Dielectric spectroscopy characterization of relaxation process in Ni/epoxy composites

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Abstract

Nickel (Ni)/epoxy composites with different Ni filler additions were prepared, and the dynamic dielectric properties of the composites were investigated using broadband dielectric spectroscopy spectrometer with the frequency range 1-10⁷ Hz at the temperature of -20-200 °C. The dielectric properties as a function of temperature and frequency show three relaxation processes: (1) Maxwell interfacial polarization at low frequencies; (2) a primary α -relaxation process at near glass transition temperature (T_g); and (3) ionic conduction relaxation at the middle frequencies between 100 °C and 200 °C. Detailed studies of modulus spectrum suggest non-Debye type of relaxation mechanism for the composites. The Cole-Cole plots exhibit the contribution of filler concentration effect in the modulus characteristics of the Ni/epoxy composites. Alternating current (AC) conductivity and electric modulus studies support the hopping type of conduction in the composites, and frequency dependent AC conductivity data obey Jonscher's power law.

Key Words: A. Polymers; A. Metals; A. Semiconductors; D. Dielectric response.

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1. Introduction

The recent advances in flexible and green electronic devices lead to an intense research activity in the area of multifunctional materials [1, 2]. The main requirements are related to the obtaining of flexible, high dielectric constant (k), breakdown strength, low dielectric loss, environmental friendly and light weighted electron components. These types of electric components can be used in a large number of applications such as: artificial muscles, energy storage, flexible electronics, embedded capacitor and sensors [1-5]. The mechanical and electrical requirement of flexible electronic devices can be achieved using polymer matrix composites (PMCs). Polymers are appealing as matrices due to their flexibility, high dielectric strength, low cost and easy processing. Their major drawback for electronics applications is their low value of permittivity. However, using different types of conductive fillers, such as metal fillers (i.e., Aurum, Silver, Copper, Aluminum) [6-12], carbon fillers such as carbon fibers [13-15], carbon black [16-18], graphite nanoplates [19, 20], and other types of conductors [21, 22], a significant increase in permittivity values can be obtained.

Epoxy is a good option as polymer matrix due to its good heat and chemical resistance, super mechanical and electrical properties, as well as excellent processing ability [23, 24]. As conductive filler, nickel (Ni) particle was chosen due to its effect on electrical conductivity, permittivity as well as magnetic permeability of polymer matrix [25-30]. Generally, Ni is an important ferromagnetic material, which shows diverse application as catalysts, magnetic recording medias, magnet sensors, ferrofluids, and conduction materials. Other appealing properties of Ni particles are that they are cheap and readily available. Ni particle can endow polymers with a larger dielectric permittivity as well as a high loss near percolation threshold (f_c)

due to the resultant leakage current within the composites. Few studies on development of Ni/polymer composites have been reported in the recent years. For instance, Panda et al. reported that for Ni/PVDF composites, a high effective dielectric constant of 2500 ($\tan\delta=10$) at 100 Hz was observed near the $f_c \approx 0.27$ [31]. Xu et al. compared the effect of Ni, zinc, tungsten and carbon black fillers in PVDF and found that Ni gave rise to the highest dielectric constant [25]. Yang et al. observed an enhanced value of dielectric constant from 49 to 140 when the volume fraction of nickel increases from 0% to 22% in $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ (CCTO) /PVDF composites at 100Hz and room temperature [26]. To tailor Ni/PVDF composites for applications, influences of temperature [27, 30] and Ni loading around the f_c [25, 28-30] on their properties have been investigated.

Most of the research on Ni/polymer composites done so far have been focused on the study of their dielectric behavior as a function of Ni filler content and f_c critical behavior in the vicinity of metal-insulator transition process. Up to now, the investigation on the influence of temperature on the dielectric properties of Ni/polymers has rarely been reported, and it is as important as dielectric properties at room temperature from the application point of view and requires serious attention. The study of dielectric behavior as a function of temperature and frequency is one of the most convenient and sensitive methods of investigating polymer structure. This has motivated us to consider a systematic study to explore the thermal and dielectric behaviors of Ni/epoxy composites and how the presence of Ni concentration, temperature as well as frequency affects the dielectric properties in a complex polymer matrix. Therefore, the aim of the present paper is to explore the effects of temperatures and frequencies on the dielectric properties and molecular relaxation in the Ni/epoxy nanocomposite by broadband dielectric

spectroscopy. Broadband dielectric spectroscopy with the frequency range $1\text{-}10^7$ Hz at the temperature of $-20\text{-}200$ °C, provides a highly accurate simple measurement of electrical properties of the composites.

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, the 2,4,6-tri(dimethylaminomethyl) phenol (DMP30) (Shanghai Haitai, China) was used as the cure accelerator. The flaky-shaped Ni particles (average diameter of $10\mu\text{m}$) were purchased from Shenyang Hangda Technol. Co. (Liaoning, China). The γ -glycidoxypropyl-trimethoxysilane, which has an epoxide as one of its end group, was used as the silane coupler (Nanjing Xiangfei, Chemical, China).

2.2 Surface modification of Ni particles

Prior to use, Ni particle surface was treated with silane couplers γ -glycidoxypropyl-trimethoxysilane (KH560) in order to well disperse them into the epoxy matrix. The faction of KH560 was set as 1.0% of the Ni mass. Firstly, the coupling agent and water/ethanol aqueous solution were slowly added into a round bottom flask with reflux setting, then the diluted hydrochloric acid was put into the mixture to adjust the ethanol aqueous solution pH to 3-5. After that, the mixture was stirred for 20 min, and the Ni particles were slowly added into this solution by ultrasonicing for 60 min. Then the mixture was heated to 80 °C and refluxed for 6 h while stirring and cooling to room temperature, letting it set for 2 h. Finally, the

products were filtered by ethanol and dried under vacuum at 110 °C to remove the residual solvent.

2.3 Preparation for the Ni/epoxy composites

For the preparation of the Ni/epoxy composites, the epoxy resin (D.E.R-331) was blended with the flexible epoxy (D.E.R-732), curing agent, Ni particles, and the accelerator according to the designed mass-fraction ratio (as shown in Table 1). Then, the mixture was stirred vigorously for 1 h, and the obtained homogeneous mixture was degassed for about 30 min in a vacuum to get rid of bubbles. After that, the liquid mixture was poured into a clean glass plate mold kept at 60-80 °C, and was cured in an oven at 100 °C for 1 h and 150 °C for 5 h. Finally the cured sample was left to cool down slowly to room temperature.

2.4 Characterizations

The dielectric measurement was performed on a broadband dielectric spectrometer (Novocontrol Technology Company, Germany) with an Alpha-A high-performance frequency analyzer. The measurement was carried out in the frequency range of 1-10⁷Hz below room temperature and at the -20 to 200°C range to investigate the dielectric property's dependence upon temperature. The specimens for dielectric measurements were molded in the form of circular disk (diameter = 20 mm and thickness ~1 mm). Prior to samples measurement, a layer of Al foil was placed on the upper and lower surfaces of the specimens.

Morphological observation on the samples was performed using a scanning electron microscopy (SEM, JSM-7000F, JEOL, Japan). The fractured surfaces were prepared in liquid N₂ and sputtered with gold in vacuum prior to observation.

3. Results and discussion

3.1 Dielectric permittivity

Figure 1 shows the frequency dependence of the real part of complex dielectric constant (ε') of Ni/epoxy composites at selected temperatures. Figure.1 (a) gives the variation of the dielectric constant ε' with frequency at room temperature for all examined composite. At room temperature, ε' increases remarkably with filler concentration, and slowly decreases with frequency. The inset of Figure.1 (a) presents the SEM image of 55 wt% Ni/epoxy composites. Note that the Ni particles were homogeneously distributed in composite with small trails of agglomeration and no resin fault (defeat) is observed at the interface between particle Ni and epoxy. Figures.1 (b)-(d) reflects the variation of ε' with frequency at different temperatures for pure epoxy, 40 wt% and 55 wt% Ni/epoxy, respectively. It is noticeable that there is a mutation when the temperature reaches about 70 °C. For example, at 1Hz the dielectric constant of pure epoxy rises by two orders of magnitudes as the temperature increases from 60 °C to 180 °C. The remarkable increase in dielectric constant of pure epoxy with temperature is associated with the enhanced interfacial polarization (IP). According to Maxwell-Wanger-Sillars (MWS) effect [32], for heterogeneous polymer composites, when the current flows from the interface of the composites, space charges will be accumulated, leading to interfacial polarization. This abrupt change in dielectric constant should be attributed to the glass transition movement, which often occurs in polymer materials when chain segments start to move and interact with each other. When the temperature approaches to glass transition temperature (T_g), the motion of polymer chain increases and the free charges get accumulated at the interface of the material. So, the rapid increase in dielectric constant with temperature is mainly due to the enhanced mobility of

different bound charges like induced dipoles and interfacial space charges. This thermal excitation of different bound charges with the increase in temperature is the main reason for the increase in the dielectric constant. Further, the decrease in ε' with increasing frequency is a characteristic behavior in most of dielectric materials. It is clear that the permittivity decreases monotonically with increasing frequency and, after a cross-over frequency, shows a plateau in the higher frequency region. And the cross-over frequency extends to a higher frequency with the increase in filler content. For example, the dielectric constant of pure epoxy decreases with an increase in frequency up to 180 Hz and then it becomes almost constant, while the 40 wt% Ni/epoxy extends to 4500 Hz. The low-frequency dispersion region is attributed to charge accumulation at interface between electrode and epoxy composite. At higher frequencies, the rotational motion of the polar molecules is not sufficiently rapid to attain equilibrium with the external electric field, thus leading to declined dielectric constant [33].

3.2 Dielectric loss

Figure 2 depicts the frequency dependence of the imaginary part of complex dielectric constant (ε'') of Ni/epoxy composites at selected temperatures. The ε'' is due to the contribution of three effects: direct current (DC) conductance, interfacial polarization (IP), and dipole orientation. The figures show a straight line in the low-frequency region with a slope close to -1.0, which represents the contribution of DC conductivity. From Figure.2 (a), it can be seen that in the frequency below 10^6 Hz, the dominant electron transport mechanism is DC conduction. Above 70 °C, the dielectric loss increases abruptly, suggesting that the conduction loss is dominant in the high temperature and results in larger dissipation factor. The frequency dependence of dielectric loss tangent ($\tan \delta$, $\tan \delta = \varepsilon''/\varepsilon'$) for epoxy is shown in Figure.2 (b). In

case of epoxy, a relaxation at lower frequency is primarily due to the dipole polarization, since dipoles have less time to orient themselves in the direction of the alternating field with increasing frequency. As observed in Figure 2 (b), it is apparent that the dielectric loss increases with temperature and the temperature dispersion is more prominent for lower frequencies. At $T < T_g$, the loss peak in $\tan \delta$ is very weak with no obvious shift with increasing temperature. From the inset of Figure 2 (b), the α -relaxation appearing at about 70 °C is related to the glass transition of chain segments. At $T > T_g$, the loss peak jumps to a high value and the frequency is found to shift towards higher values with increasing temperature. Thermally excited macromolecular dipoles follow faster alternations of the applied electric fields, shifting the loss peak frequency at higher values. Figures 2 (c)-(d) presents the variation of ε'' with frequency at different temperatures for 40 wt% and 55 wt% Ni/epoxy, respectively. Compared with the neat epoxy, the slope of straight line in the low-frequency region of Ni/epoxy composite is sharper than the epoxy, suggesting that there is more prominent DC conduction dominant in the electron transport mechanism. Furthermore, the value of dielectric loss of the composites decreases with an increase in the Ni content, indicating that the dielectric loss is mainly owing to thermal activated charge carriers resulting from pure epoxy matrix.

3.3 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 data was initially expressed in terms of real and imaginary part of permittivity and then 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 are minimized in the

electric modulus presentation, since electrode polarization, space charge injection and absorption of impurities can be neglected [34-37]. 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. Variation of the real M' part of the electric modulus with frequency for pure epoxy and Ni/epoxy composites at different temperature ranges is presented in Figures 3(a)-(c). As observed from Figures 3(a)-(c), the value of M' is near zero in the low frequency region, starts disperse in the mid 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 attribute to the conduction mechanism that is due to the short range mobility of charge carriers [38]. 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.

Figures 3(d)-(f) plots the frequency dependence of M'' spectra for pure epoxy and Ni/epoxy composites at various temperatures. A single peak is observed whose position shifts towards high frequency with an increase in temperature. The peaks represent the 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 carries 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) [39]. Further increase in the frequency leads to the formation of localized sites, which can trap the carriers [39]. Therefore, displacement of carriers which move within the sample by discrete hops between randomly distributed localized sites (i.e. short-range motion). Therefore, the region where peak occurs is an indicative of the transition from long-range to short-range mobility with increase in frequency. This behavior suggests that the spectral intensity of the dielectric relaxation is activated thermally in which hopping process of charge carriers and small polarons dominate intrinsically [39].

Figure 4 shows the complex electric modulus plane plots of Ni/epoxy composites at various concentrations and temperatures. It is known that due to the deviation of the dielectric relaxation from ideal Debye behavior, the electric modulus plots for dielectric materials do not always yield perfect circular or semicircular arcs, even they become asymmetric. The use of the Cole-Cole plots (M'' versus M') provides interesting information regarding the nature of the relaxation process. The empirical Cole-Cole model was used to fit the experimental results. Equation 2 is a modification of the Debye equation.

$$M^* = M_{\infty} + \frac{\Delta M}{1 + (i\omega\tau)^{1-\alpha}} \quad (2)$$

where M_{∞} , ΔM , and τ are the relaxed modulus, modulus relaxation strength and the relaxation time, respectively. α is a parameter between 0 and 1 that reflects the dipole interaction or the complexity of the system. When $\alpha=0$, the system is in the standard Debye model, corresponding to a single relaxation time. The red lines are fitting results of complex electric modulus to Cole-Cole equation. The fitting curves cannot form semicircles of idealized Debye model with single relaxation time. According to Debye theory of relaxation, the electric modulus maxima are supposed to appear in the same frequency at a particular temperature

(Figure 3(d), (e), (f)), which are not observed for the studied composites. The patterns are characterized by the presence of little asymmetric and depressed semicircular arcs whose centres do not lie on M' -axis, which also supports the non-Debye type dielectric relaxation in the composite. The influence of the concentration of Ni filler on composites at high temperature (100 °C) is presented in Figure 4 (a). In the Figure 4(a), the deformed semicircles reach the origin on the M' axis, indicating that the Ni/epoxy composites have not a blocking layer in which the charge carriers build up on the electrodes. The epoxy and 40 wt% Ni/epoxy data are well fitted with the Cole-Cole model, although the 55 wt% Ni/epoxy data do not well fitted, presenting the semicircle arc with its centre lying below the axis. And the diameter of the semicircles decreases with the increase in Ni concentration, indicating an enhancement of the material's conductivity. In the case of these composites, the low frequency arc can be ascribed to the interface between the conductive Ni particles and the insulating polymer matrix. Moreover, the variation of the semicircle radius, corresponding to the α -mode, indicates that α -mode is influenced by the filler's concentration. Furthermore, at the high frequency end, experimental results from the composites with 40 and 55 wt% contents in Ni form a suppressed semicircle, reflecting the presence of IDE (intermediate dipolar effect)-mode [40].

Figures.4 (b)-(d) displays the relationship between M' and M'' at different temperatures for the tested composites. They process a shape pf deformed arcs in low frequency with their centers positioned below the horizontal axis. This asymmetric formed of the curves plots for different temperatures is associated to the asymmetric distribution of the relaxation time [41]. For all the composites, the diameters of the semicircles marginally decrease with temperature revealing an expected insignificant increase in the composites' conductivity. As the temperature increases, the

increase in polarity is observed by Ni particles, hence resulting in the orientation of dipoles which make it more conductive.

The temperature dependence of loss peak position for all examined system and relaxation processes at elevated temperatures is illustrated in Figure.5. IDE exhibits an Arrhenius type behavior in concentrations according to the equation (3):

$$f_{\max} = f_0 \exp\left(-\frac{E_A}{k_B T}\right) \quad (3)$$

where f_0 is a pre-exponential factor, E_A is the activation energy, k_B is Boltzmann constant and T is the temperature in K . The temperature dependence of α -relaxation can be described by Vogel-Tamann-Fulcher equation (4):

$$f_{\max} = f_0 \exp\left(-\frac{B}{T - T_0}\right) \quad (4)$$

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 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 reduction of free volume. Values of activation energy of IDE and the VTF parameters T_0 and B are summarized in Table.2.

3.3 Electric conductivity

The variation of AC conductivity (σ_{ac}) of Ni/epoxy as a function of frequency at temperatures between -20 and 200 °C are exhibited in Figure 6. It can be seen that the conductivity presents frequency dispersion and the σ_{ac} gets enlarged with the increases of Ni contents as well as temperature. AC conductivity σ_{ac} due to localized states in a dielectric material can be expressed using Jonscher's power law [42]:

$$\sigma_{ac}(\omega) = \sigma_{dc} + A\omega^s \quad (5)$$

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. At higher temperatures (70 °C) σ_{dc} rises with increase in frequency and plateau like behavior is observed in the low-frequency region. The increasing trend of AC conductivity with raise in frequency at higher temperatures may be due to the space charge carriers in the material. Further, the frequency independent plateau at higher temperature indicates the DC conductivity of the material arises due to random diffusion of charge carriers followed by hopping mechanism [43]. Hence, AC conductivity obeys the Jonscher's power law, and the conductivity spectra are fitted by equation (5), plotted in Figure 6. The hopping frequency takes place at the point where the slope changes in the conductivity spectrum and it shifts to higher frequency with rise in temperature, indicating an enhancement in the carrier hopping rate of mobile charge carriers with increase in temperature [44,45]. The change in behavior of the AC conductivity, from initially flat to rapidly rising may be attributed to a change in the hopping behavior of the charge carriers, from long range to short range [46]. From the figure 6, it is clearly observed that the conductivity increases with increase of temperature in all filler loadings, which can be explained on the basis of positive temperature coefficient (PTC) character of the composites. The increase in AC conductivity with temperature can be attributed to large heat energy absorbed by the samples, thus resulting in enhanced dipole mobility.

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 (5) follow the Arrhenius law defined as:

$$\sigma_{dc} = \sigma_o \exp\left(-\frac{E_a}{k_B T}\right) \quad (6)$$

where σ_o is the pre-exponent factor, k_B is Boltzmann constant and T is the absolute temperature of the sample. The Arrhenius plot of σ_{dc} is plotted in the inset of Figure.6. 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 are obtained using a linear curve fitting method. The activation energy is found to be 0.6472 eV, 0.4472 eV and 0.4745 eV for epoxy, 40 wt% and 55 wt% Ni/epoxy, respectively.

4. Conclusions

Broadband dielectric spectroscopy has been applied to investigate the dielectric relaxation phenomena taking place in the 40 and 55 wt% Ni/epoxy polymer composites. All samples have been studied in the frequency range from 1 to 10^7 Hz and a temperature range of -20 to 200 °C. The variation of the dielectric parameters with the frequency, temperature and Ni particles concentration were explored. The results of these Ni/epoxy composites were compared with the dielectric properties of their individual polymer matrix. The dielectric permittivity of these composites increases with the Ni content and reduces with frequency at room temperature. Compared with pure epoxy, the dielectric constant of the composites increases with the concentration of filler due to enhanced interfacial polarization, whereas, the dielectric loss tangent declines. Remarkable increase in dielectric constant with temperature can be explained by the enhanced dipole and interfacial polarizations effect, while, large increase in dissipation

factor and conductivity with a temperature higher than T_g can be ascribed to the direct current conduction of thermal activated charge carriers resulting from epoxy matrix. Further, detailed studies of modulus spectrum suggest that the material exhibits non-Debye type of relaxation mechanism. The Cole-Cole plots show the contribution of filler concentration and temperature to the modulus characteristics of the composites. AC conductivity and electric modulus studies support the hopping type of conduction in the system, and frequency dependent AC conductivity data obey the Jonscher's power law.

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Table 1 Formulation of Ni/Epoxy Composite

Raw materials	Content
Epoxy(331)/g	70
Epoxy(732)/g	30
MeHHPA/g	90
DMP-30/g	1
Ni/g	Variant

Table 2 Activation energies and VTF parameters for all the tested specimens

System	α -mode		IDE
	T_0 /K	B/K	E_A /eV
Epoxy	329	52	0.2653
Epoxy+40 wt% Ni	267	124	0.1544
Epoxy+55 wt% Ni	228	233	0.3971

Fig.1. Frequency-dependent dielectric constant of (a) neat epoxy and Ni/epoxy composites at room temperature, (b) epoxy, (c) 40 wt% Ni/epoxy and (d) 55 wt% Ni/epoxy at selected temperatures.

Fig.2. Frequency-dependent dielectric loss of (a) and (b) neat epoxy, (c) 40wt% Ni/epoxy and (d) 55wt% Ni/epoxy at selected temperatures.

Fig.3. (a)-(c) Real (M') and (d)-(f) imaginary (M'') parts of electric modulus as a function of frequency for pure epoxy, 40 wt% Ni/epoxy and 55 wt% Ni/epoxy composites at different temperatures.

Fig.4. Complex plane plot Cole-Cole plots for: (a) all tested composites at 100 °C; (b) pure epoxy; (c) 40 wt% Ni/epoxy and (d) 55 wt% Ni/epoxy at selected temperatures.

Fig.5. The dependence of relaxation frequencies with the reciprocal temperature at elevated temperatures.

Fig.6. Dependence of electric conductivity for (a) epoxy, (b) 40 wt% Ni/epoxy and (b) 55 wt% Ni/epoxy on frequency. Solid lines represent the fitting to experimental data using Eq. (4). The Arrhenius plot of the σ_{dc} is shown in the inset.