



The effect of catalyst addition on the structure, electrical and mechanical properties of the cross-linked polyurethane/carbon nanotube composites

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ABSTRACT

Uniform distribution of filler particles in a polymer matrix is crucial to the improvement of properties of polymer composites. In this work, we have shown that control of the polymerization rate by addition of the catalyst (Fe(acac)₃) hinders filler aggregation and enhances electrical and mechanical properties of polyurethane/nanotube composites. Thus, a percolation threshold value of 0.02 wt % obtained for the composites with the catalyst was much lower than the value of 0.65 wt % for the composites without the catalyst. Moreover, the electrical conductivity of the catalytically prepared composites at a nanotube content of 3 wt % was two orders of magnitude higher than that of the non-catalytically prepared ones. The tensile strength of both types of composites showed an improvement at lower filler concentrations, however, the increase of filler content led to deterioration of the mechanical properties for the non-catalytically prepared composites. Structure of the composites was investigated by means of optical and scanning electron microscopy. Additionally, the current-voltage characteristics (J-E) of the composites were studied.

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1. Introduction

Polymer composites based on different kinds of nanoscale fillers are of great scientific interest in the last two decades [1–9]. The addition of small amounts of nanofillers allows one to design unique materials, which own both polymer and filler properties. However, the main obstacle to the creation of nanocomposites with high performance is the agglomeration tendency of nanofillers. To achieve a uniform distribution of nanoparticles in polymer matrix both proper dispersion of the primary aggregates and prevention of the particle agglomeration after a mixing process are necessary [1].

In order to address the first problem, application of intense mixing to prepare nanocomposites is important. Among other mixing methods, ultrasonication of nanoparticles in a low viscous medium allows one to get a proper dispersion of primary aggregates [2]. The ultrasonication finds wide use in the preparation of

composites by solution mixing [3] or *in situ* polymerization [4] methods. The second problem arises commonly in the media with a low viscosity. Thus, for the polymer composites prepared with the help of solvent addition, there is a time period between the end of mixing process and complete evaporation of the solvent. This time is long enough for the formation of the large secondary aggregates, especially when the solvent has a high boiling point. For the stabilization of the nanoparticle dispersion different methods, such as chemical modification of filler [5], addition of surfactants [6] and secondary nanoparticles [7], and polymer wrapping [8], can be used. However, in spite of the possibility to achieve a uniform distribution of nanoparticles in the polymer matrix, some drawbacks of these methods occur. On the one hand, chemical modification of the carbon nanotubes (CNT) damages a π conjugation of the carbon atoms and, subsequently, impairs the electrical conductivity of composites [9,10]. On the other hand, application of surfactants and polymer wrapping increases the contact resistance between the nanotubes [11], but without degradation of their properties.

Another approach that can interrupt filler agglomeration is an acceleration of the polymer network formation during the

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preparation of the composites by *in situ* method. One of the ways to accelerate network formation is a microwave irradiation of a prepolymer/nanofiller mixture. In work [12], the microwave treatment of polyethylene terephthalate/layered double hydroxide systems has been resulted in the uniform filler distribution. Chang et al. [13] have prepared CNT/epoxy composites by thermal and microwave curing methods. In this study, the decrease of the curing time during microwave treatment helps to achieve a uniform distribution of the nanotubes and to enhance the dielectric properties of the nanocomposites.

Furthermore, the addition of the catalyst during *in situ* polymerization of polyurethanes can significantly accelerate the urethane bonds formation and, therefore, the network formation as well [14,15]. The main focus of this study is cross-linked polyurethane/carbon nanotube (CPU/CNT) composites prepared by *in situ* polymerization with and without the addition of iron acetylacetonate ($\text{Fe}(\text{acac})_3$) as a catalyst.

2. Experimental

2.1. Materials

For the synthesis of the cross-linked polyurethanes (CPUs) the following reagents were used. Polypropylene glycol with molecular mass 1000 (PPG) (Merck) was dried under pressure of 300 Pa at 393 K for 3 h. Toluene diisocyanate (TDI) (2,4-/2,6-isomers = 80/20) (Sigma) was distilled under vacuum. 1,1,1-Tris-(hydroxymethyl)-propane (TMP) (98%, Sigma) was dried under vacuum at 313–315 K. Iron (III) acetylacetonate (99%, Sigma) was used as received. Dichloromethane (CH_2Cl_2) (Sigma) was redistilled.

The multi-walled CNTs («Specmash» Ltd., Ukraine) were made by chemical vapor deposition (CVD) method at 0.1% of mineral admixtures. Specific surface area of the nanotubes was $190 \text{ m}^2/\text{g}$, external diameter was 20 nm, length was 5–10 μm , specific conductivity σ of pressed nanoparticles (at pressure of 15 TPa) along the axis of compression was 10 S/cm.

2.2. Characterization

The reaction kinetic was controlled by the IR-spectroscopy using Fourier transform spectrometer «Tensor-37» (Bruker, Germany). Electrical conductivity of CPU/CNT composites was measured by the two probe method using an impedancemeter Z-2000 (Elns, Russia) for conductivity above 10^{-7} S/cm and an alternating current bridge P5083 (RostokPribor, Ukraine) for lower conductivity. Dependencies of current density J versus electric field strength E (current-voltage characteristics) of the composites were measured by UT804 (UNI-T, China) (for current measurements) and UT70C (UNI-T, China) (for voltage measurements) multimeters. The B5–44A (Priborelectro, Russia) was a source of stabilized voltage. Measurements of the conductivity and J – E characteristics were performed on samples with thickness of 0.5 mm and diameter of 14 mm.

Measurements of the tensile strength were carry out using 1925 RA–10 M (Uralpromtek, Russia) under load of 0.5 kN. The stretching speed was 40 mm/min. The samples in shape of the spatula were used. Size of the functional part of the sample was

$150 \times 2.5 \times 0.5 \text{ mm}^3$. The five samples for the one measurement were used.

Morphology of the composites was investigated by means of Scanning Electron Microscopy (SEM) using a Tescan MIRA III (Tescan, Czech Republic) microscope operating at 30 keV electron beam energy and by Optical Microscopy (OM) using a microscope Carl Zeiss Primo Star (Carl Zeiss, Germany). Specimens for SEM measurements were cut from *in situ* prepared composite films by knife and had size of $1 \times 5 \text{ mm}^2$. The cut surface of the specimens was covered by thin layer ($\sim 2 \text{ nm}$) of Pt. For OM measurements composite films were formed between two cover glasses. Thickness of the samples for OM measurements was adjusted by 20 μm -thick spacers.

Thermal transitions of the materials were investigated in air atmosphere in the temperature range from 123 to 473 K using DSC Q2000 (TA Instruments, USA). Thermal destruction of the samples was investigated in the temperature range from 293 to 973 K in air atmosphere using Derivatograph Q-1500D (MOM, Hungary).

2.3. Synthesis of cross-linked polyurethanes (CPU)

CPUs were synthesized in two stages. At the first stage, prepolymer (Fig. 1) based on the PPG and TDI was synthesized at 393 K during 1.5 h (percentage of isocyanate groups was 5.9%). The PPG/TDI valence ratio was 1/2.

At the second stage, the prepolymer was cross-linked with the TMP (Fig. 2).

The TMP was dissolved in the prepolymer at 343–348 K in an oil bath during 5 min with constant mixing under argon atmosphere. The prepolymer/TMP valence balance was 3/2.

CNTs were added to the reaction mass (from 0.02 to 3% wt.) as a dispersion in CH_2Cl_2 . Such dispersions of CNTs in CH_2Cl_2 were obtained by using a sonicator UZN-22/44 (UKRROSPRIBOR Ltd, Ukraine) at 22 kHz during 2.5 min. Then the dispersions of CNTs were added to the polymer reaction mass and the sonication was continued for 2.5 min. The concentration of CNTs in CH_2Cl_2 was in a range of 0.015–2.3%. The formation of CPU/CNTs composites was carried out in Petri dishes at 318 K. The solvent residues were removed from the composite films under vacuum to constant weight. For obtaining of the CPU/CNTs/ $\text{Fe}(\text{acac})_3$ composites the catalyst was initially solved in CH_2Cl_2 . Then the dispersion of CNTs in CH_2Cl_2 (as described above) was mixed with this solution conditions and added in reaction mixture.

The investigated composites were flexible films. The temperature of destruction of 10% of polymer mass was in the range from $530 \pm 2 \text{ K}$ (for CPU-0 and CPU/CNT) to $558 \pm 2 \text{ K}$ (for CPU/ $\text{Fe}(\text{acac})_3$ and CPU/CNT/ $\text{Fe}(\text{acac})_3$). The temperature of the glass transition of flexible oligoether segments in all composites was equal $263 \pm 2 \text{ K}$ (except CPU/ $\text{Fe}(\text{acac})_3$ $256 \pm 2 \text{ K}$).

3. Results and discussion

Fig. 3 represents the kinetics of chemical reaction between the prepolymer and TMP with and without addition of the catalyst $\text{Fe}(\text{acac})_3$. As clearly seen in Fig. 3, the time of NCO-groups conversion for systems with $\text{Fe}(\text{acac})_3$ addition is 5.5 times less than for the pristine ones. Hence, the catalytic effect of $\text{Fe}(\text{acac})_3$ allows to

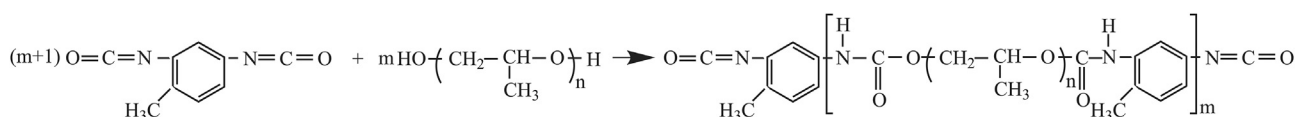


Fig. 1. Synthesis of prepolymer based on PPG and TDI.

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