THE EFFECT OF FULLERENE C_{60} 
ON THE MECHANICAL AND DIELECTRICAL 
BEHAVIOR OF EPOXY RESINS AT LOW LOADING

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PACS 81.07.Lb

Fullerene C\textsubscript{60} / epoxy polymers nanocomposites with different C\textsubscript{60} loadings (0.01-0.12 wt.\%) have been prepared. Mechanical testing shows that compared with the neat epoxy, the mechanical and toughening properties of the composites are greatly improved. The addition of fullerene C\textsubscript{60} increased the modulus of the epoxy (up to 20 \%), but the glass transition temperature was unaffected. The measured impact strength was also increased, from 38 to 115 kJ/m\textsuperscript{2} with the addition of 0.12 wt.\% of fullerene C\textsubscript{60}. The toughening mechanism has been discussed. Dielectric spectroscopy was used to investigate the influence of nanoparticles on the relaxation processes in the polymer matrix.

Keywords: epoxy resins, fullerene C\textsubscript{60}, nanocomposites, mechanical properties; dielectric spectroscopy; relaxation processes.

1. Introduction

Epoxy resins are widely used in high performance applications, such as structural adhesives, composite materials and microelectronics encapsulants. Unfortunately, most of these resins are inherently brittle. The fracture toughness of an unmodified epoxy can be enhanced with the addition of fillers and additives. In the past decade, attention has been focused on using nanoparticles as filler to overcome the trade-off encountered in traditional composite systems [1]. Such nanoparticle modification has been shown to increase the toughness and cyclic-fatigue resistance of the epoxy polymer [2], and also, due to the very small size of these fillers, not lead to a significant increase in the viscosity of the epoxy monomer [3]. The nanoparticles not only stiffen, strengthen and toughen epoxy, but also reduce the effect of flaws on mechanical performance.

In this research, we will investigate the effect of fullerene C\textsubscript{60} on the mechanical properties, fracture toughness and toughening mechanism of epoxy resins. Because of the outstanding physical properties and large specific surface area of fullerene C\textsubscript{60} [4], fullerene-based composites are expected to show significantly improved mechanical performance, when compared with neat matrix materials. A number of toughening mechanisms were proposed to explain the toughening effect of nanoparticles [5]. Recent molecular-dynamics studies have suggested that the mobility of the nanoparticles in the matrix might be crucial for introducing new energy-dissipating mechanisms that lead to enhanced toughness in the nanocomposite [6]. Here, we use broadband dielectric spectroscopy (BDS) to directly measure the influence of fullerene C\textsubscript{60} on polymer relaxations corresponding to different lengths and time scales. BDS is one of the most efficient tools for studying molecular relaxations of polymers. It covers a broad frequency
range, allowing measurement of different relaxation processes simultaneously, including secondary, and even entire chain relaxation processes under favorable circumstances [7]. In this paper, we report the synthesis of epoxy/fullerene $C_{60}$ nanocomposites, study their mechanical properties, and the data of BDS measurements.

2. Materials and Methods

A diglycidyl ether of bis-phenol F (Araldite GY285) supplied by Hunstman, UK was used as epoxy. The resin mixture was cured with a standard polyether-amine DEH24 (Dow Chemical). This resin and hardener were mixed to a ratio of 1:1. Fullerene $C_{60}$ (purity 99.9%), which was supplied from ZAO ILIP (Saint Petersburg, Russia), was used as filler. The calculated amount of filler was mixed with hardener using ultrasonic method. The resins were cured at $140 \, ^\circ C$ for 2 h and then post-cured at $160 \, ^\circ C$ for 2 h.

3. Techniques

Uniaxial tensile tests were conducted on the epoxy polymers in accordance with ISO 527 [8,9]. Tests were conducted using $4 \, \text{mm} \times 10 \, \text{mm} \times 40 \, \text{mm}$ specimens for toughness estimation and $6 \, \text{mm} \times 6 \, \text{mm} \times 40 \, \text{mm}$ specimens for compression Young’s modulus and yield stress estimation. Five specimens were taken for each sample to obtain an average value. Tensile properties were measured using a compression method on UTS 10 instrument (UTS test systeme, Germany). The acoustic modulus was measured ultrasonically using a UK-10 PM instrument (Volna, USSR) at a frequency of 200 kHz. The specimens for test were cylinders with a length of 50 mm and diameter of 10 mm.

The fracture surfaces of the epoxy polymers were studied using scanning electron microscopy (SEM). This was performed using a scanning electron microscope with Zeiss ULTRA-plus FEG-SEM instrument equipped with field-emission gun with magnification 20–2000.

Differential scanning calorimetry (DSC) measurements were performed using Netzsch DSC 204F1 instrument at a scan rate 10 K/min in temperature range 20–200 °C. The thermal gravimetric analysis (TGA) measurements were performed in an inert nitrogenous atmosphere and an oxigenous atmosphere on a Perkin-Elmer TGA-7 instrument with platinum pan using 5 mg of polymer as probe. The samples were heated 25–900 °C and the temperature was raised at the rate of 20 K/min.

Dielectric measurements were performed using a RCL WK 4270 Waynekeerr (USA) Impendance Analyzer in the frequency range from 0.01 Hz to 40 kHz at different temperatures. The instrument was interfaced with a computer and equipped with a custom-modified heating and cooling system for sequential measurement from low to high frequency.

The epoxy monomers (epoxy plus hardener) with calculated amounts of filler for nanocomposite samples were placed in a parallel-plate capacitor with 20 mm diameter, and a pair of glass fiber spacer with 50 µm diameter was used between the electrodes. This sample capacitor was heated at $140 \, ^\circ C$ for 2 h and then at $160 \, ^\circ C$ for 2 h. The sample capacitor was mounted in the fixture and placed in the thermostat under permanent vacuum of about 1 mm Hg. Temperature stabilization was about 0.1 K throughout the measurements. The experiments were carried from 100 to 458 K by 5 K steps. At each temperature, the ten chosen frequencies (1 Hz to 40 kHz) were measured.
4. Results and Discussion

4.1. The effect of fullerene C\(_{60}\) on basic properties

The SEM microscopy of all epoxy polymers, unmodified and modified with fullerene C\(_{60}\), showed that these were homogeneous thermoset polymers. The primary and secondary aliphatic amines added readily and repeatedly across the C\(_{60}\) molecule, producing complex reaction mixtures composed of numerous structures and isomers [10]. Each amination reaction reportedly added the elements R(R')N and H across \(\pi\)-bond on the fullerene C\(_{60}\). A number of regiochemistries are possible but hydroamination is preferred over 1,2- or 1,4- addition. Considerable evidence exists that radical ion-pairs form when fullerene C\(_{60}\) is mixed with an aliphatic amine. The molecules of fullerene C\(_{60}\) can incorporate up to 48 such amine functionalities [10]. Therefore, as a result of such reaction with polyether-amine hardener, the fullerene C\(_{60}\) was homogeneously incorporated into the epoxy polymer structure. The quality of fullerene C\(_{60}\) dispersion in the epoxy matrix is important because numerous studies have shown that the interfacial adhesion provided by the chemical reaction of the filler surface with the matrix is critical for nanoparticle dispersion, as well as mechanical, damping and thermal properties [11, 12]. The incorporation of fullerene C\(_{60}\) into the epoxy matrix structure was supported by TGA data (Fig.1).

The TGA results showed a tripartite degradation which began at ca 300 °C both in an inert nitrogenous atmosphere and an oxygenated atmosphere. There were not distinct differences between those two runs. However, the incorporation of fullerene C\(_{60}\) leads to a prolongation in the last stage of degradation over 700 °C (Fig.1b). Hereby, the fullerene C\(_{60}\) may act like carbon nanotube (CNT) in polymer nanocomposites, where interphase formation can be found through TGA analysis [13].

Furthermore, the glass transition temperatures were unchanged upon the addition of fullerene C\(_{60}\) (Table 1), within experimental uncertainty, compared to the value of the neat epoxy, and the value received here was equivalent to the value of epoxy found in literature (about 123–124 °C for first heating and about 130 °C for second). Hence, the incorporation of fullerene C\(_{60}\) did not change the phase structure and the crosslinked density of the epoxy thermosets in comparison with pristine epoxy polymer because the larger crosslinked density should lead to an increase of the Tg. Similar results, showing no change in Tg due to addition of nanoparticles (for example, silica nanoparticles or carbon nanotubes) was reported previously [11].

<table>
<thead>
<tr>
<th>Loading, wt.%</th>
<th>(T_g), °C</th>
<th>Acoustic Young’s modulus, GPa</th>
<th>Tensile strength (\sigma), MPa</th>
<th>Contraction at compression (\varepsilon), %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Neat epoxy</td>
<td>124</td>
<td>4.92±0.10</td>
<td>110± 5</td>
<td>7.0± 0.5</td>
</tr>
<tr>
<td>C(_{60}), 0.02</td>
<td>124</td>
<td>5.11±0.10</td>
<td>118± 5</td>
<td>8.0± 0.5</td>
</tr>
<tr>
<td>0.04</td>
<td>123.5</td>
<td>5.22±0.10</td>
<td>122± 4</td>
<td>7.5± 0.5</td>
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<tr>
<td>0.06</td>
<td>124</td>
<td>5.45±0.10</td>
<td>138± 5</td>
<td>8.0± 0.5</td>
</tr>
<tr>
<td>0.08</td>
<td>124</td>
<td>5.70±0.10</td>
<td>145± 5</td>
<td>8.0± 0.5</td>
</tr>
<tr>
<td>0.10</td>
<td>124</td>
<td>5.83±0.10</td>
<td>163± 4</td>
<td>8.0± 0.5</td>
</tr>
<tr>
<td>0.12</td>
<td>124</td>
<td>5.91±0.10</td>
<td>166± 3</td>
<td>8.0± 0.5</td>
</tr>
</tbody>
</table>
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4.2. Young’s modulus and tensile strength

Typical stress-strain curves are portrayed in Fig.2. Although the strain-stress behaviors of fullerene modified epoxy are almost identical to those of the base epoxy, the tensile strength failure strain and the ductility are all improved. Fullerene nanoparticles are able to improve strength and elongation to break simultaneously, leading to an increase of the areas under the curve, (this implies toughness enhancement in the nanotubes) which have been reported by other authors [14,15]. The Young’s modulus values, \( E \), and tensile strength measured from the tensile tests are summarized in Table 1. In spite of small amount of fullerene addition (< 0.1 wt.%), the improvement of Young’s modulus and tensile strength are about 20%, which suggests that fullerene might be a modifier of the epoxy resin system. Such improvement in modulus is similar with earlier reported results [12]. The Young’s modulus is related to the depth of atomic bond energy function where the polymer chain mobility is restricted by fillers, which contribute to an improved tensile modulus [16].

The fullerenes restrict the mobility and deformation of the matrix by introducing a mechanical restraint. According to this mechanism, the improved modulus for composites containing nanoparticles would be expected over composites containing larger particle sizes.
The yield stress of the composites is greater than that of the polymer matrix, hence, one can conclude that bonding between the fillers and the matrix is strong enough.

4.3. Toughness testing results

Results of toughness testing for the neat epoxy and fullerene modified composites are shown in Fig. 3. The values of impact strength ($G$) showed significant improvement with increasing fullerene $C_{60}$ concentration. The 0.12 wt.% fullerene $C_{60}$ loading resulted in largest increase in $G$, i.e. from 38 kJ/m$^2$ for neat epoxy to 115 kJ/m$^2$ at 0.12 wt.% loading, a threefold improvement.

The SEM samples were prepared from brittle fracture surfaces of the impact tests pieces. Pictures showed the initiation position of fractures. Examination of fracture surfaces by SEM revealed the neat epoxy to have the classic fracture surface for brittle failure (Fig. 4a) observed in highly crosslinked polymer systems [17]. The fracture surface of the test piece of pure epoxy
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Fig. 4. SEM micrographs of the fracture surfaces of the test piece of pure epoxy (a) and of the 0.1 wt.% fullerene C$_{60}$ modified epoxy (b) at magnification 200x.

was very cracked. The fracture was initiated by a small hole at the edge of the sample. River marks leading to the initial site of crack growth were detected, but substantial indication of plastic deformation in the reference material was not noted. Quantitatively speaking, the lack of plastic deformation and a cracked fracture surface well agree with relatively low toughness of the material. Inspection of the 0.1 wt.% fullerene C$_{60}$ modified epoxy confirmed the composite to display a much smooth fracture surface (Fig. 4b). This image clearly shows the occurrence of plastic deformation. The implication of the above results will be discussed further later, when toughening mechanisms initiated by the presence of the fullerene nanoparticles are described.

The ability of fullerenes to enhance the mechanical properties of epoxy resins is improved in relation to the published data for other nanoparticle-modified epoxy resins. Thus, the fracture toughness of epoxy with $\sim$ 0.1 wt.% of amine-functionalized double-walled CNT was
increased by 18% [18]. The weight fraction of Al₂O₃, SiO₂, and TiO₂ nanoparticles required to increase the fracture toughness of the neat epoxy by > 50% is nearly fifty- to one hundred-fold higher (∼ 5–20 wt.%) [19, 20]. Similarly, clay nanocomposites require the same amount (∼ 5–10 wt.%) of additives in various epoxy resins to achieve a 60% increase in toughness [21–23]. By contrast, for the case of the fullerene C₆₀ filler, we find that toughness of epoxy composites at a nanofiller weight fraction of ∼ 0.1 %.

4.4. Toughening mechanisms

The previous studies [1] have considered the toughening mechanisms induced by nanoparticles in detail. These mechanisms included (a) crack pinning, (b) crack deflection, (c) immobilized polymer around the particles, and (d) the ability of nanoparticles to induce an increased extent of plastic deformation. All these mechanisms are connected with mobility of nanoparticles in polymer matrix. We use BDS to directly measure the influence of fullerene C₆₀ on polymer relaxation corresponding to different lengths and time scales. Fig. 5 presents the temperature dependence of tan δ spectra for the fullerene C₆₀/composite (0.02 wt.% of fullerene C₆₀) measured at different frequencies. Similar to neat epoxy, we observed two relaxation processes: β and α. Both relaxation processes are well separated in these measurements, providing a good opportunity for analyzing their dependence on the fullerene C₆₀ concentration at different temperatures. The α relaxation process corresponds to the segmental mode, which is associated with the glass transition of the system, whereas the β relaxation process is connected with secondary relaxation. For all the samples investigated, we observed no qualitative changes in the shape of the nanocomposite relaxation modes with the fullerene C₆₀ additive. In order to obtain τ_max values (as τ_max = 1/(2πf_max), where f is frequency) at the temperature of maximum on the temperature dependence of tan δ for the fullerene C₆₀/ epoxy composite, a non-linear curve fitting procedure was applied to experimental curves of Fig. 5. The fitting was done using Microcal Origin 8.0. Further details about the fitting procedure are given in [24].

Fig. 5. Temperature dependence of tan δ for the fullerene C₆₀/ epoxy composite (0.02 wt.% of fullerene C₆₀); frequency 40 kHz (1); 25 kHz (2); 3 kHz (3)
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Figure 6 shows the relaxation times for the \(\beta\) relaxation processes as a function of temperature for nanocomposites. The secondary relaxation process for composites is shifted to higher temperatures compared to the same process for neat epoxy. Hence, the introduction of fullerene in an epoxy matrix leads to the restriction of molecular motions. Since the distance between cross-links in this study can be assumed as an epoxy molecule size (2–3 nm), these particles may be in motion within the matrix molecules at a similar time and length scale. As a result, the presence of fullerene hampers the molecular motions in epoxy composites because it leads to hardening of polymer chain and impedes secondary relaxation processes.

The activation energies for the \(\beta\) relaxation processes for nanocomposites were obtained from an Arrhenius plot of \(-\log \tau_{\text{max}}\) (Table 2). All epoxy composites demonstrate a 30 %

<table>
<thead>
<tr>
<th>Sample</th>
<th>Ea, kJ/mol</th>
<th>(-\log \tau_0) [s]</th>
</tr>
</thead>
<tbody>
<tr>
<td>neat</td>
<td>33.03</td>
<td>31.8</td>
</tr>
<tr>
<td>0.02% C\textsubscript{60}</td>
<td>20.46</td>
<td>21.1</td>
</tr>
<tr>
<td>0.04% C\textsubscript{60}</td>
<td>18.62</td>
<td>19.6</td>
</tr>
<tr>
<td>0.06% C\textsubscript{60}</td>
<td>18.76</td>
<td>20.5</td>
</tr>
<tr>
<td>0.08% C\textsubscript{60}</td>
<td>19.72</td>
<td>19.5</td>
</tr>
</tbody>
</table>

It is well known that secondary relaxation (\(\beta\) process) is connected with toughness of polymer [25].
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activation energy decrease with fullerene loading; this indicated that carbon nanoparticles can significantly improve energy dissipation processes in epoxy resins, probably independent of the loading level. This process can lead to domination of plastic deformation mechanism in the epoxy composite which effectively blunts the crack trip. Hence, the suggested mechanism is a major reason for the higher values of impact strength $G$ which were observed.

5. Conclusions

The mechanical and fracture properties of epoxy nanocomposites containing 0–0.12 wt.% of fullerene $C_{60}$ have been studied. Several major conclusions may be reached from the present work.

Firstly, considering the Young’s modulus of these materials, when the loading level was increased, the modulus of epoxy polymer steadily increased.

Secondly, the presence of fullerene $C_{60}$ always leads to an increase in the toughness of epoxy resins.

Thirdly, the two toughening mechanisms which were operative in all the epoxy polymers containing nanoparticles have been identified. Namely, (a) immobilized polymer around the particles, and (b) the ability of nanoparticles to induce an increased extent of plastic deformation.

References

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