The possibilities to enhance the properties of nanostructured surfaces have been demonstrated on “polymer-multiwall carbon nanotubes” composites. Carbon nanotubes are among the most anisotropic materials known and have extremely high values of the Young modulus. Influence of sp³ hybridization bonds on polymer crystallization and strengthening was investigated in composite films of polyethyleneimine, polyamide and polypropylene with multiwall carbon nanotubes. IR absorption maxima were measured after formation of composite “polyethyleneimine-carbon nanotubes” in the area of the sp³ hybridization bonds at the frequency of primary amino groups of polyethyleneimine. High IR absorption at frequencies of sp³ hybridization bonds of polypropylene, polyamide-6 with carbon nanotubes is determined by γω(CH) and γω(CH₂) vibrations as a result of the formation of C-C bonds in the polymer chains, which increases the crystallization of polymers and the strength of the composites. The IR absorption peak dependences on the carbon nanotube content at frequencies of sp³ hybridization bonds are described by a 1D Gaussian curve for the diffusion equation in the electric field. Thus, the way to improve the strength properties of “polymer-CNTs” composites is the polymer crystallization as a result of the transformation of the C-C bonds in the polymer chains supported by the resonances of the primary amino groups, γω(CH) and γω(CH₂) in the electric field between the nanotubes and polymer matrix. Tensile strength for polyamide-6 composites at 0.25 % CNT increases 1.7 times and tensile deformation – 2.3 times.

Keywords: polymer composites, multiwall carbon nanotubes, sp³ bonds, electric field

INTRODUCTION

Multiwall carbon nanotubes are among the most known anisotropic materials and have extremely high values of the Young 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 dependent 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 on-chip interconnects with a current density well above 10⁶ A/cm² [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, 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 nanotubes” composites. Influence of $sp^3$ hybridization bonds on polymer crystallization and strengthening was investigated in composite films. A connection was confirmed between the composite IR absorption at frequencies of $sp^3$ hybridization bonds and the primary amino group, $\gamma_\omega(CH)$ and $\gamma_\omega(CH_2)$ vibrations as a result of C-C bond transformation in polymer chains. The IR absorption peak dependences on the CNT content are described at frequencies of $sp^3$ hybridization bonds by a 1D Gaussian curve for the diffusion equation in the electric field. It determines the way to improve the strength properties of composite films of polyethyleneimine, polyamide and polypropylene with multiwall carbon nanotubes due to the composite crystallization supported by the resonance amino group, $\gamma_\omega(CH)$ and $\gamma_\omega(CH_2)$ vibrations in the intrinsic electric field.

EXPERIMENTAL

Carbon high purity multiwall nanotubes (CNTs) of 2 $\mu$m length and 20 nm diameter (Fig. 1 a–b) were obtained by catalytic pyrolysis of unsaturated hydrocarbons [12]. Nanoparticle morphology was investigated by the atomic force microscopy (AFM, NanoScope IIIa Dimension 3000TM, Advanced Surface Microscopy Inc.). The composites were made of polyethyleneimine, 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 were performed using a tensile machine 2167-R50 with automatic recording of the deformation diagram. Thin polymeric films (100–150 $\mu$m thick) without and with CNTs were prepared out using a Thermo HYDROPRESS.

Fig. 1. a – morphology of carbon multiwall nanotube according to the AFM data, b – fragment of carbon multiwall nanotube

Chemical states on the surface of macroporous silicon structures with nano-coatings 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 at room temperature.

RESULTS AND DISCUSSION

Intensive peaks of $sp^3$-hybrid orbitals (D), $sp^2$-hybrid orbitals (G), 2D and CH$2$ bonds were measured in the IR spectra and Raman spectra of multiwall carbon nanotubes. Fig. 2 a shows the absorption spectra of polyethyleneimine (curve 1), of the composite “polyethyleneimine – carbon nanotubes” (curve 2) and the ratio of spectra 2 and 1 (curve 3). After formation of the “polyethyleneimine – carbon nanotubes” composite intensive absorption maxima were measured in area of the $sp^3$ hybridization (D) bonds at the frequency of the primary amino group N-H(1) oscillations in PEI (Fig. 2 b, curve 1) and in area of the $sp^2$ hybridization (G) bonds for the secondary amino group N-H(2) oscillation frequencies in PEI (Fig. 2 b, curve 2).

Fig. 3 a shows IR absorption spectra of polyamide (curve 1), “polyamide – carbon nanotubes” composite (curve 2) and the ratio of the curves 2 and 1 (curve 3). After adding CNTs
Carbon sp³ hybridization bonds in composites “polymer – CNT”

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. 3 b).

Fig. 2. a – IR absorption spectra of polyethylenimine (curve 1), “polyethylenimine – carbon nanotubes” composite (curve 2) and the ratio of the curves 2 and 1 (curve 3), b – IR absorption by N-H(1) (curve 1) and N-H(2) (curve 2) bonds in composites based on polyethylenimine vs the carbon nanotube content in polymer

![Graph](image1.png)

Fig. 3. a – IR absorption spectra of polyamide (curve 1), “polyamide – carbon nanotubes” composite (curve 2) and the ratio of the curves 1 and 2 (curve 3), b – IR absorption by sp³ hybridization bonds (D) in composites based on polyamide-6 vs the carbon nanotube content in polymer

![Graph](image2.png)

From Fig. 4 a one can see that after adding CNTs (concentration of 0.25 %) to polypropylene IR absorption exceeds the absorption of polypropylene 4–8 times in antire measured spectral range. This increases the intensity of the C-C bond vibrations (835 and 1000 cm⁻¹), γ(CH₃) (A) – 970 cm⁻¹, γ(CH₂) – 1170 cm⁻¹, γ(CH) (A) on the frequency of bonds sp³ hybridization (D) – 1360 cm⁻¹, as well as fluctuations δ(CH₃) – 1380 cm⁻¹, δ(CH₂) – 1440 cm⁻¹, δ(CH) – 1470 cm⁻¹ [13, 14].

After formation of the “polypropylene – carbon nanotubes” composite intensive absorption maxima were measured in the area of sp³ hybridization (D) bonds at the frequency of γ(CH) vibrations (Fig. 4 b). Higher C-C
fluctuations, CH, CH₂ and CH₃ bond absorption correspond to higher absorption of composites at the frequencies of sp³ hybridization bonds. Table 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 the primary amino group N-H(1), γυ(CH) and γυ(CH₂) vibrations.

Table. Type and frequency of bonds in the areas of sp² and sp³ hybridizations in composites after adding multiwall carbon nanotubes to polymers

| Type of hybridization | Polyethyleneimine – carbon nanotubes | Polyamide-carbon nanotubes | Polypropylene-carbon nanotubes |
|----------------------|-------------------------------------|---------------------------|-------------------------------|
|                      | Type of bonds | Frequency, cm⁻¹       | Type of bonds | Frequency, cm⁻¹       | Type of bonds | Frequency, cm⁻¹       |
| sp³                  | N-H(1)       | 1314                   | γυ(CH₂)       | 1319                   | γυ(CH)       | 1360                   |
| sp²                  | N-H(2)       | 1572                   |               |                        |              |                        |

IR absorption by sp³ hybridization bonds in composites of polymers with multiwall carbon nanotubes has maxima (Figures 2 b, 3 b and 4 b) at its dependences on CNT content. Thus, the maxima correspond to fixed distances between nanotubes. The distance between nanotubes in composites depends on the concentration of CNT (N_CNT), its content (% CNT) and the nanotube volume (V_CNT):

\[ a = (N_{CNT})^{\frac{1}{2}} = \frac{\% \text{ CNT} \times V_{CNT}}{100} \]

The IR absorption maximum for sp³ hybridization bonds (D) of composite polyethyleneimine-carbon nanotubes (Fig. 2 b) corresponds to the average distance \( a = 0.31 \) μm between the cylindrical CNT (diameter of 20 nm, length of 2 μm). The IR absorption maximum for sp³ hybridization bonds (D) of composites polyamide-carbon nanotubes and polypropylene-carbon nanotubes (Fig. 3 b and Fig. 4 b) corresponds to the average distance \( a = 0.35 \) μm between the cylindrical CNTs. Obtained maxima can be explained by the geometric factor – characteristic volume around the cylindrical CNT at a distance of \( a/2 \) 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 growth of CNT content at \( a < a_{m} \).

Fig. 5 shows the calculated (according to Equation (1)) dependences of average distance \( a \) between CNT (curve 1), geometric...
approximation (curve 2, characteristic volume around CNT), experimental dependence from Fig. 4b 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 qualitatively only 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 electric field between the nanotubes and polymer matrix has a space charge region (SCR) of width w (Fig. 6) with surface potential Ys. We used the Poisson equation in a cylindrical coordinate system to calculate the SCR width (Fig. 6) around a cylindrical nanotube:

$$\frac{1}{r} \frac{\partial}{\partial r} \left( r \frac{\partial Y}{\partial r} \right) = -\frac{\rho_q}{\varepsilon_\varepsilon_0} e^kT,$$  \hspace{1cm} (2)

where r is the radius vector, \( \rho_q \) is the charge density, \( \varepsilon_\varepsilon_0 \) – the relative dielectric permittivity.

We used the boundary conditions for the area of the SCR width w for a cylindrical nanotube diameter d:

\[ E(d/2 + w) = 0, \quad Y(d/2 + w) = 0, \quad Y(d/2) = Y_s, \]

where \( E \) is the electric field strength, \( Y_s \) – the value of the potential on the boundary “polymer – CNTs”. Integrating Eq. (2) and using the above boundary conditions, we obtained the equation [15]:

$$\frac{16\pi\varepsilon_\varepsilon_0 Y_s w}{eq_\varepsilon d^2} - 1 + \left( 1 + \frac{2w}{d} \right)^2 \left( 1 - 2 \ln \left( 1 + \frac{2w}{d} \right) \right) = 0. \hspace{1cm} (3)$$

Fig. 7 shows dependences of the size of the space charge region w of cylindrical nanotubes calculated from Eq. (3) on their diameter at various values of the surface potential \( Y_s \). Fig. 7 shows that the SCR width w decreases with the diameter of nanotubes decrease. The length \( a = 0.31 \mu m \) between cylindrical CNT corresponds to the distance between nanotubes \( w = (a_m - d)/2 = 0.155 \mu m \) in composite “polyethylenimine – carbon nanotubes” for maximum of IR absorption (Fig. 2b) and surface potential \( Y_s = -3kT \) (79.5 mV) at the electric field intensity \( E = Y_s/w = 5.12 \cdot 10^3 \) V/cm. The
length $a = 0.35 \mu m$ between cylindrical CNTs corresponds to the distance between nanotubes $w = (a_m - d)/2 = 0.17 \mu m$ in composites “polyamide – carbon nanotubes” and “polypropylene – carbon nanotubes” (Fig. 3 b and Fig. 4 b) for maximum of IR absorption. It corresponds to surface potential $Y_S = -4kT$ (106 mV for room temperature 300 K, Fig. 7) and electric field intensity $E = Y_S/w = 6.3 \cdot 10^3 V/cm$ for $w = 0.17 \mu m$ between cylindrical CNTs (diameter of 20 nm, length of 2 $\mu m$) at maximum of IR absorption for bonds of $sp^3$ hybridization (D). The profile analysis of X-ray reflexes confirmed high crystallinity degree of investigated composite “polyamide 6 – CNTs” from 72 to 85 % [16] at the maximum of IR absorption (Fig. 3 b). Crystalline polymers demonstrate high tensile strength (30–40 MPa for composite “polyamide 6 – CNTs”).

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 $sp^3$ type C-C bonding [8]. Thus, one of the way to improve the strength properties of “polymer – CNTs” composites is the polymer crystallization as a result of the formation of C-C bonds in the polymer chains supported by the $sp^3$ hybridization bond organization in nanotubes and by resonances of the primary amino groups of polyethyleneimine, $\gamma_\omega(CH)$ vibrations of polypropylene and $\gamma_\omega(CH_2)$ vibrations of polyamide-6 (Table) in the intrinsic electric field between nanotube and polymer matrix.

CONCLUSIONS

Carbon nanotubes are among the most anisotropic materials known and have extremely high values of the Young 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 $sp^3$ hybridization bonds on polymer crystallization and strengthening was investigated in composite films. Intensive IR absorption maxima were measured after formation of composite “polyethyleneimine – carbon nanotube” in the area of the $sp^3$ hybridization (D) bonds at the frequency of N-H(1) oscillations in the primary amino groups of polyethyleneimine. In addition, high IR absorption at frequencies of $sp^3$ hybridization bonds of polypropylene, polyamide-6 with carbon nanotubes is determined by $\gamma_\omega(CH)$ and $\gamma_\omega(CH_2)$ vibrations.

The IR absorption peak dependences on CNT content at frequencies of $sp^3$ 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 % CNTs (polyamide-6 with carbon nanotubes). Thus, the way to improve the strength properties of “polymer – CNT” composites is the composite crystallization supported by $\gamma_\omega(CH)$ and $\gamma_\omega(CH_2)$ vibrations in the intrinsic electric field.

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Зв’язки sp³ гібридизації в композитах «полімер – вуглецеві нанотрубки»

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Досліджено можливості підсилення властивостей композитів «полімер – багатошарові вуглецеві нанотрубки». Вуглецеві нанотрубки є одним з найбільш анизотропних матеріалів і мають надзвичайно високі значення модуля Юнга. Оцінено вплив sp³-гібридизаційних зв’язків на кристалізацію та зміщення полімерів у композитних плівках поліетиленаміну, поліамідну та поліпропілену з вуглецевими нанотрубками. Після формування композиту «поліетиленамін – вуглецеві нанотрубки» були виміряні максимальні значення IЧ-поглинання в області sp³-гібридизаційних зв’язків на частоті первинних аміногруп поліетиленаміну. Суттєве підвищення IЧ-поглинання на частотах sp³-гібридизаційних зв’язків поліетиленаміну та поліаміду-6 з вуглецевими нанотрубками висвітлюється коливаннями, відповідно, γυ(CH) та γυ(CH3) в результаті утворення C-C зв’язків в полімерних ланцюгах, що підвищує кристалізацію полімерів та міцність композитів. Піка залежності IЧ-поглинання від волого вуглецевих нанотрубок на частотах sp³-гібридизаційних зв’язків описуються 1D-гауссовою кривою для рівняння дифузії в електричному полі. Таким чином, спосіб підвищення міцності композитів «полімер – багатошарові вуглецеві нанотрубки» - це кристалізація полімера в результаті трансформації C-C зв’язків в полімерних ланцюгах, підтриманої резонансами коливань первинних аміногруп γυ(CH) та γυ(CH3) в електричному полі між нанотрубкою і полімерною матрицею. При цьому міцність на розрив, наприклад, для композиту поліаміду-6 при 0.25 % вуглецевих нанотрубок збільшується в 1.7 рази, а деформація розтягування - в 2.3 рази.

Ключові слова: полімерні композити, багатошарові вуглецеві нанотрубки, зв’язки sp³, електричне поле

Связи sp³ гибернизации в композитах «полимер – углеродные нанотрубки»

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Исследованы возможности улучшения свойств композитов «полимер – многослойные углеродные нанотрубки». Углеродные нанотрубки являются одним из наиболее анизотропных материалов и имеют чрезвычайно высокие значения модуля Юнга. Оценино влияние sp³-гибридизационных связей на кристаллизацию и упрочнение полимеров в композитных пленках полиамидами, полипропилен и полипропилен с углеродными нанотрубками. После формирования композита «полипропилен - углеродные нанотрубки» были измерены максимальные значения ИК-поглощения в области sp³-гибридизационных связей на частоте первичных амидных групп полиамидами. Существенное повышение ИК-поглощения на частотах sp³-гибридизационных связей полиамидами и полиамид-6 с углеродными нанотрубками определяется колебаниями, соответственно, γυ(CH) и γυ(CH3) в результате образования С-C связей в полимерных цепях, что повышает кристаллизацию полимера и прочность композитов. Пики интенсивностей ИК-поглощения от содержания углеродных нанотрубок на частотах sp³-гибридизационных связей описываются 1D-гауссовой кривой для уравнения диффузии в электрическом поле. Таким образом, способ повышения прочности композитов «полимер - многослойные углеродные нанотрубки» - это кристаллизация полимера в результате трансформации C-C связей в полимерных цепях,
подержанной резонансами колебаний первичных аминогрупп, γ_а(СН) и γ_а(СН₂) в электрическом поле между нанотрубкой и полимерной матрицей. При этом прочность на разрыв, например, для композита полиамид-6, содержащего 0.25 % углеродных нанотрубок, увеличивается в 1.7 раза, а деформация растяжения - в 2.3 раза.

Ключевые слова: полимерные композиты, многостенные углеродные нанотрубки, sp³ связи, электрическое поле

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