

Hong-Ou-Mandel quantum effect on "rubber - carbon nanotubes" composites

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Introduction

We investigated influence of multiwalled carbon nanotubes (CNTs) on the characteristics of composites "rubber-carbon nanotubes". The rubber compounds filled by nanotubes were prepared on the butadiene-nitrile rubber. CNTs were obtained by the method of catalytic chemical vapor deposition (CCVD) by pyrolysis of hydrocarbons on complex metal oxide catalysts. Rubber mixtures were prepared on a laboratory mixer, mixing temperature – 100 °C, mixing time – 6 min, speed of rotation of rotors – 60 rpm. CNTs were injected into a technical carbon on a dissolver with a rotational speed of 300 rpm for 5 min in a mixer chamber of a dissolver. To assess the strength of the properties of the resulting compositions, rubber was treated in a vulcanization press at 150 °C for 20 min.

Procedure and Results

IR reflectance. Earlier we evaluated that IR reflectance peak dependences on the carbon nanotubes content in polymer composites correspond to 1D Gaussian curve for the diffusion equation in the electric field between electrons of nanotubes and protons in polymer according to "semiconductor" model of the composite structuring. And here we measured IR reflectance maxima (Fig. 1) of composites "rubber-carbon nanotubes" at 0–10 % of CNTs in the spectral area of the rubber CH deformation vibrations at frequencies 1297, 1465 and 1728 cm⁻¹ and valence vibrations at frequencies 2844 and 2916 cm⁻¹.

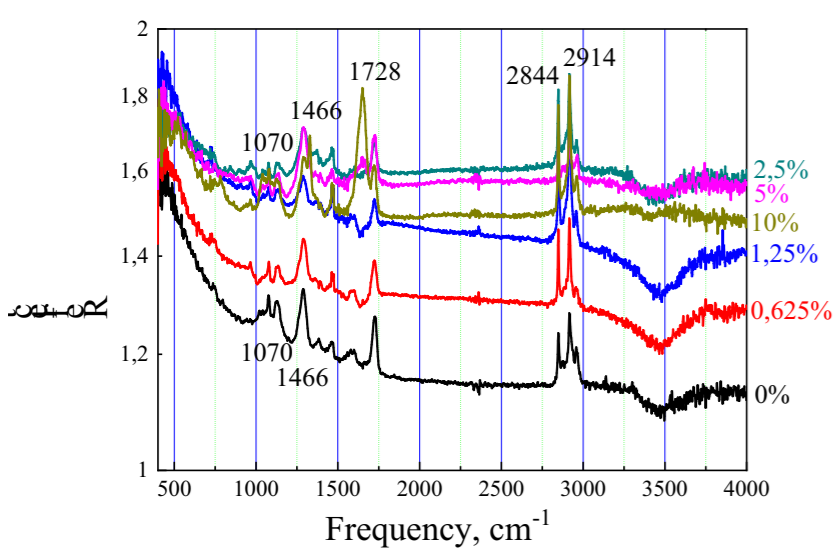


Fig. 1. IR reflectance spectra of composites "rubber - carbon nanotube" at 0–10 % of CNTs in the spectral area of CH deformation vibrations at frequencies 1466 and 1728 cm⁻¹ and CH valence vibrations at frequencies 2844 and 2916 cm⁻¹.

Fig. 2a shows dependences of IR reflectance maxima from Fig. 1 of composites "rubber - carbon nanotubes" vs. the carbon nanotube content in the area of CH deformation vibrations: 1 – 1297 cm⁻¹, 2 – 1465 cm⁻¹ and 3 – 1728 cm⁻¹; and valence vibrations: 4 – 2844 cm⁻¹ (CH₃) and 5 – 2914 cm⁻¹ (CH₂). Fig. 2b shows dependences of relative IR reflectance R/R_0 of composites "polybutadiene rubber - carbon nanotubes" on the carbon nanotube content in the area of CH₃ (curve 1, 2844 cm⁻¹) and CH₂ (curve 2, 2914 cm⁻¹) valence vibrations and relative tensile strength N/N_0 for two types of composites (curves 3–4). IR reflectance in spectral area of CH, CH₂ and CH₃ vibrations in composites "polybutadiene rubber - carbon nanotube" has maxima as dependent on CNT content.

According to 2D model of CNTs distribution, the distance between nanotubes in composites depends on the CNTs concentration (N_{CNT}), its content (wt.% CNT) and the nanotube volume (V_{CNT}):

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

The IR reflectance maxima (Fig. 2a and Fig. 2b) correspond to the average distance $a = 0.35 \mu\text{m}$ between the cylindrical CNTs. Obtained maxima can be explained by the geometric factor – characteristic volume around the cylindrical CNT at distance of $a_m/2$ from nanotubes. At $a > a_m$, the characteristic volume around CNT increases with the CNT content and N_{CNT} , IR absorption; and the characteristic volume around CNT and IR absorption decreases with growth of CNT content at $a < a_m$.

Thus, these maxima correspond to fixed distance between nanotubes. There are maxima of dependences 1–4 from Fig. 2a at 0.16, 1.25 and 2.5 wt.% CNTs and pronounced minimum at 5 wt.% CNTs. That minimum corresponds to minima IR reflectance of CH₃ and CH₂ valence vibrations. In addition, at high CNTs content (>5 wt.% CNTs) dependences 3 and 4 from Fig. 2b became almost linear and proportional to CNTs surface in composite. The introduction of CNTs in an amount of 0.1–5.0 % by weight of rubber compositions results in a significant increase in the strength characteristics and thermal stability of the compositions (Fig. 2b). This result indicates that CNT is ideal filler for composites based on polymers of different chemical composition and structure. It follows from the foregoing that the strengthening of elastomers is not an isolated phenomenon at the interlayer boundary, but is a complex colloid-chemical process of formation of the interlayer region and vulcanization structures in the carbon-rubber mesh nodes. Rubber deformation begins with redeployment of grid nodes by overcoming their physical interactions in chain structures and with a matrix, accompanied by a decrease in their functionality due to the rupture of overvoltage chains. In the final stages of destruction, nodes can also be deformed, which contributes to the dissipation of overvoltage from the interphases boundary, which additionally increases the strength of the rubber.

Fig. 3 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. 2b of the IR absorption peak in area of sp³ hybridization of "polypropylene - CNTs" composite on CNT content. The obtained geometric approximation (Fig. 3, 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 a form of a 1D Gaussian curve (Fig. 3, curve 3), which corresponds to the diffusion equation in the electric field. Surface of all nanotubes in composites S_{CNT} is proportional to the concentration of CNT (N_{CNT}) and have no peak in dependence on CNT content according curve 1 from Fig. 3.

An important role in increasing the ability to deform the grid nodes played occluded rubber and its polar modifiers reduce. Polar groups of rubbers interacting with CNT accelerate the vulcanization with sulphur, strengthen the interphone boundary and compact the transitional layers at the nodes of the rubber net, which reduces their capability to deform. With the decrease in the instauration of rubber by hydrogenation, the cross linking processes are redistributed from the interphone boundary to the entire volume of the particles, increasing the thickness of the transition layers and the functionality of the assemblies, and 30 % the strength of the rubbers.

CNTs are characterized by extremely high specific strength characteristics (breaking strength at ~ 1.8 TPA), electro- and thermal conductivity, and they have huge prospects for use in modern technologies. The feature that distinguishes CNT from other nanoparticles is the uniquely high aspect ratio (η) (ratio of length to diameter) that exceeds 10³. In this case, the percolation threshold $F\eta$ ($F\eta \approx 1/\eta$), that is, the concentration at which a continuous grid of CNTs is formed, provided they are uniformly distributed in the rubber matrix, can be ≈ 0.1 wt.%. Therefore, the use of CNTs as a modifier of filled rubbers, even with a minimum content of 0.1 wt.%, can provide an increased level of strength of rubber composites as compared to other (conventional) fillers. From this point of view, the modification of the butadiene-nitrile rubbers of CNTs is an urgent task. Solving this problem can lead to an increase in the elastic, strength properties of rubber while maintaining high processability of rubber compounds during their processing.

The introduction of CNTs into the elastomeric matrix was carried on a high-speed mixer, followed by homogenization in a wiping trivalent machine. For the maximum possible degree of dispersion of agglomerates of nanostructures, a method of ultrasonic treatment of carbon nanotubes with simultaneous functionalization of the surface of nanoparticles with surfactant IR spectra was used.

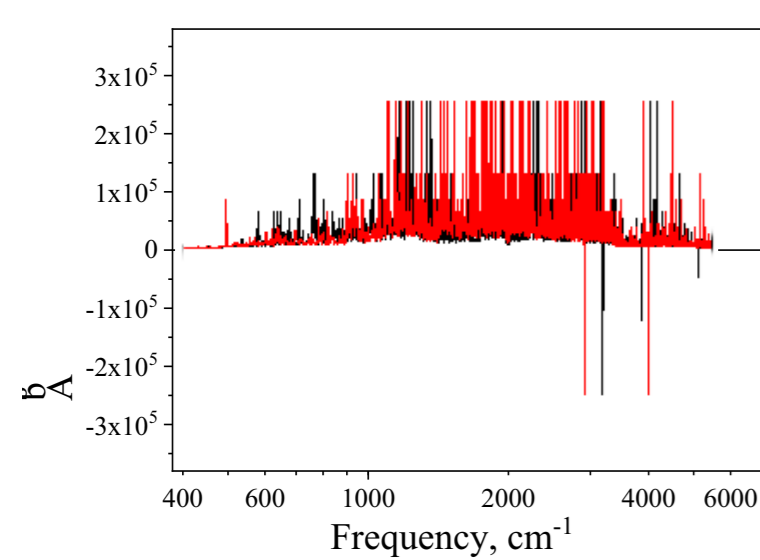


Fig. 4. IR absorption spectra of two composites "rubber - carbon nanotubes" on the base of butadiene-nitrile rubber after vulcanization: Rubber 1 (red line) and Rubber 2 (black line).

IR absorption spectra. IR absorption spectra of two composites "rubber - carbon nanotubes" after vulcanization (Fig. 4) include the giant two-polar oscillations in spectral range 3900–7000 cm⁻¹. Measurements the giant two-polar oscillations with very small half-width 0.5 cm⁻¹ (Fig. 4) testify the strong interaction of surface polaritons with photons. Moreover, it is possible to achieve a match in spectral area of CH, CH₂ and CH₃ vibrations in composites "polybutadiene rubber - carbon nanotube" and quantum entanglement of dipole-active vibrations and photon splitting according to Hong-Ou-Mandel (HOM) quantum effect. Furthermore, two-photon interference could be perspective for high-coherent optical quantum computers on composites "rubber-carbon nanotubes".

When frequencies of local oscillations of surface bonds of carbon nanotubes and modes along "nanotube-polymer" boundaries matched, then the light absorption increases 10²–10³ times (Figs. 4 and 5). Thus, vertically polarized light along carbon nanotubes and horizontally polarized light for CH, CH₂ and CH₃ vibrations resulted in beams splitting, two-photon interference and quantum Hong-Ou-Mandel effect. IR absorption spectra of composites "rubber - carbon nanotubes" on the base of butadiene-nitrile rubber without vulcanization includes one giant two-polar oscillation at 1068–1072 cm⁻¹ (Fig. 5) with half-width 2 cm⁻¹.

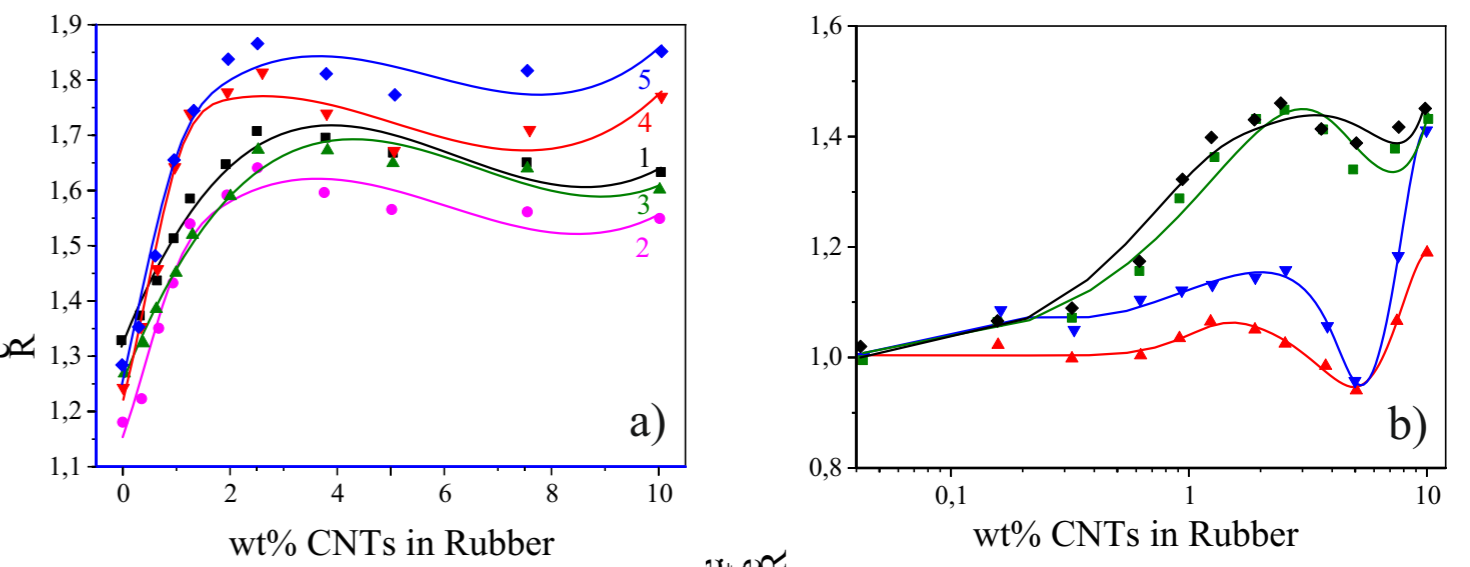


Fig. 2. a – IR reflectance maxima of composite "rubber - carbon nanotube" vs. the carbon nanotube content; b – relative IR reflectance R/R_0 (curves 1–2) and the relative tensile strength N/N_0 (curves 3–4) for composites "polybutadiene rubber - carbon nanotubes" vs. the carbon nanotube content in rubber in the area of valence vibrations CH₃ (curves 1, 3 – at 2844 cm⁻¹) and CH₂ (curves 2, 4 – at 2914 cm⁻¹).

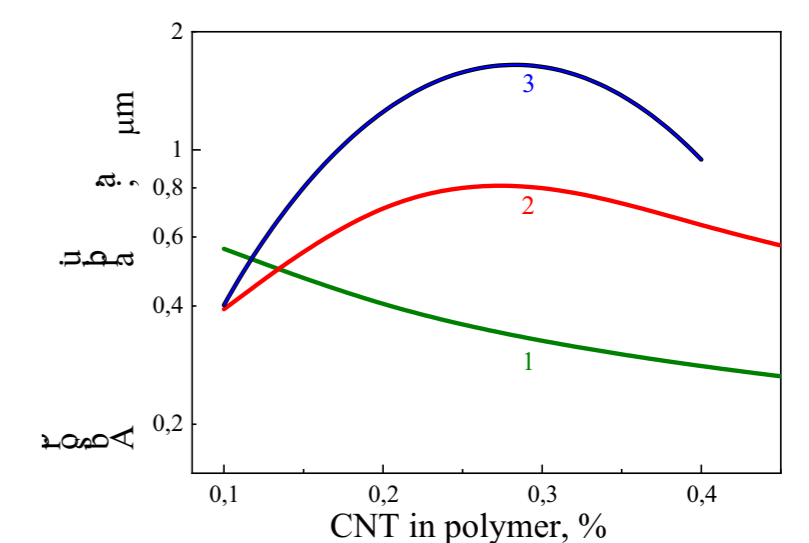


Fig. 3. The calculated dependences of average distance a between CNTs (curve 1), geometric approximation (curve 2, characteristic volume around CNT), experimental dependence from Fig. 2 b of the IR absorption peak on CNT content (curve 3).

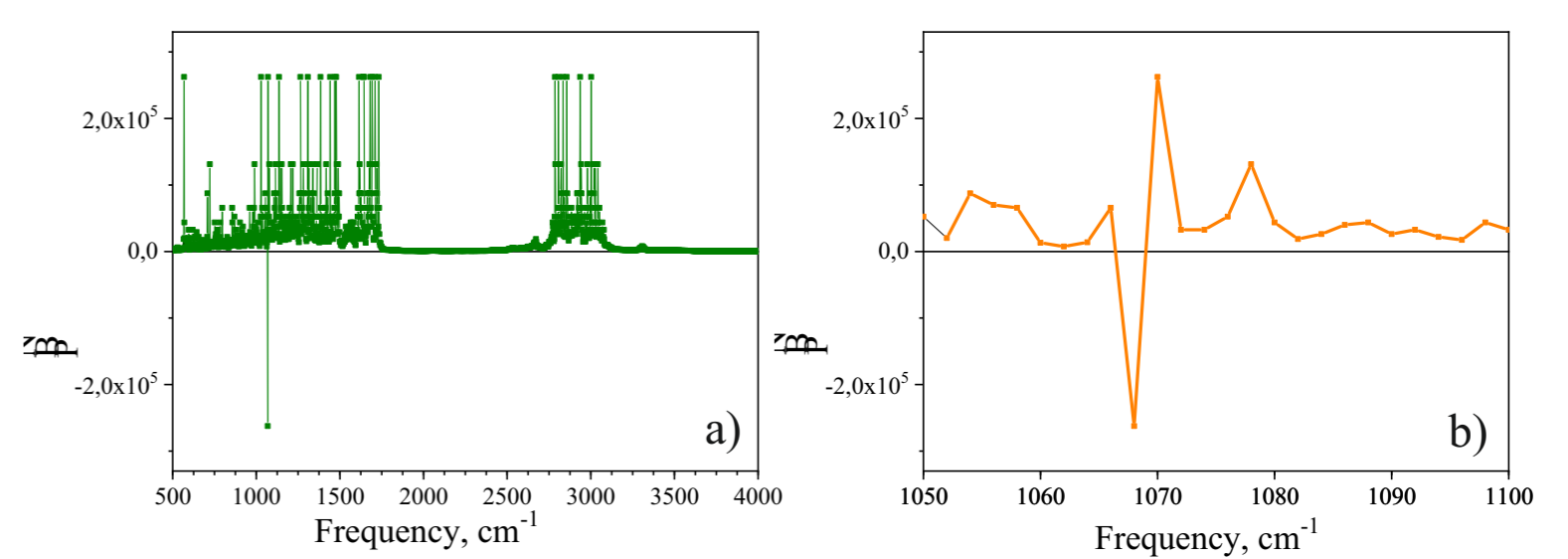


Fig. 5. a – IR absorption spectra of composites "rubber - carbon nanotubes" on the base of butadiene-nitrile rubber without vulcanization; b – fragment of IR absorption spectra of composites "rubber - carbon nanotubes" from Fig. 4 a.

Model of Hong-Ou-Mandel effect. As it is known, the amplification effect when carbon black or other active fillers is used as a filler occurs due to the formation of a "grid" as a result of the joining of active particles penetrating the entire rubber mass in all directions. That is, the rubber and the filler form two interpenetrating continuous clusters. The functional groups existing on the surface of the carbon black: -OH, -OOH, >C=O, etc., provide for chemical interaction with sulphur and rubber during vulcanization. It is believed that in the formation of the grid, only those bonds can participate that are at a distance of 0.3 nm from soot particles with an average diameter of 3 nm. At such distances, not more than 1.5 % of the total amount of unsaturated bonds in the rubber is saturated. As a result, rubber molecules become less mobile.

Obviously, CNT are more effective filler due to the shape factor. The ratio of the maximum size (length) to the minimum size (diameter) for CNT is 10³ or more times. The specific surface area of the CNT is 200 m²/g, in comparison with technical carbon, for which this value is less 100 m²/g. Polar groups of rubbers interacting with CNT accelerate the vulcanization with sulphur, strengthen the interphone boundary and compact the transitional layers at the nodes of the rubber net, which reduces their ability to deform. With the decrease in the instauration of rubber by hydrogenation, the cross linking processes are redistributed from the interphone boundary to the entire volume of the particles, increasing the thickness of the transition layers and the functionality of the assemblies, and increase for 30 % – the strength of the rubbers.

The percolation threshold (the concentration at which a continuous grid of CNTs is formed and provided uniformly distributed in the matrix) can be ≈ 0.1 wt.%. Therefore, the use of CNTs as a modifier of filled rubbers, even with a minimum content of 0.1 wt.%, can provide an increased level of strength of rubber composites as compared to conventional fillers.

Conclusions

The introduction of CNTs in an amount of 0.1–5.0 % by weight of rubber compositions results in a significant increase the strength characteristics and thermal stability of the compositions. This result indicates that CNT is ideal filler for composites based on polymers of different chemical composition and structure. We measured IR reflectance maxima of composites "rubber-carbon nanotubes" at 0–10 % of CNTs in the spectral area of the rubber CH deformation vibrations at frequencies 1297, 1465 and 1728 cm⁻¹ and valence vibrations at frequencies 2844 and 2916 cm⁻¹. IR absorption spectra of composites "rubber - carbon nanotubes" after vulcanization include the giant two-polar oscillations in spectral range 3900–7000 cm⁻¹. Measurements of the giant two-polar oscillations with very small half-width (0.5 cm⁻¹) testify the strong interaction of surface polaritons with photons. Moreover, it is possible to achieve a match in spectral area of CH, CH₂ and CH₃ vibrations in composites "polybutadiene rubber - carbon nanotube" and quantum entanglement of dipole-active vibrations and photon splitting according to Hong-Ou-Mandel (HOM) quantum effect. Furthermore, two-photon interference is perspective for high-coherent optical quantum computers on composites "rubber - carbon nanotubes".