



Reinforcement of Bisphenol-F epoxy resin composites with fluorinated carbon nanotubes

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ABSTRACT

Pristine and fluorinated carbon nanotubes (CNT) were studied by FTIR, TGA, Raman spectroscopy, transmission and scanning electron microscopy. Influence of fluorination on CNT dispersion in epoxy resin was studied by the dynamic light scattering. It was shown that fluorination favoured CNT dispersion in epoxy matrix. Mechanical properties (tensile and flexural strength and modulus, abrasion resistance, thermal diffusivity and heat conductivity), thermal stability and fracture texture of epoxy resin (Bisphenol-F type) polymer composites with added unmodified and fluorinated CNT were studied. Insertion of pristine and fluorinated CNT into epoxy matrix did not influence composites thermal stability below 275 °C and resulted in a very small worsening of thermal stability over 275–375 °C range. Insertion of both pristine and fluorinated CNT into epoxy matrix resulted in composites reinforcement but fluorinated CNT were more efficient in reinforcement than pristine CNT. The best reinforcement was obtained for 0.1 wt % CNT fluorinated at 150 °C. Tensile strength and modulus were increased by 50% and 74% respectively, flexural strength and modulus were increased by 60 and 66% respectively. Obtained in the frames of the current research results on a relative reinforcement exceed data from available literature data. Insertion of both pristine and fluorinated CNT into epoxy matrix did not improve composite conductivity. Insertion of 0.5 wt % fluorinated CNT into composites resulted in +25% increase of the thermal diffusivity. Fluorinated CNT are more effective than pristine CNT. Presence of both pristine and fluorinated CNT did not influence thermal conductivity. Fluorinated CNT were more effective in abrasion decrease than pristine CNT. The best results – abrasion decrease by 33% – was obtained for the composites with 0.1 wt % fluorinated CNT.

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1. Introduction

At present time carbon nanomaterials especially single-walled (SWCNT) and multi-walled (MWCNT) carbon nanotubes are widely used as fillers to reinforce polymer composites [1–5]. In many cases low polarity of the carbon nanomaterials surface and also polymer matrix adhesion between fillers and polymer matrix

is too low to provide marked reinforcement [6–8]. Moreover, carbon nanotubes (CNT) tend to agglomerate in a polymer matrix [9]. To increase surface energy and adhesion properties fillers should be modified. A wide variety of modification methods are applied to modify carbon nanomaterials: plasma/plasma chemical treatment, monomers grafting, acid treatment, etc. Review on the influence of those methods on the reinforcing properties of various fillers will be presented below. One of the most prospective methods is the direct fluorination, i.e. treatment with gaseous fluorine at elevated temperature [10–15]. For the case of thermoplastic polymers insertion of fluorinated SWCNT into polymer matrix (1, 0.5 and 10 wt% of SWCNT in polyethyleneoxide, polyamide-6 and

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polypropylene respectively) resulted in increase of the tensile strength by a factor of 3, 3.3 and 2.7 respectively [16–18]. Module was highly increased also. The effect of nonfluorinated SWCNT was much less pronounced. It was shown [19,20] that fluorinated multiwalled CNT are effective in reinforcement of bulk ultrahigh molecular weight polyethylene and Bisphenol-A epoxy composites. In Ref. [20] epoxy resin (diglycidyl ether bisphenol-A type) polymer composites with added unmodified and fluorinated CNT were studied by FTIR, TGA, DSC and electron microscopy. Composites tensile and flexural strength were measured. Insertion of 0.1 wt % of CNT fluorinated at 150 °C into polymer matrix resulted in the composite tensile strength increase by 35% as compared with unfilled composites. Flexural strength of composite filled with 0.2 wt% fluorinated at 150 °C CNT was increased by 58% as compared with unfilled composite. Unmodified CNT were less effective in composite tensile and flexural strength improvement as compared with fluorinated CNT. In the present research we have used the same reinforcing nanoparticles as in Ref. [20] (namely fluorinated CNT) but another polymer matrix – epoxy resin of bisphenol-F type was used. The fluorinated CNT were used for Bisphenol-F epoxy composites for the first time. In Ref. [1] bisphenol A epichlorohydrin-based epoxy resin was reinforced by insertion of 0.5 wt % of single-, double- and multiwalled CNT mixture in a laminate composed from epoxy resin and carbon fabric. Reinforcement has been resulted in an increase of the tensile strength and module by 18 and 24% respectively.

2. Materials and methods

2.1. Materials

Multi-walled carbon nanotubes were purchased from “Nanotechcenter Ltd” (Tambov, Russia). Their internal and external diameters were equal to 4–8 nm and 8–15 nm and length exceeded 2 μm. Total amount of admixtures after purification did not exceed 1%. CCP Epoxy Resin BFE-170 Bisphenol-F type (Chang Chun Plastics Co., LTD, China) and polyaminoamide L-19 hardener (CHIMEX Limited, Russia). Total amount of admixtures after purification did not exceed 1%. CCP Epoxy Resin was used to fabricate composites. Fluorine had less than 0.1 vol % of admixtures (mainly O₂).

2.2. CNT treatment

CNT fluorination has been carried out in a closed reaction vessel at 0.7 bar fluorine pressure. That pressure was chosen for the following reason. Increase of fluorine pressure resulted in fluorination rate acceleration but at higher than 0.8–0.9 bar pressure local ignitions took place because the heat released in the reaction cannot be quickly dissipated by gas phase or reactor walls. Also previously we have found that at treatment temperature around 150–200 °C the CNT structure was not disturbed and rather high degree of fluorination (CF_{0.2}–CF_{0.4}) could be reached [11]. At the temperature above 250 °C some destruction of fluorinated CNT was observed [15]. Treatment duration was varied over 10 min to 2 h. It was shown that fluorination degree at 2 h treatment markedly exceeded one at 150 °C so 2 h treatment duration was chosen. Fluorine was inserted into heated reactor and its pressure was maintained constant within accuracy 5%.

2.3. Composites fabrication

Sample for testing were fabricated in “Lepta-550-30” silicon compound casting moulds. Epoxy resin was mixed with hardener “Polyam-B10” (100 g of resin and 81.1 g of hardener) in «EXAKT 80E » three-roll mill and undergone sonication, evacuated,

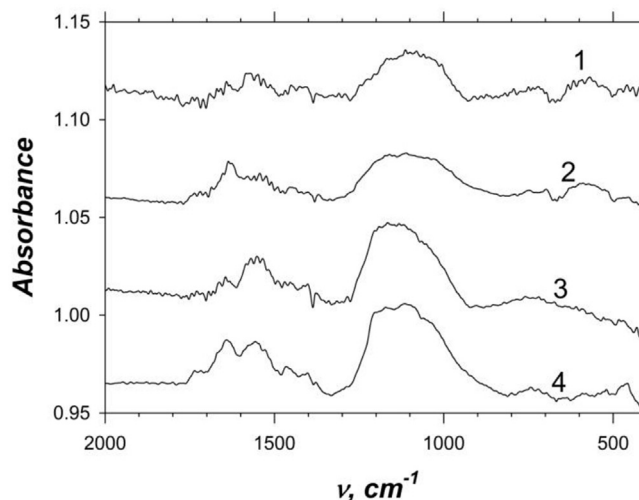


Fig. 1. FTIR spectra of virgin (1) and fluorinated with undiluted fluorine at pressure 0.7 bar. Treatment temperature and duration were as follows: 150 °C and 2 h (2), 150 °C and 10 min (3), 250 °C and 2 h (4).

transferred to casting moulds, evacuated and was cured during 12 h at 25 °C, 6 h at 40 °C and 6 h at 100 °C.

2.4. Testing procedures

To measure IR spectra of KBr pellets containing CNTs FTIR spectrometer FT-02 Lumex Ltd, Saint Petersburg, Russia was used. 1000 scans at 4 cm⁻¹ resolution were collected to measure 1 spectrum over 4000–400 cm⁻¹ spectral range. Texture of composite fracture was studied by scanning electron microscope JEOL JSM-6610LV at accelerating potential 20 kV. To avoid charge accumulation polymer surface was coated with Pt layer several nm in thickness. The CNT structure was studied by transmitting electron microscope JEOL JEM-1400. The testing CNT were dispersed in ethanol by FisherScientificFB 15048 dispergator and deposited onto copper grids. STA 449 F3 Jupiter (Netzsch) was used to study thermal stability. Heating rate was equal to 10 °C per minute over room temperature to 1000 °C range. Mechanical properties of

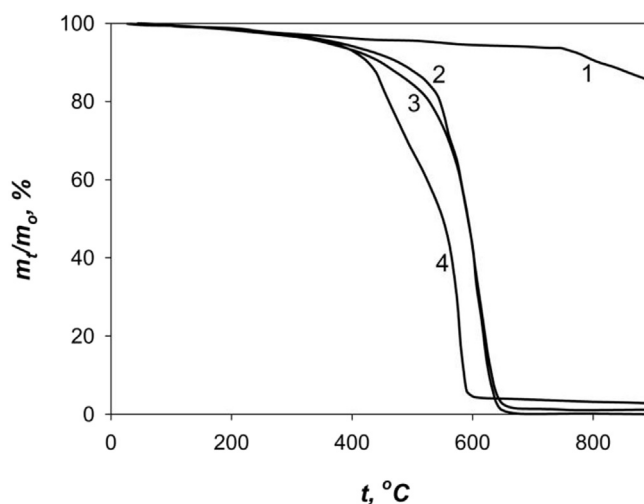


Fig. 2. TGA data measured in argon environment for pristine (1) and fluorinated with fluorine pressure 0.7 bar CNT (2–4). Temperature and treatment duration: 150 °C and 2 h (2), 150 °C and 10 min (3), 250 °C and 2 h (4).

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