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Synthesis and characterization of PMMA/PEG-TPE semi-interpenetrating polymer networks

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Abstract Two-component semi-interpenetrating polymer networks (Semi-IPNs) of thermoplastic urethane elastomer based on poly(ethylene glycol) and polymethyl methyacrylate were synthesized by the sequential technique. The Semi-IPNs obtained were characterized with respect to their mechanical properties such as tensile strength, elongation. Glass transition temperatures were carried out using dynamic mechanical thermal analysis. Phase morphology was studied by scanning electron microscopy. The effect of the compositional variation on the above-mentioned properties was examined. The results demonstrate that the components are immiscible, phase separation at the micrometer scale is observed, the extent of interpenetrating is dependent on variations in composition.

Keywords Semi-IPN · PMMA/PEG-TPE · Polyurethanes · Mechanical property

Introduction

In the manufacture of propellants, a polymeric substance is frequently employed as a binder to hold together fuel and oxidizer compounds of the propellant. The binder, the content can get to 12–20 wt% in the solid propellant, imparts dimensional stability and structural integrity to the grain and also acts as fuel during combustion [1, 2].

Hydroxyl terminated polybutadiene (HTPB) liquid prepolymers find extensive application as binders in composite solid propellants for launch vehicle technology since 1970s [2]. However, the crosslinked elastomers must be cast within a short period of time after addition of the curative. Disposal of a cast, crosslinked

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propellant composition is difficult, and usually is accomplished by burning, which poses environmental problems [3]. In view of the inherent disadvantages associated with the use of crosslinked elastomeric polymers as binder materials, there has been considerable interest in developing thermoplastic elastomers suitable as binders for propellants [4, 5]. Typical of these materials is the random block copolymer [poly(3-azidomethyl-3-methyloxetane]–poly[3,3-bis(azidomethyl)oxetane], also known as poly(AMMO/BAMO). However, the mechanical property of the azido solid rocket propellant is weak because of the structure of azido binder [6–8]. As a result, many thermoplastic elastomers fail to meet important requirements.

PEG is one of the most widely used polymeric binders in solid rocket propellants [9, 10] and its two-component networks with urethane linkages between PEG and isocyanate have also been used as the binder of rocket propellants, i.e. nitrate ester plasticized propellants, having excellent low-temperature mechanical properties [11, 12]. However, it has low rigidity when the PEG-TPE is plasticized with a large amount of nitrate ester. The rigidity is necessary for maintaining the dimensional stability, which is an important requirement for application of gun propellants. Interpenetrating polymer networks (IPNs) are a combination of two or more polymers in network form, with at least one such polymer polymerized and/or cross-linked in the immediate presence of the others according to the independent mechanism [13, 14]. Compositional variables are known to affect the degree of phase segregation, phase mixing, and hard-segment domain organization, and accordingly the polymer properties. Such systems were widely investigated [15, 16] and have been used in a variety of applications, pervaporation membrane [17–19], biomedical application [20], sound and vibration damping materials [8, 21, 22], and so on. Using as the binder of propellants, IPNs based on PEG-TPE are less reported in literature.

In this study, poly(ethylene glycol) based polyurethane thermoplastic elastomer were prepared firstly making use of good compatibility of PEG with gun propellant and Semi-IPNs based on PEG-TPE and polymethyl methacrylate (PMMA) were further synthesized. The properties were investigated with a view to developing improved materials for gun propellant applications by combining the mechanical properties of PMMA with the high elasticity of PEG-TPE. Although the solubility parameters of the two polymers are fairly close, the system is very immiscible, and coarsely phase separates existed in the system.

Experimental section

Materials

4′4-Diphenylmethane diisocyanate was obtained from Aldrich Chemical Co. (MDI, 98%, USA). All other chemicals were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). Poly(ethylene glycol) (PEG, 98%, molecular weight $M_n = 1{,}500\ \mathrm{g\ mol^{-1}}$) was dehydrated by vacuum distillation at 90 °C for 2 h. Methyl methacrylate (MMA, 98%) was stored over 4 Å molecular sieve for at least 2 weeks prior to use, its inhibitor, hydroquinone, approximately 100 ppm, was not removed. Benzoyl peroxide (BPO, 90%) was recrystallized in anhydrous ethanol. Ethylene glycol (EDO, 99.9%), ethylene glycol dimethacrylate (EGDMA, 90%) were used without further purification.

Preparation of PEG-TPE and PMMA

PEG-TPE was prepared as follows by using MDI (12.516 g, 0.05 mol) and PEG (15 g, 0.01 mol). The reaction was carried out at 90 °C with the continuous pass of dry nitrogen gas. After the theoretical –NCO value were reached, EDO (2.484 g, 0.01 mol) was added to the system, the mixture was poured into a mold and finally cured at 120 °C for 4 days.

PMMA was typically synthesized with MMA under BPO initiator. After homogeneous mixture of MMA (30 g, 0.3 mol), BPO (0.15 g, 0.5 wt% based on MMA) and EGDMA(0.9 g, 3 wt% based on MMA) reacted for 2 h at 60 °C under nitrogen, the mixture was poured into a mold and kept at 70 °C for 24 h and the reaction medium was finally cured at 120 °C for 4 days.

The prepared PEG-TPE and PMMA samples were used for comparison with PMMA/PEG-TPE Semi-IPNs.

Preparation of PMMA/PEG-TPE Semi-interpenetrating polymer networks

The PEG-TPE was prepared as described above, after the theoretical –NCO value were reached, the required quantities of EDO, MMA monomer, EGDMA, BPO initiator was introduced to the system, then thoroughly mixed to initiate MMA polymerization at 60 °C for 0.5–1 h. The mixture was then poured into the mould and kept in a nitrogen circulated oven, initially at 70 °C for 24 h and subsequently at 120 °C for 4 days to facilitate the complete network formation. The chemicals dosages are same as described above.

Characterization

Infrared (IR) spectra of the polymer films were obtained using Bruker Tensor 27 Fourier transform infrared spectrometer (FTIR). The spectra were obtained over the frequency range of 4,000–400 cm^{-1} at a resolution of 4 cm^{-1}. The mechanical properties of the Semi-IPNs were measured using Instron-3367 Materials laboratorial instrument according to ASTM D882 at ±25 °C. The sample was cut into dumb-bell shapes with a gauge length of 75 mm, widths between 6 and 14 mm, and sample thickness between 0.5 and 1 mm. Samples were elongated at a continuous strain rate of 10 mm/min. Dynamic mechanical investigation was performed using a Q800 V7.0 dynamic mechanical analyzer at a heating rate 3 °C/min. The samples were tested in the bending mode at a fixed frequency of 1 Hz from -100 to 150 °C. The surface morphology was obtained on a JSM-6380LV scanning electron microscope (SEM). Microphotographs were taken on the fracture surface which was made by cutting the specimen in knife then coated with gold powder.

Results and discussion

FTIR analysis

As in Fig. 1, the Semi-IPN showed characteristic peaks in the wave number region 3,420–3,220 cm^{-1} and 1,740–1,660 cm^{-1}, which correspond to secondary urethane –NH and –CO stretching group. The peak of hydrogen-bonded carbonyl ester group of PMMA is also in this region. The relatively weak peaks were observed in the region 3,050–3,020 cm^{-1}, indicating the presence of aromatic ring of MDI. Therefore, the FTIR absorption bands indicate the presence of both the PEG-TPE and PMMA in this Semi-IPN.

Mechanical properties analysis PMMA/PEG-TPE (weight ratio, the same hereinafter)

Figure 2 shows the effect of weight composition of PMMA/PEG-TPE on tensile strength, elongation at break. As it was shown, the curve for PEG-TPE is typical of elastomers. The same types of stress–strain curves are observed for Semi-IPNs with a PMMA content of 0–40 wt%. The tensile strength of the Semi-IPNs lies in the range 1.93–5.55 MPa and has no significant increase. This implies that PEG-TPE forms a continuous phase in these samples, and that PMMA is dispersed in the PEG-TPE continuous phase.

As the PMMA content was above 50 wt%, it is observed that tensile strength increases, whereas, elongation at break decreases with increasing PMMA contents. A steep increase in tensile strength implies that the higher degree of physical entanglement and hydrogen bond formation or phase transfer produced between PEG-TPE and PMMA. The curve of the Semi-IPNs containing 50 wt% PMMA is

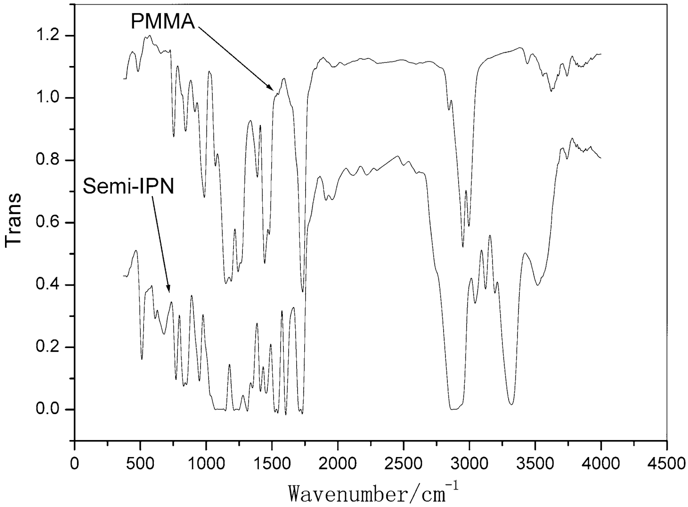

Fig. 1 FTIR spectra of PMMA and Semi-IPN

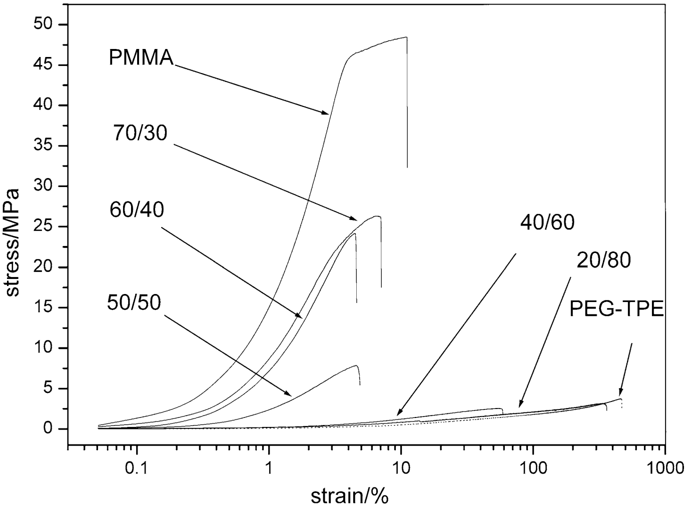

Fig. 2 Stress strain curves of PMMA/PEG-TPE Semi-IPNs

typical of amorphous polymers containing an elastomeric phase as filler, suggesting that phase transfer occurs and PMMA gradually forms a second continuous phase in Semi-IPNs with increasing PMMA content.

Dynamic mechanical thermal analysis (DMTA)

The dynamic mechanical properties of samples are expressed as the tangent (tanδ) vs. temperature in Fig. 3 and loss modulus versus temperature in Fig. 4, respectively. Over the temperature range from −50 to 150 °C, two distinct

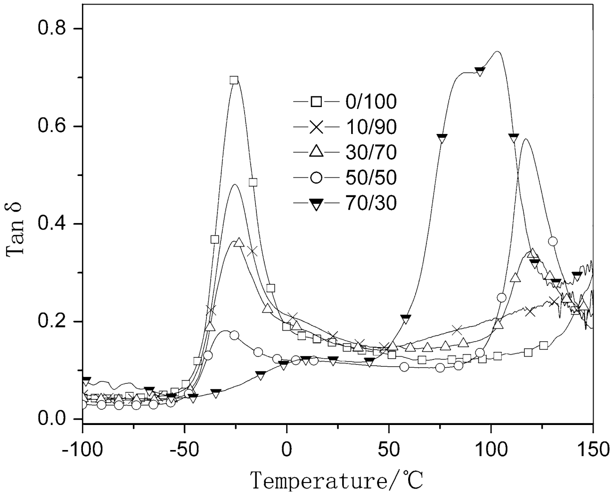

Fig. 3 Dynamic tan δ versus temperature for PMMA/PEG-TPE Semi-IPNs

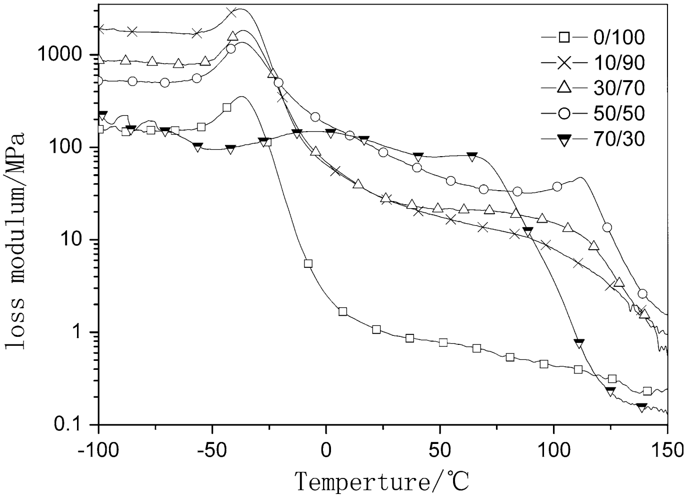

Fig. 4 Loss modulus versus temperature for PMMA/PEG-TPE Semi-IPNs

transition peaks are observed at −25 °C (T_{g1}) and 110 °C (T_{g2}). The α peak at low temperature has been widely accepted as the glass transition of PEG-TPE's soft segments, and the corresponding temperature is the soft segment's glass transition temperature. Another α peak observed in high temperature attributes to the glass transition of PMMA, and the corresponding temperature is the glass transition temperature of PMMA.

The separation between two tan δ peaks indicates a less degree of compatibility in the system. The height of PEG-TPE's soft segment tan δ peak decreases and magnitude keep invariable as the PMMA content increases, indicating the segment movement of PMMA less affect on that of PEG-TPE, and the reasonable explanation is physical entanglement decrease the peak height. The peak magnitude of PMMA tanδ peaks shift towards PEG-TPE and broaden, indicating some "forced" miscibility between the two polymers in the phases [23].

As shown in Fig. 4, the width and intensity of the loss modulus peak are different with different weight ratio of PMMA/PEG-TPE Semi-IPNs, a shoulder at the left-hand side of the peak should be the result of the immiscibility between PMMA and PEG-TPE segment.

The intensity of the loss modulus peak increases as the PMMA content decreases. This is due to the dissolution of PMMA chain into the PEG-TPE matrix phase and then the formation of a micro-heterogeneous PEG-TPE domain. Usually, the heterogeneous morphology causes a broader glass transition peak. For the system with 50 wt% PMMA, another loss modulus peak appears at a high temperature in addition to the main peak. This indicates that the PMMA gradually forms continuous phase and exhibits its intrinsic properties. It is in accord with the result of tensile testing.

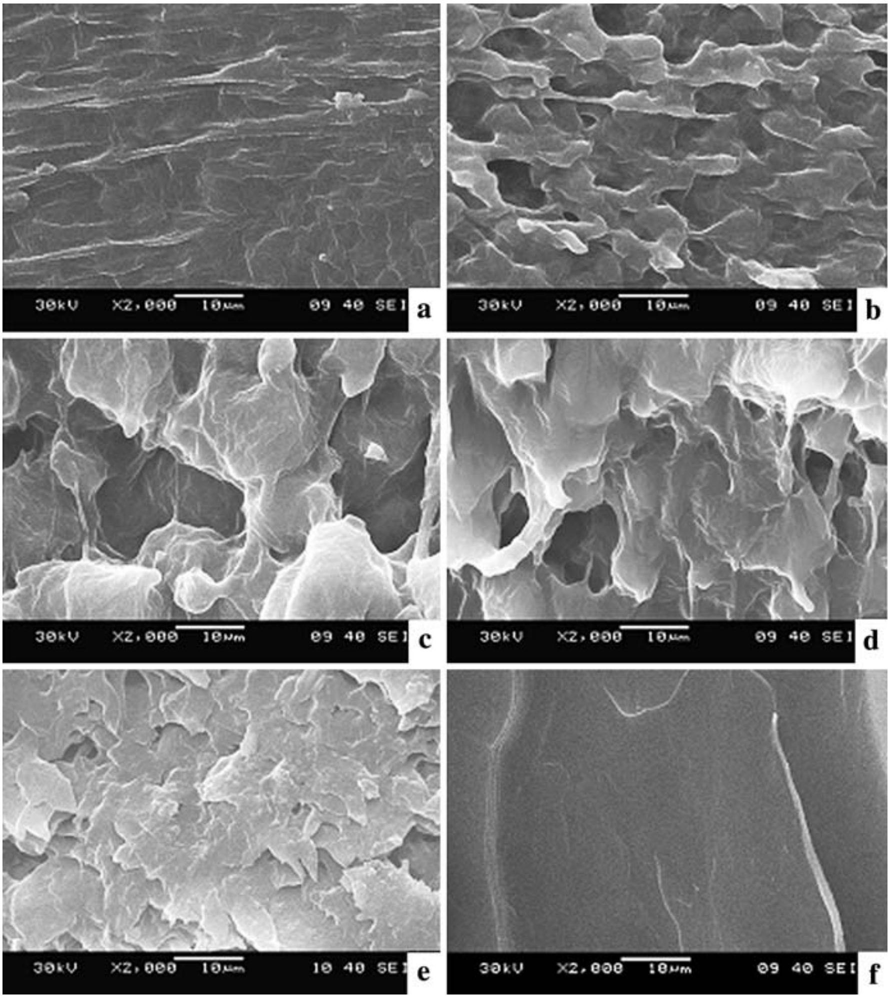

Fig. 5 The scanning electron micrographs of fracture surface of the PMMA/PEG-TPE Semi-IPNs. **a** PEG-TPE; **b** 10/90; **c** 30/70; **d** 50/50; **e** 70/30; **f** PMMA

Scanning electron micrograph (SEM)

Figure 5 shows the scanning electron micrographs of the fracture surface of PMMA/PEG-TPE Semi-IPNs at various PMMA contents.

The PEG-TPE exhibited a rough microstructure because it was a flexible material with the segregation of hard and soft segments in Fig. 5a. The pure PMMA expressed the smooth and glossy microstructure because it was a brittle material in Fig. 5f.

In these Semi-IPNs, the separate small domains of PMMA in the PEG-TPE matrix were observed with PMMA content increasing to 30 wt%. The Semi-IPNs show complicated domain structures, while the PMMA content is up to 50 wt%, indicating phase separation in the composition range. It is due that the phase separation in the networks depends on the miscibility of both constituent polymers and the polymerization condition. Finally, the micrograph for the Semi-IPN with 70 wt% PMMA in Fig. 5d show PMMA become a matrix containing phase domains of PEG-TPE, which indicates an inversion of phases occurred in this range.

These results are in agreement with the result of the mechanical properties above 50 wt% PMMA, the stress–strain curve of Semi-IPNs sharply changed as shown in Fig. 2.

Conclusions

A series of Semi-IPNs of PMMA/PEG-TPE could be prepared by sequential polymerization and obtained Semi-IPNs are tough and turbid. Mechanical properties of Semi-IPNs were improved with the increase of PMMA content. The two components are immiscible and two distinct α peak transformation were observed, that demonstrates the components are immiscible, the extent of network interpenetrating is dependent on variations in composition. A partial or complete phase inversion may occur as the PMMA content gets to 50 wt%. The morphological investigations show that the Semi-IPNs have complicated domain structures indicating phase separation occurred, which is agreed with mechanical properties of the Semi-IPNs.

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