AN INVESTIGATION OF THE EFFECT OF NANO ALUMINA ON THE ELECTRICAL AND THERMAL PROPERTIES AND MORPHOLOGICAL BEHAVIOR OF THE CAST EPOXY NANO COMPOSITE

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Abstract: This paper investigates the effect of nano alumina, which is a stiff material with high thermal conductivity, on properties of cast epoxy composite filled with silica flour by performing experiments to measure breakdown strength, thermal stability and morphological behaviour. To accomplish this, different weight percent of nano alumina was added to the epoxy/silica system and electrical test was carried out on different temperatures. It was observed that in glassy region presence of nano alumina increased dielectric strength due to high surface area while at temperature range above glass transition temperature, interaction between filler and matrix dominated dielectric strength of composites. Study on thermal properties of cast epoxy systems showed that nano alumina increased thermal stability of composites. Also, it was found that the 5 wt% specimen had the highest Tg among nano composite samples. Study of morphology indicated that alumina particles located at silica flour and epoxy matrix interface.

1 INTRODUCTION

Recently, polymeric nanocomposites are significantly applied in the field of electrical insulation due to their capability to resist against the electrical, thermal and mechanical stresses. Epoxy resin, which possesses characteristics such as high modulus, low creep, reasonable thermal stability, excellent dielectric properties and good dimensional stability, is a preferred alternative for electrical insulations [1-10]. Cast epoxy, which is said to be a multi-sided insulating material, can be applied as switchgears, bushing, rotating machines and/ or transformers because of their chemical stability and excellent dielectric properties [11-14].

To obtain an epoxy system with desired properties, lots of hardeners with amine, phenolic and/or anhydride groups, each of which get special characteristics to the resin, can be used for curing and making crosslink among chains.

Anhydride hardener which has characteristics such as low viscosity, good transparency, excellent electrical insulation properties and providing high network Tg, is an appropriate curing agent for casting resins which has electrical applications [2, 15-17].

A common way to reinforce an epoxy resin for desired application is to incorporate inorganic fillers into the neat resin. Recently, lots of researches have been investigated the effect of incorporation of different types of nanoparticles such as nanoclay, graphite nanofibre, carbon nanotube, cellulosic fibre and nano alumina on the characteristics of thermosets such as epoxy and it has been realized that some properties and behaviour of composites are affected by particle size, concentration and shape of nanofillers [3, 18-24]. Alumina (Al_2O_3) could be suitable filler for epoxy composites due to its outstanding properties like hardness, wear-resistant, excellent dielectric properties, resisting against strong acid and alkali attack at elevated temperatures, good thermal conductivity, excellent size and shape capability, high strength and stiffness [25].

The objective of this paper is to investigate the effect of nano alumina on the electrical and thermal properties of cast epoxy resin based on bisphenol A filled with silica flour and finding out if shape and size of particles of alumina could impact on the morphological behaviour of the system.

2 EXPERIMENTAL

2.1 Material

A low viscosity liquid epoxy resin based on bisphenol A named Araldite CY 228 with epoxy equivalent weight of 5.00-5.30 (Eq/kg) was obtained from Huntsman, Germany. The hardener was a dicarboxylic anhydride named HY 918 (Huntsman, Germany). The applied accelerator was a tertiary amine named DY 062. Two types of mineral fillers with different size were used in specimens. The micro size filler was silica flour W12 and the nano size filler was aluminium oxide (purity > 99.9 %, in gamma phase) with an average size of 40 nm and average surface area about 40 m^2/g. All materials were used in their as-received state.

2.2 Mixing and moulding

Preparation of samples was done by vacuum casting process. The formulation of prepared samples is illustrated in Table 1. Firstly nano filler was dried under vacuum for 12 h at 140 ˚C. Then it mixed with resin and the mixture was added to the hardener in vacuum casting system. The micro filler and accelerator were added as well. Then the mixture was casted in the moulds with dimensions of 4×150×150 mm^3

2.3 Characterization

2.3.1. Differential Scanning Calorimetry (DSC)
To analyze thermal and physical properties of the epoxy composite, DSC test was carried out by 2920 MDSC, model V2.6A, with Aluminium sample holders under nitrogen atmosphere. Samples with weight around 8-12 mg were heated with rate of 5 ˚C/min from room temperature to 170 ˚C.

2.3.2. Breakdown test
The electrical breakdown test was carried out with a needle-plate electrode, which provides a non-uniform field. The electrode was made of tungsten with a tip radius of 2 µm and the gap distance of 2mm. the experiment was done with 50-Hz-AC-voltage in ramp testes with a continues rising speed of 2 kV/s. The measurements were carried out at the temperatures 23, 90, 150 and 180 ºC.

2.3.3. Thermo gravimetrical analysis (TGA)
It is an appropriate technique to study the thermal properties of polymeric materials such as thermal stability and thermal degradation which is affected by the type and structure of the material and fillers used in it. In this technique, changes of sample mass are measured as a function of temperature or time. Thermal stability of the composite was studied by TGA-PL, under nitrogen atmosphere at the flow rate of 10 ˚C/min within a temperature range of room temperature to 600 ˚C.

2.3.4. Scanning electron microscopy
To study morphological behaviour of the epoxy nano composite, scanning electron microscopy (SEM) was used. The specimens were fractured in the liquid nitrogen. The gold coated surface of samples was inspected by Cambridge 360, SEM, using a voltage of 20 kV.

3 RESULT AND DISCUSSION

3.1 Differential scanning calorimetry

DSC is a good technique to analysis thermal behaviours and transitions of samples. Figure 1 depicts glass transition temperature for cast epoxy systems with different contents of nano alumina which was obtained from DSC.

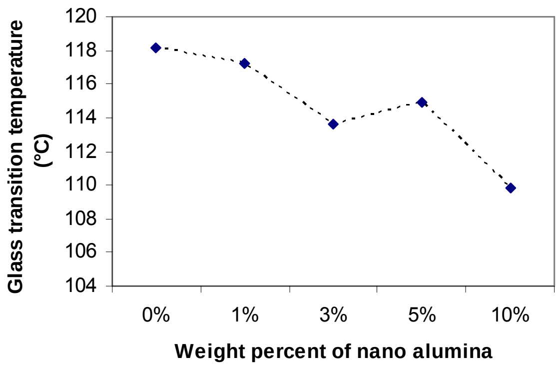

Figure 1: Glass transition temperatrue of cast epoxy systems vs. nano particle concentration

Glass transition temperature (Tg) is a characteristic of a system that represents interactions between components in the sample [26-28]. As the obtained results show, A0 possesses the highest Tg because silica flour has a strong interaction with epoxy matrix. Also, it is clearly seen that generally addition of nano alumina to the cast epoxy system reduces Tg.

Table 1: Formulation of prepared sample

Sample	Resin CY 228 (pbw[1])	Hardener HY 918 (pbw)	Accelerator DY62 (%)	silica flour (W12) (pbw)	Nano alumina (Al_2O_3) (wt %)
A0	100	85	1	345	0
A1	100	85	1	345	1
A3	100	85	1	345	3
A5	100	85	1	345	5
A10	100	85	1	345	10

[1-] Part by weigh

It has been found that interactions between nano particles and matrix form two polymeric layers around particles which have crucial influence on Tg of a nano composite.[26-27]. The first nanolayer includes immobile chains which tightly bonded to the particles and the second layer is made of chains which form looser bonds with particles that lead to higher chain mobility and determine Tg of system. When 1% nano alumina adds to the system, interparticle distances are large and chains mobility in the second nanolayer is high which causes a reduction in Tg of the system. Increasing nano filler content to 3% induces volume fraction of chains which make the second layer and leads to more reduction of Tg of system.

Increasing nano alumina to 5% leads to an increment in Tg which is due to overlapping of restricted regions around nano particles. In other words, as interparticle distances decreases, loosely bound chains are affected by immobile chains tightly bound to surface of particles and raise Tg of system. In fact, 5% of nano alumina is critical concentration in which distances among particles are in optimum amount; while more addition of nano alumina leads to further decreasing interparticle distance which reduces thickness of second layer and convert it to restricted region with immobile chains that do not have function on Tg. Therefore, reduction of volume fraction of loosely bound chains reduces Tg of composite. Moreover, 10% nano alumina is a high concentration and the interparticle distances are small enough that make clusters of nano particles though chains and reduces degree of crosslinking in the system.

3.2 Electrical properties

The breakdown test was carried out at several temperatures to provide a simple comparison between breakdown voltages of a sample in different temperatures as well as between the breakdown strength of samples with different contents of fillers in a same temperature and different ones. Figure 2 shows breakdown voltage vs. temperature for three samples with different contents of nano alumina. It is seen that at 23 ºC addition of 5% nano alumina leads to 5% reduction in breakdown voltage which is due to increasing electrical conductivity that occurs as a result of presence of impurities in form of ions or electrons in system [7, 11, 13-14, 29]. However, 10% loading nano particle leads to 10% increment of dielectric strength because the system is closely packed by nano particles which can act as scattering sites and capture energy from electrons that get accelerated by applied field [3]. Therefore, A10 requires higher voltage to failure.

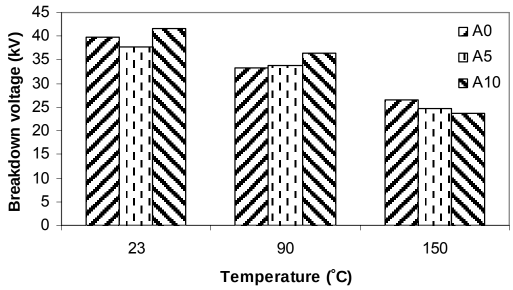

Figure 1: Histogram of breakdown voltage of samples vs. temperature

As temperature raise, molecular motion increases and rearrangement of free volumes induces electron transports which lead to electron avalanche breakdown [29]. So breakdown voltage at 90 ºC is lower than that at room temperature. At 90 ºC, which is still below Tg of systems, it is seen that breakdown voltage is increased with nano alumina loading. High specific surface area of nano particles absorbs energy from electrons and retards breakdown. However, at 150 ºC dielectric strength is reduced by increasing nano alumina. In plastic region by increasing chain mobility, redistribution of free volume enhances which facilitates movement of electrons and impurities [29]. So nano composite which has more content of particles leads to higher electrical conductivity. Moreover, result of dielectric strength at 150 ºC is according to Tg of cast epoxy composites. It is suggested that at regions above Tg, the breakdown strength follows the interactions between filler and matrix. Therefore, reduction of crosslink density in A10 which occurs as a result of high content of nano particles reduces Tg as well as dielectric strength. Meanwhile, absence of nano alumina in A0 which leads to strong interface interaction between silica particles and epoxy matrix causes high Tg and dielectric strength at 150 ºC. Nevertheless, more study is required for certainty about relation between Tg and dielectric strength in plastic regions.

3.3 Thermo-gravimetrical analysis

Using of thermo-gravimetrical analysis (TGA) is an appropriate technique to analyze thermal stability of composites. Figure 3 shows the result of TGA in the form of residue weight vs. temperature for cast epoxy systems. It is taken from Figure 3 that 0.01 % of weight was lost at about 150 ˚C which is due to lose of humidity. It is also clearly seen that the major of weight loss was in the range of 370-440 ˚C which is belonged to the loss of bisphenol A group [4, 30]. Figure 3 also reveals that presence of nano alumina in the composite enhanced thermal stability of the system. To explain the higher thermal stability of samples filled with nano alumina it should be considered that alumina is a mineral material which has high thermal conductivity (about 35 W/m°K [25]) that can transform heat in the composite and prohibit of locally thermal defection in the system. Moreover, nano particles that are well dispersed among chains inhibit diffusion of the volatile decomposition products; so the whole decomposition process occurs at higher temperatures.

It is taken from Figure 3 that A1 has the highest thermal stability among other samples since the initial decomposition temperature, when 1% of sample decomposes and the residue weight of A1 at 600 ˚C is higher than other samples. In addition, loss weigh of A1 is more gradual rather than others. It is due to uniform dispersion of nano alumina in the matrix while further increasing nano alumina content forms agglomeration that causes micro voids and lead to penetration of volatile. As it can be seen, A3 decomposes at lower temperate in compare to A1 which can be due to poor dispersion of nano particles that leads to easy volatile diffusion. Also, the initial decomposition temperatures of A5 and A10 are less than other samples because of forming agglomeration in the matrix. Moreover, high concentration of nano particles in A10 could reduce cross link density which induces free volume and helps to easy escape of volatile.

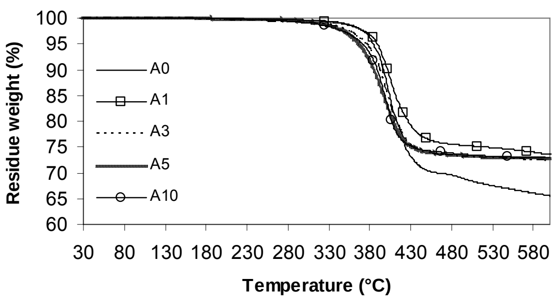

Figure 3: TGA curves of cast epoxy systems in the range of 30-600 ºC

3.4 Morphological behaviour

Scanning electron microscopy (SEM) is a useful technique to study morphological behaviour of nanocomposites, which helps to better understanding obtained results. SEM images of samples are shown in Figure 4a-d. Figure 4a shows fabric of A0 (in magnification of 1000×) which indicates good adhesion and uniform dispersion of silica flour in the epoxy matrix. The interface interaction between silica particles and epoxy chains is strong and there is noting to show separated phases or debonding regions between filler and matrix. Sample A1 is appeared in Figure 4b which shows a rougher surface rather than A0 and represents dispersion of micro and nano particles in the matrix. Comparison between A0 and A1 reveals that dispersed phase is embossed on the matrix as nano alumina is added to the composite It can be supposed that nano alumina located between polymeric chains and silica particles to loose their interactions. In addition, increasing nano particles content leads to formation of aggregation. Figure 4c, which belongs to A5, indicates that particles are tightly located to each other and make clusters which can provide paths for escaping volatiles.

Micrograph of A10 is shown in Figure 4d which indicates poor dispersion of nanoparticles. Separated phases and agglomeration are clearly seen in Figure 4d which is as a result of high concentration and dense distribution of alumina particles that could reduce crosslink density of chains in the matrix.

4 CONCLUSION:

Study on the electrical, thermal and morphological properties of cast epoxy systems with different concentration of nano particles provides following conclusions:

- Dielectric strength of samples filled with nano alumina is decreased with increasing temperature. However, presence of nano alumina retards dielectric breakdown since it absorbs energy of exited electrons which could cause electron avalanche in system. As temperature passed the Tg, interaction between filler and matrix determined the breakdown strength of composits.
- Increasing nano alumina in cast epoxy system up to 5% decreased Tg of nano composite since interparticle distance is large and mobility of chains does not affect by restricted region, On the other hand, volume fraction of loosely bound chains at 10% of nano alumina is low enough that reduces Tg. So, 5% of nano alumina is an optimum concentration in which loosely bound chains overlap and increase Tg.
- Thermal stability of epoxy composites increases with addition of nano alumina to the system. Also, good dispersion of nano particles leads to higher thermal stability; otherwise, formation of agglomeration provides paths for diffusion of volatile.
- Interaction between silica four and epoxy chains is strong until alumina particles locate at their interface and emboss filler in the matrix

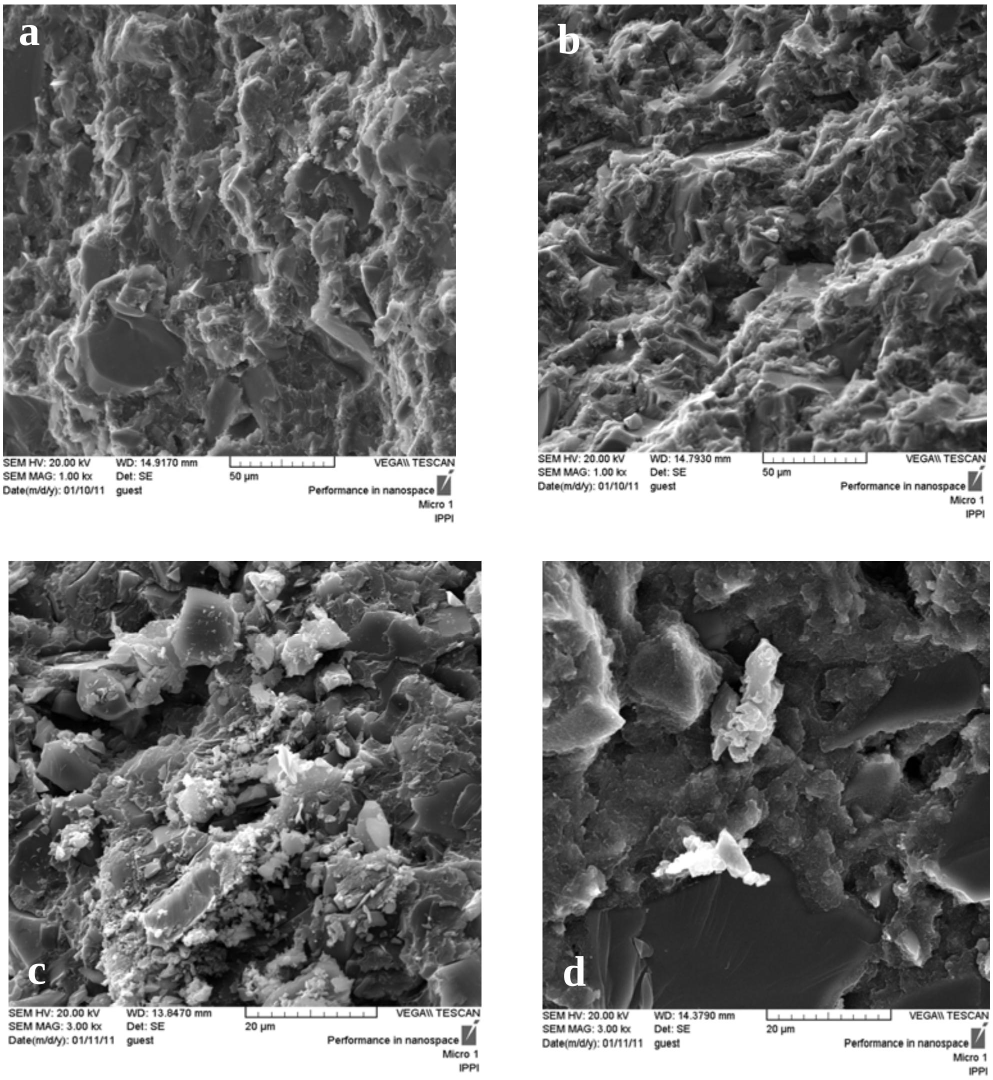

Figure 4: SEM micrographs of cast epoxy systems: a) A0 with magnification of 1000×; b) A1 (1000×); c) A5 (3000×);d) A10 (3000×).

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