

BaTiO₃/(PU/UP-IPNS)复合材料的相容性、力学性能和阻尼性能研究

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摘要: 以水热法合成的 BaTiO₃ 纤维和同步法制备的互穿聚合物网络为原料, 采用原位分散聚合法获得了一系列 BaTiO₃/(PU/UP-IPNs) 复合材料。采用傅立叶变换红外分光光度计跟踪考察了 IPNs 的聚合过程, 用透射电镜观测了 IPNs 及其复合物的形貌。结果表明, IPNs 中两相相畴尺寸在纳米级范围内, 在此基础上, 实现了 BaTiO₃ 纤维状的复合。动态力学性能的检测结果表明, 相较纯 IPNs, 复合材料的阻尼损耗模量和阻尼损耗因子值均有所提高, 且在低温区均出现了肩峰。复合物的最大损耗因子值均大于 0.4, 在约 50 °C 范围内, E'' 值提高 100 MPa。力学性能检测结果表明, IPNs 中的连续相是决定材料力学性能的主要因素; 有机/无机组分间混溶性的降低, 使 BaTiO₃/IPNs 复合材料的抗张强度和断裂伸长率均下降。

关键词: 互穿聚合物网络(IPNs); BaTiO₃ 纤维; 复合材料; 阻尼性能; 相容性

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Morphology, Mechanical and Damping Properties of BaTiO₃/(PU/UP-IPNs) Composites

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Abstract: A series of BaTiO₃/Interpenetrating polymer networks (IPNs) composites, composed of BaTiO₃ fibers synthesized by hydrothermal method and simultaneous IPNs based on polyurethane (PU) and unsaturated polyester resin (UP), were prepared by *in-situ* polymerization process. Fourier transform infrared spectroscopy (FTIR) was used to trace polymerization process of IPNs and transmission electron micrographs (TEM) was used to characterize the morphology and miscibility among multiple phases of IPNs and composites. The results indicated that the domains between two phases in IPNs were constricted in nanometer scales, and BaTiO₃ dispersed in composites mostly with fiber structures. The damping property studies of IPNs and composites revealed that, the value of loss factor ($\tan\delta$) and loss modulus (E'') detected by dynamic mechanical thermal analyzer (DMTA) both increased with the adding amounts of BaTiO₃ in composites, and the shoulder peak of $\tan\delta$ and E'' curves both appeared apparently at low temperature ranges. Maximum $\tan\delta$ values of all composites were above 0.4 and the maximum E'' values of composites increased above 100 MPa in nearly 50 °C ranges compared with that of IPNs. The mechanical properties study showed that the continuous phase of IPNs accounted for the major mechanical properties and the adding of BaTiO₃ both decreased the values of tensile strength and elongation at break of composites.

Key words: interpenetrating polymer networks (IPNs); barium titanate (BaTiO₃) fiber; composites; damping property; morphology

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0 Introduction

Polymer blends, with two or more kinds of polymer components, can exhibit many outstanding properties to the system formed and have been a valid and important means for materials' modification^[1]. Due to its linear network with excellent elasticity, abrasive resistance and, particularly high damping property at transition temperature ranges, polyurethane has been used extensively in sound and vibration damping areas as polymer matrix. But the characteristics of narrow transition temperature ranges (often within 20~30 °C and at low temperature ranges) restrict its application fields^[2]. Interpenetrating Polymer Networks are an intimate blend of two network polymers with special properties brought about by permanent interlocking of chains through chemical crosslinks^[3]. IPNs usually form large amounts of phase-separation structures in system. As a consequence, the degree of interpenetrating and morphology in the polymer networks influences the damping properties greatly and often enlarges the transition temperature ranges^[4]. So much work has been carried out on the synthesis and morphology of IPNs. Up to now, lots of studies on the microphase separation behavior and structure character have been focused on multicomponent polymer systems^[5]. Researches have shown that the applications of IPNs can be enlarged greatly by mixing inorganic components into the system to obtain polymer-based reinforced composites^[6-9]. Generally speaking, the properties of the composites mixed with two or more components depend not only on the inorganic material selected, but also on the morphology and interfacial property of the composites^[10-13].

In this study, PU/UP-IPNs with nanometer domain sizes were prepared and then mixed with BaTiO₃ fiber synthesized by hydrothermal process. The surface modification of BaTiO₃ and the composite technique were optimized. The morphology and microphase separation behavior, the damping and the mechanical properties of composites are characterized and discussed.

1 Experimental

1.1 Preparation of IPNs

3.64 g toluene diisocyanate (TDI) precursor (TDI

content: 9%) and different amounts of UP resin (21.00 g, 14.00 g or 9.00 g, free of inhibitor) were added respectively into the system composed of 17.86 g PU prepolymer (dehydrated before use), benzoyl peroxide (BPO, 1% by weight of UP) and ethyl acetate (30% by volume of PU). Then dimethylaniline (DMA, 2% by weight of UP) and dibutyl dilaurate (0.5% by weight of PU) were added. The mixtures thus obtained were stirred for 10 to 20 min and then cast into a mold. The molar ratio of -NCO/-OH in PU network were 1.2:1.0. The weight ratios of PU/UP in IPNs were 50/50, 60/40 and 70/30, respectively.

1.2 Synthesis of BaTiO₃ fiber

BaTiO₃ fiber was synthesized by hydrothermal process^[14]. 12 g K₂Ti₄O₉ fibers were immersed into 30 mL 1 mol·L⁻¹ HCl solution for 1 week after stirring thoroughly, then the mixture was filtered under vacuum and dried. 12 g Ba(OH)₂·8H₂O was then added into the above system. All the components were poured into a hot reaction vessel with 30~50 mL distilled water. The above mixture was heated at 140 °C for 24 h and rinsed with hot water to neutral and then dried at room temperature. The BaTiO₃ fiber thus obtained was calcined at 1200 °C for 2 h.

1.3 Composite technique

BaTiO₃ fibers (2%, 25% and 70% by weight of composites) were treated with coupling agents (vinyltriethoxysilane, 1% by weight of BaTiO₃) in ethyl acetate (30% by volume of IPNs) and then added into 70/30PU/UP-IPNs once its contents were thoroughly mixed. Then the system was ground slightly for about 25 min and dispersed for 20 min under supersonic wave, then cast in mold.

1.4 Properties testing

The FTIR analysis was performed on Nicolet-5DX FTIR spectrometer by casting the homogeneous systems composed of TDI precursor, PU prepolymer, UP, and BPO-DMA onto a KBr crystal plate. The -NCO / -OH ratio (in mole) and PU/UP component ratio (by weight) were 1.2:1.0 and 60/40, respectively. BaTiO₃ fibers were observed by KYKY-1000B scanning electron microscope (SEM). The phase morphologies of IPNs and composites were examined by Nippon Electron 1200-EX transmission electron microscope (TEM). The samples were cut into 100 nm thick sections and stained in OsO₄ (2%wt.) solution for 12

hours. The -NCO/-OH molar ratio and PU/UP component weight ratios were 1.2:1.0 and 70/30. Damping properties, represented by the values of dynamic storage modulus (E'), loss modulus (E'') and loss factor ($\tan\delta$), were measured by DMTA-V dynamic mechanical thermal analyzer. The measurements were made at 100 Hz in the range of $-75\sim 150\text{ }^{\circ}\text{C}$ at a heating rate of $10\text{ }^{\circ}\text{C}\cdot\text{min}^{-1}$. Tensile strength, elongation at break of IPNs and composites of small size dumb-bells were measured by Nippon Shimadzu DSS-10T-S tester at room temperature at a crosshead speed of $5\text{ mm}\cdot\text{min}^{-1}$ according to China's Reference Method (GB4456-84). Data were taken as average of at least five measurements.

2 Results and discussion

2.1 IR analysis

The FTIR spectra of IPNs at various reaction times are shown in Fig.1. As shown in the figure, the intensity of characteristic absorption peaks of -NCO (2278 cm^{-1}), -OH (3400 cm^{-1}), -NH (3350 cm^{-1}), and -NHCO (1528 cm^{-1}) decreases during the polymerization. In this study, the intensity changes of the absorption peak at 2278 cm^{-1} and at 965 cm^{-1} represent the change of -NCO group and -C=C- group, respectively^[15]. The disappearance of -NCO absorption peak is a little faster than that of -C=C- absorption peak during early stages, but slower at later stages of the reaction as seen from the conversion data of -NCO and -C=C- calculated from IR spectra in Table 1. This indicates that during the formation of IPNs, although attempts were made to form the two networks simultaneously, the formation of PU was faster at early stages. This is mainly because that the UP polymerizes through free radical mechanism, and the initiation step tends to make it proceed slowly before moving into the propagation step. Whereas, the hydrogen transfer polymerization of PU could undergo rapidly at early stages. So PU forms the continuous phase in the system. Grafting between the two networks might occur through the reaction between isocyanate groups of PU and hydroxyl or carboxyl groups of UP. Such a system may be considered as grafted IPNs. The chemical crosslink structures formed lead to shorter distance between two networks and increase the extent of interpenetration, and thus decrease the domain sizes

of the two phases to nanometer scales. So the component ratios of IPNs can be adjusted in relative wide ranges without phase separation, and thus leading to better miscibility and the improvement of other integrated properties.

Table 1 Conversion data of -NCO and -C=C- at various reaction time calculated from FTIR spectra

| t/h | 1/10 | 1 | 3 |
|--------------------------|------|-------|-------|
| Conversion rate of -NCO | 2.56 | 6.48 | 21.85 |
| Conversion rate of -C=C- | 1.82 | 11.35 | 16.76 |

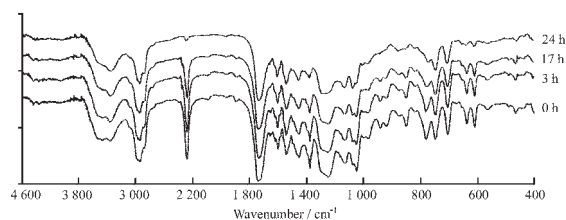


Fig.1 IR spectra of PU/UP IPNs at various reaction time

2.2 Morphological properties

TEM photographs of PU/UP-IPNs are shown in Fig.2. As shown in Fig.2(a) and (b), PU appears as white phase and presents as continuous phase with globules of UP dispersion. The globules were generated from the first-stage phase separation due to immiscibility of components during polymerization. The fine structures in the system were caused by the second-stage phase separation after polymerization. This is mainly due to the fact that increase of viscosity and crosslinking density can make the second-stage phase separation occur in narrow scales, and form nanometer globules. Although the interpenetration and entanglement structures between two networks increase the compatibility, the network formed later can just act as the filler of the first formed one. However, through varying the component ratios and controlling the formation rates of the two networks to complete the polymerization processes almost simultaneously, the extent of the first-stage phase separation can be effectively locked. The SEM photographs of BaTiO₃ fibers and TEM photographs of composites with 25%(wt.) BaTiO₃ are shown in Fig.3. As shown in Fig.3(a), the length of fibers was approximately $50\sim 80\text{ }\mu\text{m}$. And in composites, BaTiO₃ fibers are well-dispersed in the matrix, mostly with the original structures as seen from Fig.3(b).

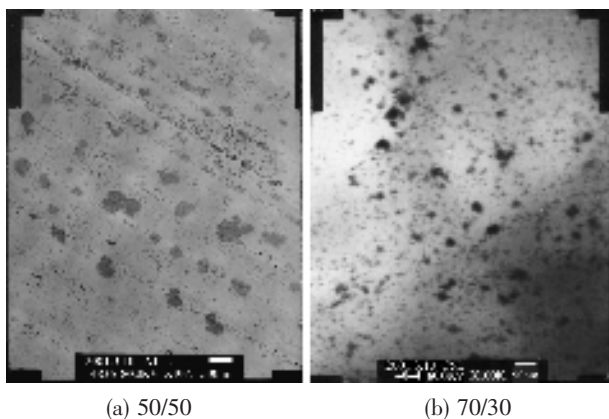


Fig.2 TEM of IPNs with various modified PU/UP component ratios (wt./wt.)

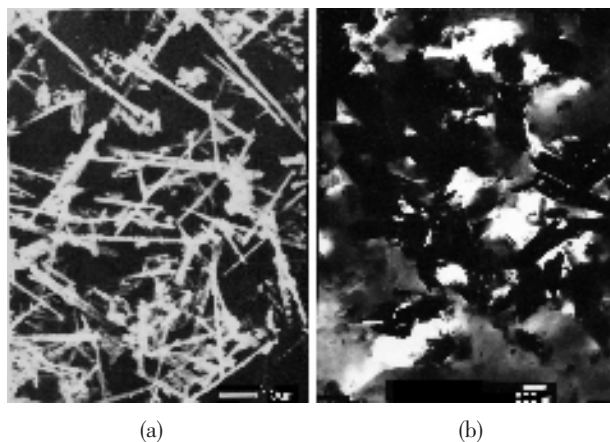


Fig.3 SEM of BaTiO₃ fibers (a) and TEM of BaTiO₃/(PU/UP-IPNs) composites (b)

2.3 Damping properties

A series of dynamic mechanical spectra were obtained by changing PU/UP ratios. Fig.4 (a) and (b) show the change of loss factor and loss modulus with UP content. It is obvious that the dynamic mechanical spectrum curves change with composition, i.e. with the increase of PU, the values of $\tan\delta$ shift toward lower temperature. The values of loss modulus increase with PU content. The above results indicate that the multi-component system formed can broaden damping temperature ranges and enlarge the areas below $E'' \sim T$ curves. All the samples show only one expanded transition temperature ranges with higher peak $\tan\delta$ value (above 0.4). This indicate that better interpenetration and apparent entanglement effects led by the additional cross-linking structures in systems make a larger mid-peak width and areas below $E'' \sim T$ curves. The broadened transition temperature ranges show good miscibility between polymer components. Mean-

while, based on Rouse-Bueche theory^[16], such single broadened peaks do not mean a homogeneous system formed. This is mainly because the ranges of $\tan\delta$ curves are relatively expended with slightly changed values of E'' .

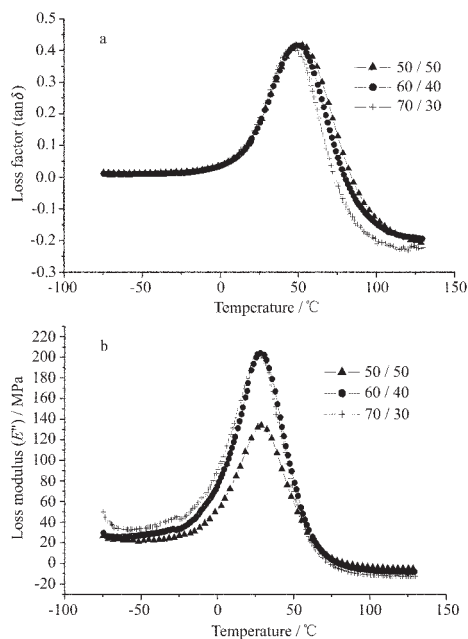


Fig.4 Loss factors curves (a) and loss modulus curves (b) of PU/UP IPNs with different component ratios (w/w)

The dynamic mechanical behaviors of composites with various BaTiO₃ ratios are shown in Fig.5. As seen from the figure, the $E'' \sim T$ and $\tan\delta \sim T$ curves both change with the same tendency. The maximum values of E'' and $\tan\delta$ increase with the introducing of BaTiO₃, and shoulder peaks appeared at lower temperature ranges ($-20 \sim 30^\circ\text{C}$). Especially for the sample containing 70% BaTiO₃, the shoulder peak occurs apparently at nearly -10°C , and maximum value of E'' increases above 10^2 MPa. The above results indicate that the introduction of BaTiO₃ increases the damping property due to the additional frictional damping mechanism between BaTiO₃ and polymer matrix. But the miscibility decreases with unsymmetrical $\tan\delta$ curves. This is caused by the fact that, when a small amount of BaTiO₃ is added, the properties of the materials are contributed mainly by matrix; with the increase of BaTiO₃, $\tan\delta$ peak values shift towards higher temperature ranges. This illustrates that the introduction of the inorganic component can contribute the frictional action between fibers and IPNs, so can fur-

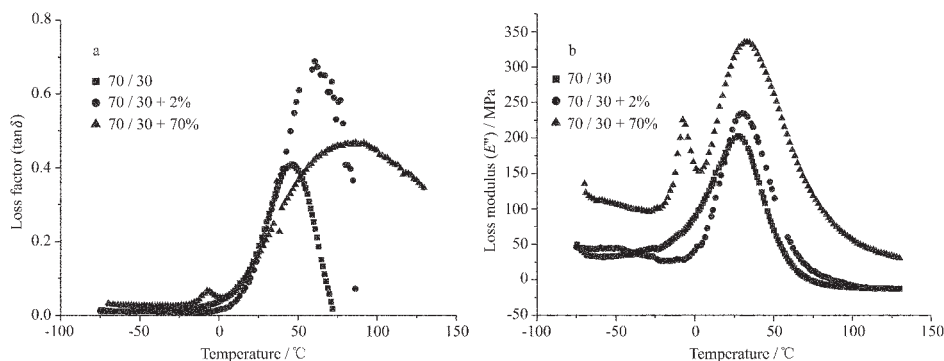


Fig.5 Loss factors curves (a) and loss modulus curves (b) of 70/30 PU/UP IPNs with different amounts of BaTiO₃ fibers (*w/w*)

ther increase the vibration energy loss of the resulting composites.

2.4 Mechanical properties

The mechanical results of PU/UP-IPNs with various amounts of BaTiO₃ fibers are shown in Table 2. As shown in the table, tensile strength (σ) increases, and elongation at break (ε) decreases with UP content

in IPNs. The higher ε and lower σ values indicate that the first formed networks commonly determine the mechanical properties of the system. And all the samples' σ and ε decrease with the increase of BaTiO₃ amounts in composites led by less miscibility between IPNs and BaTiO₃ fibers.

Table 2 Mechanical properties of PU/UP-IPNs with various amounts of BaTiO₃ fiber

| PU/UP component ratios (<i>w/w</i>) | BaTiO ₃ / IPNs component ratios (<i>w/w</i>) | Tensile strength (σ) / MPa | Elongation at break (ε) / % |
|---------------------------------------|---|-------------------------------------|---|
| 50/50 | 0/100 | 3.21 | 77.27 |
| 50/50 | 2/100 | 3.15 | 75.02 |
| 50/50 | 7/100 | 2.89 | 69.12 |
| 50/50 | 10/100 | 2.87 | 64.95 |
| 50/50 | 15/100 | 2.48 | 58.47 |
| 70/30 | 0/100 | 2.70 | 95.04 |
| 70/30 | 2/100 | 2.32 | 89.05 |
| 70/30 | 7/100 | 2.58 | 87.46 |
| 70/30 | 10/100 | 2.49 | 87.52 |
| 70/30 | 15/100 | 2.44 | 83.34 |

3 Conclusions

IR, TEM and DMTA results indicate that domains of the IPNs are in nanometer scales by simultaneous interpenetrating techniques and by introduction graft structures into networks. By these, it can create chemical crosslinking in addition to physical interlinks between two networks and further decrease the distance between phases and constrains the domain sizes of IPNs in nanometer scales. The influence of PU/UP ratio on damping properties indicates that the changing of damping behavior with temperature is in similar changing trends with the increase of the PU/UP ratios. This is mainly because that the PU networks usually act as continuous phase and UP as filler in systems. So with the increase of PU content, both

tanδ and E'' increase. The samples all show significantly expanded transition temperature ranges. The introduction of BaTiO₃ into system increases the damping properties, but decreases the miscibility with unsymmetrical peak in tanδ~*T* curves. The PU/UP ratios have influence on tensile strength and elongation of the system. The tensile strength and elongation at break of composites decrease with the increase amount of BaTiO₃ fibers results in the less miscibility of composites compared with IPNs.

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