

The effect of MDI on the impact strength of the POM/TPU : 85/15 blends is shown in Figure 2, from which it can be seen that by increasing the amount of MDI, up to 3 parts per hundred rubber (phr), the impact strength of the blends increases and then decreases. The increase of strength can be the result of crosslinking (**Scheme 1**) of TPU and the compatibilizing effect of MDI, which reduced the TPU particle size and increased the compatibility. Isocyanate groups of MDI react by the end hydroxyl group of the POM chains. On the other hand, isocyanate groups can react by the urethane

Table IV Hardness of POM/TPU Blends

TPU content in the blends (wt %)	0	5	10	15	20	30	40
Hardness (Shore A)	80	79	77	75	74	71	68

Table V Effect of MDI on POM/TPU : 85/15 Blends

MDI content (phr)	0	0.5	1	2	3	4
Hardness (Shore A)	75	76	78	80	82	79

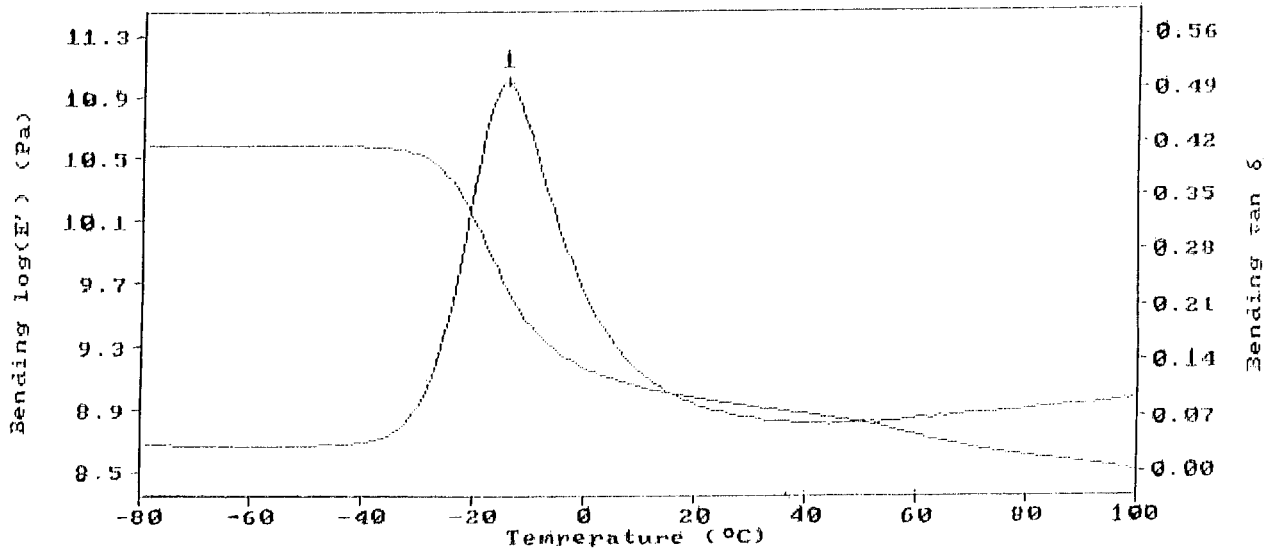


Figure 6 Storage modulus and tan δ traces of pure TPU.

group in the TPU chains, the result of which is a block copolymer (Scheme 2). By increasing the amount of MDI to more than 3 phr, the homopolymer of MDI with low molecular weight can be formed, which decreases the impact strength.

Figures 3, 4, and 5 show the tensile strength, modulus, and elongation at break of the blends, respectively. It can be seen that by increasing the amount of the TPU, the tensile strength and the modulus both decrease, but the elongation at break increases up to 30% then decreases. The addition of MDI to the POM/TPU : 85/15 blends

increases the tensile strength, Young's modulus, and elongation at break up to 3 phr, after which value these properties decrease (Table III). The reasons, as mentioned before, can be attributable to crosslinking and the compatibilizing effect of MDI. MDI in low concentration mostly acts as a crosslinking agent. For this reason we can see decreases in elongation at break at low MDI concentrations up to 2 phr (compared with that of blends without MDI), and then it increases because, in high concentration, the compatibilizing effect of MDI is predominant.

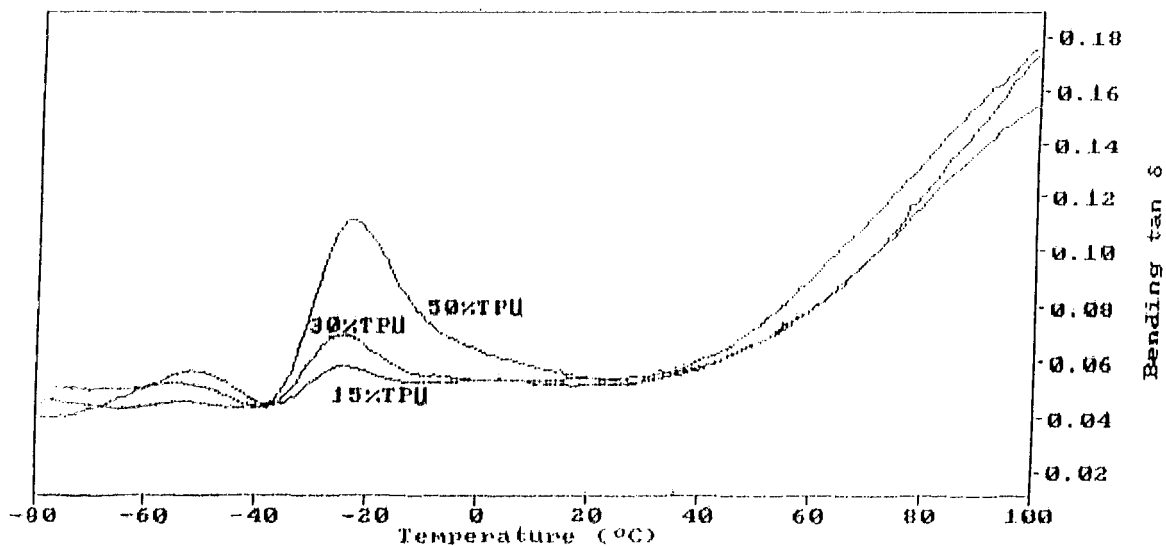


Figure 7 Tan δ traces of POM/TPU (85/15, 70/30, and 50/50) blends.

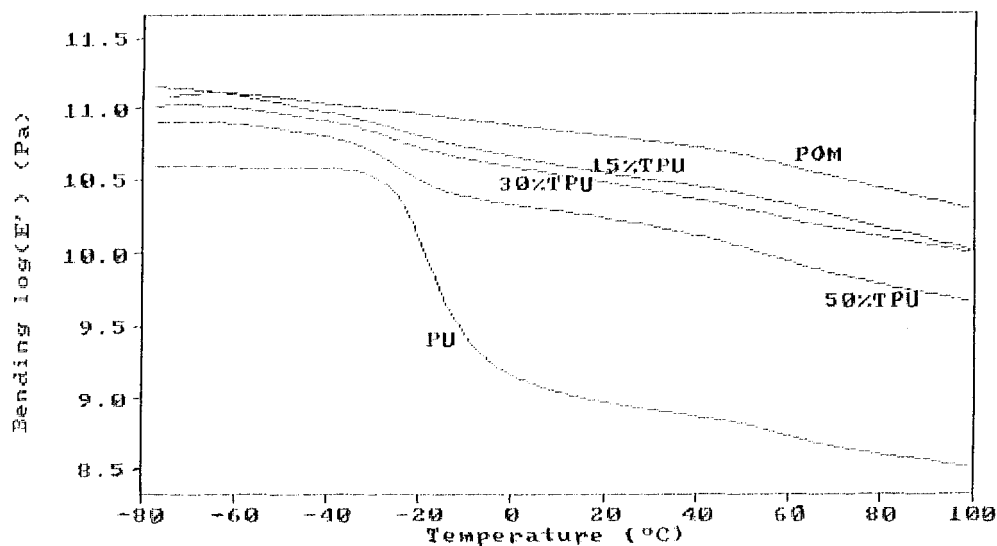


Figure 8 Storage modulus of POM/TPU blends with varying TPU content.

Table IV shows the hardness of the blends. It is obvious that by increasing the TPU content the hardness decreases, although it should be noted that the decrease in hardness is not too significant, especially up to 15% TPU in the blends. The effect of MDI content on hardness of POM/TPU : 85/15 blends is shown in Table V. It can be seen that by increasing the MDI contents (up to 3 phr), the hardness increases and then decreases. In low concentration of MDI, resulting from the crosslinking of TPU, the hardness is increased, and in high concentration of MDI (more than 3

phr) crosslinking is decreased and the homopolymer of MDI with low molecular weight is formed, resulting in a reduction in hardness.

Thermal Behavior

The DMTA traces show that POM/TPU blends are partially miscible. Figure 6 shows the bending storage modulus and $\tan \delta$ traces of pure TPU. It can be seen that the glass-transition temperature (T_g) of the TPU is about -15°C and from a similar curve for POM T_g was -73°C . The $\tan \delta$ traces of

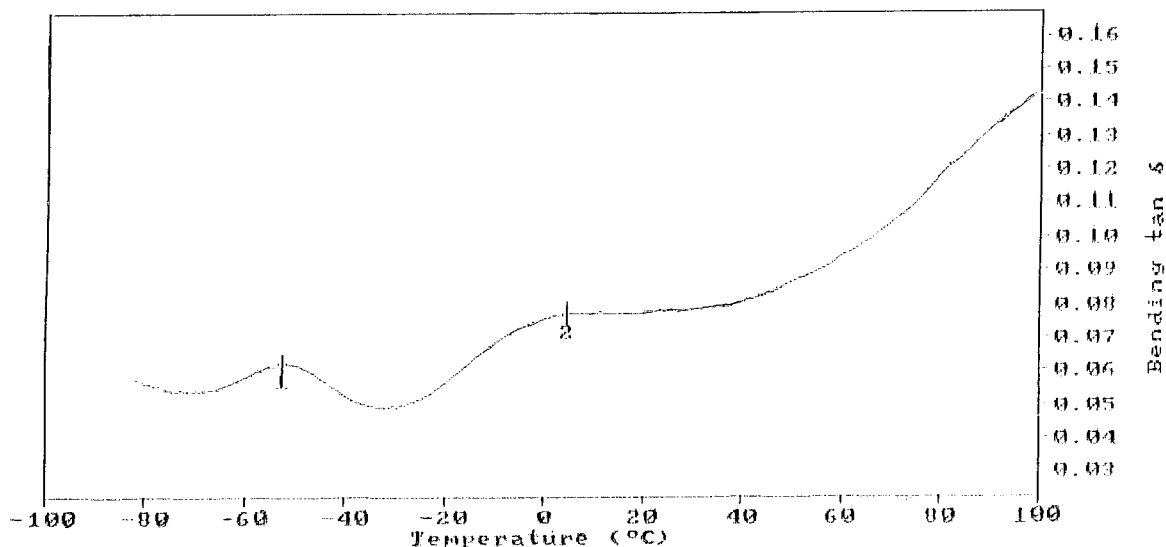


Figure 9 $\tan \delta$ traces of POM/TPU : 85/15 blends with 3 phr MDI.

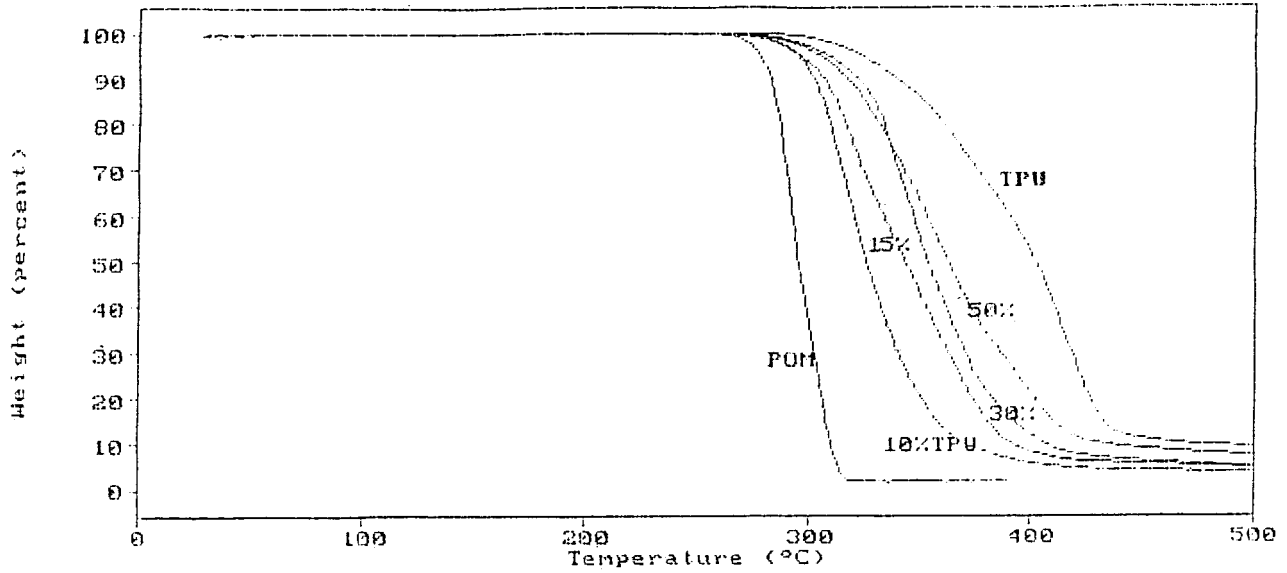


Figure 10 Thermal stability of POM, TPU, and POM/TPU blends.

the POM/TPU blends are shown in Figure 7, in which the traces of $\tan \delta$ show the shifts of the T_g values of TPU and POM toward each other, indicating partial miscibility of the blends. More shifts can be seen in the POM/TPU : 85/15 blend, which is correlated with better impact strength in this concentration of TPU. Figure 8 shows the storage modulus of POM/TPU blends. It can be seen that by increasing the TPU content (up to 50%) the storage modulus decreases, although not

significantly, thus indicating that POM is still the matrix phase and TPU is the dispersed phase. It means no phase inversion occurs, which correlates with the morphology observation.

Figure 9 shows the $\tan \delta$ trace of POM/TPU : 85/15 blends with 3 phr MDI. A comparison of Figure 9 and Figure 7 leads to the conclusion that by addition of 3 phr MDI to the blend, the height and damping energy increase, which correlates with the impact improvement of the blends. Our

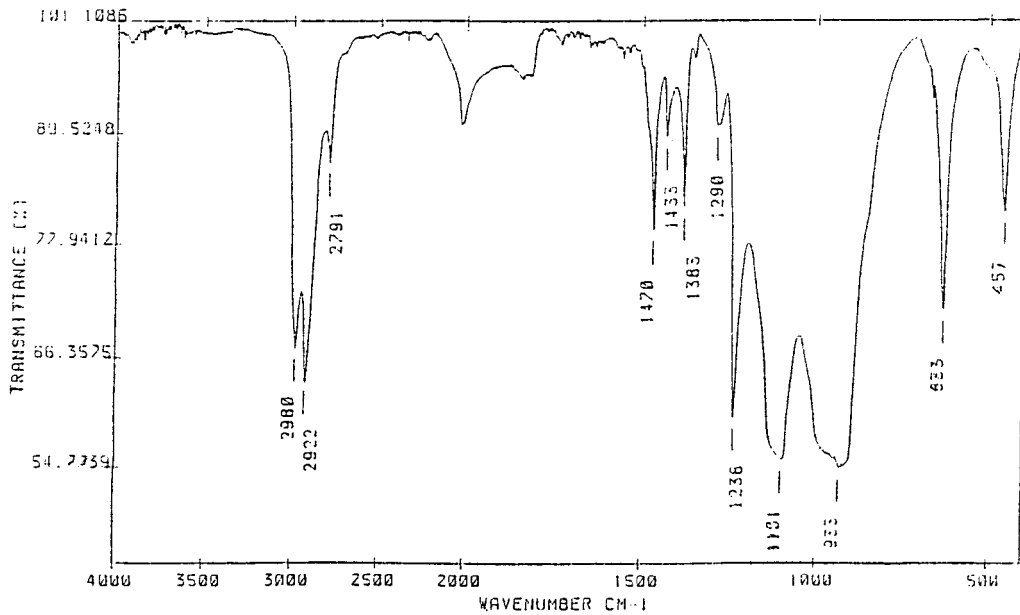


Figure 11 FTIR spectrum of POM.

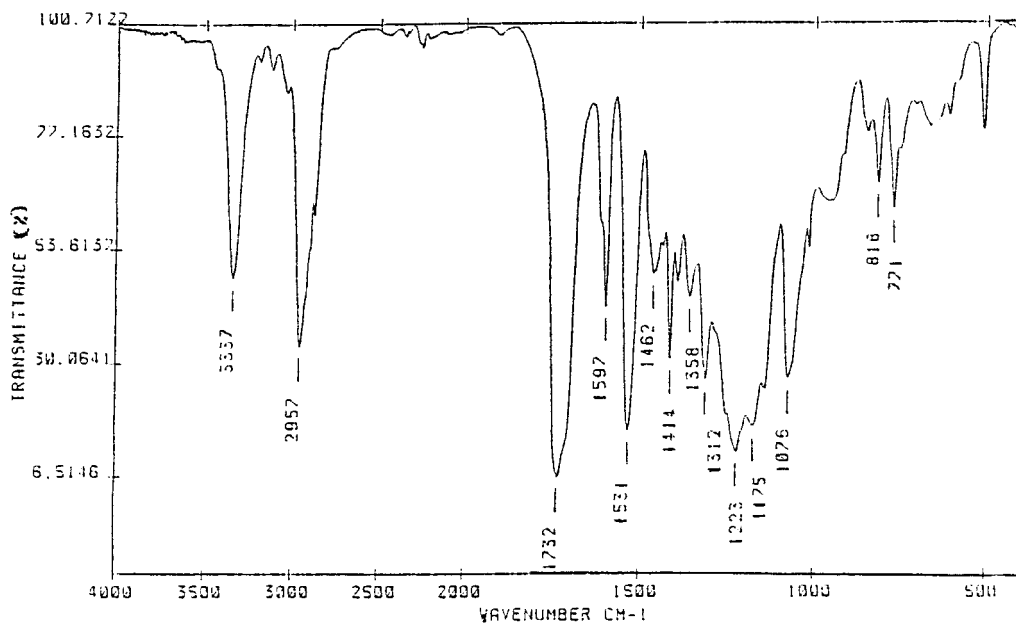


Figure 12 FTIR spectrum of TPU.

results show maximum height and damping are at 3 phr of MDI. Figure 9 also shows increasing in T_{g} of the TPU, which is the result of crosslinking of the TPU with MDI, as mentioned earlier.

Figure 10 shows the thermal stability of POM, TPU, and POM/TPU blends with varying TPU content. It can be seen that POM has a lower decomposition temperature than that of TPU (at

about 270°C) and has a sharp decomposition rate. By adding TPU to POM, the thermal stability and decomposition rate of the blends are improved.

FTIR Studies

Partial miscibility of the POM/TPU blends was also studied by FTIR. Figures 11, 12, and 13 show

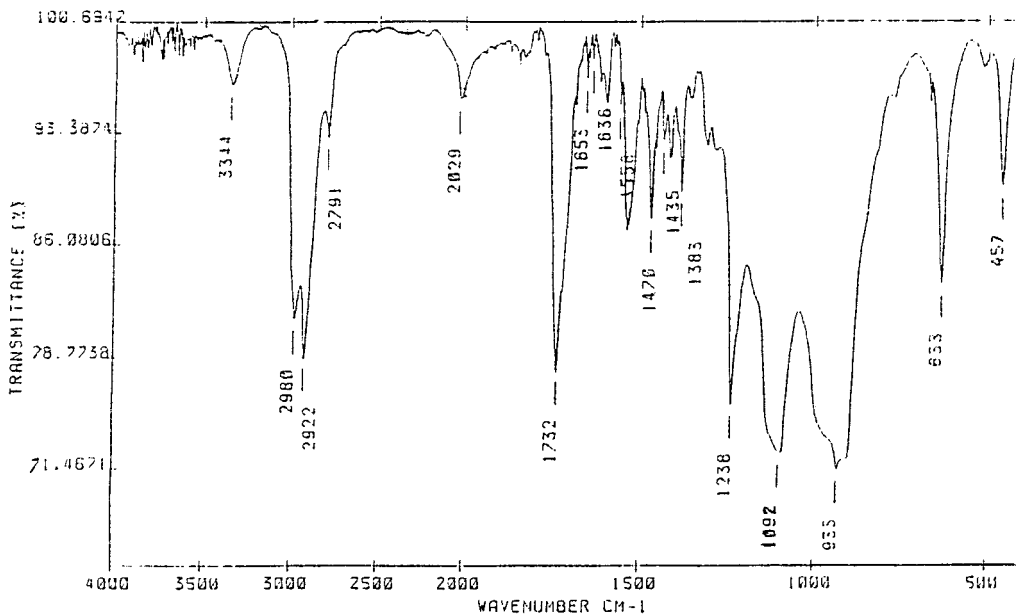


Figure 13 FTIR spectrum of POM/TPU : 85/15 blends.

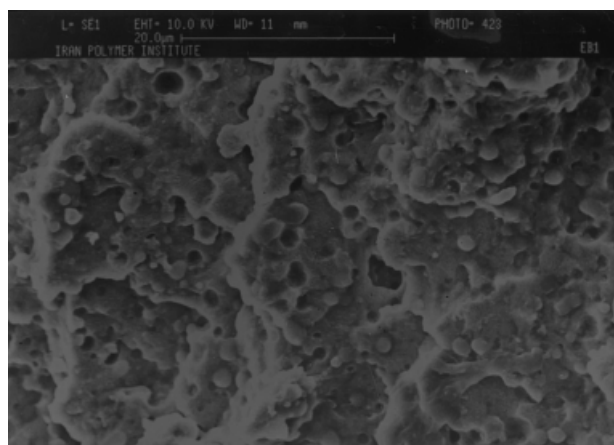
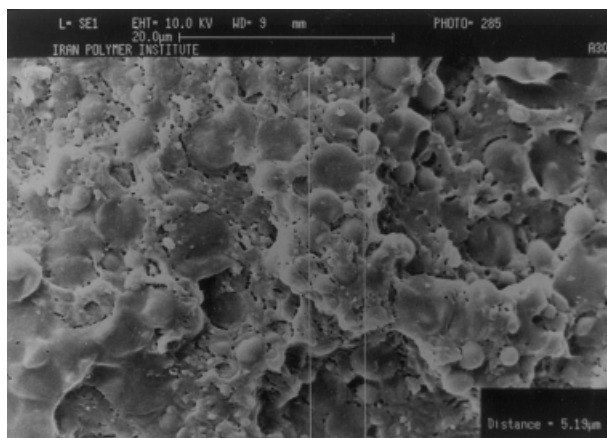
Table VI Wave Number (cm^{-1}) of N—H and C—O Groups of TPU, POM, and the Blends

POM/TPU (w/w)	Wave Number of C—O (cm^{-1})	Wave Number of N—H (cm^{-1})
100/0	1101	—
0/100	—	3337
95/5	1094	3339
85/15	1092	3344
70/30	1092	3339
50/50	1094	3339

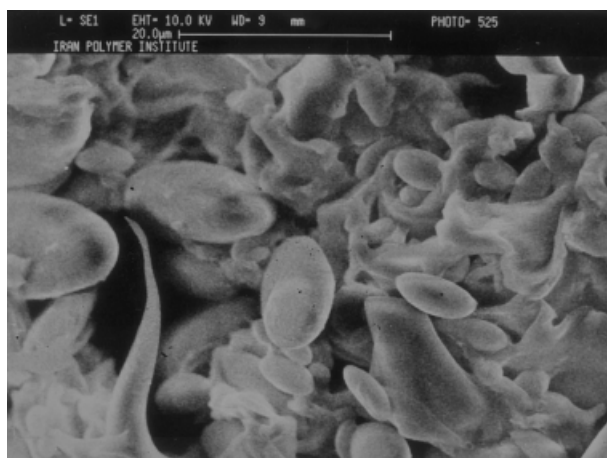
FTIR spectra of POM, TPU, and POM/TPU : 85/15 blends, respectively. It can be seen that the wave number of the N—H group in TPU and the C—O group in POM have been changed in the blend, which can be attributed to hydrogen bonding of the N—H group and the C—O group of POM and, as a result, better miscibility in the blends. Chiang and Huang⁴ also reported similar trends in POM/TPU blends. Table VI shows the wave number of NH and CO groups in POM, TPU, and the blends. As shown in this table more shift is related to the POM/TPU : 85/15 blend, which confirmed and is correlated to our results in impact strength and thermal behavior. MDI has no effect on the wave numbers of NH and CO groups.

Morphology Observation

The notched Izod fracture surfaces of the blends at room temperature were studied by using SEM. Figures 14, 15, and 16 show SEM micrographs of

**Figure 14** SEM micrograph of the fracture surface of POM/TPU : 85/15 blends.**Figure 15** SEM micrograph of the fracture surface of POM/TPU : 70/30 blends.

the fracture surfaces of the POM/TPU : 85/15, POM/TPU : 70/30, and POM/TPU : 40/60 blends, respectively. It can be seen that in all compositions, even in POM/TPU : 40/60 blends, that POM is the matrix and TPU is the dispersed phase. The TPU particles, up to about 30%, are spherical and then become more stretched and egg-shaped in appearance (Fig. 16). In the POM/TPU : 85/15 blend the particles are small and particle distribution is uniform, which correlates with better impact strength at this composition. As shown in Figure 17, by addition of 3 phr MDI to the POM/TPU : 85/15 blend, the fracture surface is characterized as a tough fracture surface. In blends with MDI more small particles can be seen and the particle distribution is more uniform than that in blends without MDI, which correlates with improvement in impact strength.

**Figure 16** SEM micrograph of the fracture surface of POM/TPU : 40/60 blends.

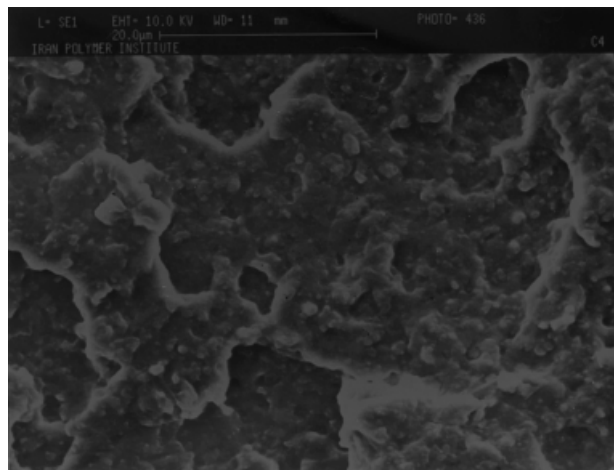


Figure 17 SEM micrograph of the fracture surface of POM/TPU : 85/15 blends with 3 phr MDI.

CONCLUSIONS

The maximum impact strength (about 10-fold more than that of pure POM) can be achieved in POM/TPU : 85/15 with 3 phr MDI as crosslinking agent and a compatibilizer. Dynamic mechanical and FTIR studies showed the partial miscibility of POM/TPU blends and that MDI improved the miscibility.

The SEM micrographs of the fracture surfaces of the samples showed the two-phase morphology of the blends and that the TPU is dispersed in POM as a matrix phase. Phase inversion of the POM/TPU blends occurred at a ratio of more than

POM/TPU : 40/60 and, up to this ratio, the TPU was still the dispersed phase. The shape of the TPU particles, up to 30%, is spherical and then changed to being egg-shaped. Using 3 phr MDI in the POM/TPU : 85/15 blends reduces the particle size of the TPU and improves the particle size distribution.

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