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Influence of Nano-SiO_2 and BN on Space Charge and AC/DC Performance of Epoxy Nanocomposites

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Abstract—**In this paper, the high purity bisphenol-A diglycidyl ether (DGEBA) epoxy resin (D.E.R 332), which is mainly used as filament winding, electrical laminates and encapsulation applications, was used as a host. The epoxy resins were loaded with nano-SiO_2 and nano-BN in different loading concentrations, and then test of the AC/DC breakdown strength has been performed. It has been observed that the presence of untreated nano-fillers will decrease the AC/DC breakdown strength of nanocomposites. This may be caused by field enhancement resulting from agglomeration of un-treated nano-fillers. The influence of filler concentration and surface treatment, especially the filler type, of particles on AC, DC breakdown strength and space charge has been investigated. Moreover, it has been widely recognised that the presence of moisture in nanocomposites has detrimental effect on the electrical performance. Therefore, the water absorption of epoxy nanocomposites and its impact on electrical performance has also been considered.**

Keywords—nanocomposites; epoxy resin; fillers; space charge; breakdown

I. INTRODUCTION

Epoxy resin is one of the most commonly used thermosetting materials. Due to their reactive epoxy group, they can react with many curing agents/hardeners and form three dimensional cross-linking network structures, resulting in good adhesion, excellent mechanical and dielectric properties, as well as chemical stability [1]. It is well known that the injection of space charge into polymers will significantly affect insulation properties. It has been shown in literature, that presence of injected space charge may result in the breakdown [2, 3]. Therefore, it's very important to consider the presence of space charge when studying the insulation properties of polymers. Recently, many researchers have introduced the nanoparticles into epoxy resins, in order to improve their physical, chemical and electrical properties, with varying degrees of success. Because of the extremely large surface area of nano-sized particles, it is expected that polymer materials with even a relative small nano-filler loading concentration will still result in a strong effect on dielectric properties of the resultant composites. Owing to these complex influence factors, the initial attempts did not gain the expected results but weak properties of nanocomposites instead, which may result from agglomeration and poor interfaces. Some of them showed that nano-fillers could prevent space charge from accumulating in the epoxy nanocomposites [4]. In this paper the effect of nano-SiO_2 and BN on space charge and breakdown has been studied in terms of filler type, loading concentration and surface treatment on insulating properties of epoxy nanocomposites.

II. EXPERIMENTAL DETAILS

A. Materials

The samples were prepared using high purity bisphenol-A diglycidyl ether (D.E.R. 332, density 1.16 g/cm^3) along with polyetheramine hardener (Jeffamine D-230, density 0.948 g/cm^3) supplied by Huntsman. This was used as the base polymer material. The filler particles used in the present study are commercially available untreated SiO_2 and BN fillers provided by Sigma-Aldrich. C8 treated Nano-SiO_2 was introduced, which has previously been used in [5]. 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.

B. Process

The epoxy nanocomposites samples with different loading concentrations of nano-fillers (untreated SiO_2, C8 treated SiO_2 and BN) in 0.5wt%, 1wt%, 3wt% and 5wt% were prepared. Before preparation, in order to reduce its viscosity, the epoxy resin was pre-heated to 50 ºC in oven (1 atm). Then the appropriate amount of epoxy resin and hardener were weighed out, and degased separately by using vacuum oven (103 Pa, 50 ºC) 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 50 ºC for 15 min. The composite was degassed at 103 Pa and 50 ºC for 30 min. After being degased, the mixture was subsequently cast under nitrogen atmosphere in an aluminium mould. The samples were cured at 120 ºC for 4 hours [6]. The samples were stored in a desiccator under vacuum until use.

According to the results of TGA, there is no significant weight loss between 100 and 300 ºC, which means the samples tested are all relatively dry. FEG-SEM was used to illustrate the dispersion of nano- particles in the epoxy nanocomposites as shown in Fig. 1. The obvious agglomeration of particles was appeared in C8 treated SiO_2 samples shown in Fig. 1(a). Moreover, in Figure 1(d), matrix did not show good structure and a large number of particles were located around the defect positions. This may lead to deteriorated insulation properties in epoxy nanocomposites. In addition, particles of C8 treated SiO_2 samples showed relative good dispersions as shown in Figure 1 (b) and Figure1 (c).

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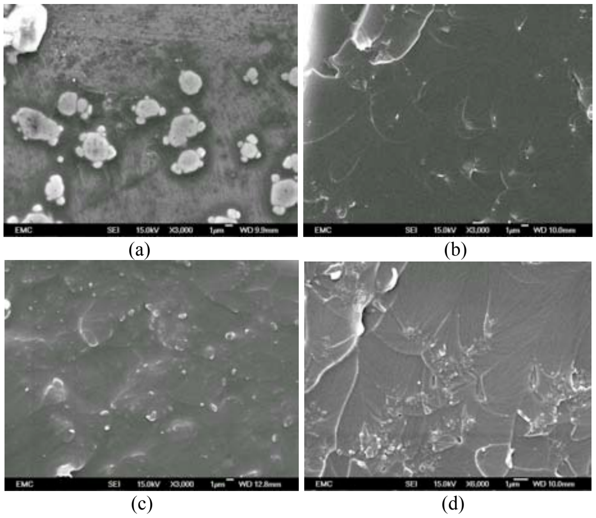

(a) (b)

(c) (d)

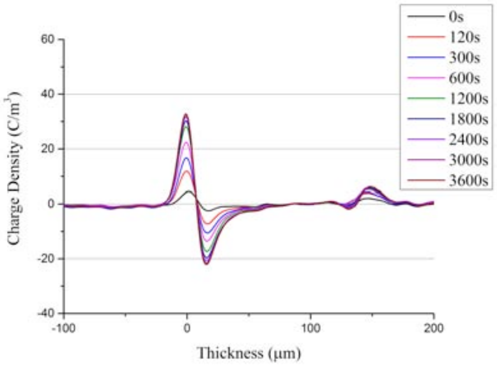
Fig. 1. SEM image of epoxy nanocomposites (a) C8 treated-0.5wt%; (b) C8 treated SiO_2-1wt%; (c) C8 treated SiO_2-3wt%; (d) untreated SiO_2-3wt%.

III. RESULTS AND DISCUSSIONS

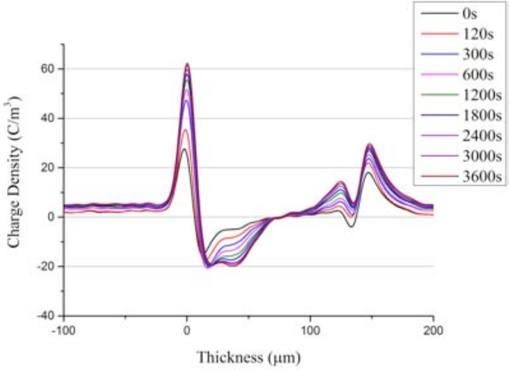
A. Space Charge Measurement

The PEA technique was used to measure the distribution of space charge in epoxy nanocomposites. The applied electric field is 40 kV/mm so that the voltage of 5-6 kV has been applied on samples with thickness of ~140 μm at room temperature (approximately 20 ºC) for 60 minutes. In this paper, the results from "volts-on" measurements were used but the influence of the capacitive charge due to the applied voltage was removed.

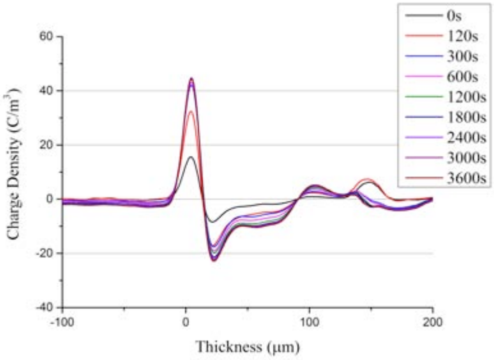
The "volts-on" space charge measurement results on specimens in different nano-SiO_2 loading concentrations and surface treatment are built-up as shown in Figure 2. It is obvious that some homocharges present adjacent to the cathode in pure epoxy and the amount of homocharges increases with time. The presence of homocharges can be attributed to charge injection from both electrodes. Heterocharges may occur due to the charge separation process in the specimen but play little role. When compared to the pure sample, space charge distribution in the C8 treated specimen with 0.5wt% SiO_2 shows difference. In addition to the presence of homocharges near to the cathode, they also appear in the region close to the anode. The results with 1wt% and 3wt% show similar charge distributions, with C8 treated specimens. Moreover, with the increase of loading concentration, the amount of positive charge presented in the middle of samples and increases. It is also noticed that the initial charge build-up rate in C8 treated nano-SiO_2 samples increases with filler concentration. A negative peak close to the anode develops as shown in treated 3wt% and 5wt% (the latter not shown here) and its magnitude increases with time. This may be caused by the movement of injected electrons. Similar observation was found [7]. However, for untreated nano-SiO_2 samples with 3wt% loading concentration, heterocharges present at two electrodes and both positive and negative charges appeared in the middle of the sample. The exact reason is not known but it may be related to the non-homogeneous distribution of nano-SiO_2 particles.



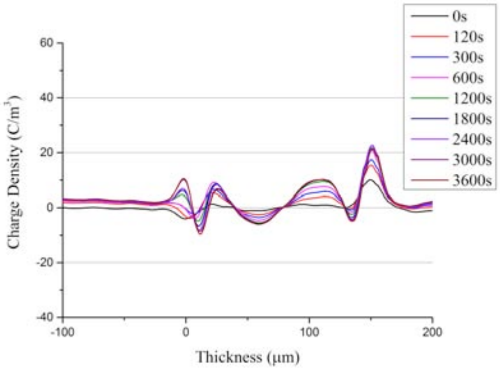
Pure epoxy



Treated-0.5wt%

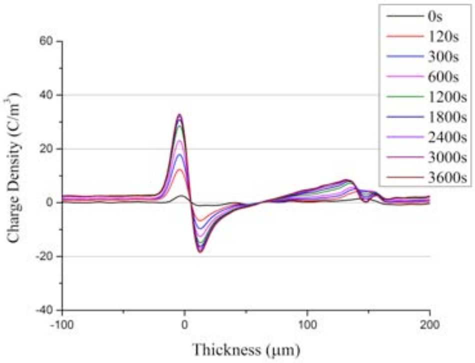


Treated-3wt%

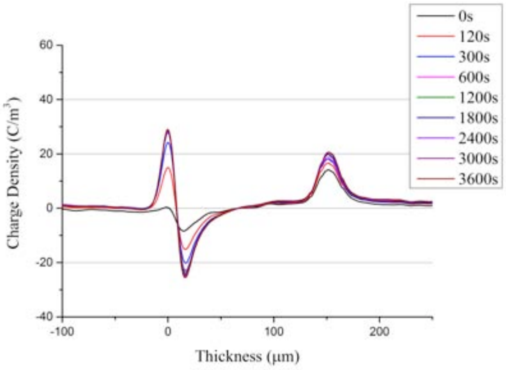


untreated-3wt%

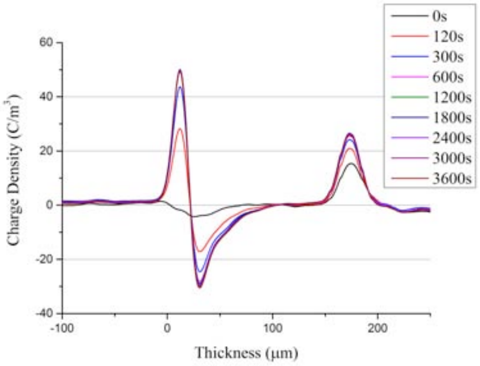
Fig. 2. Charge build-up in epoxy-SiO_2 nanocomposites at 40 kV· mm^{-1}.



0.5 wt%



1 wt%



5 wt%

Fig. 3. Charge build-up in epoxy-BN nanocomposites at 40 kV· mm^{-1}.

Fig. 3 shows the space charge accumulation in nano-BN samples in each loading concentration. Obviously, in nano-BN samples, charges were dominated by homocharges. It can be seen the initial charge build-up rate near the cathode in each sample is similar and the magnitudes of charges increases slightly with loading concentration. Moreover, positive charges in the middle of 0.5wt% BN samples are observed but not in any other samples. The magnitude of the injected electrons seems to increase with the loading concentration. Comparing with SiO_2 base nanocomposites there are some differences in terms of charge distribution and magnitude.

B. Breakdown Measurement

The breakdown test was performed based on ASTM standard D149-87. The breakdown strengths of epoxy samples at 50 Hz were measured with a ramping rate of 50 V/s. DC breakdown strength was measured with a ramp of 100 V/s with positive polarity. The test points selected were uniformly distributed on each sample and total of 25 breakdown data were collected for each type of sample. The average thickness of samples is ~70 μm. All the samples were checked after breakdown tests and they all had a punctured hole. The data were analysed by Weibull 7++ Software.

A typical AC breakdown Weibull plot for nano-BN composites with different loading concentrations is shown in Figure 4. AC breakdown strength of pure epoxy samples is 222.7 kV· mm^{-1}. It can be observed that all nanocomposites show a decrease in AC breakdown performance. AC breakdown results for all the specimens are summarised in Table 1. For epoxy nanocomposites with untreated nano-SiO_2, a slight decrease in breakdown strength with loading concentration is observed. Compared with untreated samples, samples of C8 treated SiO_2 shows lower breakdown strength with lower loading concentrations but improved AC breakdown strength in high filler loading concentration.

The nanocomposites samples loaded with nano-BN are very similar to untreated nano-SiO_2 ones and exhibit a reduction in breakdown strength. The least reduction in the breakdown strength of nano-BN is at 53.1 kV· mm^{-1} and 5wt% samples showed the worst properties with 67.9 kV·mm^{-1} lower than pure epoxy resin samples. The differences between two types of nano-fillers may be caused by the different shape of particles and volume percentages. Because, in same loading concentration but different densities, filler volume percentage in BN composites is smaller than in SiO_2-epoxy [8]. The larger volume can make SiO_2 act as barriers for the penetration of the charge carriers through the bulk of the sample [9].

Fig. 5 shows a typical Weibull plot for DC breakdown of nano-BN epoxy composites with different loading concentrations. The full results of DC breakdown, including SiO_2 based nanocomposites, are summarised in Table 2. The DC breakdown strength of pure epoxy samples is 502.1 kV· mm^{-1}. It can be obviously seen that all the epoxy nanocomposites showed the worse DC breakdown performances. For treated and untreated SiO_2 epoxy nanocomposites, the same trend can be seen. C8 treated samples show worse performance of DC breakdown strength than untreated, but becomes better from 3wt%. This may result from agglomeration of particles in untreated samples in relatively high filler loading concentrations which is observed in SEM results. The agglomerated fillers will act as defects in nanocomposites and lead to low breakdown strength.

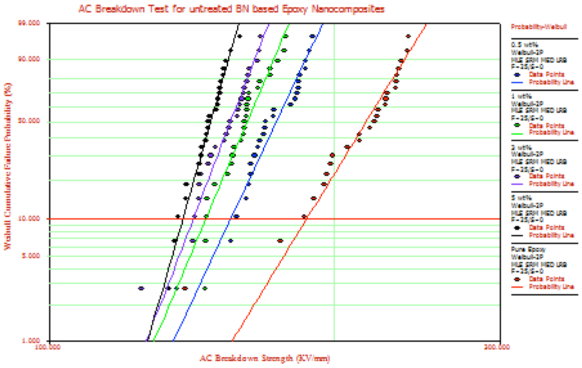


Fig. 4. AC Breakdown of Nano-BN epoxy composites.

TABLE 1 Weibull parameters for AC breakdown of nanocomposites

Samples	Scale parameter (η) (kV·mm^{-1})	Shape parameter (β)
Pure epoxy	222.7	12.9
C8_0.5wt%	165.9	10.2
C8_1wt%	170.6	24.1
C8_3wt%	166.9	17.4
C8_5wt%	182.0	15.9
0.5wt%	185.4	13.5
1wt%	184.1	13.3
3wt%	183.9	11.9
5wt%	171.2	15.3
BN_0.5wt%	177.6	16.8
BN_1wt%	165.1	18.6
BN_3wt%	158.2	20.6
BN_5wt%	150.0	27.5

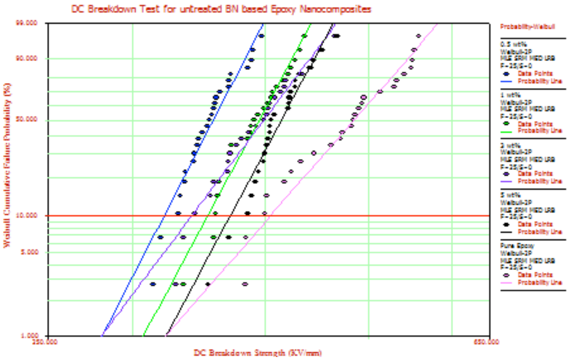


Fig. 5. DC Breakdown of Nano-BN epoxy composites.

TABLE 2 Weibull parameters for DC breakdown of nanocomposites

Samples	Scale parameter (η) (kV· mm^{-1})	Shape parameter (β)
Pure epoxy	502.1	10.4
C8_0.5wt%	402.7	14.0
C8_1wt%	436.2	20.5
C8_3wt%	410.7	21.0
C8_5wt%	366.2	26.2
0.5wt%	424.3	10.2
1wt%	441.4	10.6
3wt%	373.3	20.0
5wt%	332.2	32.4
BN_0.5wt%	364.8	17.6
BN_1wt%	403.3	16.9
BN_3wt%	410.9	12.0
BN_5wt%	423.3	16.9

The nanocomposite samples loaded with nano-BN are very similar to nano-SiO$_2$. However, the DC breakdown strength exhibited a slight increase from 1wt%. The differences between two types of nano-fillers may be mainly caused by the volume percentage of particles and permittivity. The volume percentage acted as the main factor that makes SiO$_2$ samples perform better in breakdown strength up to 3wt% as discussed earlier. However, with the increase of filler loading concentration, BN based nanocomposites showed the higher breakdown strength than that of SiO$_2$. The samples with C8 treated Nano-SiO$_2$ show worse breakdown strength in low filler loading concentrations and better in higher ones, which may be caused by different matrix structures shown in SEM results. It is not clear how the surface treatment can result in this difference in structures. Therefore, further work will be carried out on this part in the future.

IV. CONCLUSIONS

The introduction of nano-sized SiO$_2$ seems to lead to space charge accumulation in samples and the magnitude of charges is likely to increase within the loading concentrations. Moreover, the surface treatment has significantly hindered the charge accumulation when compared to the untreated samples. And the presence of nano-BN particles may result in charge accumulation in samples. Within the increase of filler loading concentration, although the magnitude of homochages adjacent to the cathode increased, there appears a reduction of space charge accumulation in the samples.

The presence of both nano-sized SiO$_2$ and BN in epoxy nanocomposites shows an obvious reduction in the AC/DC breakdown strength. It is inconclusive what influence of the space charge accumulation has on the dielectric breakdown behavior of epoxy resin at this point.

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