

Nanocomposite Films Based on Functional Copolymers with Embedded Carbon Nanotubes

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The conductive nanocomposite films based on functional reactive copolymers and bifunctional alcohols with embedded multiwall carbon nanotubes have been obtained via spin-coating of component suspension followed by thermal treatment. The study of the processes of polymer film formation witnesses that film cross-linking occurs owing to the reactions of peroxide groups presented in the structure of copolymers as well as due to the interactions between maleic anhydride groups of copolymers with bifunctional alcohols. The conductivity of formed polymer nanocomposites has been studied and their percolation threshold has been determined. It has been shown that conductive properties of the nanocomposites depend on the specific surface of carbon nanotubes, as well as on composite composition and obtaining conditions.

Keywords: Reactive copolymer, Carbon nanotubes, Nanocomposites, Conductivity, Percolation threshold.

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1. INTRODUCTION

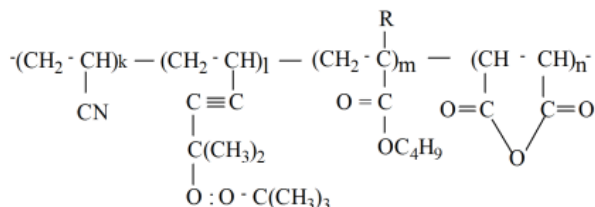
With the development of technologies of the new nanofiller creation the possibility of obtaining polymer composite materials filled with carbon nanotubes (CNT) has attracted increasing attention. CNT possess the unique gamut of specific properties – for example they can have metallic conductivity as well as be semiconductor or dielectric depending on their structure and diameter [1]. Such composites with the wide spectrum of unique properties can be used as chemical and biological sensors, accumulator electrodes, supercapacitors, aerospace structural materials [2]. Due to the high electron affinity CNT are the effective tools to improve the characteristics of photo-voltaic devices on polymer basis. Hence, both obtaining and the study of the properties of polymer nanocomposites with embedded CNT is the actual task for the scientists working in the field of material science.

In general, CNT introduction into polymers divides in three methods, namely: "in situ" polymerization [3]; mixing in melt [4]; mixing in solution [5]. Each of these methods has both advantages and disadvantages. So, when "in situ" polymerization is used the creation of grafted polymer layer around CNT provides the improvement of their surface interaction with polymer as well as the uniformity of their distribution in polymer matrix, but on the other hand – hinders the formation of contacts between CNT and, in such a way, diminishes composite conductivity. Direct mixing of components without solvent use is the main advantage of mixing in melt because this technique is environmentally friendly and simple for the application. But in this case the equipment providing significant shear stress is necessary. Melting in solution is the widespread method of the formation of composites filled with CNT. The advantages of this method are caused by system low viscosity that provides CNT even distribution in polymer matrix. As our previous studies reveal surface-active reactive copolymers synthesized at organic chemistry chair of Lviv Polytechnic National University are able

to adsorb on the surfaces of various nature and allow to obtain composite materials with filler uniform distribution in polymer matrix [6]. The aim of this work is to study the processes of obtaining and the properties of conductive film polymer nanocomposites on the basis of reactive copolymers and carbon nanotubes.

2. EXPERIMENTAL

Reactive heterofunctional peroxide-containing copolymers (RC) on the basis of acrylonitrile (AN), peroxidic monomer 5-tert-butylperoxy-5-methyl-1-hexen-3-yne (PM), maleic anhydride (MA), butyl acrylate (BA) and butyl methacrylate (BMA) were used for the formation of thin polymer films.



where R – H, CH₃.

RC synthesis was carried out via radical copolymerization of corresponding monomers in ethyl acetate (monomer total concentration – 3 mol/l) at 333K in the presence of lauroyl peroxide as initiator ($C_{in}=2 \cdot 10^{-2}$ mol/l) [7]. The composition and some characteristics of synthesized copolymers are presented in Table 1.

The content of peroxide fragments in RC was determined via the thermal decomposition of peroxide containing RC at 483K under argon, followed by gas chromatographic analysis of the decomposition final products. The MA subunit content in RC was determined using a reverse potentiometric titration of carboxylic groups [8]. The AN subunit content was determined via elemental [C, H, N] analysis.

Polyethylene glycols (PEG) with different molecular weight, namely PEG-200, PEG-400 and diethylene gly-

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col (DEG) were purchased from Aldrich and used as received.

Table 1 – Composition and some colloidal-chemical characteristics of synthesized copolymers

№	Copolymer composition, %mol.					γ_s^d *, mN/m	γ_s^h *, mN/m	γ_s^* *, mN/m	In-trins. visc.** dl/g
	AN	PM	BA	BMA	MA				
1	35.0	5.9	31.8	-	27.3	17.8	22.7	40.5	0.107
2	44.1	8.3	27.9	-	19.7	19.0	16.2	35.2	0.089
3	27.8	-	-	27.5	44.7	22.2	13.3	35.5	0.159

* γ_s , γ_s^d , γ_s^h - surface free energy of polymer films, its dispersion and polar components respectively.

** intrinsic viscosity in acetone at 293K

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Multiwall carbon nanotubes Baytubes C-150 (Bayer Material Science AG, Germany, $S_{sp}=167$ m²/g), Fibermax (Fibermax Composites, Greece, $S_{sp}=198$ m²/g), Nanocyl NC-7000 (Nanocyl S.A., Belgium, $S_{sp}=239$ m²/g) were used for nanocomposite filling.

For obtaining nanocomposite films 5% solution of RC and PEG in dimethyl formamide was prepared at the molar ratio [MA links in RC]:[PEG-200] = 8:1. Certain amount of CNT was added to the solution and the dispersion was carried out by magnetic stirrer during 30 min. followed by ultrasonification using UZDN-4A disperser during 1 min. Obtained dispersion was deposited onto glass slides applying spin-coating technique ($\omega = 2000$ rpm) at ambient temperature. Slides with composite films were cured in two stages at 373 K and 393 K during 1 hour for each stage. Three-layer films were used to study conductive properties of nanocomposites.

Content of gel-fraction in polymer films without CNT was determined as a residue after extraction of their soluble fraction in a Soxhlet extractor by dioxane till constant weight of the residue, approximately during 12 hours.

The micrographs of polymer films with embedded CNT were obtained using optical microscope Jenaval (Carl Zeiss, Jena, Germany).

In order to study conductive properties of polymer films with embedded CNT the copper strips 5mm wide and 0.5 μ m thick were sputtered on both sides of the glass slide (18x18 mm) with polymer nanocomposite films via vacuum magnetron deposition using VUP-5M-01 plant (SELMI, Sumy, Ukraine). These strips served as contacts for the resistance determination. The resistance of the nanocomposite films placed between two contacts was measured using Practitronic MV-40 Teraohmmeter (Germany) or M890G multimeter (Zhangzhou Lihao Electronic Co., China) depending on its value. The specific resistance was calculated using the equation $R_{sp} = R \cdot l/d$, where R – determined conductivity (Ohm), l – the distance between contacts (mm), d

– the width of glass slide (mm).

3. RESULTS AND DISCUSSION

Obtained data witness that synthesized RC form cross-linked films owing to reactions of peroxide groups presented in their structure as well as due to the interactions between RC maleic anhydride groups with bifunctional alcohols (PEGs). To form cross-linked structures at the expense of peroxide groups exclusively, a high-temperature treatment (≥ 393 K) of the films is necessary (Table 2). However, even at this temperature gel-fraction value does not exceed 40%.

Table 2 – Dependence of gel-fraction value of polymer films-based on RC-1 on their composition and formation conditions

№	PEG	Mole ratio [PEG]: [MA links]	Gel-fraction, %	
			353 K	393 K
1	-	-	1,9	16,1
2	PEG-200	1:8	8,7	91,7
3	PEG-200	1:4	5,3	24,7
4	DEG	1:8	6,2	78,2
5	PEG-400	1:8	5,4	88,1

The introduction of PEGs into the RC solution from which the film is formed allows to obtain at 393K polymer films with cross-linking degree of 80-90%. The study of the influence of PEG molecular weight on the cross-linked film formation process witnesses that the highest values of gel-fraction are observed with PEG-200. In the case of diethylene glycol and PEG-400 use as curing agent, the cross-linking degree of films is lower. Evidently, the length of PEG-200 chain is optimal for the proceeding of acylation reaction of PEG with maleic anhydride groups, while in the case of PEGs with shorter or longer chains steric obstacles hinder the formation of intermolecular bonds at the expense of this reaction. Besides, it has been shown that optimal PEG to MA ratio is equal to 1:8. The increase of this ratio to 1:4 causes the decrease of gel-fraction, evidently, because of unbonded PEG.

On the basis of functional copolymers nanocomposite films with embedded CNT have been formed. The micrographs of these films witness that in studied polymer matrix CNT are rather agglomerated (Fig. 1) due to the low compatibility of CNT surface with matrix polymer.

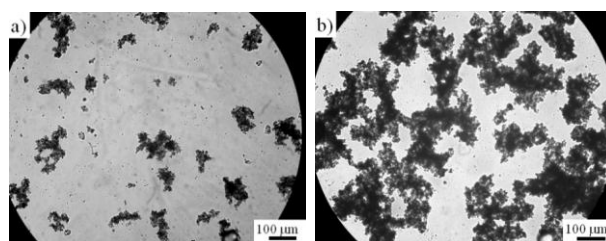


Fig. 1 – Micrographs of nanocomposite films on the basis of RC-1 filled with CNT Baytubes obtained via spin-coating of unheated dispersions: 0.5% CNT (b), 2.0% CNT (d)

With the rise of CNT concentration from 0.2% up to 1.0% the agglomerate amount increases and after reaching 2% concentration they form continuous network of conductive filler (Fig. 1d) i.e. the infinite conductive cluster is formed from the isolated clusters.

Table 3 – Dependence of conductivity of nanocomposites with embedded CNT Baytubes C150 on their composition

N _o	Polymer	C _{CNT} , %	Dispersion heating	l, cm	d, cm	R, Ohm	R _{sp} , Ohm
1	RC-2	2.0	+	0.52	1.57	3.0·10 ⁹	9.1·10 ⁹
2	RC-2	3.0	+	0.55	1.45	1.6·10 ⁸	4.2·10 ⁸
3	RC-1	2.0	+	0.51	1.85	1.0·10 ¹⁰	3.6·10 ¹⁰
4	RC-1	2.0	–	0.50	1.70	6.4·10 ⁴	2.2·10 ⁵
5	RC-1	3.0	–	0.52	1.98	2.0·10 ³	7.6·10 ⁴
6*	RC-1	2.0	–	0.50	1.96	4.4·10 ⁵	1.7·10 ⁶
7**	RC-1	2.0	–	0.50	1.90	2.0·10 ⁴	7.8·10 ⁴
8	RC-3	2.0	–	0.48	2.1	2.1·10 ⁴	9.2·10 ⁴

Such segregated system has to provide the sharp increase of conductivity. These data coincides well with the results of the study of conductivity dependence on CNT concentration (Fig. 2, Table 3). At CNT concentration equal to 0.2-1% electric resistance reaches the tens of gigaohms while at C_{CNT} = 2% we observed extreme (up to 5-6 orders of magnitude) decrease of the resistance. This concentration evidently corresponds to the percolation threshold for studied nanocomposite. With further CNT content increase the monotone decrease of resistance value is observed.

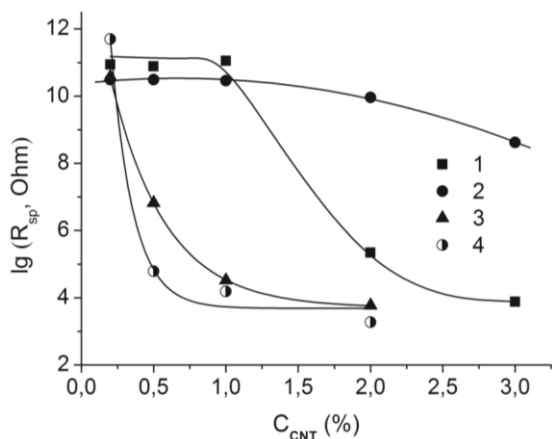


Fig. 2 – Dependence of the resistance of nanocomposite films based on RC-1 on CNT concentration in semi-logarithmic coordinates: film of initial dispersion without thermal treatment (1, 3, 4); film after dispersion thermal treatment in ampoule at 393 K during 4 hours (2); CNT Baytubes (1, 2), Fibermax (3), Nanocyl (4)

In order to improve the compatibility of CNT surface with polymer matrix and to prevent of CNT agglomeration it was necessary to modify nanotube surface. Taking into account that the RC forming polymer films is polyfunctional substance and contain in its structure diverse functional groups (including peroxide fragments, which are able to generate free radicals at elevated temperatures and to provide "grafting to" of polymer molecules) we decided to modify CNT surface "in situ" via thermal treatment of CNT dispersion in RC solution.

One can see (Fig. 3) that as a result of thermal treatment of initial dispersion the nanocomposite films are formed, in which conductive filler is distributed rather evenly and CNT large agglomerates are practically absent. Thus, such modification of filler surface enhances its compatibility with matrix polymer and provides disaggregation of carbon nanotubes as well as

their uniform distribution in the composite.

At the same time such modification does not promote the formation of segregated system with continuous network of conductive filler. As a result percolation threshold in the studied range of CNT concentrations is not reached – specific resistance decreases only by 1-2 orders (Fig. 2, Table 3). Evidently, polymer immobilized on CNT surface create thin insulating layer in the points of contact between nanotubes that causes the increase of electric resistance.

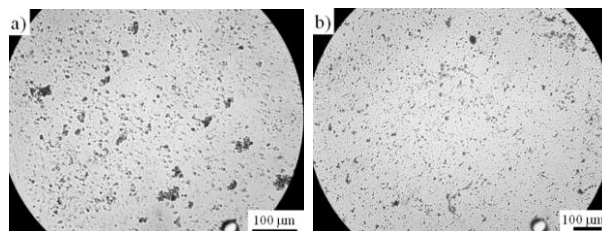


Fig. 3 – Micrographs of nanocomposite films on the basis of RC-2 filled with CNT Baytubes obtained via spin-coating of heated dispersions: 1.0% CNT (a), 2.0% CNT (b)

It has to be pointed that thermal treatment of nanocomposite films influence their conductive properties as well. One can see (Table 3, sample 6) that in the case of unheated film at C_{CNT} = 2% the value of specific resistance is equal to 1.7·10⁶ Ohm that witnesses about inadequately formed network of conductive filler. After thermal treatment (Table 3, sample 7) the specific resistance decreases more than by one order of magnitude. Obviously, the structurization of polymer matrix that occurs during thermal treatment provides better contacting of filler particles due to the compacting of film structure. As a result this causes the increase of conductivity.

Copolymer composition influence slightly both the percolation threshold value and the value of resistance in this point. It is interesting that the use of non-peroxide RC allows to reach percolation threshold at C_{CNT} = 2% and resistance value in this point equal <100 kOhm. It can witness in favor of our assumption that the reaction of PEG hydroxyl group acylation by RC anhydride subunits is the main reaction providing the formation of network polymer structures. Hence, the formation of spatial 3D network by RC macromolecules is the significant factor influencing the conductive properties of nanocomposite films.

The study of the dependence of percolation threshold on CNT specific surface reveals (Fig. 2, curves 1, 3,4) that with the increase of specific surface from 160 m²/g up to 200-240 m²/g the percolation threshold de-

creases and is equal to 0.2-0.5% i.e. at this concentration CNT continuous network is formed in polymer matrix and in the case of Nanocyl NC-7000 nanotubes that are characterized by higher specific surface the denser network is formed and percolation threshold value is lower as compared with other types of CNT.

4. CONCLUSIONS

The results of performed studies witness that the method proposed allows to obtain conductive nanocom-

posite films and percolation threshold value at which the conductivity increases sharply depends on CNT specific surface, nanocomposite structure and formation technique. It has been shown that the modification of CNT surface with reactive copolymers "in situ" provides disaggregation of carbon nanotubes and their uniform distribution in polymer matrix, but insulating adsorption layer formation in the points of the contacts between CNT causes the decrease of obtained nanocomposite conductivity.

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