

STRUCTURE, ELASTIC AND ELECTRICAL PROPERTIES OF POLYETHYLENE (PE) / CARBON NANOTUBE (CNT) NANOCOMPOSITES

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Abstract

In the paper results of an investigation of properties of polyethylene (PE) modified with multiwall carbon nanotubes (CNT) are presented. Two types of modifiers were used: multiwall CNTs and polymer concentrate containing 31.6 wt.% of nanotubes in the polyethylene matrix. Results on the influence of CNTs on the structural (crystallinity), thermal (thermal stability), electrical (AC conductivity) and mechanical properties (yield stress, strength, elastic modulus and ultimate elongation) of PE matrix composites were obtained. A theoretical analysis of elastic properties of the PE/CNT composite was carried out by using the Mori–Tanaka theory of an equivalent medium. The calculation results were compared with experimental data.

1 Introduction

Polymer nanocomposites, consisting of CNT additives and polymer matrices, including thermoplastics, thermosets and elastomers, are considered to be an important group of perspective materials for many engineering applications. CNT filler possesses remarkable mechanical, electrical, chemical and other properties revealing huge potential applications of CNT/polymer nanocomposites in sports industry, building and automotive sectors, electrical appliances and other areas of national economy [1].

However, there is important setback in development of CNT/polymer nanocomposites, generally by the problems to achieve good dispersion of CNTs in polymer matrix. For example due to high aspect ratios, CNTs are easy agglomerated in polymer matrices. Consequently in the fabrication process of composites, spatial CNT dispersion in polymer matrices is a crucial characteristic for ensuring high exploitation properties. CNT/polymer nanocomposites can be processed by using common polymer processing methods like *in situ* polymerization, solution casting and melt blending. Melt blending is used to fabricate most of the polymer matrix composites. Comparing with other fabrication processes it is simple and most suitable for industrial production [2].

As described in this paper, CNT/PE nanocomposites are fabricated by using melt blending process. Considerable improvements in mechanical, electrical and thermophysical properties of these nanocomposites are achieved in comparison with pure PE.

2 Experimental

2.1 Materials

As matrix material middle density polyethylene of trademark *Egycroptene MD 3804 U* (Citicon Industrial Ltd., Hong Kong) with density of 0.938 g/cm³ and melt flow index of 4.0 g/10 min. was used.

As additives two types of CNT fillers were used: a) multi-walled carbon nanotubes - *Baytubes C 150 P* (CNT-1: Bayer MaterialScience, Germany) with average length > 1µm, outer mean diameter ~ 13 nm and density of 1.3 – 1.5 g/cm³; b) high-density polyethylene based concentrate *Nanocyl 9000* (CNT-2: Nanocyl S. A., Belgium), fabricated by *in situ* polymerization method and containing 31.6% multiwall carbon nanotubes of trademark *NC 7000* with average diameter of 9.5 nm and length of 1.5 µm.

2.2 Manufacturing

The procedure of manufacturing of specimens of a PE/CNT composites consisted in the following. First, the constituents of the composition were mixed by using two-roll mills at 160°C for 7 min. The resulting blend was mechanically milled and pressed at 160°C on a Carver hydraulic press into 100 × 80 × 1.5-mm plates, which were then cut into flat dumbbell-type specimens, corresponding to EN ISO 527-2:1996 [3]. In total, four different PE based compositions with nanotube concentrations of 0, 1, 2, and 5 wt.% were prepared.

2.3 Testing

Tensile stress-strain characteristics were determined by using *Zwick/Roell BDO020* universal testing machine (speed of the upper moving clamp – 1 mm/min. for Young's modulus *E* determination and 50 mm/min for measuring of stress-strain characteristics at yield and at break (σ_Y , ε_Y , σ_B and ε_B respectively)).

Differential scanning calorimetry (DSC) measurements were carried out by using *Mettler Toledo DSC 1/200W* equipment. Glass transition temperature (T_g) was determined within temperature scans from +25°C to +200°C at heating rate 10°C/min.

Thermogravimetric analysis (TGA) measurements were made by using *Mettler Toledo TGA1/SF* equipment. Changes in weight in relation to change in temperature from +25°C - +800°C were determined at heating rate 20°C/min.

The measurements of dielectric properties of the specimens were carried out by using *Novocontrol Concept 40* broadband dielectric spectrometer. Dielectric measurements of the

selected polymer nanocomposites were performed in a wide frequency region (from 10^{-2} to 10^6 Hz). Real part of AC conductivity (σ') was analyzed.

2 Results

2.1 Thermal analysis

The results of DSC measurements of the investigated nanocomposites are presented in Fig. 1. Although nanotubes can favor an increase in the nucleation of PE crystallites, the conformational restrictions of macromolecules at the interphase evidently lead to some decrease of crystallinity degree χ of the composites.

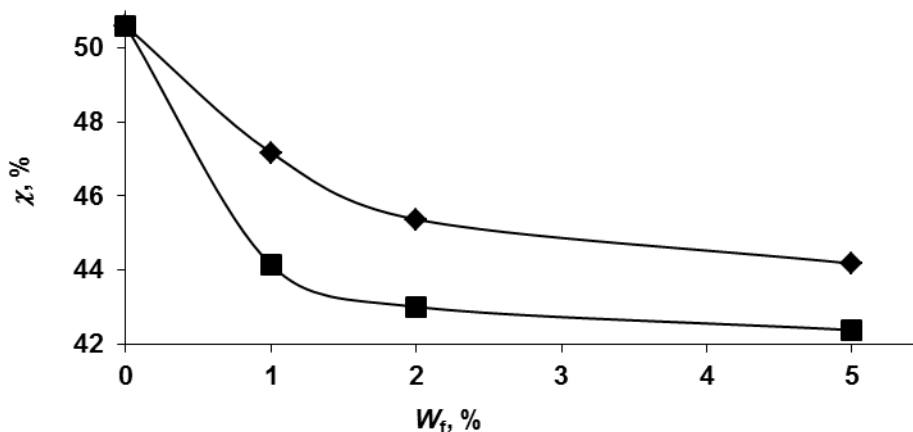


Figure 1. Crystallinity degree χ of PE and PE nanocomposites with CNT-1 (◆) and CNT-2 (■) as function of nanofiller content W_f .

As one can see the dependence $\chi(W_f)$ appears to be considerably nonlinear for both nanocomposites. First, at $W_f = 1\%$, a noticeable drop in χ is observed; later, at $W_f > 1\%$, the change in χ is not so significant. Furthermore, the χ changes of the composites, modified with CNT-2, are somewhat greater (by $\sim 5\%$) than those, characteristic for the composites, modified with CNT-1. Evidently this is connected with dispersability issues of CNTs in a polymer matrix, which will be discussed later.

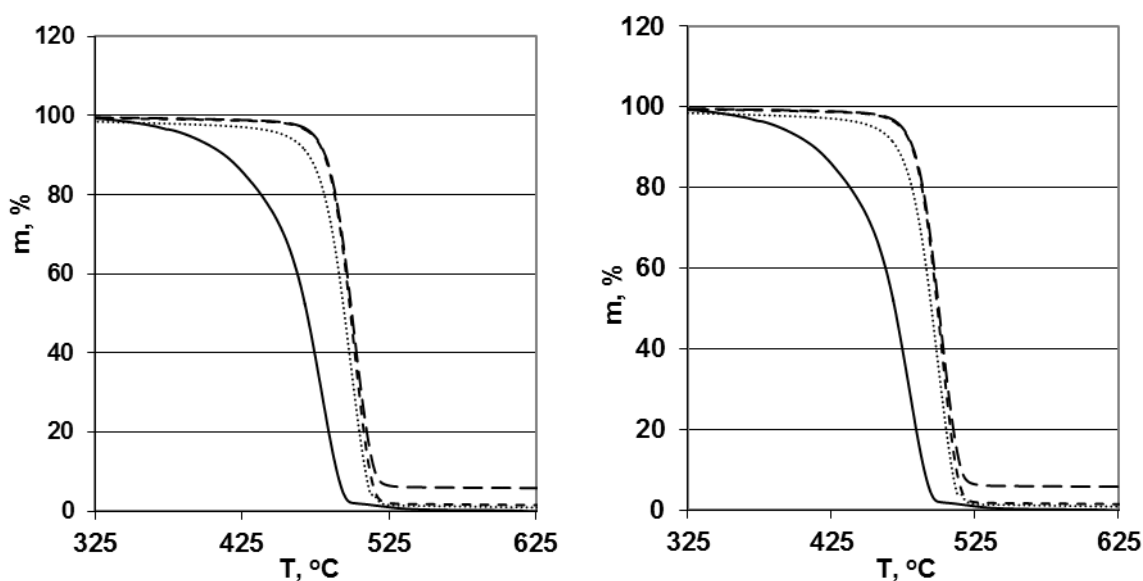


Figure 2. TGA curves of PE and PE nanocomposites with CNT-1 (a) and CNT-2 (b) at various nanofiller weight contents W_f : 0% (—), 1% (⋯), 2% (- -) and 5% (- -).

The results of TGA measurements (Fig.2.) of the investigated composites are summarized in Fig. 2. As one can see, TGA curves are shifted to higher values by increasing CNT content in the polymer matrix. For an example, 50% weight loss temperature $T_{50\%}$ is shifted to higher temperatures by $\sim 50^{\circ}\text{C}$ in respect to pure PE. Besides it no considerable differences between CNT-1 and CNT-2 modified composites are observed. These results most probably are explained with CNT thermal properties as shown also in some other investigations [4]. Evidently CNTs improve thermal stability of nanocomposites by dissipating applied heat through the all sample volume in that way making it more resistant to thermal degradation.

2.2 Mechanical analysis

The effect of CNT concentration on the indices of stress-strain properties of the investigated compositions are summarized in Table 1. With increasing CNT content, the values of σ_Y and σ_B monotonically grow. Increase of E along with addition of CNTs is not so expressed. In the case of the nanocomposite containing CNT-1, some decrease of E at higher W_f is even observed. According to literature the reason for the decreased efficiency of reinforcement of the material appears mainly because of the worsening of nanotube dispersion by increasing filler content. There are evidences made by other authors [5], showing that at higher nanofiller contents (usually above 3-6 wt. %), composite contain clusters (even entanglements) of nanotubes randomly crimped and aggregated in bound bunches. From the composite theory it is also well known that elastic modulus of a nanocomposite is a function of the theoretical elastic modulus of the filler, aspect ratios of the fillers and the degree of fiber alignment.

W_f , %	E, Mpa		σ_Y , MPa		σ_B , MPa	
	CNT-1	CNT-2	CNT-1	CNT-2	CNT-1	CNT-2
0	610		15.2		11.2	
1	694	695	16.4	16.7	12.6	12.1
2	612	908	17.9	17.9	13.4	12.8
5	580	960	17.4	20.1	14.4	15.0

Table 1. PE/CNT-1 and PE/CNT-2 composite stress-strain properties as function of CNT weight content W_f

The further theoretical analysis of the elastic properties of the composite examined in the present study has been performed in order to estimate the potential effect of reinforcement under the conditions of totally uniform dispersion of nanotubes in a polyethylene matrix.

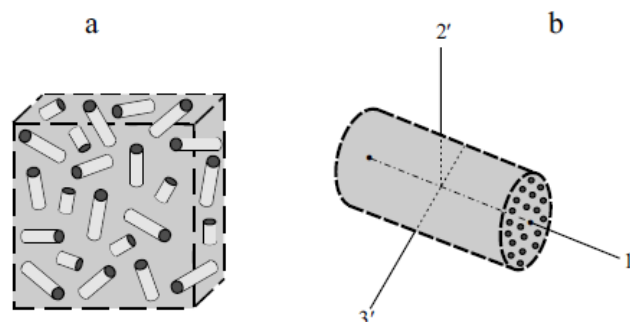


Figure 3. Schematics of a composite with randomly oriented nanotubes (a) and a representative structural element (b).

To analyze a composite material reinforced with randomly oriented individual nanotubes (Fig. 3a) let us separate from the composite a representative structural element including the polyethylene matrix and unidirectionally oriented nanotubes (Fig. 3b).

Let's assume that the constituents of the composite are isotropic, linearly elastic, and strongly bonded together. As in [6], the tensor of effective rigidity C^* of the structural element can be expressed in the form

$$C^* = C_m + V_f (C_f - C_m) \dots A \quad (1)$$

where C_f and C_m are the rigidity tensors of nanotubes and the matrix, V_f is the volume fraction of nanotubes in the composite, and A is the strain concentration tensor, which, according to the *Mori-Tanaka* method [7], is presented as

$$A = A^* \dots [(1 - V_f)I + V_f A^*]^{-1} \quad (2)$$

The tensor A^* is found by using the *Eshelby* solution [8]

$$A^* = [I + S \dots (C_f - C_m) \dots (C_m)^{-1}]^{-1} \quad (3)$$

where S is the *Eshelby* transformation tensor, depending on the shape of inclusions and the *Poisson* ratio of matrix; I is the fourth-rank unit tensor with components $I_{ijkl} = 0.5(\delta_{ik}\delta_{jl} + \delta_{il}\delta_{jk})$, and δ_{ik} is the *Kronecker* symbol.

Tensor relations (1) and (2) in an expanded form for determining the components of rigidity tensor C^*_{1111} , $C^*_{2222}=C^*_{3333}$, $C^*_{1122}=C^*_{3311}$, C^*_{2233} , $C^*_{1212}=C^*_{3131}$, and $C^*_{2323}=0.5(C^*_{2222} - C^*_{2233})$ of the transversely isotropic structural element (see Fig. 3b) are given in [9]. The tensor of effective rigidity C_{ijkl} of a composite with a random orientation of nanotubes (see Fig. 3a) is obtained by averaging the rigidity tensor C^* of the structural element over all spatial directions in the composite [10]:

$$C_{ijkl} = \frac{1}{30} [2(2C^*_{mmnn} - C^*_{nnnn}) \delta_{ij}\delta_{kl} + (3C^*_{mmnn} - C^*_{nnnn})(\delta_{ik}\delta_{jl} + \delta_{il}\delta_{jk})] \quad (4)$$

Calculation results for the concentration dependence of the elastic modulus E of polyethylene reinforced with randomly oriented nanotubes presented below were obtained according to the known relation for isotropic materials

$$E = C_{1111} - \frac{2C_{1122}^2}{C_{1111} + C_{1122}} \quad (5)$$

Let us now compare the experimental data with the calculations. The characteristics of the unfilled polyethylene (the elastic modulus $E=0.61$ GPa and *Poisson* ratio $\nu=0.35$) were determined experimentally. The 6-8% reduction in the degree of crystallinity of the polyethylene matrix in the composite revealed by the DSC could probably lead to some decrease in E ; however, in the calculations, this effect was neglected. The geometrical parameters of CNTs were assumed according to the manufacturer's data. As elastic characteristics of the nanotubes ($E_f=600$ GPa and $\nu_f=0.25$), the average values over the range of data for multiwall CNTs cited most frequently in the literature [11] were taken.

The calculation results and experimental data of *PE/CNT-2* composite are presented in Fig. 4. The elastic modulus of the composite with uniformly dispersed and randomly oriented

individual straight nanotubes, calculated according to Eq. (3) (curve 1), appeared to be much higher than the experimental one (curve 2). With increasing W_f , the disagreement between the calculation and experimental results grows. At W_f , equal to 1, 2, and 5%, the calculated values of E exceed the average experimental data by 9, 21, and 70%, respectively. The calculation results proved to be close to the confidence interval (according to the root-mean-square error) of test points only in the range of W_f not exceeding 1%.

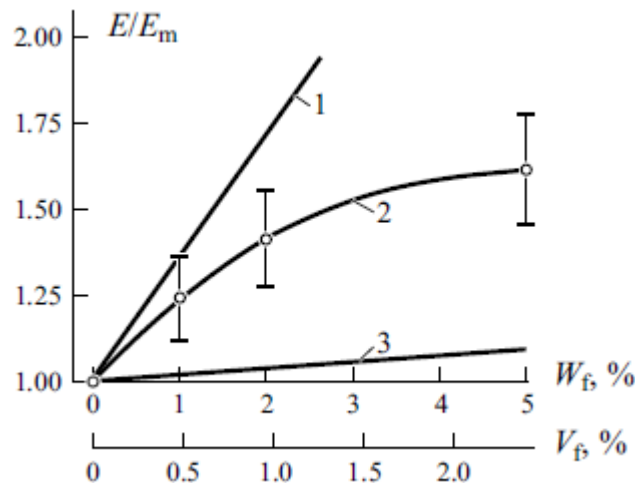


Figure 4. Relative elastic modulus E/E_m as a function of content of nanotubes by weight W_f and by volume V_f : 1 — calculation of a composite with uniformly dispersed nanotubes, 2 — experimental data, and 3 — calculation of a composite with undispersed particles of a nanotube concentrate.

The discrepancy between the calculated and experimental data indicates that, with growing content of nanotubes, the distinction between the actual morphology of CNTs in the material and the composite structure adopted in our calculations becomes more and more significant.

To complete the analysis of elastic properties, let us calculate the elastic modulus of a composite with uniformly distributed particles of a nanotube concentrate in the initial (undispersed) state. First, the effective elastic characteristics of concentrate particles are determined. It is assumed that nanotubes 1.5 μm in length and 9.5 nm in diameter are randomly oriented in the particles. According to the manufacturer's data, the content of nanotubes in the particles is 31.6%. Performing calculations following the procedure described earlier, it is possible to determine the elastic characteristics of particles: the elastic modulus $E_c = 24.3$ GPa and Poisson ratio $\nu_c = 0.254$. Then it is assumed that the concentrate particles are distributed uniformly in the polyethylene matrix. The particles are considered spheroidal with aspect ratio $l_c/d_c = 1$. Now, it is possible to find the volume content of such particles in relation to W_f and, using the known values of E_c and ν_c , calculate E of the composite. The calculation results are shown in Fig. 4 (curve 3).

As seen, the effect of reinforcement with undispersed concentrate particles proves to be rather insignificant. At $W_f = 5\%$, the increase in E , compared with that of the unfilled polyethylene, makes only 16%, while the experimental gain at the same value of W_f reaches 60% (see curve 2 in Fig. 4). This allows us to believe that the preparation of the compositions was accompanied by a significant dispersion of nanotubes. However, it should be mentioned that

the reinforcement potential of the material has not been completely realized, which is confirmed by the great discrepancy between curves 1 and 2 (see Fig. 4).

2.2 Dielectric spectroscopy

Dielectric spectroscopy measurements at frequency range from 0.1 Hz to 1 MHz indicate sharp increase in real part of AC conductivity σ' (see Fig. 5) at CNT W_f over 2 % and 1 % for PE/CNT-1 and PE/CNT-2 composites, respectively. Above these CNT concentrations the AC conductivity levels off and shows independence from the applied frequency (except the higher frequency region) indicating that the conductivity percolation threshold of the composite is reached; it could be assumed that conductivity of the investigated systems is now controlled by the CNTs network within the polymer matrix.

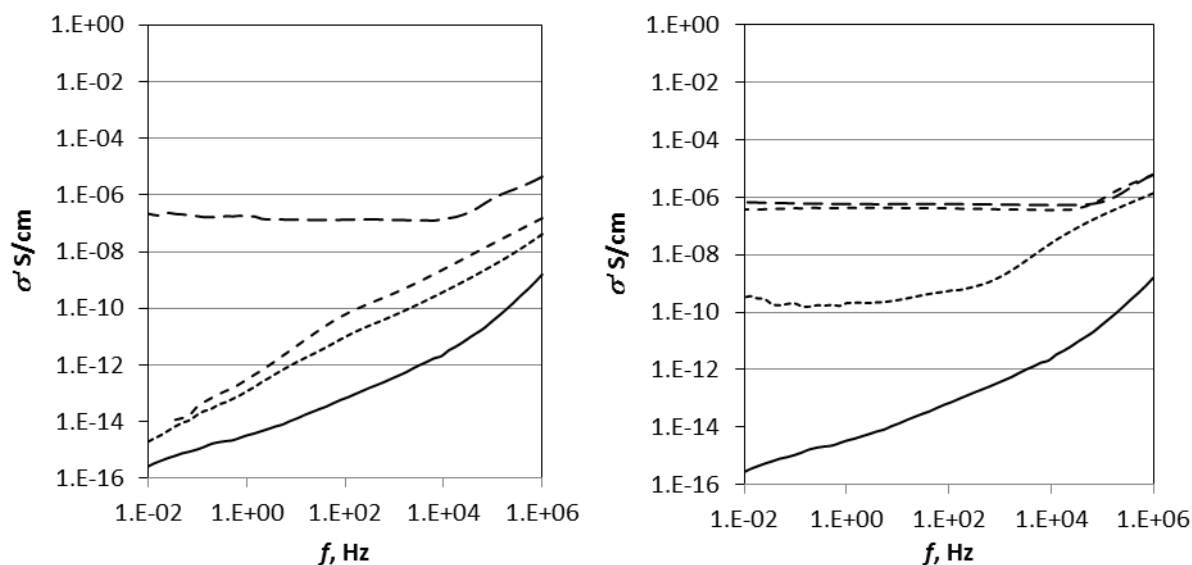


Figure 5. AC conductivity of PE and PE nanocomposites with CNT-1 (a) and CNT-2 (b) at various nanofiller weight contents W_f : 0% (—), 1% (···), 2% (- -) and 5% (- - -).

Conclusion

CNT containing PE nanocomposites with enhanced mechanical and electrical properties have been prepared by melt mixing method.

DSC results point to a marked decrease of the degree of crystallinity of the polyethylene matrix with increasing content of CNTs.

TGA results show increased thermal stability of CNT containing composite materials compared with pure PE matrix.

Dielectric spectroscopy results show that percolation threshold in the investigated nanocomposites is initiated above W_f 1% and 2% for the nanocomposites containing CNT-2 and CNT-1 respectively.

The introduction of nanotubes in rather small amounts (up to 2% of W_f) allows improve also stiffness and strength of the material. At higher CNT contents modification efficiency is somewhat reduced, most probably due to reduced dispersion quality and agglomeration of CNTs in the polymer matrix. These results have been justified by corresponding theoretical calculations.

Acknowledgements

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