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EFFECT OF CARBON NANOTUBE FUNCTIONALISATION ON THE STRENGTH PROPERTIES OF NANOCOMPOSITE CRYOGELS BASED ON POLYVINYL ALCOHOL

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Abstract. *The paper investigates the effect of carbon nanotube (CNT) functionalisation on the strength properties of nanocomposite cryogels based on polyvinyl alcohol (PVS). The functionalisation of CNTs using different functional groups focuses on improving the adhesion of nanotubes and polymer matrix. It can significantly improve the mechanical properties of the obtained composites. During the experiment we performed tensile strength tests with different concentrations of unmodified, oxidised (CNT-COOH), and polyvinyl alcohol modified (CNT-PVS) carbon nanotubes. Hence, the introduction of CNTs and CNT-COOH into the PVA cryogel matrix causes a significant increase in the strength properties. However, a statistically significant difference in the strength properties of composites with CNTs and CNT-COOH was only at a concentration of 0.1%. At the same time, the introduction of CNT-PVC up to a concentration of 0.5% enhances the strength characteristics of cryogels. The further increase in the concentration of CNT-PVC causes a decrease in the tensile strength.*

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Introduction

Polyvinyl alcohol (PVA) cryogels are macroporous heterophase gels formed through cryostructuring (freeze-thaw) process of PVA solution [1]. PVA cryogels have a number of unique properties such as biocompatibility, non-toxicity, porosity, high water content, and simple production methods. Therefore, they are widely used in biomedicine [2].

However, the current application of such materials is limited by their poor mechanical properties, namely the lack of the required strength. The properties of the resulting PVA cryogels are easily adjustable and depend on the concentration of the PVA stock solution, the molecular weight of the polymer, the number of cryostructuring cycles, and the solvent

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composition. A number of scientific papers by Lozinskii [1, 3] and publications by foreign authors [2, 4-6] have studied these dependencies in detail.

The production of polymer nanocomposite materials is a trend in modern applied chemistry. They are obtained by introducing nanoparticles into polymer matrixes to change their operational properties.

To obtain PVA nanocomposite cryogels, we used single-walled carbon nanotubes (SWCNTs) as a filler for cryogel polyvinyl matrix. They appear as cylindrical molecules made of coiled sheets of graphene [7]. SWCNTs are promising components of modern nanocomposite materials due to their unique physical and mechanical properties [8].

The introduction of CNTs into the polymer matrix can improve the physical and mechanical properties of nanocomposite materials. However, the high surface energy of CNTs and their low affinity to polar polymer matrices allows their agglomeration. It can negatively affect the final properties of the composite. Indeed, to obtain a high-quality nanocomposite material, it is necessary to ensure a uniform distribution of CNTs in the volume of the polymer matrix [8].

Two groups of methods are used to reduce the size of agglomerates and enhance the interaction of CNTs with the dispersion medium: mechanical (e.g., ultrasound treatment) and chemical (grafting of functional groups by chemical reaction) one. According to the authors [9, 10], a uniform distribution of CNTs in the polymer matrix can be obtained by combining mechanical methods with chemical treatment of CNTs.

Nowadays, there are a number of studies on the preparation and properties of nanocomposite materials based on PVA and CNTs [11-14]. The nanocomposite materials containing CNTs exhibit properties that differ significantly from those of pure PVC. These changes are due to the interaction of CNTs with the polymer matrix. It causes changes in the operational properties of the samples and provides new opportunities for their application in various fields.

The purpose of this study is to evaluate the effect of CNT functionalisation on the strength properties of polyvinyl alcohol-based nanocomposite cryogels.

The object of the study is nanocomposite cryogels prepared of 15% aqueous solutions of PVC with a molecular weight of 89000 Da containing CNTs.

The subject of the study is the durability limit of PVC/CNT-based nanocomposite cryogels.

Main body

The presence of CNTs in the polymer matrix volume can significantly change the mechanical properties of PVC cryogels. At the same time, the aggregation ability of CNTs can negatively affect the characteristics of the obtained material. Chemical functionalisation of CNTs causes the formation of functional groups on their surface. These groups can increase their affinity to the polymer matrix and contribute to better distribution and reduce the risk of agglomeration [8].

We obtained the oxidation product (CNT-COOH) by oxidation of CNTs with a 1:3 mixture of concentrated nitric and sulfuric acids. The oxidation reaction of CNTs causes the formation of polar oxygen-containing functional groups, mainly carboxyl groups, on the surface of nanotubes. Their presence is confirmed by the signal in the region of 1732.44 cm^{-1} on the IR spectrum (Fig. 1), corresponding to the valence vibrations of the C=O bond in the carboxyl group.

Also an increase in the oxygen content of the oxidation product was recorded by CHNOS analysis from 4.43% for CNTs to 18.95% for CNT-COOH.

The authors of [15] performed the esterification reaction of CNT-COOH with polyvinyl alcohol, resulting in the product CNT-PVC, soluble in hot water. It allows us to assume the formation of the most uniform dispersion in water to obtain nanocomposite materials. The oxygen content with the synthesised CNT-PVC modification increased to 37.04% according to CHNOS analysis. It is due to the presence of the polymer cross-linked with CNTs.

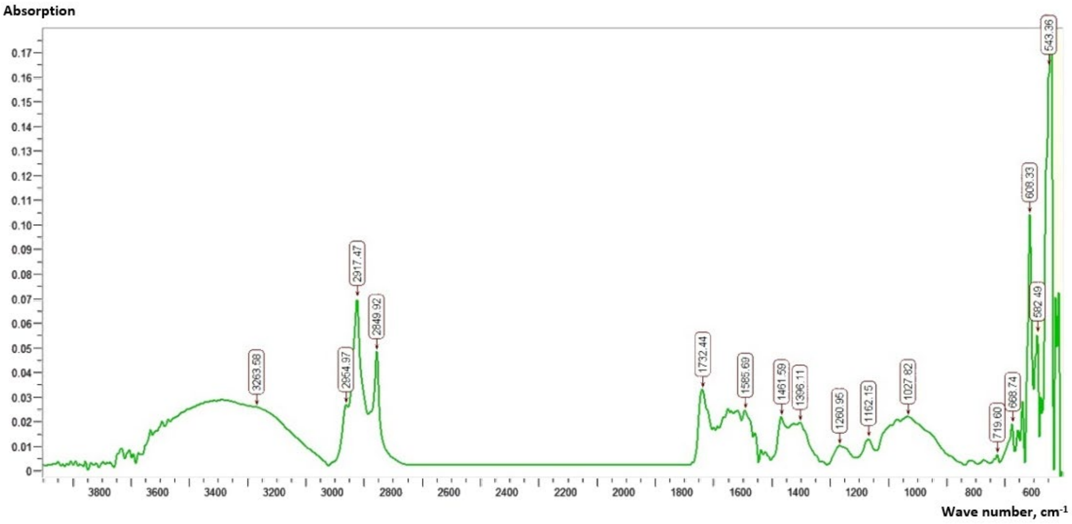

Fig. 1. IR spectrum of CNT-COOH

CNTs, CNT-COOH in amounts of 0.1; 0.5 and 1% and CNT-PVC in amounts of 0.5; 1 and 2% were used as filler for the polyvinyl matrix obtained from a 15% aqueous polymer solution. Figure 2 shows the dependence of the tensile strength of PVC/CNT nanocomposite cryogels on the CNT concentration.

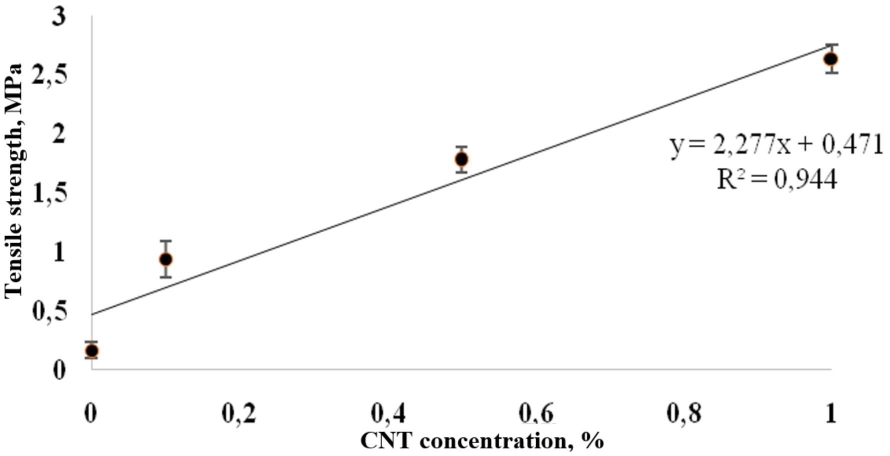

Fig. 2. Dependence of strength of aqueous nanocomposite cryogels based on 15% PVC/CNT on CNT concentration

Fig. 2 shows the increase in tensile strength by introducing CNTs in 15% polyvinyl matrix in the amount of 1% was about 15 times from 0.17±0.07 MPa to 2.64±0.12 MPa.

The presence of polar functional groups on the surface of CNTs causes an improved distribution of nanoparticles in polar media. Generally, the introduction of CNT-COOH would cause an even greater increase in the strength properties of PVC-based cryogels compared to the use of the original CNTs. Nanocomposite cryogels from aqueous 15% PVC_{89} solutions containing CNT-COOH were prepared to test the hypothesis. Figure 3 summarises the results of the strength tests.

Indeed, raise of the concentration of CNT-COOH increases the strength characteristics of the materials. However, a comparative analysis of the effect of CNTs and CNT-COOH on the ultimate strength of nanocomposites showed a statistically significant difference in the strength characteristics at a nanoparticle concentration of 0.1%. At the same time, the differences in strength were insignificant in the range of higher nanotube concentrations (0.5%; 1%) (Fig. 4).

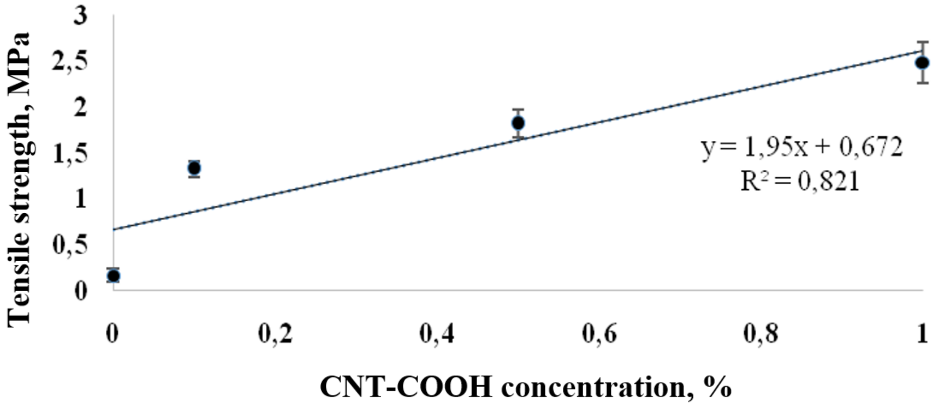

Fig. 3. Dependence of strength limit of aqueous nanocomposite cryogels based on 15% PVC/CNT-COOH on CNT-COOH concentration

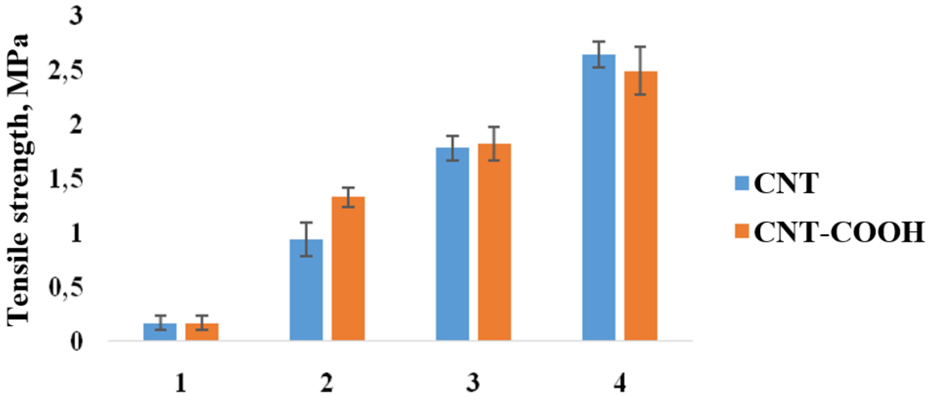

Fig. 4. Comparison of the strength of aqueous nanocomposite cryogels based on 15% PVC_{89} at different modifications of CNTs: 1 - 0%; 2 - 0.1%; 3 - 0.5%; 4 - 1%

We were able to obtain nanocomposite cryogels with modified CNT-PVCs from aqueous 15% PVC_{89} solution with nanoparticle concentrations of 0.5%; 1% and 2%. Figure 5 shows the results of physical-mechanical tests.

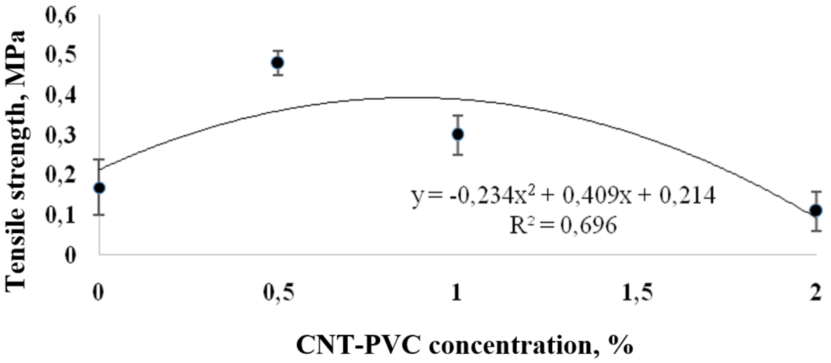

Fig. 5. Dependence of the strength of aqueous nanocomposite cryogels based on 15% PVC_{89}/CNT-PVC on the concentration of CNT-PVC

According to the diagram (Figure 5), the tensile strength of the materials raised with increasing CNT-PVC concentration up to 0.5% almost 3 times, from 0.17±0.07 MPa to 0.48±0.03 MPa. However, further increase in CNT-PVC content up to 2% causes a decrease in strength properties to 0.11±0.05 MPa.

Conclusions

Chemical functionalisation of carbon nanotubes using a mixture of concentrated sulphuric and nitric acids and the esterification reaction of oxidised carbon nanotubes with polyvinyl alcohol significantly improves the distribution of nanoparticles in the polar dispersion medium. The introduction of original and oxidised carbon nanotubes into cryogel aqueous 15% polyvinyl matrix (PVC_{89}) causes an increase in the tensile strength of the samples by about 14-15 times at a filler concentration of 1%. A statistically significant difference in the strength characteristics of nanocomposite cryogels containing original and oxidised carbon nanotubes can be observed only at low concentration (0.1%). The differences in strength properties become statistically insignificant at high concentrations. The introduction of carbon nanotubes modified with polyvinyl alcohol causes an increase in strength characteristics by almost 3 times at a concentration of 0.5%. However, with further increase in the content, a significant decrease in the tensile strength is observed. The results obtained indicate the possibility to achieve maximum mechanical properties using original and oxidised carbon nanotubes. This provides opportunities for further research towards tuning the properties of nanocomposites.

Experimental part

We used the following substances without further purification: polyvinyl alcohol with a molecular weight of 89000 Da with a degree of hydrolysis of *O*-acyl groups of 99% (Sigma-Aldrich, USA); single-walled carbon nanotubes with a diameter of 1.6±0.4 nm, length > 5 µm, and carbon content ≥ 93% as the main component (Sigma-Aldrich, USA); nitric acid, 70% aqueous solution (Sigma-Aldrich, USA); sulphuric acid, 98% aqueous solution (Reakhim, Russia); 1,3-dicyclohexylcarbodiimide (DCC) (Sigma-Aldrich, USA); 4-dimethylaminopyridine (DMAP) (Sigma-Aldrich, USA); hydroxybenzotriazole (HOBT) (Sigma-Aldrich, USA); acetone (Reakhim, Russia); dimethyl sulphoxide (DMSO) (Sigma-Aldrich, USA); distilled water.

Methodology for preparation of nanocomposite cryogels based on polyvinyl alcohol and carbon nanotubes

We disintegrated the CNT suspension in distilled water for 15 min under the action of ultrasonic homogeniser Q500 (Qsonica, USA) with an output power of 500 W, frequency 20 kHz, and oscillation amplitude 20%. We added a weight of dry PVC to the obtained dark dispersion and stirred by heating to 95 °C until a homogeneous suspension was formed. After that, we divided the obtained mixture between two glasses with a fixed gap of 1 mm, incubated at -40 °C for 24 hours, and then gradually thawed for 24 hours at room temperature. We treated the samples with one cycle of cryostructuring, after that we washed with distilled water from the residues of uncrosslinked polymer and CNTs for a day.

Oxidation of carbon nanotubes

We treated a 0.3 g CNT suspension with a mixture consisting of 10 mL of concentrated nitric acid and 30 mL of concentrated sulfuric acid (1:3 ratio). We performed the reaction for 6 hours in a Sapphire ultrasonic bath with an operating frequency of 35 kHz. We filtered the oxidation product, washed with distilled water to neutral medium, and air dried to constant weight.

Functionalisation of carbon nanotubes with polyvinyl alcohol

We dissolved suspensions of 0.4 g DCC; 0.066 g DMAP; and 0.13 g HOBT in 15 mL DMSO. We added a 0.166 g weight of oxidised CNTs to the solution, and then the resulting mixture was ultrasonically treated in a Sapphire ultrasonic bath for 1 hour. We then added a solution consisting of 0.166 g of PVC and 10 mL of DMSO to the reaction mixture and continued ultrasonic treatment for 24 hours. The resulting dark mixture was centrifuged at 7200 rpm. We conducted the precipitation of modified CNTs by adding acetone to the supernatant. We purified the sample by dissolution in hot water followed by dialysis process for 3 days and precipitation in acetone. We washed the precipitate with acetone and dried in air to constant weight.

Investigation of mechanical properties of nanocomposite cryogels

We evaluated the mechanical properties of the obtained materials under uniaxial tensile conditions according to ISO 37:2017 at 37°C. We prepared samples for the study on a ZCP 020 punching press (ZwickGmbH&Co. KG, Germany) in the form of rectangular plates using a specially shaped knife B083. It conforms to ISO 37:2017 (n = 7-8) without considering the choice of direction due to the isotropic material properties. We measured the thickness with a thickness gauge - TP with an error tolerance limit of ±0.01 mm with a clamping force not exceeding 1.5 N. We conducted the study on a universal testing machine Z series (ZwickGmbH&Co. KG, Germany) using a transducer with a nominal force of 50 N, the selected traverse speed of 50 mm/min. We assessed the ultimate strength of the material by the maximum tensile stress (MPa) considering the cross-sectional area of the sample. We evaluated the elastic-deformational properties of the samples by relative elongation corrected for the fracture pattern of the samples (%) and Young's modulus calculated in the range of elongation required to obtain the final product (0 to 125% elongation).

IR spectroscopy

We recorded the infrared spectra of CNTs on an Infralum FT-08 infrared spectrometer (Lumex, Russia) using a multiple disturbed total internal reflection attachment with a ZnSe prism. We grinded CNT samples with potassium bromide in a microstocke. IR spectra were recorded in the range 4000-500 cm^{-1} with a resolution of 4 cm^{-1} and an accumulation time of 256 scans.

CHNOS-analysis

We determined the content of carbon, hydrogen, sulphur, and oxygen by high-temperature oxidation on an automatic elemental analyser ThermoFlash 2000 manufactured by ThermoScientific (USA).

Statistical analysis of data

We performed statistical analyses of the data using GraphPadPrism 8.0 (GraphPadSoftware, San Diego, CA, USA). We assessed the normality of the distribution using the Kolmogorov-Smirnov criterion. An ANOVA with a posteriori test was used for normally distributed variables to determine differences between groups. We used the Kruskal-Wallis test for non-normally distributed variables to determine differences between groups. We have presented results either as mean and standard deviation or median and interquartile range where it is appropriate. We considered differences to be statistically significant at $p < 0.05$.

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