Internal Structure of Amorphous Electrospun Nanofiber: Oriented Molecular Chains

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The properties of polymeric nanofibers are determined by their internal structure. Although electrospun nanofibers have been widely applied in many fields, their internal structure is still not extensively reported, especially for amorphous nanofibers, which cannot be analyzed by studying the morphology of the crystal lamellar such as the crystalline nanofibers. In this study, the internal structure of electrospun amorphous polycarbonate (PC) nanofibers is investigated. The phase contrast and transmission electron microscopy images show that PC nanofibers exhibit a cylinder-like structure composed of molecular chains that are highly oriented along the fiber axis. This interesting cylinder-like internal structure may be the result of evaporation-induced phase separation in the polymer solution jet and the high strain rate in the electrospinning process. The variation of mechanical properties of PC nanofibers agrees well with the varied internal structure of the nanofibers with different fiber diameters. Due to the high degree of molecular orientation, as-spun PC nanofibers exhibit superior elastic modulus (6.2 GPa) and strength (780 MPa). The cylinder-like structure provides an insight into the internal structure of an amorphous electrospun nanofiber, which helps optimize the mechanical performance of amorphous nanofibers and fiber-based devices.
Therefore, understanding the formation and evolution of polymer supramolecular assembly and the internal structure of nanofibers is important for optimizing the performance of polymer fiber-based systems and devices.

Among the methods for fabricating polymer nanofibers, electrospinning (ES) has been regarded as the most efficient. In the ES process, a polymer solution drop is elongated and stretched by electrostatic forces, leading to an extended chain conformation in the nanofibers. For crystalline polymeric nanofibers, the internal structure can be demonstrated by the morphology of the crystal structure using wide-angle X-ray diffraction, selected-area electron diffraction or other methods. However, for amorphous ones, the internal structure is more difficult to determine because of the lack of an ordered and detectable substructure.

In this work, we investigated electrospun nanofibers of polycarbonate (PC)—an extensive applied amorphous engineering polymer. The substructure of its nanofibers was determined by polarized Fourier transform infrared spectrometry (PFTIR), polarized Raman spectra, an atomic force microscope (AFM), and a transmission electron microscope (TEM). We also describe the effects of varied orientations on mechanical performance of the PC nanofibers.

2. Experimental Section

2.1. Membrane Preparation

Electrospun nanofibers were fabricated from a solution with 16% w/w of PC dissolved in a mixed solvent of tetrahydrofuran and dimethyl formamide in the ratio of 7:3 (v/v). Hexadecyl trimethyl ammonium bromide (CTAB) was added to the solution to increase its conductivity with the content of 0.2% w/w of PC. The PC nanofibers were electrospun at room temperature, ambient humidity, with a solution feed rate of 0.6 mL h\(^{-1}\), and an applied voltage of 18 kV.

2.2. Membrane Characterization

The morphologies of electrospun nanofibers were observed using a scanning electron microscope (Keysight 8500 FE, USA) after gold coating. The phase contrast and internal structure images of the nanofibers were obtained by the tapping mode of an AFM (Keysight 7500, USA) and a transmission electron microscope (TEM). The electrospun PC nanofibrous membranes for PFTIR and polarized Raman spectrum were collected using a rotating drum with a line speed of 4 m s\(^{-1}\). Specimen preparation for tensile testing was shown in Figure S1 (Supporting Information) and the tests were carried out by a nanotensile tester (Keysight T150 UTM, USA) with a 500 mN load range and 50 nN load resolution. All the specimens were stretched to failure at a strain rate of 10\(^{-3}\) s\(^{-1}\) with a gauge length of 5 mm. More details about the experiments are provided in the Supporting Information.

3. Results and Discussion

ES polymer nanofibers with smaller diameters tend to have higher degree of molecular orientation. However, reported electrospun PC fibers have an average diameter of 2–3 \(\mu m\), which makes them less likely to form oriented structures. Diameters of ES fibers are affected by the combined actions of the surface tension of the solution, applied voltage, receiving distance, and so on. To reduce the fiber diameter, CTAB was dissolved into the solution to increase the electrostatic force during electrospinning. In this way, the fiber diameter was dramatically decreased to 349 nm, and the fiber surface was smooth (Figure S2, Supporting Information).

The molecular orientation of nanofibers can be identified by PFTIR through the chemical bond vibration. In specific, the molecular orientation of aligned PC nanofibers collected from a rotating drum can be obtained quantitatively by determining the dichroic ratio, \(R = A_\parallel / A_\perp\), where \(A_\parallel\) and \(A_\perp\) are the parallel-polarized and perpendicular-polarized infrared absorbance intensity respectively for a specific vibration component. As shown in Figure 1, the absorbance bands of 1240 and 1190 cm\(^{-1}\) are caused by vibration of C–O on the backbone of PC.\(^{10}\)

Figure 1. a) PFTIR spectra of the PC membrane composed of aligned PC nanofiber and b) polarized Raman spectra of a single PC nanofiber. \(A_\perp\) and \(A_\parallel\) represent the parallel and perpendicular directions to the axis of fiber, respectively.
which is oriented almost parallel to the chain direction. The $R$ values of these two bands are 1.25 (1240 cm$^{-1}$) and 1.36 (1190 cm$^{-1}$) and the fact that both are greater than 1 indicates that the molecular chains align along the fiber axis of the PC nanofiber. Meanwhile, absorbance band caused by ring stretch showed negative dichroism (cf., Figure 1a), which also demonstrated orientation of PC molecular chains. Furthermore, the result of polarized Raman spectroscopy of a single nanofiber exhibited positive dichroism of C=O band (cf., Figure 1b), again indicating that the PC molecular chains were orientated along the fiber axis.

Substructures within the PC nanofiber can be seen in the AFM phase contrast image and TEM images of the nanofiber (Figure 2a–c). One can see that cylinder-like structures orient along the nanofiber axis. The shape of the structure is in good agreement with the theoretical deduction of the internal structure of the amorphous nanofiber. The reason is that the nanofiber is a composite consisting of ellipsoid-like anisotropic regions surrounded by thin amorphous polymer layers. PC is an amorphous polymer whose molecular chain cannot crystallize like crystalline polymers, such as polycaprolactone, do in the ES process. The PC molecular chains undergo stretching and elongation as the solvent continuously evaporates. Consequently, phase separation occurs in the ES process, leading to a cylinder-like structure inside the PC fibers.

At beginning, because the PC molecular chains are surrounded by large numbers of solvent molecules, they have the ability to move and stretch (Figure 2d Stage I). As the solvent evaporation-induced phase separation develops, the crimping and entanglement of the PC molecular chains increases due to the minimum energy principle facilitating the formation of aggregates of stretched molecular chains or spinodal structures (Figure 2d Stage II).

Along with continuous evaporation of the solvent, the ES jet begins to solidify, accompanied with the solidification of highly stretched molecular chain bundles or spinodal structures (dashed box in Figure 2d Stage III), which take a shape of irregular fibrils or cylinders with diameters of ≈20 nm. Two factors promote the formation of this structural orientation. The first is the strong elongation caused by the electrostatic force, which stretched the molecular chains during the ES process. The second is the action of solvent molecules, which provide the molecular chain with spaces and enable them to move and form the orientation structure after complete solvent evaporation. Nanofibers with larger diameter have a lower orientation degree of the molecular chain than those with smaller diameter (Figure 2b,c). After annealing at 120 °C for 2 h (under $T_g$), polarized Raman spectra of the single PC nanofiber was slightly different from that of untreated one (cf., Figure S3, Supporting Information), and the orientation structures became
less acute (cf., Figure S4, Supporting Information). As the annealing temperature was increased to 160 °C (above \(T_g\)), all the organized structures vanished completely after 2 h annealing. This was caused by relaxation of the molecular chains during annealing.

For electrospun amorphous polymer nanofibers, the morphologies of the orientated structures of molecular chains have not been reported. We believe that the result we got might be related to the addition of CTAB. As shown in Figure 3, almost all the fibers containing 0.2% of CTAB showed the cylinder-like structure, yet hardly any fiber with no CTAB showed this structure. The addition of CTAB increased the flexibility of the PC molecular chain and led to enhanced chain mobility, which was well demonstrated by the viscosity of the PC solution with different content of CTAB (cf., Figure S5, Supporting Information). The viscosity of the PC solution decreased with increased CTAB concentration, indicating that the CTAB improved the mobility of PC chains and favored the formation of orientated molecular chain structures during the ES process.

Mechanical properties of electrospun nanofibers are greatly affected by the orientation of the molecular chains.\(^{11,12}\) As shown in Figure 4a, fibers with smaller diameters exhibited a higher tensile modulus and strength but lower elongation at break. Besides the size effect,\(^ {10}\) an oriented structure gains higher resistance to axial tensile force due to molecular chain orientation in the direction of applied stress.\(^ {13}\) The reason is that the stretch of an oriented structure leads to deformation of chemical bonds (the length of the bonds and the angles between the bonds along the chain backbone), which supplies a much greater force than that supplied by action between chain molecules (van der Waals forces).\(^ {16}\)

Interestingly, different from bulk PCs,\(^{17}\) there are two approximate linear stages and no strain hardening stage for electrospun PC nanofibers. Before and after yielding, stress increases approximately linearly with the increase of strain, and the slope before yielding is larger than that after yielding. This is related to the deformation and slippage of both the molecular chains and the oriented structure. In the elastic deformation stage, the deformation of the molecular chains and the oriented structure caused by applied stress is reversible, and the applied load is evenly borne by the oriented structures contributing to the first linear stage. After this stage, under further stretch, a crimped molecular chain becomes straight, and oriented structures begin to slip, which creates voids. With continuous stretching, the voids are elongated and new voids form, which leads to a plateau in the second linear stage where a small increase of applied stress causes significantly more elongation. Under a certain applied stress, nanofibers will fracture, due to fracture and destruction of both the molecular chains and the oriented structure.

Varied degrees of orientation have significant effects on the mechanical properties of fibers. The relationship between mechanical properties and varied fiber diameters are shown in Figure 4b–d. The trend of the elastic modulus and tensile strength with varied fiber diameters corresponds with the power law function, and the elongation at break corresponds with the Boltzmann function (dashed line in each figure). By virtue of these orientation structures, the elastic moduli and tensile strengths of as-spun PC nanofibers in our tests reached 6.2 GPa and 780 MPa, which were both nearly three times as high as those of bulk PCs.\(^ {17}\)

4. Conclusions

In summary, the molecular orientation structures, caused by strong elongation and evaporation of solvent during the ES process, took the shape of irregular fibrils or cylinders with a diameter of \(\approx 20\) nm and tended to exist in thinner fibers. Those structures exhibited higher resistance to axial tensile force and led to a superior elastic modulus and tensile strength, which facilitates preparation of nanofibers with ultrahigh strength. This study provides direct insight
into the internal structure of amorphous nanofibers, which favors tuning the mechanical performances of polymer fiber-based systems and devices.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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