

THERMAL INDUCED MORPHOLOGICAL CHANGES OF POLY(ETHYLENE OXIDE) NANOFIBROUS WEBS

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Abstract

The crystallinity of fibres prepared by electrospinning shows lower level in comparison with samples processed by common technologies such as moulding or film casting. Thus, the attempts to improve the structure of electrospun fibres in order to increase physical and mechanical properties of nonwoven webs are obvious. Post-process thermal treatment is one of the possibilities of the crystallinity enhancement that can be easily included to the finishing operation of final products. For the experiment we used poly(ethylene oxide) representing electrospun-friendly material and two solvents - methanol and water, both ensuring good electrospinnability. It is demonstrated that a choice of polymer solvents plays a significant role in fibre diameter and their capabilities to resist applied heat. However, in all cases the enhancement of crystallinity is detected at the short time of thermal exposure.

Keywords: PEO nanofibres, degree of crystallinity, electrospinning

1. INTRODUCTION

Poly(ethylene oxide) (PEO) is a nontoxic water soluble, highly crystalline polymer with glass transition temperature around -50 °C which assures the extensive chain flexibility [1]. Electrospinning of PEO solutions at room temperature was widely studied in recent years resulting in many research works describing PEO nonwoven webs with various fibres size and molecular orientation depending on the chosen processing parameters [2, 3], solvents [4] and solutions properties [5].

Generally, the crystallinity and molecular orientation of electrospun fibres is compared to samples prepared by common processing technologies (moulding or film casting) much lower [6]. Macroscopic alignment of fibres was already reached either by rotating mandrel collector [1] or by counter electrode plates integration [7, 8]. However, macroscopic alignment is not always connected with the orientation on microscopic level and the degree of crystallinity remains almost the same. The structure formation during the electrospinning process is indeed a complex issue. Among the most critical parameters affecting the crystallization process belong the degree of chain orientation/relaxation and the rate of solvent evaporation [9].

Post-processed thermal treatment seems to be the technique that can lead to the both evaporation of residual solvent and the crystalline phase increase [10]. For this phenomenon is typical the reduction in interlamellar distance which is also known as lamellar thickening. However, an amorphous and crystalline phase rearrangement can be accompanied with thermooxidation process in the solid state [11]. Compared to pure hydrocarbon polymers (like poly(ethylene) and poly(propylene)) PEO is more sensitive towards thermal oxidation [12]. In this context, scission of the chains during this process also induces the morphological

changes that can be reflected in overall crystallinity degree. Thus, the proper temperature-time condition for post-process thermal treatment should be established.

2. EXPERIMENTAL

2.1. Material

Poly(ethylene oxide) (PEO), $M_w = 300,000$ g/mol was purchased from Sigma Aldrich (USA). Polymer was dissolved in distilled water and methanol at 9 wt.%. PEO solutions were prepared using a magnetic stirrer (Heidolph MR Hei-Tec, Germany) with the help of a (teflon-coated) magnetic cross. The stirrer was used for 48 hours with mixing rate 250 rpm at 25 °C in water solution and 35 °C in methanol solution.

2.2. Electrospinning

The nanofibrous webs were created by the laboratory device consisted of a high voltage power supply (Spellman SL70PN150, USA), a carbon steel stick of a diameter of 10 mm with a drop of polymer solution (0.2 ml), and a motionless flat metal collector. The electrospinning process was carried out at a voltage of 25 kV with the tip-to-collector distance fixed at 200mm at ambient conditions at 20 ± 1 °C with a relative humidity of 38 ± 3 %.

2.3. Thermal treatment of the nanofibrous web

In order to avoid any structural transformations of prepared samples, electrospun webs were immediately after electrospinning process cooled down to -75°C (significantly lower than T_g of PEO at -54 °C) and stored at this temperature for further experiments. Then, the PEO nanofibrous webs were exposed to thermal treatment at the temperature of 60 °C for a specified period of time. The induced structural changes were simultaneously measured by wide-angle X-ray diffraction.

2.4. Characterization of the nanofibrous web

Characteristics of the nanofibrous webs were evaluated using a Vega 3 high resolution scanning electron microscope (Tescan, Czech Republic). A conductive coating layer was applied before imaging. For a determination of the mean fibre diameter, the Adobe Creative Suite software was used 300 measurements were done at 3 different images.

Crystallinity of prepared samples was characterized by wide-angle X-ray diffraction (WAXD). Diffractograms were recorded on Philips diffractometer (XPertPRO, Netherlands) equipped with hot stage. Measurements were done in reflection mode in the 2θ range of 10 - 35° with nominal resolution of 0.03° at selected temperatures and quasi-logarithmic sampling frequency.

3. RESULTS AND DISCUSSION

The diameter of nanofibres depends on various factors: (i) polymer characteristics (molecular weight and topology of polymer macromolecules), (ii) solvent characteristics (vapour pressure, surface tension, viscosity), (iii) solution properties (concentration, viscosity and elasticity of solution), and (iv) electrospinning parameters (electric field strength, tip-to-collector distance, temperature and humidity). For both the water and the methanol solution, identical PEO and process parameters were used.

Figure 1 shows the micrographs of the pristine electrospun fibres and fibres upon 4-hours treatment at the temperature of 60 °C. As can be seen, the initial smooth surface and diameter of fibres are rather intact upon the thermal treatment in given time interval. However, the finer fibres resulting from water solution tend to surface roughening, breaking and re-joining. This indicates thermodynamic instability of the fibres. Surface roughening can be even ascribed to the process so-called chemi-crystallization. This phenomenon has been

already described and explained for several polymers and is connected with chain scission in surface layer. Released macromolecular segments can then be incorporated into already existed crystallites, which result in surface shrinkage and cracking, especially at the lamellae borders.

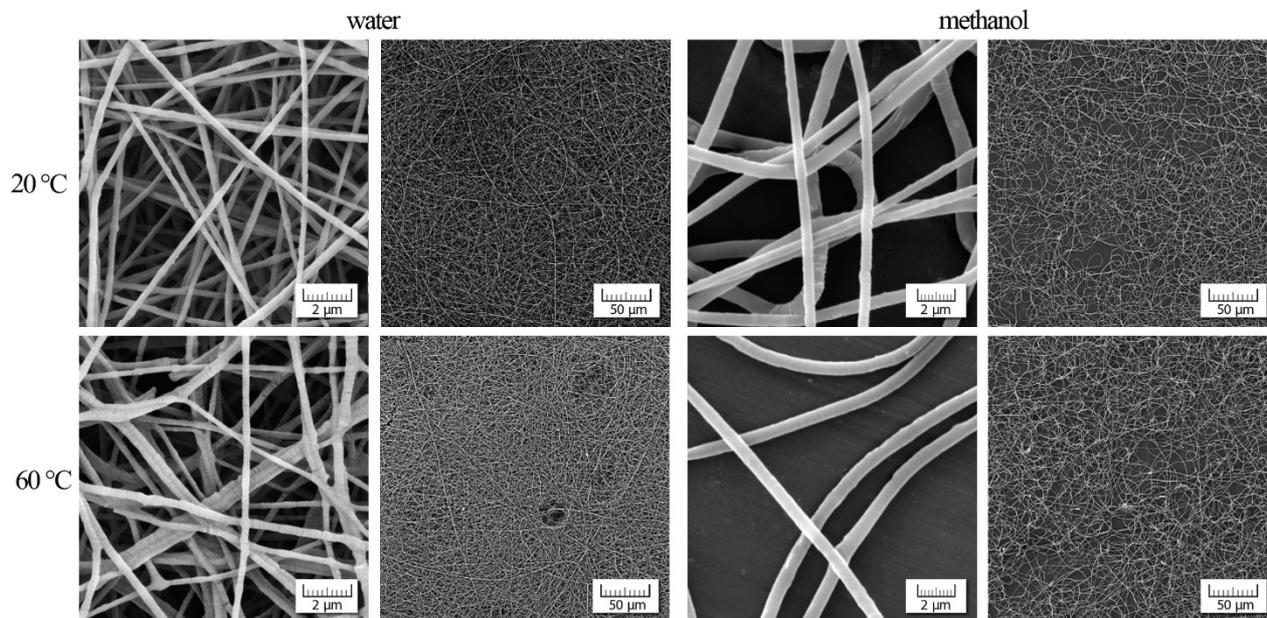


Figure 1 The temperature effect on the morphology of fibres created from PEO solutions

Since the structure of thermal-treated nanofibrous webs consist of well-identified separated fibres, it enables to perform image analysis and calculate fibre diameters. **Table 1** shows the influence of used solvent on resulting fibre diameters and the effect of 4-hours treatment at 60 °C. As can be seen, fibres electrospun from methanol solution exhibit significantly larger diameter. Thus, in this case, the main parameter controlling the fibre thickness is the evaporation kinetics of a given solvent represented by vapour pressure; ejected jets from Taylor cone can be drawn in electric field until the evaporation of solvent and fibre solidification. Moreover, the diameter variation after 4-hours treatment at the temperature of 60 °C is statistically insignificant. In other words it means that no extensive shrinkage of oriented amorphous portion occurred. Although electrospun fibres exhibit generally high amount of amorphous phase [1, 6, 7] in the given experiment, the level of crystallinity is sufficiently high to stabilize nanofibrous webs dimensionally.

Table 1 Average diameter of fibres immediately after electrospinning process (at 20 °C) and after thermal treatment at 60 °C

Solvent	Diameter of pristine fibres [nm]	Standard deviation [nm]	Diameter of thermal treated fibres [nm]	Standard deviation [nm]
Water	234	32	303	79
Methanol	768	140	858	73

Crystallinity development in nanofibres upon thermal treatment can be non-destructively studied by wide-angle X-ray diffraction. Typical X-ray pattern is shown in **Figure 2**. Sharp reflections in a diffractogram correspond to PEO crystallites. On the other hand, wide diffused halo is an evidence of amorphous phase. For precise determination of crystallinity, the diffractograms was resolved into separated crystalline peaks and amorphous halo.

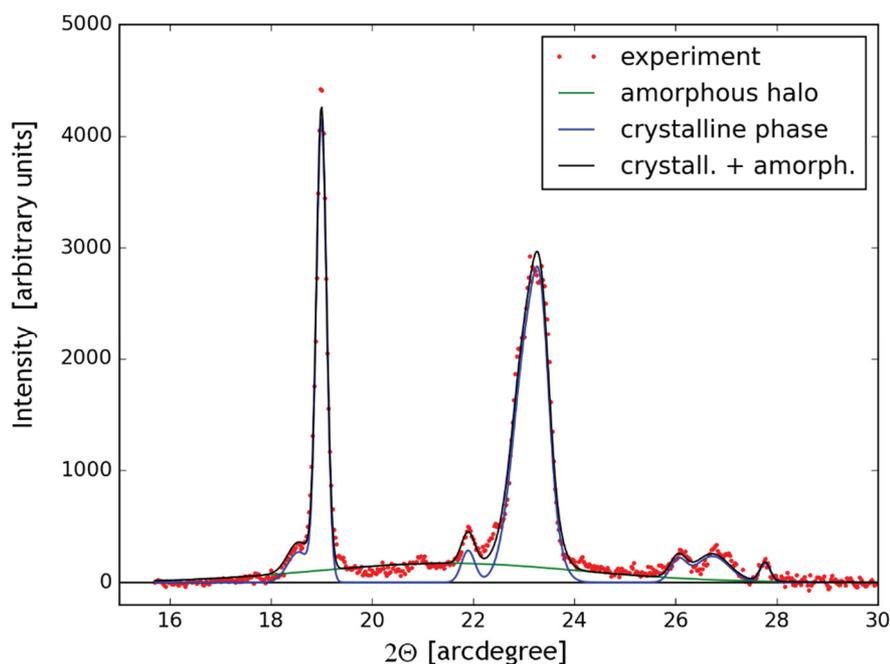


Figure 2 Diffractogram of nanofibrous PEO sample resolved into crystalline peaks and amorphous halo

While crystalline peaks can be unambiguously identified, the maximum of amorphous halo varies with temperature and need to be experimentally assessed. For these purposes, X-ray patterns were measured in melt state at various temperatures and the maximum of individual amorphous halo at given temperature was assessed. In **Figure 3**, position of maximum of amorphous halo as a function of temperature is shown. It can be seen that under given experimental conditions, the maximum of amorphous halo is a linear function of temperature. Then, the maximum position can be extrapolated to solid state, i.e. into the temperatures below 60 °C, and the diffractogram can be successfully resolved into individual crystalline peaks and amorphous halo.

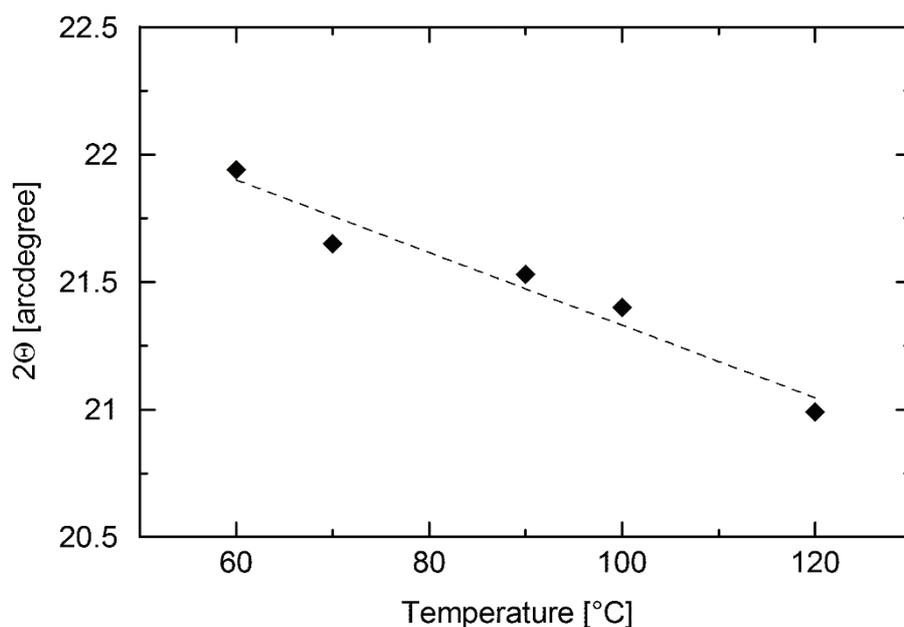


Figure 3 Position of amorphous halo as a function of temperature of melted PEO

As shown in **Figure 2**, each crystalline peak and amorphous halo is fitted by individual Gauss function and the number of fitted peaks within the X-ray pattern was kept for all the diffractograms under study. Then, the crystallinity of the samples was calculated as a ratio between the sum of crystalline peak areas and the area of the whole X-ray pattern and plotted in time of thermal treatment (see **Figure 4**).

It was already described [13] that rapid uniaxial stretching of polymer during the electrospinning process hinders the development of crystalline structure in fibres. Thus fibres with smaller diameter show generally lower level of crystalline content. Indeed in **Figure 4**, an increase in crystallinity with increasing fibre diameter is observed from comparison of fibres from methanol (approx. 800 nm) and water (approx. 250 nm) solution. It is also obvious that in both cases the crystallinity increases in given period of time. In the case of fibres prepared from methanol solution the crystallinity rose by another 12 per cent. Fibres prepared from the water solution showed slightly lower crystalline content increase (by 10 per cent). Nevertheless, the largest structural rearrangement occurs within the first hour of thermal treatment, representing the fundamental step from application point of view.

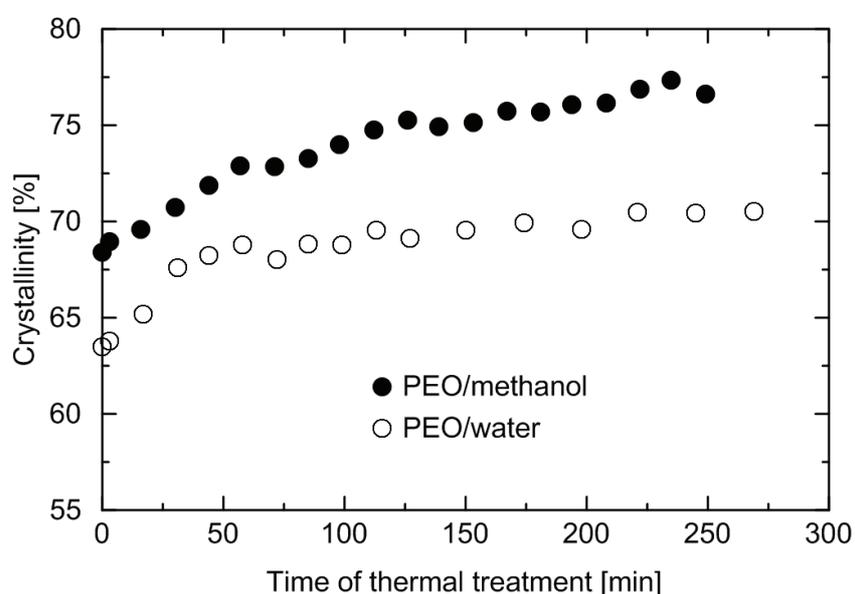


Figure 4 The crystallinity evolution upon 4-hours thermal treatment at 60 °C

4. CONCLUSION

The PEO nanofibres prepared by electrospinning process from methanol and water solution were analyzed and compared. Then, post-process thermal treatment was applied in order to increase their crystallinity content. It was shown that the resulting diameter of electrospun PEO nanofibres depends on the solvent used. The finer fibres from water solution possess lower crystallinity and, as a consequence, are seen to be less thermodynamically stable. Nevertheless, in both cases the crystallinity increases upon the 4-hour thermal treatment. The most pronounced structural changes proceeds within the first hour of thermal treatment.

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