

Characterization and Properties of Thermoplastic Polyether Elastomer/Polyoxymethylene Blends Prepared by Melt-Mixing Method

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Abstract—Thermoplastic polyester elastomer is a block copolymer comprising polyester hard segments and polyether soft segments. The soft section gives elasticity, making it rubbery; the hard section gives the same processing properties and mechanical strength as engineering plastic has. In this paper, the thermoplastic polyester elastomer/polyoxymethylene composites were prepared by melt extrusion and the content of thermoplastic polyester elastomer in the blends was 5, 10, 15, 20 and 25 wt %, respectively. The compatibility of composites was studied by DSC, FTIR, SEM and DMA. The mechanical tests showed that the notched impact strength and the elongation at break of the blends were significantly better than pure polyoxymethylene.

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INTRODUCTION

Copolyoxymethylene resin (POM), also named polyacetal, a kind of widely used engineering plastics, is synthesized by polymerization of triformaldehyde as a monomer (trioxane) and dioxane or ethylene oxide as a comonomer [1]. Due to strong intermolecular forces and high crystallinity that can reach above 70% [2], POM resin has many excellent properties, such as high tensile strength, flexural modulus, excellent self-lubricating creep. However, the toughness of POM is not so good and at low temperatures (<0°C) the polyacetal products become brittle and this may limit its application. For example, the fastener of automobile's side door or safety belt are mostly made of POM resin. If used in warmer zones, such as in tropical, subtropical and temperate regions, the material of above products can be general brand polyacetal. However, in subfrigid zones or frigid zones, the modified POM toughened by various elastomers must be used which can work at low temperature for a long time. Another shortage of this high crystalline structure is the problem of mold shrinkage [3], because the crystallization rate and the crystallinity of POM are higher than of most other resins. Dimensional stability of POM resin products is worse than that of others. For example, the mold shrinkage of POM is 1.9–2.3, while that of acrylonitrile butadiene styrene resin (ABS) is 0.4–0.7 and

polycarbonate is 0.8. Through modification research, the low temperature performance and high shrinkage of POM can be improved by, for instance, toughening modification or filling modification, etc.

The most effective way to improve impact strength, enhance low temperature resistance and reduce mold shrinkage of POM resin is using thermoplastic elastomers or structural plastics of high flexibility [3]. These soft materials could not only absorb or disperse stress and energy acting on the modified POM, but also reduce the crystallinity of POM. It could be explained by the crazing phenomenon [4, 5]. Like other elastomer toughening materials, POM compounds toughened by the soft materials had the similar sea-island structure [6], which provides the composites with high toughness and good notched impact strength [7–9]. When these modified materials are subjected to stress, white cracks occur at the interface between the rubber particles and the base resin, that is the craze. When the materials are destroyed by the stress, the formation of craze will absorb a lot of energy, which giving the materials high impact strength. In addition, adding elastomer to POM resin could reduce the crystallization rate and crystallinity, thereby improving the dimensional stability of the materials [10].

Many toughened POM materials modified by different elastomers have been reported in literature. For

Table 1. Experimental formula of POM/TPEE blends

Sample	1	2	3	4	5	6
POM	100	95	90	85	80	75
TPEE	—	5	10	15	20	25
1010	0.25	0.25	0.25	0.25	0.25	0.25
White oil	Appropriate amount					

example, these elastomers could be poly(lactic acid) [11, 12], acrylate elastomer [13, 14], poly(ethylene oxide) [15, 16], ABS [17], acrylonitrile butadiene elastomer [18], methyl methacrylate-styrene-butadiene copolymer [19], polyolefin elastomer [20], thermoplastic polyurethane [21–23] and so on. Among these materials, thermoplastic polyurethane was the most widely used one, because the soft segment of polyurethane had good toughness and the hard segment was compatible with POM. However, the tensile modulus and low temperature resistance of thermoplastic polyurethane were not as good as that of other materials such as thermoplastic polyester elastomer (TPEE) [24–26] or thermoplastic polyamide elastomer [27–29] that would ultimately affect the comprehensive properties of modified POM.

In this article, TPEE was used as a flexibilizer to modify POM and prepare TPEE/POM blends by melt-mixing method. The characterization and properties of the blends were fully investigated. The goals of this study were to research the effects of the blend ratio on properties and morphology of the TPEE/POM system and to enhance the performances of POM through melt blending.

EXPERIMENTAL

Materials

TPEE (CH4132) with shall hardness equal to 38, melt flow index 14.598 g/10 min at 190°C/2.16 kg, brittle point of -50°C, melting point of 156°C was purchased from SUNPLAS Co., China. The

POM (MC90) was manufactured by Methanol Branch of Shenhua Ningxia Coal Industry Group., China, with melt flow index of 9.142 g/10 min at 190°C/2.16 kg, density of 1.40 g/cm³, melting point of 165–168°C, $M_w = 180$ and dispersity of 2.7.

Antioxidant (Irganox 1010) was purchased from Rianlon Corporation, China. The melting point is 120°C, volatile matter content is $\leq 0.5\%$, ash content is $\leq 0.1\%$.

White oil (industrial grade 15#) was supplied by Petrochina Corporation, China.

Sample Preparation of POM/TPEE

Blends of TPEE and POM were prepared in a twin screw extruder with the ratio of screw length to diameter equal to 40 and diameter 26 mm (ZSK26, Coperion GMBH, Germany). The proportions of TPEE and POM in the experiment were respectively 5/95, 10/90, 15/85, 20/80, 25/75 (Table 1). To prevent TPEE and POM oxidative degradation during melting extrusion, 2500 ppm Irganox 1010 was added to each experiment. A proper amount of white oil was also needed in order to improve the dispersion of antioxidant.

Test Methods

Melt Flow Rate (MFR) of the POM/TPEE materials was measured by melt index instrument (JJ-Test Materials Testing Industry CO., LTD, China, Type: MFI-2322). According to the international-standard test method for Melt Index (ISO 1133), the test temperature was 190°C and the test sample load was 2.16 kg [30].

The tensile and bending test splines were molded by injection using HAAKE MiniJet-II. The mold model of tensile spline was 557-2298, the mold model of bending spline was 557-2296: 80 × 10 × 4 mm. The tensile properties of the specimens were characterized by the test according to ISO527-2 and the bending properties according to ISO178:2001 on Universal Material Testing Machine (INSTRON 5966). The stretching rate was 50 mm/min and the bending speed was 2 mm/min. An Impact testing machine (INSTRON CEAST 9050) was used for measuring notched Charpy strength (the mold model of Impact testing spline is 557-2296: 80 × 10 × 4 mm). All of the test samples were placed in the Constant Climate Chambers (BINDER, Model KBF 240) for 40 h state adjustment at 23 ± 2°C and 50 ± 5% relative humidity. The above mechanical tests were also performed at 23 ± 2°C and 50 ± 5% relative humidity.

DSC was performed on a NETZSCH DSC 200F3. The measurements were conducted in nitrogen atmosphere (20 mL/min) with a heating and cooling rate of 20 deg/min. The samples were heated from 30 to 200°C and then maintained at 200°C for 5 min to eliminate their thermal history. The samples were subsequently cooled down to 30°C and stayed in this temperature for 5 min before being reheated back to 200°C [31].

FTIR spectra of the specimens were carried out on a BRUKER Vertex 70 FTIR spectrometer (Bruker Daltonics Inc.). The test specimens were made into small pieces of films by using melt-pressing method operated on the thermal platform [32, 33].

The sample was fractured in liquid nitrogen, etched by the mixed solvent (the ratio of acetone to chloroform was two to three) at 40°C for 8 h, and then dried in a vacuum at 60°C. The surface of the sample was

coated with a thin layer of gold. Phenom PRO PW-100-016 scanning electron microscope was used at 10 kV [34].

The experimental investigations were carried out on a NETZSCH 242E DMA system in nitrogen atmosphere (50 mL/min). During testing, the scanning frequency was 5 Hz, the heating rate was 3 deg/min and the range of temperature was from -100 to 100°C [35]. The spines were molded by injection; the mold model was 557-2296: $60 \times 10 \times 3$ mm.

RESULTS AND DISCUSSION

Usually if two different thermoplastic materials are mixed by melt blending, the MFR of the product will differ from that of the two raw materials. As shown in Table 2, with the increase of TPEE content, the MFR of POM/TPEE composite is increased gradually.

It is well known that the toughness of polyformaldehyde can be significantly improved by blending

Table 2. Melt index of the POM/TPEE blends

Sample	1	2	3	4	5	6
MFR, g/10 min	9.142	9.273	9.480	9.522	9.712	10.146
Content of TPEE	0	5%	10%	15%	20%	25%

modification with elastomers. In this paper, the thermoplastic polyether ester CH4132 is used as a modifier to improved the toughness of POM MC90. Unlike general rubber-based elastomers, vulcanization is not required and TPEE can provide better toughness and melt fluidity for the TPEE/POM blends. Figure 1a shows that if the content of CH4132 is increased, the toughness of composite materials (notched Charpy impact strength and elongation at break) will be improved accordingly. At the same time, the rigidity and strength of blends (tensile strength and flexural modulus) will be reduced as exhibited in Fig. 1b. From the curve of notched Charpy impact strength, the

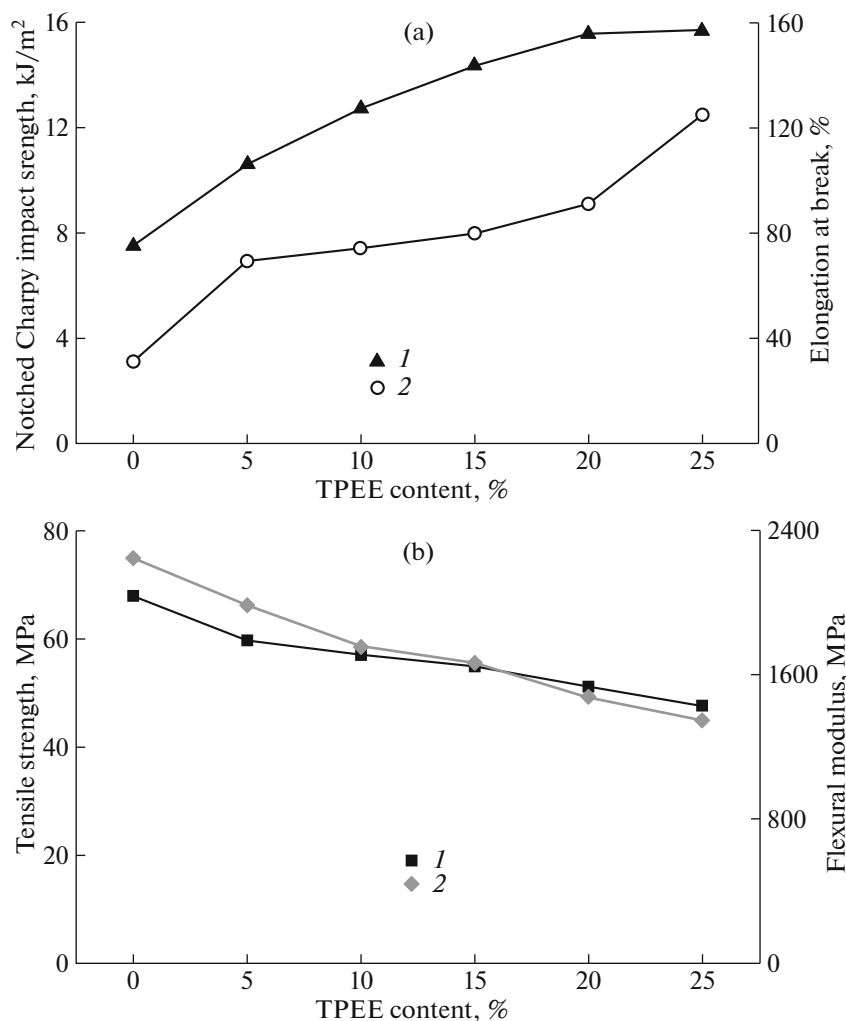


Fig. 1. Mechanical performances of TPEE/POM with different content of TPEE: (a) (1) notched Charpy impact strength and (2) flexural modulus curves; (b) (1) tensile strength and (2) elongation at break curves.

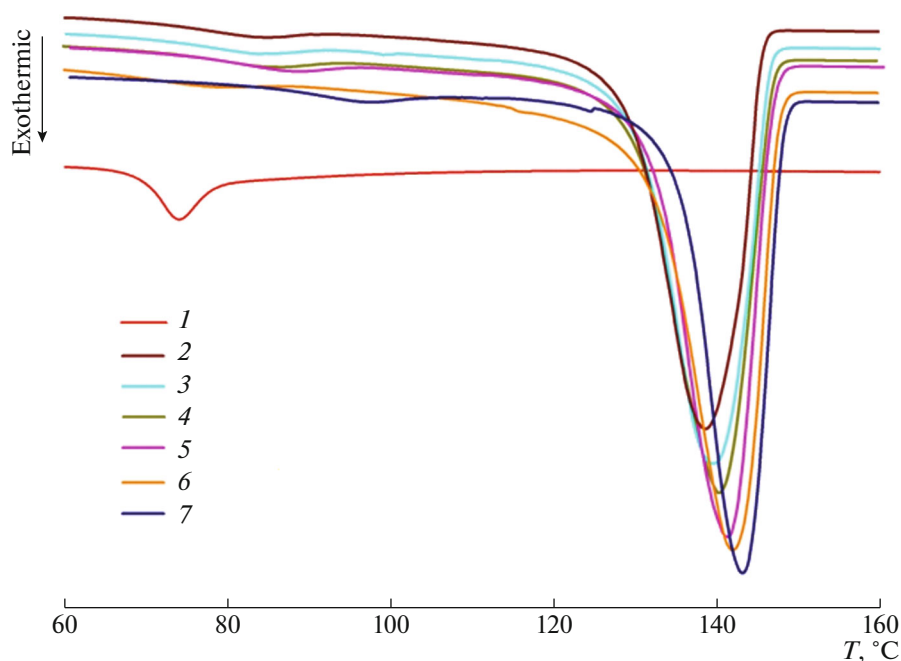


Fig. 2. (Color online) DCS crystallization exothermic curves of (1) pure TPEE, and TPEE/POM blends: (2) 25/75, (3) 20/80, (4) 15/85, (5) 10/90, (6) 5/95, and (7) pure POM.

value of the modified POM blend containing 20 parts of CH4132 reached 15.57 kJ/m^2 , which is twice the value of POM MC90.

The influence of the content of CH4132 on the crystallization behavior of the POM blends is evaluated by means of DSC analysis (Fig. 2). The crystallization peak temperature of MC90 is 143°C and that of CH4132 is 71°C , which means for pure MC90 and pure CH4132 the former is easier to crystallize than the latter during the cooling process from high temperature to low temperature. Second the area of crystallization peak of MC90 is significantly larger than that of CH4132, that is to say the crystallinity of the former is obviously higher than that of the latter. This is because there are some hard segments and most soft segments in TPEE CH4132, the hard segment is crystalline but the soft segment is amorphous. At last for the TPEE/POM blends, the crystallization temperature of which shift toward the low temperature zone with the increase of CH4132 content from 143 to 138°C .

Figure 3 compares the FTIR spectra of POM, TPEE and TPEE/POM blend. The characteristic bands of TPEE observed at 2844 and 2925 cm^{-1} can be assigned to the CH stretching on the benzene ring of the TPEE chain; band at 1720 cm^{-1} represents the stretching vibration of the carboxyl group; bands at 1408 and 1520 cm^{-1} are assigned to C–C absorption of benzene rings; band at 727 cm^{-1} is the bending vibration peak of CH on the benzene ring.

The bands at 2844 and 2925 cm^{-1} are assigned to the CH stretching of POM molecular chain; at

1238 cm^{-1} represents the C–C absorption of comonomer (such as dioxolane or epoxyethane); bands at 1081 and 881 cm^{-1} are assigned to the C–O and C–O–C absorption of POM; band at 632 cm^{-1} is assigned to the OH bending.

The characteristic bands of TPEE and POM as shown above can also be found on FTIR of the blend sample, but the positions of some characteristic bands have slightly drifted and the areas have also changed. These results indicate that it is feasible to prepare TPEE/POM composite mixed evenly by melt blending.

The morphological structures of fractured surface TPEE/POM blends etched by solvent are shown in Fig. 4. Figures 4a–4d exhibit the cross-sectional morphology of the polyoxymethylene blend samples with different TPEE content accordingly. The cross-section voids are formed after the TPEE elastomeric particles have been etched. In case of the blend containing 5% TPEE, a small number of TPEE elastomeric particles are dispersed in the POM matrix. When the TPEE content is increased to 10%, the TPEE elastomeric particles in the blend are increased correspondingly. At TPEE content to 15%, large number particles are uniformly dispersed on the matrix resin. If continue to increase the TPEE content to 20%, the size of the TPEE particles becomes larger, which indicating that TPEE particles are agglomerated to a certain extent in the polyoxymethylene matrix. These SEM tests show us TPEE can be easily dispersed in the POM matrix by melt mixing.

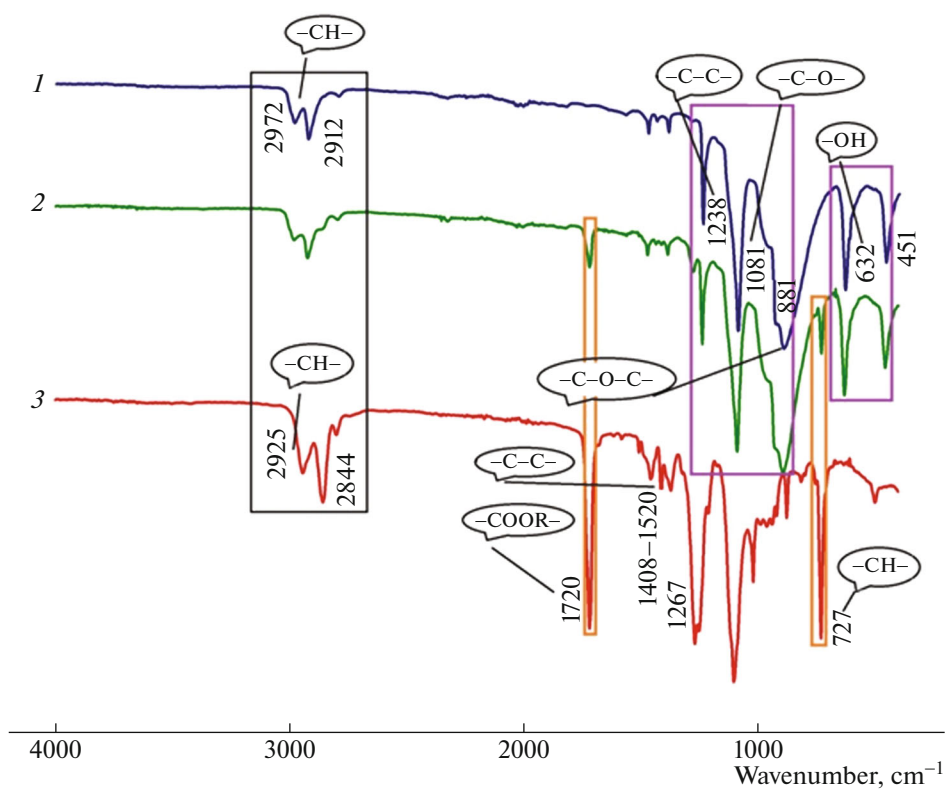


Fig. 3. (Color online) FTIR absorbance of (1) pure POM, (2) TPEE/POM (15/85), and (3) pure TPEE.

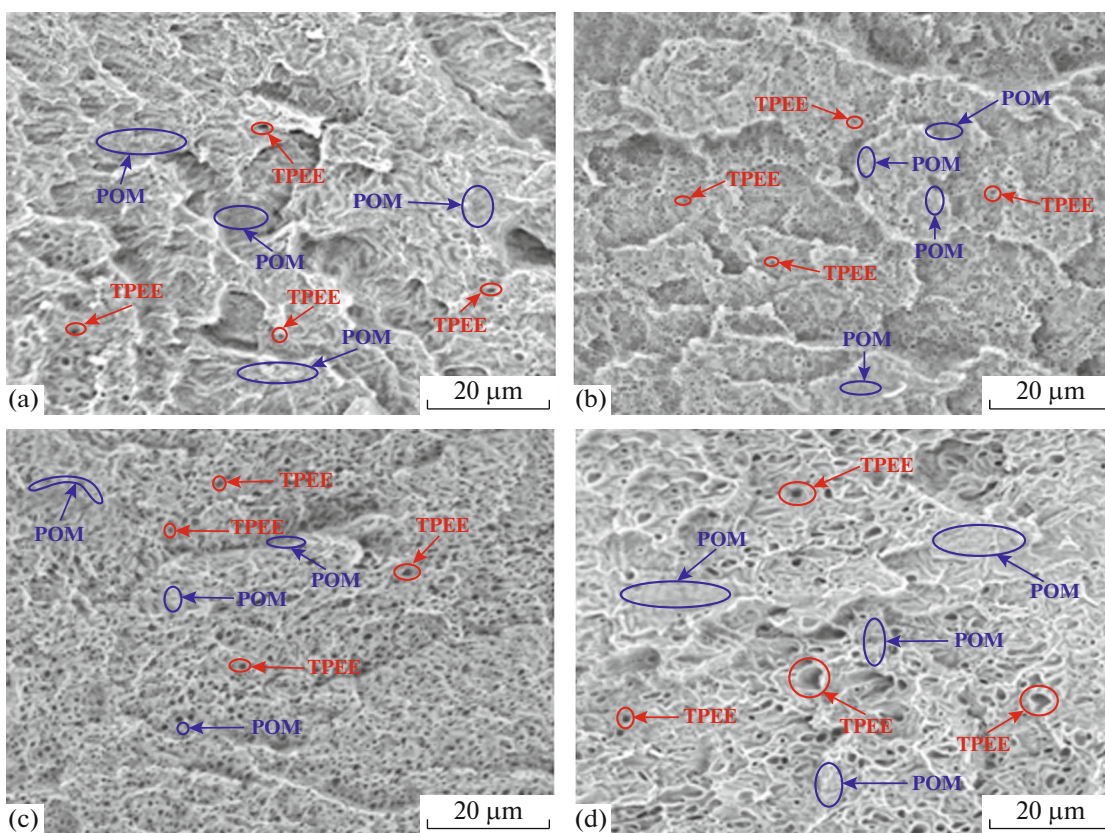


Fig. 4. (Color online) SEM images of TPEE/POM. TPEE content: (a) 5, (b) 10, (c) 15, (d) 20%. The TPEE particles were marked by the red arrows and the POM matrix was marked by the blue ones.

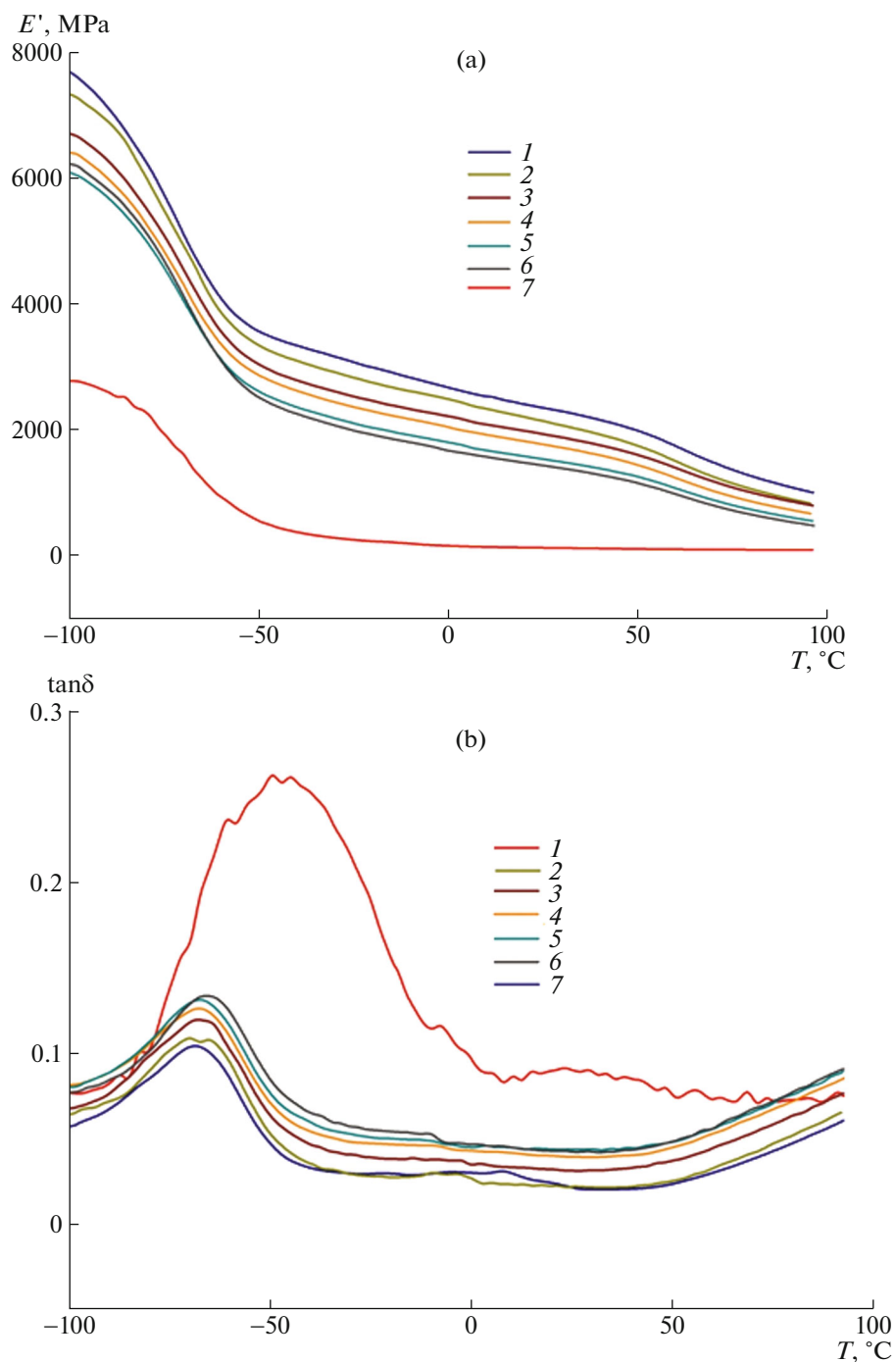


Fig. 5. (Color online) DMA of spectrum of (1) pure TPEE, POM, and TPEE/POM blends: (2) 25/75, (3) 20/80, (4) 15/85, (5) 10/90, (6) 5/95, and (7) pure POM. (a) E' curves and (b) $\tan \delta$ curves of TPEE/POM blends.

In this paper, the storage modulus E' and the loss tangent $\tan \delta$ of TPEE, POM and TPEE/POM blends at 5.00 Hz vibration frequency are studied by using dynamic mechanical analyzer. As is seen from Fig. 5a, the E' value of the pure POM is the highest in the test range from -100 to 100°C , but it is the smallest for the pure TPEE. For the TPEE/POM blends, the E' value lies between that of the POM and TPEE, and

decreases with the increase of TPEE content in the blend.

Figure 5b shows that the glass transition temperature T_g and $\tan \delta$ of the pure TPEE are higher than that of pure POM, and the $\tan \delta$ of the TPEE/POM blends increase regularly with the increase of TPEE content. The T_g of the blends drifts slightly to the right side of

the transverse axis with the increase of TPEE content. This is due to the better flexibility of POM molecule than that of TPEE, so the T_g of POM is lower than that of TPEE. In addition, TPEE contains amorphous polyether soft segments, which show the viscoelasticity of rubber materials, so the $\tan \delta$ of TPEE is much larger than POM and it increases with the rise of TPEE content in the blends.

CONCLUSIONS

This research is devoted to preparation and analysis of the properties of the novel melt TPEE/POM blends with varied component weight ratios. The DSC curves showed POM is easier to crystallize than TPEE and the crystallization temperature of the TPEE/POM blends shifted toward the low temperature zone with the increase of TPEE content. The FTIR results indicated that the characteristic bands of TPEE and POM can be observed in the spectra of the blends. From SEM images, the microparticles constituted by TPEE can be seen and the number of particles is related to the content of TPEE in the blends. The DMA results showed that there is one glass transition temperature which is between the two pure materials (TPEE and POM). The mechanical test results showed that the notched impact strength of the blend containing 20% TPEE reached 15.57 kJ/m², which is double of the POM. The above research results illustrate that TPEE is a good toughening modifier for POM.

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