

Interfacial Reaction and Its Influence on Phase Morphology and Impact Properties of Modified-Polyacetal/Thermoplastic Polyurethane Blends

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ABSTRACT: The cationic polymerization of 1,3,5-trioxane, 1,3-dioxolane and a small amount of 2-hydroxyacetic acid (HAA) was carried out, and the resulting modified-polyacetal (POM) was blended with thermoplastic polyurethane (TPU) in melt. The results of ^1H NMR analysis indicated that HAA was almost incorporated in the modified-POM, and that the resulting carboxyl end-group and hydroxyl end-group in the modified-POM reacted with TPU during the melt blending. There were many boundary layers between the cavities and matrix in the modified-POM/TPU (82/18 by weight) blend that was etched with tetrahydrofuran (THF), and the diameter of the cavities became $\sim 0.3\text{--}1\ \mu\text{m}$ long when the blending time reached 10 min. The results

of scanning electron microscopic (SEM) observation and dynamic mechanical analysis (DMA) indicated that the modified-POM/TPU blend had a good compatibility because of the interfacial reaction between the modified-POM and TPU phase in the blend. The modified-POM/TPU blend exhibited higher Charpy impact strength when compared with a normal-POM/TPU blend; the toughness of the modified-POM/TPU blend attributed to the good compatibility between the two phases. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 100: 4375–4382, 2006

Key words: polyacetal; modification; blends; morphology; impact resistance

INTRODUCTION

Polyacetal (alternatively called polyoxymethylene (POM)) is a major engineering thermoplastic of industrial importance. POM is toughened with thermoplastic polyurethane (TPU) so as to widen its engineering applications industrially, such as clips, cramps, springs, and snap-fit parts. Several researchers^{1–13} investigated the toughened POM/TPU blends focusing on physical properties, fracture behavior, and toughening mechanism. It was reported that the toughness of the POM/TPU blends depend on the concentration of TPU,^{2–4,6,8,9,11} the interparticle distance of dispersed TPU phase^{10,13} and the compatibility between POM and TPU.^{12,13} With regard to compatibilizers for the POM/TPU blends, Mehrabzadeh et al. reported that 3% of diphenylmethane diisocyanate (MDI) in the POM/TPU (85/15 by weight) blend reduced the particle size of TPU and achieved the maximum impact strength,¹² and Gao et al. reported that polystyrene-*block*-poly(ethylene-butylene)-*block*-polystyrene grafted with maleic anhydride (SEBS-*graft*-MA)

enhanced the interfacial interaction between POM and TPU.¹³

Several modified-POM samples have been prepared, containing a variety of reactive groups as side chain branches from the main polymer backbone and as terminal groups on the polymer chain.^{14–20} Wissbrun reported that the POM copolymer of trioxane with epichlorohydrin comonomer reacted with thio glycolate to give modified-POM with carboxylic derivatives.¹⁹ Hermann et al. prepared a POM copolymer of trioxane with 2-hydroxyacetic acid methyl ester and reported that it incorporated carboxylic derivatives in POM.²⁰ Such modified-polymers with various functional groups, as well as compatibilizers, have potential as further improvement of mechanical properties of the POM/TPU blends from the viewpoint of interfacial reaction between POM and TPU, but the reaction and properties of the modified-POM in the POM/TPU blends have not been investigated so far. Moreover, the POM copolymer, prepared by cationic polymerization, possesses a hydroxyl end-group on the polymer chain,²¹ but the interfacial reaction of the hydroxyl end-group in the POM/TPU blends has not been investigated.

In this study, we prepared a novel modified-POM, namely, POM copolymer of trioxane and 1,3-dioxolane, with a small amount of 2-hydroxyacetic acid, and blended the modified-POM with TPU in melt. We investigated the interfacial reaction between modi-

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fied-POM and TPU in the blends focusing on the variation of concentration of functional groups in the modified-POM during the melt blending, and its influences on the phase morphology and impact properties of the modified-POM/TPU blends.

EXPERIMENTAL

Preparation of POM samples

To prepare the modified POM sample (POM-2), the cationic polymerization of 1,3,5-trioxane (TOX) with 1,3-dioxolane (DOX; 4.0 mol %) was carried out in the presence of 2-hydroxyacetic acid (HAA; 0.10 mol %) by using boron trifluoride as a catalyst. A continuous type reactor was used for the polymerization, and the reactor temperature was controlled to 80°C. The purified HAA was predissolved in DOX and was fed into the reactor. In the polymerization, DOX was used for the insertion of an occasional carbon-to-carbon linkage in the polymer chain for thermal and chemical stability of polymers. A small amount of dimethoxymethane was used for the adjustment of molecular weight as a chain transfer agent. The normal-POM sample (POM-1) was similarly prepared except the polymerization took place in the absence of HAA. Discharged raw polymers from the reactor were poured into a triethyl amine aqueous solution and then left overnight at room temperature so as to deactivate the catalyst. Polymers that resulted were posttreated by using an extruder at 200°C to remove unstable fractions.

Preparation of POM/TPU blends

The ether based TPU, Mirastran P480MSUD, was supplied by Nippon Mirastran Co. (Japan). Pellets of POM and TPU were dried in a vacuum oven before the melt blending. The POM/TPU (82/18 by weight) blends were prepared by melt blending in a TOYOSEIKI Labo Prastomill at 200°C. The melt blending was carried out for 5, 10, and above 10 min (partially). Screw rotational velocity was controlled to 50 rpm. To prevent thermal oxidative degradation of the samples, all experiments were performed with a nitrogen flow.

Polymer characterization

Fourier transform infrared (FTIR) spectra were obtained by using a Perkin-Elmer Spectrum One using KBr disks at room temperature. The samples were purified by dissolving in 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP) and reprecipitating with methanol before analysis. We tentatively confirmed that the polymer was insoluble in methanol, whereas HAA was soluble. The purified samples were dissolved in HFIP

again and were cast on KBr disks. The resulting disks were dried in vacuum.

To analyze the incorporation of DOX and HAA in the samples, ^1H NMR spectra were obtained at 35°C on a Bruker Avance 400 spectrometer operated at 400 MHz. The samples were purified by dissolving in HFIP and reprecipitating with methanol before analysis, and prepared by dissolving the samples in HFIP- d_2 . The deuterated solvent was used to provide an internal lock signal. The chemical shift was referenced to TMS as an internal standard. The mol composition of polymer was determined by using the following equations:

$$(\text{DOX}) = \{(A_{\text{C}_2\text{H}_4\text{O}}/2)/[(A_{\text{CH}_2\text{O}} + A_{\text{CH}_2\text{OC}_2\text{H}_4\text{O}} - A_{\text{C}_2\text{H}_4\text{O}}/2)/3 + A_{\text{C}_2\text{H}_4\text{O}}/2]\} \times 100 \quad (1)$$

$$(\text{HAA}) = \{A_{\text{CH}_2\text{COO}}/[(A_{\text{CH}_2\text{O}} + A_{\text{CH}_2\text{OC}_2\text{H}_4\text{O}} - A_{\text{C}_2\text{H}_4\text{O}}/2)/3 + A_{\text{C}_2\text{H}_4\text{O}}/2]\} \times 100 \quad (2)$$

where (DOX) is the mol % of DOX, (HAA) is the mol % of HAA and A_x represents the corresponding protons peak area.

To analyze the hydroxyl end-group concentration of the samples,^{22,23} ^1H NMR spectra were obtained at 45°C. The samples were trimethylsilyl-derivatized by dissolving in HFIP together with *N,O*-bis(trimethylsilyl) trifluoroacetamide and pyridine at room temperature, and held for 0.5 h. The resulting products were dried with a nitrogen flow, and prepared by dissolving the samples in HFIP- d_2 . The hydroxyl end-group concentration of polymer was determined by using the following equation:

$$(\text{OH}) = \{(2A_{\text{TMS}}/9)/[(A_{\text{CH}_2\text{O}} + A_{\text{CH}_2\text{OC}_2\text{H}_4\text{O}} - A_{\text{C}_2\text{H}_4\text{O}}/2)/3 + A_{\text{C}_2\text{H}_4\text{O}}/2]\} \times 100 \quad (3)$$

where (OH) is the mol % of hydroxyl end-group and A_{TMS} represents the peak area of protons of the trimethylsilyl unit whose chemical shift is at ~ 0.2 ppm.

Melt flow indexes (MFI) of the samples were measured at 190°C with a load of 2.16 kgf according to ASTM D-1238 on a melt indexer (Takara Kogyo Co., Japan). Weight-average molecular weight (M_w) was estimated from the following equation²⁴:

$$\text{MFI} = 1.30 \times 10^{18} \times M_w^{-3.55} \quad (4)$$

Phase morphology observation

Scanning electron microscopic (SEM) observation was performed on a HITACHI S-4700 at room temperature. The blended samples were cryogenically fractured in liquid nitrogen and etched with tetrahydrofuran (THF) for 1 h at room temperature so as to etch

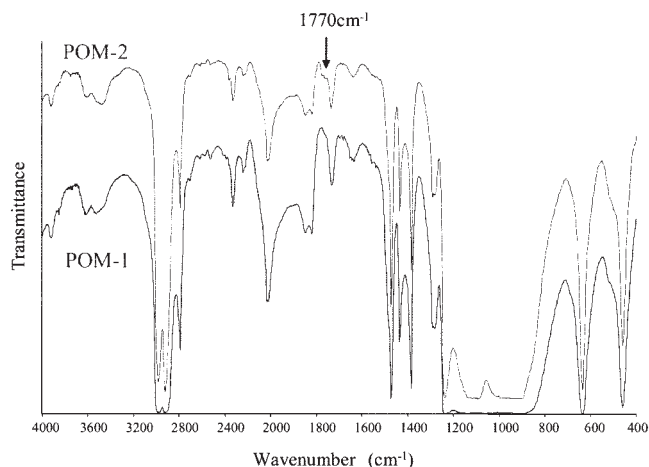


Figure 1 FTIR spectra of POM-1 and POM-2.

the TPU portion selectively. We tentatively confirmed that TPU was soluble in this condition. Resultant samples were washed by distilled water and acetone, and dried in a vacuum oven. Thereafter they were ion-sputtered with platinum and palladium in vacuum.

Evaluation of mechanical properties

Charpy impact strength test was carried out conforming to ISO-179/1eA. The specimens ($80 \times 10 \times 4 \text{ mm}^3$) were molded by using an injection-mold machine, and 45° -notch were made. The Charpy impact strength was measured with an impact tester (Yasuda Seiki Seisakusho Co., Japan) at room temperature. Five specimens of each sample were tested and the average values were reported.

Dynamic mechanical analysis (DMA) data of compression-molded specimens, 0.8 mm thick, were obtained with a Rheometric Scientific Solids Analyzer RSAIII equipped with liquid nitrogen cooling facilities. All experiments were performed at a heating rate of $6^\circ\text{C}/\text{min}$ and a frequency of 1 Hz under a nitrogen atmosphere. A small three-point bend clamp, whose support-to-support span was 40 mm long, was chosen for this investigation.

Evaluation of thermal behavior

Differential scanning calorimetric (DSC) measurements were performed with samples on a Perkin-Elmer DSC-7. About 10 mg of samples were used for these measurements. All experiments were performed under a nitrogen atmosphere. The samples were held at 200°C for 1 min to remove any thermal history, and cooled to 100°C at $10^\circ\text{C}/\text{min}$ to observe crystallization temperature (T_c) and the heat of crystallization (ΔH_c), they were then heated to 200°C at $10^\circ\text{C}/\text{min}$ to observe the melting point (T_m) and the heat of fusion

(ΔH_m). The instrument was calibrated with both indium and benzene.

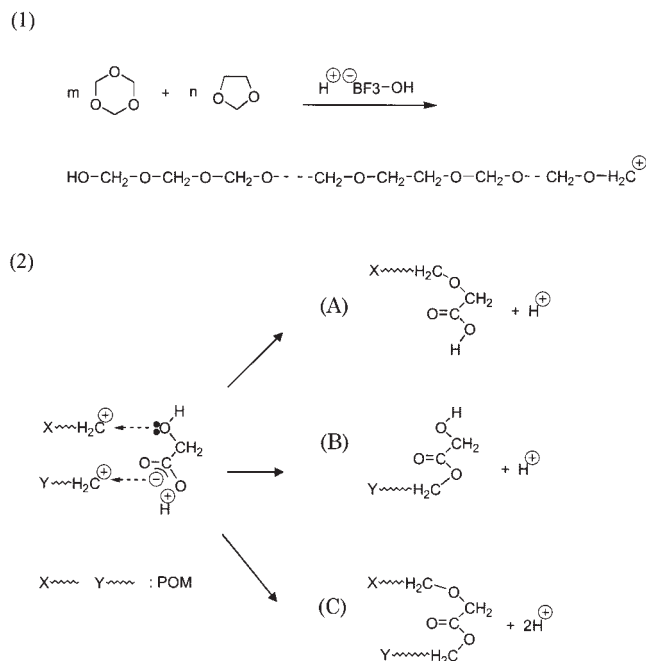
RESULTS AND DISCUSSION

Characterization of polymers

The polymer samples were characterized by using FTIR and ^1H NMR spectroscopy. Figure 1 shows the FTIR spectra of POM-1 and POM-2. In both the spectra, the absorption bands at $940\text{--}1100$, 1480 , and $2850\text{--}2950 \text{ cm}^{-1}$ were assigned to C—O—C stretching, CH_2 deformation and C—H stretching, respectively. In the POM-2 spectrum, the characteristic shoulder band at 1770 cm^{-1} was observed, and this band was assigned to the carbonyl group attributed to the incorporated HAA in POM-2.

During the cationic ring-opening copolymerization of TOX and DOX, the cationic active sites are expected to undergo chain transfer with HAA as shown in Scheme 1. The chain transfer reaction would be involved in three cases: (A) chain transfer with a hydroxyl end-group in HAA, which generates a carboxyl end-group in POM, (B) chain transfer with a carboxyl end-group in HAA, which generates a new hydroxyl end-group adjacent to the methylene-carboxylate unit in POM, and (C) chain transfer with both a hydroxyl and carboxyl end-group in HAA, which generates an ester unit in POM.

Figure 2 shows the ^1H NMR spectra of POM-2 and the corresponding magnified region. The new signal



Scheme 1 Polymerization of TOX and DOX in the presence of HAA: (1) cationic ring-opening copolymerization; (2) chain transfer to HAA.

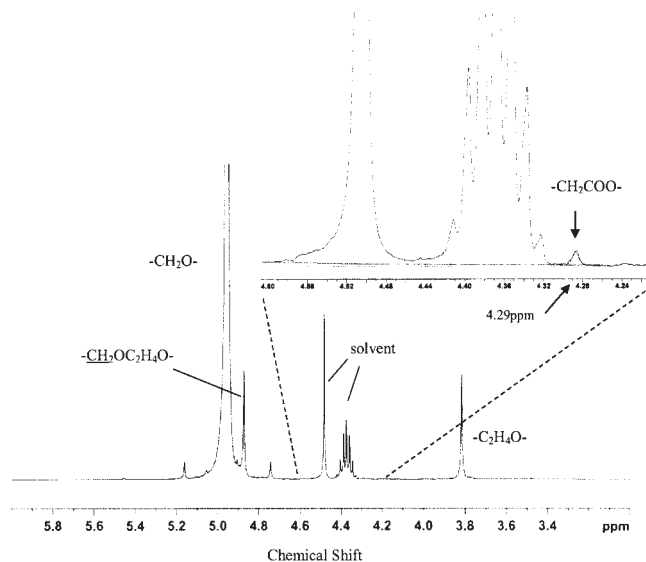


Figure 2 ^1H NMR spectrum of POM-2 and corresponding magnified region.

at 4.29 ppm was detected in the magnified spectrum. We tentatively confirmed that the signal of the methylene protons in HAA appeared at 4.26 ppm. Taking into account the chemical formula, the chemical shifts of the methylene protons adjacent to the carboxylate unit in both (A) and (C) were assigned to the signal at 4.29 ppm. On the other hand, those in both (B) and residual HAA were assigned to the signal at 4.26 ppm, and they were not detected in the spectrum as shown in Figure 2. Therefore, the NMR results imply that the HAA was incorporated as (A) and/or (C) in POM-2.

Table I shows the characterization results. The incorporated HAA content, calculated from the signal at 4.29 ppm, was equal to the fed amount, indicating that HAA was almost incorporated in POM-2. The DOX contents of both polymers were nearly equal to the fed amount. The hydroxyl end-group of POM-2, which was analyzed with the trimethylsilyl-derivatized sample, was higher as compared with POM-1, and the weight-average molecular weight of POM-2, estimated from MFI, was lower than that of POM-1. These results indicate that the generated protons during the

TABLE I
Characterization of Samples

Sample	POM-1	POM-2
DOX (mol %)	4.2	4.4
HAA ^a (mol %)	0	0.10
OH ^b (mol %)	0.16	0.22
MFI (g/10 min)	4.8	12.5
M_w^c	8.14×10^4	6.22×10^4

^a Methylene-carboxylate unit concentration.

^b Hydroxyl end-group concentration.

^c Estimated from MFI.²⁴

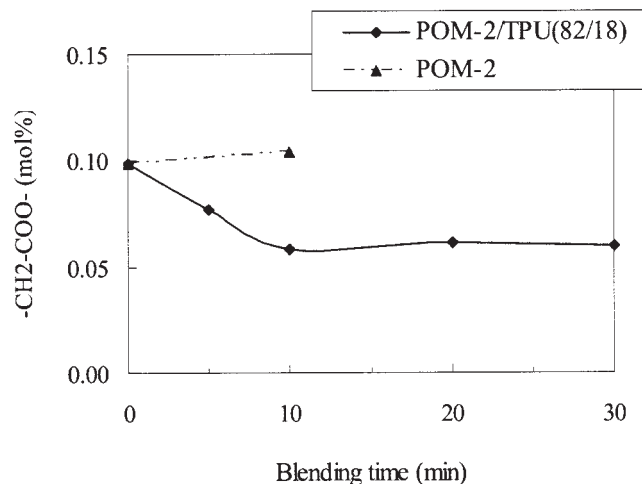


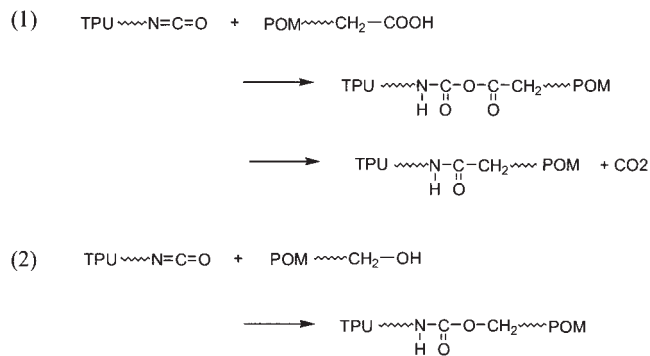
Figure 3 Blending time dependence on the concentration of methylene-carboxylate unit in POM-2/TPU (82/18) and POM-2.

chain transfer in each case, as shown in Scheme 1, were capable of reinitiation, and formed a hydroxyl end-group in POM.²⁵

NMR monitoring of functional groups

The variation of a methylene-carboxylate unit (carboxyl end-group and ester unit) concentration in POM during the melt blending was monitored. Figure 3 shows the blending time dependence on the mol % of the methylene-carboxylate unit, which was calculated from the signal at 4.29 ppm in the ^1H NMR spectra, in the POM-2/TPU blend. The mol % of the methylene-carboxylate unit in the POM-2/TPU blend decreased with prolonging the blending time up to 10 min, where ~ 0.04 mol % of decrease was detected, and then kept an almost constant value when the blending time was over 10 min. On the other hand, the mol % of the methylene-carboxylate unit in POM-2 did not decrease, when the blending time reached 10 min, as shown in Figure 3 for reference. TPU slightly decomposes at a higher temperature around 200°C ,^{26,27} and a small amount of isocyanate exists in TPU. The experimental results indicate that the carboxyl end-group in POM-2 [Scheme 1(A)] partially reacted with the isocyanate end-group contained in TPU during the melt blending [Scheme 2(1)].²⁸ In Figure 3, the constant value after 10 min was attributed to the ester unit, which was less reactive with TPU, in POM-2 [Scheme 1(C)].

The variation of hydroxyl end-group concentration in POM during the melt blending was also monitored. Figure 4 shows the blending time dependence on the mol % of the hydroxyl end-group, which was analyzed with the trimethylsilyl-derivatized sample, in the POM/TPU blends. The mol % of the hydroxyl



Scheme 2 Reaction in POM/TPU blends during the melt blending: (1) carboxyl end-group in POM-2 versus isocyanate end-group in TPU; (2) hydroxyl end-group in POM-1 and POM-2 versus isocyanate end-group in TPU.

end-group in both the POM/TPU blends decreased at 5 min, where ~ 0.07 mol % of decrease was detected, and then kept an almost constant value over 5 min. The decrease concentration of the hydroxyl end-group in each POM/TPU blend was almost the same during the melt blending. On the other hand, the mol % of the hydroxyl end-group in POM-2 did not decrease, when the blending time reached 10 min, as shown in Figure 4 for reference. These results indicate that the hydroxyl end-group in POM also partially reacted with the isocyanate end-group contained in TPU [Scheme 2(2)],²⁸ and that, in the case of the POM-2/TPU blend, both carboxyl and hydroxyl end-groups in POM-2 reacted with TPU during the melt blending.

Phase morphology of blends

The difference of phase morphology between the POM-1/TPU blend and POM-2/TPU blend was investigated. Figure 5 shows the SEM micrographs of

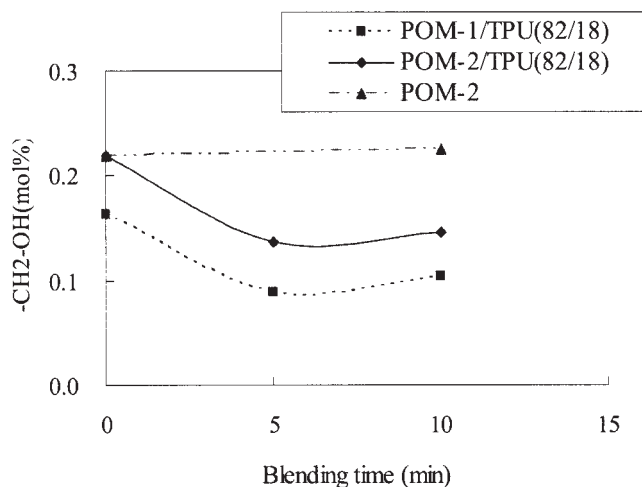
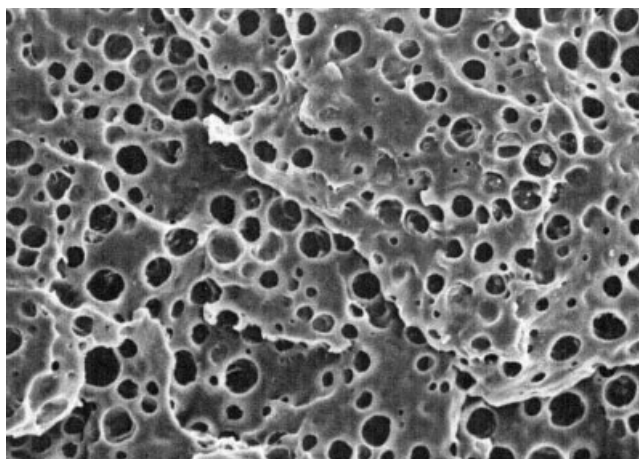
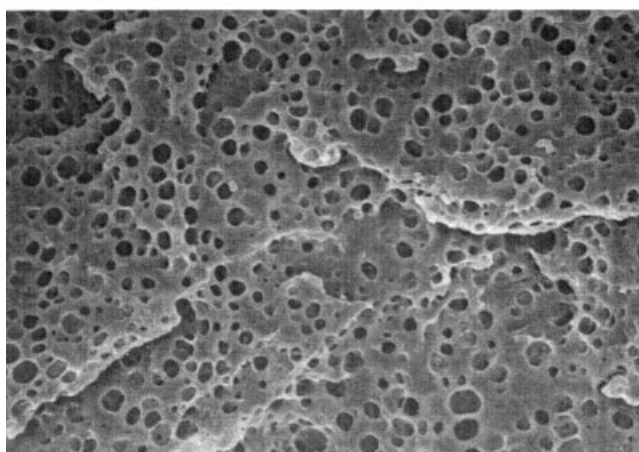


Figure 4 Blending time dependence on the concentration of hydroxyl end-group in POM/TPU (82/18) and POM-2.



(a)



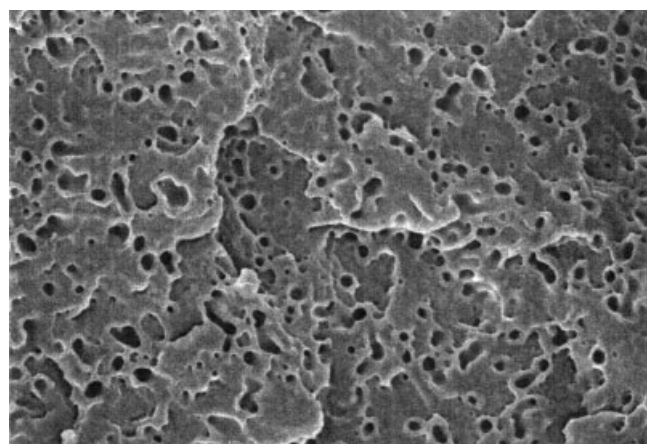
(b)

10 μm

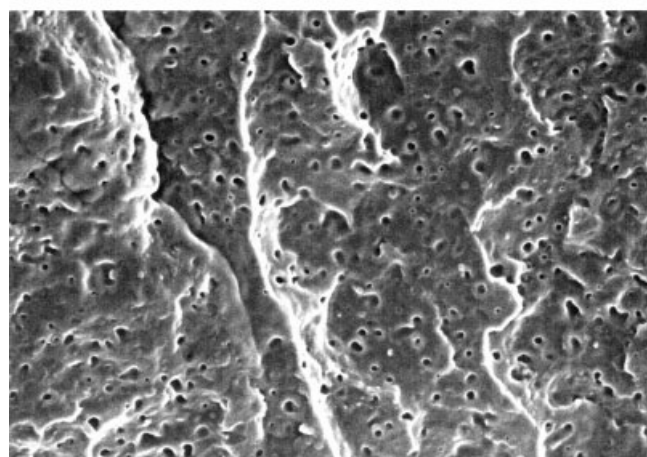
Figure 5 SEM micrographs of POM-1/TPU (82/18) etched with THF for 1 h: (a) blended for 5 min; (b) blended for 10 min.

the POM-1/TPU blend after etching. There are many sunken cavities in the matrix, and these cavities indicate the extracted TPU phase with THF. In this island-sea morphology, POM was the matrix and TPU was the dispersed phase. When the blending time reached 5 min, the diameter of the cavities was $\sim 1\text{--}3$ μm long in the POM-1/TPU blend [Fig. 5(a)]. When the blending time reached 10 min, the diameter of the cavities became $\sim 1\text{--}2$ μm long [Fig. 5(b)] and was slightly smaller as compared with the 5 min-blended one. The distribution of the cavities in the 10 min-blended sample was more uniform than that of the 5 min-blended sample.

Figure 6 shows the SEM micrographs of the POM-2/TPU blend after etching. It was clear that the diameter of the cavities in the POM-2/TPU blend was



(a)



(b)

10 μm

Figure 6 SEM micrographs of POM-2/TPU (82/18) etched with THF for 1 h: (a) blended for 5 min; (b) blended for 10 min.

smaller than those in the POM-1/TPU blend. When the blending time reached 5 min, the diameter of the cavities was $\sim 1 \mu\text{m}$ long in the POM-2/TPU blend, and the shape of the cavities was obviously irregular [Fig. 6(a)]. There were many boundary layers between the cavities and the matrix, and this morphology did not appear in the POM-1/TPU blend. These boundary layers were obviously insoluble in THF for 1 h. When the blending time reached 10 min, the diameter of the cavities became $\sim 0.3\text{--}1 \mu\text{m}$ long [Fig. 6(b)] and was relatively smaller as compared with that of the 5 min-blended sample. There were many boundary layers between the cavities and the matrix, similar to the 5 min-blended sample, as shown in the magnified photograph (Fig. 7).

These results from the observations imply that the interfacial reactant between POM-2, both carboxyl and

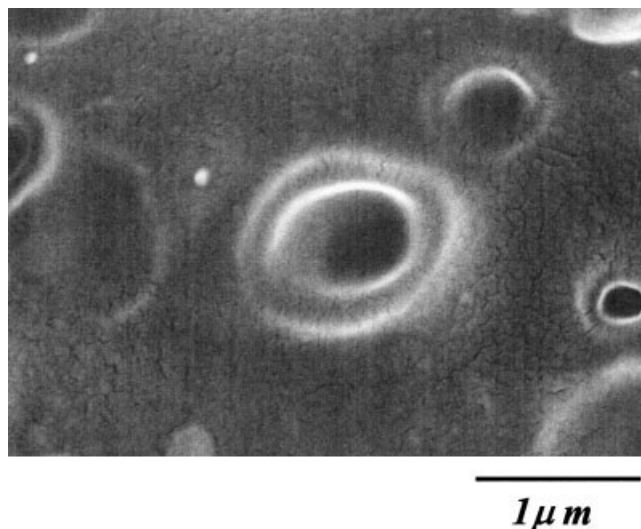


Figure 7 Magnified photograph of Figure 6(b).

hydroxyl end-groups, and TPU act as a high-potency compatibilizer between the dispersed phase and the matrix, resulting in the strong interfacial adhesion between two phases. With prolonging the blending time up to 10 min, the further interfacial reaction between POM-2, especially the carboxyl end-group, and TPU would promote the small diameter and uniform distribution of the dispersed TPU phase in the POM-2/TPU blend. On the other hand, in this work, the dependence of the decrease concentration of the hydroxyl end-group on the phase morphology was not clearly observed in the POM-1/TPU blend as shown in Figure 5; the 10 min-blended sample had smaller and more uniform cavities, but it had nearly the same decrease concentration of the hydroxyl end-group as compared with the 5 min-blended sample. It is interesting to compare the results with those obtained for the samples that have a different extent of reaction of the hydroxyl end-group, to further clarify the influence of the decrease concentration of the hydroxyl end-group on the phase morphology.

Impact properties of blends

The difference of the impact properties between the POM-1/TPU blend and the POM-2/TPU blend was

TABLE II
Impact Properties of POM and Blends

	Charpy notched impact strength ^a (kJ/m ²)	
	POM	POM/TPU (82/18) ^b
POM-1	6.1	12.5
POM-2	5.8	20.6

^a Tested at room temperature.

^b Blended at 200°C for 10 min.

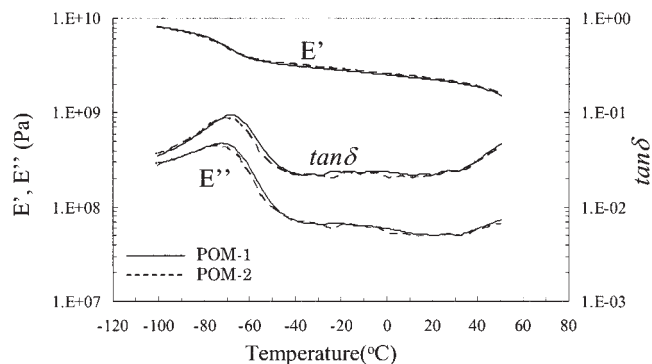


Figure 8 DMA test results at 1 Hz for POM-1 and POM-2.

investigated. Table II shows the impact strength of the 10 min-blended POM/TPU and POM. The POM-2/TPU blend exhibited a good impact-resistance property, and had higher Charpy impact strength as compared with the POM-1/TPU blend. The results indicate that the toughness of the POM-2/TPU blend attributed to the good compatibility because of the interfacial reaction between POM-2 and TPU^{12,13}; in the POM-2/TPU blend, the TPU phase adhered with the POM-2 matrix would stop craze growth and form a barrier to the expansion of crazing.¹²

Figure 8 shows the curves of the storage modulus (E'), loss modulus (E'') and loss tangent ($\tan \delta$) versus the temperature of the compression-molded specimens for POM-1 and POM-2. Both polymers showed almost the same curves respectively, and their glass-transition temperature (T_g) was approximately -70°C as shown in the curves of $\tan \delta$ and E'' . Figure 9 shows the DMA results of the compression-molded specimens of the 10 min-blended POM/TPU blends. The T_g of TPU was observed at around -50°C , and the T_g peak of TPU in the POM-2/TPU was larger than that in the POM-1/TPU as shown in the curves of $\tan \delta$ and E'' . This result correlates with the fact that the damping energy of the POM-2/TPU blend was higher than that of the POM-1/TPU blend, corresponding to the

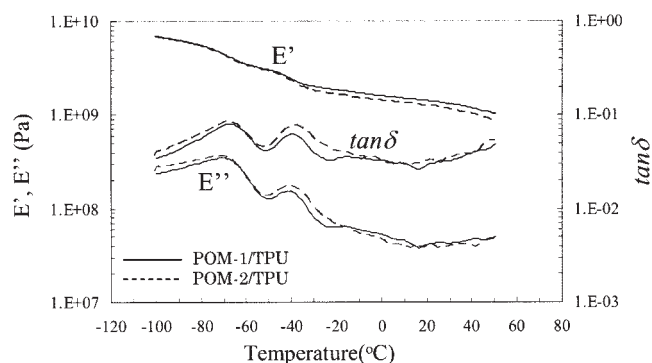


Figure 9 DMA test results at 1 Hz for POM/TPU (82/18) blended for 10 min.

TABLE III
DSC Analysis of POM and Blends

Sample	T_m ($^\circ\text{C}$)	T_c ($^\circ\text{C}$)	ΔH_m (J/g)	ΔH_c (J/g)
POM-1	166.0	144.2	146.6	139.6
POM-1/TPU (82/18) ^a	165.4	145.2	123.0	117.3
POM-2	165.9	144.2	149.5	145.9
POM-2/TPU (82/18) ^a	165.4	143.7	119.4	115.2

^a Blended at 200°C for 10 min.

good impact-resistance property of the POM-2/TPU blend.¹² Moreover, the E' of the POM-2/TPU blend was slightly lower than that of the POM-1/TPU blend over -40°C , indicating that the POM-2/TPU blend became softer as compared with the POM-1/TPU blend. These DMA results indicate that the POM-2/TPU blend had good compatibility because of the interfacial reaction between POM-2 and TPU in the blend.

Table III shows the DSC analytical results of the 10 min-blended POM/TPU and POM. The melting temperature (T_m) and crystallization temperature (T_c) of POM-1 and POM-2 was almost the same. The heat of fusion (ΔH_m) and the heat of crystallization (ΔH_c) of the POM/TPU blends became relatively lower because of the blending with TPU. There was a slight difference in thermal behavior between both blends; the crystallization temperature (T_c) of the POM-2/TPU blend slightly lowered as compared with POM-2, whereas those of the POM-1/TPU blend slightly heightened as compared with POM-1. Moreover, the heat of fusion (ΔH_m) and heat of crystallization (ΔH_c) of the POM-2/TPU blend were slightly lower than those of the POM-1/TPU blend. These results correspond to the difference of the E' in both blends as mentioned earlier, also attributed to the difference of the interfacial reaction between the POM and TPU phase in both blends.

CONCLUSIONS

The cationic polymerization of TOX, DOX, and a small amount of HAA was carried out, and the resulting modified-POM (POM-2) was blended with TPU in melt. The results of the ^1H NMR analysis indicate that HAA was almost incorporated in the polymer, and that the resultant carboxyl end-group and hydroxyl end-group in POM-2 partially reacted with TPU during the melt blending. There were many boundary layers between the cavities and the matrix in the POM-2/TPU (82/18) blend that was etched with THF, and the diameter of the cavities became $\sim 0.3\text{--}1\ \mu\text{m}$ long when the blending time reached 10 min. The results of SEM observation and DMA indicate that the POM-2/TPU blend had good compatibility because of the interfacial reaction between the POM-2 and TPU phase

in the blend. The POM-2/TPU blend exhibited higher Charpy impact strength as compared with a normal-POM (POM-1)/TPU blend; the toughness of the POM-2/TPU blend attributed to the good compatibility between the two phases.

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