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Effect of Molecular Weight on the Properties of Polyethyleneglycols Doped with Multiwalled Carbon Nanotubes

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The aim of this study is to analyze the changes in the structure, thermal properties and electrophysical behavior of polyethylene glycol doped with multiwalled carbon nanotubes. The differential scanning calorimetry and electrical conductivity methods were used to study influence of doping multiwalled carbon NTs on the properties of polyethylene glycol of different molecular weights, Mw (PEG-400, PEG-1000, PEG-10000). Dependencies of the polymers degree of crystallinity and temperature behavior of conductivity on the concentration of NTs were researched. The obtained data indicates a strong influence of the molecular weight of PEG on the spatial distribution of NTs and electrical conductivity of researched systems.

Keywords: multiwalled carbon nanotubes, polyethylene glycol, DSC, degree of crystallinity, electrical conductivity.

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1. INTRODUCTION

Polyethylene glycol (PEG, H-[-OCH₂CH₂-]ₙ-OH) is a promising material due to its own high solvation capacity. The electrolytes, created on its base, can be used in various electrochemical devices, in lithium batteries, flexible electrochromic displays, etc. [1]. However, an ionic conductivity of these systems need to be strengthened. The solution to this problem is doping electrolyte based on PEG with carbon nanotubes (NTs) [2, 3]. Detailed studies of the structure and properties of polyethylene glycol doped with NTs have been conducted previously [4-6]. The aim of this study is to analyze the changes in the structure, thermal properties and electrophysical behavior of PEG doped with multiwalled carbon nanotubes.

2. MATERIALS AND METHODS

The multiwalled carbon nanotubes (MWCNT) may be imagined as the combination of the concentric cylinders. In principle, the number of multiple rolled layers in MWCNTs is not restricted, however, commonly they contain 10 – 20 layers. The interlayer distance in MWCNTs is close to the distance between graphene layers in graphite (≈ 0.34 nm). MWCNTs were prepared from ethylene using the chemical vapour deposition (CVD) method (NV Spetsmash Ltd., Kyiv, Ukraine) with FeAlMo as a catalyst. They were further treated by alkaline and acidic solutions and washed by distilled water until reaching the distilled water pH values in the filtrate. The typical outer diameter d of MWCNTs was ≈ 30-50 nm, their length l was ≈ 5-10 μm and mean aspect ratio was $a=l/d ≈ 100$-300.

Polyethylene glycol (PEG) is the typical polyglycol with many different applications. The term glycol is reserved for low molecular weight polymer while the term oxide is used for high molecular weight polymer. At room temperature PEGs with a molecular weight, M_w, up to 600 are fluids, PEGs with a molecular weight between 800 and 2000 are pasty, and with molecular weights above 3000 the PEGs are solids. Degree of PEG crystallinity, χ, increases with increasing of molecular weight. PEG is a hydrophilic nonionic polymer and it has the remarkable solubility in water.

The melting temperature, T_m, and melting enthalpy, ΔH_m, were measured with a TA Q2000 Instrument (TA Instruments Ltd. West Sussex, England) in the regime of heating from 273 K to 333 K at the heating rate, V_h, of 2 K/min. The samples (20-30 mg) were packed in the aluminium pans. The fractional crystallinity of polymer composites, χ_{DSC}, was calculated as:

$$\chi_{DSC} = \frac{\Delta H_m}{\Delta H_m^0} \qquad (1)$$

where ΔH_m is the heat of melting of the composite under investigation and ΔH_m^0 is the heat of melting of 100% crystalline polymers (=188.4 J/g for PEG [7]).

The electrical conductivity, σ, was estimated by the inductance, capacitance and resistance (LCR) meter 819 Instek, 12 Hz–100 kHz (Instek America Corp. Chino, CA, USA) in a cell equipped with two horizontal platinum electrodes (diameter of 12 mm, interelectrode space of 0.5 mm). The applied external voltage was U = 1.275V. The measuring frequency of 10 kHz was chosen in order to avoid polarization effects on the electrodes and the electric field-induced asymmetric redistribution of MWNTs between the electrodes.

The optical microscopy images were obtained using an OI-3 UHL 4.2 microscope (LOMO, Russia). The microscope detector unit was interfaced with a digital camera and a personal computer.

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3. RESULTS

3.1 Microstructure

Fig. 1 shows examples of microscopic images for samples PEG-400, PEG-1000, PEG-10000 on fixed-NTs concentration (0.1 %wt) and various times of ultrasonic dispersion. Studies have shown that increasing the dispersion time contributed to the «loosening» of NTs aggregates and improving uniformity of its spatial distribution. In addition, most dense aggregates were observed for PEG-400, while for PEG-10000 recorded more uniform distribution of NT on sample volume.
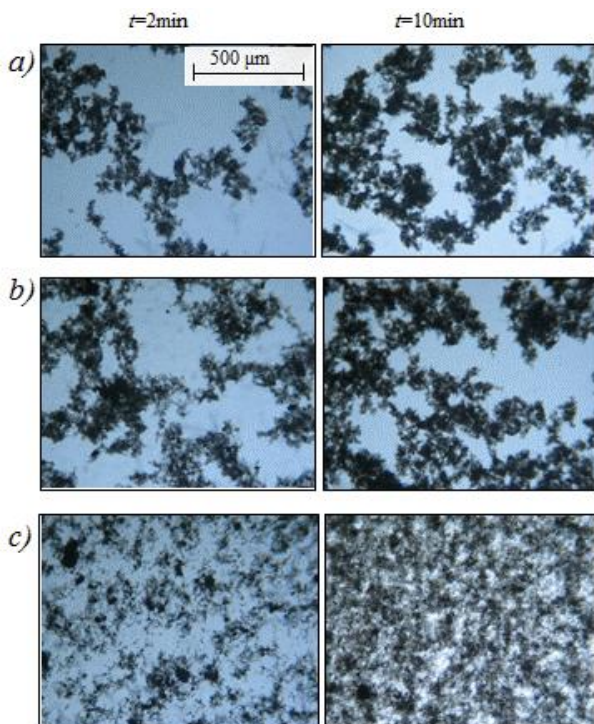

Fig. 1 – Microstructure of samples PEG-400 (a), PEG-1000 (b), PEG-10000 (c) doped with NTs (0.1 %wt) in case of two different time of dispersion: left column - 2 min., right column - 10 min. of ultrasonic dispersion. The sample temperature was 338 K

3.2 Thermal characteristics

The examples of the estimated from the DSC data thermal characteristics (temperature, T_m, and enthalpy, ΔH_m, of melting) and the degree of crystallinity, χ_{DSC}, for the samples are presented in the Table 1.

The increase of crystallinity of PEG-400 in the concentration 1.5 % wt MWCNTs was explained by the fact that the nanotubes serve as the centres of heterogeneous nucleation of crystalline phase.

With increase of the concentration of these centres the crystallization rate and degree of crystallinity of the polymer matrix are also increase. As the result a more perfect structure of the polymer with a higher degree of crystallinity was realized. At $C_n \approx 0.2$ % wt the processes of thermal motions of macromolecular chains are restricted owing to the presence of well-developed surface of nanotubes. The presence of steric barriers for macromolecules of PEG-400 results in losing of their mobility and thus in ability to form a crystalline struc-

ture. This behavior is also observed for PEG-1000. However, for highly crystalline PEG-10000 increase in the concentration of NT leads only to a decrease in the degree of crystallinity. This can be explained by the destruction of highly crystalline structure due to the introduction of MWCNTs.

Table 1 – Thermal characteristics (temperature, T_m, and enthalpy, ΔH_m, of melting) and the degree of crystallinity, χ_{DSC}, obtained for the samples PEG-400, PEG-1000, PEG-10000 +MWCNTs from the DSC method

	$T_m \pm 0.1$, K	ΔH_m, J/g	χ_{DSC}, %
	PEG 400		
0%NT	248,7	44,21±2,2	23,4±1,1
0,2% NT	245,8	38,3 ±1,9	20,3±1,0
1,5% NT	249,6	52,03 ±2,6	27,6±1,5
	PEG 1000		
0% NT	310,5	135,1 ±4,1	71,7±2,1
0,2% NT	308,8	122,9 ±3,6	65,2±1,9
1,5% NT	308,9	133,9 ±4,1	71±2,1
	PEG 10000		
0% NT	335,7	170 ±3,4	90,2±1,8
0,2% NT	336,4	161,3 ±3,2	85,6±1,6
1,5% NT	335,9	158,1 ±3,1	83,92±1,6

3.3 Percolation behaviour of electrical conductivity

Doping of PEG by nanotubes noticeably affect the system electrophysical behaviour. Figure 2 presents temperature dependencies of electrical conductivity of PEG with different molecular weight undoped (dashed lines) and doped (solid lines) with 0.1 % wt MWCNTs. For PEG 400 sample no significant hysteresis in the heating-cooling cycle was observed. However, for PEG 1000 and PEG 10000 samples the hysteresis loop in the heating-cooling cycle in the vicinity of the melting-freezing temperatures was observed.

In general, with increasing molecular weight of the polymer, M_w, and increasing the degree of its crystallinity a significant decrease in electrical conductivity was observed. This effect can be attributed to a decrease in electrical charge mobility with increase of the crystallinity.
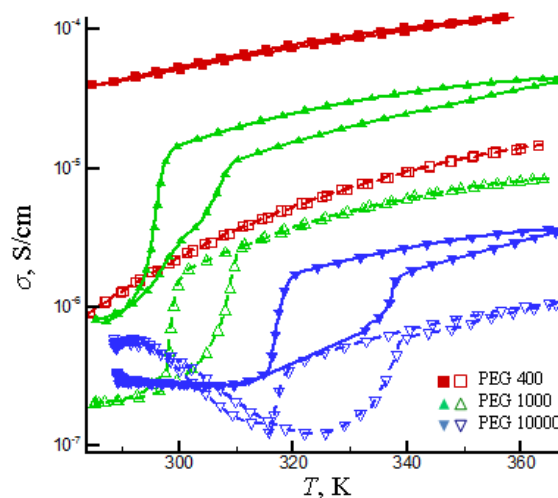

Fig. 2 – Electrical conductivity, σ, versus the temperature, T, for different undoped PEG (dashed lines, open symbols) and PEG doped (solid lines, closed symbols) with 0.1 % wt MWCNTs

The rather unexpected effect was observed in temperature dependence of electrical conductivity for the PEG 10000 sample. In the vicinity of the melting-freezing temperatures the electrical conductivity passed through a minimum. The negative temperature coefficient of conductivity in the vicinity of 290-325 K can be explained by the effect of the temperature on the conductive pathways in a polymer matrix in this temperature interval.

Fig. 3 shows the concentration dependence of the reduced conductivity σ / σ_0 ($\sigma_0 = \sigma$ ($C = 0$)) for the three samples. Analysis of the figure 3 shows that the relative contribution of nanotubes in composites electrical conductivity for polymers of different molecular weights are similar, i.e. in the selected coordinate system all three depending's fit into a single universal curve.
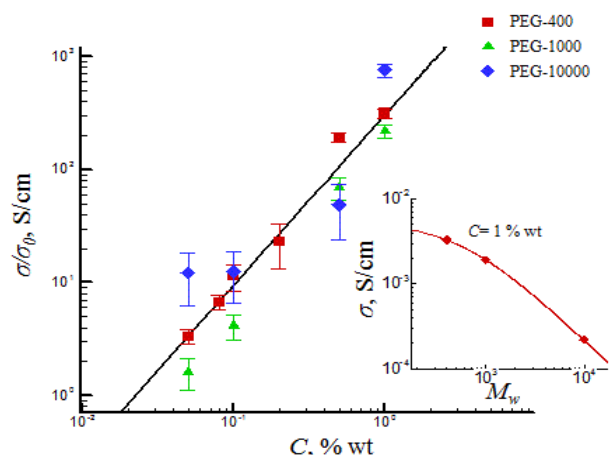

Fig. 3 – Relative electrical conductivity σ / σ_0 ($\sigma_0 = \sigma$ ($C = 0$)) versus the concentration of MWCNTs, C, for PEG with different molecular weight at a temperature $T = 363$K. The solid line corresponds to the percolation approximation using equation (2). In the inset - the dependence of σ versus molecular weight, M_w, at $C = 1\%$ wt.

The percolation theory predicts the following scaling law for the concentration dependence of electrical conductivity [8]:

$$\sigma \propto \left(C - C_p \right)^t, \ C > C_p \qquad (2)$$

where t is a critical conductivity exponent, and C_p is a percolation concentration of the conductive filler. Analysis of experimental data in Fig. 3, allows us to get the critical exponent of electrical conductivity $t = 1.5 \pm 0.15$.

4. CONCLUSION

Thus, analysis of the results shows that with increasing molecular weight of polyethylene glycol and increasing its degree of crystallinity, the spatial distribution of the nanotubes becomes more homogeneous, but with greatly reduced of electrical conductivity of such systems.

Note that the found value of the critical conductivity exponent, t is smaller than classic value $t \approx 2$, the random percolation in three-dimensional systems [8]. In our opinion, this could mean some (such as planar) character of ordering NTs in studied PEG-systems. The significant decrease in sample conductivity was observed even at much higher concentrations of MWCNTs above the percolation threshold (see inset to Fig. 3).

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