Dynamic Mechanical Response in Epoxy Nanocomposites Incorporating Various Nano-Silica Architectures

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Abstract—This paper is a continuation of the previous work where the dielectric response (BDS) of epoxy nanocomposites filled with three types of nano-silica architectures, namely core (SiO$_2$), core-shell (SiO$_2$-SiO$_2$) and hollow (h-SiO$_2$) was investigated. These samples were filled based on their respective nanoparticle surface area, keeping it theoretically constant across all samples. The aim is to better understand the molecular dynamics and physical mechanisms in dielectric nanocomposites to contribute towards developing materials with tailored properties. The samples were characterised based on their dynamic mechanical behaviour (DMA) and their $T_g$ was measured by DSC. Unlike BDS, there is no additional relaxation peak observed in DMA thermographs besides the conventionally known $\alpha$ and $\beta$. The $T_g$ of the samples increases as the size of the nanoparticles decreases. Analysis of the height, width and intensity of the tan $\delta$ relaxation peak suggests reduction in the localised modes of motion as the size of the nanoparticles increases. Similarly, characterization of the tan $\delta$ of $\beta$ relaxation reveals a internally plasticised nanocomposite system. The $T_g$ values obtained from DSC do not vary significantly across the samples. These key findings are discussed in details and demonstrate by providing further evidence that the additional relaxation observed in BDS measurements is potentially due to the presence of hydrogen bond interactions between the polymer matrix and the fillers. However, no significant impact on the viscoelastic-mechanical properties of the nanocomposites is evident.

I. INTRODUCTION

Insulating materials are subjected to various stresses throughout the operation of power equipment, including electrical, thermal, and mechanical stress. Since the insulating material must endure these tribological and electro-thermal stresses, it is often reinforced with fillers, resulting in a composite material [1], [2], [3]. Many complex high-performance polymer nanocomposites are being fabricated to fit these multifunctional applications. Nanoparticles with complex designs, such as core-shell, multi-shell, and hollow architecture, are increasingly used as filler materials due to their advantages over conventional nanoparticles [4]. This, however, also results in complicated molecular dynamics.

In a prior study, whilst investigating core-shell (SiO$_2$-SiO$_2$) and hollow (h-SiO$_2$) nanoparticles filled epoxy nanocomposites an additional relaxation termed the Si$_{OH}$ relaxation was observed in broadband dielectric spectroscopy (BDS) [5]. This was attributed to the hydrogen bonding interaction of the hydroxy ether group produced during the curing reaction and the silanols (Si-OH) present on the surface of the nanoparticles. Keenan et. al [6] observed a similar relaxation phenomena in a dynamic mechanical analysis (DMA) thermograph. This was attributed to the hydrogen bonding interactions between the adsorbed water molecules and hydroxy ether groups side chains of the cured epoxy resin; thereby, creating regions of varying density in the matrix.

As a continuation of previous research, the aim of this study is to understand the SiO$_2$, SiO$_2$-SiO$_2$ and h-SiO$_2$ nanoparticles filled epoxy nanocomposites from a dynamic mechanical perspective by analysing their material deformation characteristics and flow behaviour. Materials react to applied stress or strain fields by dispersing the energy either as a irreversible response in form of a viscous flow, by storing the energy, or by a mixture of the two [7]. The dynamic mechanical approach detects variations in both contributions as a function of temperature or deformation rate and presents the spectrum of relaxation processes that influence the viscoelastic behaviour of the nanocomposite. Understanding the correlation between mechanical (DMA) and polarization (BDS) behaviour of these samples could provide a coherent and comprehensive understanding of the Si$_{OH}$ and other relaxation phenomena observed these epoxy nanocomposite samples.

II. EXPERIMENTAL

A. Materials

A diglycidyl ether of bisphenol-A (DGEBA) based epoxy resin, commercially known as DER 332, with an epoxide equivalent molar mass of 172-176 g mol$^{-1}$ was used in this study, obtained from Sigma Aldrich. An amine hardener, Jeffamine D-230 from Huntsman, with a hydrogen equivalent molar mass of 60 g mol$^{-1}$ was used to cure to the resin. A theoretically optimal ratio was maintained to ensure complete reaction between the epoxide and amine groups. Silica (SiO$_2$) nanoparticles of size 5-20 nm in diameter were obtained from Sigma Aldrich. Further, for the synthesis of SiO$_2$-SiO$_2$ and h-SiO$_2$ nanoparticles all the other chemicals used, namely tetraethyl orthosilicate (≥ 90%, TEOS),...
hexadecyltrimethylammonium bromide (CTAB), ammonium oxide and poly (acrylic acid sodium salt) (PAA – Na, M.W. 5100 gmol⁻¹), were also obtained from Sigma Aldrich [8]. All the quoted data are taken from the datasheets provided by the suppliers.

**B. Sample Preparation**

Core-shell nanoparticles (SiO₂-SiO₂) and hollow nanoparticles (h-SiO₂) were synthesized using the Stöber method [9]. A detailed procedure for the synthesis has been published elsewhere [10]. The nanoparticle loading ratios were adjusted so that the total shell-polymer interfacial area of the nanoparticles can be found elsewhere [10]. Information regarding the average sample size, particle weight used, the corresponding weight percentage and the density of the different nanoparticles for the selected surface area of 5.80 m² is provided in Table 1. For the preparation of the epoxy nanocomposites, a standard solvent method was followed. The method has been reported in a prior publication [8].

**TABLE I: Approximate nanoparticle weight percentages required for a surface area of 5.80m² based on their average size and packed density**

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>wt. %</th>
<th>Density (g cm⁻³)</th>
<th>Average Size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>0.15</td>
<td>2.2</td>
<td>15 (5-20)</td>
</tr>
<tr>
<td>SiO₂-SiO₂</td>
<td>1</td>
<td>2.1</td>
<td>35 (30-45)</td>
</tr>
<tr>
<td>h-SiO₂</td>
<td>1.05</td>
<td>1.32</td>
<td>60 (57-72)</td>
</tr>
</tbody>
</table>

**C. Material Characterization**

After calibrating the instrument using high purity indium, a Mettler Toledo DSC820 differential scanning calorimetry (DSC) was used to determine glass transition temperatures (T_g). In all cases, a 4.5 mg sample was utilised in a two-step heating cycle, where the first cycle used to erase the sample’s thermal history and the second cycle used to determine the reported T_g, which was taken from the inflexion point in the heat flow curve.

For DMA measurements, a Mettler Toledo DMA/SDTA861 was employed. This equipment was used in tension mode with a maximum force of 10 N or 3 µm maximum level and a 150% auto offset. Measurements were taken in isothermal steps of 10 °C, for a temperature range of -100 °C to 160 °C along with a frequency sweep of 10⁻¹ Hz to 10² Hz. BDS measurements presented in this study are taken from a prior publication for comparison [5].

**III. RESULTS AND DISCUSSION**

Figure 1 presents the DMA – tan δ and E'' spectra and BDS – ε'' spectra for the reference - unfilled epoxy and SiO₂, SiO₂-SiO₂, h-SiO₂ filled epoxy nanocomposites between the temperature range of -100 °C – 160 °C along with derived imaginary permittivity (ε'') spectra from BDS for a frequency range of -160 °C – 160 °C at a frequency of 10 Hz illustrating different relaxation phenomena and the T_g values from DSC for reference - unfilled epoxy sample and epoxy nanocomposite samples filled with SiO₂, SiO₂-SiO₂ and h-SiO₂.

**Fig. 1:** DMA - tan δ and loss modulus (E'') spectra for a temperature range of -100 °C – 160 °C along with derived imaginary permittivity (ε'') spectra from BDS for a frequency range of -160 °C – 160 °C at a frequency of 10 Hz illustrating different relaxation phenomena and the T_g values from DSC for reference - unfilled epoxy sample and epoxy nanocomposite samples filled with SiO₂, SiO₂-SiO₂ and h-SiO₂.

DMA, one being the primary relaxation phenomenon, denoted as α, and the other being the sub-glassy relaxation process, known as β relaxation. However, in BDS measurements an additional SiOH relaxation can also be observed in case of SiO₂-SiO₂ and h-SiO₂ filled epoxy nanocomposite samples. Unlike the research by Keenan et. al [6], since the SiOH relaxation is not distinctly visible in the DMA thermograph, it is possible that it has little effect on the viscoelastic behaviour of the samples. Further examination of the molecular structure by analysing the tan δ peaks, on the other hand, may reveal possible effects on the bulk characteristics.

The α relaxation originates from the macromolecular chain motions, which are frequently linked to the T_g [11]. All of the samples have single, well-defined α relaxation peaks, indicating that their respective cross-linked networks have no phase separation. To understand the relaxation features, factors such as the width and intensity (height) of the relaxation peaks.
were analysed, the results are presented in Table 2.

**TABLE II: Values of different parameters for α relaxation obtained from DMA – tan δ vs. temperature and E’ vs. temperature plots. T\_g; tan δ peak position, Intensity: tan δ peak maxima, Width: full width at half maxima (FWHM) of tan δ and storage modulus (E’)**

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>T_g (°C)</th>
<th>Intensity</th>
<th>Width (°C)</th>
<th>E’</th>
</tr>
</thead>
<tbody>
<tr>
<td>Unfilled Epoxy</td>
<td>93.88</td>
<td>0.81</td>
<td>21.61</td>
<td>15.68</td>
</tr>
<tr>
<td>SiO_2</td>
<td>92.70</td>
<td>0.79</td>
<td>21.64</td>
<td>15.34</td>
</tr>
<tr>
<td>SiO_2-SiO_2</td>
<td>91.14</td>
<td>0.73</td>
<td>22.52</td>
<td>16.20</td>
</tr>
<tr>
<td>h-SiO_2</td>
<td>90.33</td>
<td>1.02</td>
<td>14.67</td>
<td>18.04</td>
</tr>
</tbody>
</table>

From Table 2, it can be observed that as the size of the nanoparticles increases and their concentration reduces, the T\_g reduces. Interfacial interactions between the host polymer and the filler are known to be a deciding factor impacting the bulk properties of the system. The concentration of the filler significantly influences the volume of the inter-phase. An increase in the nanoparticle concentration, as the distance between the particles decreases, may lead to an overlap of these interphal nanolayers; therefore, increasing the volume of the immobilised chains and increasing the T\_g of the nanocomposite when compared to an unfilled polymer or a less filled composite [12]. Consequently, it has been reported in the literature that the E’ of filled polymer samples in the rubbery region is usually higher than their respective unfilled reference samples. However, the presented values of E’ illustrate contrary results. As the concentration of the nanoparticles decreases, the value of E’ increases. When compared to an unfilled epoxy sample, there is a notable rise in case of SiO\_2-SiO\_2 filled sample and a considerable increase in h-SiO\_2 filled sample. This implies that the increase in E’ in the present case might not originate from the overlapping of the interfacial regions.

It has been demonstrated experimentally in various published literature that the T\_g increases with increase in the crosslink density (\(\varphi\)) and the tan δ peak shifts towards higher temperatures. However, the tan δ peak width and intensity reduce with increasing \(\varphi\). This is assumed to be due to the reduction in the distribution of the localised modes of motion, and the decrease in the concentration of the groups with the freedom of rotational and translational modes of molecular motion, respectively [13]. Here the epoxy nanocomposite samples have tendentially lower T\_g than the unfilled reference sample. As the size of the nanoparticles increases, which leads to reduced nanoparticle concentration, the T\_g is reduced, implying a reduced \(\varphi\).

Further, the tan δ peak intensity and width were determined by using a Gaussian fit function. Intensity of tan δ is frequently used to represent the internal friction of the polymer matrix; based on this stronger interfacial interaction usually lower the value of intensity and shift the tan δ peak to higher temperatures. No significant change in the intensity of the tan δ peak can be observed for samples filled with SiO\_2 and SiO\_2-SiO\_2 when compared with unfilled sample. However, a significant change is observed in case of h-SiO\_2. One interpretation could be that the reduction in the T\_g value implies more chain segments in motion at the same time; therefore, increasing the internal friction and the loss modulus, resulting in higher value of the tan δ peak.

Unlike SiO\_2 and SiO\_2-SiO\_2 filled sample, the width of the h-SiO\_2 filled sample reduces significantly. However, this is contrary to the discussion above where reduction in T\_g implied a lower degree of cross-linking. A reduce is in width correlates to an increase in T\_g. Nevertheless, it is plausible with bond formations which do not affect the T\_g of bulk but do constrain molecular motions. Alternatively, this would also justify the increase in the intensity of the tan δ peak as these additional constrains would reduce the distribution of localised modes of motion; thus potentially increasing the concentration of groups having a similar modes of motion.

Covalent bonds and hydrogen bonds are known to show such behaviour [14]. However, covalent bonds between the filler, fictionalised or non-fictionalised, and the polymer matrix has been shown to noticeably increase the T\_g of the sample. Nevertheless, weak attractive bonds such as the hydrogen bond do not significantly affect the T\_g of the sample. In a study by Lin et al. [15] two types of SiO\_2 nanoparticles i.e. hydrophobic and hydrophilic filled in poly (vinyl acetate) were investigated. It was reported that in case of hydrophilic-SiO\_2, with Si-OH bonds on its surface, hydrogen bond interactions with the carbonyl group of the matrix were observed. However, even at a loading ratio of 30 wt%, the T\_g remained more or less constant, with a maximum variation of ~2K. The presence of these hydrogen bonds would also explain the increase in E’ with reduced concentration of the filler nanoparticles. In a separate study [5], it has been demonstrated that h-SiO\_2 has the highest concentration of Si-OH on its surface followed by SiO\_2-SiO\_2 and SiO\_2; thus, providing further evidence to the interpretation of increased E’.

The β relaxation is often attributed to the crankshaft motion of the glyceryl segments in epoxy-amine networks [16]. The relaxation features obtained from the E” vs. temperature profile such as the height, width and the intensity are presented in Table 3.

Considering the position of β maxima, a significant shift towards higher temperature is observed in case of h-SiO\_2 as compared to the other samples, implying slower segmental dynamics. The distribution of molecular modes reduces in weakly cross-linked systems [13]. This leads to a decrease in the width and intensity of the β transition peak, accompanied by the faster segmental dynamics. However, the width of the E” peak for β relaxation has increased significantly, which along with slower segmental dynamics implies a highly cross-linked network. However, the T\_g for this system is the lowest. Furthermore, the DSC values presented in Figure 1 do

**TABLE III: Values of different parameters for β relaxation obtained from DMA – E” vs. temperature plots. β maxima: position of E” maxima, Intensity: E” peak maxima and Width: FWHM of E”**

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>β Maxima (°C)</th>
<th>Intensity</th>
<th>Width (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Unfilled Epoxy</td>
<td>-45.26</td>
<td>121.86</td>
<td>54.00</td>
</tr>
<tr>
<td>SiO_2</td>
<td>-45.21</td>
<td>133.71</td>
<td>50.44</td>
</tr>
<tr>
<td>SiO_2-SiO_2</td>
<td>-45.63</td>
<td>148.90</td>
<td>56.11</td>
</tr>
<tr>
<td>h-SiO_2</td>
<td>-40.15</td>
<td>152.01</td>
<td>66.19</td>
</tr>
</tbody>
</table>
not show any significant change and are within the limits of experimental error (±2 °C). In case of SiO₂ filled sample the β maxima position does vary but the intensity increase and the width of the peak reduces. Such behaviour is generally observed in internally plasticised systems when the addition of filler causes an increase in free volume [13]. Like h-SiO₂, similar observation can be made in SiO₂-SiO₂ filled system; however, on a smaller scale.

In accordance to the arguments presented and the observed features, the presence of hydrogen bonds is likely in form of a weakly attractive interactions between the filler surface and the host polymer matrix. As these bonds affect both the α and the β relaxation behaviour, it is clear that these interactions involve the hydroxyster groups. Therefore, in combination with BDS it is apparent that the Si-OH relaxation is rather a polarization phenomena in the SiO₂-SiO₂ and h-SiO₂ filled systems and does not have any significant effect on the viscoelastic-mechanical properties of the bulk system.

IV. CONCLUSION

Three epoxy nanocomposite samples were characterised via. DMA and DSC, each sample was filled with a distinct architecture of nano-silica i.e. SiO₂, SiO₂-SiO₂ and h-SiO₂ and had a comparable total nanoparticle surface area. In a prior study, an additional relaxation peak was observed, termed as SiOH, in BDS measurements. It was attributed to the hydrogen bonding interaction between the hydroxyster groups of the cured epoxy resin and the silanols on the surface of the nanoparticles. However, such a peak was not observed in DMA thermographs. Further analysis of tan δ peak characteristics demonstrate that the width of the tan δ for α in case of h-SiO₂ filled system decreases but its intensity increases along with an increase in the value of E’. Similarly, the width of the tan δ peak for β relaxation increases significantly with respect to unfilled epoxy accompanied by faster segmental dynamics. Such a behaviour is generally observed for internally plasticised systems. Consequently, in accordance to these observations it was determined that the presence of weak covalent bonds in the SiO₂-SiO₂ and h-SiO₂ filled systems, particularly hydrogen bonds, is evident. This correlates well with the conclusions of the prior study. However, these bonds do not have any significant impact on the viscoelastic-mechanical properties of the nanocomposite. This is also further evidenced by the DSC Tg measurements where no significant changes are observed across all samples.

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REFERENCES