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# Polymer Nanocomposites Containing Fullerene C60 Nanofillers

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**Summary:** The effect of fulleroids (fullerene $C_{60}$, mixture of $C_{60}/C_{70}$ and fulleroids soot which used for fullerenes production) and carbon fillers (carbon black, graphite) on mechanical properties of polymer nanocomposites based on reactoplasts (epoxy resins) and thermoplasts (polyamide-12) was investigated. The nanocomposites were prepared by in situ polymerization. It was found that additives of these fillers did not influenced on the properties of reactoplasts. Therefore, the tensile modulus and tensile strength of thermoplast based polymer nanocomposites are improved by about 30-40% with loading of 0.02-0.08 fulleroids materials. Best results were obtained for a mixture of $C_{60}/C_{70}$.

**Keywords:** epoxy resins; fullerenes; nanocomposites; polyamide-12; tensile strength

## Introduction

Polymer nanocomposites have attracted enormous interest of the materials research scientists because these composites promise substantial improvement of mechanical properties at very low filler loadings. In addition, nanocomposites are compatible with conventional polymer processing, thus avoiding costly lay up required for the fabrication of conventional fiber-reinforced composites. Because of their excellent physical properties, nanosize in diameter, low density fullerene $C_{60}$ has been considered as ideal reinforcing fillers in polymer nanocomposites with multifunctions.[1] In this communication, we describe our investigation of nanocomposites comprised by polyamide 12 (PA-12) and epoxy resins (as matrices) and fullerene $C_{60}$ or fulleroid and carbon materials. The challenges for developing high-performance fullerene $C_{60}$/polymer nanocomposites are (i) homogeneous dispersion/solution of fullerene $C_{60}$ in the polymer matrix and (ii) strong interfacial interactions so as to effect efficient load transfer from the polymer matrix to the fullerene $C_{60}$.

## Experimental Part

### Materials

As fillers were used fullerene $C_{60}$ (purity 99.9%), mixture of fullerenes $C_{60}/C_{70}$ (containing 68% of fullerene $C_{60}$, 30% of fullerene $C_{70}$, high fullerenes (together about 2%)) used as starting materials for separating of individual fullerenes, and fullerene soot (contain of fullerenes about 10.5%) which was supplied from ZAO ILIP (Sankt Petersburg, Russia). Fullerene soot is ultra dispersed carbon forming at voltaic arc of graphite in inert gas atmosphere at fullerene production with particles diameter 0.5-2.0 μm.

Carbon black (trade mark K354) with middle diameter of initial aggregates of 28-35 nm and graphite (trade mark GMZ MG-1) with purity 99.9999) was supplied from FGUP NIIEI (Electrougli, Russia).

The epoxy resins used in this investigation was supplied from ZAO Chimexs Ltd (Russia) under the trade name XT-155A for resins and XT-155B for catalyst. The calculated amount of fullerenes was solved

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in catalyst and the resins and catalyst was ultrasonically mixed. The curing was conducted at temperature 100 °C for 2 h.

The PA-12 based polymer nanocomposites were obtained by polymerization of fine mechanically mixture of lauryl lactam (Aldrich) with calculated amount of filler using phosphoric acid as catalyst at 100 °C for 12 h by method.[2]

### Procedures

The density for all samples was obtained using a water displacement method. Tensile properties were measured using a compression method on UTS 10 (UTStestsysteme,Germany) at a compression rate of 2 mm/min or ultrasonically using a UK-10 PM instrument (USSR) at a frequency of 200 kHz. Test specimens for the tensile test were half cylinders with a length of 10-12 mm and diameter of 10 mm for compression method, whereas for the ultrasonic tests we used specimens in a form of cylinder with a length of 50 mm and diameter of 10 mm. 5 specimens were taken for each sample to obtain an average value.

## Results and Discussion

### Thermoset Matrix

Epoxy resins have been used in variety of applications. Although the advantage of the poly-functional reactivity of most epoxy systems leads to a high cross-linking density and meets the required matrix rigidity for applications, the brittleness and combustibility of these materials can be problematic and limit their potential applications. Additives or modifiers such as nanopowders, nano-tubes, and layered silicate clays[3–5] have been generally used to improve their physical and mechanical properties. It was found that if modifiers contain functional groups which can form chemical bonds with the polymer matrix, a very high degree of exfoliation of the nanofillers can be achieved, thereby enhancing the physical properties.[6]

It is known that catalyst for epoxy resin curing is polyamine. The fullerene $C_{60}$ light and quickly react with amine group and incorporate up to 48 such unit.[7] It leads to increase of local density of amino in curing agent. As results the obtained materials are brittle because of the local high cross-link-density. In the Table 1 and Figure 1 are given mechanical and acoustic properties of epoxy resins loading with fullerenes. As follows from Table 1, for all the tested samples Young's modulus is systematically higher than compression Young's modulus. This effect is well known for elastic properties of solid polymers. According to Vettegren et al.,[8]when a polymer sample is subjected to acoustic (high frequency) deformation, its strained interatomic bonds have no opportunity to relax; a sample behaves like a 'real solid' and exhibits a high elasticity value. Under static or low rate deformation, the strained interatomic bonds have enough time for

**Table 1.**
Effect of loading on mechanical properties of polymer nanocomposites based on thermoset matrix.

| Loading, wt% | Acoustic Young's modulus, GPa | Compression Young's modulus, GPa | Tensile strength σ, MPa | Contraction at compression ε, % |
|---|---|---|---|---|
| Pure XT-155 | 4.92 ± 0.10 | 1.86 ± 0.07 | 110 ± 5 | 7.0 ± 0.5 |
| $C_{60}$, 0.01 | 5.41 ± 0.10 | 1.86 ± 0.15 | 108 ± 5 | 8.0 ± 0.5 |
| 0.02 | 5.22 ± 0.10 | 1.83 ± 0.03 | 110 ± 4 | 6.5 ± 0.5 |
| 0.03 | 5.95 ± 0.10 | 1.81 ± 0.10 | 108 ± 5 | 7.0 ± 0.5 |
| 0.04 | 5.90 ± 0.10 | 1.53 ± 0.12 | 105 ± 5 | 7.0 ± 0.5 |
| 0.05 | 5.83 ± 0.10 | 1.86 ± 0.04 | 109 ± 4 | 7.0 ± 0.5 |
| 0.06 | 5.51 ± 0.10 | 1.70 ± 0.13 | 106 ± 3 | 7.0 ± 0.5 |
| $C_{60}$/$C_{70}$ mixture, 0.0 | 6.02 ± 0.10 | 1.89 ± 0.02 | 102 ± 2 | 8.0 ± 0.5 |
| 0.02 | 5.50 ± 0.10 | 1.64 ± 0.11 | 99 ± 2 | 8.0 ± 0.5 |
| 0.03 | 5.93 ± 0.10 | 1.59 ± 0.05 | 106 ± 8 | 8.0 ± 0.5 |
| 0.04 | 5.92 ± 0.10 | 1.83 ± 0.09 | 112 ± 4 | 8.0 ± 0.5 |
| 0.05 | 5.68 ± 0.10 | 1.78 ± 0.12 | 107 ± 5 | 8.0 ± 0.5 |

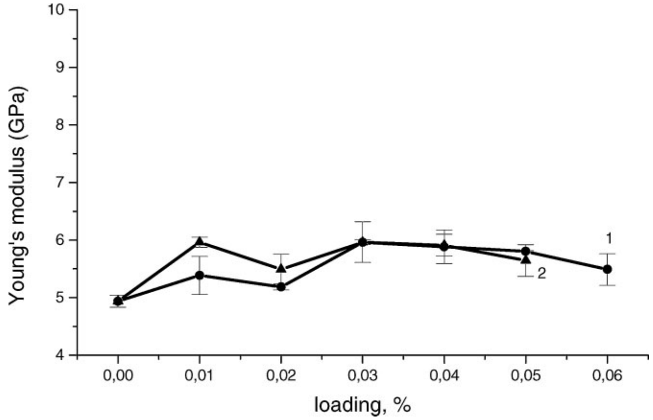

***Figure 1.***
Effect of pure fullerene $C_{60}$ (1) and of fullerenes $C_{60}/C_{70}$ mixture (2) content on acoustic Young's modulus of epoxy resins.

relaxation; this results to reduction of the Young's modulus value. It can be observed that there is no significant difference of the unmodified epoxy resins and the polymer composites reinforced with fullerenes. Compared with that of neat epoxy, the tensile strength, elongation at break, and modulus of nanocomposites were practically unchanged. This is attributed to the general infectivity of small spherical nanofillers at reinforcing hard materials or loss of fullerene nano nature as results chemical including it in polymer matrix. This analysis gives the first clue as to limited modulus enhancement of thermosets reinforced with nanoparticles.This observation is interesting as it indicates the modified fullerene $C_{60}$ do not change mechanical properties of this polymer system.

## Thermoplast Matrix

Modulus enhancement of polymer nanocomposites at loading depends on intrinsic properties of matrix and fillers as well as interactions between matrix and filler. Our fabrication strategy of thermoplast polymer nanocomposites synthesis starts by dispersing fillers in monomer followed by polymerization the monomers by standard method for lauryl lactam. It is known that at nanocomposites synthesis *in situ* polymerization have many advantages over other methods (solution and melt blending, mechanochemical pulverization etc).[9] Note that at cationic polymerization fullerene $C_{60}$ is chemically stable and stay unchanged. With increasing of fullerene $C_{60}$ concentration the color of composites is more and more orange. Observed that the films prepared from syndiotactic PMMA containing fullerene $C_{60}$ have the same color. X-ray diffraction analysis of the films revealed the formation of st-PMMA/$C_{60}$ inclusion complexes in which the $C_{60}$ molecules were encapsulated within a helical st-PMMA cavity.[10] PA-12 molecules a helical too and the size of helical cavity is about the same as st-PMMA. It allows us to conclude that the similar inclusion complex forms in the case of PA-12/$C_{60}$ .It clone of polymer and fullerene $C_{60}$ and may to clarify it reinforced effect.

It was supported by solving composite in benzyl alcohol and recording UV spectrum. The original spectrum of fullerene $C_{60}$ was obtained. The distinct solvatochromic effect was observed for nanocomposites. Thus the fullerene $C_{60}$ is soluble in PA-12 matrix and forms true solution.

The mechanical properties of thermoplastic nanocomposites were investigated. The tensile mechanical properties of these composites are summarized in Table 2 and Figures 2- 3. As fillers were used fullerene $C_{60}$, mixture of fullerenes $C_{60}/C_{70}$,

**Table 2.**
Effect of loading on mechanical properties of polymer nanocomposites based on thermoplast matrix.

| Loading, wt% | Acoustic Young's modulus, GPa | Compression Young's modulus, GPa | Tensile strength σ, MPa | Contraction at compression ε, % |
|---|---|---|---|---|
| Pure PA-12 | 2.42 ± 0.19 | 0.846 ± 0.070 | 67 ± 5 | 16 ± 1 |
| C60, 0.02 | 2.61 ± 0.06 | 1.007 ± 0.043 | 72 ± 5 | 20 ± 2 |
| 0.04 | 2.96 ± 0.08 | 0.978 ± 92 | 69 ± 5 | 17 ± 1 |
| 0.06 | 2.84 ± 0.12 | 0.998 ± 0.071 | 71 ± 6 | 22 ± 2 |
| 0.08 | 2.48 ± 0.06 | 1.035 ± 0.079 | 68 ± 4 | 28 ± 2 |
| $C_{60}/C_{70}$ mixture,0.02 | 3.44 ± 0.13 | 1.087 ± 0.019 | 84 ± 5 | 32 ± 2 |
| 0.04 | 3.30 ± 0.18 | 1.012 ± 0.045 | 75 ± 5 | 19 ± 1 |
| 0.06 | 3.51 ± 0.14 | 0.820 ± 0.038 | 110 ± 5 | 30 ± 2 |
| 0.08 | 3.41 ± 0.16 | 1.081 ± 0.065 | 96 | 23 ± 3 |
| graphite, 0.1 | 3.49 ± 0.10 | 1.075 ± 0.058 | 67 ± 5 | 14 ± 1 |
| 0.2 | 3.16 ± 0.18 | 0.947 ± 0.016 | 65 ± 10 | 14 ± 1 |
| 0.5 | 3.00 ± 0.10 | 0.962 ±0.018 | 111 | 39 ± 2 |
| Carbon black 0.1 | 3.20 ± 0.11 | 875 ± 0.049 | 71± 1 | 17 ± 2 |
| 0.2 | 2.80 ± 0.20 | 0.969 ± 0.064 | 85± 8 | 34 ± 2 |
| 0.5 | 2.90 ± 0.05 | 0.746 ± 0.042 | 100 ± 11 | 46 ± 2 |
| Fulleroid soot 0.1 | 2.98 ± 0.07 | 0.725 ± 0.078 | 85 ± 15 | 42 ± 2 |
| 0.2 | 3.07 ± 0.13 | 0.899 ± 0.092 | 110 | 33 ± 2 |
| 0.5 | 2.65 ± 0.21 | 1.007 ± 0.026 | 66 ± 2 | 24 ± 2 |

fullerene soot and for comparison such traditional fillers as carbon black and graphite. Compared with that of neat PA-12 the Young's modulus were increased at 20-40% for all polymer composites. The more enhanced tensile mechanical properties were found for polymer nanocomposites enforced by fulerene $C_{60}/C_{70}$ mixture. It may be mainly attributed to the combination of two factors. The fullerene $C_{60}$ is soluble in polymer matrix but fullurene $C_{70}$ is not. Insoluble fillers have a tendency to form agglomerates and as results poor dispersed in polymer matrix. It is known that combination loading of two fillers one of which is good dispersed and other one poor leads to more enhanced mechanical properties.[11] Overall, the addition of fullerene fillers to the PA-12 matrix had a more profound effect than loading such fillers as carbon black, graphite, and fullerene soot. This is attributed to the better dispersion and changes in morphology, which is caused by the presence of fullerene $C_{60}$.

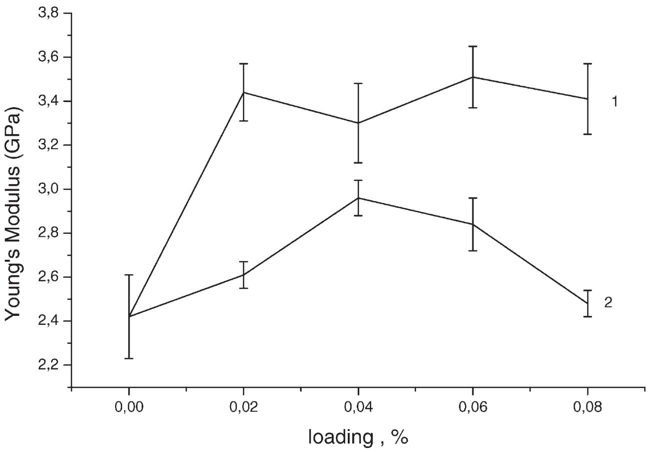

**Figure 2.**
Effect of mixture of fullerene $C_{60}/C_{70}$ (1) and pure fullerenes $C_{60}$ (2) content on acoustic Young's modulus of PA-12.

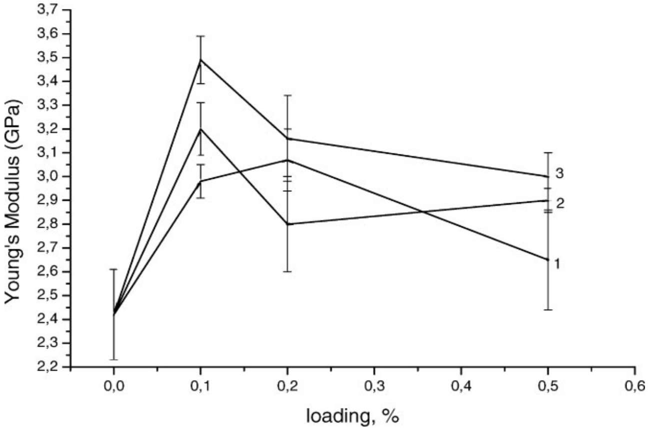

***Figure 3.***
Effect of fulleroid soot (1), carbon black (2) and graphite (3) content on acoustic Young's modulus of PA-12.

## Conclusion

Polymer nanocomposites loading with fulleroid materials were synthesized and its mechanical properties were studied. Relationships between loading and mechanical performance were established using tensile testing. It was found that the fullerenes and fulleroid materials are more efficient in the reinforcement of soft polymers (PA-12) compared to hard polymers (epoxy resins). Tensile analysis of PA-12 based polymer nanocomposites revealed the tensile modulus and tensile strength are improved by about 30-40% with loading of 0.02-0.08 fulleroids materials. Best results were obtained for a mixture of $C_{60}/C_{70}$.

[1] M. Prato, *J.Mater.Chem.* **1997**, *7*, 1097.

[2] Ger.431981 **1964**, BASF AG, invs.: J. Kunde, H. Wilhelm, F. Mertes, E. Schwartz,

[3] H. J. Yu, L. Wang, Q. Shi, G. H. Jiang, Z. R. Zhao, X. C. Dong, *Prog. Org. Coat.* **2006**, *55*, 296.

[4] Y. Ye, H. Chen, J. Wu, L. Ye, *Polymer.* **2007**, *48*, 6426.

[5] D. P. R. Kint, G. Seeley, M. Gio-Batta, A. N. Burgess, *J. Macromol. Sci. Part B. Phys.* **2005**, *44*, 1021.

[6] Y. W. Chen-Yang, Y. K. Lee, Y. T. Chen, J. C. Wu, *Polymer.* **2007**, *48*, 2969.

[7] A. Hirsch, "*The chemistry of fullerenes*", Thieme, New York 1994, 468 p.

[8] V. I. Vettegren, S. V. Bronnikov, L. N. Korzhavin, S. Ya. Frenkel, *J. Macromol. Sci. Part B. Phys.* **1990**, *29*, 285.

[9] M. Moniruzzaman, K. I. Winey, *Macromolecules.* **2006**, *39*, 5194.

[10] M. Kawauchi, T. Kawauchi, T. Takeichi, *Macromolecules.* **2009**, *42*, 6136.

[11] Yu. S. Lipatov, "*Physico-chemical background of polymer loading*", Chimia, Moscow **1991**, 260 p (In Russian).