Effect of C<sub>60</sub> Fullerene Additives on the Structure and Mechanical Properties of Thin Organic Glass Films

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Abstract—We have studied the effect of small additives of C<sub>60</sub> fullerene on the mechanical properties (strength, Young’s modulus, elongation at break) of thin organic glass films tested for uniaxial extension.

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Polymers filled with dispersed particles exhibit a qualitative change in the mechanical properties when the filler particle size is decreased below a certain level and the material becomes a nanocomposite [1]. In real materials, the transition from composite to nanocomposite is “smeared” under the influence of various factors, primarily because of an unavoidable distribution of filler particle dimensions and/or due to the aggregation of particles. Using the molecules of C<sub>60</sub> fullerene (with diameters of ~0.7 nm [2]) as a filler, it is possible to eliminate at least the first factor.

We have studied the effect of dispersed C<sub>60</sub> fullerene particles on the mechanical properties of thin organic glass films. The choice of this polymer matrix is related to its simplicity and the inherent structural homogeneity on a supramolecular level. Indeed, the small-angle X-ray diffraction patterns of organic glasses typically exhibit constant reflection intensity over the entire range of scattering angles [3].

The organic glass used in this study represented atactic poly(methyl methacrylate) (PMMA) obtained by radical block polymerization, with a viscosity-average molecular weight of M<sub>n</sub> = 8.5 × 10<sup>4</sup>. Fullerene-containing carbon black was synthesized in arc discharge using the Krätschmer–Huffman method [4]. A mixture of C<sub>60</sub> and C<sub>70</sub> fullerenes was extracted from the deposit with toluene and separated by preparative chromatography techniques, which yielded the target fullerene black containing 99.7% of C<sub>60</sub> molecules [5]. Thin (10–12 µm thick) films for mechanical testing were prepared by casting from pure PMMA and mixed PMMA–C<sub>60</sub> solutions in toluene. The content of C<sub>60</sub> in the PMMA films was varied from 1 to 10%.

The mechanical properties of samples, including the tensile strength (stress at break) σ<sub>b</sub>, elongation at break ε<sub>b</sub>, and elastic (Young’s) modulus E were determined from the averaged stress–strain diagrams (σ(ε) curves) obtained for a series of 5–6 samples on a VRPS-1 testing machine operating at a deformation rate of 12 mm/min. The samples had a conventional double-pad shape with a working section length of 22 mm and a width of 1.9–2.0 mm.

The possible aggregation of fullerene molecules in the PMMA matrix was studied using X-ray diffraction in the small- and wide-angle X-ray scattering (SAXS and WAXS, respectively) modes. The SAXS and WAXS measurements were performed in the transmission geometry on KRM-1 and DRON-2 instruments, respectively, using Ni-filtered CuK<sub>α</sub> (λ = 0.1542 mm) radiation.

Figure 1 shows a series of averaged stress–strain diagrams obtained for uniaxial extension of PMMA films with various concentrations of C<sub>60</sub>. These data reveal the following features in the behavior of the mechanical properties of fullerene-doped PMMA films. The most significant change takes place upon the introduction of only 1% of fullerene, which leads to an approximately fivefold growth in the tensile strength and a twofold increase in both the elastic modulus and elongation at break. The strength keeps growing (albeit at a lower rate) with the further increase in the fullerene content. Substantial changes in the strength and elastic modulus were observed for the fullerene concentration increased up to about 3%. The further increase in the C<sub>60</sub> content to 5% brings practically no changes, while the introduction of 10% C<sub>60</sub> even leads to a decrease in...
the elastic modulus (at still high values of the elongation at break).

The SAXS (Fig. 2) and WAXS (Fig. 3) patterns remain virtually unchanged (to within the sensitivity of these methods) when the content of C$_{60}$ in the PMMA matrix increases up to 5%. The absence of visible changes in the character of X-ray diffraction in the samples containing 1–5% C$_{60}$ is probably related to a weak or completely absent aggregation of C$_{60}$ molecules, so that the majority of fullerene is dispersed on a molecular level. It is only the introduction of 10% C$_{60}$ that leads to an increase in intensity on the primary beam side of the SAXS patterns (Fig. 2), which is evidence for increasing inhomogeneity of the system. The WAXS patterns of these films exhibit the appearance of two sharp halos (or diffuse reflections), which is indicative of the nucleation of a crystalline fullerene phase.

The estimation of interplanar distances using the aforementioned diffuse reflections yields 0.7 and 0.5 nm. The values of interplanar spacings corresponding to the closest values calculated for C$_{60}$ crystals are given in the table. Only the second distance is manifested in the real diffractogram of C$_{60}$ fullerite by a strong (220) reflection from to a face-centered cubic (fcc) lattice (or the (110) reflection from a hexagonal close-packed (hcp) lattice). The other distance is not manifested in the diffractogram of crystalline C$_{60}$ despite the fact that it corresponds to the results of calculations for (200) reflections of the fcc lattice [6–10]; we believe that the absence of these reflections at room temperature is explained by chaotic rotations of C$_{60}$ molecules at $T > 260$ K [7–10].

According to the results of calculations, the (200) reflections belong to the most intense ones for the fcc C$_{60}$ lattice [6]. Therefore, the corresponding planes are involved in the nucleation of a crystalline C$_{60}$ phase. This process must also take place in solutions, but the presence of a PMMA matrix leads to “freezing” of the structure of nuclei, arrests their further growth, and prevents chaotic rotation of C$_{60}$ molecules. All these factors probably lead to the manifestation of scattering in the vicinity of (200) reflections of the