

The Effect of Resin/Hardener Stoichiometry on the Electrical Properties of Silicon Nitride/Epoxy Nanocomposites

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Abstract— The effect of resin/hardener stoichiometry was investigated for both unfilled epoxy and nanocomposite samples. The results indicate that incorporating silicon nitride nanofiller, which contains amine groups on its surface, has a significant influence on the resin/hardener reaction. At 2 wt.% of nanofiller, it was estimated that the powder contains amine groups equivalent to around 5 wt.% of the hardener mass, which results in the displacement of the optimum resin/hardener mass ratio by the same amount (~5 wt.%). The dielectric spectra showed that the β relaxation is directly related to the hydroxyether groups that are generated by the reaction between the epoxy and the amine groups. Therefore, the relaxation strength is proportional to the crosslinking density and consequently related to the glass transition temperature. The DC conductivity increases considerably as a result of incorporating silicon nitride nanofiller when not compensating for its impact on the resin/hardener stoichiometry. This might be related to the increase in the amine content of the material caused by the amine groups existing on the surface of the nanoparticles. When the stoichiometry effect is taken into account, the DC conductivity decreased to a value that is comparable to that of the unfilled polymer.

Keywords—nanocomposites; epoxy; silicon nitride; stoichiometry; glass transition temperature; dielectric spectroscopy; DC conductivity;

I. INTRODUCTION

Research interest in utilizing nanotechnology for dielectric applications has grown immensely in the last decade. Many research groups worldwide have been conducting research to explore the potential of this technology to improve the performance of insulating materials and investigating the underlying mechanisms that control the behaviour of so-called nanodielectrics. It is widely accepted that the electrical performance of nanodielectrics is strongly influenced by the interactions that occur between the surface of the nanoparticles and the encapsulating polymer, i.e. within the interphase region [1]. These interactions are intensified by increasing the specific surface area of the particles, i.e. reducing the particle size, and by dispersing the particles efficiently within the matrix material [2, 3]. However, if these interactions have a negative impact on dielectric performance, the effective dispersion will also aggravate this. Nanoparticle surface chemistry is an important factor that affects both interphase interactions and nanoparticle dispersion. Many studies have tried to modify the surface

chemistry of nanoparticles before introducing them into the base polymer and some of these have reported improved electrical properties. However, the underlying mechanisms are not well understood, with different studies referred them to different factors, such as better particle dispersion [4], removal of polar moieties [5] and the introduction of electron traps [6].

For epoxy based nanocomposites, particles are incorporated into the resin before the curing process, which allows the particles to interact with the active as supplied resin or hardener. Any chemical reaction between the particles and the resin or the hardener will affect the reaction stoichiometry and thus result in a different network structure after curing.

Silicon nitride (Si_3N_4) is covered by amine and hydroxyl groups [7, 8]; both of these groups, particularly the amine, can react with the epoxy groups in the resin. Thus, this makes silicon nitride inherently compatible with an epoxy matrix and results in good particle dispersion, as can be observed from the scanning electron microscope images shown in a previous study [9]. The reaction between the amine groups on the surface of the particles and the epoxy groups will, however, reduce the epoxy groups available for reaction with the hardener, and consequently affect the stoichiometric ratio. Therefore, detecting an influence of the silicon nitride on the resin/hardener stoichiometry will be considered as evidence of reactions between the functional groups covering the surface of the silicon nitride nanoparticles and the epoxy groups from the resin.

This study therefore set out with the objective of investigating the effect of adding a silicon nitride nanofiller on the resin/hardener stoichiometry and the consequences of this for the electrical performance of the resulting materials.

II. EXPERIMENTAL

A. Materials and samples preparation

The silicon nitride (Si_3N_4) nanopowder utilised in this study was obtained from Sigma Aldrich. The supplier specifies a spherical shape and a particle size < 50 nm. The epoxy resin used here was the diglycidyl ether of bisphenol-A (DGEBA) based resin, DER 332, obtained from Sigma Aldrich, and the hardener was the aliphatic diamine hardener, Jeffamine D 230, from Huntsman. The epoxy equivalent molar mass of DER 332

is ~ 174 g/mol and the amine hydrogen equivalent molar mass of Jeffamine D230 is 60 g/mol. Thus, the theoretical resin:hardener stoichiometric ratio is 1000:344. Throughout this paper, the resin:hardener ratio is identified using a parameter termed the hardener percentage (HP) which is defined by the following relation:

$$HP = \frac{\text{mass of the hardener used}}{\text{hardener stoichiometric mass}} \%$$

where the hardener stoichiometric mass is the hardener mass following the stoichiometric ratio (344:1000). The samples are identified using a code consisting of three elements, the first refers to the epoxy resin, the second refers to the hardener percentage and the third refers to the nanofiller weight percentage (wt.%). For example, E/100-H/2-SiN refers to an epoxy cured with 100 % hardener percentage (stoichiometric ratio) and containing 2 % silicon nitride; E/80-H/0 refers to epoxy cured with 80 % hardener percentage without any filler. The unfilled epoxy sample, which employs the theoretical stoichiometric resin/hardener ratio (i.e. sample E/100-H/0), is taken as a reference for all other samples.

To prepare the unfilled epoxy sample, the required masses of the resin and the hardener were mixed using a magnetic stirrer for 15 min and then the mixture was degassed for 20 min before being injected into a metallic mould with an ~ 200 μm thick spacer. For nanocomposite samples, the filler was first dispersed into the resin using a probe sonicator for 45 min and then the mixture was heated at 100 $^{\circ}\text{C}$ for 3 h, to stimulate any possible reaction, before the hardener was added and the above epoxy preparation procedure was followed. Based on the manufacturer's instructions, all samples were first cured in a fan oven at 80 $^{\circ}\text{C}$ for 2 h and then post-cured at 125 $^{\circ}\text{C}$ for 3 h.

B. Differential Scanning Calorimetry

The crosslink density of all sample was evaluated by determining the glass transition temperature (T_g) using a Perkin Elmer DSC 7 differential scanning calorimeter (DSC). Two repeated DSC scans were performed for each material using specimen about 10 mg in mass at a heating rate of 10 $^{\circ}\text{C}/\text{min}$. T_g was deduced from the second DSC scan, as the temperature corresponding to the maximum gradient of the heat capacity. The first scan was performed to erase the thermal history of the sample.

C. Dielectric spectroscopy

Dielectric spectroscopy was performed using a Solatron 1296 dielectric interface along with a Schlumberger SI 1260 impedance/phase gain analyser on specimens 30 mm in diameter. Before testing, each specimen was sputter coated with gold on both sides to provide a better sample/electrode contact. All measurements were performed at room temperature (~ 23 $^{\circ}\text{C}$) over the frequency range 0.1 Hz - 1 MHz.

D. DC Conductivity measurements

DC conductivity was evaluated by measuring the current passing through the material of interest, using a Keithley 6487 picoammeter. The specimen was placed between opposing circular electrodes with a diameter of 20 mm. Samples were sputtered coated with gold and stored dry in a vacuum desiccator before any measurements were made. However,

there was no environmental control during the measurements process itself. All measurements were performed at a temperature of 30 $^{\circ}\text{C}$ and an electric field of 42.5 kV/mm.

III. RESULTS AND DISCUSSION

A. The Glass Transition Temperature

Figs. 1 and 2 respectively present DSC second scan data obtained from unfilled epoxy formulations and equivalent nanocomposites. From these traces, the T_g was determined and the resulting data are presented in Fig. 3. For the unfilled epoxy samples, as expected, the maximum T_g occurs at the theoretical stoichiometric ratio ($HP = 100$ %). However, deviations to either side cause T_g to decrease, but not in a totally symmetric way; initially, T_g decreasing more sharply for the formulations with $HP < 100$ % than for $HP > 100$ %. A comparable form of behaviour has been reported elsewhere [10, 11] for similar resin and hardener systems.

For the nanocomposite samples, a different trend can be observed. Here, T_g does not decrease sharply for $HP < 100$ %, instead it decreases for $HP < 90$ %. Comparing the nanocomposite and the unfilled epoxy samples at an HP value of 90 % shows that T_g for the samples containing the silicon nitride nanofiller is significantly higher. This implies that the effective amine groups : epoxy groups ratio is higher than 90 % for the nanocomposite sample. Similarly, for sample E/100-H/2-SiN, it can be deduced that the actual hardener percentage is higher than 100 %, which explains the smooth decrease of T_g compared with the equivalent unfilled sample (E/100-H/0). For sample E/80-H/2-SiN, the 2 wt.% Si_3N_4 cannot compensate for the 20 % reduction in the hardener and, consequently, its T_g is significantly reduced. From these results, it can be deduced that 2 wt.% nano- Si_3N_4 has an equivalent effect to around 5 wt.% of hardener. Fig. 4 shows T_g results for all samples after shifting the HP 5 wt.% to the right for the nanocomposite samples. Clearly, T_g results obtained from the nanocomposite samples are equivalent to their counterparts from the unfilled samples, after increasing the HP by 5 %, which reinforces the hypothesis adding 2 wt.% of nano- Si_3N_4 is, from a reaction stoichiometry perspective, comparable to 5 wt.% of hardener.

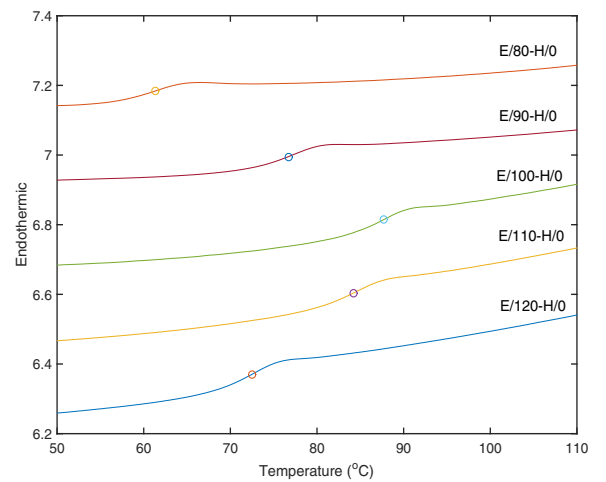


Fig. 1. DSC second scan traces obtained from unfilled epoxy samples with different formulations; the circles superimposed on the curves indicate T_g .

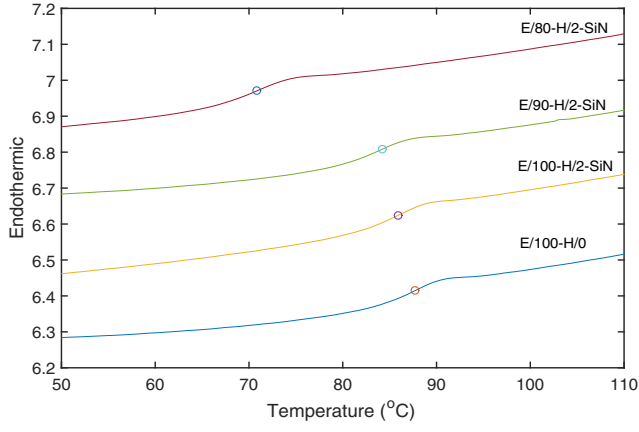


Fig. 2. DSC second scan traces obtained from nanocomposite samples prepared with different resin stoichiometries; the circles superimposed on the curves indicate T_g .

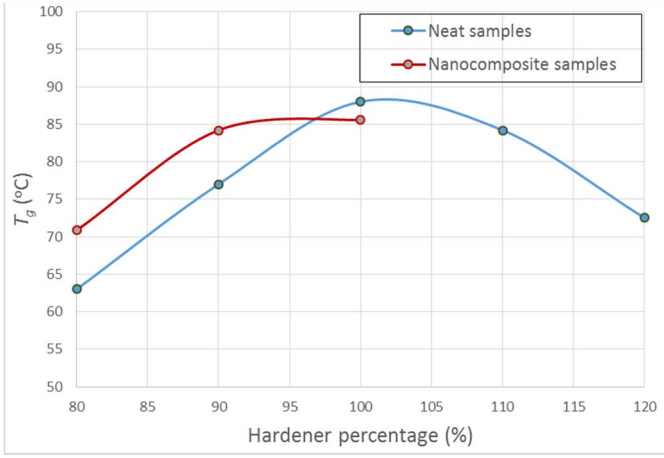


Fig. 3. The glass transition temperature for all samples.

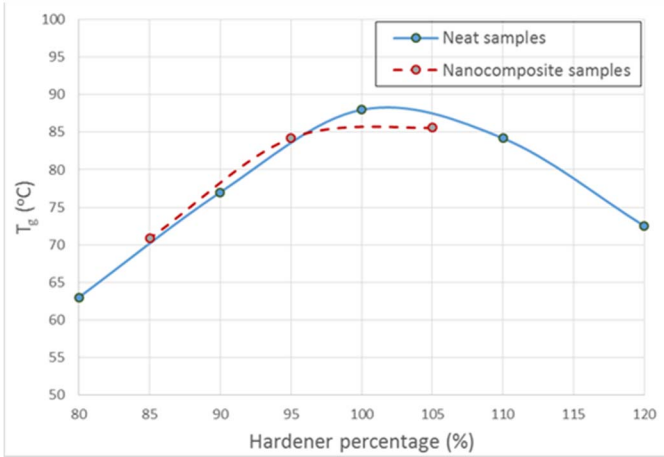


Fig. 4. The glass transition temperature for all samples after shifting the HP 5% to the right for the nanocomposite samples.

B. Dielectric spectroscopy

Fig. 5 shows dielectric spectra obtained from nanocomposite samples, along with the reference sample (E/100-H/0). A broad β relaxation can be detected for all

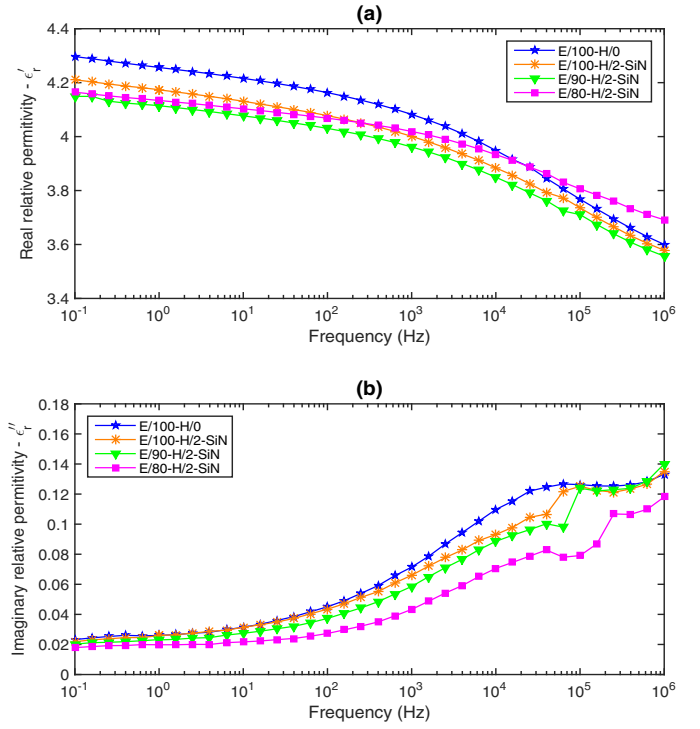


Fig. 5. Dielectric spectra for nanocomposites samples compared with the reference sample, (a) real permittivity and (b) imaginary permittivity.

samples, which peaks around 5×10^4 Hz. This relaxation is associated with the crankshaft rotation of the hydroxyether group that is produced at each crosslink point by the reaction between epoxy and amine groups [12, 13]. Thus, a higher crosslinking density implies a higher concentration of generated hydroxyether groups and, consequently, a stronger β relaxation. Therefore, the β relaxation is directly related to the crosslinking density of the network and consequently would be expected to correlate with the glass transition temperature. The imaginary permittivity, Fig. 5 (b), shows this relation where the relaxation strength decreases for the samples with lower T_g and vice versa. The nanofiller does not have a noticeable influence on the dielectric spectra over the frequency range shown at the measurement temperature.

C. DC Conductivity

The effect of the nanofiller and the different resin/hardener ratios on charge mobility was investigated by measuring the DC conductivity of the nanocomposite samples along with the reference unfilled epoxy. The resulting data are presented in Fig. 6 and show that sample E/100-H/2-SiN has a considerably higher DC conductivity compared with the other samples. This might be related to its higher amine content, where the effective hardener percentage for this sample is expected to be greater than 100 %, due to consumption of epoxy groups through reaction with amine groups on the surface of the nanoparticles. The other nanocomposite samples exhibit a slight increase in the DC conductivity compared with the unfilled epoxy, see Table 1. However, the data for these three samples are overlapping and within experimental uncertainties.

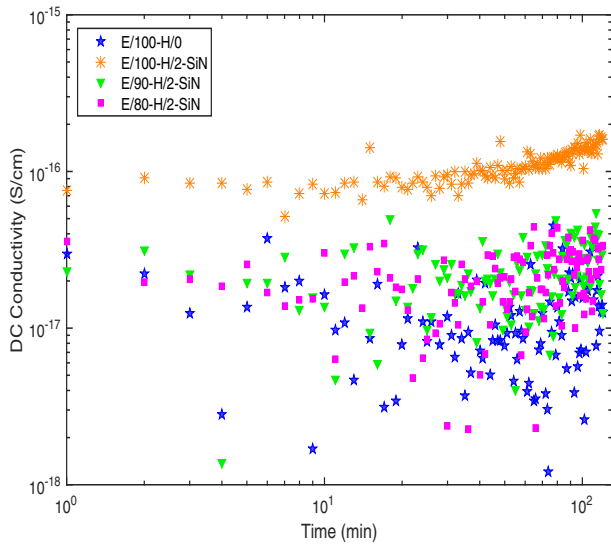


Fig. 6. DC conductivity for nanocomposite samples compared with the reference sample.

TABLE I. DC CONDUCTIVITY AVERAGED OVER 2 HOURS.

Sample code	E/100-H/0	E/100-H/2-SiN	E/90-H/2-SiN	E/80-H/2-SiN
DC conductivity (S/cm)	1.0×10^{-17}	11.1×10^{-17}	2.1×10^{-17}	1.7×10^{-17}

The variation of DC conduction current with time is generally expected to take the form $I = A e^{-bt}$ [14]. However, from Fig. 6, it is evident that the behaviour of E/100-H/2-SiN is very different from this in that a clear increase in conductivity with time is evident beyond ~60 min. Comparable behaviour has been seen elsewhere and discussed in terms of two processes: trap filling effects [15]; absorption of water influencing charge injection from electrodes [16]. The origin of the process shown here is currently unclear, but an investigation into the influence of water on charge transport dynamics in epoxy/silicon nitride nanocomposites is currently underway.

IV. CONCLUSION

The interactions between a nanofiller and the base polymer can significantly affect the performance of nanocomposite systems. Particularly for nanocomposites based on thermosetting polymers, chemical interactions between the nanoparticles and either the resin or the hardener could change the reaction stoichiometry and, therefore, result in the development of different network structures. Thus, particle dispersion is not the only factor which affects the performance of the nanocomposites. Other factors like the chemical content could affect the electrical performance considerably, as was observed by the increase in the DC conductivity caused by the

excess amine group resulting from introducing the silicon nitride nanofiller.

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