

Influence of Nanofillers on Electrical Characteristics of Epoxy Resins Insulation

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Abstract— Epoxy resin is widely used in high voltage apparatus as insulation. Fillers are often added to epoxy resin to enhance its mechanical, thermal and chemical properties. The addition of fillers can deteriorate electrical performance. With the new development in nanotechnology, it has been widely anticipated that the combination of nanoparticles with traditional resin systems may create nanocomposite materials with enhanced electrical, thermal and mechanical properties. In the present paper we have carried out a comparative study on dielectric properties and space charge behaviour of epoxy resin/nanocomposites with nano-fillers of SiO_2 and Al_2O_3 . The epoxy resin (LY556), commonly used in power apparatus, was used to investigate the dielectric behaviour of epoxy resin/nanocomposites with different filler concentrations. The epoxy resin/nanocomposite thin film samples were prepared and tests were carried out to measure their dielectric permittivity and tan delta value in frequency range of 1Hz- 1MHz. The space charge behaviours were also observed by using the pulse electroacoustic (PEA) technique. In addition, traditional epoxy resin/microcomposites were also prepared and tested and the test results were compared with those obtained from epoxy resin/nanocomposites.

Keywords-nanocomposites, epoxy resin, nanofillers, dielectric properties, space charge.

I. INTRODUCTION

Epoxy resin is one of the most commonly used thermosetting materials in high voltage apparatus as insulation due to its excellent mechanical, electrical properties and chemical stability. In recent years, the nano reinforced epoxy resin has attracted a wide interest as it enhances the epoxy's properties significantly. Researches on nano reinforced epoxy resin composites have been carried out ceaselessly. The recent investigation has shown that the epoxy/nanocomposites demonstrate some advantages in both mechanical and dielectric properties [1, 2] comparing with pure resin system and epoxy with micrometer-size fillers. One of the interesting observations was that over a wide range of frequencies, the dielectric permittivity values in epoxy nanocomposites are normally lower than both base resin and epoxy with micrometer-size fillers at lower concentrations (depend on filler type and size) [1]. For both TiO_2 and ZnO nano fillers, as the loading filler concentration increases, the permittivity of epoxy nanocomposites increases as well [2]. Earlier researches also showed that the presence of nano fillers in epoxy resin

affects the space charges accumulation in epoxy resin. Epoxy nanocomposites seem to accumulate less charge compared with filler-free epoxy resin [3]. It was also observed that epoxy nanocomposites have faster charge dynamics, especially for negative charges [4].

The purpose of the present paper is to study the effects of nano-size fillers on space charge behaviors and dielectric permittivity of epoxy/nanocomposites. It aims to investigate the effects of the filler type, concentration and size on epoxy/nanocomposites' dielectric properties. Both SiO_2 and Al_2O_3 nano fillers are used in this study. The permittivity of epoxy/nanocomposites with different concentrations is measured and the pulsed electroacoustic technique is used to monitor space charge behaviors of the samples.

II. EXPERIMENTAL DETAILS

A. Materials

The material used in this study to produce epoxy resin specimen was Araldite LY556 (Bisphenol-A type) and the hardener HY917 (anhydride type hardener), supplied by Huntsman. The epoxy resin system is widely used in practice and has an advantage of low viscosity at room temperature. Both nanoparticles of silicon dioxide (average diameter 25nm) and aluminium oxide (diameter 30-40nm) supplied by NanoAmor were used as fillers. Micro-sized SiO_2 fillers supplied by Huntsman were also used to show how filler size influence the dielectric properties of epoxy resin.

B. Process

The mould used to produce epoxy/nanocomposites consists of two metal plates, with a polymer film spacer in the middle. The thickness of epoxy specimens is controlled by the thickness of the spacer. For this study the thickness of spacer used is 200 μm . The plate surface was polished to achieve even and smooth sample surfaces. To help release the specimen from the mould after curing, both the plate surface was smeared with a very thin layer of silicon grease.

The suggested mix ratio of araldite and hardener 1: 0.9 (by weight), and the concentration of accelerator is 1 parts in per 100 parts epoxy resin. The epoxy resin specimens (200 μm) with loading concentrations of nano-fillers (both SiO_2 and

Al₂O₃) 0.1wt%, 0.3wt%, 0.5wt%, 1wt%, 3wt% and 5wt% were produced. Pure epoxy resin specimens and specimens with micro-size SiO₂ fillers were also prepared for comparison purpose. Before the process of preparing epoxy resin specimen, epoxide needs to be pre-heated to 40°C in an oven to reduce its viscosity. Then both epoxy resin and hardener were taken into beakers separately. To remove the gas bubbles, both of them need to be degassed in a vacuum oven for 1h at 40°C before mixing. After the completion of degas process, the fillers (micro and nano) were dispersed into epoxy resin slowly with hand stirring. The hardener was added into the resulting epoxy/nano-filler solutions and then the mixture was stirred with both high speed mechanical mixer (at 600 rpm) and ultrasonic liquid processor for 1h each. The mixture was degassed in the vacuum oven for another 20 min at 40°C to remove gas bubbles generated during the mixing process. After degassing, the mixture was poured into the mould. Then the mould was placed into the oven at 80°C to cure for 4h followed by 4h post-cure at 120°C. Finally removing the cured resin from the mould, the 200µm specimen was ready for testing.

Scanning electron microscope (SEM) was used to exam to dispersion of nano-size filler in the epoxy/nanocomposites. The even dispersion of nano-size filler in the resin can be seen from Fig. 1. Therefore it is confirmed that the filler dispersed uniformly in the result specimens.

III. RESULTS AND DISCUSSIONS

A. Dielectric Spectroscopy Measurement

The dielectric permittivity of epoxy/nanocomposites was measured over a wide range of frequency using dielectric spectroscopy (Solatron 1260). During all the measurements, the temperature was maintained at room temperature. Thus the influence of temperature on results can be ignored.

For both epoxy/nanocomposites with SiO₂ and Al₂O₃ nano fillers and with different concentrations, the variations of dielectric permittivity as a function of frequency are shown in Fig. 2.

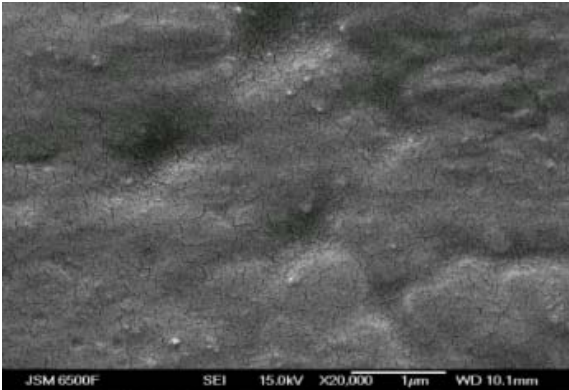


Figure 1. SEM Image of the Epoxy-SiO₂ Nanocomposite

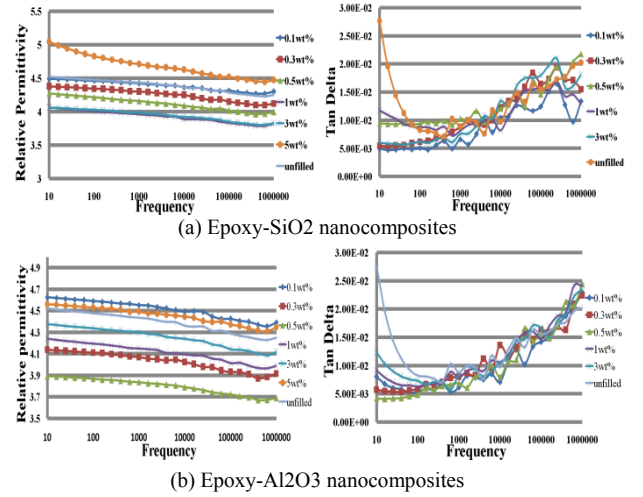


Figure 2. Variations of permittivity and Tan Delta with respect to frequency

In the present case, the effective permittivity of the epoxy/nanocomposites is governed by the polarization associated with epoxy and nano SiO₂/Al₂O₃ particles, as well as the interfacial polarization at the interface between epoxy and nano particles. It is also well known that the frequency of the measurements will influence the polarization process. Thus as expected, it can be seen from Fig. 2, both epoxy-SiO₂/Al₂O₃ nanocomposites and unfilled epoxy show a decrease in effective permittivity with increasing frequency. In a typical epoxy resin system, the permittivity of epoxy is determined by the number of orientable dipoles present in the system and their ability to orient under an applied electric field [5, 6]. As in the epoxy chain, most of the free dipolar functional groups are able to orient under lower frequency of applied field. Thus the epoxy composites tend to have higher permittivity in lower frequency range. When the frequency of the applied voltage increases, it will become more difficult for larger dipolar groups to orient themselves. Thus the effect of dipolar groups on the permittivity is reducing continuously as the frequency increasing. Moreover, the increasing of frequency of the applied field will also result in reducing of SiO₂/Al₂O₃ fillers' inherent permittivity [7]. The combination of both effect results in the reduction of epoxy/nanocomposites' permittivity with increasing frequency.

There is another interesting observation from both Fig.2 (a) and Fig. 2 (b). For both epoxy- SiO₂/Al₂O₃ nanocomposites, the permittivities of the composites with 0.1% nano filler loading are similar to the unfilled epoxy. It also can be seen from Fig. 2 (a), the permittivity for epoxy-SiO₂ nanocomposites decrease as the filler concentration increases, and the relative permittivity reaches its lowest value when the loading concentration is between 1% and 3%. Then the permittivity of epoxy-SiO₂ nanocomposites begins to increase as filler concentration increases further more. Fig. 2 (b) shows a similar observation on epoxy-Al₂O₃ nanocomposites, with

the lowest permittivity occurs between 0.5% and 1%. This observation is surprising as most of the earlier investigations showed that lower loading concentration (even much less than 1%) of nano-size fillers will lead to lower permittivity [2]. Earlier study also stated that the permittivity of epoxy/nanocomposites increases with increasing nano filler concentration in epoxy. However, there are also similar observations in the literature where the nanocomposites' permittivity drops at lower concentration and then increases again as the filler concentration increases to a high value (more than 0.5%) [8]. Reduction of effective permittivity with increasing nano SiO₂ filler concentration may be caused by the following reason. The interaction between nano SiO₂ filler and epoxy chain reduces the mobility of epoxy chain in the bulk material, which will result in decreasing of the effective permittivity of epoxy/nanocomposites. When a small amount of nano filler is loading into epoxy, due to the interaction between filler and epoxy chain, the thin immobile nano layers can be formed. Those thin immobile nano layers will restrict the mobility of the epoxy chain [9]. As the loading concentration increases, more immobile nano layer formed and the mobility of epoxy chain decreased continuously, resulting in reducing of nanocomposites' permittivity. Moreover, the influence of the filler's inherent permittivity on resulting nanocomposites' permittivity increase as the loading concentration increases. The permittivity of two phase dielectric satisfies the Lichtenecker-Rother mixing rule (1):

$$\text{Log } \epsilon_c = x \text{ Log } \epsilon_1 + y \text{ Log } \epsilon_2 \quad (1)$$

where, ϵ_c is the resultant composite permittivity, ϵ_1 and ϵ_2 are the permittivity of filler and epoxy and x, y are concentrations of filler and polymer.

It can be obtained from the rule that the influence of filler permittivity on nanocomposites increases as the filler concentration increases. Thus as nano SiO₂ filler has a lower permittivity compared with unfilled epoxy, the increasing concentration of the filler will result in reducing of nanocomposites' permittivity. Fig. 2 (b) also gives similar observations. It also needs to be noticed that epoxy-Al₂O₃ nanocomposites have higher permittivity compared with nanocomposites with nano SiO₂ fillers. This is because nano Al₂O₃ particles have a high permittivity than nano SiO₂ particles. So the type of nano fillers also has a significant influence on nanocomposites' permittivity.

The variation of tan delta value in both epoxy- SiO₂ / Al₂O₃ composites are also presented in Fig. 2. The tan delta value in both epoxy- SiO₂ / Al₂O₃ nanocomposites decrease at lower frequencies (less than 100Hz). It can also be obtained from Fig.2 that the tan delta value of unfilled epoxy is higher than epoxy-SiO₂/Al₂O₃ nanocomposites in this frequency range. However, when the applied frequency is higher than 100Hz, there is a continuous increase in tan delta value in both epoxy-SiO₂ / Al₂O₃ nanocomposites with increasing frequency. Moreover, there is no significantly difference in tan delta

value between unfilled epoxy and both epoxy-SiO₂/Al₂O₃ nanocomposites.

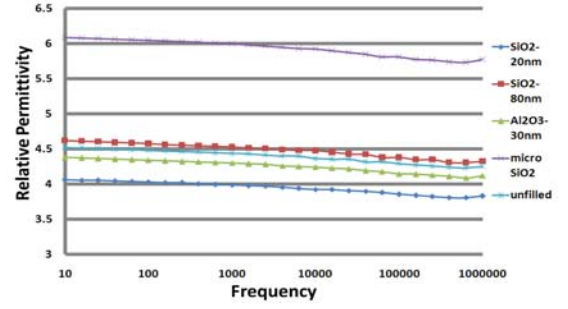


Figure 3. Variations of permittivity with respect to filler size

The influence of filler size on epoxy/nanocomposites' permittivity can be seen from Fig. 3. The composite with micro-size filler seems to have a higher permittivity than the nanocomposites. This is probably due to immobility of epoxy chain in nanocomposites due to a strong interaction at the interface.

B. Space Charge Measurement

The Pulsed electro-acoustic (PEA) system was used for measuring the space charge accumulation in epoxy nanocomposites. A voltage of 6kV had been applied to specimens with approximately 0.2mm thickness (The applied field is 30kv/mm) at room temperature (approximately 20°C) for 90 minutes. In the present case, the results from "volts-off" measurements were used to investigate the charge accumulation in the specimens. The "volt-off" measurement measures charge formation immediately after the applied voltage has been removed.

The "volts-off" space charge accumulation of specimens with different nano SiO₂ filler concentrations is shown in Fig. 4. It can be seen from Fig. 4 (a), a large amount of homocharges is observed adjacent to both electrodes for unfilled epoxy. As the duration of the applied voltage increases, the amount of charge in the specimen increases as well. Charges are dictated by homocharges, which means that the charge injection takes

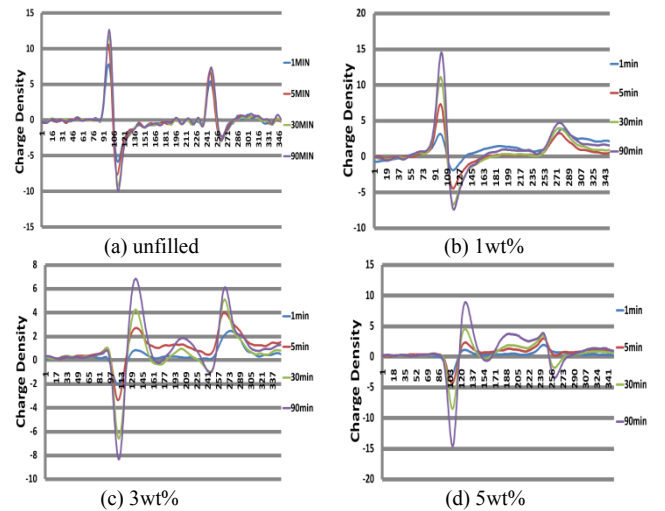


Figure 4. Charge build-up in epoxy-SiO₂ nanocomposites at 6KV

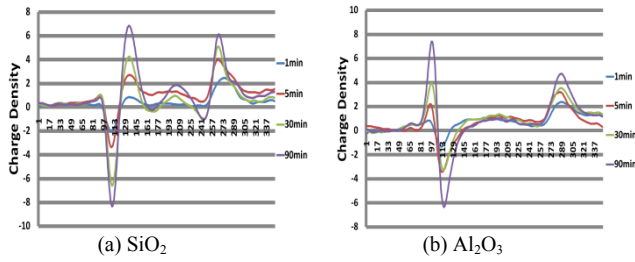


Figure 5. Charge build-up in 3wt% epoxy-SiO₂/Al₂O₃ nanocomposites

place from both electrodes. The heterocharges which is caused by ionization process may also present in the specimen. However, as the PEA system only measures the net charges, so it might be covered by the charge injection. Compared with the unfilled samples, Fig. 4 (b) shows a similar charge distribution in specimen with 1% nano SiO₂ filler. However, It is noticed that 1% nanocomposite has a slower initial charge build-up rate. The magnitude of charges in 1% samples is slightly less than that in the unfilled one. The reason for such decreasing in the magnitude of space charge is either the presence of nano filler has hindered the charge injection or more heterocharges are generated due to the ionization process. As the presence of the nano SiO₂ fillers, the heterocharges generated by ionization process should increase. Thus more heterocharges accumulated closed to the electrodes. The small amount of heterocharges will cancel out with some of the injected charges. Therefore the net charges observation from the PEA system shows a small decrease in the magnitude of space charges. As shown in Fig. 4 (c), when the filler concentration increases to 5%, space charge distribution is very different. There is a positive peak close to the cathode as a result of heterocharges accumulation. Thus it is believed that the increasing concentration of nano filler will result in more heterocharges formation. When the more the fillers are added into the epoxy sample, the more heterocharges are accumulated adjacent to the cathode as shown in Fig. 4 (d).

Fig. 5 shows the observation of space charge accumulation in both epoxy-SiO₂/Al₂O₃ nanocomposites with 3% filler concentrations. It can be seen clearly that charges are dictated by homocharges in epoxy-Al₂O₃ nanocomposites, whereas in epoxy-SiO₂ composites, charges are dominated by heterocharges. But there is a small amount of positive charge presence in the middle of both samples. The difference in charge formation between two nanocomposites is caused by the amount of heterocharges accumulated adjacent to the electrodes. Thus compared with Al₂O₃ particles, the same amount of SiO₂ particles seems to have a better enhancement on the ionization process in nanocomposites.

IV. CONCLUSION

Both the dielectric permittivity and space charge accumulation in epoxy nanocomposites loaded with different concentration of nano size SiO₂ and Al₂O₃ fillers have been investigated using dielectric spectroscopy and the PEA method. The following conclusion may be drawn based on this study.

The permittivity for both epoxy-SiO₂/Al₂O₃ nanocomposites decreases at lower concentration (less than 1%). The relative permittivity of nanocomposites appears to have a minimum value with a threshold filler concentration (1wt% for nano SiO₂ and 0.5wt% for nano Al₂O₃). When the filler content is above the threshold value, the permittivity of nanocomposites begins to increase with filler concentration. The epoxy-Al₂O₃ nanocomposite has a higher permittivity than epoxy-SiO₂ nanocomposites as the Al₂O₃ particles have a higher inherent permittivity. Moreover, the increase in filler size will lead to a larger permittivity as well.

The presence of nano particles seems to enhance the ionization process inside the sample, especially at higher filler concentrations. The filler type also has a significant influence on space charge accumulations. It can also be observed that higher content of nano size filler (5wt% for SiO₂) will lead to more complicated charge accumulation.

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