Dielectric relaxation dynamics of Al/epoxy micro-composites

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Abstract

The dynamic dielectric properties of the Al/epoxy composites were investigated by means of broadband dielectric spectroscopy spectrometer with the frequency range 1-10⁷ Hz at the temperature of -20-200 °C. Three relaxation processes are detected in the dielectric spectra as a function of temperature and frequency: (1) Maxwell interfacial polarization (IP) at low frequencies and high temperatures; (2) a primary α -relaxation process near T_g at the middle frequencies; and (3) Intermediate dipolar effect (IDE) relaxation at high frequencies above -20 °C. The dynamics of all the recorded processes include contributions from both polymer and the inorganic reinforcing phases. The analyses of loss tangent and electric modulus spectrum of the composites indicate that the chain segmental dynamics of the polymer are accompanied by the absorption of energy given to the system. Finally, the alternating current (AC) conductivity spectra support the hopping type of conduction in the composites and the ionic conduction relaxation processes are observed also.

Key Words: Polymers, elastomers and plastics; Semiconductors; Dielectric response.

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1. Introduction

As a kind of functional materials, polymer matrix composites (PMCs) with high dielectric constant (k), breakdown strength, energy density, and low dielectric loss, have attracted the attention of researchers as advanced technological materials such as artificial muscles, energy storage, flexible electronics, embedded capacitor and sensors [1-4]. However, their major drawback for electronics applications is their low value of permittivity (i.e., <10) [5, 6]. Therefore, a key issue is to enhance the dielectric constant of polymers while retaining other excellent performances. To solve this problem, one common strategy is to add high k ceramic fillers such as BaTiO_3 or PbTiO_3 into the polymer matrix. Generally, the k of the composites could be obviously improved only by adding up to 50 vol. % of these fillers. Unfortunately, the mechanical and processing properties are greatly deteriorated owing to the high loading of fillers, and it is difficult to control the dielectric constant by precisely adjusting the filler content [5-9]. Another widely used strategy is to prepare percolative polymer composites by introducing high electrical conductivity particles such as metal (i.e., Aurum, Silver, Copper, Aluminum) [10-17] and carbon fillers [18-23] into a polymer. Based on the percolation theory and mini-capacitor model, when the volume fraction of conductive filler increases to the percolation threshold, dielectric constant of the composites can be dramatically enhanced [24,25]. However, a critical problem of this kind of composites is that they generally have very high dielectric losses, bringing about huge energy wastage and low reliability in service [26]. Therefore, the development of polymer composites with high dielectric permittivity but low dielectric loss is important for practical engineering applications [15, 17, 27-28].

To solve this problem, some useful strategies have been proposed. Nowadays, commonly used one is preparing the conductor-insulator core-shell structured particle to avoid the connection of

conductors and thus reduce the dielectric loss. As previously reported, surface self-passivated aluminum (Al) particles are often chosen as the filler to fabricate the core-shell structured Al (Al@Al₂O₃)/polymer composites with high permittivity but low dielectric loss [13, 20, 29-32]. The metal core is used to increase the dielectric constant owing to its interfacial polarization or Maxwell-Wagner-Sillars effect (MWS), while the insulator shell serves as a barrier layer to control the dielectric loss efficiently through blocking the electron transfer between adjacent metal cores [10, 11, 20, 31, 32]. Due to this special structure, a low dielectric loss and conductivity can be obtained compared with that of a neat epoxy resin [17]. The obtained Al/polymer composites have combined the advantages of ceramics/polymer system and percolative composite, presenting a high dielectric constant and a low dielectric loss [20].

Most of the researches on Al/polymer composites done so far have focused on the study of their dielectric behavior as a function of Al filler content and the percolation threshold (P_c) critical behavior in the vicinity of metal-insulator transition process. Up to now, the investigation on the dynamic dielectric properties of Al/polymers has been rarely investigated, and it is as important as dielectric properties at room temperature from the application point of view and requires serious attention. This has motivated us to conduct a systematic study on the dynamic dielectric behavior of core-shell structured Al/epoxy composites, and on how the presence of filler concentrations of particles, temperature as well as frequency affects the dielectric properties in a complex polymer matrix. Broadband dielectric spectroscopy with wide temperature (from -20 to 200 °C) and frequency (1-10⁷ Hz) ranges provides a highly accurate and powerful measurements for the investigation of molecular mobility, electrical conductivity mechanisms, interfacial effects and dielectric properties in polymers and complex systems. Therefore, the present research is expected to provide a deeper

insight into the dynamic thermal and dielectric behavior of the Al/epoxy composite.

2. Experimental

2.1 Materials

A diglycidyl ether of bisphenol A-type epoxy resin (D.E.R.-331, Dow Crop.) with an epoxy value of 0.52-0.54 was chosen as the polymer matrix in this study. Epoxy resin and curing agent with trade names D.E.R-732 (Dow Crop) and methylhexahydrophthalic anhydride (MeHHPA) (Shanghai Shengyuan, China), were used for the preparation of the composite systems. Besides, 2,4,6-tri(dimethylaminomethyl) phenol (DMP30) (Shanghai Haitai, China) was selected as the cure accelerator. The average diameter of 1-2 μ m aluminum particles was purchased from Xuzhou Hongwu Nano Co. (Jiangsu, China). Besides, in [this](#) study, the silane coupler was γ -glycidoxypropyl-trimethoxysilane, which had an epoxide as one of its end group, supplied by Nanjing Xiangfei, Chemical, China.

2.2 Surface modification of Al particles

The surface treatment for Al particles by using the silane couplers γ -glycidoxypropyl-trimethoxysilane were carried out as the following steps [33]: (i) Ethanol aqueous solution (95 wt% concentration) and silane coupling agent (1.0 wt% of the Al mass) were added into a bottom flask with reflux setting. (ii) The mixture was followed by sonication and addition of diluted hydrochloric acid to adjusting the ethanol aqueous solution pH to 3-5 and stirring for 20 minutes. (iii) And the Al particles were added into the solution by ultrasonication for 60 minutes. (iv) The mixture was heated to 80 °C and refluxed for 6 h while stirring and then cooling to room temperature, setting for 2 h. (v) The products were filtered by ethanol least three times and dried under vacuum at 110 °C for 10 h.

2.3 Preparations for the Al/epoxy composites

The preparations for Al/epoxy composites were carried out as follows [33]. For the preparation of Al/epoxy composites, the main epoxy, curing agent (MeHHPA), and the accelerator (DMP30) were mixed according to the weight ratio of 100:85:1, while the main epoxy matrix is made of D.E.R-331 and D.E.R-732 with a weight ratio of 7/3. Then, the blended mixture was ultrasonicated for 30 min at 40 °C and stirred vigorously for 1 h, and the obtained homogeneous mixture was degassed for about 30 min in a vacuum condition to get rid of bubbles. After that, the liquid mixture was poured into a clean glass plate mold kept at 60-80 °C, and then cured in an oven at 110 °C for 1 h and 150 °C for 5 h, respectively. Afterwards the cured sample was left to cool down slowly to room temperature. Thus, the epoxy-based composites with Al particles concentrations ranging from 5 to 70 wt% were prepared.

2.4 Characterizations

The dielectric measurements of the samples were recorded by using a broadband dielectric spectrometer (Novocontrol Technology Company, Germany) with the frequency range 1-10⁷ Hz at the temperature from -20 °C to 200°C. The specimens for dielectric measurements were molded in the form of circular disk (diameter = 20 mm and thickness ~1 mm). A layer of Al foil was placed on the upper and lower surfaces of the specimens prior to measurements.

The morphology of the prepared samples as well as the dispersion of fillers in the composites was studied using a scanning electron microscopy (SEM, JSM-7000F, JEOL, Japan). The fractured surfaces were prepared in liquid N₂ and were sputtered with gold in vacuum prior to observation.

Differential scanning calorimetry (DSC) (DCS 200PC, Netzsh Crop., Selb, Germany) measurements were performed in order to evaluate the glass to rubber transition temperature (T_g) for

the sample. Measurements were conducted in a nitrogen atmosphere, from -20°C to 200°C, at a heating rate of 10°C/min.

3. Results and discussion

3.1 Surface morphology

The SEM picture in Fig.1 presents the morphological characteristic of the produced system. The surface untreated 50 wt% Al/epoxy composite is shown in Fig.1 (b) and the surface modified 50 wt% Al/epoxy composite is given in Fig.1(c). It can be clearly seen that the untreated composite has rounded smooth pits which were formed after Al particles had been pulled off from the matrix, while in Fig.1(b), the homogeneous distribution of Al particles in the polymer matrix with small trails of agglomeration. This can be attributed to the use of coupling agents improving the interfacial bond strength between Al particles and epoxy resin, and decreasing the voids and defects at the phases interfaces. It was reported that good dispersion along with homogeneous packing of ceramic filler is likely to exhibit higher dielectric constant [34].

3.1 Dielectric permittivity and loss

Broadband dielectric spectroscopy (BDS) was employed for investigation on different molecular relaxation processes in epoxy composites. All the samples were examined by means of BDS over a wide temperature from -20°C to 200°C and frequency from 1 to 10⁷ Hz. Fig.2 presents three dimensional plots of the real (ϵ') part of the dielectric permittivity and the dissipation factor ($\tan\delta$) as a function of frequency and temperature for 50 wt% Al/epoxy composites. Polymer matrix composites are expected to exhibit relaxations originating from both the polymer matrix and the filler. Fig. 2(a) reveals that the dielectric permittivity diminishes with frequency, as a result of the inertia of the dipolar moments in the system to follow the alternation of the applied field, reflecting the

reduction of polarization. Three different relaxations are observed in the spectra of $\tan\delta$ of the examined composites as a function of frequency and temperature. They are denoted, with increasing temperature at constant frequency, as intermediate dipolar effect (IDE), α relaxation and interfacial polarization (IP) relaxation.

Above $-20\text{ }^{\circ}\text{C}$, a relaxation process named intermediate dipolar effect (IDE) is detected at high frequency for all examined composites. This mechanism has been previously observed in epoxy based system [35, 36]. This exact relaxation mechanism can not be explained unambiguously, which will be discussed and analyzed later.

As temperature increases above $70\text{ }^{\circ}\text{C}$ a well formed relaxation peak appears, and is in accordance well with the glass transition temperature (T_g) area in the DSC analysis (given in Fig.3). It can be seen that the DSC heat capacity curve of the microcomposite exhibits a typical transition shoulder with T_g of about $70\text{ }^{\circ}\text{C}$. This relaxation can be attributed to the glass transition movement (α -relaxation), which often occurs in polymer materials when chain segments start to move and interact with each other. In general, α mode (the related glass to rubber transition) is a process in which corresponds to micro-Brownian segmental motion of the polymer chain and specifically gauche transitions that leads to the rearrangement of the dipole around the chain that is perpendicularly to the skeleton of the main polymer [37].

When further increasing the temperature, both ε' and $\tan\delta$ increase abruptly especially in lower frequency due to the space charge effect. In the low frequency and high temperature region (1-1kHz and temperature greater than $120\text{ }^{\circ}\text{C}$), dielectric properties are controlled either by chains mobility, or charge transfer process (space charge polarization) [38, 39]. This relaxation mechanism, also known as Maxwell-Wanger-Sillars (MWS) effect or interfacial polarization (IP), originates from

the electrical heterogeneity of the system. This relaxation process refers to charge carriers (e.g., electrons and holes) accumulated at the interfaces in multicomponent polymer systems, when the current flows from the interface of the composites, leading to interfacial polarization [40]. The dissipation factors in Fig.4 illustrate these processes occurring in the high temperature regions.

3.2 Electric modulus plots

In polymer matrix composites, electrical relaxation phenomena arise from interfacial effects, phase transitions, and polarization or conductivity mechanisms. In this study, the recorded dielectric properties data were initially expressed in terms of real and imaginary part of permittivity and then can be transformed, via equation (1), to the electric modulus formalism. Large variations in the real and imaginary part of permittivity at low frequencies and high temperatures can be minimized in the electric modulus presentation, since electrode polarization, space charge injection and absorption of impurities can be neglected [41-44]. Electric modulus is defined as the inverse quantity of complex permittivity:

$$M^* = \frac{1}{\varepsilon^*} = \frac{\varepsilon'}{\varepsilon'^2 + \varepsilon''^2} + i \frac{\varepsilon''}{\varepsilon'^2 + \varepsilon''^2} = M' + iM'' \quad (1)$$

where, ε' , M' , and ε'' , M'' are the real and imaginary parts of dielectric permittivity and electric modulus, respectively. Variations of the real M' part of the electric modulus with frequency for pure epoxy and Al/epoxy composites at different temperature ranges is presented in Fig. 5. As observed from Fig. 5, the value of M' is near zero in the low frequency region, starts disperse in the middle frequency region and reaches maximum in the high frequency region for all temperatures. M' approaches zero at low frequency, confirming the presence of electrode polarization in the studied temperatures. A depression of the M' modulus with temperature at high frequency is observed, which may be attributed to the conduction mechanism, attributable to the short range mobility of charge

carriers [45]. In addition, the curves show a decrease in the maximum value of M' and a shift in the dispersion region towards higher frequencies with increasing temperature, indicating that the conduction mechanism is dominated by the hopping process.

Fig. 6 shows the frequency dependence of M'' spectra for pure epoxy and Al/epoxy composites at high temperatures. Obviously, the M'' spectra of the sample clearly show relaxation peaks at the temperatures between 100 and 200°C, accompanied by the stepwise transitions from low to high values in M' (seen in Fig.5). A single peak appearing in the low frequency is observed whose position shifts towards the high frequency range as the temperature increases. These peaks represent the α -relaxation process. The peaks in M'' vs. frequency plots are related to the conductivity relaxation of the materials. It is known that at lower frequencies, charge carriers can move freely to a longer distance (i.e. ions can perform successful hopping from one site to another executing long-range mobility) up to a certain frequency (frequency maximum) [46]. Further increase in the frequency leads to the formation of localized sites, which can trap the carriers [46]. Therefore, the region where peak occurs is an indicative of the transition from long-range to short-range mobility with an increase in frequency. This behavior suggests that the spectral intensity of the dielectric relaxation is **thermally** activated in which hopping process of charge carriers and small polarons dominate intrinsically [46]. Compared with the pure epoxy, the low-frequency M'' peak in Fig.6 (b) is broader, due to more free charge motions in the Al/epoxy composites.

Above T_g , the shift of α -relaxation is detected and measured as shown in the inset of Fig.6. The temperature dependence of the α -relaxation is non-linear behavior and involves an apparent activation energy that increases with decreasing temperature. This behavior is modeled by the Vogel-Tamann-Fulcher (VFT) equation (2):

$$f_{\max} = f_0 \exp\left(-\frac{B}{T-T_0}\right) \quad (2)$$

where f_0 is a pre-exponential factor, B is a constant, and T_0 is Vogel temperature or ideal glass transition temperature. In the literature [47], it is well-accepted that the dynamic of glass to rubber relaxation process follow the VFT relation, since relaxation rate increases rapidly with decreasing temperature due to the reduction of free volume. The parameters obtained by fitting the experiment data of $f_{\max}$ of α -relaxation are $T_0=360\text{K}$, $B=24.61\text{K}$ for epoxy, and $T_0=329\text{K}$, $B=57.96\text{K}$ for 50 wt% Al/epoxy microcomposites, respectively.

Cole-Cole plots of the complex electric modulus at different filler concentration and temperatures are presented in Fig.7. In Fig.7, the depressed-shaped semicircles reach the origin of the graph coordinates, indicating that the Al/epoxy composites have not a blocking layer in which the charge carriers build up on the electrodes [48]. Namely, the electrode polarization is tiny, can be ignored. Fig.7 (a) shows the effect of filler loading on Cole-Cole plots at high temperature. It can be found that IP is recorded as a small hump of the trace at low frequencies, close to the origin of the graph. The semicircle behavior of the Cole-Cole plot is reduced with the increase in Al loading, which reflects the influence of concentration of the inclusions at the α -mode. The decrease in M' with respect to filler shows the increase in conductivity and less lossy response. At the high frequency end, experimental results from the all examined composites form a suppressed semicircle, reflecting the presence of intermediate dipolar effect (IDE)-model [35,49]. Fig.7 (b) depicts the Cole-Cole plot of 50 wt% Al/epoxy at high temperature region.

3.3 Electrical conductivity

To further explore the effect of temperature on dielectric properties of epoxy based polymers, alternating current (AC) conductivity measurements were carried out at temperatures ranging from

-20 to 200°C. Fig. 8 shows the variation of AC conductivity (σ_{ac}) of pure epoxy and 50 wt% Al/epoxy composites as a function of frequency. The nature of variation of σ_{ac} with frequency exhibits dispersion throughout the chosen frequency range. Also, the values of σ_{ac} increase with rise in frequency as well as temperature. AC conductivity due to localized states in a dielectric material is expressed in equation (3) using Jonscher's power law [50]:

$$\sigma_{ac}(\omega) = \sigma_{dc} + A\omega^s \quad (3)$$

where ω is the angular frequency, σ_{dc} is the DC conductivity when $\omega \rightarrow 0$, A is pre factor, and s is frequency exponent lying between 0 and 1. Both A and s are weakly dependent on temperature. The values of the index s are obtained from the slopes of the plots in the low frequency region, which always comes out to be less than 1 and are decreasing with the raise in temperature. This observation is consistent with correlated barrier hopping model [51]. At high frequency, conductivity has almost the same value irrespective of temperature. However, the effect of measuring temperature is prominent at the lower frequencies. The low frequency and high temperature plateau observed in σ_{ac} corresponds to the DC conductivity (σ_{dc}). In the low frequency, the extra-polarization of the conductivity spectrum appears at a particular temperature, which is attributed to the long range translational motion of the charge carriers. As the temperature is increased, the DC part of the conductivity spectra shifts towards higher frequency side and leads to a change in the mechanism of electric conduction. The conductivity begins to increase after the frequency exceeds the critical frequency called hopping frequency ($f_{hopping}$). The hopping frequency, at which the conductivity relaxation begins to appear, is observed to shift to higher frequencies with rise in temperature, indicating an enhancement in the carrier hopping rate of mobile charge carriers with an increase in temperature.

In the hopping process, the carrier mobility is temperature dependent, which is usually characterized by activation energy. The values of σ_{dc} obtained from the fitting of the experiment data at different temperatures using equation (4) follow the Arrhenius law is defined as:

$$\sigma_{dc} = \sigma_o \exp\left(-\frac{E_a}{k_B T}\right) \quad (4)$$

where σ_o is the pre-exponent factor, k_B is Boltzmann constant and T is the absolute temperature of the sample. The fact that T_g occurs at about 80 °C (as shown in Fig. 3) indicates that the cooperative dipole relaxation (α -relaxation) appears in the same temperature range where the charge carrier mobility is strongly activated (MWS polarization and σ_{dc}). The conductivity activation energy of the conductivity influenced by temperature is the minimum energy required to overcome the potential barrier in the composite system. The linear curves called Arrhenius plots shown as straight lines (plotted in the Fig.9) are obtained using a linear curve fitting method. The activation energy is found to be 1.397 eV and 1.067 eV for epoxy and 50 wt. % Al/epoxy composite, respectively. The decrease in the activation energy of Al/epoxy composite is supposed to be easy movement of charge carries due to the homogeneous distribution of micro Al particles in the polymer matrix which makes the chains more soften and increases the mobility of the segmental motion.

4. Conclusions

Al/epoxy composite with core-shell structured Al additions were prepared by solution mixing method. Homogeneous dispersion of Al filler was observed by SEM. The dielectric properties as a function of temperature and frequency show three relaxations processes: (1) IP resulting from the electric heterogeneity of the system at low frequencies and high temperatures; (2) a primary α -relaxation process attributed to the glass transition movement at near T_g at the middle frequencies; and (3) IDE relaxation at high frequencies above -20 °C. Broadband dielectric spectroscopy shows

that the multiple dielectric processes in the Al/epoxy microcomposites correspond to ionic conductivity, interfacial polarization and α -relaxation as the frequency increases for temperature above T_g , respectively. The α -relaxation peak shifts towards higher frequency with increasing temperature due to the increase in the mobility of charge carriers. The IP and ionic conduction relaxation modes exhibit an Arrhenius type dependence on reciprocal temperature, while α -relaxation follows the VTF model. Large increase in the dissipation factor and conductivity with temperature is mainly attributed to the DC conduction of thermally activated charge carriers resulting from epoxy after T_g . The observed temperature-dependent relaxation of chain segments indicates a thermally activated behavior of the relaxation time.

Acknowledgements

The authors gratefully acknowledge the financial supports from the National Science Foundation of China (51577154), Shaanxi Provincial Natural Science Foundation, China (Nos. 2016JM5014, 2014JM2043), the Scientific Research Program Funded by Shaanxi Provincial Education Commission (Nos. 14JK1485, 15JK1451), the Key Laboratory of Engineering Dielectrics and Its Application, Ministry of Education, Harbin University of Science and Technology (JZK201301), and the Foundation for Key Program of Ministry of Education, China (212175).

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Fig.3. DSC curves for pure epoxy and 50 wt% Al/epoxy composite.

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Fig.5. Real part of electric modulus as a function of frequency for (a) pure epoxy and (b) 50 wt% Al/epoxy composite at different temperatures.

Fig.6. Imaginary part of electric modulus as a function of frequency for (a) pure epoxy and (b) 50 wt% Al/epoxy composites at different temperatures. Insert: Reciprocal temperature dependence of the M'' (VFT behavior) of the Al/epoxy composites.

Fig.7. Complex plane plot Cole-Cole plots for: (a) examined composites at 150 °C and (b) 50 wt% Al/epoxy composites at high temperatures.

Fig.8. Frequency dependence of the ac conductivity in (a) epoxy and (b) 50 wt% Al/epoxy composites at temperatures from -20 °C to 200 °C.

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