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Preparation and characterization of polyketone (PK) fibrous membrane via electrospinning

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ABSTRACT

In this study, the aliphatic polyketone (PK) fibrous membrane was successfully prepared from the solution by electrospinning process at room temperature. As solvents for PK polymer, the mixed solvents of trifluoroacetic acid (TFA) and dichloromethane (MC) were used. Electrospun PK fibrous membrane was characterized by scanning electron microscope (SEM), wide angle X-ray diffraction (WAXD), differential scanning calorimetry (DSC), Fourier transform infrared spectrophotometer (FT-IR), and Raman spectroscopy, and compared to the corresponding cast PK film. The crystal structures of electrospun PK fiber and solvent cast PK film were characterized by WAXD. The result indicated that the crystal structure of cast PK film was assigned to α-form, while the crystal structure of PK fibrous membrane corresponded to β-form, which was attributed to fast crystallization during electrospinning process. Accordingly, the crystallinity of electrospun PK fibrous membrane was lower than that of solvent cast PK film. To confirm further these crystalline structures, FT-IR and Raman spectroscopy were employed.

1. Introduction

Aliphatic polyketone (PK) is a family of polymers prepared by the polymerization of α-olefins and carbon monoxide in a perfectly 1:1 alternating sequence using palladium catalysts. The simplest aliphatic polyketones can be regarded as a homopolymer of the repeat unit $-(CH_2-CH_2-C{=}O)-$. These polymers are semi-crystalline thermoplastics and a class of polymers of great current interest, due to their excellent properties like fast crystallization, high tensile strength, high chemical and wear resistance, very low permeability and good impact behavior over a broad temperature range [1–3]. These properties make polyketone a suitable material for engineering applications. X-ray diffraction study of the crystalline structure of aliphatic polyketones has been reported. For instance, the original crystalline morphology for polyketone determined by Chatani et al. [4,5] is directly analogous to the unit cell of polyethylene, but with the *c*-axis increased by three times to account for the carbonyl group. Lommerts et al. and Klop et al. [6,7] reported a denser phase in polyketones. This denser phase (density 1.383 g cm^{-3}) was designated alpha (α), and original Chatani structure (density 1.297 g cm^{-3}) was beta (β). Both crystalline structures are orthorhombic with all-trans chain conformations, but there is a difference between the modes of chain packing. In α form, the carbonyl groups are closer together than in β one. Also, the angle between the molecular plane and the *bc* plane is 26° for the α form whereas it is 40° for the β form. The different crystalline structures are shown in Fig. 1.

Electrospinning is a powerful method for preparing nanofibers owing to simplicity, versatility as well as the feasibility of mass production as applied various organic polymers [8]. This technique employs a high-voltage supply with a polymer solution or melt that can make polymeric fibers with diameters ranging from a few microns to nanometers [8,9]. A number of organic polymers including natural and biomaterial polymers have been successfully spun to micro- or nano-scale fibers using electrospinning process [10]. These nanofibrous membranes prepared by electrospinning process have many applications due to their excellent properties such as very small pores, larger surface area, and higher porosity compared with regular fibers which produced by conventional melt and wet spinning process [11]. However, PK fibers using electrospinning have not been reported to date. In this study, poly-

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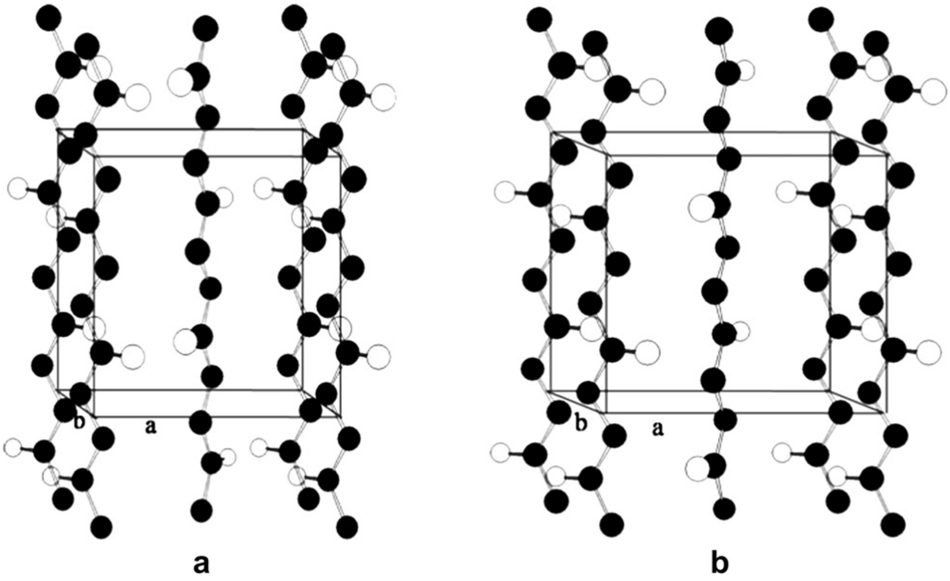

Fig. 1. View of the different crystal structures of PK; (a) PK-α; and (b) PK-β.

ketone nanofibrous membrane was successfully prepared using electrospinning process from the solution. The characterization of polyketone nanofibrous membrane was investigated using various techniques.

2. Experimental

2.1. Materials

Poly (ethylene ketone) (PK, intrinsic viscosity (IV) ~2.3) was supported by Hyosung Corporation (Republic of Korea). The intrinsic viscosity was measured by Ubbelohde viscometer at room temperature. The solvent used was hexafluoroisopropanol (HFIP). The polymer solution for electrospinning was prepared by using the mixed solvents of trifluoroacetic acid (TFA, pK_a ~0.3) and dichloromethane (MC). In case of mixed solvents, the composition of these TFA/MC mixtures was expressed as the mass fraction of TFA (ϕ_{TFA}). All chemicals were used without further purification.

2.2. Electrospinning

All solutions prepared were poured in a 5-mL plastic syringe attached to a capillary tip of about 0.6 mm in inner diameter. The copper wire connected to an anode was inserted into the solution, and a cathode was attached to a grounded rotating metallic collector wrapped with Al-foil. The tip to collector distance (TCD) was 15 cm and the applied voltage was 10 kV. The electric field was produced by a high-voltage power supply (HAR-100*12, Matsusada. Co., Japan) capable of generating voltages up to 100 kV.

2.3. Characterization

Solution properties, such as viscosity and surface tension, were measured with a Rheometer (DV-I, Brookfield. Co., USA) and surface tension meter (CBVP-Z, Kyowa Interface Science Co., Ltd, Japan), respectively. The morphology of electrospun fibers was observed with scanning electron microscopy (SEM, VE-8800, Keyence Co., Japan). The crystal structure of solvent cast PK film and electrospun PK nanofibers were evaluated by WAXD (X-ray Diffractometer, Rigaku Co., Japan) operating at 40 kV and 150 mA using Cu kα radiation. Scan were recorded over a 2θ range of 5–50°. Differential scanning calorimetry (DSC, Q100, TA Instruments, USA) curves were recorded under N_2 gas at a heating speed of 20 °C/min from 25 to 300 °C. All samples were dried under vacuum overnight before measurement. To monitor the conformation of the polymer chains, Raman spectroscopy were employed. The Raman spectra were recorded with a Raman spectrometer (Hololab 5000, Kaiser Optical Systems Inc., USA), and argon laser at 532 nm, with a Kaiser holographic edge filter. Typically 50 mW of laser light was used at the sample with a ×50 long distance microscope objective. Integration times were around 40s, and the spectral resolution was 1.2 cm^{-1}. In addition, Fourier Transform infrared spectroscopy (FT-IR, Thermo Nicolet Avatar 370, Thermo Fisher Scientific Inc., USA) was acquired, and the spectra were recorded from 600 to 4000 cm^{-1} at a resolution of 4 cm^{-1}.

3. Results and discussion

In the electrospinning process, solution properties determine the limited boundaries for the formation of electrospun fibers due to variations in the viscosity and surface tension [11]. PK is one of the polyolefin is in general difficult to electro-spin ~ and poor electrical conductivity [12]. Therefore, in this study, the solution concentration and mixture ratio of solvents were investigated to find an optimum spinning condition of the PK solution on electrospinning. Fig. 2 shows SEM images of PK fibers electrospun from the solution with various concentrations. As seen in SEM images, the average diameter of electrospun PK fibers increased as increasing the solution concentration. The average diameter of PK fibers electrospun from 6 wt% solution was the smallest (about 300 nm), and the diameter distribution of electrospun PK fibers was narrower. However, the spinnability was not good, presumably due to the lower viscosity (see Table 1).

As shown in Table 1, dramatic increase in viscosity of PK solution (TFA mass fraction, $\phi_{TFA} = 0.4$) was observed as increasing the solution concentration while the surface tension slightly increased. The spinnability of the PK fibers electrospun from the 12 wt% solution was the most stable. The fiber diameter was found to be about 800 nm and its distribution was narrower. When the solution concentration was further increased to ca. 14 wt%, it wasn't formed

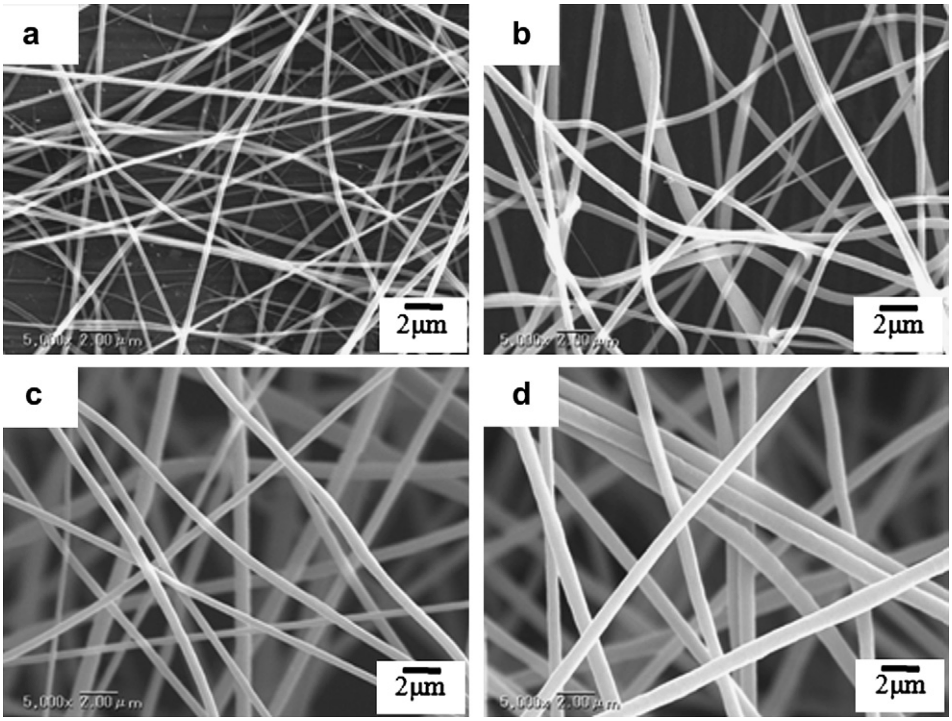

Fig. 2. SEM images of PK nanofibers electrospun from the solutions at different concentrations ($\phi_{TFA} = 0.4$); (a) 6 wt%, (b) 8 wt%, (c) 10 wt%, and (d) 12 wt%. The deposition time for each sample was about 5 min.

nano-scale fiber, and the resultant PK fibers exhibited ribbon-like morphologies. As a result, it was concluded that the optimum solution concentration for PK electrospinning was ca.12 wt%.

In this study, TFA in the mixed solvents of TFA and MC was used as a good solvent for PK polymer. It would appear that the PK polymer solution (~ 12 wt%) dissolved in 100% TFA ($\phi_{TFA} = 1.0$) gave a good electrical conductivity, but too high viscosity and thus results in a poor electrospinnability. That is, because TFA is a strong acid, it was therefore estimated that the conductivity of PK solution increased as increasing the ϕ_{TFA}, then resulted in lower fiber diameter and good spinnability. In contrast, when ϕ_{TFA} further increased, the viscosity of PK solution drastically increased and the average fiber diameter increased despite higher conductivity of PK solution at higher ϕ_{TFA} (Fig. 3).

In addition, MC was used as a co-solvent for decreasing the viscosity of PK solution. To study the effect of the mixed solvents on solution properties of PK polymer, the viscosity and surface tension of the PK solutions dissolved in various ϕ_{TFA} were investigated, respectively. The results are shown in Fig. 3. As ϕ_{TFA} increases, the viscosity increases sharply while the surface tension decreases slightly. Interestingly, average fiber diameter of PK fibers initially decreased dramatically, then goes through a minimum around $\phi_{TFA} = 0.4$–0.5, and finally increased gradually. Fig. 4 shows SEM images of PK fibrous membrane electrospun from PK solutions at various ϕ_{TFA}. In case of $\phi_{TFA} = 0.4$, average fiber diameter was about 800 nm, which was a little bigger than that of $\phi_{TFA} = 0.5$. Moreover, the amount of fiber spinning was larger and spinnability was more stable. By the analysis of SEM observation and solution properties, it was found that the optimum ϕ_{TFA} was about 0.4.

In the past, Chatani et al. [4,5], Lommerts et al. [6], and Klop et al. [7] demonstrated X-ray diffraction patterns for PK polymers. In this study, WAXD patterns of both electrospun PK fibers and as-cast PK films were measured, and the results were shown in Fig. 5. Solvent cast PK film clearly showed typical crystalline peaks at $2\theta = 21.75°$, $17.38°$, $24.65°$, $25.97°$, $31.47°$, $37.87°$, $39.38°$, and $41.84°$, corresponding to the primary (110) reflection, and the (101), (111), (200), (210), (103), (212), and (301) reflections at room temperature, respectively. These indicate that solvent cast PK films show completely the α-form, while electrospun PK fibers exhibit only the β-form, indicative of three reflections such as (110), (201), and (210) reflections at $2\theta = 21.66°$, $25.44°$, and $29.19°$, respectively. These distinctive differences in crystalline structures can be attributed to

Table 1
Viscosity and surface tension of PK solutions in terms of the different polymer concentrations ($\phi_{TFA} = 0.4$). The temperature was at about 25° C.

Concentration [wt%]	Viscosity [cP]	Surface tension [mN/m]
6	90	20.9
8	234	22.2
10	541.4	23.2
12	943.3	23.9
14	1725	24.7

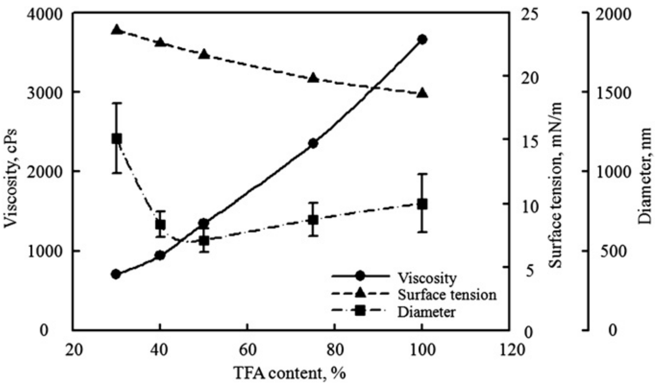

Fig. 3. Viscosity and surface tension of PK solutions dissolved in various ϕ_{TFA}, and average fiber diameter of PK fiber electrospun from the corresponding PK solutions. The concentrationof all PK solutions was 12 wt%.

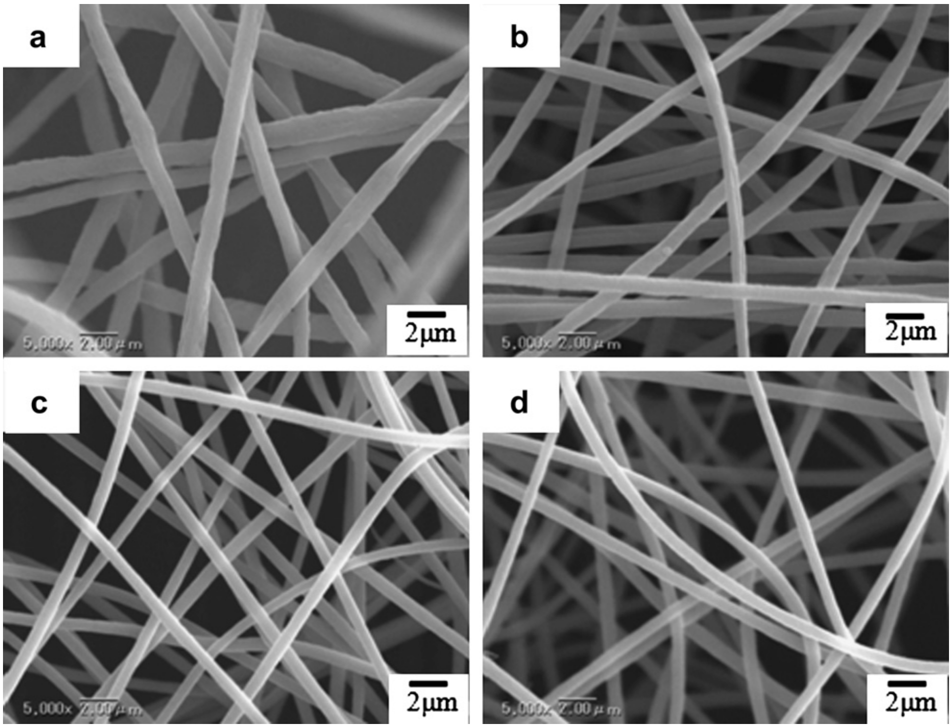

Fig. 4. SEM images of PK nanofibers electrospun from the 12 wt% solutions dissolved in various ϕ_{TFA}; (a) $\phi_{\mathrm{TFA}} = 0.3$, (b) $\phi_{\mathrm{TFA}} = 0.4$, (c) $\phi_{\mathrm{TFA}} = 0.75$, and (d) $\phi_{\mathrm{TFA}} = 1.0$. The deposition time for each sample was about 5 min.

the kinetics of the crystallization process (fast crystallization) during electrospinning process.

Fig. 6 shows DSC curves (1st scan) of both electrospun PK fiber and solvent cast PK film. In case of solvent cast PK film, the endothermic peak of melting point (at 252 °C) slightly shifted to higher temperature compared to electrospun PK fiber. The heat of fusion (ΔH_m) of solvent cast PK film at this peak was 142 J/g, while the electrospun PK fiber was 136 J/g. As mentioned previously, the stability of α-form is higher than β-form, due to the higher phase density and strong intermolecular interactions. In addition, solvent cast PK film showed a small endothermic peak at 107 °C, which was assigned to α-β phase transition [7], while a small endothermic peak around 110 °C wasn't observed for the electrospun PK fiber, suggesting that electrospun PK fiber was completely β-form.

Raman and FT-IR are well known to be sensitive methods to determine molecular and chain conformation. As mentioned previously, crystalline structures of α-form and β-form are orthorhombic with all-trans chain conformations, but there is a difference between the modes of chain packing. The main difference between α and β forms is that the adjacent chains in the α-form lie on the same plane, while the planes in the β-form are twisted. In the α-form, carbonyl groups belonging to neighboring chains are aligned on the plane, so each oxygen atom are close to the carbonylic carbon of the next chain. This arrangement could be

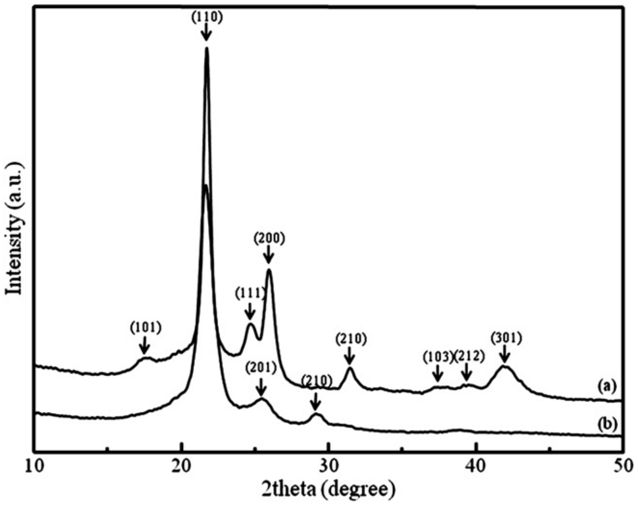

Fig. 5. WAXD patterns of (a) solvent cast PK film and (b) electrospun PK fiber. The concentration of all PK solutions was 12 wt% ($\phi_{\mathrm{TFA}} = 0.4$).

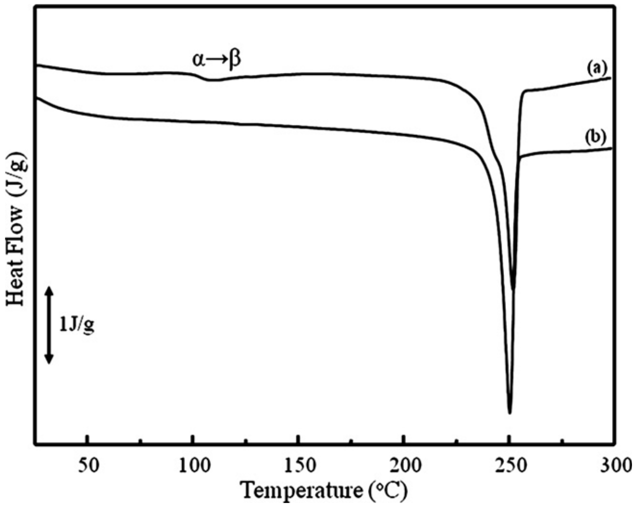

Fig. 6. DSC curves (1st scan) of (a) solvent cast PK film and (b) electrospun PK fiber. The concentration of all PK solutions was 12 wt% ($\phi_{\mathrm{TFA}} = 0.4$).

therefore compatible with the formation of intermolecular dipole-dipole bonds [6]. Furthermore, the PK-α structure is denser than the β one because the inter-atomic distances are shorter. As a result, intermolecular hydrogen bonds between C═O and CH_2 groups inside α structure are plausible [13].

All bands corresponding to α and β form of PK in the Raman spectra have been well assigned previously [3], and referred them in this study. Fig. 7 shows the Raman spectra of electrospun PK fiber and solvent cast PK film over the ranges from 1000 to 1800 cm^{-1}. Fig. 7 shows two sharp peaks around 1100 cm^{-1} tentatively attributed to C–C stretching (ν) motions, a sharp band at 1260 cm^{-1} which could be assigned to–CH_2– twisting (γ_t), and a group of bands 1340-1480 cm^{-1} assigned to -CH_2- bending (σ). Furthermore, the intense band around 1710 cm^{-1} is attributed to C═O stretching (ν). Specifically, a group of bands 1340–1480 cm^{-1} shows distinctive differences between samples and the insect shows the enlarged view. According to Lagaron et al. [3], the band at 1440 cm^{-1} is assigned to one component of the splitting arising from α-form crystal, while the band at 1430 cm^{-1} is assigned to it arising from β-form crystal.

As seen in Fig. 7, it was therefore found that solvent cast PK film is assigned to α-form, while electrospun PK fiber corresponds to β-form. Moreover, the band at 1412 cm^{-1} in solvent cast PK film, which is shifted to higher wavenumber compared to electrospun PK fiber (at 1418 cm^{-1}), is assigned to the other component of the splitting for both polymorphs (α- and β-form crystals). Compared to solvent cast PK film, relative intensity in splitting band at 1440 cm^{-1} observed for electrospun PK fiber was dramatically diminished, which could be arisen from decreasing in interchain interaction associated with the cell expansion [14], suggesting that electrospun PK fiber has a dominant β-form, while solvent cast PK film clearly showed two splitting bands at both 1412 and 1440 cm^{-1} indicating a dominant α-form.

Fig. 8 shows FT-IR spectra of electrospun PK fiber and solvent cast PK film, respectively. In case of electrospun PK fiber, the relative intensity of the CH_2 scissoring at 1408 cm^{-1} was much smaller than that of the CH_2 wagging at 1331 cm^{-1}, while in the solvent cast PK film the intensity of these peaks was almost same. In addition, CH_2 twisting at 1261 cm^{-1} would appear that these differences are caused by the difference of phase density. As mentioned previously [7], the packing of polymer chains in the PK-α structure is denser than that in the PK-β structure, resulting in the scissoring motion being stronger than the wagging motion in the α-form.

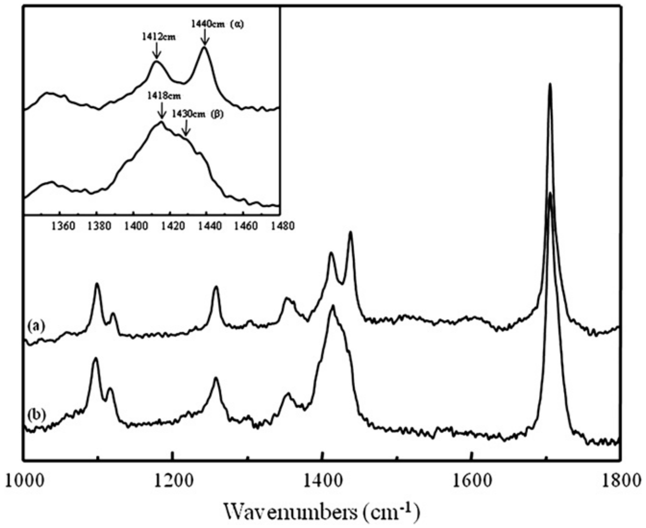

Fig. 7. Raman spectra of (a) solvent cast PK film and (b) electrospun PK fiber in the range 1000-1800 cm^{-1}. The concentration of all PK solutions was 12 wt% ($\phi_{TFA} = 0.4$).

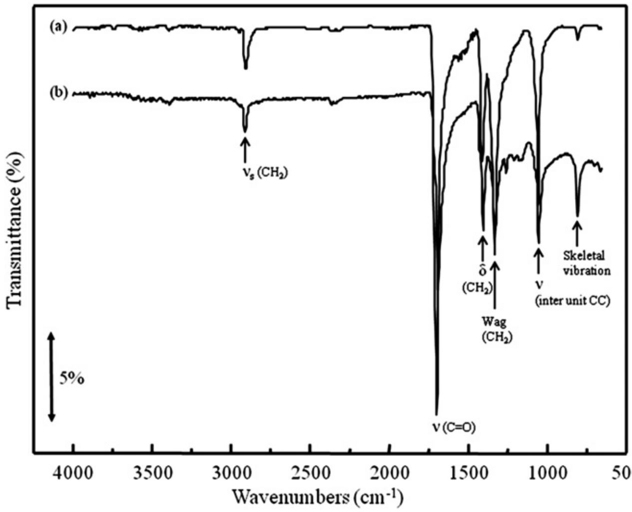

Fig. 8. FT-IR spectra of (a) electrospun PK fiber and (b) solvent cast PK film. The concentration of all PK solutions was 12 wt% ($\phi_{TFA} = 0.4$).

4. Conclusion

In this study, PK nanofibers have been successfully electrospun in the form of a fibrous membrane from the solutions which were dissolved in various ϕ_{TFA}. As demonstrated by SEM, the morphology and diameter of the resultant fibers were dependent on the solution properties, such as concentration, and mixture ratio of solvents. The optimized concentration and mixture ratio of solvents for electrospinning were found to be 12 wt% and $\phi_{TFA} = 0.4$, respectively. The crystal structure of electrospun PK nanofiber and solvent cast PK film were characterized by WAXD. The result indicated that the crystal structure of PK cast film corresponded to α-form, while the crystal structure of electrospun PK fibrous membrane was assigned to β-form. This was attributed to the kinetics of the crystallization process (fast crystallization) during electrospinning process, and the crystallinity of electrospun PK fibrous membrane was lower than that of cast film. Furthermore, the attribution of these crystalline structure were also confirmed by Raman and FT-IR spectroscopy.

Acknowledgements

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