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O.M. Shevchuk, N.M. Bukartyk, R.Yu. Petrus, V.S. Tokarev  
Lviv Polytechnic National University,  
Department of Organic Chemistry

## POLYMER NANOCOMPOSITE FILMS EMBEDDED CARBON NANOTUBES

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The conductive nanocomposite films on the basis of reactionary copolymers with embedded carbon nanotubes were received. The percolation threshold of obtained nanocomposites was determined and it was shown that its value depends on the size of specific surface of nanotubes, composition and conditions of composite obtaining.

**Key words:** reactionary copolymers, carbon nanotubes, conductive nanocomposites, percolation threshold.

Одержано струмопровідні нанокомпозитні плівки на основі реакційноздатних кополімерів з вбудованими вуглецевими нанотрубками. Визначено поріг перколяції одержаних нанокомпозитів і показано, що його значення залежить від величина питомої поверхні нанотрубок, складу та умов одержання композиту.

**Ключові слова:** реакційноздатні кополімери, вуглецеві нанотрубки, струмопровідні нанокомпозити, поріг перколяції.

**Problem definition.** With the development of technologies of the new nanofiller creation the possibility of receiving the polymer composite materials filled with carbon nanotubes (CNT) has attracted increasing attention. The 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, super-capacitors, aerospace structural materials [2]. Due to the high electron affinity the CNT are the effective tools to improve the characteristics of photo-voltaic devices on polymer basis. Thus, both receiving and studying of the properties of polymer nanocomposites with embedded CNT is the actual task for the scientists working in the field of material science.

**State of the paper.** In general, the CNT introduction into polymers divided in three methods, namely: 1) “in situ” polymerization [3]; mixing in melt [4]; mixing in solution [5]. Each of these methods has both advantages and disadvantages. When “in situ” polymerization is used the creation of grafted polymer layer around CNT provides the improvement of their surface interaction with polymer molecules as well as the uniformity of their distribution in polymer matrix, but from the other hand – hinder the formation of contacts between nanotubes and, in such a way, diminishes composite conductivity. The direct mixing of components at high temperature 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 high-performance 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 reactionary copolymers synthesized at organic chemistry chair of Lviv Polytechnic National University are able to absorb on the surfaces of various nature and allow receiving the composite materials with filler uniform distribution in polymer matrix [6].

**The aim** of this paper is to study the processes of receiving and studying the properties of conductive film polymer nanocomposites on the basis of reactionary copolymers and carbon nanotubes.

**Experimental part.** Reactionary heterofunctional peroxide copolymers (RC) on the basis of 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. The 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.

Table 1

Composition and some colloidal-chemical characteristics of synthesized copolymers

| № | Copolymer composition, %mol. |     |      |      |      | $l_s^d$ , mN/m | $l_s^h$ , mN/m | $l_s$ , mN/m | Intrins. viscosity 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                   |

The content of peroxide fragments in RC was determined via the thermal decomposition of peroxide 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.

The estimation of the components of FC surface energy was performed by the method of two liquids using known equation [9]:

$$1 + \cos \theta = 2 \left[ \frac{(\gamma_s^d)^{0.5} \cdot (\gamma_l^d)^{0.5}}{\gamma_l} + \frac{(\gamma_s^h)^{0.5} \cdot (\gamma_l^h)^{0.5}}{\gamma_l} \right] \quad (1)$$

where  $\gamma_s$  – surface energy of solid, mN/m;  $\gamma_l$  – surface energy of liquid, mN/m;  $d, h$  superscripts indicate the dispersion (London) and polar (hydrogen) components respectively;  $\theta$  – limiting wetting angle. The FC overall surface energy and its components were calculated after solving the system of two equations using determined wetting angles of substrate with two liquids. The following values of the surface energy

components of used liquids were used for calculations: water –  $\gamma_l = 72.8$  mN/m,  $\gamma_l^d = 21.8$  mN/m,  $\gamma_l^h = 51.0$  mN/m; methylene iodide –  $\gamma_l = 50.8$  mN/m,  $\gamma_l^d = 48.5$  mN/m,  $\gamma_l^h = 2.3$  mN/m [9].

The multiwall carbon nanotubes of such brands as Baytubes C-150 (Bayer Material Science AG, Germany,  $S_{sp}=204\text{m}^2/\text{g}$ ), Fibertex (Fibertex Composites, Greece,  $S_{sp}=230\text{m}^2/\text{g}$ ), Nanocyl NC-7000 (Nanocyl S.A., Belgium,  $S_{sp}=250\text{--}300\text{m}^2/\text{g}$ ).

For receiving the nanocomposite films 5% solution of RC and PEG-200 in dimethyl formamide were 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 dispergator during 1 min. The received dispersion was deposited onto glass slides applying spin-coating technique ( $\omega = 2000$  rpm) at ambient temperature. The 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.

The micrograph of polymer films with embedded CNT was received using optical microscope Jenaval (Carl Zeiss, Jena, Germany).

In order to study the conductive properties of polymer films with embedded CNT the copper strips 5mm wide and 0.5  $\mu\text{m}$  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 (SEIMI, 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:

$$R_{sp} = R \cdot l/d \quad (2)$$

where  $l$  – the distance between contacts (mm),  $D$  – the width of glass slide (mm)

**Results and discussion.** The micrographs of received nanocomposite films witness that in studied polymer matrix the CNT are rather agglomerated (Fig. 1) due to the low compatibility of CNT surface with matrix polymer.

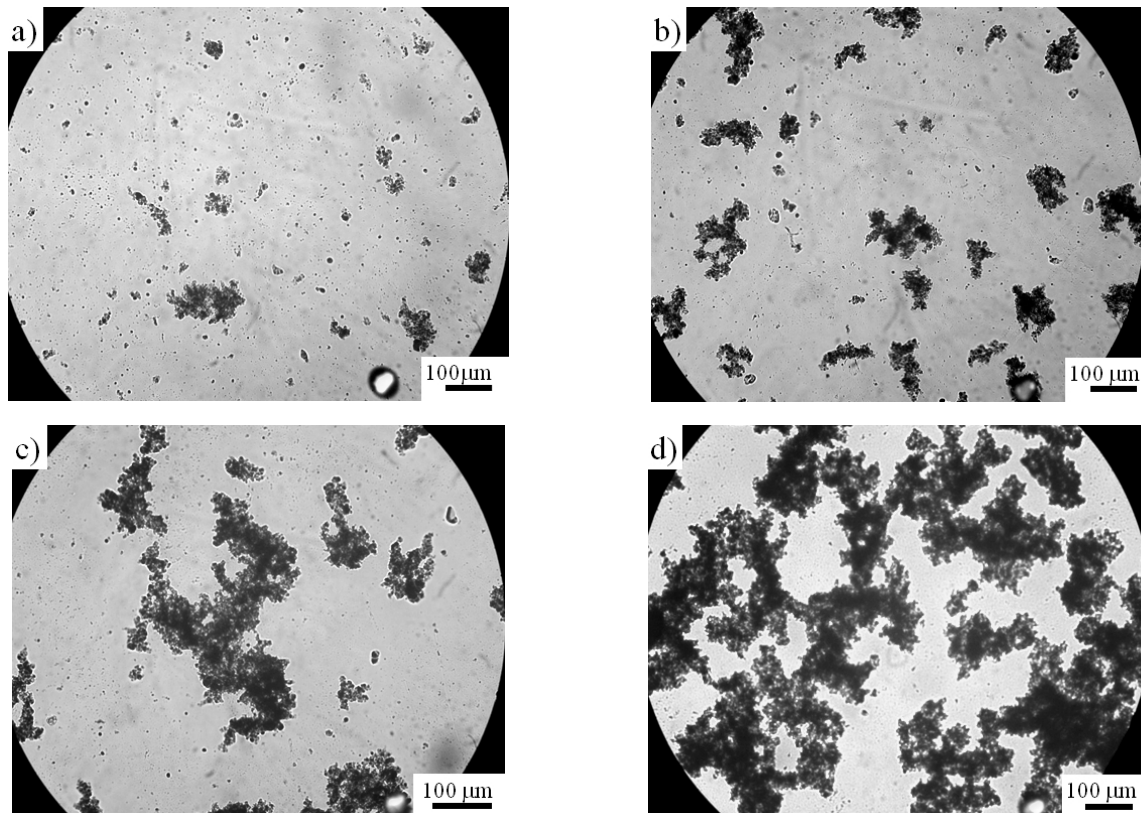


Fig. 1. Micrographs of nanocomposite films on the basis of RC-1 filled with CNT Baytubes received by spin-coating of unheated dispersions: 0.2% CNT (a), 0.5% CNT (b), 1.0% CNT (c), 2.0% CNT (d)

With the rise of CNT concentration from 0.2% up to 1.0% the agglomerate amount increases and after reaching 2% concentration they begin to form continuous network of conductive filler (Fig. 1d) i.e. the infinite conductive cluster is formed from the separate isolated clusters. 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 2). At CNT concentration equal to 0.2-1% electric resistance reaches the tens of gigaohms while at  $C_{\text{CNT}} = 2\%$  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.

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 contains 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” by 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 desaggregation of carbon nanotubes as well as their uniform distribution in the composite.

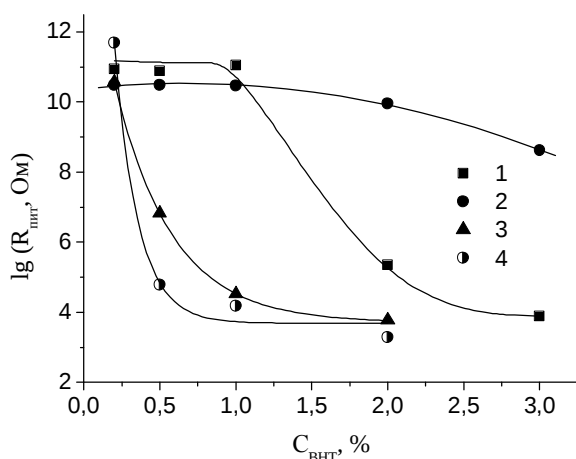


Fig. 2. Dependence of the nanocomposite film resistance on the basis of RC-1 on CNT concentration in semi-logarithmic coordinates: film of initial dispersion without thermal treatment (1, 3, 4); film after dispersion thermal treatment in ampoule at 393 K during 4 hours (2); CNT Baytubes (1, 2), Fibermax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

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 2). Evidently, polymer immobilized on CNT surface create thin insulating layer in the points of contact between nanotubes that causes the increase of electric resistance.

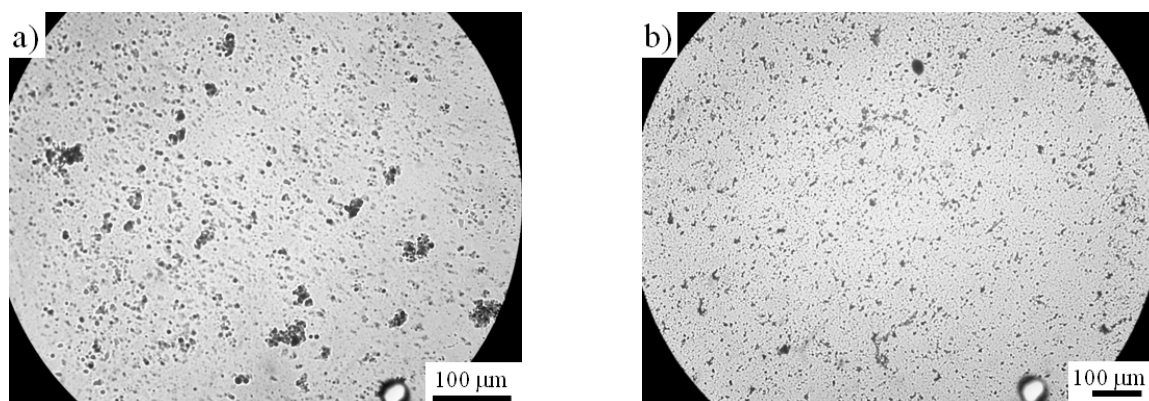


Fig. 3. Micrographs of nanocomposite films on the basis of RC-1 filled with CNT Baytubes received by spin-coating of heated dispersions: 1.0% CNT (a), 2.0% CNT (b)

It has to be pointed that thermal treatment of nanocomposite films influence their conductive properties. One can see (Table 2, sample 6) that in the case of unheated film at  $C_{CNT} = 2\%$  the value of specific resistance is equal to  $1.7 \cdot 10^6$  Ohm that witnesses about inadequately formed network of conductive filler. After thermal treatment (Table 2, 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.

The copolymer composition slightly influences both the percolation threshold value and the value of resistance in this point. It is interesting that the use of non-peroxide RC allows reaching 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. Thus, the formation of spatial 3D network by RC macromolecules is the significant factor influencing the conductive properties of nanocomposite films.

Table 2

**Dependence of the conductivity of nanocomposites with embedded CNT on their composition**

| №   | Polymer | $C_{CNT}$ , % | Dispersion heating | l, cm | d, cm | R, Ohm              | $R_{sp}$ , Ohm      |
|-----|---------|---------------|--------------------|-------|-------|---------------------|---------------------|
| 1   | PK-2    | 2.0           | +                  | 0.52  | 1.57  | $3.0 \cdot 10^9$    | $9.1 \cdot 10^9$    |
| 2   | PK-2    | 3.0           | +                  | 0.55  | 1.45  | $1.6 \cdot 10^8$    | $4.2 \cdot 10^8$    |
| 3   | PK-1    | 2.0           | +                  | 0.51  | 1.85  | $1.0 \cdot 10^{10}$ | $3.6 \cdot 10^{10}$ |
| 4   | PK-1    | 2.0           | –                  | 0.50  | 1.70  | $6.4 \cdot 10^4$    | $2.2 \cdot 10^5$    |
| 5   | PK-1    | 3.0           | –                  | 0.52  | 1.98  | $2.0 \cdot 10^3$    | $7.6 \cdot 10^4$    |
| 6*  | PK-1    | 2.0           | –                  | 0.50  | 1.96  | $4.4 \cdot 10^5$    | $1.7 \cdot 10^6$    |
| 7** | PK-1    | 2.0           | –                  | 0.50  | 1.90  | $2.0 \cdot 10^4$    | $7.8 \cdot 10^4$    |
| 8   | PK-3    | 2.0           | –                  | 0.48  | 2.1   | $2.1 \cdot 10^4$    | $9.2 \cdot 10^4$    |

\* The film was not heated.

\*\* The film (sample № 6) was heated at 373K and 393K during 1hour respectively.

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  $200 \text{ m}^2/\text{g}$  up to  $230\text{--}300 \text{ m}^2/\text{g}$  the percolation threshold decreases and is equal to  $0.2\text{--}0.5\%$  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.

**Conclusions.** The results of performed studies witness that the proposed method allows receiving the conductive nanocomposite films and percolation threshold value at which the conductivity increases sharply depends on the CNT specific surface, nanocomposite structure and formation technique. It was shown that the modification of CNT surface with reactionary copolymers “*in situ*” provides desaggregation 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 received nanocomposite conductivity.

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