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Reinforcement of epoxy resin composites with fluorinated carbon nanotubes

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ABSTRACT

Epoxy resin (diglycidyl ether bisphenol-A type) polymer composites with added unmodified and fluorinated carbon nanotubes (CNTs) were studied by FTIR, TGA, DSC and electron microscopy. Composites tensile and flexural strength were measured. CNTs fluorination markedly (by a factor of 2.26) increased its specific surface. Fluorination did not influence CNTs thermal stability below 260 °C and did not worsen thermal stability of filled composites. Insertion of 0.1 wt% of CNTs fluorinated at 150 °C into polymer matrix resulted in the composite tensile strength increase to 89.6 ± 4.1 MPa (35% increase as compared with unfilled composites). Flexural strength of composite filled with 0.2 wt% fluorinated at 150 °C CNTs was increased to 199.7 ± 4.8 MPa (+58% as compared with unfilled composite). Obtained reinforcement values exceeded all the available literature reinforcement data reported for epoxy composites based on epoxy resins similar to used in the current project. Unmodified CNTs were less effective in composite tensile and flexural strength improvement as compared with fluorinated CNTs. Insertion of fluorinated CNTs into a polymer matrix increased glassy temperature and did not influence the composites thermal stability. Surface of composites cuts was studied by electron microscopy technique. The reinforced composites can be applied in several industries: aviation, automotive, wind turbine propeller blades, for producing yachts and boats etc.

1. Introduction

At present time carbon nanomaterials especially single-walled (SWCNTs) and multi-walled (MWCNTs) carbon nanotubes are widely used as fillers to reinforce polymer composites [1]. 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 [2–4]. Moreover, CNTs tend to agglomerate in a polymer matrix [5]. 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 [6–11]. For the case of thermoplastic polymers insertion of fluorinated SWCNTs into polymer matrix (1, 0.5 and 10 wt% of SWCNTs in polyethyleneoxide, polyamide-6 and polypropylene respectively) resulted in increase of the tensile strength by a factor of 3, 3.3 and 2.7 respectively [12–14]. Module was highly increased also. The effect of nonfluorinated SWCNTs was much less pronounced. In [1] bisphenol A epichlorohydrin-based epoxy resin (similar to used in our research) was reinforced by insertion of 0.5 wt% of single-, double- and multiwalled CNTs 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

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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%. Epoxy resin ED-22 (GOST 10587-84) based on diglycidyl ether of bisphenol-A type and "Polyam-B10" hardener were used to fabricate composites. Fluorine had less than 0.1 vol% of admixtures (mainly O_2).

2.2. CNTs treatment

CNTs fluorination has been carried out in a closed reaction vessel at 0.8–0.9 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 CNTs structure was not disturbed and rather high degree of fluorination ($CF_{0.2}$–$CF_{0.4}$) could be reached [7]. At the temperature above 250 °C some destruction of fluorinated CNTs was observed [11]. 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%. Pristine CNTs were designated as "TM". Index "F" indicates that the CNTs were fluorinated. Samples TM-F26, TM-F28 and TM-F30 were treated at temperatures 250, 150 and 100 °C respectively. Treatment duration was equal to 2 h (TM-F26, TM-F28) and 10 min (TM-F30).

2.3. Composites fabrication

Sample for testing were fabricated in "Lepta-550-40" silicon compound casting moulds. Composites were mixed in «EXAKT 80E» three-roll mill and undergone sonication. Epoxy resin was mixed with hardener "Polyam-B10", evacuated, transferred to casting moulds, evacuated and was cured inside heated thermostate during 5 h. The composites composition was designated as ER + (percentage of filler) where "ER" means pristine epoxy composition (epoxy resin + hardener).

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. Influence of fluorination on the CNTs surface chemical composition was studied by XPS spectrometer PHI 5500 ESCA (Perkin Elmer). Texture of composite cuts 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 1–2 nm in thickness. TGA Instruments Q600 was used to study thermal stability in air flow. Heating rate was equal to 10 °C per minute over room temperature to 1000 °C range. DSC was performed by calorimeters NETZSCH DSC204F1 and STA 449F3 Jupiter (Netzsch) in Ar atmosphere with heating rate 10 °C per minute over 35–420 °C range. Mechanical properties of composites were investigated by testing machine "Testometric M350-5AT" at 50 mm/min (tensile strength) and 20 mm/min (flexural strength). Specific surface was measured by sorption meter SORBTOMETR-M (Russia). BET method (GOST 2340-90) and multipoint method STSA (ASTM D5816) were applied.

3. Results and discussion

3.1. FTIR spectroscopy

IR spectra of virgin and fluorinated CNTs are shown in Fig. 1. Baseline was corrected by application of multi-point correction method from "GRAMS-32" software. All the spectra in Fig. 1 were corrected with respect to KBr absorption. Fluorination of CNTs resulted in a formation of a wide diffuse band over 1300–900 cm^{-1} with maximum at 1200 cm^{-1} which is due to absorption of covalent C—F_x bonds [7–8,15] and in an increase of the 1720–1700 cm^{-1} band which can be attributed to C=O groups formation due to an oxygen admixture in used fluorine [16]. Intensity of that band is increased with treatment temperature which can be due to increase of the structure defect amount.

3.2. Influence of fluorination on the CNTs specific surface

CNTs fluorination resulted in a marked increase of CNTs specific surface. Pristine CNTs have specific surface equal to 105 m^2/g. CNTs treatment at 150 and 250 °C resulted in a specific surface increase to 238 (increased by a factor of 2.26 as compared with pristine CNTs) and 166 m^2/g values. Increase of the CNTs specific surface could enhance the reinforcing effect of CNTs which will be used as composites fillers.

3.3. XPS study

XPS spectra of pristine and fluorinated CNTs are shown in Fig. 2. Several bands can be separated (mixture of Gauss and Lorentz functions was applied for fitting) and assigned [17,18]. The resulting fitting line is not presented at the Fig. 2 because it coincides with the experimentally measured spectrum (dotted line) within accuracy of the line width. Areas of peaks 1, 2, 3 and 4 correspond to 74:4:7:15 sequence. Band 1 corresponds to C atoms surrounded only by C atoms without attached F atoms. Bands 2 relates probably to C atom without attached F atom surrounded by three (sp^2 hybridization) or four C atoms (sp^3 hybridization) with attached F atom. Band 3 corresponds to C atom with attached F atom surrounded with two C atoms with attached F atoms. Band 4 corresponds to C atom with attached F atom surrounded with three C atoms with attached F atoms. Chemical composition C:O:F of CNTs are as follows: 98:2:0 for the pristine CNTs and 78:1.3:20.7 for fluorinated at 150 °C CNTs (TM-F28).

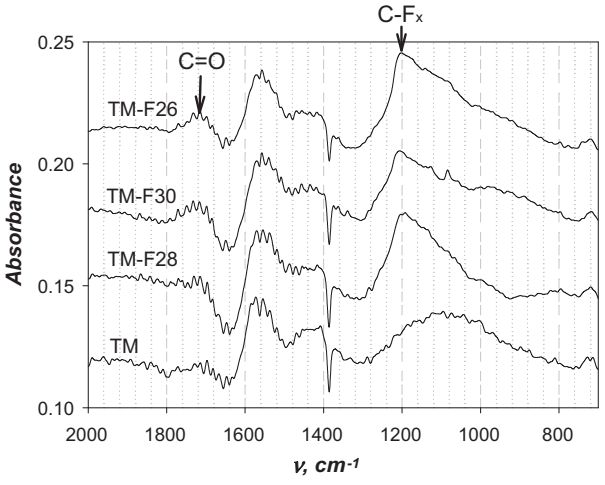

Fig. 1. Spectra of virgin (TM) and fluorinated (TM-F26, TM-F28, TM-F30) CNTs. Treatment conditions are indicated in the point 2.2.