

Influence of Water Absorption on Dielectric Properties of Epoxy SiO₂ and BN Nanocomposites

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Abstract—It is well known that epoxy resins would absorb water when left in ambient conditions. A number of hydrophilic nano-particles also absorb water, like nano-SiO₂, because of their surface hydroxyl groups resulting from the manufacture process. The water uptake will affect dielectric properties of the nanocomposites. However there was conflict report on the amount of water uptake by the unfilled and nano-filled epoxy resin systems. In the present paper, the epoxy resin was filled with surface treated, as well as, untreated nano-SiO₂ and nano-BN. The relative humidity is controlled by the desiccator (dry samples), de-ionized(100% RH) water and climate chamber. The dielectric properties will relate to the hydration of samples. Measurements of dielectric spectroscopy cover the range of frequency from 10⁻²-10⁵ Hz. Dielectric spectroscopy also showed different capacitance and permittivity at low frequencies, as well as $\tan\delta$, which depend on the hydration and temperature. It was observed from the results that permittivity, capacitance and $\tan\delta$ of pure epoxy were strongly affected by the water absorptions. All these results are used to analyse how different variables, like surface treatment, filler type and filler loading concentration, can influence the water absorption. It will allow us to extract the influence of water absorption on dielectric properties of epoxy nanocomposites.

Keywords—epoxy nanocomposites; water uptake; nano-fillers; temperature; dielectricscopy; dielectric relaxation; permittivity; $\tan\delta$

I. INTRODUCTION

Epoxy resin is a widely used thermosetting material in many areas, such as insulation, mechanical manufacturing and chemical anti-corrosion. Owing to its three dimension cross-linking network structures, it has good adhesion, excellent mechanical, chemical stability and dielectric properties [1]. Many researchers have introduced nano-fillers in order to improve dielectric properties of the material. However, water absorption will occur in humid environment and will result in overall deterioration in dielectric properties [2]. And the loaded fillers may exacerbate, resulting from free volume and hydroxyl groups on surface of nano-particles [3]. In the present paper, the water uptake of different nanofillers in various loading concentrations and influence of water absorption on the dielectric properties of epoxy and its nanocomposites were investigated.

II. EXPERIMENT DETAILS

A. Material

The samples were prepared using bisphenol-A diglycidyl ether (D.E.R. 332, density 1.16 g/cm³) along with polyetheramine hardener (Jeffamine D-230, density 0.948 g/cm³) supplied by Huntsman. This was used as the base polymer material. The filler particles used in the present study are commercially available untreated SiO₂ and BN fillers provided by Sigma-Aldrich. C8 treated Nano-SiO₂ was introduced in order to eliminate the hydroxyl groups on surface of SiO₂ particles, which has previously been used in [4]. The average particle size (APS) of nano-silica is 20 nm, according to datasheets. BN particles are hexagonal and with the average part size of 150 nm, according to datasheets. The filler loading concentration in each kind of samples is 0.5wt%, 1wt%, 3wt% and 5wt%. The thickness of sample is 0.145 ± 0.005 mm and the thin film samples was coated with gold on both sides before dielectric spectroscopy tests.

In the process of sample preparation, in order to reduce its viscosity, the epoxy resin was pre-heated to 323 K in oven (1 atm). Then the appropriate amount of epoxy resin and hardener were weighed out, and resin was degassed by using vacuum oven (103 Pa, 293K) for 15 min. The ratio of epoxy and resin was 1000:344. The resin was then injected into the small glass vessel contains nano-particles and mixed. The mixture was then sonicated, with cooling breaks in order to avoid too much heat build-up, which may initiate curing or decompose the resin. Then the hardener was added and the compound mixed at 600 rpm and 323 K for 15 min. The composite was degassed at 103 Pa and 323 K for 30 min. After being degassed, the mixture was subsequently cast under nitrogen atmosphere in a steel mould. The samples were cured at 393 K °C for 4 hours [5]. The samples were stored in a desiccator under vacuum until use.

B. Dielectric Spectroscopy Measurement

The dielectric measurements were over a frequency range from 10⁻² to 10⁵ Hz by using Solartron 1260 Dielectric Interface. The temperature of the measurements was in a range from 293 - 333 ± 1 K. All the samples were placed between two electrodes with diameter 32 mm. A voltage of 1 V RMS was used. The accuracy of measurements is within 2%.

C. Relative Humidity Control

There are three relative humidity conditions in the test.

- 0% RH: All the samples were controlled in the vacuum oven (103Pa, 333 K) for 72h and then stored in vacuum desiccator with dried silica gel at 293 K. The TGA result of samples can show the samples were relatively dried before testing observed in Fig. 1. It can be observed that pure 100RH samples began to lose weight from around 413K and loss of weight percentage is about 2%;
- 60% RH: All the samples were exposed in RH climate chamber at 293 K, and actual RH is from 56 to 62%;
- 100% RH: All the samples were immersed in de-ionized water for 10 days before testing at 293 K.

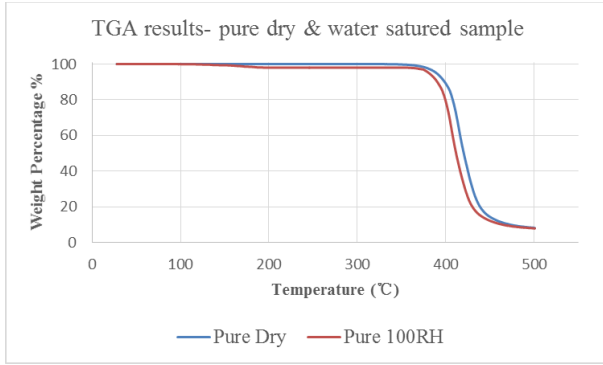


Fig. 1. TGA result of dried and water saturated pure samples

III. RESULTS AND DISCUSSIONS

A. Water Diffusion in Samples

Water diffusion in epoxy and its nanocomposites was measured at 293 K. The samples were removed from humid environment periodically and measured using microbalance, and then put them back. The measurements were continued until weight becomes stable, in about 10 days. The water diffusion in epoxy and its nanocomposites may act as Fickian diffusion behavior. The water uptake, M , is a function of time shown in equation (1) [6]:

$$M = \int_0^t J dt = \sqrt{\frac{4Dt}{\pi}} (B \cdot C) \quad (1)$$

where J is the flux of moisture, B is a constant of integration; D is the water diffusion coefficient, according to the nature of the materials; and C is the humidity of environment. The water diffusion in epoxy and its nanocomposites can be plotted as percentage increase in mass versus the square root of time. The water diffusion in pure and each type of nanocomposites in loading concentration of 3wt% in both 60%RH were shown in Fig. 2. It can be observed that the water absorption reaches quasi-equilibrium after 3days, which is about 2.5×10^5 s and $500 \text{ s}^{0.5}$ in Fig. 2. Prior to this stage, the water diffusion follows Fickian's law. After this, another much slower process comes into plots. This process is described by the later flatter portion of the curves [3]. According to Fig.2, the lower equilibrium state of C8 SiO₂ samples may be caused by the removed hydroxyl groups from surface treatment, when compared to

untreated SiO₂ (unSiO₂) and BN samples. However, the water uptake is still higher than the pure samples, owing to that the surface treatment cannot remove all the hydroxyl groups on particle surface.

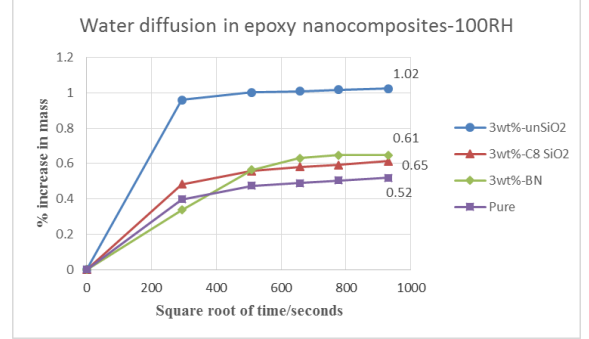


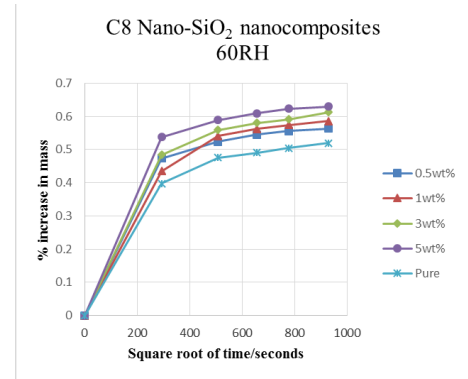
Fig. 2. Water diffusion in epoxy and its nanocomposites (60% RH, 293K)

B. Water Uptake

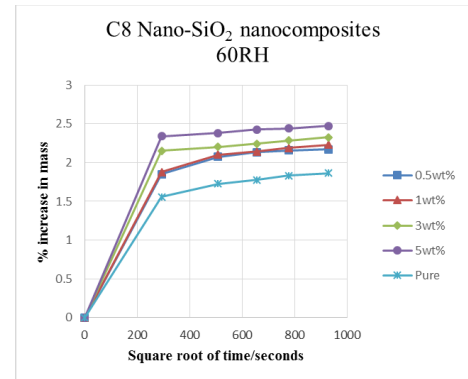
The water uptake, H_w , can be calculated by equation (2):

$$H_w = \left| \frac{M_w - M_d}{M_d} \right| \times 100\% \quad (2)$$

where M_w is the weight of water absorbed samples and M_d is the weight of dry samples. The water uptake of C8 SiO₂ samples in each loading concentration at 60% RH and 100% RH at 293K are shown in Fig.3. And the increases in mass of all epoxy samples in each humidity are shown in Fig. 4.



(a)



(b)

Fig. 3. Water uptake of C8 SiO₂ samples and matrix, (a) 60% RH and (b) 100% RH, 293K

In Fig.3, it is noted that water uptake of samples increases with nanofiller loading concentration in both 60% RH and 100%RH, which was also observed in results of water uptake of untreated SiO₂ and BN samples. As shown in Fig 4, the water uptake in each sample increases with relative humidity. Those may be caused by free volume in interfacial areas around nano-particles where water may locate and hydrogen bonds form owing to hydroxyl groups, which will rise with the increase in nanofiller loading concentrations [7, 8, 9].

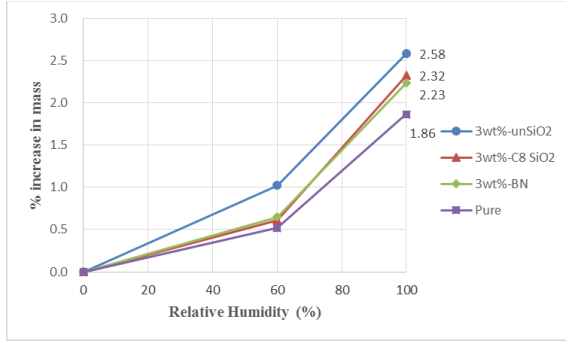
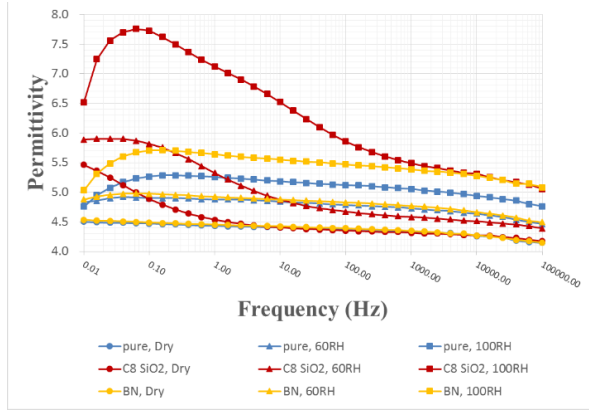
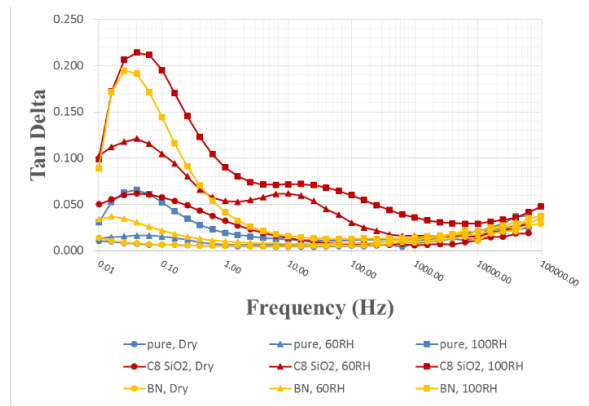


Fig. 4. Water uptake of C8 SiO₂ samples and matrix, 100% RH, 293K



(a)

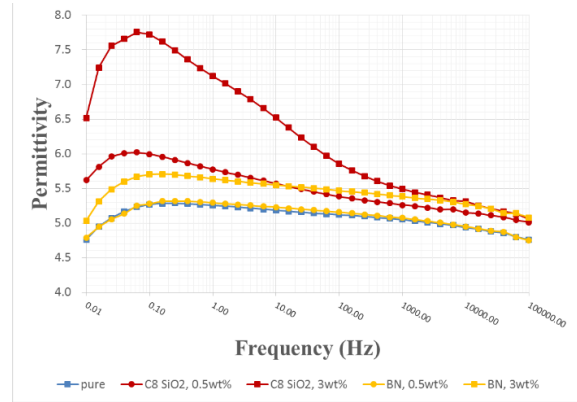


(b)

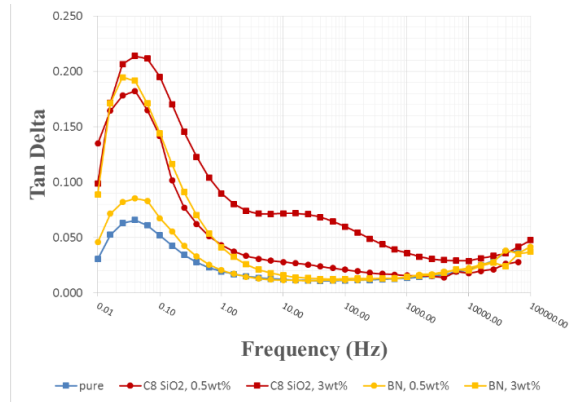
Fig. 5. (a) Real relative permittivity and (b) tan δ in C8 SiO₂, BN and pure samples exposed to 0%, 60%, 100% RH, fillergrade of 3wt%, 333K

C. Real Relative Permittivity and Loss Tangent

The real relative permittivity and tan δ are plotted in Fig. 5 as a function of frequency, RH value, filler types in filler loading concentration of 3wt% at 333K. It is noted that a large increase in permittivity at low frequencies shown in Fig. 5 (a), which become more obvious with growth of RH value. This surge of permittivity refers to the “electrode polarisation” mechanism, which is related to the existence of free charges. When applying an electric field, free charges will move towards the electrodes and lead to the conducting-like phase in material. This effect is well-known in dielectricscopy [10]. However, the permittivity shows reduction in pure, C8 SiO₂ and BN samples in 60% RH and 100% RH, adjacent to frequency of 0.01Hz. This is caused by presence of water, since this phenomenon is not shown in dried samples.



(a)



(b)

Fig. 6. (a) Real relative permittivity and (b)tan δ in C8 SiO₂, BN and pure samples exposed to 100% RH in fillergrade of 0.5wt%, 3wt%, 333K

The loss tangent is shown in Fig 5 (b). The value of tan δ increases with RH value as well. Mid-frequency relaxation peaks at a range of 0.01 Hz to 1 Hz can be seen. This, not shown in dry samples in Fig. 5(b), may result from water in samples. In addition, the C8 SiO₂ samples have extra relaxation peaks at frequency from 1 Hz to 100 Hz. Because this kind of peaks did not show in pure and BN samples, which have few hydroxyl groups when compared to C8 SiO₂ ones, it may be caused by the bonded water [11]. And the variations in different filler loading concentrations show an overall increase

with filler loading concentration in both permittivity and $\tan\delta$ of samples, shown in Fig. 6. Those differences in plot may be caused by fraction of free volume and the number of hydroxyl groups, related to the filler loading concentrations [12].

D. Mid Frequency Relaxation

Two kinds of water present in epoxy and its nanocomposites [8, 13]. Free water is located in free volume holes, cracks and crevices in matrix. It also stays in and can get through the matrix-nanofiller interfacial areas. And the bonded water is bond to the hydroxyl in nanocomposites, forming hydrogen-bonded clusters [11]. As shown in Fig 7 and discussed before, mid frequency relaxation peaks are related to the presence of water compared to dried samples and loss peak shifts towards higher frequencies with increasing temperature. And the extra relaxation peaks only in C8 SiO₂ samples at frequency range is from 1 Hz to 100 Hz, which may result from bonded water and can be further proved by Arrhenius plot shown in Fig 8.

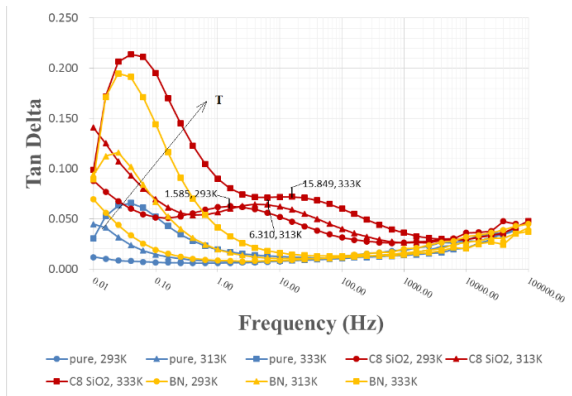


Fig. 7. $\tan\delta$ in C8 SiO₂, BN and pure samples exposed to 100% RH in fillergrade of 3wt%, temperature range from 293K to 333K

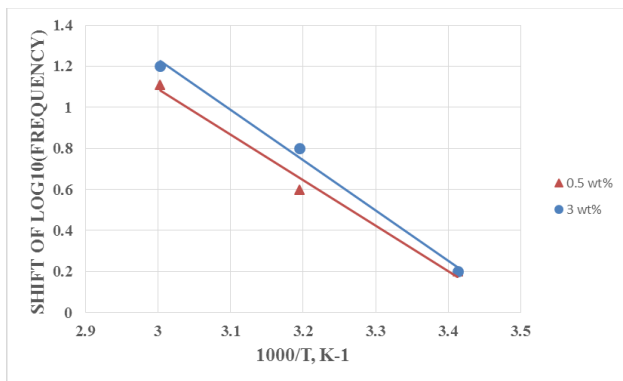


Fig. 8. Arrhenius plot indicating charge transport activation energy

According to Fig.8, the activation energy of the extra mid frequency relaxation in water saturated 0.5wt% and 3 wt% C8 SiO₂ nanocomposites is 2.22eV and 2.44 eV respectively. The activation energy can show the strength of local interactions around water molecules [11]. Owing to the increase of filler loading concentration, there will be more hydroxyl groups interacted with water and lead to an increase in the activation

energy. Therefore, it is believed that the extra relaxation peak in C8 SiO₂ is caused by the bonded water.

IV. CONCLUSION

According to the present work, conclusions can be made as below:

- Filler Loading Concentration: water uptake, permittivity and $\tan\delta$ of nanocomposites increases with the nanofiller loading concentration;
- Surface Treatment: C8 treatment can eliminate large number of hydroxyl groups and leads to a lower water uptake compared with the untreated SiO₂ samples. However, it cannot remove all the hydroxyl groups;
- Filler Type: the different permittivity of two fillers lead to the different dielectric properties between BN and C8 SiO₂ samples; BN samples show better performance on avoiding absorbing water, even compared to surface modified SiO₂ samples.

Future work will be carried on untreated nano-SiO₂ samples in order to investigate the peak of permittivity at range of 0.01 Hz to 0.1 Hz and influence of filler type on dielectric properties.

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