Formation of carbon sp³ hybridization bonds in local electric fields of composites "polymer-CNT"

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Abstract

Carbon nanotubes are among the most anisotropic materials known and have extremely high values of Young's modulus. The possibilities to enhance the properties of nanostructured surfaces were demonstrated on "polymer-multiwall carbon nanotube" composites. Influence of sp³ hybridization bonds on polymer crystallization and strengthening was investigated in composite films of polyethyleneimine, polypropylene and polyamide with multiwall carbon nanotube" to enhance the strength properties of "polymer-multiwall carbon nanotube" composites is the composite crystallization and sp³ C-C tetrahedrons organization between nanotubes supported by resonance $\gamma_{\omega}(CH)$ and $\gamma_{\omega}(CH_2)$ vibrations in the intrinsic electric field 6·10³ V/cm between nanotube and polymer matrix. Tensile strength for polyamide-6 composites at 0.25% CNT increases 1.7 times and tensile deformation – 2.3 times. Copyright © 2018 VBRI Press.

Keywords: Polymer composites, multiwall carbon nanotubes, sp³ bonds, electric field.

Introduction

Multiwall carbon nanotubes are among the most anisotropic materials known and have extremely high values of Young's modulus [1]. Carbon nanotube aspect ratio of length to diameter is more than 10³; this distinguishes it from other nanoparticles. New composites with carbon nanotubes (CNTs) as additives were studied intensively during the last decade. Composites are characterized by extremely high specific strength properties [2], electrical and thermal conductivity [3]. The presence of CNT in the matrix improves the composite biocompatibility [4]. CNTs exhibit both semiconducting and metallic behavior depending on their chirality [5]. Researchers have successfully demonstrated field-effect transistors based on semiconducting CNTs [6]. Metallic CNTs have been considered as a potential solution for onchip interconnects with a current density well above 10^{6} A/cm^{2} [7]. The connection of CNTs to silicon has been realized, using polyethyleneimine (PEI) as a binding material between them [8]. Chemical hydrogen bonding and electrostatic interaction between PEI, CNTs, and silicon effectively connect CNTs to silicon. Electric transport at this junction shows a tunneling behavior,

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which verifies PEI as a molecular link between CNT tips and silicon. Narrow-band luminescence has been observed at the short-wavelength edge of the luminescence spectrum of polyethylene and polytetrafluoroethylene. The characteristics of this luminescence permit its assignment to the radiation emitted in recombination of ruptured C-C bonds in polymer chains [9]. The photoluminescence of polyethyleneimine with carbon multiwall nanotubes on silicon structures was investigated in [10]. High photoluminescence intensity of composite was measured due to low non-radiative proton recombination [11] on boundary microporous layer and "polymer-nanoparticles" nanocoating.

In this paper, the opportunities to enhance the properties of nanostructured surfaces are demonstrated on "polymer-multiwall carbon nanotube" composites. Influence of sp³ hybridization bonds on polymer crystallization and strengthening was investigated in composite films. It was confirmed connection between the composite IR absorption at frequencies of sp³ hybridization bonds and the amino group, $\gamma_{\omega}(CH)$ and $\gamma_{\omega}(CH_2)$ vibrations as a result of C-C tetrahedron formation. The IR absorption peak dependencies on the

CNT content at frequencies of sp³ hybridization bonds are described by a 1D Gaussian curve for the diffusion equation in the electric field. It determines the way to improve the strength properties of "polymer-CNT" composites due to the composite crystallization supported by the resonance amino group, γ_{ω} (CH) and γ_{ω} (CH₂) vibrations in the intrinsic electric field.

Experimental

Carbon high purity multiwall nanotubes (CNTs) of 2 μ m length and 20 nm diameter (**Fig. 1**) were obtained by catalytic pyrolysis of unsaturated hydrocarbons [12]. Nanoparticle morphology was investigated by the atomic force microscopy (AFM, NanoScope IIIa Dimension 3000TM, Advance Surface Microscopy Inc.).

The composites were made of PEI, polypropylene and polyamide filled by a mixture of CNTs with the polymer powder and dried; the samples were formed by hot pressing. Compression and tension tests of the polymeric materials and their composites was performed using tensile machine 2167-R50 with automatic recording of the deformation diagram. Thin polymeric films (100-150 μ m thick) without and with CNTs were prepared out using Thermo HYDROPRESS.

Chemical states on the surface of macroporous silicon structures with nanocoatings were identified by IR absorption spectra using a PerkinElmer Spectrum BXII IR Fourier spectrometer in the spectral range of 300-8000 cm⁻¹. The optical absorption spectra were measured at normal incidence of IR radiation on the sample. Raman spectra of macroporous silicon structures with nanocoatings of PEI with multiwall carbon nanotubes were measured using a Horiba Jobin-Yvon T64000 spectrometer. The IR absorption ang Raman spectra measurements were carried out in air at room temperature.



Fig. 1. Morphology of multiwall nanotubes according to the data of the atomic force microscopy.



Fig. 2a. IR absorption (1) and Raman (2) spectra of multiwall carbon nanotubes.

Results and discussion

Intensive peaks of sp^3 -hybrid orbitals (D), sp^2 -hybrid orbitals (G), 2D and CH₂ bonds were measured in the IR spectra (Fig. 2a, curve 1) and Raman spectra (Fig. 2a, curve 2) of multiwall carbon nanotubes.

Fig. 2b shows the absorption spectra of PEI (curve 1), the composite "PEI-carbon nanotubes" (curve 2) and the ratio of spectra 1 and 2 (curve 3).

After formation of the PEI-CNT composite intensive absorption maxima were measured in area of the sp^3 hybridization (D) bonds at the frequency of N-H(1) oscillations in the primary amino groups of PEIs and in area of the sp^2 hybridization (G) bonds for the N-H(2) oscillation frequencies in secondary amino groups of PEIs.



Fig. 2b. IR absorption spectra of PEI (1), "PEI-CNT" composite (2) and its relation (3).



Fig. 3a. IR absorption spectra: 1-polyamide-6, 2-composite "polyamide-6 - carbon nanotubes" and 3 - the ratio of the curves 1 and 2.

Fig. 3a shows IR absorption spectra of polyamide (curve 1), "polyamide-carbon nanotubes" composite (curve 2) and the ratio of the curves 1 and 2 (curve 3).

From Fig. 3a one can see that after adding CNTs (concentration of 0.25%) to polypropylene IR absorption exceeds the absorption of polypropylene 4-8 times in all measured spectral range. This increases the intensity of the C-C bond vibrations (835 and 1000 cm⁻¹), γ_r (CH₃) (A) - 970 cm⁻¹, γ_{ω} (CH₃) - 1170 cm⁻¹, γ_{ω} (CH) (A) on the frequency of bonds sp³ hybridization (D) - 1360 cm⁻¹, as well as fluctuations $\delta(CH_3) - 1380 \text{ cm}^{-1}$, $\delta(CH_2) - 1440$ cm^{-1} , $\delta_a(CH_3) - 1470 cm^{-1}$ [13, 14].

Fig. 3b presents the ratio of IR absorption spectra of "composite/polymer" for films of polypropylene (PP) curve 1, polyamide-6 (PA6) - curve 2) and polyamide-12 (PA12) - curve 3. After adding CNTs to polymers (concentration of 0.25%), IR absorption of "composite/polymer" films exceeds that of polymer films essentially. Higher C-C fluctuations, CH, CH₂ and CH₃ bond absorption correspond to higher absorption of composites at the frequencies of sp³ hybridization bonds.



Fig. 3b. Ratio of IR absorption spectra of "composite/polymer": 1 – polypropylene, 2 – polyamide-6, 3 – polyamide-12.

| Table 1. Types of bonds for IR absorption growth at frequencies | | | | | | | | |
|--|-----|--------|---------------|-------|--------|----|----------|--------|
| of sp ² | and | sp^3 | hybridization | after | adding | to | polymers | carbon |
| nanotubes. | | | | | | | | |

| Type of bonds | Frequency, cm ⁻¹ | | | | | |
|-----------------------------------|-----------------------------|--|--|--|--|--|
| Polypropylene | | | | | | |
| $\gamma_{\omega}(CH)$ | 1360 | | | | | |
| Polyamide-6 | | | | | | |
| $\gamma_{\omega}(CH_2)$ | 1319, 1406 | | | | | |
| Polyamide-12 | | | | | | |
| γ _ω (CH ₂) | 1357 | | | | | |

Table 1 shows type and frequency of bonds for the IR absorption growth at frequencies of sp³ hybridization after adding carbon nanotubes to polymers. Thus, higher absorption of composites at the frequencies of sp³ hybridization bonds is due to $\gamma_{\omega}(CH)$ and $\gamma_{\omega}(CH_2)$ vibrations (Table 1).

IR absorption by sp³ hybridization bonds (D) in composites of polymers with multiwall carbon nanotubes has maxima (Fig. 4) at its dependencies on CNT content. Thus, the maxima correspond to fixed distance between nanotubes. Distance between nanotubes in composites depends on the concentration of CNT (N_{CNT}) , its content (% CNT) and the nanotube volume (V_{CNT}):

$$a = (N_{CNT})^{1/2} = (\% \text{ CNT}/100V_{CNT})^{1/2}$$
 (1)

The IR absorption maximum for sp³ hybridization bonds (D) of composites (Fig. 4) corresponds to the average distance $a = 0.35 \,\mu\text{m}$ between the cylindrical CNT (diameter of 20 nm, length of 2 um).

This maximum can be explained by the geometric factor - characteristic volume around the cylindrical CNT at a distance of $a_m/2$ from nanotubes. As $a > a_m$, the characteristic volume around CNT increases due to increasing of the content of CNT (% CNT, N_{CNT}), IR absorption increases too. The characteristic volume around CNT and IR absorption decreases with CNT content at $a < a_{\rm m}$,



Fig. 4. IR absorption by sp³ hybridization bonds (D) in composites based on polypropylene (1) and polyamide-6 (2) vs CNT content in polymer.



% CNT in polymer

Fig. 5. Calculated dependences of average distance *a* between CNT (1), geometric approximation (2) - characteristic volume around CNT; experimental dependence from Fig. 4 of the IR absorption peak of sp³ hybridization of "polypropylene - CNTs" composite (3) and its approximation (4) on CNT content.

Fig. 5 shows the calculated (according to Eq. (1)) dependences of average distance a between CNT (curve 1), geometric approximation (curve 2, characteristic volume around CNT), experimental dependence from Fig. 4 of the IR absorption peak of sp³ hybridization of "polypropylene-CNTs" composite (curve 3) on CNT content. The obtained geometric approximation (Fig. 5, curve 2) explains only qualitatively the experimental dependence of IR absorption peak in bonds sp³ hybridization (D) of "polypropylene-carbon nanotube" composite on the CNT content. This relationship is more nonlinear and has the form of a 1D Gaussian curve (Fig. 5, curve 4), which corresponds to the diffusion equation in the electric field. The length $a = 0.35 \,\mu\text{m}$ between cylindrical CNT corresponds to the distance between nanotubes $w = (a_{\rm m} - d)/2 = 0.17 \ \mu {\rm m}$ for maximum of IR absorption.

The electric field between the nanotubes and polymer matrix has a space charge region (SCR) width w (Fig. 6).

We used the Poisson equation in a cylindrical coordinate system to calculate the SCR width (Fig. 6) around a cylindrical nanotube:

$$\frac{1}{\mathbf{r}}\frac{\partial}{\partial \mathbf{r}}(\mathbf{r}\frac{\partial Y}{\partial \mathbf{r}}) = -\frac{\rho_q}{\varepsilon\varepsilon_0}\frac{e}{kT}$$
(2)

where r is the radius vector, ρ_q is the charge density. We used the boundary conditions for the area of the SCR width w for a cylindrical nanotube diameter d: E(d/2 + w) = 0, Y(d/2 + w) = 0, $Y(d/2) = Y_S$, where E is the electric field strength, Y_S - the value of the potential on the surface of the nanotube. Integrating Eq. (2) and using the above boundary conditions, we obtained the equation [15]:

$$\frac{16\varepsilon\varepsilon_0 Y_S w}{eq_V d^2} - 1 + \left(1 + \frac{2w}{d}\right)^2 \left(1 - 2\ln\left(1 + \frac{2w}{d}\right)\right) = 0$$
(3)

Fig. 7 shows dependences of the size of the space charge region of cylindrical nanotubes calculated from Eq. (3) on their diameter at various values of the surface potential. It is shown in Fig. 7 that the SCR width w

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decreases with the diameter of nanotubes decrease. Surface potential $Y_s = -4kT$ (106 mV) and electric field intensity $E = Y_S / w = 6.3 \cdot 10^3$ V/cm corresponds to $w = 0.17 \,\mu\text{m}$ for cylindrical CNTs (diameter of 20 nm, length of 2 µm) maximum at IR absorption peak for bonds of sp³ hybridization (D).

Carbon nanotubes are divided into two main groups: (1) the molecular associated nanotubes linked through weak interactions, van der Waals forces, and (2) nanotubes with additional strong covalent sp³ type C-C bonding [8]. Thus, one of the way to improve the strength properties of "polymer-CNT" composites is the polymer crystallization.

For our case, the polymer crystallization depends on sp³ C-C tetrahedrons organization between nanotubes due to $\gamma_{\omega}(CH)$ and $\gamma_{\omega}(CH_2)$ vibrations (**Table 1**) in the intrinsic electric field. Really, the profile analysis of Xray reflexes confirmed high crystallinity degree of investigated "polymer-CNT" composites - from 72% to 85% [16].

Crystalline polymers demonstrate high tensile strength. Experimental dependences of the IR absorption peak of sp³ hybridization (Fig. 8, curve 1) and tensile strength of "polyamyde-6-CNT" composite (Fig. 8, curve 2) have the same peak at CNTs content of 0.25%. Tensile strength of PA6-CNT system with CNTs content of 0.25% is 30-40 MPa (Fig. 8).



Fig. 7. Dependences of SCR width w around cylindrical nanotubes on its diameter for surface potential Ys: 1 - 12 kT; 2 - 8 kT; 3 - 4 kT.



Fig. 8. Experimental dependence of the IR absorption peak of sp³ hybridization (1) and tensile strength of "polyamyde-6-CNT" composite (2) on CNT concentration.

Conclusions

Carbon nanotubes are among the most anisotropic materials known and have extremely high values of Young's modulus. The possibilities to enhance the properties of nanostructured surfaces were demonstrated on the "polymer-multiwall carbon nanotube" composites and composite nanocoatings on macroporous silicon structures.

Influence of sp³ hybridization bonds on polymer crystallization and strengthening was investigated in composite films. Intensive IR absorption maxima were measured after formation of the "PEI-CNT" composite in the area of the sp³ hybridization (D) bonds at the frequency of N-H(1) oscillations in the primary amino groups of PEIs. In addition, high IR absorption at frequencies of sp³ hybridization bonds of polypropylene, polyamide-6 and polyamide-12 with CNTs is determined by γ_{ω} (CH) and γ_{ω} (CH₂) vibrations as a result of C-C tetrahedron formation.

The IR absorption peak dependencies on CNT content at frequencies of sp³ hybridization bonds are described by a 1D Gaussian curve for the diffusion equation in the electric field. The electric field intensity between nanotubes and polymer matrix is equal to $6.3 \cdot 10^3$ V/cm at 0.25% CNT. Thus, the way to improve the strength properties of "polymer-CNT" composites is the composite crystallization supported by γ_{ω} (CH) and γ_{ω} (CH₂) vibrations in the intrinsic electric field.

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Author's contributions

Conceived the plan: L. Karachevtseva, M. Kartel, W. Bo; *Performed the expeirments:* Y. Sementsov, V. Trachevskyi, O. Lytvynenko *Data analysis:* L. Karachevtseva, V. Onyshchenko; *Wrote the paper:* L. Karachevtseva, M. Kartel, M. Kartel, V. Onyshchenko. Authors have no competing financial interests.

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