Effect of electrospinning solution parameters on the properties of nonvolven fibrous material based on polyhydroxibutyrate

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Abstract. In the present work, the influence of technological parameters of poly-3-hydroxybutyrate solution on the process of electrospinning of ultrathin fibers has been studied. It was established that the electrical conductivity and viscosity of the polymer solution largely determine the geometry and morphology of ultrathin fibers. Modification of solutions with ionic electrolyte and hydrolytic agent reduces the initial molecular weight of the polymer and leads to an increase in the viscosity of the system. It’s shown that the inputting of CNT leads to the orientation of the polymer macrochains in the amorphous phase. As a result, there are increases in mechanical, sorption properties and resistance to oxidative, thermal-oxidative and hydrolytic degradation. The fibers obtained will find application in biomedicine.

1. Introduction
One of the economically appropriate and technologically advanced methods of forming nanoscale and ultra-thin polymer fibers is the method of electrospinning (ES) [1]. The main advantages of ES are the relatively low cost of apparatuses, simple equipment, variability of fiber synthesis conditions, and diversity of fiber types and articles prepared on the basis of them [2]. The forming of polymer nanofibers under the conditions of electrodynamic interactions and viscoelastic deformations allows to alter their various structural and morphological characteristics, create a high specific surface area, adjust their mechanical properties and porosity, as well as adjust their mechanical properties and porosity with a wide range of diffusion parameters.

2. Materials and measurements
In this work PHB with a molecular mass (MM) of 300 and 460 kDa (BIOMER, Germany) was used. Chloroform (CF) as a solvent. Tetrabutylammonium iodide [CH3(CH2)3]4N (TBAI) was used in electroforming as an addition to increase the electric conductivity of the forming solution. Formic acid (FA) was added to adjust the viscosity and electric conductivity. Carbon nanotubes (CNTs) were obtained at the Lomonosov Moscow State University of Fine Chemical Technologies.
ES of nonwoven fiber materials on the basis of PHB was performed on a pilot laboratory unit ES-1 (Russia) at a dynamic viscosity of solution of 9 P (0.9 Pa·s), specific bulk conductivity of $10^{-3}$ (Ohm·m)$^{-1}$, volumetric flow rate of the forming solution of $(10-12) \times 10^{-5}$ g/s, electric field voltage of 15 kV, interelectrode distance of 18 cm, and capillary diameter of 0.1 mm.

The diameter distribution of the fibers obtained from a PHB solution in CF/FA (0.9 : 0.1) in addition of the TBAI electrolyte was studied by light and electron microscopy (MBI-6 optical microscope and Hitachi TM-1000 scanning electron microscope). The thermophysical and thermal characteristics (the temperatures of the start of the thermo and thermooxidative destruction) of fibers on the basis of PHB were obtained using Perkin Elmer Pyris 6 DSC (United States) differential scanning calorimeter. IR spectroscopy was performed on a Nicolet 6700 spectrophotometer (USA).

The strength of PHB fibrous materials was probed on an RM31 tensile testing machine in accordance with TC 25.061065-72 using samples with a size of $4 \times 1$ cm$^2$ cut from the nonwoven fibrous material. The kinetics of UV aging was studied on the same samples utilizing a Feutron 1001 artificial weathering chamber (Germany) equipped with a UV source—a high-pressure mercury lamp with a power of 385 W. The distance from the lamp to the samples was 30 cm.

3. Results and discussion

A large number of factors responsible for the various stages of electrospaying pose a challenge for researchers and technologists to identify among them the most significant, dominant characteristics, the modification of which affects the structure, morphology, porosity and geometry of the fibers to the greatest extent. During the ES-process, a high-voltage electric field creates free ionic charges that migrate along the jet of polymer solution from one electrode to another. In organic nonionic polymer solutions with the low dielectric constant, the concentration of such ions is extremely low, that determines the low values of the electrical conductivity of the spinning system. The PHB solution in nonpolar CF presents the same situation [3].

Previously, we studied the effect of electrical conductivity and viscosity on the ES-process of a binary solution of PHB in chloroform (CF) [4]. Particularly, it was found that the low electrical conductivity of the PHB solution prevents the formation of uniform fibers that, that is clearly demonstrated in Fig. 1 A, B.

Due to the heterogeneity of the fiber diameter and its characteristic thickenings, which are sporadically arising ellipse-like structures, tetrabutylammonium iodide (TBAI) was introduced into the polymer solution to increase the electrical conductivity, which made it possible to obtain cylindrical fibers without noticeable knots and thickenings. However, a high electrolyte content relative to the polymer concentration in the solution led to a variation of the properties of PHB and an increase in the defectiveness of the PHB fibers formed. To decrease the concentration of TBAI, FA was added to the spinning polymer solution as an modifying additive, which made it possible to reduce the TBAI content in the system by approximately 5 times. In this case, the addition of FA as an organic electrolyte not only led to an increase in the electrical conductivity of the solution, but also created a solvating effect that enhanced the dissociation of salt and increased the electrical conductivity of the system by more than 400%, see Fig. 1.

However, it should be noted that the input of an acid, as a hydrolytic agent, into a polymer solution leads to the development of acid hydrolysis of PHB, the breaking of the main chain and, consequently, to a change in its molecular weight. To obtain the uniform fiber diameter, it is necessary to optimize the electrical conductivity by selection of the appropriate electrolyte and its concentration in the spinning polymer solution, which was demonstrated by us as an example of a pair of TBAI-FA electrolytes.

Figure 2 shows the dependence of the PHB fiber diameter on its electrical conductivity in chloroform in the presence of a TBAI electrolyte. As the additive that enhances electrical conductivity, FA was used. Curves 1 and 2 show minima of the dependence of the average fiber diameter on electrical conductivity for two different acid concentrations, where the most perfect, cylindrical shape of the fiber with the smallest diameter is observed.
The range of conductivity values located to the left of the minimum <30 μS/cm (I) does not allow one to obtain a strictly cylindrical fiber geometry, while the range of values of this characteristic to the right of the minimum >90 μS/cm (III) is characterized by the electrosinning of PHB fibers of a deformed tortuous shape. The range of conductivity near the minima for both curves of 50 and 70 μS/cm (II), respectively, ensures the electrosinning of fibers homogeneous in thickness with a minimum number of defects.

Figure 1. The dependence of the electroconductivity of the solution of PHB in chloroform on the formic acid content. Inset: micrographs of PHB fibers obtained both in the absence of (A) and in the presence of tetrabutylammonium iodide, 5 g/l (B).

Figure 2. The dependence of the average diameter of ultrathin fibers on the electroconductivity of the spinning solution PHB-chloroform-electrolyte (TBAI) in the presence of FA: 1 - 3.2% and 2 - 5.3%.

One of the key characteristics of the ES-process is the viscosity of the molding solution [5]. In the range of concentrations below 4 wt. %, at low values of viscosity, in the ES-process a mixture of fibers and spherical particles was formed, while an increase in viscosity corresponding to a concentration of 10 wt. % led to the termination of the ES-process. When using FA as an additional electrolyte, its hydrolytic effect on PHB should be taken into account even in non-aqueous environments, i.e. in an organic solvent with a low dielectric constant. Indeed, fig. 3 shows a rather
sharp decrease in the viscosity of the PHB solution in the presence of FA. As expected, in the absence of this hydrolytic agent, the viscosity of PHB in chloroform remains constant for more than 1200 hours (curves 4 and 5).

Figure 3. The time dependence of the dynamic viscosity (A) and its reciprocal value (B) for the PHB solution in the CF-FA-TBAI mixture (1 - MM = 350 kDa, 2 - MM = 450 kDa and 3 - 850 kDa) and in CF (4 - 850 kDa and 350 kDa).

The kinetic curves of the decrease in the viscosity of the system allow to take into account the final time of fiber production (from 30 to 45 minutes) to estimate the reduce in the average viscosity molecular weight of the polymer upon the ES-process completion, i.e. by the time when ultrathin fibers have already formed, and volatile components, including the hydrolytic agent (FA), are removed because of evaporation. The residual content of CF and FA in ultrafine fibers was 0.011 and 0.014 wt%, respectively.

A comparative analysis of the IR spectra of PHB and PHB - TBAI-FA fibers (see fig. 4) showed that, considering the error in the baseline of the spectra, the presence of an electrolyte does not lead to significant changes in the chemical composition of the polymer. In both spectra, all characteristic peaks practically overlap each other. It should be noted only a decrease of the peak areas 1280 and 1227 cm$^{-1}$ characterizing the crystalline phase in the PHB–TBAI–FA sample. It indicates a decrease in fiber degree of crystallinity with electrolyte, compared with the initial PHB.

The linear character of the inverse value of the time dependence of viscosity (Fig. 3 B) shows that the kinetics of hydrolytic degradation of PHB in the presence of FA obeys a first-order equation, which is often observed with acid catalysis of cleavage of ester bonds belonging to natural and synthetic polyesters in a quasi-homogeneous medium. In the process of breaking ester bonds in poly-$\alpha$-hydroxyacids (PLA, PHA, PHGA) and in poly-$\beta$-hydroxyacids (PHB, PHBV), the molecular weight decreases, in particular, in accordance with equation (1):

$$\frac{1}{M_n} = \frac{1}{M_{n0}} + \frac{1}{M_0} k t$$

where $M_n$ and $M_{n0}$ are the number average molecular weight of the polyester at time $t$ and at the initial time, respectively, $k$ is the constant associated with the constant of hydrolysis of the polyester in a homogeneous medium, $M_0$ is the coefficient of transition from medium viscosity to number average molecular weight. The reduction of the molecular weight of PHB is associated with a change in dynamic viscosity directly through the Mark-Houwink-Kuhn equation. For the PHB solution in chloroform studied, this ratio has the form of an exponential equation with an indicator approaching 1 ($0.82 \pm 0.14$).

$$[\eta] = 7.7 \cdot 10^{-5} x M_n^{0.82}$$
By substituting equation 2 into equation 1, one can obtain a close to linear relationship between the reciprocal viscosity and the contact time of the polymer with the FA solution in chloroform, which is observed in Fig. 3.

The inputting of CNT into the spinning solution significantly changes the physical and mechanical properties of the final nonwoven fibrous material, increasing both the breaking length ($L_{av}$, m) and the average elongation ($\varepsilon,%$)

The base modification of crystallites melts at 176-179 °C; a slight change in the melting temperature indicates that the crystallite sizes practically do not change regardless of the concentration of CNTs. With inputting of a modifying additive, the temperature of the onset of thermal degradation rises. It can be noted that the modifying additive works as a thermostabilizer. Higher temperatures for the onset of thermal degradation of nonwoven materials with CNTs, as compared to unmodified nonwoven materials, indicate the presence of adhesive interaction between PHB and the surface of CNT particles (Table 1).

Nonwoven material on the basis of PHB undergoes noticeable photo-oxidative degradation over 120 min of UV exposure in air. The induction period of photooxidation is apparently associated with the time of oxygen diffusion into the bulk of the fiber.

| Table 1. The effect of the recipe on the physicomechanical properties of the fibrous material. |
|-------------------------------------------------|------|--------|-------|
| Recipe            | $T_m$, °C | Induction period, min | $L_{av}$, m | $\varepsilon$, % |
| PHB               | 176,7     | 120       | 724   | 20,8  |
| PHB + 0,01% CNT   | 177,8     | 120       | 1652  | 87,0  |
| PHB + 0,1% CNT    | 178,6     | 150       | 1403  | 105,3 |

In details, the effect of low concentrations of CNTs on the properties and characteristics of nonwoven materials will be considered in our next article, which is planned for publication.

4. Conclusion

The characteristics of the polymer solution largely determine the geometry and morphology of the ultrafine fibers of PHB obtained by the ES. The conversion from a drop-like product to fibrillar structures depends on such important properties of the spinning solution as electrical conductivity and
viscosity. To obtain cylindrical fibers, a number of modifying low-molecular-weight additives, such as TBAI and FA, were added to a PHB solution in chloroform, which enhanced the electrical conductivity of the system. Besides, an increase in the viscosity of solutions by increasing the concentration and/or molecular weight of the polymer also leads to an improvement in the homogeneity of the fiber thickness and affects the diameter and width of the distribution of ultrathin fibers in diameter. Modification of solutions by an ionic electrolyte (TBAI) and hydrolytic agent (FA) reduces the initial molecular mass of the polymer and leads to an enhance in the viscosity of the system as a response to the gyrolytic process. The fibers resulting have found their application in biomedicine.

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