Influence of BaTiO$_3$ on damping and dielectric properties of filled polyurethane/unsaturated polyester resin interpenetrating polymer networks

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A series of BaTiO$_3$ fiber and nanopowder unfilled and filled interpenetrating polymer networks (IPNs) composed of polyurethane (PU) and unsaturated polyester resin (UP) are prepared by simultaneous polymerization process. The effect of PU/UP component ratios, the types and amounts of BaTiO$_3$ filled, the polarization treatment to filled IPNs, on the damping properties are investigated by dynamic mechanical thermal analyzer (DMTA). The morphology and microstructures of unfilled and filled IPNs are examined by transmission electron microscope (TEM). The dielectric loss and dielectric constant at different temperatures are studied by AC impedance analyzer. Moreover, the relationship between damping and dielectric properties is discussed in terms of dielectric constant and dielectric loss measured. The results show that the PU/UP component ratios in IPNs, the types of filler, and the amount of nanopowder added all affect the damping behaviors and degree of phase separation of unfilled and filled IPNs. Through polarization treatment, the filled IPNs exhibit synergistic action in systems caused by elastomeric damping mechanism, interfacial frictional damping mechanism and piezoelectric damping mechanisms. The maximum value of E'' of filled IPNs with 70% BaTiO$_3$ increase above 100 MPa and the temperature ranges of tan $\delta > 0.3$ is higher than 100°C compared with unfilled IPNs. Moreover, the maximum value of E'' and the temperature ranges of tan $\delta > 0.3$ increases dramatically after polarizing process. The dielectric properties and its relation with damping properties studies reveal that the temperature ranges exhibit excellent consistency of maximum dielectric loss and dielectric constant with damping loss factor.
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1. Introduction

Interpenetrating polymer networks (IPNs) are a combination of two or more networks polymers synthesized in juxtaposition [1]. As one kind of polymer alloys, IPNs provide the possibility of effectively producing advanced multi-component polymeric systems with new property profiles and so have been studied extensively [2–4]. Since the existence of mutual entanglement, forced compatibility, synergism of the networks and cellular, dual-phase continuous microstructure in systems, up to now, IPNs has been the promising technique of preparing materials with broad glass transition temperature (T_g) ranges and so have shown excellent damping performances [5, 6]. But through interpenetrating technique, the materials can only show enlarged T_g ranges. The areas under loss modulus (E'') versus temperature curves of materials, another important index to indicate damping capabilities, cannot be

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improved greatly [7, 8]. Researches have found that other techniques, such as polymer blends, copolymers and filled with inorganic materials into IPNs can contribute large E'' values and improve areas under E'' versus T curves [9, 10]. Especially, if the filled inorganic material is of dielectric and/or piezoelectric properties and can transform mechanical energy into electric energy, then into heat energy and release from system, it can contribute excess damping ability to IPNs besides frictional damping ability between organic and inorganic phase, so materials with better damping properties can thus obtained effectively. Unfortunately, investigations of filled IPNs have been studied somewhat less intensively, although such researches are of great importance [11, 12]. Up to now, there are no works dealing particularly with piezoelectric and/or dielectric properties of fillers on damping properties of IPNs.

In this paper, a series of $BaTiO_3$ fiber and nanopowder unfilled and filled interpenetrating polymer networks (IPNs) are prepared by simultaneous polymerization process of polyurethane (PU) and unsaturated polyester resin (UP). The effect of PU and UP component ratios in IPNs, the types and amounts of $BaTiO_3$, the polarization treatment to filled IPNs on the damping properties of 70/30(mass) PU/UP IPNs are investigated. The dielectric properties such as dielectric loss and dielectric constant are detected. Moreover, the relationship between damping and dielectric properties is somewhat revealed. The filled IPNs are polarized with high voltage and small current, and protected by silicon oil to investigate the synergistic action of elastomeric damping, interfacial frictional damping and piezoelectric damping mechanisms in systems.

2. Experimental
2.1. Materials
The polyurethane/polyester IPNs studied in this work contain two reactive parts (the polyurethane and polyester phase) designated as x/y IPNs (x stands for the % weight of polyurethane and y the weight of polyester). The polyurethane phase is formed by polyol (with an -OH index of 120 mg KOH/g) and 2,4-tolylene diisocyanate(TDI) precursor (with TDI content (% weight) of 9%). Chemical Factory of Harbin Institute of Technology supplies them both. Before use, polyol and TDI precursor were dehydrated and degassed at 80°C in a vacuum for 1.5 h. The polyester phase consists of a resin formed by phthalic anhydride, maleic anhydride and propylene glycol. The resin (contains 35% styrene as UP's comonomer), uses benzoyl peroxide(BPO) as initiator and cobalt salt as promoter. Dibutyltin dilaurate(DBTL) is used as catalyst of PU phase and ethyl acetate as solvent to adjust the viscosity of IPNs.

2.2. Preparation of barium titanate fiber and nanopowder
The barium titanate fiber was prepared by hydrothermal process [13, 14]. In a typical experiment, 23% weight of distilled water was added into the mixtures of K_2CO_3

and TiO_2, which was in the molar ratio of 1:3. After mixed for 1 h, the system were spread on a platinum plate and dried at 80°C for 72 h, calcined at 1000 for 100 h, then cooled down quickly to room temperature and immersed in distilled water for 1 week. The $K_2Ti_4O_9$ fiber thus obtained was then immersed in HCl solution ($10^3 \cdot molm^{-3}$) for 1 week after stirring thoroughly, then filtered under vacuum and dried. $Ba(OH)_2 \cdot 8H_2O$ was then added into the above system with the same amount. All the components were poured into hydrothermal reaction vessel with a weight amount of distilled water. The products were heated at 140°C for 72 h and rinsed with hot water to neutral and then dried at room temperature. The $BaTiO_3$ fiber thus obtained was then changed from cubic system to tetragonal system after calcining at 1200°C for 2 h. And $BaTiO_3$ nanopowder was gained by grinding the fibers slightly for 0.5 h.

2.3. Preparation of PU/UP IPNs
TDI precursor, UP resin and its promoter, solvent were added into a three-necked round-bottomed flask under nitrogen gas purge to mix for 10–20 min. Then polyol and its catalyst, UP initiator were added and stirred continuously for about 30 min until a homogeneous and transparent mixture formed. Then the viscose mixture was poured into a mold and cured at room temperature for 24 h. The molar ratio of −NCO/−OH was 1.2, with 0.1% weight of dibutyltin dilaurate(DBTL) in PU phase. The weight ratio of UP resin, BPO and cobalt salt was 100:1:2, with 10–30% weight of ethyl acetate in system. A series of IPNs were prepared by varying the component ratios of PU and UP in system.

2.4. Preparation of $BaTiO_3$ filled PU/UPR IPNs
$BaTiO_3$ fiber/nanopowder, with 2% weight of vinyl triethoxysilane as coupling agent in 30% weight of ethyl acetate, was added into 70/30IPNs once all the components in IPNs were thoroughly mixed. Then the filled system was grinded for about 25 min and dispersed for 20 min under supersonic wave treatment, then cast in mold. A series of filled IPNs were obtained by varying the amount of fiber/nanopowder added. Among them, the 70% $BaTiO_3$ nanopowder filled IPNs was coated with conducting adhesive and polarized at 100°C in silicon oil by high voltage (2 kV/mm), small currency for 1 h.

2.5. Measurements
The phase morphology observations of unfilled and filled IPNs were examined by a Nippon Electron 1200-EX transmission electron microscope (TEM). The samples were cut into 100 nm thick sections and stained in OsO_4 (2% by weight) solution for 24 h. The PU/UP component weight ratios were 50/50 and 70/30, respectively. The damping properties of materials represented by the values of dynamic storage modulus (E'), loss modulus (E'') and loss factor (tan δ) were measured

by a DMTA-V dynamic mechanical thermal analyzer (DMTA). The measurements were made at 100 Hz in the temperature range of -75–$150°C$ at a heating rate of $10°C/min$. The dielectric properties of materials were detected by HP4285 AC impedance analyzer to obtain values of dielectric constant and dielectric loss of $BaTiO_3$ nanopowder filled IPNs at fixed frequency and different temperatures.

3. Results and discussion
3.1. Damping properties
Fig. 1 shows the plots of storage modulus(E') (1a), loss modulus (E'')(1b) and loss factor (tan δ)(1c) versus temperature of various PU/UP component ratios of IPNs. As shown in Fig. 1, the PU/UP component ratio is a factor to affect damping properties of IPNs. The
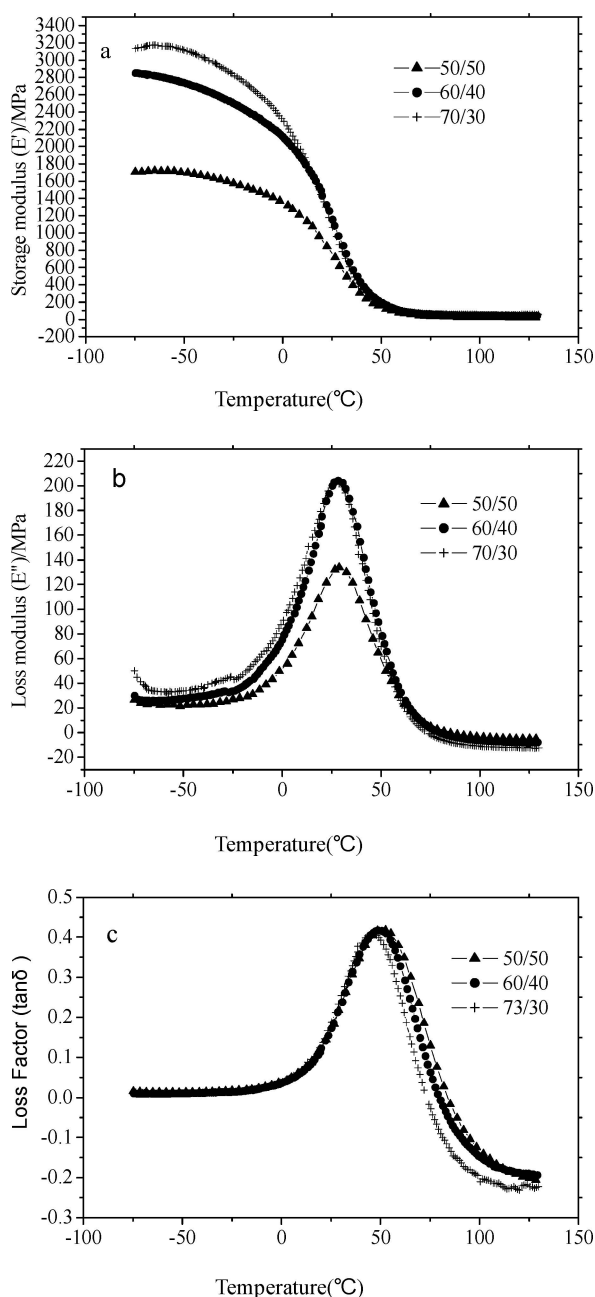

values of E' and E'' increase with that of PU content in system. The maximum value of tan δ shift toward lower temperatures. These results can be attributed to the fact that PU phase in 50/50–70/30 IPNs polymerize first and form the continuous phase. The values of E' decrease slowly between lower and higher temperature regions, led by a relative large phase separation in system with the increase of UP component concentration. The results also indicate that multi-component system can broaden the effective damping temperature range and move the range toward higher T_g range corresponding to UP content, and enlarge the areas below $E'' \sim T$ curves. All the IPNs show one expended damping peaks with maximum tan δ value higher than 0.4. These show better interpenetration and apparent entanglement effects led by better compatibility between two components of IPNs. Meanwhile, based on the Rouse-Bueche theory [15], such single broad peaks do not mean homogeneous system formed, mainly because of the fact that there appears relatively expended ranges in tan $\delta \sim T$ curves and less significant increased areas in $E'' \sim T$ curves.

Fig. 2 shows the plots of storage modulus(2a), loss modulus (2b) and loss factor(2c) versus temperature of 70/30IPNs and filled IPNs with 7%BaTiO$_3$ fiber and nanopowder. As shown in Fig. 2, with the same PU/UP component ratio and the same filler amounts, the types of fillers have a strong influence on damping properties of IPNs. As expected, the filler can both broaden the temperature ranges of maximum tan δ and the areas under $E'' \sim T$, thus increase damping properties of IPNs effectively. But compared with nanopowder, fiber has apparent damping effect besides the same interfacial frictional damping effect created by two different modulus materials (organic matrix and inorganic filler), mainly because of the larger interfacial frictional areas between chains of polymer matrix and inorganic fibers. But from Fig. 2a, it can be seen that the introducing of filler also increase the degree of phase separation in systems.

Considering the dielectric and/or piezoelectric properties of filler, in our further studies, we select BaTiO$_3$ nanopowder as filler, and change the filler amount in 70/30IPNs and polarize the 70% BaTiO$_3$ filled IPNs to investigate the influence of functional inorganic component on damping properties of materials.

Fig. 3 gives the plots of storage modulus(3a), loss modulus(3b) and loss factor(3c) versus temperature of 70/30IPNs with different amount of BaTiO$_3$ nanopowder. As shown in Fig. 3a, the rigidity of matrix and phase separation of system both increase with the increase amount of filler; in 3b, larger areas occur under $E'' \sim T$ curve for 70% filler IPNs compared with 2% one. Maximum E'' increases approximately 150MPa compared with the pure IPNs, but with an apparent shoulder peak, indicating poor miscibility in system; in 3c, maximum tan δ values of filled IPNs are higher than that of unfilled IPNs and shift toward higher temperature ranges. The higher damping properties of filled IPNs obtained mainly due to the frictional damping effect introduced by higher modulus of inorganic filler. Additionally, introducing little amount of filler into
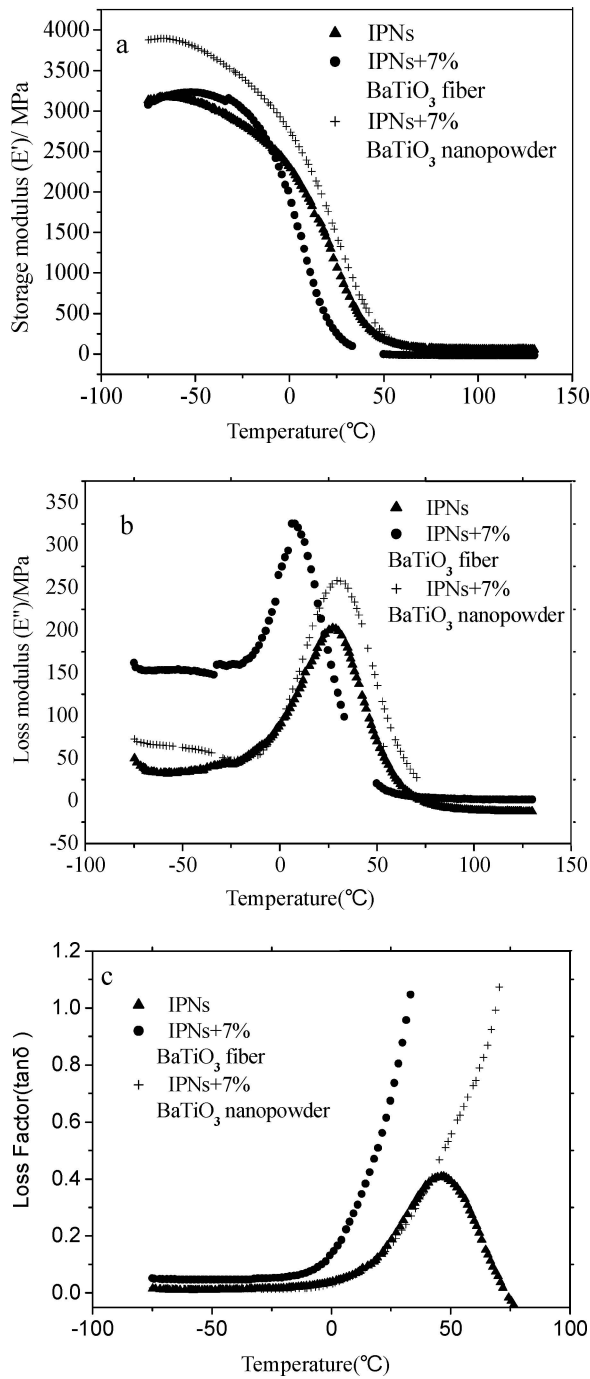
Figure 1 Storage modulus (a), loss modulus (b) and loss factor (c) versus temperature curves of PU/UP IPNs with different component ratios.

Figure 2 Storage modulus (a), loss modulus (b) and loss factor (c) versus temperature curves of 70/30IPNs with BaTiO$_3$ fiber and nanopowder.

Figure 3 Storage modulus (a), loss modulus (b) and loss factor (c) versus temperature curves of 73/30IPNs with different amount of BaTiO$_3$ nanopowder.

IPNs system can improves the damping properties effectively without decrease the phase separation significantly. But increase the amount of filler added, the phase separation increase, for example, two damping peaks appeared in tan$\delta \sim T$ curve of 70% filled IPNs shows a large phase separation in system.

Fig. 4 gives the plots of storage modulus(4a), loss modulus(4b) and loss factor(4c) versus temperature of pure IPNs, polarized and unpolarized filled IPNs with 70%BaTiO$_3$ nanopowder. As shown in Fig. 4, values of E'; E'' and tan δ of polarized filled IPNs increase dramatically compared with unpolarized one. The dramatically increase of E' may be attributed to the reinforced interaction between filler and polymer matrix and increased dual-phase continuity degree between the
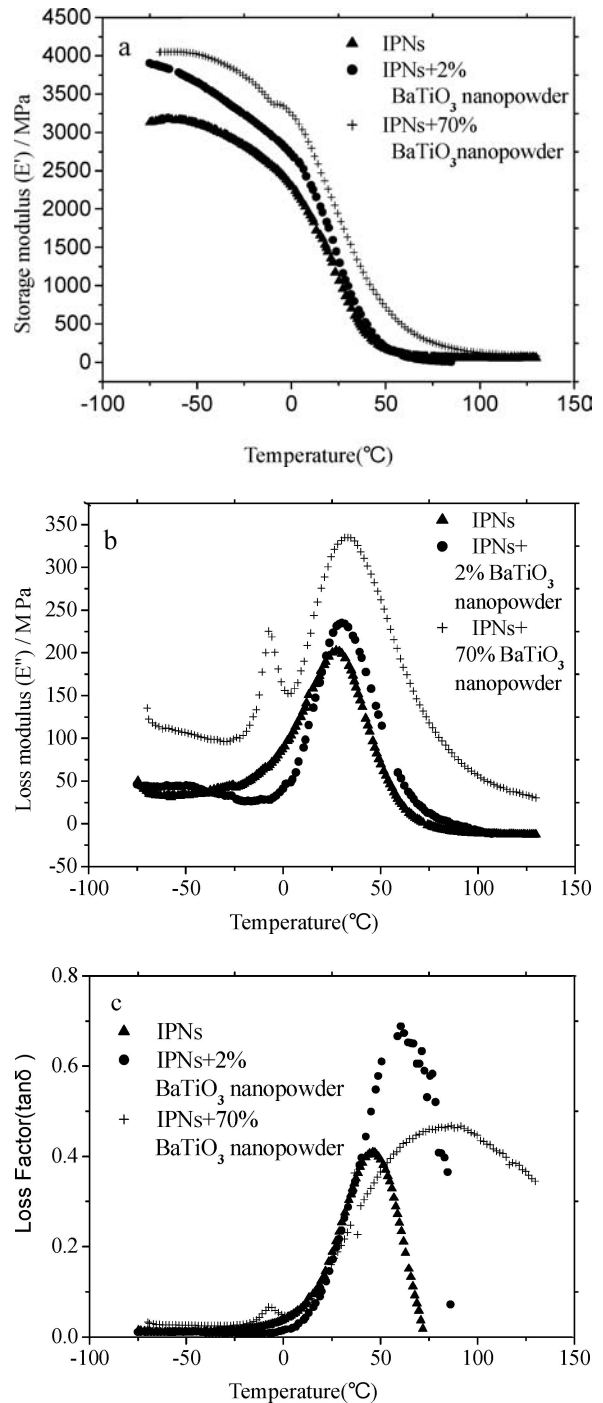
inorganic and organic parts caused by the orientation of BaTiO$_3$ from multi-domain to single-domain through polarization process. The disappearance of shoulder in $E'\sim$T curve and the decrease of shoulder in $E''\sim$T curves for polarized filled IPNs compared with unpolarized one also show the miscibility increase between BaTiO$_3$ and IPNs after polarization process. So the material can exhibit much storage modulus of filler. Maximum T_g value move toward higher temperatures. This probably attribute to the fact that the piezoelectric properties of BaTiO$_3$ can transform mechanical energy into electric energy, then conducting out of the materials, so contribute piezoelectric damping effect led by the
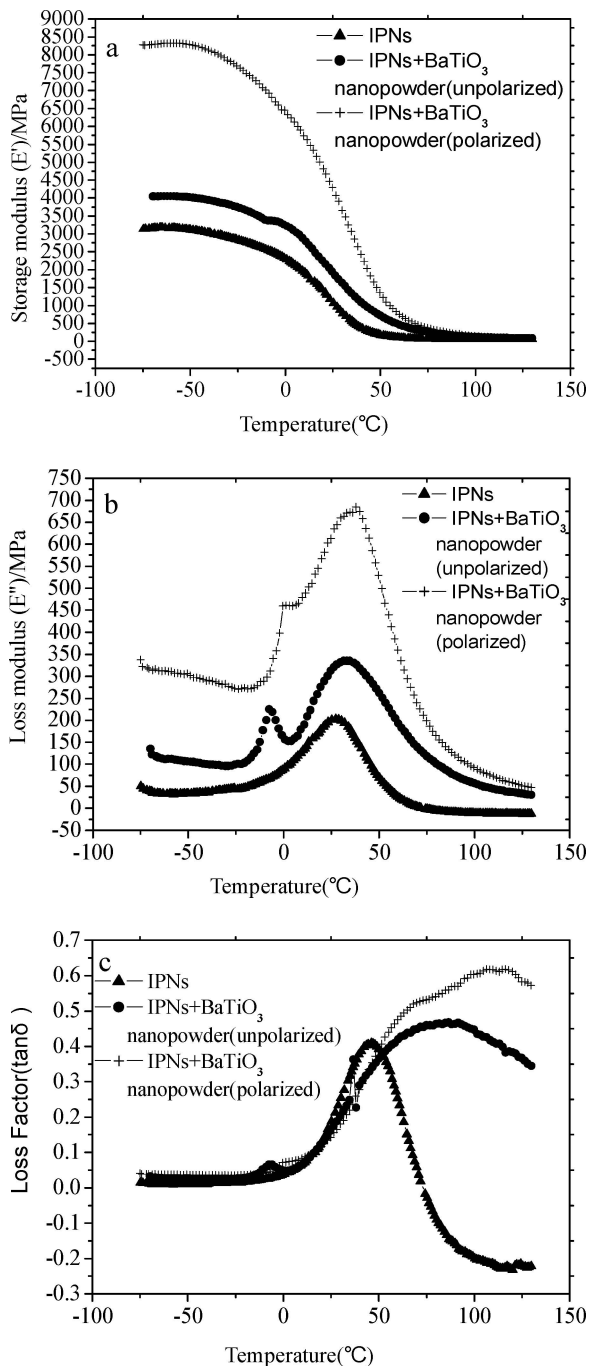
Figure 4 Storage modulus (a), loss modulus (b) and loss factor (c) versus temperature curves of unpolarized and polarized 73/30IPNs with BaTiO₃ nanopowder.

piezoelectric character of BaTiO$_3$ nanopowder to polarized filled IPNs. For the polarized filled IPNs, the values of tan δ are higher than 0.3 for a temperature range of above 100°C.

3.2. Morphology characters

TEM photographs of different PU/UP component ratios IPNs are shown in Fig. 5. The PU appears as the white phase and UP, reacted its double bond with OsO$_4$, so stained as dark phase [16]. 70/30IPNs is heterogeneous with phase domain sizes less than 50 nm, which show finer phase domains than that of 50/50IPNs. The photographs provide more direct evidence that PU forms continuous phase with globules of the UP dispersed

within it, and the compatibility of IPNs is improved by increase of PU content. The globules are generated by first-stage phase separation led by immiscibility during polymerization. The fine structures in the system are caused by second-stage phase separation after the polymerization. This is mainly due to the fact that the increase of viscosity and crosslinking density makes the second-stage phase separation occur on narrow scales, and form small globules in nanometer ranges. Although the interpenetration and entanglement structures between the two networks increase the compatibility, the network formed later can just act as the filler of the first formed one. The appearance of more continuous PU phase and small phase domain sizes of 70/30IPNs determines relative better damping properties. So the TEM results of IPNs are consistent with the damping property detection results by DMTA.
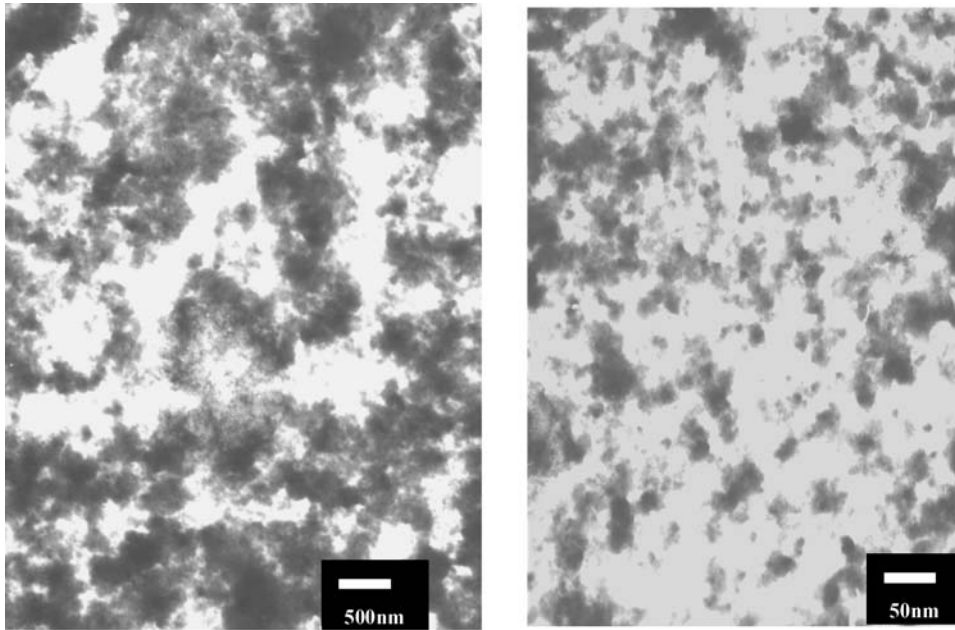
TEM photographs of BaTiO$_3$ fiber and nanopowder filled 70/30IPNs are shown in Fig. 6. As shown in Fig. 6, the fibers and nanopowders are dispersed mostly with its original structures in the matrix of polymers with larger disperse sizes compared with the UP phase in IPNs.

3.3. Dielectric properties and relation with damping properties

Figs 7 and 8 give temperature plots of dielectric constant and dielectric loss of 70% BaTiO$_3$ filled IPNs at a fixed frequency(1MHz). As shown in Figs 7 and 8, for the BaTiO$_3$ filled IPNs, there has a apparent peak at low temperature range corresponding to the dielectric constant of pure BaTiO$_3$. At temperature higher than 20°C, the overall dielectric constant increase slowly. Only when the temperature higher than 80°C, it increase quickly and the maximum dielectric loss occur at 60–70°C. The apparent changing temperature ranges for dielectric constant and dielectric loss are both consistent with the ranges of better damping properties, e.g. at 60–70°C and/or higher than 80°C, there are also greatly increased tan δ values and effectively enlarged damping areas. So the dielectric property studies of materials can give effect information related with damping properties of materials.

The existence of alternative electric field, created by force induced alternatively by alternative vibration waves at both sides of crystals, can decrease the energy of electric fields by the conducting of electric charge within the materials. So, after changing mechanical energy(vibration) into electric energy through piezoelectric effect of BaTiO$_3$, in filled IPNs, the piezoelectric materials can create dielectric loss because of the created alternating electric field, thus conduct the electric energy through dielectric loss.

Additionally, seen from the equation, $P = 2\pi U^2 f \tan \sigma A\varepsilon/d$ (where P is loss power (W), U is induction voltage(V), f is frequency (Hz), $\tan \sigma$ is dielectric loss, ε is dielectric constant, A is area (m^2) and d is thick (m) of material), the higher values of dielectric constant and dielectric loss, the higher energy loss power of materials, and thus the better damping properties of materials. Since BaTiO$_3$ possess high dielectric loss value

(a)- 50/50 PU/UPR IPNs

(b)- 70/30 PU/UPR IPNs

Figure 5 TEM photographs of IPNs with different component ratios.
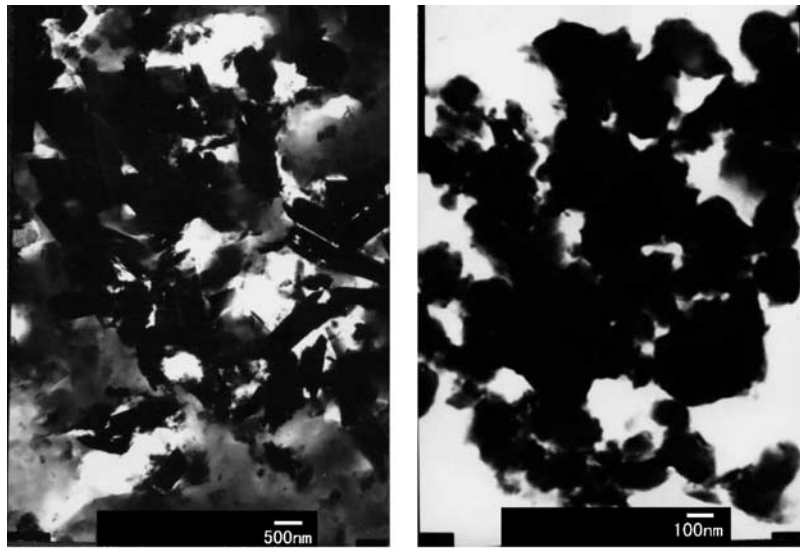
(a)-IPNs with BaTiO$_3$ fiber

(b)-IPNs with BaTiO$_3$ nanopowder

Figure 6 TEM photographs of 70/30IPNs with BaTiO$_3$ fiber and nanopowder.
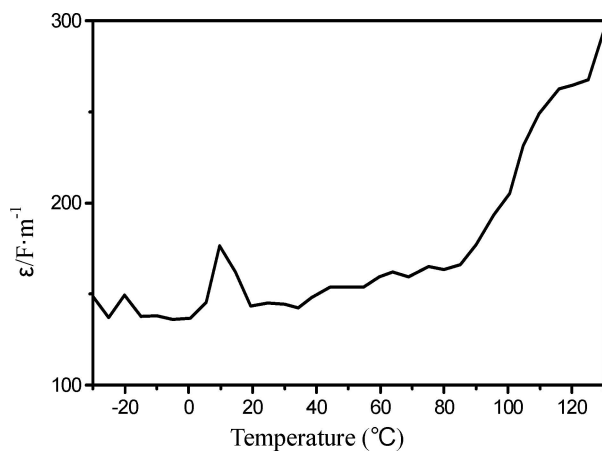

Figure 7 Dieletric constant versus temperature curve of BaTiO$_3$ nanopowder filled IPNs at 1 MHz.
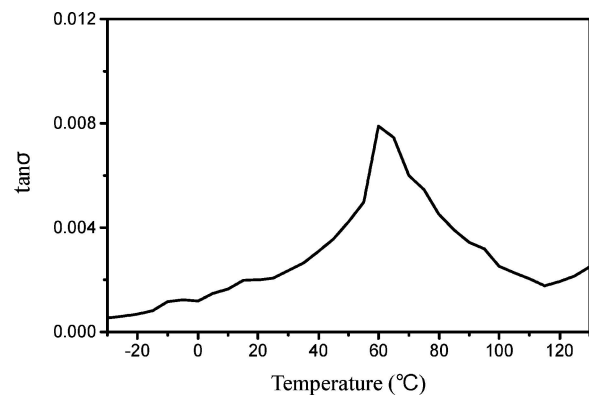

Figure 8 Dieletric loss versus temperature curve of BaTiO$_3$ nanopowder filled IPNs at 1 MHz.

(tanσ is usually 10^2), so the BaTiO$_3$ filled IPNs can obtain relative high dielectric loss, and contribute high damping properties to system. Especially, after polarization process to material, more BaTiO$_3$ create higher induction voltage, can give higher values of tan δ and larger E'' area.

4. Conclusion

The PU/UP component ratio is one factor that has influence on damping properties of IPNs. The tan δ shifts toward higher temperatures and the phase separation degree increase with the increase of UP component concentration in IPNs. The types of filler and filling amount both have great influence on maximum tan δ and E'' values of IPNs. Fiber-like filler can improve areas of E'' and shift effective damping temperatures to higher temperatures dramatically, mainly because of strong frictional action between two apparent different modulus materials(the molecular chains of polymer matrix and inorganic fibers). The small amount of filler, can improve the damping properties without sacrifice phase continuity a lot, but large amount of inorganic phase, result in shoulder at low temperatures of tan $\delta \sim T$ curve, indicating large phase separation in system. The polarization treatment to piezoelectric properties materials filled IPNs can exhibit synergistic effects caused by elastomeric damping, interfacial frictional damping and piezoelectric damping mechanisms. The dielectric properties have excellent consistency of temperature ranges of maximum values of dielectric constant, dielectric loss with loss factor. This reveals that there exist highly correlated relation between dielectric and damping properties in IPNs. Besides T_g, dielectric constant and dielectric loss are other two important factors, to determine damping properties of IPNs-based composites.

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