

Enhanced orientation of PEO polymer chains induced by nanoclays in electrospun PEO/clay composite nanofibers

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Abstract Polymer fibers composed of poly(ethylene oxide) (PEO) and nanoclay were fabricated by electrospinning. The morphology of the composite nanofibers was characterized by scanning electron microscope (SEM) and transmission electron microscope (TEM), which showed aligned nanoclays in the fibers. Polarized Fourier transform infrared (FT-IR) spectroscopy revealed that the PEO chains in the composite fibers exhibit a higher degree of orientation than that in PEO nanofibers containing no nanoclay. It is believed that spatial confinement is present in the electrospun nanofibers, which results in the enforcement of the mutual restriction. The anisotropic hierarchical nanostructure may have potential applications in optics, mechanical materials, and biomedical materials for cell culture.

Keywords Composite nanofibers · Chain orientation · Electrospinning · Platelet nanoclays · PEO

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Introduction

It is well known that electrospinning is a facile and efficient technique for fabrication of continuous polymer nanofibers [1–3] with unique features and properties, and fiber mats with nanometer size pores and high surface-to-volume ratios. In addition, it is versatile and cost-efficient to improve the functionalities of the nanofibers thus prepared by incorporating additives during the electrospinning process [4–7]. Multifunctional nanofibers can be obtained from various polymers, polymer blends, composites, sol–gels, ceramics, etc. [2, 4]. The unique properties and multifunctionality of these nanofibers have presented very interesting and appealing applications in various areas such as filters, textiles, catalysis, tissue engineering, wound healing, controlled drug release, and biochemical sensors [3, 4, 6, 8–13].

Poly(ethylene oxide) (PEO) is a cheap, water-soluble, and biocompatible polymer that has been used in composite functional materials [14], nanocomposite hydrogels [15–17], drug delivery systems [16–19], and so on. It can also be electrospun with nanoparticles such as Au nanorods (AuNRs) [20], cyclodextrin [21], and SiO₂ [22] nanoparticles, among others, to form composite fibers. Compared with these additives, clays, a kind of inorganic mineral salts which can be exfoliated into nanoclay platelets, are commonly used inorganic nanoparticles for the polymer composite with the purpose of enhancing the thermomechanic performance of the polymers [23–27]. It can also be used as the cross-linker to form PEO/nanoclay hydrogels, which have shown remarkable thermomechanical properties [28–32]. On the other hand, recent studies on co-electrospinning of AuNRs and polymers have indicated that the process can result in long-range alignment of AuNRs in electrospun nanofibers [20, 33]. It is expected that the strong shear forces caused by the solution jet flow can induce alignment of the inorganic nanoparticles therein. Meanwhile, the orientation of PEO polymer chains can also

be obtained by simply electrospinning the PEO fibers, which may be attributed to the orientation of polymer C–O backbones induced by water dipole [34]. Inspired by these facts, therefore, electrospinning of PEO nanofibers with nanoclay is particularly interesting, especially the relationship between the alignment of nanoclays and the orientation of PEO chains in the nanofibers.

In this paper, we report the nanocomposite fibers made of PEO and nanoclays via electrospinning. The morphology of the composite hierarchical fibers was characterized with SEM and TEM, and orientation of the PEO chains and nanoclays was analyzed by polarized FT-IR spectroscopy. The results indicate, for the first time, that inorganic nanoplatelets can enhance molecular orientation of polymer chains in electrospun nanofibers, which may afford unique optical and mechanical properties.

Experimental

Materials

PEO (average $M_w \sim 300,000$) was obtained from Alfa Aesar Company. Clay ($Mg_{5.34}Li_{0.66}Si_8O_{20}(OH)_4Na_{0.66}$) was purchased from Laporte Industries (UK), which was purified before use. $Na_2P_4O_7$ was bought from Tianjin Chemical Works. The clay (0.2 g) was dispersed in 5 mL deionized water with proper concentration of $Na_2P_4O_7$. When $Na_2P_4O_7$ was dissolved in water, the $P_4O_7^{2-}$ anions were attracted to the edges of nanoclay platelets because of electrostatic interactions, which led to negative charges on the surfaces of nanoclays, and the charge–charge repulsion resulted in the exfoliation of the clays in aqueous solution, as demonstrated by AFM results (Fig. S1, Supporting Information). Then, a PEO/clay mixture solution was prepared by mixing a PEO solution (0.55 g PEO in 5 mL deionized water) and a clay aqueous solution with a total volume of 10 mL. The final concentration of clay and PEO in the mixture solution was 0.02 g mL^{-1} and $5.5 \times 10^{-3} \text{ g mL}^{-1}$, respectively. Pure PEO aqueous solution was prepared by dissolving PEO in deionized water with a concentration of 0.14 g mL^{-1} .

Electrospinning

PEO fibers and PEO/clay nanocomposite fibers were electrospun from a PEO aqueous solution (14 wt%) and a mixture solution of PEO (5.5 wt%) and clay (2.0 wt%), respectively. The solution was placed in a pipette equipped with a 16-G, flat-tipped, stainless steel needle and was pumped to the needle by a syringe infusion pump at a flow rate of 0.3 mL h^{-1} . High voltages of 10 kV were applied to the needle during electrospinning. The working distance between the tip of the syringe needle and the collector was 18 cm. The collectors were two parallel grounded Si wafers with a 5-mm gap. The

random fibers were collected on the Si wafers, while the aligned fibers were suspended in the gap between the parallel wafers. All experiments were carried out at ambient temperature with a relative humidity of approximately 30 %.

Characterizations and measurements

The morphology of random fiber mats and aligned fibers was assessed using a JEOL S-4300 field emission SEM operating at an accelerating voltage of 10 kV. Samples for the SEM analysis were dried under vacuum at room temperature for 24 h and then sputter-coated with gold palladium for 60 s. The dispersion of plate-like clay in the nanofibers was detected by a JEOL JEM 2100 TEM.

Polarized FT-IR spectroscopy measurements were carried out on a Bruker IFS-66 V/S spectrometer in conjunction with Hyperion 3000 microscope equipped with a MCT detector, with a gold wire grid polarizer (Specac) mounted between the sample and the detector. The fiber bundle direction was defined as the reference (parallel) direction. Each spectrum was acquired with 128 scans at 2 cm^{-1} resolution. The area of a selected band was obtained by curve fitting the spectrum using the software OPUS 6.5, with a residual RMS error less than 0.002.

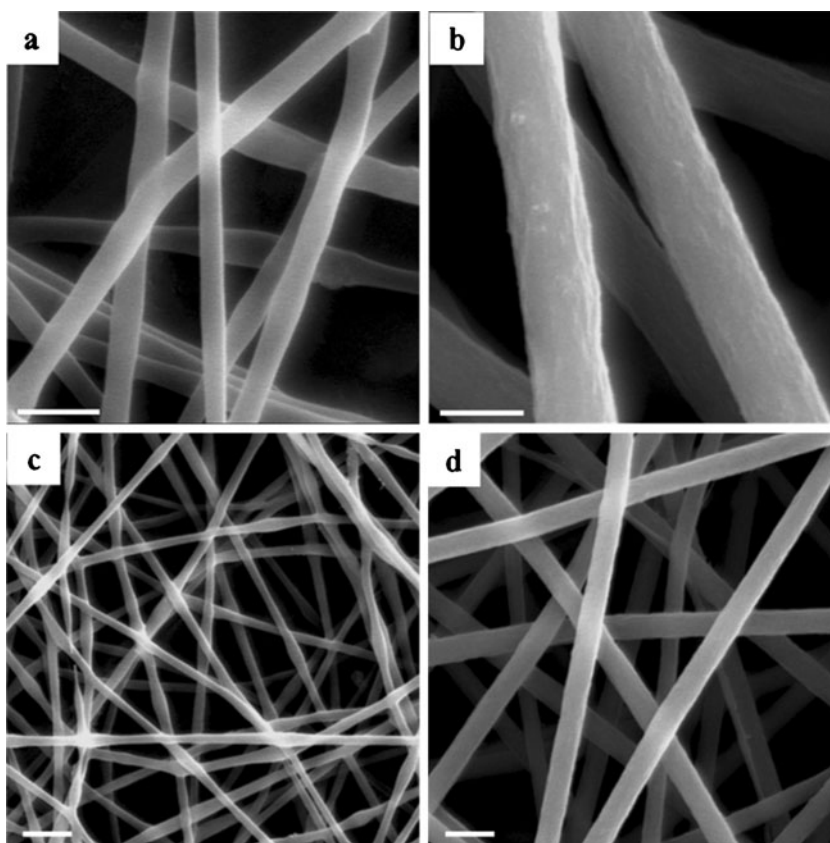
Results and discussion

For the PEO used in the experiment (average $M_w \sim 300,000$), when the solution concentration was $5.5 \times 10^{-3} \text{ g mL}^{-1}$, it cannot be electrospun to form continuous nanofibers due to low viscosity of the solution. When the nanoclays were mixed with this PEO solution, because of the interactions between the clay nanoplatelets and the ethylene oxide units of the polymer chains, the viscosity of the solution was significantly increased. As a result, nanofibers can be produced easily from the mixture solution. In contrast, in absence of the nanoclay additive, a PEO solution of a much higher concentration (0.14 g mL^{-1}) was used in order to produce pure PEO nanofibers via the same electrospinning process.

Morphology

Figure 1 presents SEM images of nanofibers electrospun from pure PEO solution and mixture solution containing nanoclays of 0.02 g mL^{-1} concentration, respectively, under the same electrospinning conditions. There are no beads in either electrospun PEO nanofibers or PEO/clay composite nanofibers. All the pure PEO fibers have smooth surface. However, the surface of composite nanofibers was rough. In addition from the SEM images (Fig. 1b, d), it can be seen that clay addition leads to a broader distribution in diameter of the composite fibers, which is in agreement with previous

Fig. 1 SEM images of nanofibers electrospun from PEO (**a, c**) and PEO/clay (**b, d**). Scale bars are 500 nm in **a** and **b**, and 1 μm in **c** and **d**



study [35]. This can be attributed to the increase of viscosity because of inserted volumes of the nanoclays. Under the same electrospinning conditions, the difference of nanofibers diameter is mainly because of the difference of surface tension which resulted from the differential viscosities of PEO and PEO/clay solutions.

As shown in Fig. 2, the TEM images provided detailed evidence of the dispersion of clays in the composite nanofiber, from which we can see that the nanoplatelets are aligned parallel to the fiber axis. It is believed that during the process of electrospinning, the high voltage was applied to the solution, and the solvent substantially volatilized at the long working distance, which resulted in the increase of the viscosity of the jet flow. Under the sustained electric shearing forces, the nanoplatelet orientated well along the direction of fiber axis as schematically depicted in Fig. 2c [36].

Polarized FT-IR spectroscopy analysis

Because of electrostatic interaction, electrospun nanofibers can form parallel array perpendicular cross the gap between two parallel Si wafers, both grounded [37]. This was verified by optical microscopy (data not shown). From the SEM micrographs (Fig. 3), it can be seen that for both PEO and PEO/clay composite, the nanofibers align almost parallel to each other and form bundles. Next, the orientation of PEO

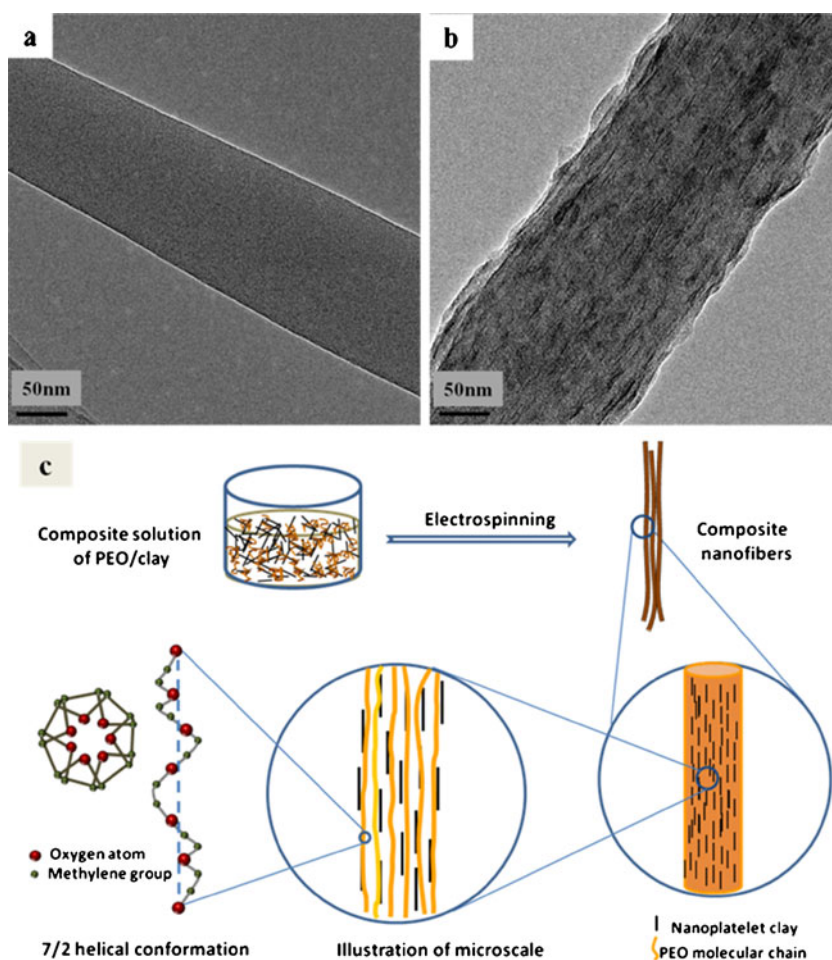
chains in the nanofibers was analyzed by polarized FT-IR spectroscopy.

PEO chains in the crystalline state adopt a 7/2 helix structure, the internal rotations of the succession bonds (O–CH₂–CH₂–O) constructing a *trans*, *gauche*, and *trans* conformation. IR spectrum is an accurate reflection of conformation of molecular chains through detecting chemical group vibrations, and polarized IR spectroscopy provides a powerful method to evaluate chain orientation at molecular level. Generally, the infrared dichroic ratio, R , is calculated from the equation of $R=A_{\parallel}/A_{\perp}$, A_{\parallel} and A_{\perp} being the absorbances of a specific peak in the parallel and perpendicular spectra, respectively. In fibers, polymer chains are assumed to be uniaxially oriented, and the Herman orientation function F can be determined from the infrared dichroism of the specific band,

$$F = \frac{3 \langle \cos^2 \theta \rangle - 1}{2} = \frac{R - 1}{R + 2} \cdot \frac{R_0 + 2}{R_0 - 1}$$

where $R_0 = 2 \cos^2 \alpha$, α is the angle between the transition dipole moment vector and the chain axis, and θ is the angle between the chain axis and the fiber axis (reference direction). Thus, the average orientation of the polymer chains can be characterized by θ . A random orientation is implied by $\theta = 54.7$, while a perfect parallel orientation of the chains along the fiber axis is indicated by $\theta = 0$. Figure 4a displays IR spectra of nanofibers of PEO and PEO/clay composite in

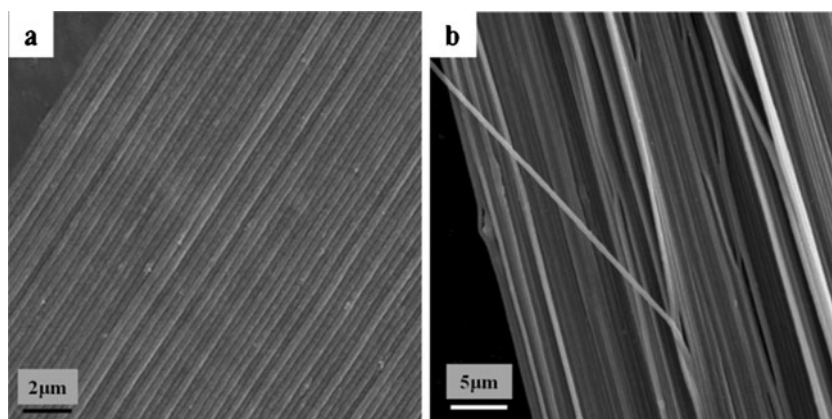
Fig. 2 TEM images of **a** an electrospun PEO fiber and **b** an electrospun PEO/clay fiber (scale bars 50 nm). **c** Illustration of structure formation in the experimental process: the clays are random exfoliating in the composite solution, and after electrospinning, they are nearly parallel to the fiber's axial direction. Also shown is the schematic representation of 7/2 helical conformation of PEO polymer chain [36]



the 1,400–900 cm^{-1} range. In both spectra, characteristic PEO bands are clearly identified. The assignments of these bands have been well established in the literature [38–42]. In particular, the band at 1,360 cm^{-1} is perpendicular and ascribed to the mixture of CH_2 symmetric wagging and C–C stretching modes; the band at 1,342 cm^{-1} is parallel and associated with CH_2 asymmetric wagging vibration; the 1,240 cm^{-1} band is also parallel and is assigned to CH_2

asymmetric twisting; and the strongest band at 1,102 cm^{-1} , which is parallel, is due to C–O stretching vibration; the doublet at 962 ($//$) and 943 (\perp) cm^{-1} are considered to arise from CH_2 rocking of a *gauche* ($\text{OCH}_2\text{CH}_2\text{O}$) group. An additional band at $\sim 1,000$ cm^{-1} assigned to Si–O stretching is observed in the spectrum for the PEO/clay composite nanofibers, which is an indication of the presence of nanoclays in the composite fibers. Polarized FT-IR spectra of

Fig. 3 SEM images of aligned pure PEO fiber bundle (**a**) and aligned PEO/clay fiber bundle (**b**). Excellent parallel alignment of the nanofibers can be seen from the images



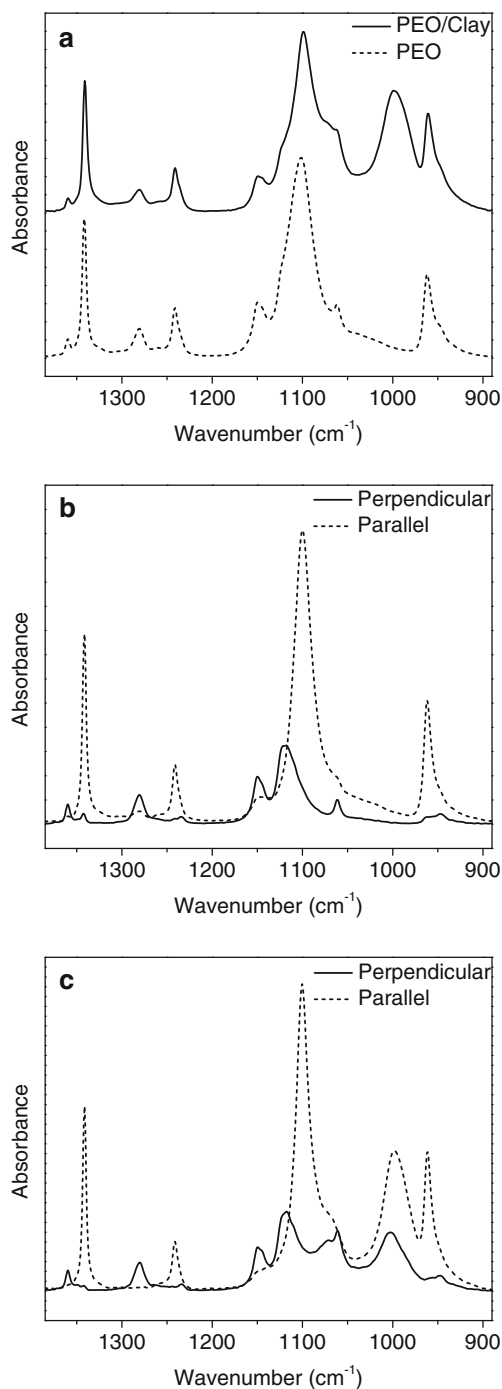


Fig. 4 FT-IR spectra of PEO and PEO/clay composite fiber bundles in the 1,400–900 cm^{-1} range (a) and polarized spectra of PEO fibers (b) and PEO/clay fibers (c)

PEO and PEO/clay fibers are shown in Fig. 4b, c, which are consistent with parallel orientation of PEO chains along the fiber axis. The band at $1,342\text{ cm}^{-1}$ due to CH_2 wagging, which is clean and with the transition dipole moment vector parallel to the chain axis, was used to calculate the degree of orientation quantitatively of the PEO chains in the fibers.

For the PEO fibers, $R=29.3$, $\theta=14.7$, and $F=0.90$, whereas for the PEO/clay nanocomposite fibers, $R=152.3$, $\theta=6.5$, and $F=0.98$. The results indicate that there was significant uniaxial orientation of the polymer chains in the PEO nanofibers when collected between the electric parallel Si wafers, and the nanocomposite fibers exhibited a much higher R and a lower θ than pure PEO nanofibers. In the electrospinning process, a high voltage was added to the solution, and at the long working distance, the solvent largely vaporized, which resulted in increase of the viscosity. Under sustained shear stress, the nanoplatelets orientated well along the fiber axis and anisotropic nanofibers were formed. The reason of higher orientation of molecular chain in the composite nanofibers than in pure PEO may be attributed to the mutual restriction between the PEO molecular chains and the clay nanoplatelets under the shear stress. In this situation, the nanoclays can enhance the orientation of PEO molecular chains in electrospun nanofibers, which was due to the special nanoplatelet structure of clay. In fact, similar orientation of clay nanoplatelets was observed in fibers obtained by hand-drawing PEO/clay solution. In addition, when the electrospun composite nanofibers were treated by solvent vapor for 3 s, the platelet nanoclays in the fibers became randomly oriented (Fig. S2 in Supporting Information), presumably because of the release of the limiting effects during the dissolution process. Furthermore, spherical nanoparticles were found to exert little effects in enhancing the orientation of PEO molecular chains (Fig. S3 and S4 in Supporting Information).

Conclusion

In summary, we have fabricated PEO/clay composite nanofibers by electrospinning technique. Both the polymer chains and the nanoclay platelets exhibited well alignment in the nanofibers which was revealed by TEM and polarized FT-IR measurements. The clay can enhance the ordered molecular architecture of the electrospun nanofibers. Therefore, mutual restriction between PEO molecular chain and nanoclay was the efficient cause of the orientation of both. Restricted space was formed during electrospinning, which resulted in the enforcement of the mutual restriction. The hierarchically well-aligned electrospun PEO/clay composite nanofibers may be used as a biomedical material for cell culture and are referential to other systems, which could broaden nanocomposite studies for future work.

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