

Preparation and Properties of Nano-Al₂O₃ Particles/Polyester/Epoxy Resin Ternary Composites

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ABSTRACT: This article presents the results of an experimental study on the preparation and properties of new ternary composites composed of nano-Al₂O₃ particles, polyester, and epoxy resin. The ternary composites were prepared by the addition of the nano-Al₂O₃ particles in a binary matrix, with elevated viscosity, of the epoxy resin modified by the polyester. The nano-Al₂O₃ particles were previously located and dispersed in the polyester phase. The study showed that the ternary system was a type of nanoscale dispersed composite with high strength and toughness as well as modulus, combined with excellent dielectric and heat-resistance properties. All related properties of the composites were remarkably superior to those of both the binary matrix and the unmodified epoxy resin. © 2002 John Wiley & Sons, Inc. *J Appl Polym Sci* 83: 70–77, 2002

Key words: nanocomposite; polyester; reinforcement

INTRODUCTION

Epoxy resin is widely used for the matrix of composites and electronic components, due to its excellent adhesive and dielectric properties. However, its usage has been greatly limited in complicated environments because of accompanying disadvantages, in particular, its poor toughness, which causes warping and cracking of products loaded by impact, thermomechanical fatigue, and shrinking stress during the preparation and service of the products. With the development of more highly integrated components and structures, it is important to develop new toughened modified dielectric epoxies with high heat resistance.

Rubber materials have been used to modify epoxy resins,^{1–3} which results in increased toughness of the composite. However, the toughening was obtained at the cost of a decreased modulus and glass transition temperature, namely, the reduction of the heat resistance of the modified epoxy resins, which resulted directly from the lower modulus and the glass transition temperature of the rubber materials.

An inorganic nanoparticle is an excellent toughening and reinforcing material to develop new nanocomposites.^{4–6} It is well known that the structures and properties of a polymer are greatly different from those of inorganic nanoparticles. For example, polymer materials possess low specific gravity, excellent dielectric properties, and high specific strength, and the inorganic nanoparticles have great rigidity, a good heat-resistance property, and high surface binding energy. Therefore, much effort has been made to obtain new nanocomposites with excellent comprehensive

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properties combined with those of both the polymer materials and the inorganic nanoparticles.

Various methods have been employed to prepare polymer-layered silicate (or clay) nanocomposites, for example, *in situ* intercalative polymerization. In this technique, the layered silicate is swollen within the liquid monomer so that polymer formation can occur between the intercalated sheets.^{7,8} Polymerization can be initiated either by heat or radiation, by the diffusion of a suitable initiator, or by a catalyst fixed through cationic exchange inside the interlayer before the swelling step by the monomer. In another way, layered silicate can be mixed with the polymer matrix in the molten state, that is, melt intercalation. If the layer surfaces are sufficiently compatible with the chosen polymer, the polymer can crawl into the interlayer space and form either an intercalated or an exfoliated nanocomposite.⁹ Additionally, the layered silicate can also be exfoliated into single layers using a solvent in which the polymer is soluble, namely, exfoliation-adsorption from the polymer in solution^{10,11} or a prepolymer in solution,¹² or by emulsion polymerization.¹³ It is well known that such layered silicates, owing to the weak forces that stack the layers together, can be easily dispersed in an adequate solvent. The polymer then adsorbs onto the delaminated sheets, and when the solvent is evaporated, the sheets reassemble, sandwiching the polymer to form an ordered multilayer structure. Moreover, the technique of template synthesis has been also used for the synthesis of double-layer hydroxide-based nanocomposites.¹⁴ However, even with all the methods mentioned above, there are very few studies on the formation of nanocomposites by directly adding nanoparticles into the polymer; knowledge about this field and what can or cannot be accomplished is still very incomplete.

The comprehensive properties of nanocomposites depend not only on how the properties of each component are related, but also on the morphologies of the microphase structure of the nanocomposites.¹⁵⁻¹⁸ In general, however, it is difficult to obtain epoxy-based nanocomposites with uniform dispersed phases and good interfaces by common blend methods because the inorganic nanoparticles tend to be agglomerated and separated from the epoxy matrix.

To obtain nanoscale dispersion epoxy composites, it is possible to modify the epoxy resin to be interpenetrated networks with another engineering plastic to avoid the agglomeration of the nanoparticles. Engineering thermoplastics are novel

modifying materials for epoxy resins from the viewpoint of the maintenance of mechanical and thermal properties. Modifications of epoxy resins with various types of ductile thermoplastics have been studied to improve the toughness of epoxy resins.^{19,20} In a previous article, aromatic polyesters, prepared by the reaction of phthalic or isophthalic acids and α,ω -alkanediols, were used to reduce the brittleness of epoxy resin.²¹ It should be pointed out that the synthesized aromatic polyesters had only lower molecular weight, and the investigation results exhibited that the fracture toughness increased with increase of the molecular weight of the polyester. Therefore, commercial polyester with a high molecular weight was used in this investigation, which was convenient and effective. In addition, polyester was used mainly for the dispersing medium of the nanoparticles because it is impossible for the nanoparticles to be dispersed directly at the nanoscale in the epoxy resin.

Therefore, the research on the ternary composites composed of thermoplastic polyester, rigid nano- Al_2O_3 particles, and epoxy resin is a relatively novel approach in this article. The investigation was performed with its focus on the preparation and properties as well as the microphase structures of the ternary composites.

EXPERIMENTAL

Materials

The bisphenol A type of epoxy resin was commercially available as E-6101; its epoxy value was 0.43N/100 g. The average molecular weight of poly(ethylene terephthalate) (polyester, PET) was 1.9×10^4 ; its melting temperature was 259°C. *O*-Benzene dicarboxyl anhydride, an analysis reagent, was used for the curing reagent. Nano- Al_2O_3 particles were supplied by The Institute of Physics in Beijing, China Academy of Science, with an average length of 40 nm and average diameter of 10 nm.

Preparation of the Specimens

Epoxy resin and polyester were added into an enamelware cup with stirring and heating. The mixing operations were carried out at 250°C for 10 min at a stirring rate before the polyester was resolved completely. After the mixture was cooled to 200°C, the Al_2O_3 nanoparticles and *o*-benzene

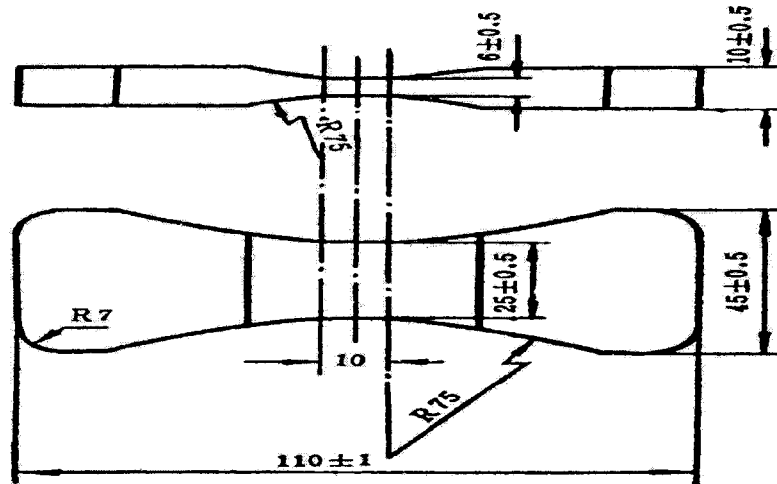


Figure 1 Specimen size of tensile strength test.

dicarboxyl anhydride were added and stirred uniformly. The mixture was poured into a preheated mold at once and put it into a vacuum oven at 200°C for 4 h. Subsequently, the prepared composites specimens were taken out of the oven and then cooled at room temperature and taken from the mold.

Mechanical Properties

Experiments were completed to measure the impact strength of the composites by no-notch specimens. All tests were performed on a Charpy-560 impact strength testing machine using 120 × 10 × 15-mm no-notch specimens. Five specimens of each composition were tested and the average values of the data are reported.

The tensile strength and modulus were measured using a mechanical testing machine (Instron-1195, Britain) at 22°C. The size of the specimen is shown in Figure 1. A tensile speed of 2 mm/min was applied in the tests. Five specimens of each composition were tested and the average values of the data are reported. Dynamic mechanical analysis was performed with a DuPont DMA 982 instrument between -150 and 250°C at a heating speed of 5°C/min at frequency of 5 Hz.

Dielectric Properties

All dielectric losses were measured using a dielectric loss measuring set (TR-10C type, Ando Electric Co. Ltd., Japan). The circle specimen of $\phi 50 \times 1$ mm was placed on the testing circuit bridge. When a balance was reached on the testing circuit bridge, the electric effect that acted on the cured

epoxy material was equivalent to that on the circuit as shown in Figure 2. The dielectric loss value is given by eq. (1):

$$T_g \delta = \frac{1}{\omega R_x C_x} = \frac{1}{2\pi f R_x C_x} \quad (1)$$

where R_x is the electric resistance at the balance state; C_x , the capacitance at the balance state; f , the frequency of the alternating current; and ω , the phase of the alternating current.

Morphology Observation

Some slices with a thickness of 70 nm were first cut off with a slicing machine (LKB NOVA, Sweden) and then dyed with OsO_4 to enhance the contrasting color of the photographs. Finally, the phase structures of the composites were observed by a transmission electron microscope (JEM-2000EX, Japan).

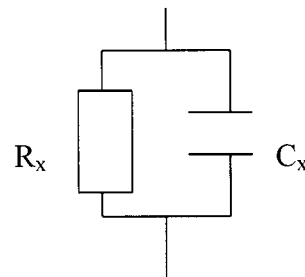


Figure 2 Equivalence circuit in the circuit bridge.

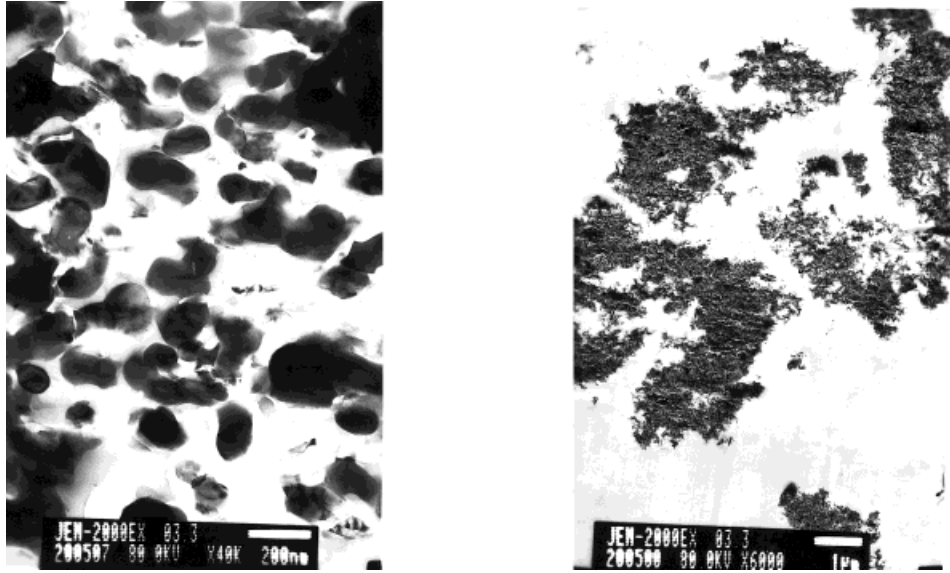


Figure 3 TEM photographs of ternary composites: (a) $\times 40\text{K}$; (b) $\times 6\text{K}$.

RESULTS AND DISCUSSION

Choice of Binary Matrix for Dispersion of Nanoparticles

Generally, it is impossible that nanoparticles are dispersed directly at nanoscale into epoxy resin. When mixed, the added nano- Al_2O_3 particles are easily separated from the epoxy matrix, that is, during the initial curing stage of the mixture, the rapid deposition of the particles resulted from their great difference in the specific gravity with epoxy resin, which had very low viscosity when the curing temperature was 200°C . Additionally, the nanoparticles with a large specific surface, driven by their great mutual-action forces, have a strong tendency to agglomerate in epoxy with low viscosity. Therefore, it was important to enhance the viscosity of the curing system at the beginning of the reaction.

To increase the initial viscosity of the curing system and avoid quick sedimentation of nano- Al_2O_3 particles in the epoxy matrix, three engineering plastics, that is, PET, PC, and PA6, were considered as candidates in the experimental determination of a suitable binary matrix, that is, the modified epoxy resin by either plastic. It needs to be noted that the selected engineering plastics should benefit both to disperse the nano- Al_2O_3 particles in the binary matrix and to maintain both the mechanical and the dielectric properties of the modified epoxy resins. After numerous tests, polyester was selected as the best

among the three engineering plastics. The appropriate proportion of the polyester added in the epoxy resin to produce the binary matrix was determined to be 16 phr (mass added parts relative per hundred parts matrix resin) polyester and 100 phr epoxy resin for the dispersing of the nanoparticles.

TEM Observation of the Micromorphology of the Ternary Composites

The microphase structures of the composites were examined by TEM observation, as shown in Figure 3. The nanoscale dispersion of the nano- Al_2O_3 particles in the binary matrix was observed, as shown in Figure 3(a). It is interesting that the nanoparticles were dispersed and located only in the polyester and could not be found in the epoxy resin as shown in Figure 3(b), that is, the nanoparticles were previously captured by the polyester phase.

Mechanical Properties of the Ternary Composites

The impact strength σ_I , tensile strength σ_T , and modulus E of the unmodified cured epoxy resin and the binary matrix are listed in Table I. The results show that the mechanical properties of the binary matrix were greatly promoted compared with those of the unmodified epoxy resin, but the glass transition temperature of the binary matrix

Table I Mechanical Property of Unmodified Epoxy Resin and the Binary Matrix

Specimens	σ_I (kJ m ⁻²)	σ_T (MPa)	E (GPa)	T_g (°C)
A	6.91	36.7	2.50	111
B	16.44	67.85	2.84	111

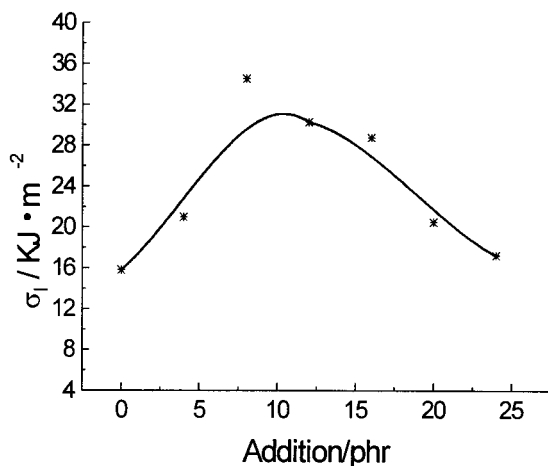
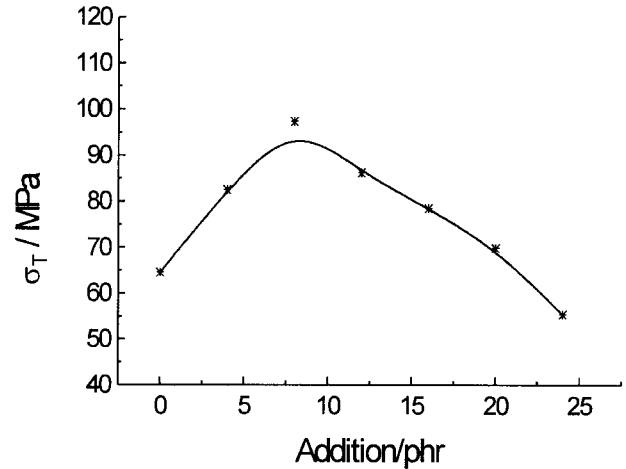
A is unmodified cured epoxy resin; B is the binary matrix.

was unchanged relative to that of the unmodified epoxy resin.

The relationships between the impact strength and the addition of nanoparticles are shown in Figure 4. The impact strength of the ternary composites was remarkably increased when 4 phr of the nanoparticles was added. The maximum impact strength was achieved when the addition of the nanoparticles was 8 phr. When the addition of the nanoparticles was over 8 phr, the impact strength of the composites was decreased with increase in the addition of the nanoparticles.

The variation of the tensile strength of the composites with the addition of nanoparticles exhibits a similar tendency to that of the impact strength, as showed in Figure 5. It needs to be noted that the maximum of the tensile strength also emerged at the point of addition of the 8 phr nanoparticles.

The maximum impact strength of the composites was 34.52 kJ/m², which was increased up to about 110% more than that of the binary matrix and 400% relative to that of the unmodified epoxy resin. Also, the composites have a maximum ten-

**Figure 4** Impact strength as a function of the addition of nanoparticles.**Figure 5** Tensile strength of composites versus addition of nanoparticles.

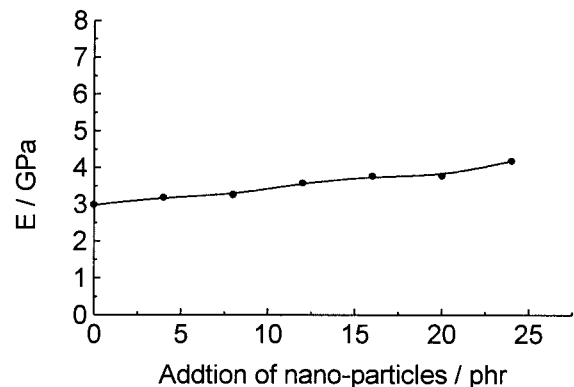
sile strength of 97.34 MPa, which was elevated to 44 and 165%, corresponding to those of the binary matrix and the unmodified epoxy resin, respectively. These results indicated that the mechanical properties of the composites were drastically improved by the addition of nano-Al₂O₃ particles dispersed in the binary matrix.

The elastic modulus of the composites almost increased linearly with increase of the addition of the nanoparticles as shown in Figure 6, that is, because of the addition of nanoparticles with greater rigidity than that of the binary matrix, the elastic modulus of the ternary composites was higher than that of the binary matrix and much higher than that of the unmodified epoxy resin.

Dynamic Mechanic Analysis (DMA)

Flexural Storage Modulus (E')

Figure 7 shows the flexural storage modulus of the composites as the function of the tempera-

**Figure 6** Elastic modulus versus addition of nanoparticles.

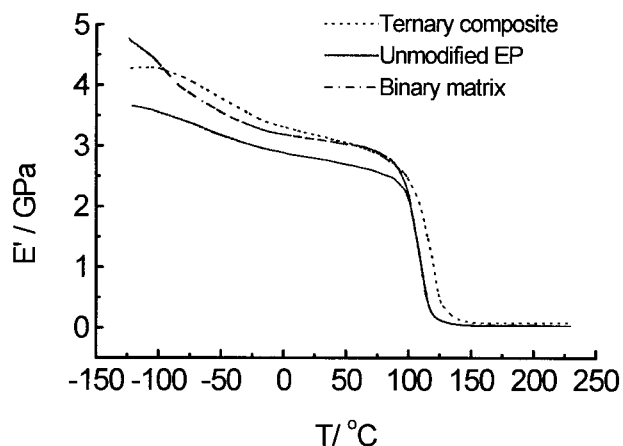


Figure 7 Variation of flexural storage modulus with temperature. Ternary compositions: 8 phr of nanoparticles:16 phr PET:100 phr EP. DNA: 16 phr of nanoparticles:100 phr EP. Unmodified EP: pure cured EP.

ture. The flexural storage modulus of the ternary composites was greatest when the temperature was within -80 to $+100^{\circ}\text{C}$. It should be noted that the flexural storage modulus of the unmodified epoxy resin almost linearly decreased with increase in the temperature, which suggested that there is a higher uniform crosslinked network density in the unmodified cured epoxy resin that consisted of only one phase. As can be seen in Figure 7, two kinds of a decline tendency emerged in the binary matrix and the ternary composites, that is, these curves showed two transformation stages, which indicated that the binary matrix and the ternary composite systems possessed an uneven phase structure. The cured epoxy resin was regarded as the the continuous phase and other compositions as the dispersed phase.

Flexural Loss Modulus (E'')

The variations of the flexural loss modulus with temperature are plotted in Figure 8. Two loss peaks emerged within -120 to $+250^{\circ}\text{C}$. The low-temperature loss peak or the T_{β} transition depends on the toughness of the material tested. The higher the peak, the better the toughness of the materials. Also, the broader peak band on the plots corresponds to the longer relaxation motion of the molecular chain segments in the polymer matrix. Figure 8 also shows that the low-temperature toughness of the chain segment of the ternary composites was best among the three systems.

The high-temperature loss peak or the T_{α} transition represents the corresponding glass transi-

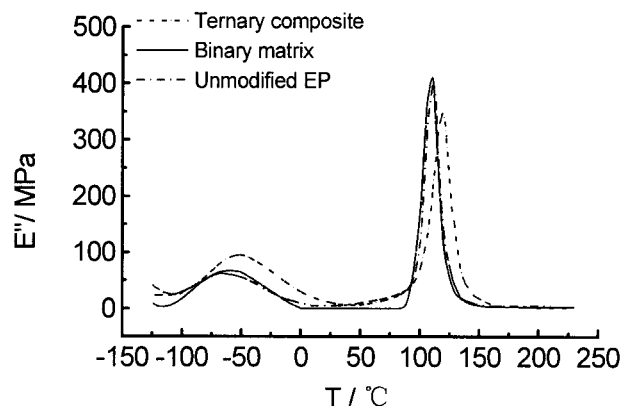


Figure 8 Relationship between flexural loss modulus and temperature. The same composition as in

tion temperature T_g . The higher the glass transition temperature, the better the heat resistance of the material. The glass transition temperature of the ternary composites was 119°C , 8°C higher than both of the other two systems (about 111°C). Therefore, the ternary composites have good heat resistance by the addition of high heat-resistant nanoparticles.

Dielectric Properties of the Ternary Composites

The dielectric property of the composites was excellent. The dielectric loss was about 10^{-4} when the temperature was below 120°C , as shown in Figure 9. A small dielectric loss peak emerged within 120 – 160°C . Also, the dielectric loss rapidly increased when the temperature was over 160°C . The lower the frequency of the electric field, the greater the loss value of the materials.

The dielectric loss of the dielectrics in the alternating current field is defined as eq. (2):

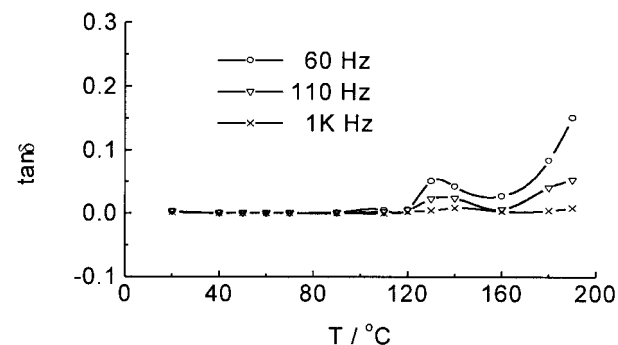


Figure 9 Dielectric loss of ternary composites as functions of temperature. Composition: 8 phr nanoparticles:16 phr polyester:100 phr epoxy resin.

$$T_g \delta = \frac{j_a}{j_c} \quad (2)$$

where j_a and j_c are the resistant electric current density and the capacitive electric current density given by eqs. (3) and (4), respectively:

$$j_a = \left(\gamma + \frac{\omega^2 \tau^2 g}{1 + \omega^2 \tau^2} \right) E_m e^{i\omega t} \quad (3)$$

$$j_c = \left(\omega \varepsilon_\infty + \frac{\omega \tau g}{1 + \omega^2 \tau^2} \right) E_m e^{i\omega t} \quad (4)$$

where g is the initial conductivity of the absorbing electric current density; ω ($= 2\pi f$; f is the frequency), the phase of the alternating current; γ , the conductance; τ , the relaxation time; E_m , the electric-field strength; t , the time; and ε_∞ , the dielectric constant at high frequency.

The conductance loss can be neglected when the temperature is below 120°C. Dielectric loss is described as eq. (5) (ref. 22):

$$T_g \delta = \frac{\omega \tau \Delta \varepsilon}{\varepsilon_s + \varepsilon_0 \omega^2 \tau^2} \quad (5)$$

where ε_s is the dielectric constant at low frequency. Therefore, dielectric loss decreased with increase of the frequency of the electric field.

When temperature increased to some level, the effect of temperature on the electric loss cannot be neglected again. The relationship between conductance and temperature is expressed as eq. (6):

$$\gamma = A e^{-B/T} \quad (6)$$

where T is the temperature and A and B are constants. Equation (6) indicates that conductance increased with increase of the temperature.

The dielectric loss of materials resulted from polarization loss and conductance loss caused by the electric field. When the testing temperature was low, the electric conductivity of materials can be neglected and the dielectric loss was caused mainly by polarization loss, which was relatively small. With increase of the temperature, the conductance loss of materials also increased. At the same time, polarization loss still existed. With further increase of the testing temperature, the conductance loss became greater and greater and the polarization loss decreased because relaxation times decrease with increase of the temperature.

So, a small peak appeared within a certain temperature range. As temperature further increased, the polarization loss can be neglected and the dielectric loss was mainly a conductance loss and drastically increased.

CONCLUSIONS

In this investigation, new toughened and reinforced ternary composites were prepared with the nano- Al_2O_3 particles dispersed in the binary matrix, namely, the modified epoxy resin by the polyester. The main results can be summarized as follows:

1. The ternary composites were prepared by the addition of the nano- Al_2O_3 particles in the binary matrix, with elevated viscosity, of the epoxy resin modified by the polyester. Also, the nano- Al_2O_3 particles were previously absorbed and dispersed in the polyester phase.
2. The mechanical properties of the composites were drastically improved by the addition of nano- Al_2O_3 particles dispersed in the binary matrix, which have their maximum impact and tensile strengths with 8 phr nano- Al_2O_3 particles. Also, the elastic modulus of the ternary composites almost linearly enhanced with increase of the addition of the nano- Al_2O_3 particles.
3. The ternary composite was an excellent dielectric material with low dielectric loss, about a 10^{-4} order of magnitude at temperature below 120°C.
4. The heat resistance of the ternary composite is better than that of the unmodified epoxy resin or binary matrix. Its glass transition temperature was 8°C higher than that of the unmodified epoxy resin.

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