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 weight % 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 weight % 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.

Keywords: *Carbon nanotubes, Polymers, Particle-reinforced composites, Mechanical properties, Direct fluorination*

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 weight % 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 weight % 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 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 volume % 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 ($CF_{0.2}$ to $CF_{0.4}$) 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 hours. It was shown that fluorination degree at 2 hours treatment markedly exceeded one at 150°C so 2 hours 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 hours (TM-F26, TM-F28) and 10 minutes (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 hours. 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 to 420°C range. Mechanical properties of composites were investigated by testing machine "Testometric M350-5AT" at 50 mm/minute (tensile strength) and 20 mm/minute (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 the 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.

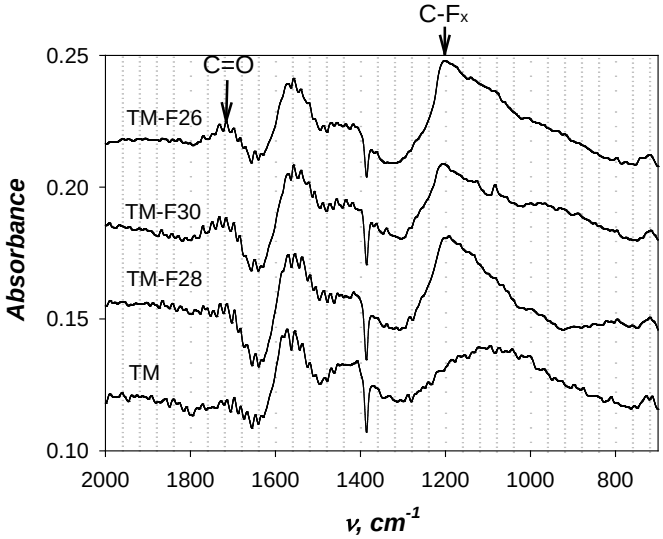

Fig.1. Spectra of virgin (TM) and fluorinated (TM-F26, TM-F28, TM-F30) CNTs. Treatment conditions are indicated in the point 2.2.

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^oC 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 the figure 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 figure 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^oC CNTs (TM-F28).

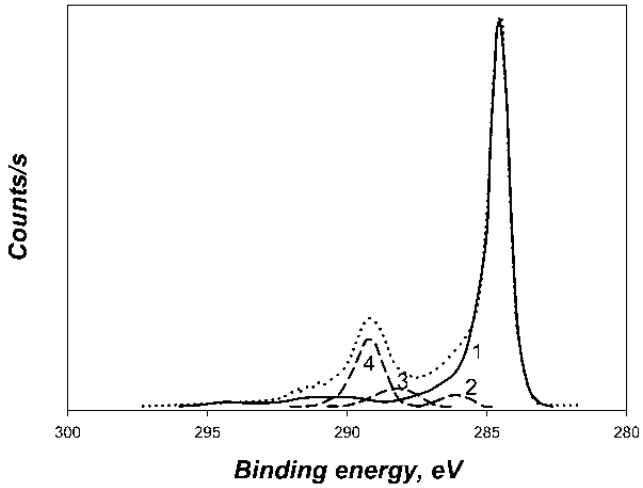

Figure 2. XPS spectra of pristine (solid line) and fluorinated at 150°C (1, dotted line) CNTs. 2, 3 and 4 – fitted bands for fluorinated CNTs. The resulting fitting spectra is not presented at the figure 2 because it coincides with the experimentally measured spectrum (dotted line) within accuracy of the line width.

3.4. TGA of virgin and fluorinated CNTs.

TGA results for virgin and fluorinated CNTs measured in air are shown in the Fig.3. CNTs fluorinated at 250°C are much less stable as compared with CNTs fluorinated at 100-150°C. Pristine CNTs are more stable than fluorinated ones because C-C triple bond energy in CNTs markedly exceeds C-F bond energy. Below 250-300°C thermal stability of pristine and fluorinated CNTs are close each to other. Unfilled composites started to degrade at 250°C (see figure 11 below) so fluorination should not influence thermal stability of filled composites below 250°C.

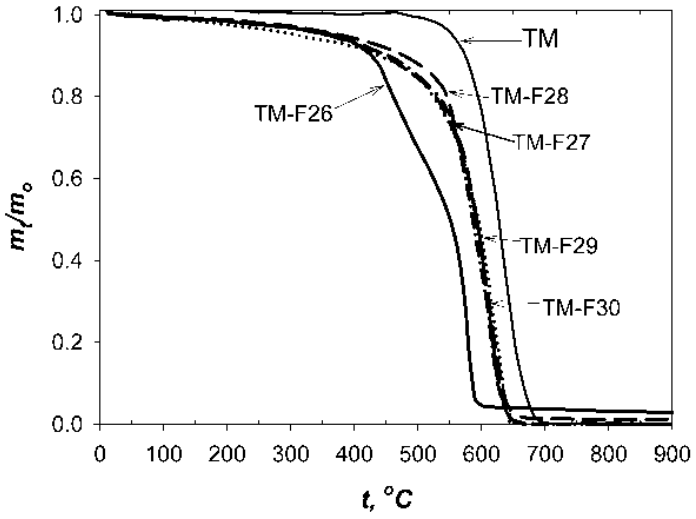

Fig.3. TGA of virgin CNTs and fluorinated CNTs (TM-F26 - TM-F30).

3.5. SEM data of composites fracture.

Epoxy resin is rather fragile polymer material so its destruction is accompanied with localization of stresses on its surface or inside its bulk. The stress is localized in defects region and stress increase results in a formation and rise of cracks. The texture of cured unfilled epoxy resin is rather flat (figs. 4-5). The sample destruction via fragile mechanism was initiated by cracks formation (fig.4, left top corner of the left photo) which have flake-like structure (fig.4). Except destruction via fragile mechanism there exist local regions destructed via flow mechanism (fig.5) which can be due to a lowered concentration of polymer chains crosslinks and higher plasticity of cured epoxy resin.

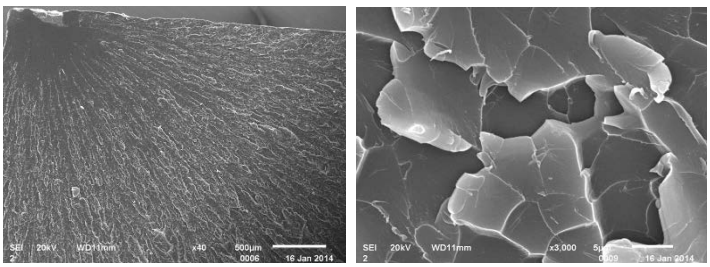

Fig.4. Cut of the destructed unfilled composite. Scale from left to right: 500 and 5 μm.

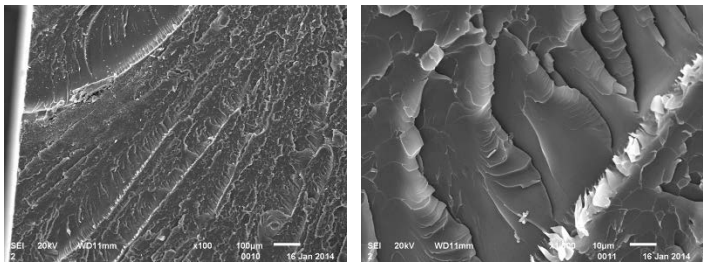

Fig.5. Cut of the unfilled composite destructed via flow mechanism. Scale from left to right: 100 и 10 μm.

Destruction mechanism of ER+0.1%TM composite (epoxy resin matrix with 0.1 weight % of virgin CNTs) is similar to one of unfilled composite (fig.6). Flake-like relief (which is probably due to CNTs covered with polymer matrix material) was observed on the flakes surface contrary to unfilled composites. CNTs directed outside of the composite bulk were not observed. It might be due to rather good adhesion between CNTs and polymer matrix. Destruction via flow mechanism is illustrated in the fig.7. In some places finger-like structures arose due to a polymer bulk pulling. Composite plasticization can be explained if CNTs are considered as a solid-phages hardener [19]. In this case amount of crosslinks at CNTs-polymer matrix boundary layer will be reduced and that region will possess higher mobility.

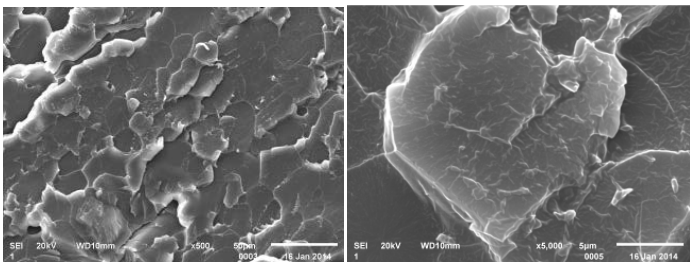

Fig.6. Cut of the polymer composite containing 0.1 weight % of virgin CNTs. Destruction via fragile mechanism. Scale from left to right: 50 and 5 μm.

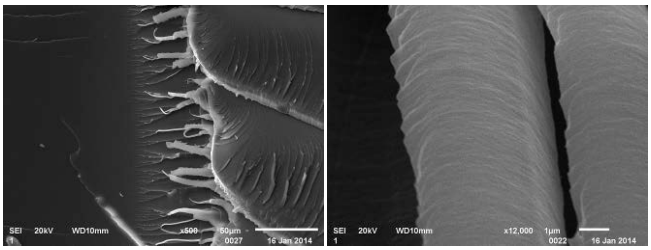

Fig.7. Cut of the polymer composite containing 0.1 weight % of virgin CNTs. Destruction via flow mechanism. Scale from left to right: 50 and 1 μm.

For the case of composite containing 0.5 weight % of virgin CNTs the prevailing mechanism of destruction became plastic destruction (via flow mechanism), as shown in fig.8. Flakes boundaries became less sharp and their size tends to decrease. Finger-like structures (similar to fig.7) were well visualized. At high resolution CNTs agglomerates (5-7 μm in size) became visible. They are placed above composite surface. It means that CNTs were removed from the bulk as a whole without their destruction. Hence at least part of virgin CNTs did not take part in composite reinforcement.

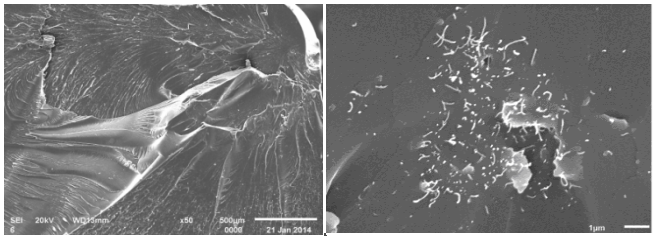

Fig.8. Cut of the polymer composite containing 0.5 weight % of virgin CNTs. Scale from left to right: 500 and 1 μm.

Composite cut with inserted 0.1% fluorinated CNTs (TM-F28) is to some extent similar to composite with 0.5% of virgin CNTs but finger-like structures were not detected (fig. 9). It can be due to CNTs surface functionalization which resulted in number of crosslinking between CNTs and epoxy bulk increase as compared to composites filled with virgin CNTs. So plasticity of the epoxy bulk can be decreased as compared with epoxy filled with virgin CNTs.

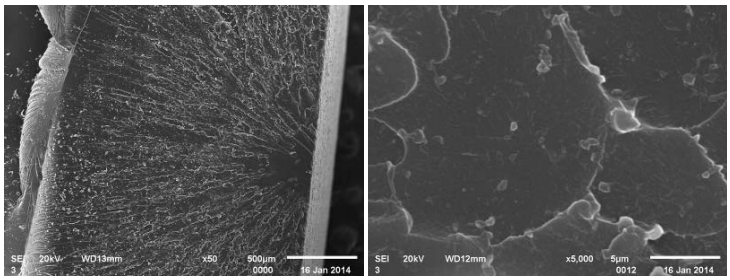

Fig.9. Cut of the polymer composite containing 0.1 weight % fluorinated CNTs (TM-F28). Scale from left to right: 500 and 5 μm.

Surface of the composite cut with inserted 0.5% of fluorinated CNTs (TM-F28) is shown in the fig.10. The surface has the most roughness as compared with other studied composites. “Flakes” are of large size and longitudinal shape. Finger-like structures were not observed. CNTs outside of the composite

bulk were not detected. It means that fluorinated CNTs exhibit good adhesion with epoxy resin and during destruction are not removed from the polymer bulk.

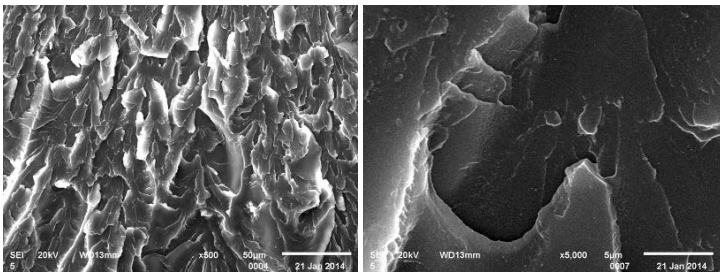

Fig.10. Cut of the polymer composite containing 0.5 weight % of fluorinated CNTs (TMF-28). Scale from left to right: 50 and 5 μm.

3.6. TGA and DSC of composites.

TGA data of composites are shown in the fig.11. At temperature below 260°C CNTs additions does not influence (and does not worsen) composite thermal stability.

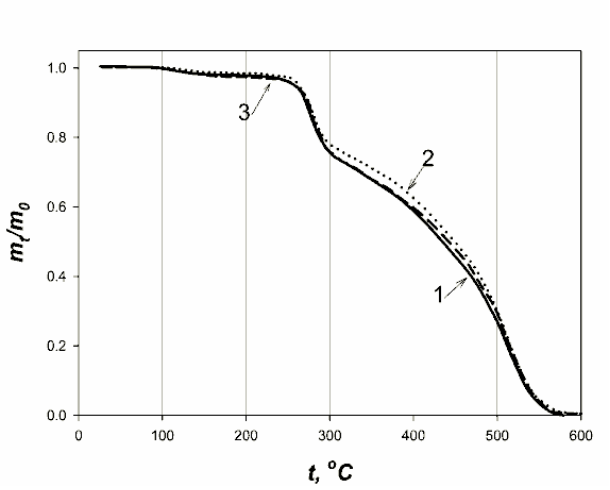

Fig.11. TGA of composites in air environment. 1 (solid ine) - unfilled composite, 2 (dotted line) and 3 (dashed line) – composite filled with 0.1 weight % of virgin CNTs and with 0.1 weight % fluorinated at 150°C CNTs respectively.

Composites glass transition temperature can be calculated from the DSC data shown in the fig.12. For all the composites transition over glassy temperature takes place not at a point but over some temperature interval. So the middle of a flexure on the DSC curves was assigned to a glassy temperature [20]. For all the composites (except ER+0.1%TM) insertion of CNTs resulted in glassy temperature increase. Unfilled epoxy resin has a glass temperature 110.9°C, composites ER+0.1%TM and 0.5%TM - 108.7 and 125°C glass temperature. Composites filled with fluorinated CNTs exhibited 113.0°C (ER+0.1%TM-F28) and 121.3°C (ER+0.5%TM-F28). According to [19] CNTs insertion into epoxy matrix resulted in chemical conversion degree increase and improved net of chemical crosslinks formation. It is evident that filled composites will possess increased glassy temperature as compared with unfilled ones.

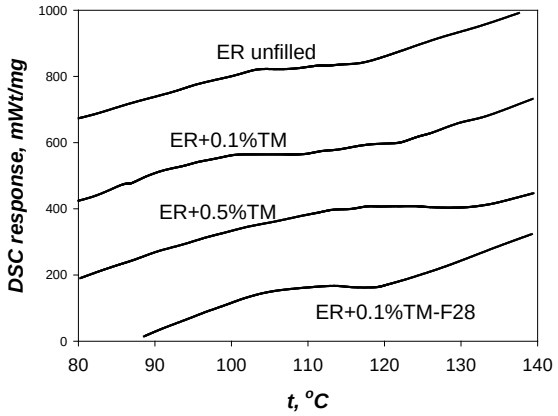

Fig.12. DSC data of composites. Composites composition is indicated in the graph.

3.7. Mechanical properties of composites.

3.7.1. Tensile strength.

Tensile strength of composites is shown in the fig.13 together with available literature data for the composites based on the epoxy resin Bisphenol-A type (similar to used in the current research) are shown. In [5, 19, 21-32] the following fillers were used: carbon nanotubes and nanofibers (pristine, silanizied, carboxilated, aminated, plasma-modified, treated with acids), soot, graphite, organic clay, ABS-copolymer. In our research insertion of 0.01% of both pristine and fluorinated CNTs resulted in a tensile strength decrease. Composites with 0.1% of fluorinated at 150°C CNTs (TM type) exhibited maximum tensile strength – 89.6±4.1 MPa (for the unfilled epoxy tensile strength was equal to 66.1±2.4 MPa) and exceeded one for unfilled composite by 35%. Increase of the fluorinated CNTs content to 0.5% resulted in a tensile strength drop to 60.8±3.6 MPa. Increase of CNTs fluorinating temperature to 250°C did not result in reinforcement of composites. For the case of pristine CNTs maximum reinforcement effect was observed for 0.5% CNTs: tensile strength 84.0±2.3 MPa, which was smaller than one for the case of 0.1% fluorinated CNTs addition. Maximum tensile strength value for reinforced composites based on bisphenol-A epoxy resin known from literature data is equal to 90 ± 6.8 MPa [27]. That value was obtained for 6.4% CNFs content. We have reached the same reinforcement using 64 times smaller filler amount (i.e. 0.1%). Modulus value 1644±76 MPa was reached for the case of 0.1% fluorinated CNTs addition (+33% as compared with unfilled composite.

3.7.2. Flexural strength

Influence of fluorinated CNTs addition on composite flexural strength is shown in the fig.14 together with literature data. According to literature review data [33-38] maximum reported in literature flexural strength value for composites based on bisphenol-A epoxy resin is equal to 139.7±1.98 MPa [38]. Fig. 14 presents the experimental results on the composites flexural strength. Maximum flexural strength value 199.7±4.8 MPa (+58% increase with respect to unfilled composite) was obtained in our research for composite with 0.2 weight % CNTs fluorinated at 150°C. Obtained value exceeds maximum reported in literature value by 43% for bisphenol-A composites similar to those used in our research. But obtained in [38] reinforcement was reached for 5 weight % filler concentration as compared with 0.2% in our research. Module of composite with 0.2% fluorinated at 150°C CNTs was equal to 3603±86 MPa and exceeded module for unfilled composite by 13%. Pristine CNTs are less effective in reinforcement: maximum flexural strength was obtained for epoxy composite contained 0.5 weight % pristine CNTs: 152.3±8.1 MPa (module 3217±170 MPa).

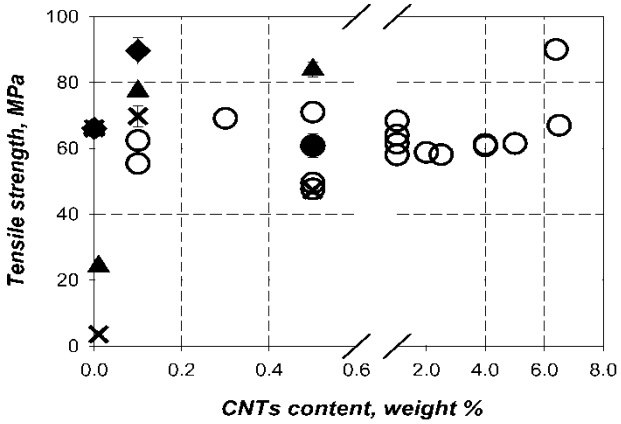

Fig.13. Tensile strength (MPa) vs CNTs content in epoxy resin (weight %). Triangles – pristine CNTs addition, squares – TMF-28 addition (CNTs fluorinated at 150°C), crosses – TM-F26 addition (CNTs fluorinated at 250°C). Open circles – literature data [5, 17-29] for Bisphenol-A based composites similar to one used in the current research.

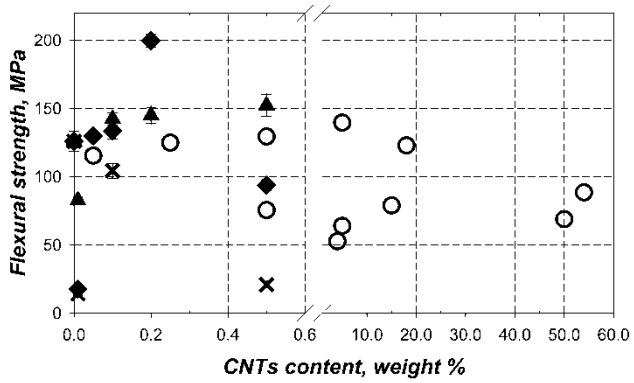

Fig.14. Flexural strength (MPa) vs CNTs content in epoxy resin (weight %). Triangles – pristine CNTs addition, squares – TM-F28 addition (CNTs fluorinated at 150°C), crosses – TM F26 addition (CNTs fluorinated at 250°C). Open circles – literature data [30-35] for Bisphenol-A based composites similar to one used in the current research.

4. CONCLUSION

Both pristine and fluorinated CNTs can be effectively used to reinforce epoxy-based composites when their concentration in composite is around 0.1-0.2 weight %. Both tensile and flexural strength and modulus were markedly improved. Fluorinated CNTs are more effective as fillers as compared to pristine ones. It was confirmed by mechanical tests and electron microscopy study. Fluorination resulted in an increase of the CNTs specific surface. Fluorinated CNTs surface became more polar and the specific surface was increased so the adhesion between CNTs and matrix (epoxy resin) was improved and mechanical properties were simultaneously improved. Application of CNTs fluorinated at 150°C provides higher increase of both tensile and flexural strength than CNTs fluorinated at 250°C. Probably treatment at 250°C resulted in a surface damage of CNTs. Obtained in the current research tensile and flexural strength of based on Bisphenol-A epoxy composites reinforced with fluorinated CNTs markedly exceeded all the available literature data for epoxy composites when the CNTs concentration is below 5 weight %. Fluorinated CNTs as fillers did not worsen composites thermal stability and resulted in a slight glassy temperature increase.

ACKNOWLEDGEMENT

The research has been partially supported by the grant of the Russian Foundation of Basic Research 13-03-12086-OFI-M and State Contract #16.711.2014/K from the Ministry of Education and Sciences of Russian Federation.

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