Available online at www.sciencedirect.com

SCIENCE DIRECT®

Polymer 46 (2005) 2297–2305

polymer

www.elsevier.com/locate/polymer

Influence of interphase and moisture on the dielectric spectroscopy of epoxy/silica composites

Yangyang Sun, Zhuqing Zhang, C.P. Wong*

School of Materials Science and Engineering, Georgia Institute of Technology, Atlanta, GA 30332, USA

Received 21 July 2004; received in revised form 6 December 2004; accepted 12 January 2005

Abstract

Epoxy/silica composites have been used widely as the electronics packaging materials. This paper tested the thermal properties, moisture absorption and dielectric properties of pure epoxy and epoxy composites with micron-sized silica and nano-sized silica. The master curve of the dielectric loss factor was obtained by time–temperature superposition principle. Results showed that the nano-composite had a much higher loss factor, lower glass transition temperature and higher moisture absorption than other samples. By the analysis of the origin of the dielectric response in epoxy/silica composite, the reason for the different dielectric relaxation behaviors of the nano-composite, the micron-composite, and the pure epoxy was discussed.

Keywords: Dielectric properties; Loss factor; Nano-composite

1. Introduction

The great majority of integrated circuits are packaged by the silica-filled epoxy composites called epoxy molding compounds (EMCs). The EMCs have been very popular in the microelectronics industry for almost 30 years because of their superior mechanical and electrical properties with the low cost and easy processing ability [1]. With the advances in nano-science and nano-technology, there is an increasing interest in polymer nano-composites both in scientific research and engineering applications. For example, epoxy/silica nano-composites have been used as the electronics and optical packaging materials [2–5]. Compared with the traditional composites containing micron-sized fillers, the nano-composites have good optical property due to the small filler size.

The electrical characteristics of microelectronic devices, such as signal attenuation, propagation velocity and cross talk, are influenced by the dielectric properties of the packaging materials. An important role of packaging materials is to ensure the electrical insulation of the silicon chip and of circuit pins. Ideally, a low conductivity is needed to avoid current leakage, a low dielectric constant (ε') to minimize the capacitive coupling effects, and a low loss factor (ε'') to reduce electrical loss. So it is necessary to understand the dielectric behaviors of nano-composites.

The dielectric properties of materials can be measured by applying a sinusoidal voltage to samples. This electric field produces polarization within the sample, causing oscillation that is at the same frequency as the field but with a phase angle shift (θ). The phase angle shift is measured by comparing the applied voltage to the measured current. The measured response is separated into a complex form ($\varepsilon*$) that can be separated into capacitive and conductive components giving the real part of permittivity (ε') and loss factor (ε''):

$$\varepsilon* = \varepsilon' - j\varepsilon'' \tag{1}$$

For the solid epoxy materials, there are two bulk effects that influence the dielectric property: ionic conductivity and molecular dipole orientation. So these effects lead to:

$$\varepsilon' = \varepsilon'_{\text{dipole}} + \varepsilon'_{\text{ion}} \tag{2}$$

$$\varepsilon'' = \varepsilon''_{\text{dipole}} + \varepsilon''_{\text{ion}} \tag{3}$$

---

* Corresponding author. Tel.: +1 404 894 8391; fax: +1 404 894 9140.
E-mail address: cp.wong@mse.gatech.edu (C.P. Wong).

0032-3861/$ - see front matter © 2005 Published by Elsevier Ltd.
doi:10.1016/j.polymer.2005.01.041

The dipole orientation in epoxy comes from the motion of polar groups under electric field in epoxy structure. From the classic Debye theory, the following equations are obtained

$$\varepsilon'_{\text{dipole}} = \varepsilon_\infty + \frac{\varepsilon_s - \varepsilon_\infty}{1 + w^2\tau^2} \tag{4}$$

$$\varepsilon''_{\text{dipole}} = \frac{(\varepsilon_s - \varepsilon_\infty)wt}{1 + w^2\tau^2} \tag{5}$$

where ε_∞ is the dielectric permittivity at infinite frequency, ε_s is the static dielectric permittivity at zero frequency, w is the angular frequency, and τ is the relaxation time. Due to the cross-linking nature of the cured epoxy, the molecular motions are hindered by the cross-linking network. When the dielectric measurement was taken under a low temperature, for example, below the glass transition temperature, the molecules lose their long-range segmental mobility. The dipolar relaxation due to the segmental movement and orientation with the electrical field cannot contribute to the dielectric response. Under this circumstance, the relaxation time (τ) to achieve a polar orientation can become very large. So for a glassy state epoxy, the dipolar relaxation due to long-range molecular mobility does not dominate the material dielectric behavior. However, there exist local relaxation processes associated with the dipolar orientation of the side groups pending to the main polymer chain. These relaxation processes can contribute to the dielectric properties.

Another effect, ionic conductivity, comes from the motion of ions under the electric field and is independent of applied frequency. Due to the synthesis reaction of Bisphenol A epoxy from the starting materials of epichlorohydrin, the residual chloride ions and corresponding cations inevitably exist in the epoxy. The concentration of Cl^- ions in the epoxy was reported to be about 0.02 wt%, and these impurity ions actually play a remarkably role in the ionic conductivity. Ionic conductivity is also related to the polymer mobility and increases dramatically with increasing temperature. Therefore, it usually dominates the dielectric properties at low frequency and high temperature. Neglecting the dipole term, the loss factor can be derived as follows [6]:

$$\varepsilon'' = \frac{\sigma}{w\varepsilon_0} \tag{6}$$

As the results from ionic conductivity, the interfacial effects between electrode and epoxy polymer due to the dielectric measurement become obvious with the increasing of conductance of the epoxy. The so-called electrode polarization can happen by the accumulation of ion layers on the electrodes.

The effect of ionic conductivity on the dielectric behavior considering electrode polarization can be illustrated as follows [7]

$$\varepsilon'_{\text{ion}} = C_0 Z_0 \sin\left(\frac{n\pi}{2}\right) w^{-(n+1)} \left(\frac{\sigma}{\varepsilon_0}\right)^2 \tag{7}$$

$$\varepsilon''_{\text{ion}} = \frac{\sigma}{w\varepsilon_0} - C_0 Z_0 \cos\left(\frac{n\pi}{2}\right) w^{-(n+1)} \left(\frac{\sigma}{\varepsilon_0}\right)^2 \tag{8}$$

where σ is the ionic conductivity, ε_0 is the permittivity of the free space, C_0 is the capacity of the cell in air, Z_0 is the constant depending on the interface of electrode and epoxy polymer, and n is the real number alternating between 0 and 1.

From the above analysis, we can see that for glassy state epoxy that does not contain polar side groups, the loss factor of the dielectric behavior is dominated by the ionic conductivity. At temperature higher than T_g of the epoxy, the dielectric relaxation due to the long-range segmental mobility becomes obvious. However, the low frequency response can be greatly influenced by the ionic conductivity as well. For the epoxy/silica composite, on the other hand, the heterogeneity introduces an extra degree of complexity. The dielectric property of the composites has been investigated by various methods accounting for the interfacial relaxation. The Maxwell–Wagner mixing rule has been widely employed for the calculation of the dielectric constant of a polymer/filler composite [8]. From M–W rule, the dielectric constant of a mixture of plates aligned parallel to the electrodes can be considered as two capacitors in series with the frequency dependent dielectric properties taking the similar form of the Debye equations (Eqs. (4) and (5))

$$\tau = \frac{\varepsilon_1 d_2 + \varepsilon_2 d_1}{\sigma_1 d_2 + \sigma_2 d_1} \tag{9}$$

$$\varepsilon_\infty^{\text{M-W}} = \frac{\frac{d_1 + d_2}{\varepsilon_0}}{\frac{d_1}{\varepsilon_1} + \frac{d_2}{\varepsilon_2}} \tag{10}$$

$$\varepsilon_s^{\text{M-W}} = \varepsilon_\infty^{\text{M-W}} \left(1 + d_1 d_2 \frac{\frac{1}{\sigma_1}\sqrt{\frac{\varepsilon_1}{\varepsilon_2}} - \frac{1}{\sigma_2}\sqrt{\frac{\varepsilon_2}{\varepsilon_1}}}{\frac{d_1}{\sigma_1} + \frac{d_2}{\sigma_2}}\right) \tag{11}$$

where d is the thickness of layer and the subscripts 1 and 2 denote the two components of the composite.

However, the M–W rule is only true when the properties of the two phases in the mixture are similar. Bruggeman developed an equation that can represent the dielectric property of ellipsoid particles in a different medium as following

$$f\left(\frac{\varepsilon_1 - \varepsilon}{\varepsilon_1 + 2\varepsilon}\right) + (1 - f)\left(\frac{\varepsilon_2 - \varepsilon}{\varepsilon_2 + 2\varepsilon}\right) = 0 \tag{12}$$

where f is the volume fraction of higher resistivity material.

This equation is basically a statistical mixture of two complex properties, giving values of the dielectric constant,

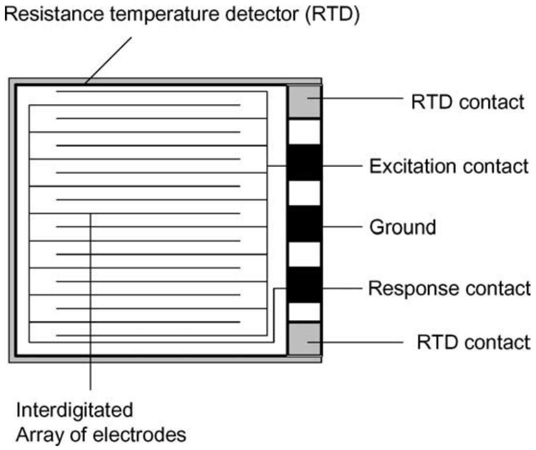

Fig. 1. Electrode design of the single surface sensor used in the experiment.

dielectric loss and ionic conductivity of two phases through complex algebra.

Although with the help of theoretical model we can roughly predict the dielectric property of material, the results are influenced by many other factors, which are not taken into account. Therefore, experimental evaluations are needed to explore the dielectric property of epoxy and its composites in the microelectronics application.

2. Existing work

Previous research about the dielectric property of epoxy and its composite has found that the water absorbed into the materials has great influence to the dielectric loss [9]. A general trend is to observe an increase in loss factor and dielectric constant under the influence of moisture uptake [10,11]. Experiments showed that with around 1 wt% water gain in the pure epoxy, the loss factor could increase by more than 20% while the dielectric constant could increase about 10%. Same trends were also observed for epoxy/silica composites [12], but changes in the dielectric properties were more severe, which was usually explained by the interfacial polarization mechanism. These results depended on the filler density, shape, as well as its surface treatment.

Some authors proposed that the interphase region between the filler and epoxy matrix played an important role in determining the dielectric properties of composite materials [13,14], and the epoxy/silica composite can be considered as a three-phase system, including the silica, epoxy and interphase region. This indicated that the effective dielectric constant of composite was dependent on the dielectric constant ratio between filler and polymer, and the degree of interaction between filler and polymer as well. With the experimental data and molecular dipole polarization calculations, they showed that the addition of silane coupling agent could form chemical bonding and improve the interphase interaction in the composite, so the interphase dielectric constant can be increased.

Although, the general trend of observation is an increase in the dielectric constant and loss factor upon water absorption, there are also few papers reporting the reverse effect, i.e. a decrease in the loss under the influence of humidity, which was especially observed for low water concentrations [15,10]. It has been argued that reduction in loss due to a decrease in segmental mobility (segments length increased due to the water absorption).

In this paper, we focus on the filler size influence to the dielectric properties of epoxy/silica composite. Silica with nano-scale size was used as the fillers in our experiments. A different dielectric behavior of nano-composite is expected because of the extremely small size and high surface area of nano-sized fillers.

3. Experiments

Silica (SiO_2) nano-particles (average diameter 100 nm, from Nippon Chemical) and micron-sized silica (average diameter 3 μm, from Nippon Chemical) were used as-received. The epoxy used was diglycidyl ether of Bisphenol-A (EPON828, from Resolution Performance Products). It has low chloride content around 0.01–0.02 wt% according to the manufacture's information. The hardener was hexahydro-4-methylphthalic anhydride (HMPA, from Lindau Chemicals). The weight ratio of epoxy to hardener was 1:0.75. 1-Cyanoethyl-2-ethyl-4-methylimidazole (2E4MZ-CN, from Shikoku Chemicals Corporation) was used as the catalyst at 1 wt% based on the total weight of the epoxy and hardener. All the chemicals were used as received. The filler loading was 20 wt%. The blank resin was used as the control sample.

The dielectric properties of the epoxy/silica composite were measured by a dielectric analyzer (DEA 2970, TA Instruments). The single surface sensor was used for the DEA experiments. The electrode design of the sensor is based on a co-planar interdigitated-comb configuration, as shown in Fig. 1. The space between the electrodes is measured as 100 μm, and the width of each electrode is 150 μm. The uncured liquid resin was coated on the sensor surface and flowed into the spaces between the electrodes. The sample geometry between the electrode channels can be precisely controlled and the contact between sample and electrode was also very intimate. After coating, the liquid sample was cured in a convection oven at 150 °C for 1 h. The DEA experiments were performed from 35 to 250 °C with a stepping temperature of 5 °C and a frequency sweep from 0.01 to 100,000 Hz varying logarithmically. The dielectric permittivity (ε') and dielectric loss factor (ε'') were calculated by the pre-installed software.

After the first test, all the samples were put in an 85 °C/85% RH temperature–humidity aging chamber for 5 days. The aged samples with moisture gain were tested for a second time with DEA following the same procedure. Then, the samples were dried in the convection oven at 120 °C for

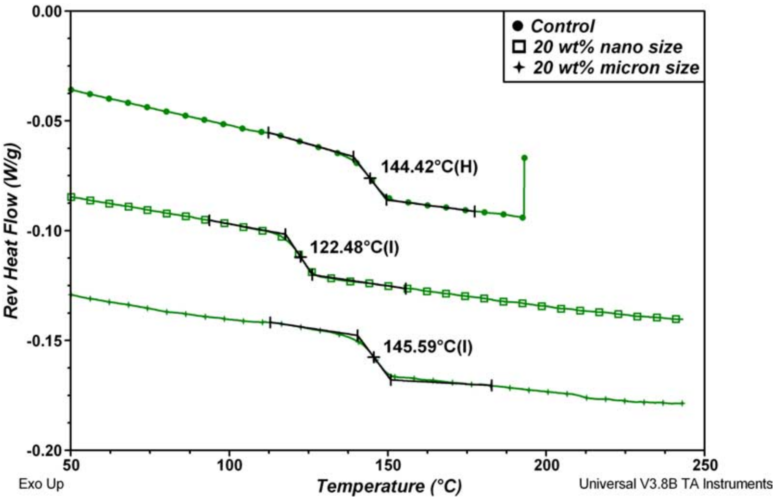

Fig. 2. DSC measured T_gs of the silica composites and the blank resin.

6 h for water desorption. The dried samples were tested for the third time with DEA.

The cured bulk samples were subjected to temperature-humidity aging at 85 °C and 85% RH. The samples were taken out of the aging chamber and the increased weight due to moisture uptake was recorded daily.

The curing behavior and glass transition temperatures of the epoxy composites were characterized by a modulated differential scanning calorimeter (DSC Q1000, TA Instruments). A sample of approximately 10 mg was sealed in a hermetic aluminum pan. Dynamic scanning experiments were conducted with a ramp rate of 5 °C/min, from ambient temperature to 250 °C to obtain the curing heat flow diagram of the composite. The cured sample was left in the DSC cell and cooled to room temperature. Then, the sample was reheated to 200 °C at 5 °C/min with a temperature modulation of ±1 °C/min to obtain the second heat flow diagram. From the step change of the reversible heat flow of the second diagram, the glass transition temperature (T_g) was determined.

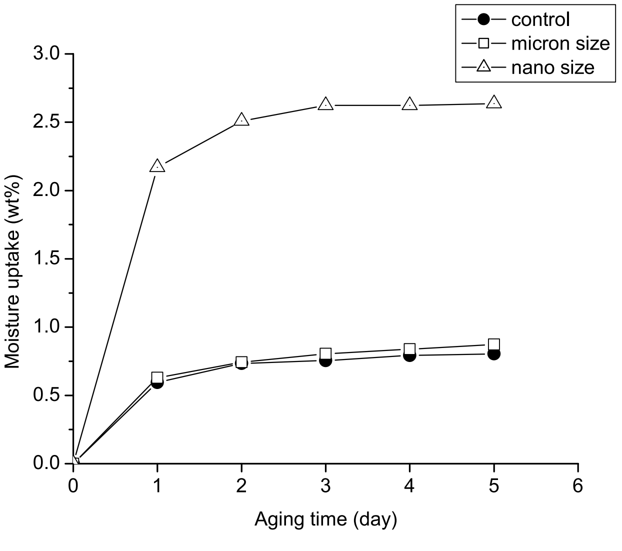

Fig. 3. Moisture absorption of three materials as aging time.

4. Results and discussions

4.1. Glass transition temperature

The thermal properties of the samples were measured by DSC. The T_gs of the silica composites with nano- and micron-sized fillers are shown in Fig. 2. The micron-sized filler did not have a significant effect on the T_g of the composites while the nano-sized filler had an appreciable impact. Compared to the control sample, the 20 wt% nano-composite showed a T_g depression by more than 20 °C while the 20 wt% micron-composite showed no change in T_g. The T_g depression behavior due to the nano-sized fillers was investigated elsewhere [16], in which different types of nano-particles were studied. It was found that the T_g depression was related to the enhanced polymer dynamics due to the extra free volume at the resin–filler interface.

4.2. Moisture absorption

Silica composites were also characterized in term of moisture absorption. Fig. 3 shows the moisture absorption of composites with 20 wt% filler as a function of time after the moisture uptake was normalized to polymer weight percentage. The behaviors of control sample were also shown. As can be seen from Fig. 3, micron-sized filler did not alter the moisture absorption behavior of the polymer matrix. However, the nano-composite showed a dramatic increase in moisture uptake. This can be due to several possible reasons. First of all, the nano-sized silica was synthesized via sol–gel reaction. The hydrophilic nature of the nano-sized silica surface tends to attract moisture. Compared to the micron-composite, the nano-composite has

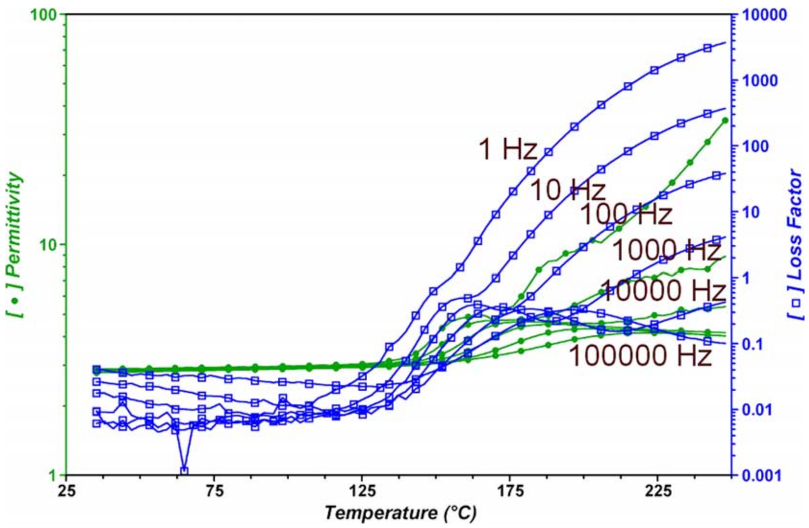

Fig. 4. Dielectric property of the control sample after curing.

a much larger interface area between the filler and the resin, and therefore, larger number of sites to attract moisture. And finally, the increased polymer dynamics in the nano-composite also helps the moisture diffusion.

4.3. Dielectric properties

Figs. 4–6 shows the DEA results of the control sample and the silica composites after curing. These three figures exhibit a similar behavior in the dielectric relaxation as shown by the change of the loss factor with the temperature and the frequency. Nevertheless, the transition temperature of the nano-composite marked by the peak of loss factor at each frequency appears to be lower than those of the control sample and micron-composite at corresponding frequencies. This result is consistent with the observation from DSC as shown in Fig. 2 since the transition temperature of the dielectric property reflects the known glass transition temperature of the polymer [17]. It is also observed that dielectric permittivity and the loss factor of the nano-composite at low frequencies are much higher than those of the control sample and micron-composite.

The mechanical and dielectric response of the polymeric material follows the time–temperature superposition (TTS) principle [18,19]. Briefly, the dielectric permittivity of solid material is a complex function of two variables: frequency and temperature. A complete representation should, therefore, comprise two ‘three dimensional’ plot of $\varepsilon'(f,T)$ and $\varepsilon''(f,T)$. These are cumbersome and are, therefore, seldom employed. The prevailing method of the representation consists of plotting the frequency dependence with temperature as a parameter or vice versa. It makes no difference whether one is plotting the frequency response or the temperature response in the appropriate coordinates. One can obtain an identical loss peak which moves to higher temperature with increasing frequency, or conversely, to

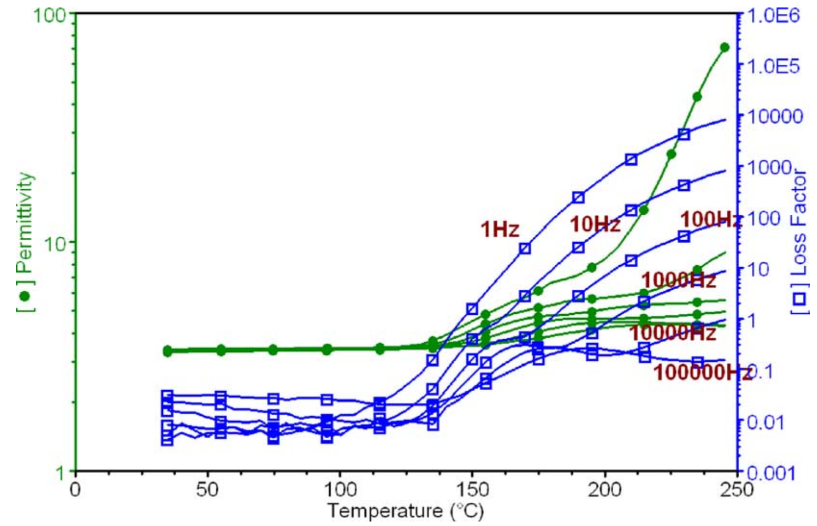

Fig. 5. Dielectric property of the epoxy/silica micron-composite after curing.

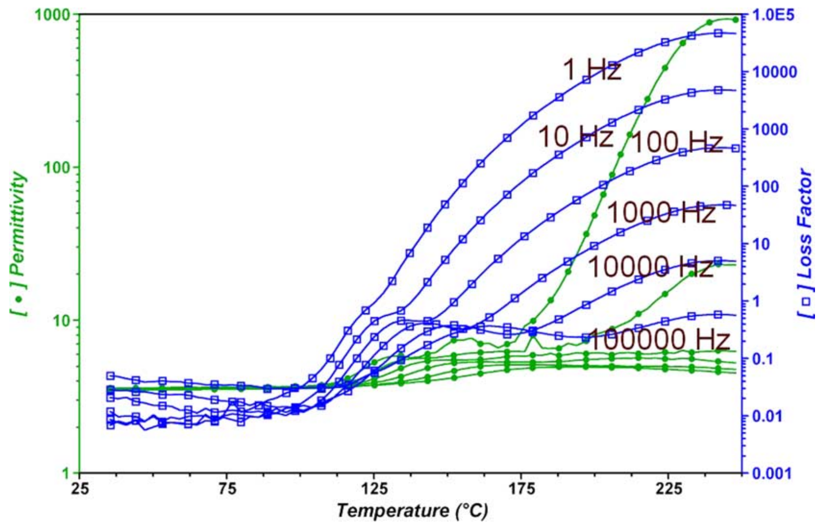

Fig. 6. Dielectric property of the epoxy/silica nano-composite after curing.

higher frequency with increasing temperature. If the dielectric response curves in a log–frequency plot at different temperatures are shifted horizontally, a master curve can be constructed to describe the dielectric behavior at a large time/frequency range at a particular temperature (reference temperature). The horizontal shifts are called shift factors (α_T) which follow the Williams–Landel–Ferry (WLF) equation [20] (Eq. (13)).

$$\log \alpha_T = -\frac{c_1(T - T_{ref})}{c_2 + T - T_{ref}} \tag{13}$$

In the current study, the reference temperature was chosen as the $T_g + 25$ °C of each sample. Fig. 7 shows the shift factors of TTS for nano-composite sample, which is in good agreement with the WLF equation. The parameters in the WLF equations for all the three samples are shown in Table 1. It can be seen that these constants take similar values for all three samples.

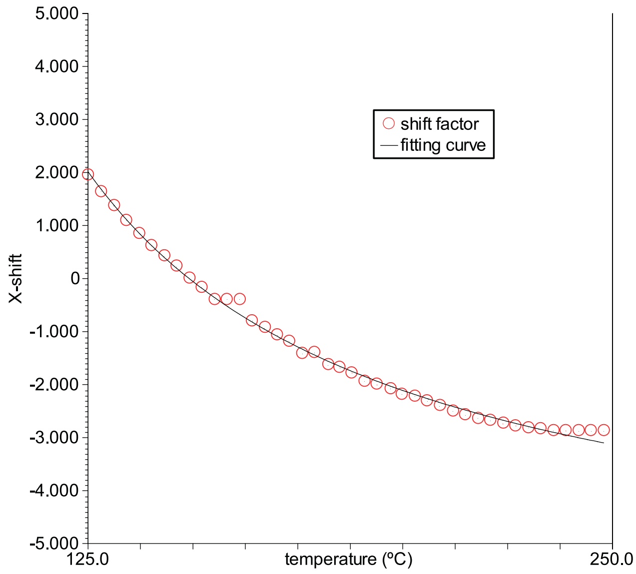

Fig. 7. Shift factors of TTS for nanocomposite sample.

By curve shifting, master curves were obtained for the three samples at temperature of 150 °C as shown in Fig. 8. As can be seen in the figure, at the entire frequency range, the nano-composite possesses a much higher loss factor than the other two samples. At a low frequency range (less than 10^2 Hz), the loss factor of the micron-composite appears to be higher than that of the control sample, but still lower than that of the nano-composite. It is also noticed that the loss peaks of the control sample and the micron-composite are observed at similar frequency range (around 1–10 Hz) while the loss peak of the nano-composite occurs at a much higher frequency (lower temperature by the TTS principle). The increased polymer mobility due to the extra free volume at the filler–resin interface increased the loss at 10^2–10^8 Hz and lowered the transition temperature of dipolar relaxation as indicated by the loss peak. The low frequency loss appeared to be linear in a log–log plot of the loss factor to the frequency with a slope of nearly -1, suggesting that the loss is associated with DC conductivity as shown in Eq. (6). A plot of the low frequency (1 Hz) loss factor and the ionic conductivity of the three samples in Fig. 9 also shows that the increased loss of the composites at low frequency and high temperature is due to the increased ionic conductivity. It is possible that the addition of the silica fillers brought more contaminants into the system that enhanced the ionic conductivity. The sol–gel synthesized nano-sized silica contains more contaminants from the solution reaction and,

Table 1
Constant parameters of WLF equation for three samples

Sample	Reference temp. (°C)	C_1	C_2
Nano-composite	150	6.1	97.81
Control	170	5.3	87.34
Micron-composite	170	5.6	107.0

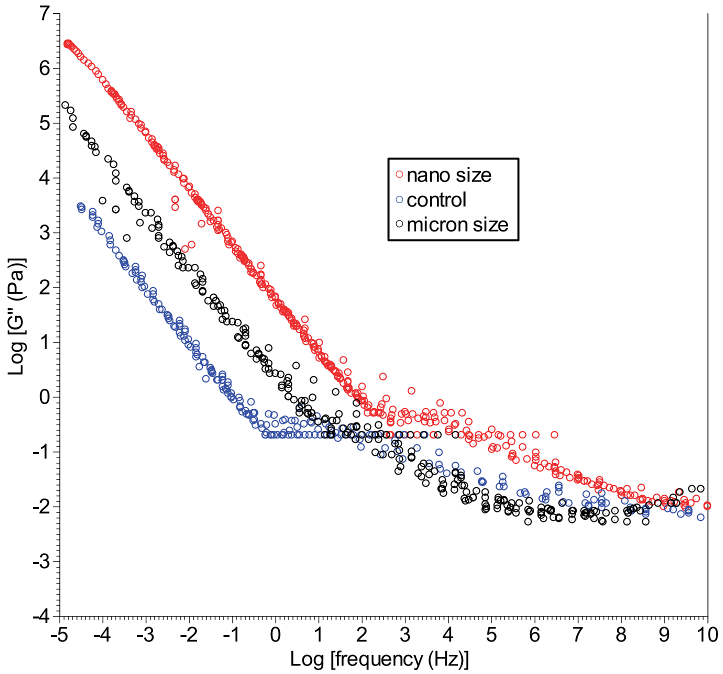

Fig. 8. Master curves of loss factor at 150 °C for three samples after curing.

therefore, the nano-composite displayed a higher ionic conductivity and, therefore, higher loss at low frequency range.

The humidity aging influence was also investigated by comparison of loss factors of samples with different history. Figs. 10 and 11 shows the loss factor of the three samples before and after aging at a humidity chamber. Before moisture absorption, three samples had similar loss factor at low temperature due to the low polymer mobility. However, the silica filled composites, regardless the filler size, have much higher loss factor after aging in 85 °C/85% humidity chamber with moisture absorption than the control sample. Although, the amount of moisture absorption of the micron-composite was similar to that of the control sample as shown in Fig. 3, the composite materials with heterogonous structure and interface between filler and polymer displayed the interfacial relaxation which was enhanced with the absorbed water on the silica surface. Therefore, the moisture absorption of the silica composite significantly increased the loss factor. From Fig. 11, it is also observed that the trapped water can be desorbed as the temperature increasing in the micron-sized composite, which corresponded to the decrease of loss factor in the temperature range 70–110 °C. On the

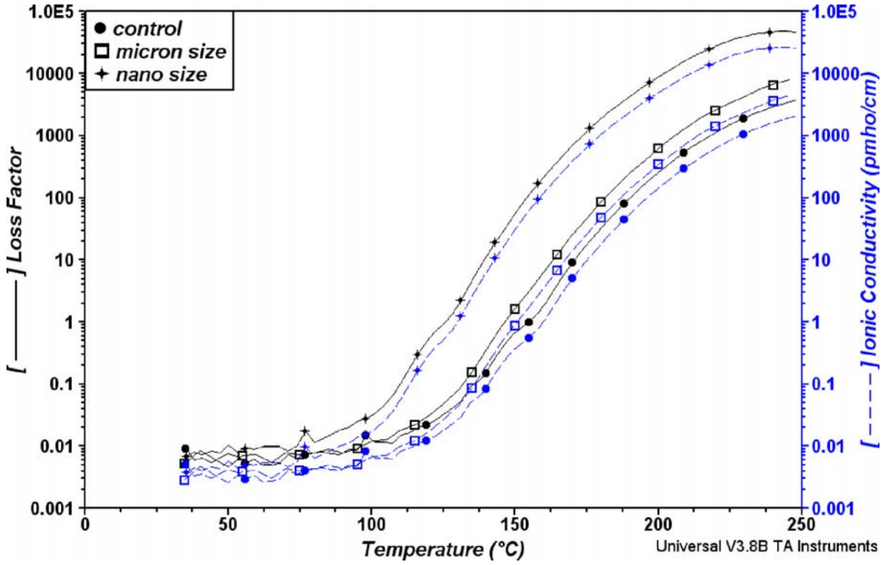

Fig. 9. Loss factor and ionic conductivity of the three samples at 1 Hz.

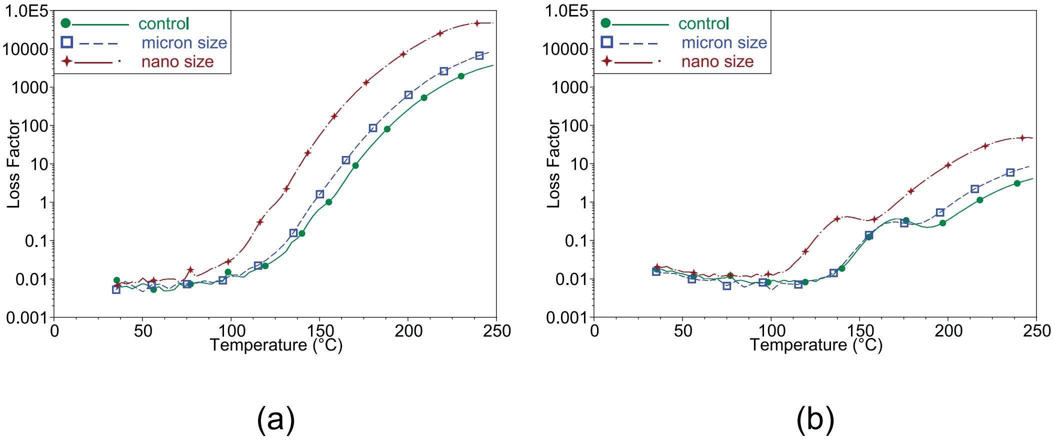

Fig. 10. Loss factor of three samples after curing (a) 1 Hz; (b) 1000 Hz.

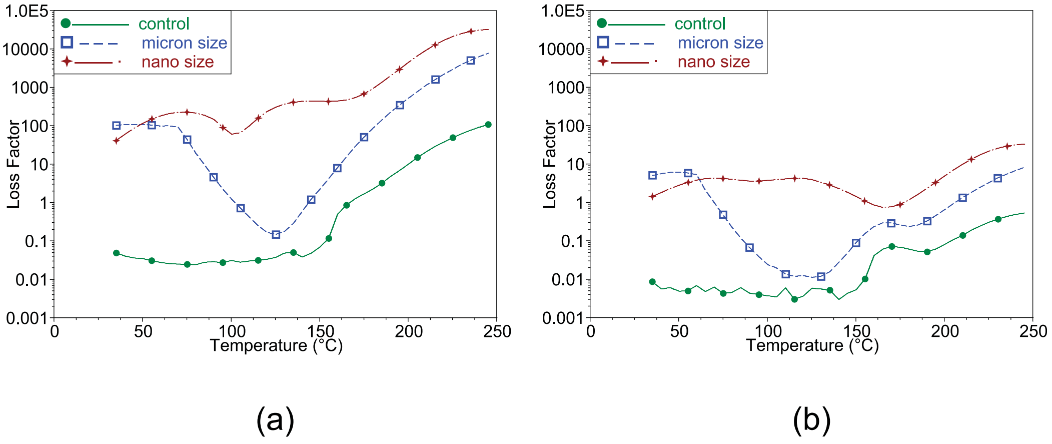

Fig. 11. Loss factor of three samples after aging under humidity (a) 1 Hz; (b) 1000 Hz.

other hand, the decrease in loss factor of the nano-composite happened at a high temperature, which indicates that desorption is more difficult with a higher surface area of the nano-sized silica with hydrophilic nature that retains moisture. Even at temperatures higher than T_g of the nano-composite when the polymer mobility is high, the moisture desorption rate is still slow. Fig. 12 showed the loss factor of three samples after drying in the thermal oven for 6 h. The dielectric property can be fully recovered after moisture desorption.

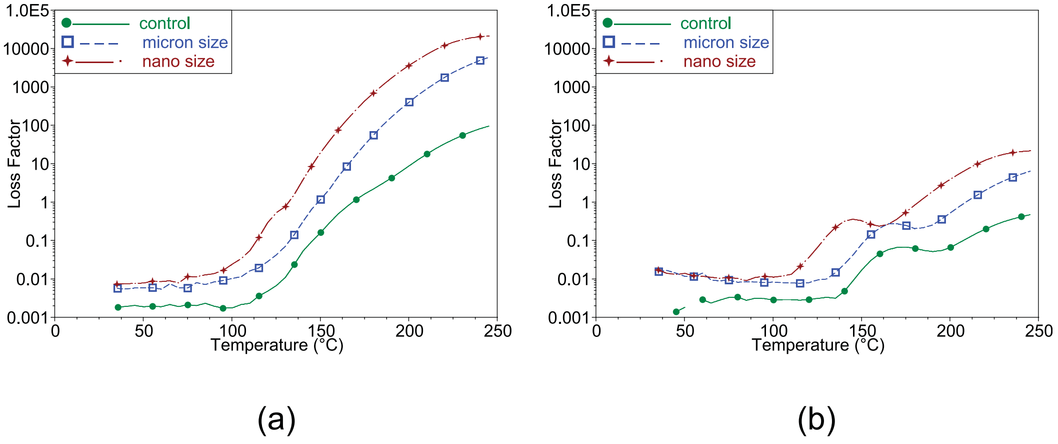

Fig. 12. Loss factor of three samples after drying (a) 1 Hz; (b) 1000 Hz.

5. Summary

This paper presented the theory models for the dielectric behaviors of solid materials. The existing work for the dielectric property of epoxy and epoxy/silica composite were briefly summarized with a focus on the ionic contribution and the water influence to the loss factor. Experimental measurements were conducted and showed that the nano-composite had a higher dielectric loss at low frequency due to enhanced ionic conductivity caused by the contaminants from the sol–gel synthesized nano-sized silica. The relaxation temperature of the nano-composite was lower than those of the micron-composite and the control samples due to the extra free volume at the filler–resin interface that assists the polymer mobility. The moisture had different effects on the pure epoxy and epoxy composite in dielectric loss, which can be explained by the combined effect of ionic conductivity and interfacial interaction in materials.

References

[1] Lee SM. Epoxy resin. New York: Marcel Dekker Inc; 1988, p. 783.
[2] Gross K, Hackett S, Larkey D, Schultz W, Thompson W. Proceedings of the international symposium on microelectronics, Denver, CO. September 2002, p. 234–38.
[3] Gross K, Hackett S, Schultz W, Thompson W. Proceedings of the 53th electronic components and technology conference, New Orleans, LA. May 2003, p. 951–56.
[4] Zhou Y, Shi FG. Proceedings of the ninth symposium on advanced packaging materials, Atlanta, GA March 2004, p. 100–2.
[5] Sun Y, Wong CP. Proceedings of the 54th electronic components and technology conference, Las Vegas, NV June 2004, p. 477–83.
[6] Williams EPM, Seferis JC, Wittman CL, Parker GA, Lee JH, Nam JD. J Polym Sci, Polym Phys 2004;42:1.
[7] Kranbuehl DE, Delos S, Yi E, Mayer J, Jarvie T, Winfree W, et al. Polym Eng Sci 1986;26:338.
[8] Vo HT, Shi FG. Microelectron J 2002;33:409.
[9] Myslinski P, Lazowski Z. Mater Chem Phy 1993;33:139.
[10] Maxwell ID, Pethrick RA. J Appl Polym Sci 1983;28:2362.
[11] Bosma TJ, Lebey T, Pouillres V, Chenerie I, Ai B, Rieus N. J Phys D: Appl Phys 1995;28:1180.
[12] Gonon P, Sylvestre A, Teysseyre J, Prior C. Mater Sci Eng B 2001;83: 158.
[13] Todd MG, Shi FG. J Appl Phys 2003;94:4551.
[14] Todd MG, Shi FG. Microelectron J 2002;33:627.
[15] Reid JD, Lawrence WH, Buch RP. J Appl Polym Sci 1986;17:1771.
[16] Sun Y, Zhang Z, Moon KS, Wong CP. J Polym Sci, Polym Phys 2004; 42:3849.
[17] Brabdrup J, Immergur EH. Polymer handbook. London: Wiley; 1989. p. VI/241.
[18] Struik LCE. In: Brostow W, Corneliussen RD, editors. Failure of plastics. Munich: Hanser; 1986, chapter 11.
[19] Jonscher AK. In: Dielectric Relaxataion in Solds. London: Chelsea, Dielectrics Press; 1983 [chapter 3, 101].
[20] McCrum NG, Read BE, Williams G. Anelastic and dielectric effects in polymeric solid. New York: Dover; 1967.