The effect of imidization conditions on the structure and properties of fibres from partially crystallized polyimide

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Abstract. In this work, the two-stage process for producing polyimide fiber from polyamic acid (PAA) by wet spinning was used. Polyimide fibers were obtained by thermal and chemical imidization. The effect of the imidization method (chemical and thermal) on morphology, chemical structure, thermal stability and mechanical properties of polyimide fibers was investigated. A number of research methods were used in the work, such as Fourier transform infrared spectroscopy (FT-IR), scanning electron microscopy (SEM), differential scanning calorimetry (DSC), thermogravimetric analysis (TGA) and determination of strength characteristics.

1. Introduction
Polyimide fibers in addition to high strength and elastic modulus have good resistance to elevated temperatures, radiation, as well as low coefficient of linear thermal expansion and high chemical resistance [1]. Such a favorable combination of the above properties allows one to use polyimide fibers for creating fire-resistant fabrics, for protective clothing, aircraft interiors or in composite materials in the aviation or automotive industry [2]. An application of polyimide materials as heat-resistant first-vapor and gas separation membranes for industrial filter elements is of particular interest. Therefore, the polyimide fibers are very promising for obtaining hollow fiber porous membranes for gas separation and liquid filtration [3].

The two-stage wet spinning method (coagulation method) is the most widely used for the production of polyimide (PI) fibers. In the two-stage method, the fiber is formed from a solution of the prepolymer, namely polyamic acid (PAA), then the PAA fiber is converted into PI fiber due to its thermal or chemical imidization. Typically, the imidization temperature of PAA is selected in the range from 300°C to 350°C. To carry out imidization at room temperature, a mixture of aliphatic carboxylic acid anhydrides and tertiary amines is prepared [4,5]. Earlier in our work, using a mixture of acetic anhydride, triethylamine and benzene, we obtained PI powder from a PAA solution [6]. A feature of the imidization process is the release of imidized water. With this method of producing a polyimide fiber, it is highly likely to form a porous structure both during the formation of the fiber and the subsequent removal of water from the PAA fiber during its cyclization to the polyimide. This circumstance can adversely affect the strength properties of the PI fibers obtained from the PAA fibers [7]. Nevertheless, in some applications, the presence of porosity in PI fibers can play a certain positive role, as, for example, in obtaining filter elements in the form of hollow fiber membranes. In this case, a certain structure is required for filtering [8]. However, information concerning the effect of the PAA imidization method
on the porosity, morphology and properties of the polyimide fibers based on crystallizing polyimides is insufficient in the literature. In this regard, the aim of the present work was to investigate the effect of imidization conditions on the structure and properties of the fibers from partially crystallized polyimide.

An additional novelty and relevance of the work is to conduct studies on the synthesized, crystallizable polyimide based on diamine 4,4'-bis (4-aminophenoxy) diphenyl (diamine BAPB) and 1,3-bis (3 ', 4-dicarboxy dianhydride phenoxy) benzene (R). A feature of R-BAPB polyimide is controlled crystallization and recrystallization during processing into the final material, which was repeatedly shown in [9, 10, 11] using films, coatings and binders for composite materials.

2. The experimental part

2.1. Materials and methods

The following monomers were used for R-BAPB synthesis: 1,3-bis (3 ', 4-dicarboxyphenoxy) benzene dianhydride (R dianhydride), melting point $T_m=163-165^\circ C$, (TechChemProm LLC), dried at $140^\circ C$ in vacuum; diamine 4,4-bis (aminophenoxy) diphenyl (BAPB), $T_m=198-199^\circ C$, (VWR International), dried at $140^\circ C$ in vacuum.

The solvent for the synthesis of PAA was specially prepared, dried (over CaH2) and distilled: N-methyl-2-pyrrolidone, boiling point -202°C, density $d_{20} = 1.024 \text{ g/cm}^3$, refractive index $n_{D20} = 1.4684$ from Sigma-Aldrich Co. LLC (St. Louis, USA).

The fibers were formed from a solution of PAA by the wet method at the PIFV-01 installation (Institute of Macromolecular Compounds, Russian Academy of Sciences). The deposition of PAA fibers was carried out in coagulation bath of the following composition: ethylene glycol / ethanol with a volume ratio of 50:50. Monofilament was formed through a die with a diameter of 0.15 mm with various degrees of die drawing (from 0% to 100%). The formed fiber was washed in distilled water, then, dried at the temperature of $50^\circ C$ for 3 min.

To confirm the chemical structure of the PI formed after the imidization of PAA, one used an IRA-Affinity-1S IR Fourier spectrometer (a Michelson-type single-beam interferometer with an incidence angle of 30°), the spectral range (7800 - 350 cm$^{-1}$); signal to noise ratio (> 30,000:1 ); the maximum resolution is 0.5 cm$^{-1}$.

To determine the phase transition temperatures (melting and glass transition) of the obtained polyimide fibers, the differential scanning calorimeter DSC 204 F1 instrument (NETZSCH) was used. The fibers were tested by the DSC method in the temperature range from 30 to 400°C in an inert atmosphere (argon), the temperature rise rate was 10°C/min. NETZSCH Proteus® software was used to determine the glass transition temperature $T_c$, the melting temperature $T_m$, and the melting enthalpy $\Delta H_m$. Thermogravimetric analysis (TGA) using the TG 209 F1 device (NETZSCH, Germany) was done to measure the temperatures of thermal degradation of polyimide fibers. The fibers were tested in the temperature range from 30 to 700°C at a rate of temperature rise of 10°C/min in an inert atmosphere (argon).

The morphology of polyimide fibers were studied using a SUPRA 55VP scanning electron microscope (Carl Zeiss, Germany). To analyze the structure of the polyimide fiber, its cryo-cleavage in liquid nitrogen was made. Before placing the samples inside the microscope chamber, a thin conductive layer of platinum was sputtered onto their surface. The accelerating voltage was 5 kV.

The mechanical properties of polyimide fibers were determined at room temperature using an INSTRON 5943 universal tensile testing machine. The tensile speed of the fibers was 10 mm/min and the base length of the fiber samples was 30 mm. The average values of the modulus of elasticity, strength and deformation at break were calculated on at least 10 samples of polyimide fibers of each type.
2.2. Results and discussions

The synthesis of PAA was carried out by reacting dianhydride R with diamine BAPB in a solution of an amide solvent of methylpyrrolidone according to the scheme described in [12]. During the synthesis, the equimolar ratio of monomers was strictly observed. The resulting polyamidoxylot solutions were filtered and evacuated. The concentration of PAA in the MP solution was 16 wt. %.

Formed PAA fibers were converted to PI by thermal and chemical imidization. Thermal imidization consisted in heating PAA fibers at the temperatures of 100°C, 200°C, and 300°C for 1 hour at each temperature. Chemical imidization of PAA fibers was carried out in a bath with the solution containing an equimolar amount of acetic anhydride and triethylamine. Next, the fiber was washed from the imidization mixture by treatment in sulfuric ether and ethyl alcohol. After that, the fiber was dried at a temperature of 50°C for 12 hours.

Figure 1 shows the IR spectra of samples of PAA fibers subjected to thermal and chemical imidization. From the decrease in the relative intensity of the C = O bands of the vibrations of the H-bonded amid acid groups (1645-1656 cm⁻¹) and from the increase in the relative intensity of C = O vibrations of the imide cycle (1720 cm⁻¹), relative to the C_ar-C_ar vibrations of the aromatic ring (1593 cm⁻¹), one can estimate the degree of conversion of the amic-acid groups of the former polymer into imide, i.e. about the degree of imidization:

![Diagram](image-url)

**Figure 1.** FT-IR spectra of the PI fibers: 1 – initial PAA; 2 – chemically imidized PAA; 3 – thermally imidized PAA.
To quantify the degree of imidization by IR spectroscopy, we selected the C = O vibration bands of the imide ring, which are of high intensity, and a chemically imidized fiber sample as a reference sample with a 100% degree of imidization. In this sample, the C = O band of vibrations at 1660 cm⁻¹ of the amic-acid fragment is absent in the spectra, while the relative intensity of the C = O vibrations band of the imide cycle is maximum (Figure 1). Thus, as follows from the spectra, the maximum degree of imidization (100%) is characteristic of a chemically imidized one. The thermally imidized fiber is only slightly inferior to the chemically imidized fiber, while the fiber heated at 300°C has an imidization degree of 98%. However, the difference in the spectra and the degree of imidization between the chemically and thermally imidized PAA fibers is insignificant.

![Figure 2. SEM micrographs of PI fibers: a - thermally imidized PAA; b - chemically imidized PAA.](image)

![Figure 3. DSC curves of PI fibers obtained by the method of 1,2 - 1 and 2 heating chemical imidization; 3,4 - 1 and 2 heating thermal imidization.](image)

The PI fiber obtained by thermal imidization has a developed rough porous surface. However, the internal structure of the fiber is quite dense and without the presence of large visible pores (Figure 2). A quite different picture is observed for the PI fibers obtained by chemical imidization. The internal structure of this fiber is more loose and porous. The formation of such porosity is probably due to the fact that, in the process of chemical cyclization, the imidizing mixture diffuses into the fiber, loosens it and forms pores.

DSC curves of PI fibers obtained by chemical and thermal imidization are shown in Figure 3. The PI fibers are characterized by endothermic melting peaks in the range from 316 to 319. It indicates that a crystalline phase is present in the PI fibers studied. However, the melting peak area for PI fiber obtained
by chemical imidization is much lower. This may be due to the fact that in the case of thermal imidization, the crystallization process is accelerated by heat treatment. To calculate the degree of crystallinity of PI fibers, we used the melting enthalpy $\Delta H_m$ determined earlier [10] for R-BAPB with a crystallinity of 100%, which was 90 J • g$^{-1}$. This suggests that the degree of crystallinity of PI fibers obtained by thermal imidization is $\sim$ 27%, and after chemical imidization it is $\sim$ 7% (Table 1). The glass transition temperatures of the fibers were determined only when they were reheated (2nd DSC scan). Upon repeated scanning of the fibers, endothermic melting peaks on the DSC curves are absent (Figure 3). The glass transition temperature of the PI fiber obtained by chemical imidization is slightly higher than that thermally imidized (Figure 3 and Table 1) and lies in the range of $\sim$ 208-210$^\circ$C. The temperature of thermal degradation of the PI fiber obtained by chemical imidization exceeds by 16 degrees a thermally imidized sample (Table 1). This is probably due to the occurrence of a more complete cyclization of amic acid units during chemical imidization (see Figure 1).

| Table 1 Thermal characteristics of PI fibers. |
| Sample | $T_g$ (°C) | $T_m$ (°C) | $\Delta H$ (J/g) | The crystallinity degree (%) | Temperature of destruction (weight loss $\tau_5$) (°C) |
|--------|------------|------------|-----------------|-----------------------------|------------------------------------------|
| PI chemimide | 210 | 319 | 6.1 | 7 | 514 |
| PI thermimide | 208 | 316 | 24.3 | 27 | 498 |

Analysis of the mechanical properties of the PI fibers showed that the fibers obtained by chemical imidization have lower strength characteristics and have less deformation at break compared to thermally imidized analogues (table 2). This fact is due to the loose porous structure of the fiber (see Figure 2).

| Table 2. Mechanical properties of the PI fibers produced by thermal and chemical imidization. |
| Sample | $\sigma$ (MPa) | $E$ (MPa) | $\varepsilon$ (%) |
|--------|---------------|----------|------------------|
| R-BAPB thermimide | 118.2±6.0 | 3116±110 | 82.35±14.17 |
| R-BAPB chimimide | 97.8 ± 4.51 | 2824± 87 | 47.67 ± 9.89 |

3. Conclusions
In the present work, we conducted a comparative study of the effect of the PAA imidization method on the structure and properties of PI fibers. In the case of thermal imidization of the fibers, the degree of imidization is close to chemically imidized analogues. The thermally imidized fiber has higher crystallinity degree than chemically imidized one. Using SEM, it was found that chemical imidization produce more loose and porous internal structure of the fiber. The study of the mechanical properties of the PI fibers showed that the best characteristics were obtained on the PAA fibers subjected to the thermal imidization.

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