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Synthesis of nanocomposite cryogels based on polyvinyl alcohol and carbon nanotubes

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Abstract

The high-strength nanocomposite cryogels based on polyvinyl alcohol (PVA) and carbon nanotubes (CNTs) have been synthesised and studied. To overcome the problems related to CNTs agglomeration in polar solvents, which limits their uniform distribution over the polymer matrix, cryogel composition was optimised to achieve high strength characteristics. To obtain uniform CNT dispersions, homogenisation in solvents (water, dimethyl sulphoxide (DMSO) and a mixture of DMSO/water = 80 : 20 by volume) in combination with ultrasonic treatment was used. During the experiment, cryogel samples were stretched uniaxially, which allowed us to obtain the ultimate strength values for each sample. Data processing was performed using STATISTICA 10 software. Using regression modelling, the Dependences between the ultimate strength of nanocomposites and synthesis parameters (the concentration of initial PVA solution, its molecular weight, water content in the solvent, and the concentration of CNTs) were established using regression modelling. The obtained regression equation was adequate with respect to Fisher's criterion, and determination coefficient was $R^2 = 0.81$, which confirms the accuracy of the model and its applicability for predicting the strength characteristics of cryogels. In addition to regression analysis, the dependences of the Harrington desirability function on synthesis parameters were analysed. This approach allowed us to identify optimal components ratio for obtaining PVA/CNT nanocomposite cryogels, which significantly increased the efficiency of developing materials with high strength properties. The results of the study emphasise the importance of taking into account various factors when optimising synthesis conditions and also offer new prospects for further research in the area of polymer composites.

Keywords: cryogels, polyvinyl alcohol, carbon nanotubes, optimisation

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INTRODUCTION

During the recent decades, much attention is paid to the development of new composites with improved mechanical and functional characteristics, which is especially urgent in the area of biomedical technologies. One of the most promising directions is considered to be development of materials based on cryogels, which can be used in various areas including tissue engineering, systems drug delivery, and biocompatible implants. Cryogels are porous structures with unique properties, such as high permeability for liquids, light weight, and the ability to recover after deformation [1]. Nevertheless, traditional cryogels often possess limited mechanical characteristics, which may limit their application.

The relevance of the present investigation is due to the necessity to develop new materials, which will be able to meet the requirements of modern medicine and provide high application efficiency.

Polyvinyl alcohol (PVA) is one of the most widespread polymers for preparing cryogels for biomedical applications because of its high biocompatibility. In spite of positive characteristics, cryogels based on PVA can demonstrate insufficient strength for certain applications [2]. In particular, some areas of biomedicine, for example, such as cardiovascular surgery, require materials with tensile strength within the range of 0.5–5 MPa [3, 4]. It should be noted that we have succeeded in achieving the maximal strength (~4 MPa) for the cryogel obtained from 15 % aqueous solution of PVA with molecular mass 146 000 Da after five freezing-thawing cycles [5].

During the recent years, the possibility to modify polymer matrices with carbon nanotubes (CNTs) is under active investigation. These nanostructures possess high strength, light weight, and good conductivity, which allows substantial changes in the performance properties of composites [6]. The first studies aimed at the use of CNTs as a filler for PVA were carried out by the end of the XX century [7]. The authors of [8] prepared nanocomposite films CNT/PVA (1 wt% CNT) and determined that the composite films possess the characteristics different from the properties of initial PVA and CNT. The introduction of CNTs into PVA renders electric conductance to the matrix, thus opening new outlooks for the application of composites. Investigation of the electric properties of composite materials based on PVA and CNT has been described in [8]. As shown in [9, 10], the addition of CNTs to PVA can also change the mechanical characteristics of the polymer material. For instance, even a small amount of CNTs added (not more than 0.25 wt%) improves the strength characteristics of nanocomposites. So, PVA modification with CNTs can accelerate the process of manufacturing materials with improved mechanical characteristics because it allows achieving the necessary strength only after one freezing-thawing cycle.

In the present work, we consider the possibility to make composite cryogels based on PVA and CNTs for application in biomedicine, in particular cardiovascular surgery. These nanocomposites should possess increased strength, so it is important not only to study the strength characteristics of the nanocomposite cryogels but also to analyse the dependence of the ultimate strength on synthesis parameters. This will make it possible to optimise cryogel composition and improve the characteristics of the final material. Unlike for previous studies in which mainly the effect of CNT concentration on the strength was investigated, this work deals with determining interrelations between the main synthesis parameters (concentration of initial PVA solution, composition of the solvent, the molecular mass of PVA, CNT concentration) and the ultimate strength of the composite cryogel.

The goal of the present work was to obtain nanocomposite cryogels based on polyvinyl alcohol and carbon nanotubes, to study and analyse their strength characteristics to optimise the composition (components ratio) of the cryogel.

EXPERIMENTAL

Materials

In the work, we used PVA (hydrolysis degree 99.9 %) with different molecular masses: 89 000 Da (PVA_{89}) and 146 000 Da (PVA_{146}); dimethylsulphoxide (DMSO); single-wall CNTs (diameter: 1.6±0.4 nm, length: more than 5 μm). All components were obtained according to the catalogue of Sigma-Aldrich (USA). Twice distilled water was also used for the synthesis of cryogels.

Synthesis of nanocomposite cryogels CNT/PVA

To obtain CNT/PVA nanocomposites, a weighted portion of CNTs was disintegrated in one of the solvents (water, DMSO or a mixture of DMSO/water at a ratio of 80 : 20 by volume) for

15 min under the action of ultrasonic homogeniser Q500 (Qsonica, USA) with the output power 500 W, frequency 20 kHz. A weighted portion of dry PVA was added to the dark-coloured uniform dispersion of CNT to achieve the concentrations of 7, 10, 12, 15 wt% (for PVA_{146}) and 10, 15, 20 wt% (for PVA_{89}). The choice of the indicated PVA concentrations was based on the data reported in [5]. In addition, the concentrations of CNTs (0.1, 0.5 and 1 wt%) and water (100, 20, 0 % by volume) were varied. The mixture was stirred at heating till the complete dissolution of the polymer. Then the mixture was cooled to room temperature. After that, the suspension was poured between two glasses with a gap of 1 mm to standardise sample thickness, and subjected to a single freezing-thawing cycle (cryostructuring), which included cooling to −40 °C (24 h), exposure at (−2)−(−5) °C (12 h), and then at 8 °C (12 h). After cryostructuring cycle completion, the samples were washed with distilled water from residual polymer and DMSO for 24 h.

Assessment of mechanical characteristics

The mechanical properties of resulting materials were assessed under the conditions of uniaxial extension according to ISO 37:2017 at a temperature of 37 °C. The samples for investigation were prepared with a punching press ZCP 020 (Zwick GmbH & Co. KG, Germany) using a knife of special shape (B083, meeting the standard ISO 37:2017) without taking into account the direction because the properties of materials are isotropic. The studies were carried out using a universal test machine of Z series (Zwick GmbH & Co. KG, Germany) and a sensor with nominal force 50 N, the chosen velocity of traverse movement was 50 mm/min. The ultimate strength of the material was determined from the maximum tensile strain (MPa) taking into account the cross section area of the sample. The stress-strain properties of the samples were assessed from the relative elongation corrected, taking into account the pattern of sample destruction (%) and Young's modulus. Sample thickness was measured using a thickness meter TR 10-60 (Russia) with the acceptable error threshold ±0.01 mm (hold-down pressure not more than 1.5 N).

Statistical data analysis

By means of uniaxial extension, 32 samples of CNT/PVA nanocomposite cryogels were studied. For each of samples, 5 parallel measurements of ultimate strength were made. Statistical analysis of the data was performed using STATISTICA 10 software package (Statsoft Inc., USA). To optimise mechanical properties, we used the method of desirability function, which involves the transformation of response function (ultimate strength) into a dimensionless desirability scale (D), with the values varying from 0 (absolutely inadmissible value) to 1 (optimal value). The individual desirability functions for each parameter were calculated automatically in STATISTICA 10 software package, and the total desirability function was calculated as the geometric mean of the individual desirability functions.

RESULTS AND DISCUSSION

Synthesising cryogel nanocomposites based on PVA and CNTs, researchers face the problem of non-uniform distribution of CNT in hydrophilic solvents and polymers. This is associated with the hydrophobic nature of nanoparticles surface, which causes their agglomeration and the formation of coils. Various methods are used to solve this problem, for example, chemical functionalisation of CNTs (e.g. oxidation) and ultrasonic treatment [11]. However, the use of aggressive chemicals can have a negative effect on the properties of nanotubes, causing their damage and shortening, which, in turn, may worsen the strength characteristics of the material [12].

In the present work, to achieve uniform distribution of CNTs in the polymer matrix, we chose DMSO and its mixture with water (80 : 20) as solvents. This allowed us to obtain uniform CNT dispersions under ultrasonic action. Distribution of CNTs in water (without DMSO) with the help of ultrasound allowed us to obtain the dispersions that remained stable for several hours; as a result, water-based nanocomposites were also obtained. The DMSO/water ratio (80 : 20 by volume) was chosen based on the results of previous investigation [5], where it was shown that, unlike for other studies ratios, this composition helps achieve the highest ultimate strength for PVA cryogels without additives.

As mentioned previously, in spite of high biocompatibility, non-toxic nature, and the possibility to vary mechanical characteristics within a broad range, which provides the attractiveness of PVA-based cryogels for biomedical applications, they do not always meet the strength requirements. In particular, for some materials used in biomedicine, the tensile strength of about 5 MPa is required, while for the cryogel based on 15 % aqueous solution of PVA_{146}, obtained after five freezing-thawing cycles, the strength of ~4 MPa was achieved. It is necessary to mention that there are physical limitations affecting experimental results, which do not allow going beyond the indicated limits: the concentration of initial PVA solution – from 10 to 20 wt% for PVA_{89} and from 7 to 15 wt% for PVA_{146}, the maximal CNT content – not more than 1 wt%, the molecular mass of PVA – within the range of 89 000–146 000 Da. These limitations are due to several factors. For the low concentration of PVA solution, unstable cryogels are formed, or they are not formed at all. On the other hand, preparation of highly concentrated PVA solutions is hindered because of its limited solubility and high viscosity of the solution, which brings complications to the dissolution process. The high concentration of CNT hampers PVA dissolution, forming additional obstacles for achieving its necessary concentration, and this becomes another limiting factor.

As a result of the tests of mechanical characteristics of nanocomposite cryogels formed within a single cryostructuring cycle, the following value ranges were determined: tensile strength was 1.3–3.7 MPa, Young's modulus varied within the range of 0.05–0.31 MPa, and elongation at failure was measured within the range of 370–560 %. It should be noted that the ultimate strength of nanocomposites turned out to be higher than that for cryogels without additives. Thus, the introduction of 1 wt% CNT into 15 % aqueous cryogel with PVA_{89} resulted in an increased in strength characteristics by a factor of ~15.5, while the addition of 0.5 % CNT into 12 % PVA_{146} dispersed in the mixture DMSO/H_2O = 80 : 20 by volume caused an increase in the strength by a factor of almost two.

To reveal the dependence, regression modelling was used, which allowed us to determine the effect of all parameters varied during the synthesis of nanocomposite cryogels CNT/PVA on their strength characteristics.

The effect of four key factors (parameters) on the response function (Y, MPa) – the ultimate strength of nanocomposite cryogels CNT/PVA:

1) X_1 – the concentration of initial PVA solution, wt%;

2) X_2 – molecular mass of PVA, 10^{-4} g/mol;

3) X_3 – water content in the solvent, %;

4) X_4 – concentration of CNT, %.

These factors correspond to the criteria of controllability, independence, and uniqueness.

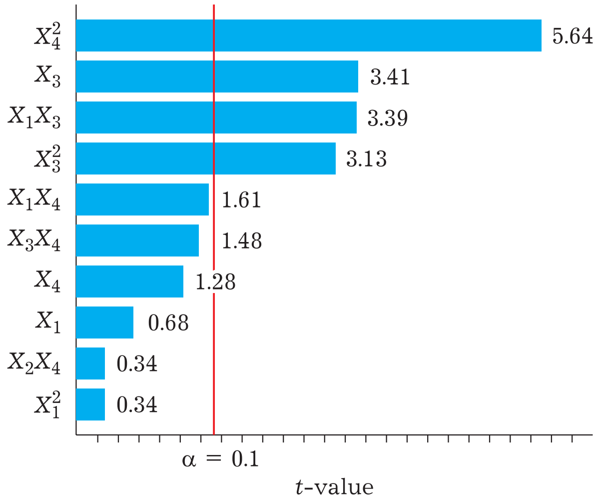

Fig. 1. Pareto diagram of statistical significance of factors at the significance level α = 0.1. Here and in Fig. 2: Y – ultimate strength of nanocomposite cryogels, X_1 – concentration of the initial solution of polyvinyl alcohol (PVA), X_2 – molecular mass of PVA, X_3 – water content in the solvent, X_4 – concentration of carbon nanotubes (CNT).

To develop the regression model, analysis of statistical significance of the factors affecting the response function Y – ultimate strength was carried out. The Pareto diagram of statistical significance of the factors (combination of factors) at the significance level $\alpha = 0.1$ is shown in Fig. 1. According to the Pareto diagram, the significant coefficients turned out to be X_4^2, X_3, X_1X_3 and X_3^2.

As a result of mathematical treatment, the regression equation was obtained:

$$Y = -1.62 + 0.52X_1 - 0.02X_1^2 - 1.01X_3 - 7.94X_4 - 1.75X_4^2 + 0.45X_1X_4 + 0.32X_2X_4 + 1.03X_3X_4$$

(determination coefficient $R^2 = 0.81$ at $\alpha = 0.1$), and its adequacy was confirmed using Fisher's criterion [13] at the significance level $\alpha = 0.1$

The criterion used to optimise the synthesis of nanocomposite cryogels CNT/PVA was the Harrington desirability function. Using this function, it is possible to choose the optimal combinations of conditions that would ensure the synthesis of nanocomposites with the best characteristics [14].

The dependence of desirability function on the parameters under study is shown in Fig. 2.

Based on the plotted dependences, several values of parameters X_1, X_2, X_3 and X_4 can be chosen to be optimal for obtaining the samples with the highest ultimate strength – 3.34, 3.15 and 2.19 MPa. The characteristics of the indicated samples are presented in Table 1. From the viewpoint of the physicochemical regularities of cryogel formation, these optimal values of parameters

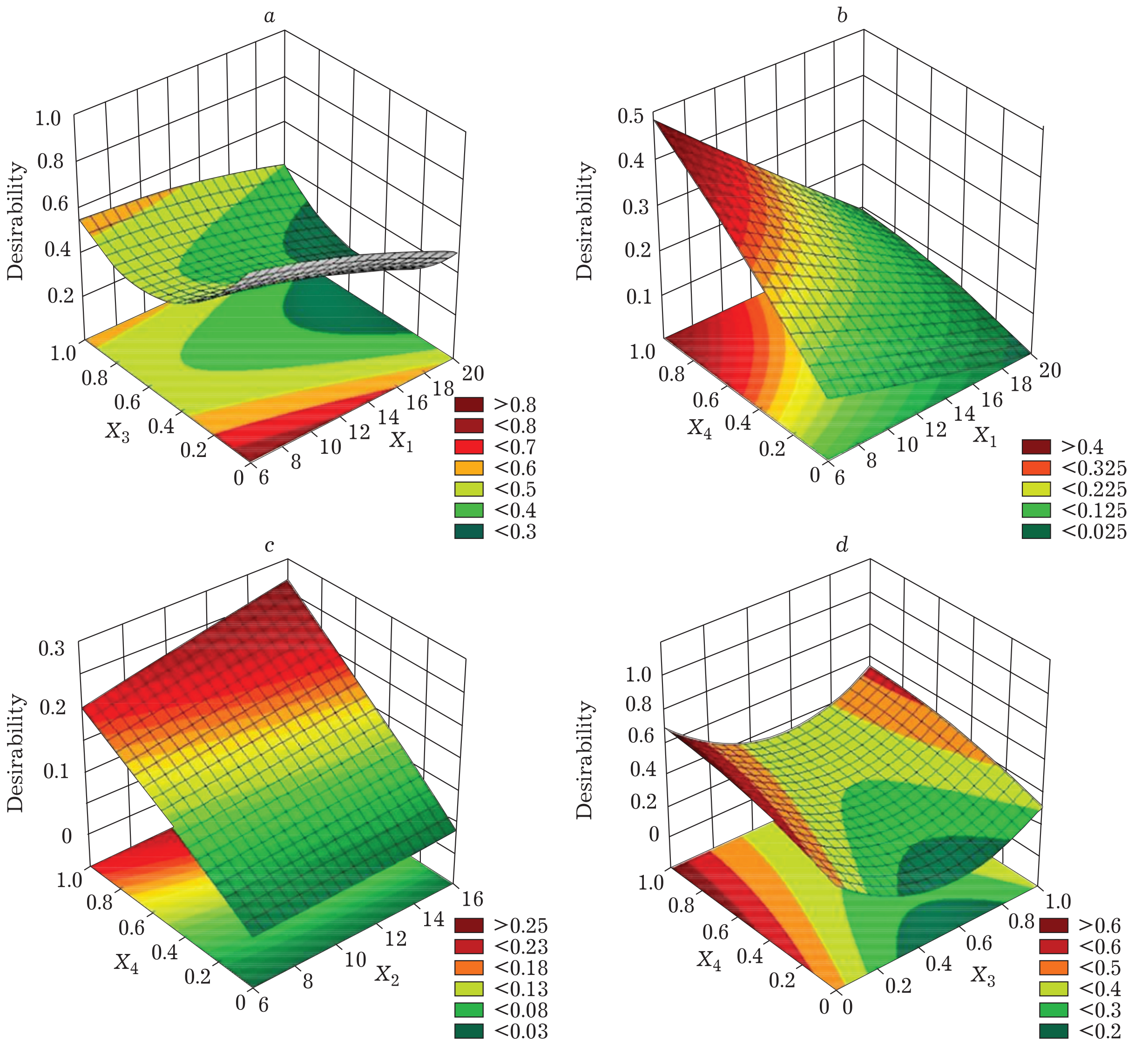

Fig. 2. Dependences of the desirability function on parameters: X_1 and X_3 (*a*), X_1 and X_4 (*b*), X_2 and X_4 (*c*), X_3 and X_4 (*d*). For designations, see Fig. 1.

provide the following advantages: the use of highly concentrated PVA solutions promotes the formation of a stronger structure due to the formation of larger number of intermolecular bonds; the use of high CNT concentration allows efficient reinforcement of the polymer matrix. In addition, the use of DMSO and its mixture with water significantly improves the uniformity of CNT distribution and, as a consequence, increases cryogel strength.

Thus, the regression model composed in the present work provides the possibility to predict the strength characteristics of nanocomposite cryogels based on CNT/PVA depending on syn-

TABLE 1

Optimal composition for obtaining nanocomposite cryogels CNT/PVA

Concentration of initial PVA solution (X_1), %	Molecular mass of PVA (X_2), 10^{-4} g/mol	Water content in solvent (X_3), %	CNT concentration (X_4), %	Ultimate strength (Y), MPa
12	14.6	0	1	2.19
20	8.9	20	1	3.15
20	8.9	0	1	3.34

Note. PVA – polyvinyl alcohol; CNT – carbon nanotubes.

thesis conditions. The use of the Harrington desirability function for optimisation allows a substantial increase in the efficiency of developing new materials that meet the modern requirements in various areas of application.

CONCLUSION

As a result of the studies, nanocomposite cryogels based on PVA and CNT with improved strength characteristics were developed and synthesised. It has been demonstrated that the reasonable approach is to apply regression modelling to establish a dependence between the ultimate strength of the obtained materials and simultaneously all parameters (the mass concentration of PVA in initial solution, the molecular mass of PVA, water content in the solvent, and CNT concentration),which allows predicting the ultimate strength for new cryogel compositions. A regression equation with determination coefficient $R^2 = 0.81$, which is adequate with respect to Fisher's F-criterion, has been developed, and this confirms the accuracy of the model. Analysis of the dependence of the Harrington's desirability function on synthesis parameters allowed us to determine the optimal components ratio to obtain nanocomposite cryogels PVA/CNT with increased ultimate strength values:

1) 1 % CNT+ 20 % PVA_{89}, 100 % DMSO, ultimate strength of CNT/PVA = 3.34 MPa;

2) 1 % CNT+ 20 % PVA_{89}, DMSO/H_2O = 80 : 20 by volume, ultimate strength of CNT/PVA = 3.15 MPa;

3) 1 % CNT +12 % PVA_{146}, 100 % DMSO, ultimate strength of CNT/PVA = 2.19 MPa.

The results of the work open new outlooks for further studies in the area of developing high-strength materials on the basis of polymer composites. The data obtained can be used to develop high-strength materials applicable in various areas, including biomedicine.

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