Polymer Bulletin 60, 129–136 (2008)
DOI 10.1007/s00289-007-0840-3

Polymer Bulletin

Dielectric properties of polymer/ceramic composites based on thermosetting polymers

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Received: 10 May 2007 / Revised version: 26 July 2007 / Accepted: 9 September 2007
Published online: 21 September 2007 –

Summary

A series of thermosetting polymer/ceramic composites were prepared. Three kinds of thermosetting polymers, i.e. cyanate resin, bismaleimide resin, and epoxy resin, were used as matrixes, and $BaTiO_3$ particles were as fillers. The dielectric properties of these composites were investigated. Experimental data of the dielectric constants were fitted to several theoretical equations in order to obtain the best-fitting equations of the dielectric constants of these composites. The result indicates that the dielectric constants of composites all increase with the increase of $BaTiO_3$ content. Using bismaleimide resin and epoxy resin as matrixes, the dielectric losses both increase obviously as the amount of $BaTiO_3$ particles is increased, but the dielectric loss of cyanate/$BaTiO_3$ composite decreases. With the increase of the frequency, the variation ranges of the dielectric constant and dielectric loss of cyanate/$BaTiO_3$ composite are both the smallest. The predications of the effective dielectric constants by Lichterecker mixing rule are in good agreement with experiment data.

Keywords

Thermosetting polymer; ceramic; composites; dielectric properties

Introduction

The study of the polymer/ceramic composites has received more and more attention worldwide [1-3]. This is because the polymer/ceramic composites can be prepared with excellent dielectric and mechanical properties at low temperature processing conditions by combining the advantages of the two phases. In addition, dielectric and other properties can be designed according to specific requirements by adjusting the relative fraction of the starting materials, treating the components with different chemical or physical methods and changing the processing techniques.

In the beginning, thermoplastic polymers such as polyvinylidene fluoride (PVDF) and poly(vinylidene fluoridetrifluoroethylene)[P(VDF-TrFE)] copolymers had been widely used as the matrixes of polymer/ceramic composites for their good dielectric and pyroelectric performances [4-6]. With the development of the electronic technology, further applications of these composites were limited because of the poor thermal stability of the matrix. Recently, thermosetting polymer/ceramic dielectric composites have been considered as the promising materials to overcome the limitation due to their excellent comprehensive properties. Epoxy /ceramic composites have been intensively investigated due to their compatibility with printed writint boards (PWBs) [7-9]. However, there have been few reports on polymer/ceramic composites using bismaleimide (BMI) or cyanate as matrix. In this work, a series of polymer/ceramic composites were prepared made of cyanate resin, bismaleimide resin, and epoxy resin, respectively. The dielectric properties of composites were investigated. Predications by theoretical equations were compared with the experimental data of the dielectric constants. According to the comparisons, the best-fitting equations of the dielectric constants of these composites were obtained.

Experimental

Materials

Bisphenol A dicyanate (2, 2'-bis (4-cyanatophenyl) isopropylidene)(BADCy) was purchased from Shanghai Huifeng Kemao Ltd. (Shanghai, China) with at least 99% (wt). 4, 4'-bismaleimidodiphenyl methane (BDM) was supplied by Northwestern Chemical Institute (Xi'an, China) and recrystallized from the chloroform/methanol mixture (volume ratio 1:1). O, O'-diallylbisphenol A (BA) was self-synthesized. Diglycidyl ether of bisphenol A epoxy resin (DGEBA (E-51, epoxide equivalent weight: 196 g/mol)) was purchased from Wu Xi Resin Plant (Wuxi, China) and its weight purity is 95% (wt). 4, 4'-diaminodiphenyl sulfone (DDS), white crystal and with purity>98%, was purchased from Third Shanghai Chemical Reagent Company (Shanghai, China). γ-aminopropyl triethoxy silane (KH-550) was supplied by Jingzhou Jianghan fine chemical Ltd.(Jingzhou, China). Barium titanate ($BaTiO_3$) was provided from Xi'an global chemical instrument company (Xi'an, China) and its average diameter of $BaTiO_3$ is 3μm. Acetone was obtained from Xi'an chemical reagent corporation (Xi'an, China).

Preparation of $BaTiO_3$ particles treated with KH-550

$BaTiO_3$ particles were first heated in an oven at 110°C for 4 hours to remove the moisture, and KH-550 was blended with acetone to form solution. And then $BaTiO_3$ particles were added in the solution. Finally, the mixture was reacted in an oven at 110°C for 3 hours.

Preparation of composites

After the mixture of a stoichiometric amount of organic monomers and $BaTiO_3$ particles was dispersed at 100ºC, the liquid mixture was precured at 150ºC with continuous stirring until a homogeneous mixture was obtained. Afterwards the prepreg was immediately cast into the glass mould that was heated at 150ºC beforehand and the air bladder in the mould was removed under vacuum at 100ºC for 30 minute. After that, the prepreg was cured at a programmed heating rate: 160ºC /2h +180ºC /2h +200ºC /2h, and then post treated at 230ºC for 4 hours. After the oven temperature was decreased naturally from 230ºC to room temperature, the composite was obtained. Table 1, Table 2 and Table 3 represent the compositions of the composites.

Table 1. Compositions of cyanate/$BaTiO_3$ composites.

Sample no.	BADCy	$BaTiO_3$
1-1	100.0	0.0
1-2	90.0	10.0
1-3	80.0	20.0
1-4	70.0	30.0
1-5	60.0	40.0
1-6	50.0	50.0
1-7	40.0	60.0

Table 2. Compositions of bismaleimide /$BaTiO_3$ composites.

Sample no.	BDM	BA	$BaTiO_3$
2-1	58.8	41.2	0.0
2-2	52.9	37.1	10.0
2-3	47.0	33.0	20.0
2-4	41.2	28.8	30.0
2-5	35.3	24.7	40.0
2-6	29.4	20.6	50.0
2-7	23.5	16.5	60.0

Table 3. Compositions of epoxy/$BaTiO_3$ composites.

Sample no.	E-51	DDS	$BaTiO_3$
3-1	80.0	20.0	0.0
3-2	72.0	18.0	10.0
3-3	64.0	16.0	20.0
3-4	56.0	14.0	30.0
3-5	48.0	12.0	40.0
3-6	40.0	10.0	50.0
3-7	32.0	8.0	60.0

Dielectric properties measurements

The dielectric properties were measured on AS2853 Impedance analyzer in the frequency ranges from 200 KHz to 60 MHz.

Results and discussion

Dielectric properties of thermosetting resin/$BaTiO_3$ composites

Figure 1 shows the dielectric constants of these three kinds of composites with various contents of $BaTiO_3$ particles. The dielectric constants all increase with the increase of $BaTiO_3$ content. When $BaTiO_3$ particles are added to 60% (wt), the dielectric constants of the composites made of cyanate resin, bismaleimide resin, and epoxy

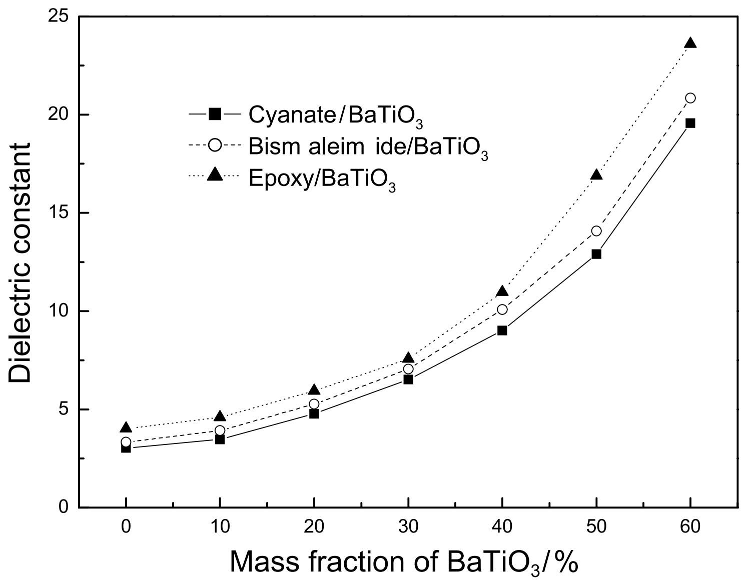

Figure 1. Dielectric constant changes with $BaTiO_3$ particles loading.

resin are 19.57, 20.085 and 23.59, respectively. Compared with pure resins, the dielectric constants of the composites are all improved by six times.

The results of the dielectric losses of these composites can be seen from Figure 2. Using bismaleimide resin and epoxy resin as matrix, the dielectric losses both increase obviously as the amount of $BaTiO_3$ particles is increased, but the dielectric loss of cyanate/$BaTiO_3$ composite decreases. The difference can be explained by the

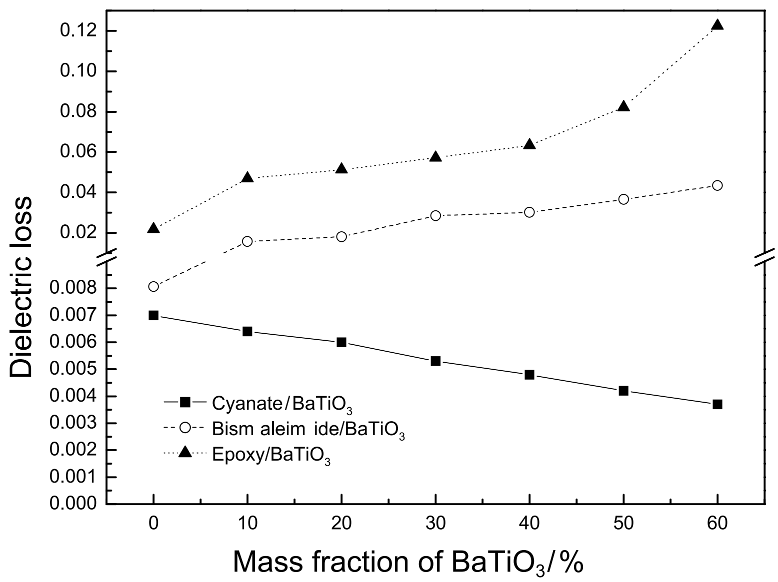

Figure 2. Dielectric loss changes with $BaTiO_3$ particles loading.

interaction between the matrix and the filler. On the surface of $BaTiO_3$ particles, there are –OH groups that can not react with bismaleimide resin and epoxy resin but react with cyanate resin to form chemical bonding, which improves the interface adhesion between cyanate resin and $BaTiO_3$ particles, thus $BaTiO_3$ particles can obviously prevent the movement of the polymer in the BADCy/$BaTiO_3$ composite. With the increase of the mass fraction of $BaTiO_3$, it is more and more difficult for polymer to move, so the dielectric loss of cyanate/$BaTiO_3$ composite decreases with the increase of the content of $BaTiO_3$ particles.

Figure 3 illustrates the effect of the frequency on the dielectric constants and dielectric losses of composites. It is shown that the variation ranges of the dielectric constant and dielectric loss of composite made of cyanate are both the smallest than those of bismaleimide/$BaTiO_3$ composite and epoxy/$BaTiO_3$ composite. This phenomenon is because the dielectric constant and the dielectric loss of cyanate resin are stablest at various frequencies compared with bismaleimide resin and epoxy resin, which can be seen clearly from Figure 4.

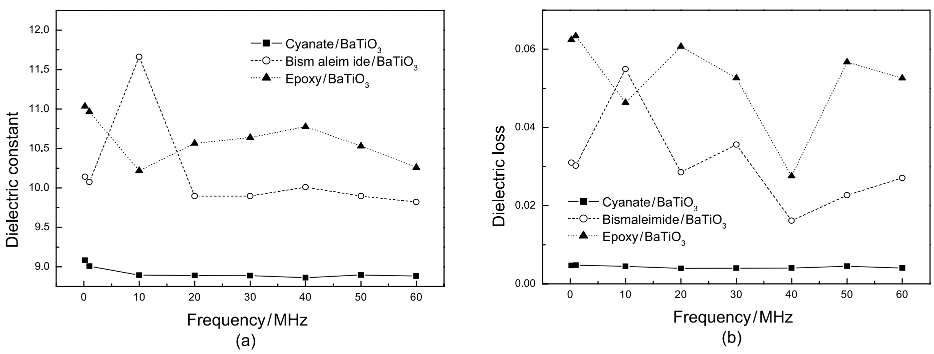

Figure 3. Dielectric properties of compositions change with the variation of the frequency.
* The content of $BaTiO_3$ particles was 40 wt%.

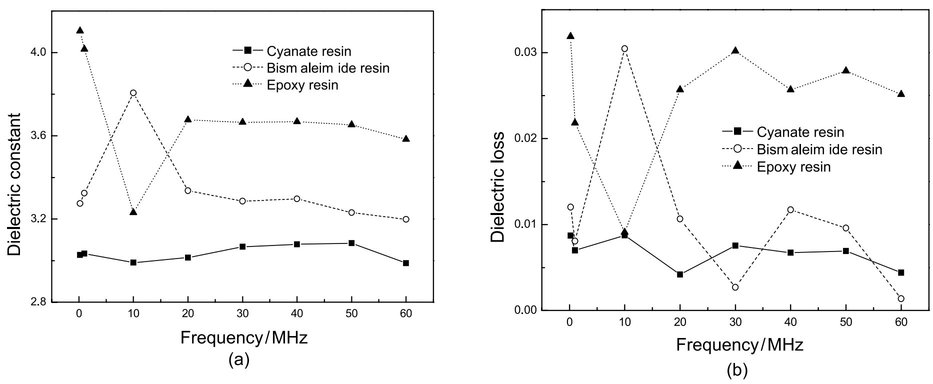

Figure 4. Dielectric properties of pure resins change with the variation of the frequency.

From above results, it can be concluded that the dielectric properties of cyanate/$BaTiO_3$ composites are the most excellent among these three kinds of composites. Besides, compared with bismaleimide resin and epoxy resin, cyanate resin provides outstanding mechanical and thermal properties. Therefore, cyanate ester resins can function as an excellent matrix material for dielectric composites.

Theoretical fitting of the dielectric constants of thermosetting resin/$BaTiO_3$ composites

It is very important for composite materials design to precisely predict the effective properties. Dielectric properties of composites are influenced with not only the dielectric constants of the components but also other factors such as the morphology, the dispersion and the interaction between the two phases. Therefore, it is necessary to predict by combining the theory and the experiment.
Considering the influence of the shape on the dielectric properties, the following equations [10-12] are often used to calculate the dielectric constant of polymer-ceramic 0-3 composites:

Yamada formula: $$\varepsilon = \varepsilon_1 (1 + \frac{\alpha\phi(\varepsilon_2 - \varepsilon_1)}{\alpha\varepsilon_1 + (1-\phi)(\varepsilon_2 - \varepsilon_1)}) \qquad (1)$$

EMT formula: $$\varepsilon = \varepsilon_1 (1 + \frac{\phi(\varepsilon_2 - \varepsilon_1)}{\varepsilon_1 + \alpha(1-\phi)(\varepsilon_2 + \varepsilon_1)}) \qquad (2)$$

Lichterecker formula: $$\varepsilon^{\alpha} = (1-\phi)\varepsilon_1^{\alpha} + \phi\varepsilon_2^{\alpha} \qquad (3)$$

Here, ε_1 is the dielectric constant of the polymer, ε_2 is the dielectric constant of the ceramic, φ is the mass fraction of the ceramic, and α is the shape parameter.
As to Yamada formula, α was taken as 3.396069 (cyanate/$BaTiO_3$ composite), 3.332278 (bismaleimide/$BaTiO_3$ composite) and 3.091588 (epoxy/$BaTiO_3$ composite) with the method of multivariate nonlinear analysis according to the experiment data. In Figure 5, the experimental data of the dielectric constants of composites are compared with predications by Yamada mixing rule. It is indicated that the predictions are lower than the experimental data in lower content of $BaTiO_3$ particles (<50%), and higher than the experimental data in higher content of $BaTiO_3$ particles (>50%). When

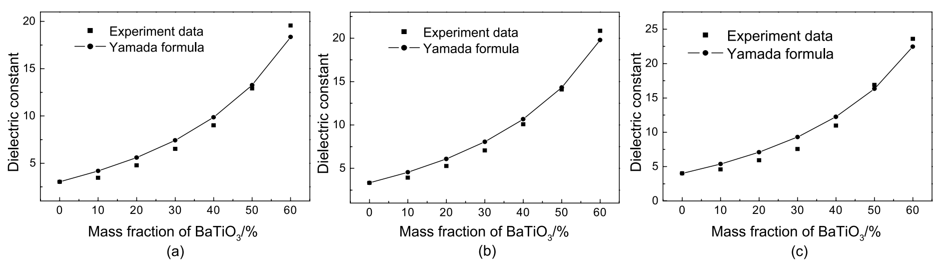

Figure 5. Comparison of the predications by Yamada formula with the experimental data (a) cyanate/$BaTiO_3$ composite (b) bismaleimide/$BaTiO_3$ composite (c) epoxy/$BaTiO_3$ composite.

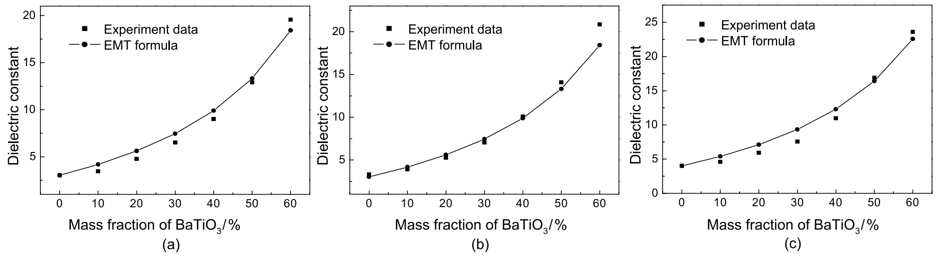

Figure 6. Comparison of the predications by EMT formula with the experimental data (a) cyanate/$BaTiO_3$ composite (b) bismaleimide/$BaTiO_3$ composite (c) epoxy/$BaTiO_3$ composite.

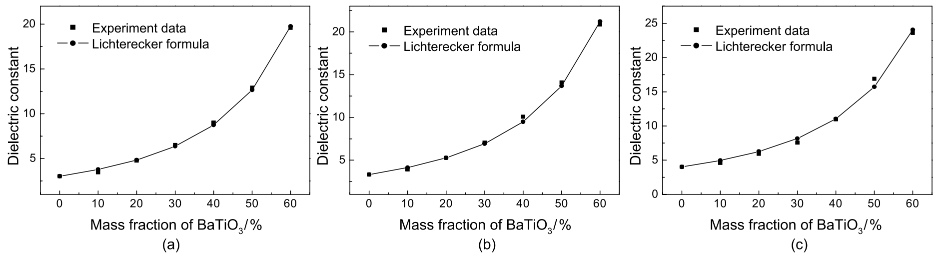

Figure 7. Comparison of the predications by Lichterecker formula with the experimental data (a) cyanate/$BaTiO_3$ composite (b) bismaleimide/$BaTiO_3$ composite (c) epoxy/$BaTiO_3$ composite.

the content of $BaTiO_3$ particles is 50%, the experimental data is equal to the predication.

With the method of multivariate nonlinear analysis, α in EMT formula was taken as 0.292947(cyanate/$BaTiO_3$ composite), 0.298440(bismaleimide/$BaTiO_3$ composite) and 0.321542 (epoxy/$BaTiO_3$ composite). The comparisons of the experimental data and predications by EMT formula are illustrated in Figure 6. The result shows that the predictions are also not consistent with the experimental data. The difference is because that this equation is based on the effective medium theory that treats the dielectric response of a heterogeneous system by assuming that each particle is, on average, surrounded by a mixture that has the assumed homogeneous medium property.

According to the experiment data, α in Lichterecker formula was taken as -0.455352 (cyanate/$BaTiO_3$ composite), -0.460039 (bismaleimide/$BaTiO_3$ composite) and -0.477392 (epoxy/$BaTiO_3$ composite). The result of predications by Lichterecker mixing rule is indicated in Figure 7. Compared with the experimental data of the dielectric constant of composites, it is shown that the predictions are in good agreement with the experimental data. Therefore, it is concluded that Lichterecker mixing rule is the best-fitting prediction of the effective dielectric constant of thermosetting resin/$BaTiO_3$ composite.

Conclusions

The dielectric properties of polymer/ceramic composites made of cyanate resin, bismaleimide resin, and epoxy resin respectively, were investigated systematically. It is shown that the dielectric constants and the dielectric losses of bismaleimid/$BaTiO_3$

composite and epoxy/$BaTiO_3$ composite increase with the increase of $BaTiO_3$ content. As to the composite made of cyanate resin, the dielectric constant increases but the dielectric loss of the composite decreases with the increase of the content of $BaTiO_3$ particles. In addition, the dielectric constant and dielectric loss of cyanate/$BaTiO_3$ composite are the most stable at various frequencies. In conclusion, the dielectric properties of cyanate/$BaTiO_3$ composites are the most excellent among these three kinds of composites. According to the comparison between the experiment data and mixing rules, Lichterecker mixing rule is the best-fitting prediction of the effective dielectric constant of thermosetting resin/$BaTiO_3$ composites.

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