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Ceramic/polymer composites with enhanced permittivity and low dielectric loss through grafting modification of polymer matrix by polyethylene glycol

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ABSTRACT

Bariumtitanate/epoxy resin (BT/ER) composite with high permittivity was obtained through graft modification on the ER matrix. Polyether polyols were employed to enhance the molecular polarity, which brought more polar oxygen atoms and produced more ester groups in the cured epoxy resin. The permittivity of epoxy matrix film was effectively enhanced (increased from 3.91 to 4.82 at 10^3 Hz) while the dielectric loss was nearly unchanged. The permittivity of the composite films containing the same amount of BT fillers improved from 18.91 to 28.73. Meanwhile, the increment of dielectric loss was not obvious. Both of the modified matrix and composite films showed excellent thermal stability.

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1. Introduction

Dielectric materials with high permittivity are of great importance for a broad range of applications in modern electronics and electrical power systems such as hybrid electric vehicles, medical defibrillators, filters, and switched-mode power supplies [1–4]. The continuous miniaturization and increased functionality of the devices demand further increase of permittivity of dielectric materials since capacitors contribute significant volume and weight to these systems. High permittivity materials, as an important material of electronic components, are receiving increasing attention [5–8].

Although percolative composite, filling conductors or semiconductors in insulating matrix, can achieve high permittivity, the dielectric loss also rapidly increases due to the insulator–conductor transition near the percolation threshold [9–11]. A better strategy, ceramic/polymer composites are preferred for applications in electronic materials because of their high dielectric strength, high permittivity and low dielectric loss. Among various species of polymer materials, epoxy resin is more attractive for these applications because of its low cost, excellent processing properties and low dielectric loss (0.002–0.01). However, the permittivity of epoxy resin is relatively low (3.5–5.0). Most of the previous research work has been focused on filling epoxy matrix with high permittivity particles (BaTiO_3 , $\text{Pb}(\text{Zr,Ti})\text{O}_3$, $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$, ZnO , etc.) and modifying interface to get improved permittivity [6,12–14].

Another method is to modify the molecular structure of epoxy matrix. Wong Ching-Ping et al. used 5 wt% Co-Acac (cobalt acetylacetonate) to promote the curing process of epoxy DER661; the results showed that permittivity of the epoxy was enhanced which had relation with the amounts of Co-Acac [15]. Our recent study [16] has shown that the permittivity of epoxy matrix was enhanced by 30% when both polyethylene glycol (PEG) and chromium acetylacetonate (Cr-Acac) were employed to graft-modify the epoxy resin. The conjugated system and induced polarizability were discussed in our previous study, while a systematic investigation on the effect of PEG amount on the enhancement of polymer matrix is still needed. In this research, emphasis was put on the effect of polyether polyols on the molecular polarity enhancement and the relation between intrinsic polarity and permittivity.

2. Experimental

First, 5 g ER (trademark E51), 0.15 g 2E4MI (2-ethyl-4-methylimidazole) and 4.3 g MeTHPA (methyl tetrahydrophthalic anhydride, curing agent for epoxy resin) were mixed at room temperature, stirring for 10 min. Then different amounts of PEG were added, respectively. Afterwards, the solution was diluted with 10 g butanone and ultrasonicated for half an hour. The resultant solution was used to fabricate films on copper foil. For preparation of BT/ER film, 20 g BT particles (average 100 nm) and 20 g butanone were added to the above resin solution, followed by ultrasonication for more than 3 h to obtain stable and uniform slurry. The slurry was used to make composite films on the copper

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foil. All the films were heated at 120 °C for half an hour to vaporize the solvent followed by the curing process at 150 °C and 180 °C for 2 h in sequence.

FTIR (Vertex 70) spectra were used to analyze the graft modification process. The dielectric behavior was measured with an impedance analyzer 4294A.

3. Results and discussions

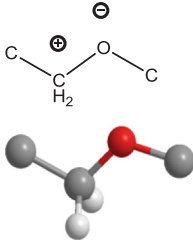
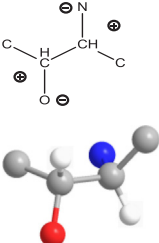
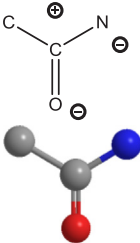
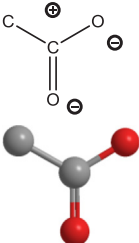
Permittivity of organic materials is determined by molecular polarization which mainly includes orientation polarization and induced polarization [17,18]. Orientation polarization is related with molecular polarity while induced polarization is caused by transfer of electrons under external electrical field. Improvement of polymer polarity will not only enhance the orientation polarization but also make electrons easier be induced. Epoxy group can react with many reagents, producing various structures, such as amine, ether, amide and ester groups. Due to different polar atoms and bond moment structures, there is obvious molecular moment difference among these groups. The group with more polar atoms and unsymmetrical structure has stronger molecular polarity, while the one with less polar atoms or symmetrical structure has weaker molecular polarity. There are many empirical approaches to compare the average molecular polarity [17–19]. A simple method is using electronegativity and bond moment to compare the molecular relative polarity. As shown in Table 1, the ester group shows stronger relative polarity than other groups. Under external electrical field, the stronger molecular polarity will enhance both of the orientation polarization and induced polarization, bringing about larger polarizability and higher permittivity.

PEG is employed to increase the molecular polarity of epoxy resin by graft modification method (Scheme 1). PEG reacts with anhydride producing one ester group. The anhydride then reacts with epoxy group producing another ester group. The above process indicates theoretically that modification with PEG improved the molecular polarizability of the epoxy resin and would result in enhanced permittivity [16]. Meanwhile, PEG increases the amount of oxygen atoms which also possess strong polarity.

As shown in Fig. 1(a), there is distinct permittivity enhancement after graft modification in the frequency range of 10^2 – 10^7 Hz. The permittivity values of all the films decrease slowly and stably with frequency increasing from 10^2 to 10^7 Hz. The permittivity of the film with 20% PEG (based on epoxy resin) at 10^3 Hz is 4.82, which is over 20% larger than that of the unmodified epoxy matrix film of 3.91. However, the permittivity is not further improved with more addition of PEG. On the contrary, it reduces to 4.64 with 30% PEG and 4.06 with 40%. The dielectric loss curves are similar (Fig. 1(a)) at frequencies below 10^4 Hz. Small differences appear above 10^4 Hz. The dielectric loss of the modified films increases faster than the unmodified one and higher PEG loading results in higher dielectric loss. PEG was grafted to the carbon chain as Scheme 1. The graft PEG brought more oxygen atoms and produced more ester groups during the curing process of epoxy resin, which increased the molecular polarity. As a result, permittivity of the epoxy graft-modified by PEG was enhanced. However, excessive PEG could react with the intermediate product and end the chain curing reaction. Consequently, the curing process was damaged and resulted in reduction of permittivity. Furthermore, the linear chain of molecule PEG is rotary and has large free volume. It makes the polar group become loose so that the dipole moves more violently in external electrical field and causes larger dielectric loss [20].

After modified with PEG, permittivity of BT/ER composites is distinctly increased. The permittivity of the composite film with 20% PEG at 10^3 Hz is 28.73, which is over 50% larger than that of the unmodified film with the permittivity of 18.91 (Fig. 1(b)). The improvement of matrix permittivity will induce prominent effect on permittivity of composite. All the dielectric loss curves (modified and unmodified ones) are very close, indicating that the enhanced permittivity for the PEG modified composite films is not accompanied with the increase of the dielectric loss (Fig. 1(b)). In composite, the polarizability mechanisms involve matrix, fillers and interfaces. The grafting of matrix with more polar groups results in polarization of more electrons and the permittivity of composites is consequently enhanced. However, the interfacial polarizability (between matrix and fillers) takes the most part of energy loss, especially with high filler loading. Although the

Table 1

(a) Single atom electronegativity.					
Atom	C	H	O	N	
Electronegativity	2.5	2.1	3.5	3.0	
(b) Simple bond moment.					
Bond	C–C	C–H	C–N	C–O	C=O
Bond moment	0	0.4	0.45	0.7	2.4
(c) Carbon atom center electronegativity and molecular moment of different groups.					
Groups	Ether group	Amine group	Amide group	Ester group	
Structure					
Electronegativity	0.2	0.6 and 0.1	2.5	3.0	
Total bond moment	1.5	1.1 and 0.85	2.85	3.1	

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