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

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Fullerene C_{60} / epoxy polymers nanocomposites with different C_{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_{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^2 with the addition of 0.12 wt.% of fullerene C_{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_{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_{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_{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 nanopartices [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_{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 °C for 2 h and then post-cured at 160 °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 mm × 10 mm × 40 mm specimens for toughness estimation and 6 mm × 6 mm × 40 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 Waynekerr (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 °C for 2 h and then at 160 °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.

TABLE 1. Effect of loading on properties of nanocomposites based on epoxy matrix

Loading, wt.%	T_g, °C	Acoustic Young's modulus, GPa	Tensile strength σ, MPa	Contraction at compression ε, %
Neat epoxy	124	4.92±0.10	110± 5	7.0± 0.5
C_{60}, 0.02	124	5.11±0.10	118± 5	8.0± 0.5
0.04	123.5	5.22±0.10	122± 4	7.5± 0.5
0.06	124	5.45±0.10	138± 5	8.0± 0.5
0.08	124	5.70±0.10	145 ± 5	8.0± 0.5
0.10	124	5.83±0.10	163 ± 4	8.0± 0.5
0.12	124	5.91±0.10	166 ± 3	8.0± 0.5

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 π-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].

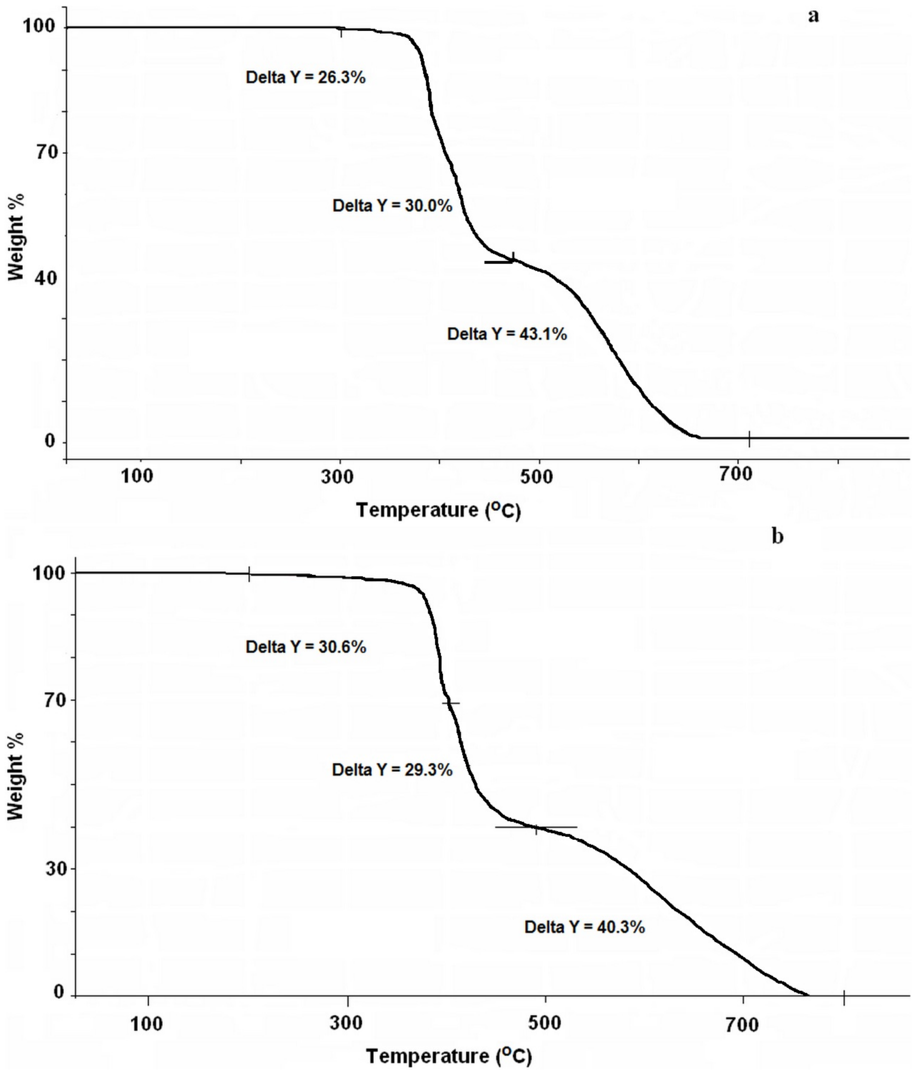

FIG. 1. TGA curve of neat epoxy (a); and with 0.1 wt.% of fullerene C_{60} (b)

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.

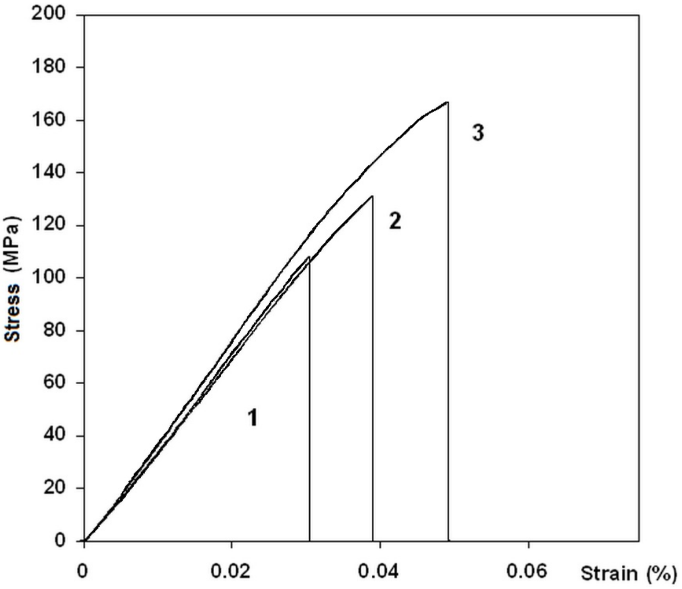

FIG. 2. Typical stress-strain curves of neat epoxy (1); with 0.04 wt.% of fullerene C_{60} (2); with 0.1 wt.% of fullerene C_{60} (3)

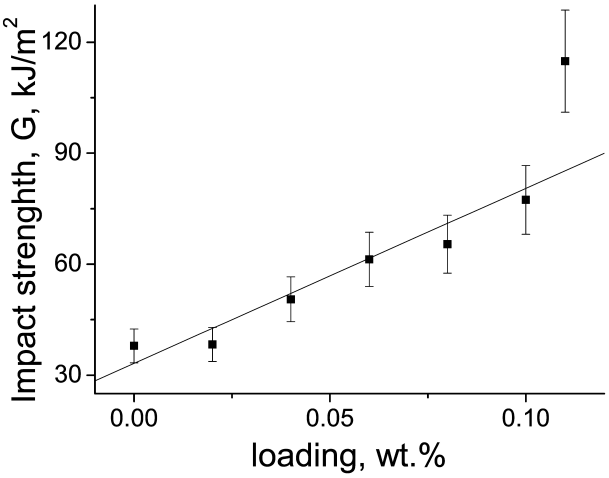

FIG. 3. The impact strength values are plotted as a function of fullerene C_{60}

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

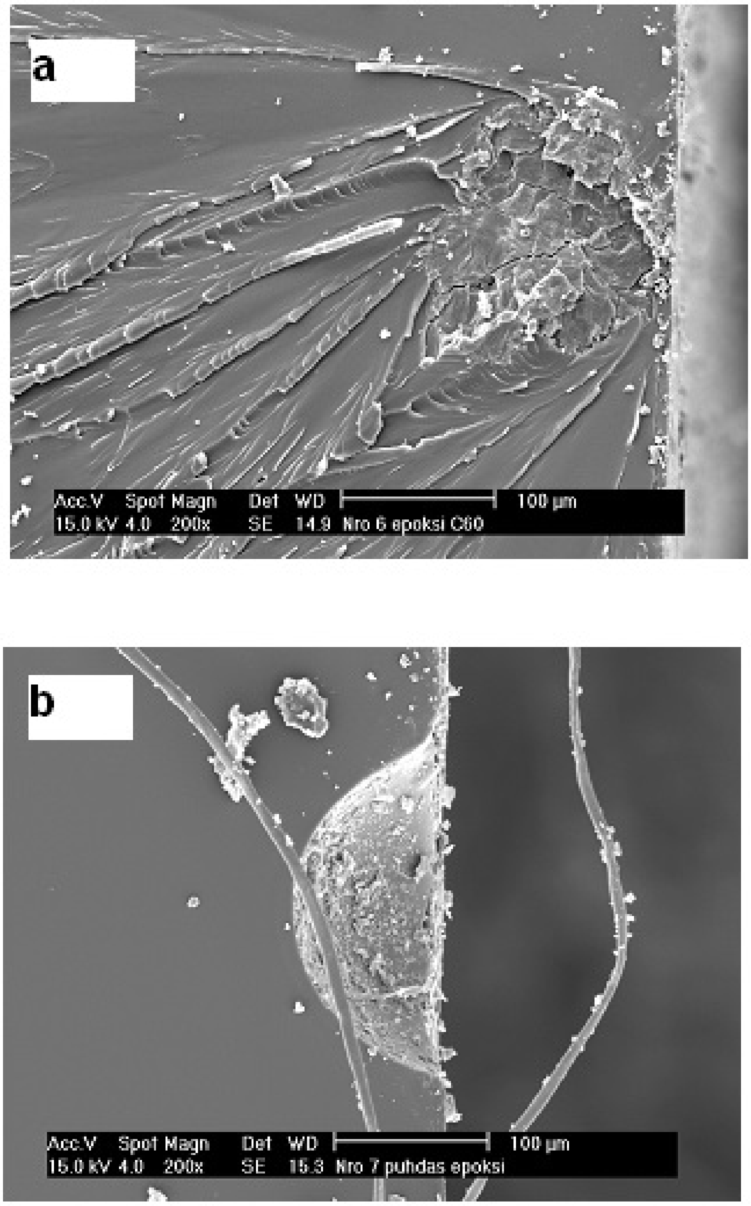

FIG. 4. SEM micrographs of the of fracture surfaces of the test piece of pure epoxy (a) and of the 0.1 wt.% fullerene C_{60} modified epoxy (b) at magnification 200

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 Al_2O_3, SiO_2, and TiO_2 nanoparticles required to increase the fracture toughness of the neat epoxy by $> 50\%$ is nearly fifty- to one hundred-fold higher ($\sim$ 5–20 wt.%) [19, 20]. Similarly, clay nanocomposites require the same amount ($\sim$ 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 C_{60} filler, we find that toughness of epoxy composites at a nanofiller weight fraction of $\sim$ 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 C_{60} on polymer relaxation corresponding to different lengths and time scales. Fig. 5 presents the temperature dependence of tan δ spectra for the fullerene C_{60}/composite (0.02 wt.% of fullerene C_{60}) 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 C_{60} 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 C_{60} additive. In order to obtain $\tau_{\max}$ values(as $\tau_{\max} = 1/2\pi f_{\max}$, where f is frequency) at the temperature of maximum on the temperature dependence of $\tan\delta$ for the fullerene C_{60}/ 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. Futher details about the fitting procedure are given in [24].

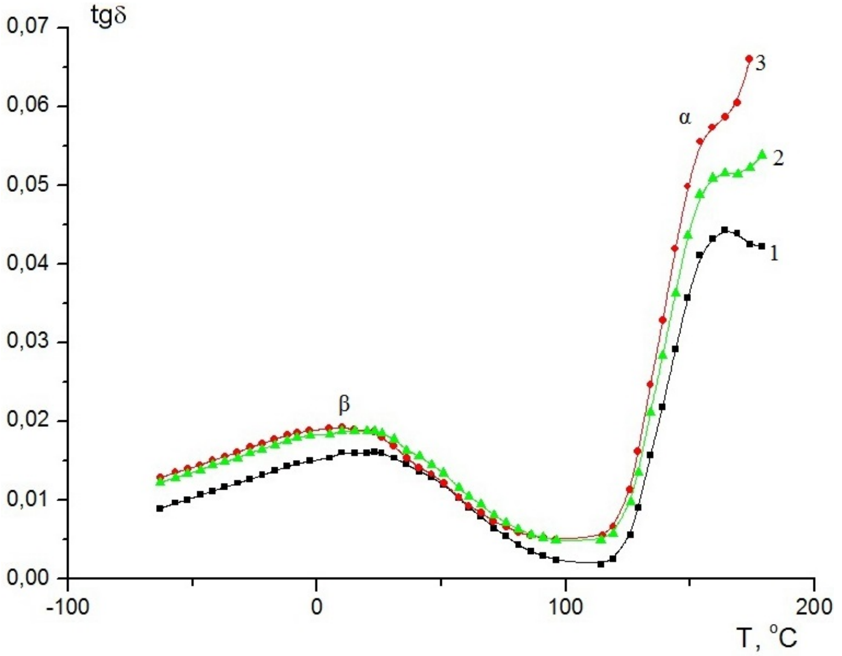

FIG. 5. Temperature dependence of $\tan\delta$ for the fullerene C_{60}/ epoxy composite (0.02 wt.% of fullerene C_{60}); frequency 40 kHz (1); 25 kHz (2); 3 kHz (3)

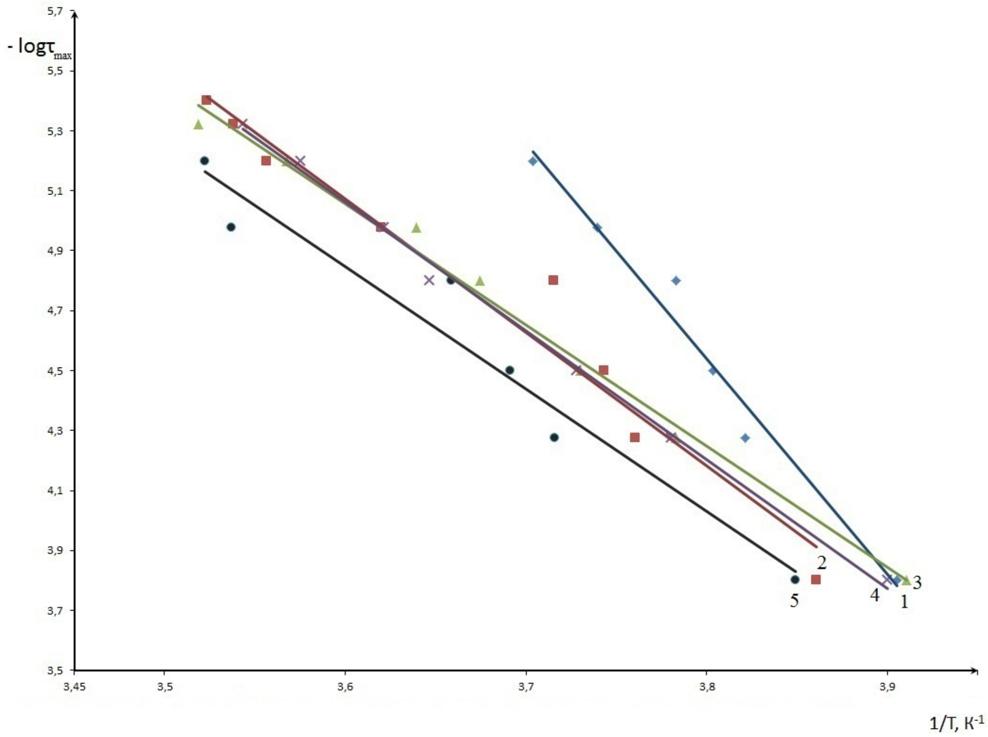

FIG. 6. Relaxation plot of $-\log\tau_{\max}$ determined from $\tan\delta$ spectra for pristine epoxy 1(♦) and for the fullerene C_{60}/ epoxy composite: 0.02 wt.% of fullerene C_{60} – 2(■); 0.04 wt.% of fullerene C_{60} – 3(▲); 0.06 wt.% of fullerene C_{60} – 4(×); 0.08 wt.% of fullerene C_{60} – 5(•)); for β process

TABLE 2. Parameters of β relaxation process of fullerene C_{60} /epoxy composites at different loading

Sample	Ea, kJ/mol	$-\log\tau_0$[s]
neat	33.03	31.8
0.02% C_{60}	20.46	21.1
0.04% C_{60}	18.62	19.6
0.06% C_{60}	18.76	20.5
0.08% C_{60}	19.72	19.5

It is well known that secondary relaxation (β process) is connected with toughness of polymer [25].

Figure 6 shows the relaxation times for the β 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 β relaxation processes for nanocomposites were obtained from an Arrhenius plot of $-\log\tau_{\max}$ (Table 2). All epoxy composites demonstrate a 30 %

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

[1] Leng J., Lau A.K.T. *Multifunctional polymer nanocomposites*. CNC Press,N-Y., 2011, 560 p.

[2] Wichmann M., Schulte K., Wagner H.D. On nanocomposites toughness. *Compos. Sci. Technol.*, *68*, P. 329–331 (2008).

[3] Roscher C. Tiny particles, huge effect: radiation curable silica nanocomposites for scratch and abrasion resistant coatings. *Eur. Coat. J.*, **4**, P. 131–141 (2003).

[4] Prato M. [60]Fullerene chemistry for material science applications. *J. Mat. Chem.*, **7**, P. 1097–1109 (1997).

[5] Hsich T.H., Kinloch A.J., et al. The mechanisms and mechanics of the toughening of epoxy polymer modified with silica nanoparticles. *Polymer*, **51**, P. 6284–6294 (2010).

[6] Gersappe D. Molecular mechanisms of failure in polymer nanocomposites. *Phys. Rev. Lett.*, **89**, P. 058301 (2002).

[7] Adachi K., Kotaka T. Dielectric normal mode relaxation. *Progr. Polym. Sci.*, **18**, P. 585–622 (1993).

[8] ISO-527-1. Plastics – Determination of tensile properties – Part 1: general principles. Geneva. International Standard Organisation (1993).

[9] ISO-527-2. Plastics – Determination of tensile properties – Part 2: test conditions for moulding and extrusion plastics. Geneva. International Standard Organisation (1993).

[10] Miller G.P. Reactions between aliphatic amines and [60]fullerene: a review. *Compt. Rend. Chem.*, **9**, P. 952–959 (2006).

[11] Ogasawa T., Ishida Y., Kasai T. Mechanical properties of carbon fiber/ fullerene dispersed epoxy composites. *Comp. Sci. Technol.*, **69**, P. 2002–2008 (2009).

[12] Rafiee M.A., Yavari F., Rafiee J., Koratkar N. Fullerene- epoxy nanocomposites – enhanced mechanical properties at low nanofiller loading. *J. Nanopart. Res.*, **13**, P. 721–731 (2011).

[13] Zhang W., Picu R.C., Koratkar N. Suppression of fatigue crack growth in carbon nanotube composites. *Appl. Phys. Lett.*, **91**, P. 193109 (2007).

[14] Kinloch A.J., Mohammed R., et al. The effect of silica nano particles and rubber particles on the toughness of multiphase thermosetting epoxy polymers. *J. Mat. Sci.*, **40**, P. 5083–5086 (2005).

[15] Hsich T.H., Kinloch A.J., Taylor A.C., Kinloch I.A. The effect of carbon nanotubes on the fracture toughness and fatigue performance of a thermosetting epoxy polymer. *J. Mat. Sci.*, **46**, P. 7525–7535 (2011).

[16] Dittanet P., Pearson R.A. Effect of silica nanoparticle size on toughening mechanisms of filled epoxy. *Polymer*, **53**, P. 1890–1905 (2012).

[17] Kinloch A., Taylor A. The toughening of cyanate-ester polymers: part 1. Physical modification using particles, fibers and woven-mats. *J. Mat. Sci.*, **37**, P. 433–466 (2002).

[18] Zhu J., Kim J., et al. Improving the dispersion and integration of single-walled carbon nanotubes in epoxy composites through functionalization. *Nano Lett.*, **3**, P. 1107–1113 (2003).

[19] Wetzel B., Rosso P., Haupert F., Friedrich K. Epoxy composites fracture and toughening Mechanisms. *Eng. Fract. Mech.*, **73**, P. 2375–2398 (2006).

[20] Blackman B.R.K., Kinloch A.J., et al. The fracture and fatigue behaviour of nano-modified epoxy polymers. *J. Mat. Sci.*, **42**, P. 7049–7051 (2007).

[21] Zerda A.S., Lesser A.J. Intercalated clay nanocomposites: Morphology, mechanics, and fracture behavior. *J. Polym. Sci. B: Polym. Phys.*, **39**, P. 1137–1146 (2001).

[22] Wang K., Chen L., et al. Epoxy nanocomposites with highly exfoliated clay: mechanical properties and fracture mechanisms. *Macromolecules*, **38**, P. 788–800 (2005).

[23] Liu W., Hoa S.V., Pugh M. Fracture toughness and water uptake of high-performance epoxy/ nanoclay nanocomposites. *Comp. Sci. Technol.*, **65**, P. 2364–2373 (2005).

[24] Nikonorova N.A., Diaz-Calleja R., Yakimansky A. Molecular mobility in comb-like copolymethacrylates with chalcone-containing side-chains. *Polym. Int.*, **60**, P. 1215–1221 (2011).

[25] Boyer R.F. Dependence of mechanical properties on molecular motion in polymers. *Polym. Eng. Sci.*, **8**, P. 161–185 (1968).