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Modification of Polymethylmethacrylate by Means of Diffusion Introduction of Single-Walled Carbon Nanotubes in Supercritical Carbon Dioxide

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Abstract—Amorphous polymethylmethacrylate has been modified by means of impregnation suspension of single-walled carbon nanotubes in alcoholic solution in supercritical carbon dioxide. Properties of the so formed composite have been studied. Thermal stability of the polymer has increased after the modification.

Keywords: nanocomposite, carbon nanotubes, polymethylmethacrylate, supercritical carbon dioxide, thermal analysis

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Carbon nanotubes have been recognized for unique set of electrical, optical, structural, and mechanical properties [1, 2]. Practical application of the nanotubes in pure form is limited due to their high price and technology complications; therefore, development of new construction materials based on polymer composites with carbon nanotubes or other nanosized dispersed fillers (graphene, fullerene, clays, etc) with polymers, steel and concrete are important. Such materials may discover improved properties compared to the initial polymer. In particular, enhancement of mechanical and thermal properties of the materials after incorporation of nanosized fillers has been reported [3–7].

According to the modern ideas of theory of materials failure, the polymers strength is determined by their structure imperfection and energy of the macromolecules thermal fluctuations. Thus, one of the approaches to develop high-strength polymer materials consists in decreasing the number of the structure defects [8] that can be attained via uniform distribution of the filler over the composite volume. Treatment of polymer with suspension of carbon nanotubes in supercritical carbon dioxide is among the most efficient methods to introduce carbon nanotubes into polymer material [9]. Besides other advantages, this process is ecologically friendly since carbon dioxide can be regenerated and does not pollute the environment. Over the recent 20 years, studies of the effect of supercritical CO_2 on physico-chemical properties of polymers have attracted substantial attention [9–14].

Efficient reinforcement of polymers with single-walled carbon nanotubes SWCNTs requires stable suspensions of SWCNTs in low-viscosity solvents. Several approaches of destruction the nanotubes aggregates and their dispersing in liquids have been developed, ultrasonication in the presence of stabilizers followed by centrifugation over the density gradient as adopted by Arnold et al. being the most widely used [15–17]. Compounds of a variety of classes [7] including bile acids and their salts soluble in water and alcohols [17, 18] can be used as the dispersion stabilizers.

Solubility of the prepared stable dispersions of carbon nanotubes in supercritical carbon dioxide over a wide range of state parameters is an important problem.

The aim of this work is the modification of polymethylmethacrylate by impregnation suspension single-walled carbon nanotubes in supercritical carbon dioxide and study the effect of addition of fillers on the thermal properties of the composite material.

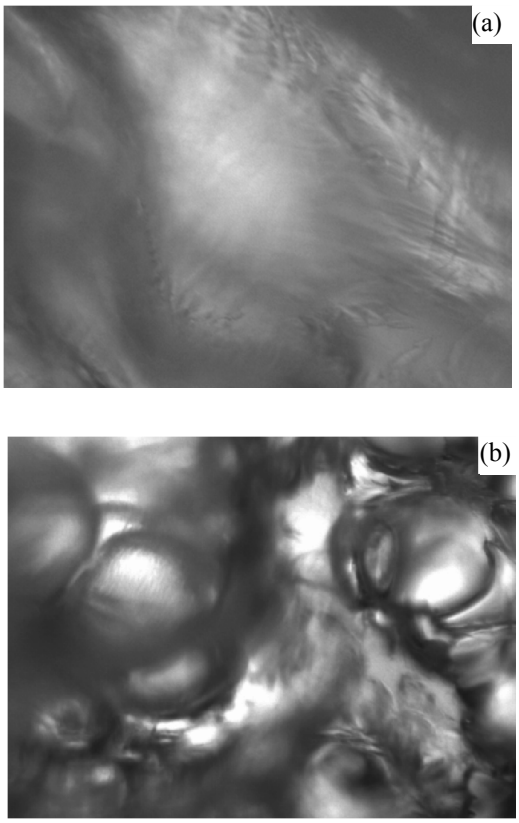

Fig. 1. Optical microscopy images of (a) initial polymethylmethacrylate (image width 0.7 mm) and (b) polymethylmethacrylate modified with single-wall carbon nanotubes (image width 0.55 mm).

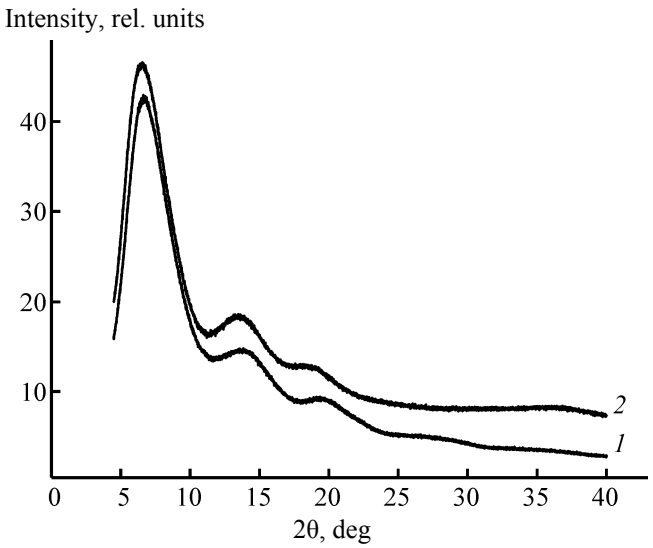

Fig. 2. X-ray diffraction patterns of (*1*) initial polymethylmethacrylate after treatment in CO_2 and (*2*) polymethylmethacrylate modified with single-wall carbon nanotubes.

As expected [19], the treatment of PMMA with SWCNT dispersion in supercritical CO_2 medium resulted in swelling of the initial polymer and porosity development, as evidenced by microscopy study of the polymer material fresh surface (cleavage in liquid nitrogen) (Fig. 1). X-ray diffraction data (Fig. 2) revealed that PMMA was amorphous both in the initial state and in the formed composite material. Indeed, the major peaks observed in the diffraction pattern of the initial sample: at $2\theta \approx 13°$ (the strongest one) and $2\theta \approx 20°$ (Fig. 2, curve *1*) were typical of amorphous PMMA [20] and reflected the local ordering of the macromolecular chains. Positions of the major peaks in the diffraction pattern of the composite remained practically unchanged as compared with those in the pattern of the initial polymer swollen in supercritical CO_2. Therefore, introduction of SWCNT did not change the local structure of PMMA.

Raman spectroscopy is one of the most accurate methods of determining the existence and structure of carbon nanotubes. The carbon nanotubes spectra contain the two frequency ranges: radial "breathing" mode, giving information on the chirality of nanotubes and their degree of aggregation, and tangential mode associated with displacements of segments of SWCNTs [21, 22].

Layer-by-layer scanning of the prepared composite revealed the uniform distribution of SWCNT over the entire volume of the resulting nanocomposite. The tangential modes were well resolved in the Raman spectra, and their blue shift was evident: $\nu = 1594$ cm^{-1} for the nanocomposite and $\nu = 1590$ cm^{-1} for the starting suspension of the nanotubes (Fig. 3). The spectral change demonstrate increased of van der Waals interactions between the single-walled carbon nanotubes and PMMA in the composites compared to the interactions between the individual single-walled carbon nanotubes in the initial suspensions. These interactions lead to a corresponding increase in the half-width of a spectral band at its half-height (FWHM).

Figure 4 shows differential curves of mass loss obtained upon heating of the initial PMMA and the SWCNT-containing composite under argon atmosphere. In the case of the initial polymer, thermal destruction included three stages, the temperatures of the fastest mass loss and the total mass loss at the corresponding stage being as follows: 177 (3%), 288 (34%), and 365°C (62%). In contrast to the initial

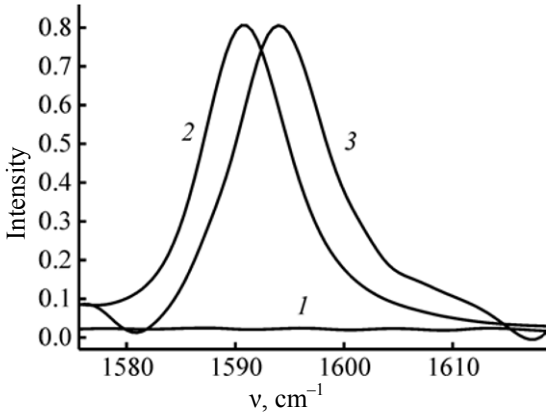

Fig. 3. Fragments of Raman spectra of (*1*) initial polymethylmethacrylate, (*2*) initial suspension of carbon nanotubes, and (*3*) polymethylmethacrylate modified with single-wall carbon nanotubes.

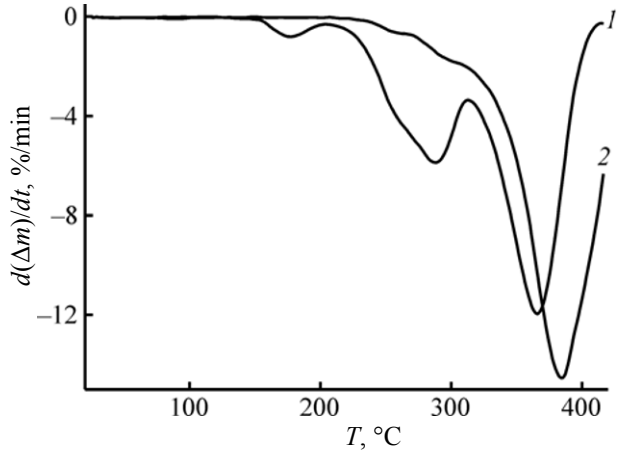

Fig. 4. Differential thermograms of mass loss of (*1*) initial polymethylmethacrylate and (*2*) polymethylmethacrylate modified with single-wall carbon nanotubes.

polymer, thermal decomposition of the nanocomposite was a single-stage process; the highest rate of mass loss being observed at 385°C, and the total mass loss being of 98%.

The low-temperature exothermic effect observed in the DSC curve of the initial polymer (114°C, Fig. 5) was not accompanied with mass loss and could be assigned to PMMA glass transition. The exothermic effect with maximum at 293°C is caused by thermolysis of PMMA, since corresponded to a significant mass loss (34%). Glass transition temperature (125°C) and the start of thermolysis (338°C) of the nanocomposite were somewhat higher than those of the initial polymer (Fig. 5).

To conclude, treatment of polymethylmethacrylate with suspension of single-walled nanotubes in supercritical carbon dioxide allows to obtain microporous material with enhanced thermal stability.

EXPERIMENTAL

Methanol (Fischer Scientific, HPLC grade, 99.95%) and cholic acid (Sigma, ≥98%) were used. Methanol was dried by the procedure described in [23]. The water content in methanol (0.001 wt %) was determined via amperometric titration by the Fischer method. Cholic acid was dried in vacuum during 48 h at 80°C. Single-walled carbon nanotubes [diameter of 1.4–1.5 nm, length of 0.5–1.0 μm, the (10, 11) chirality, semi-conductor type conductivity] were provided by Institute of Problems of Chemical Physics, Russian Academy of Sciences, Chernogolovka. Polymethylmethacrylate (M_w 996000, Aldrich) and carbon dioxide ("special pure" grade, 99.995% CO_2, <0.001% H_2O, Linde Gas) were used without further purification.

The samples were weighed using a Sartorius Genius ME235S balance with accuracy within $\pm 1 \times 10^{-5}$ g.

The polymer was modified with suspension of SWCNTs in a methanolic surfactant solution (0.036 mol/kg of cholic acid, 0.1 mg of SWCNTs on 1 mL of the solvent) prepared as described in [24]. In particular, 0.2 g of powdered PMMA and 0.5 mL of the SWCNTs suspension were placed at the bottom of a 20 mL reactor vessel; the reactor was filled with carbon dioxide at heated up to 130°C and 200 bar. Under these conditions, the sample was soaking for 24 h, and then the reactor was cooled and vented slowly.

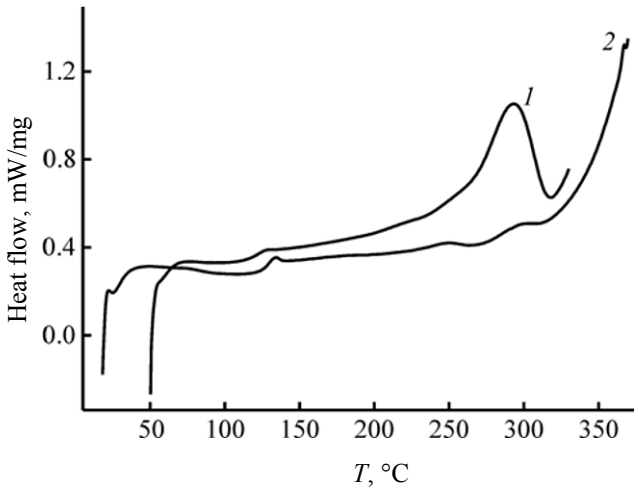

Fig. 5. DSC curves of (*1*) initial polymethylmethacrylate and (*2*) polymethylmethacrylate modified with single-wall carbon nanotubes.

Microscopy studies were performed using a Mikromed-1 binocular optical microscope with magnification of 1600×, equipped with an integrated digital video camera.

X-ray diffraction patterns were obtained using a Bruker AXS D8 Advance multifunctional X-ray diffractometer (monochromatic MoK_α radiation, λ 0.07107 nm, zirconium β-filter) at 2θ 4°–40° with 0.01° spacing. X-ray scattering intensity was recorded with a VANTEC-1 high-rate position-sensitive detector.

Raman spectra were recorded using a Bruker Vertex 70 Fourier spectrometer equipped with a Ram II Raman scattering module (excitation: Nd : YAG laser, highest output power 500 mW, wavelength 1064 nm; detecting: Ge-detector, liquid nitrogen cooling, 128 scans, the spectrum resolution was 1 cm^{-1}).

Thermogravimetry and differential thermogravimetry studies were performed using a DSC 204 F1 differential scanning calorimeter equipped with a TG 209 F1 Iris thermo balance (NETZSCH). The data were processed taking advantage of Thermokinetics Professional SW/KIN/670.01A software. A sample of 8.5±1 mg was put in a platinum crucible at 25°C and heated up to 400°C under static argon atmosphere at 10 deg/min.

DSC studies were performed using a DSC 204 F1 Phoenix differential scanning calorimeter with dynamic heat flow (NETZSCH) equipped with high-sensitive μ-sensor. The samples heat capacity was determined at 25–400°C (10 deg/min, argon atmosphere, standard aluminum crucible with a perforated lid). The sample mass was of 7±1 mg, an empty aluminum crucible used as reference. The measurements were performed with respect to the baseline recorded for a pair of empty crucibles, other conditions being the same. The calorimeter was calibrated using a set off six highly pure compounds (cyclohexane 99.96%, mercury 99.99%, biphenyl 99.5%, indium 99.999%, tin 99.999%, and bismuth 99.9995%).

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