

Thermal analysis and spectroscopic studies of electrospun nano-scale composite fibers

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Abstract The aim of this article is to develop nano-scale composite fibers from wood pulp, modified wood pulp, and polyethylene oxide (PEO). Composite fibers were developed in the diameter range of 339–612 nm. Alignment process of the composite fibers was done by electrostatic interactions between two collector disks. DSC results demonstrated a lower melting temperature of composite fibers than PEO powder. The development of crystalline structure in the composite fibers and acetylated wood pulp was poor. Thermogravimetric analysis revealed that the thermal stability of composite fibers were relatively lower than PEO powder. Fourier transform infrared spectroscopy (FTIR) showed significant differences between modified and unmodified wood pulp in the region of 960–1746 cm^{-1} . The peak intensity of acetylated wood pulp was appeared at 1746 cm^{-1} because of acetyl groups. The composite fibers demonstrated the characteristic peak of PEO since less wood pulp was incorporated in the composite system.

Keywords Softwood pulp · Polyethylene oxide · Nano-composite fibers · Electrospinning · Thermal properties · Fourier transform infrared spectroscopy (FTIR)

Introduction

Electrospinning is a novel process to generate submicron polymeric fibers in the average diameter range of 100 nm–5 μm through the action of electrostatic forces. Research interest in electrospinning area has been growing recently due to its simplicity in manufacturing nano-scale fibers [1–3].

The basic principle of the electrospinning process is based upon electrostatic force that works on the polymer solution. The polymer solution is placed in a capillary and a high voltage power source is connected to produce an electric field [1, 4]. A jet is ejected from the surface of a charged polymer solution when the applied electric field strength overcomes the surface tension. The ejected jet extends in a straight line and then undergoes a vigorous whipping motion caused by the electrohydrodynamic instability wherein the solvent evaporates, leaving behind a charged polymer fiber [5, 6]. Due to drawing, the charge density on the solution surface increased and in turn the repulsive forces are allowed to split the jet [1]. The fibers are deposited on the target ground randomly like a non-woven mat with high surface area to mass ratio (10–1000 $\text{m}^2 \text{g}^{-1}$). Due to high surface area and small diameter, they have potential application in various fields including filtration, biomedical applications, protective clothing, optical, nano-composite materials, tissue scaffolds, wound dressings and drug delivery systems, nano-sensors, liquid crystal device, and electromagnetic shielding [1, 2, 5, 7–10]. Natural fibers have drawn much attention for scientists because they are cheap, abundant, biodegradable, renewable, strong, and light in mass [11–23]. Apart from natural fibers, synthetic and biopolymers were used to develop composite fibers by an electrospinning process. Recently, Francis et al. [24] developed membrane from hydroxypropylcellulose and PEO where

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water was used as solvent. Nirmala et al. [25] generated polyamide-6/chitosan composite nanofibers using electrospinning process. Charernsriwilaiwat et al. [26] prepared nanofibers from blended chitosanhydroxybenzotriazole/polyvinyl alcohol. The developed biodegradable nanofibers may be suitable for drug delivery or tissue engineering applications. Composite fibers were also prepared from nylon 6 and polyhydroxyamide by Wang et al. [27].

However, no research has been done on wood pulp–polymer-based green nano-composite fibers obtained by electrospinning process where wood pulp has been used. The developed composite fibers have potential applications in the field of air filtration and biomedical.

The aim of this study is to generate wood pulp–polymer-based-nano-composite fibers. In this study, alignment procedure of the nano-composite fibers was investigated. Chemical modification of wood pulp was thoroughly studied in the composite fibers. Differential scanning calorimetry (DSC) studies were performed to examine the crystalline nature of the developed fibers. The thermal behavior of composite fibers was studied by thermogravimetric analysis (TG). Fourier transform infrared spectroscopy (FTIR) was employed to characterize the functional group present in the wood pulp, modified wood pulp, and composite fibers.

Experimental

Materials

Softwood pulp was supplied by Domtar (Canada). Polyethylene oxide (PEO) was obtained from Fisher Scientific (UK) with a mass average molecular mass (M_w) of 900000 g mol⁻¹. Ethanol and HPLC grade water (Sigma Aldrich) were used.

Methods

Acetylation process

Softwood pulp (WP) was dried in an oven at 105 °C for 12 h and cooled down at room temperature before use. The fibers were placed in a 250 mL round bottom flask equipped with a condenser and anhydrous CaCl₂ guard tube. The flask was then placed in a water bath at 90 °C. A mixture of acetic anhydride and pyridine (1:1, v/v) was then added to the flask and heated for 2 h. Next, 50 mL distilled water was added to the flask to convert unreacted acetic anhydride into acetic acid. The mixture was allowed to cool down to room temperature. The acetylated product was removed from the flask and washed with distilled

water until pH 7. Finally, the acetylated wood pulp (Ac-WP) was dried in an oven at 105 °C for overnight.

Solution preparation

Softwood pulp was crushed using a Wiley mill with a mesh size of 80. PEO (95 mass%) was dissolved in a mixture of water and ethanol 60/40 (v/v), and then representative wood pulp (5 mass%) was added to it and stirred continuously at 20 °C for 24 h. Finally, the solution was stored at room temperature. All formulations for composite fibers are shown in Table 1.

Mechanism of electrospinning

A high voltage DC power supply (Glassman MK35P2.0-22, New Jersey, USA) was employed to produce potential voltage of 18 kV. One electrode of a high voltage was applied to a vertically (25-gauge) blunt-ended metal needle. The blended polymer solution was fed from a syringe to a needle via Teflon[®] tubing, and the flow rate was controlled using a digital controller (positive displacement syringe pump, Harvard Apparatus M22 PHD 2000) with a flow rate of 0.20 mL h⁻¹. Green composite fibers were collected by means of an earthed collection system, which made of a copper collector plate (15 × 15 cm).

The electrospinning process is shown in Fig. 1. PEO and wood pulp solution was placed in a 5 mL syringe.

Table 1 Formulations of composite fibers including solvent (water/ethanol, v/v), solution concentration (Conc. mass%), and molecular mass of PEO (M_w)

Blends	(v/v)	Conc. mass/%	M_w /g mol ⁻¹
5/95 mass% (wood pulp/PEO)	60/40	7	900000
5/95 mass% (acetylated wood pulp/PEO)	60/40	7	900000

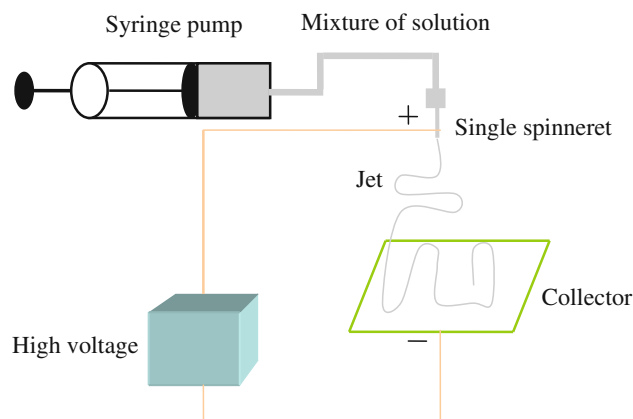


Fig. 1 Schematic diagram of electrospinning setup

The diameter of the syringe needle was 0.4 mm. The syringe then clamped to a ring stand that was 11 cm above a ground metal screen. The pump pressure was adjusted, and a voltage was applied to the needle to start the jet. The spinning process was continued for 2–5 min to collect sufficient sample.

Measurements of fibers diameter

The diameters of electrospun fibers were measured by Image-J software. The scale was set on the SEM image of the fibers. Then a straight line was drawn over the cross section of the fibers. Finally, the measurement option was selected to determine the fibers diameter.

Scanning electron microscopy (SEM)

SEM (Hitachi S-530, UK) was used to investigate the surface topography of the electrospun fibers. In order to obtain the required electrical conductivity, all samples were sputtered with gold using Gold-sputter machine. The acceleration voltage was maintained at 10 kV.

Thermal studies

Melting temperature of polymer and composite fibers were investigated using a TA instrument Q1000 DSC attached with a cooling system under a nitrogen atmosphere from 33 to 140 °C with a heating rate of 10 °C min⁻¹. TG was conducted using TA instrument Q500 with a heating rate of 10 °C min⁻¹. The samples were heated from 40 to 500 °C

to study the thermal stability of composite fibers and polymer. All tests were carried out in nitrogen atmosphere using a flowing rate of 60 mL min⁻¹.

FTIR

Bruker FTIR (Hyperion 2000) was used in ATR (Attenuated total reflectance) mode using 32 scans to identify the functional groups in wood pulp, modified wood pulp, and composite fibers. Background spectra were taken in terms of every sample before getting sample spectra. Each spectrum was documented in the range of 4000–400 cm⁻¹ with a resolution of 4 cm⁻¹.

Results and discussion

Alignment process of composite fibers

The electrospinning process was used to generate micro to nano level composite fibers. The resulting fibers were directly deposited on a target ground randomly. The fibers were deposited in a curved parallel path between two copper disks in seconds. Corresponding aligned nanofibers were appeared between the two disks following 15 s of spinning. As shown in Fig. 2, the aligned composite fibers are vertical to the axis of the collection disks and encompass a consistent diameter distribution. Alignment and stretching of the fibers are derived by electrostatic interactions between the positive electrode on the spinneret and negative grounded disks. Eventually, the green composite

Fig. 2 Alignment setup. **a** Before electrospinning spinning. **b** Aligned composite fibers on target disks after electrospinning (95 mass% PEO/5 mass% WP) at concentration of 7 mass%, and **c** SEM image of aligned nano-composite fibers

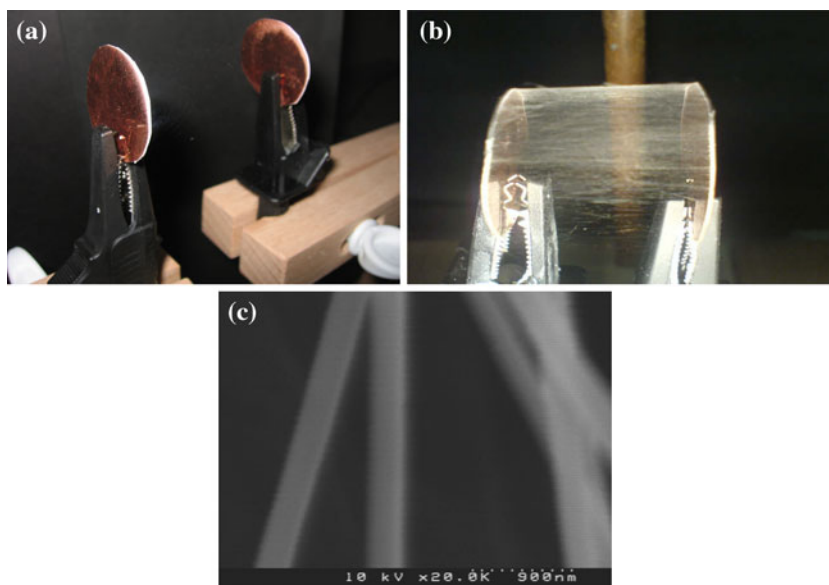
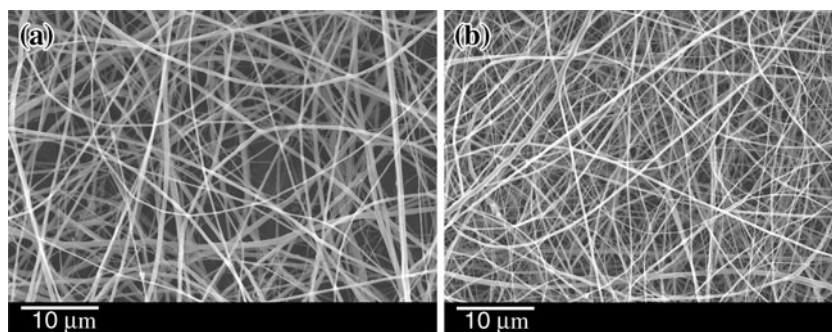


Fig. 3 SEM images of electrospun composite fibers (5% WP/95% PEO) with the same mass concentration. **a** Composite fibers (WP/PEO) and **b** Composite fibers (PEO/Ac. WP)



fibers move toward the disk collector, one end of the fiber is joined to one of the disks, and the other end of the fiber is drawn toward the opposite disk. In other words, the bending shape of the flying composite fibers is transformed into a linear shape between the grounded circular disks. Once the charged fibers have traveled into the gap between the disks, the fibers will induce opposite charges on the surface of the disks. These reverse charges will create a center of attraction of the fibers to the grounded disks, leading to the alignment of the fibers in the gap between the targeted circular disks. The composite fibers suspended across the gap remain highly charged after deposition, thus the electrostatic repulsion between the deposited and the upcoming fibers can further enhance the alignment mechanism.

Fibers morphology and diameter

The surface of both composite fibers appeared to be almost similar. As seen in Fig. 3b, it produced lower fiber diameters due to addition of Ac. WP as compared to the result of Fig. 3a. The Ac. WP improved fiber–matrix adhesion which could reduce the fibers diameter due to better drawing. Drawing takes place when the fiber exits from the spinneret and subsequently wood pulp is oriented along the length axis of fibers and polymer (PEO) is oriented at the molecular level. Thinner fibers are better as they have better mechanical properties. The diameter of aligned composite fibers was found to be between 339 and 612 nm which is shown in Fig. 2c.

Thermal properties

Figure 4 shows the DSC curves of the composite fibers and neat PEO powder. It is interesting to note that composite fibers demonstrate the melting temperature at 63 °C, whereas the neat PEO powder exhibits the melting temperature at 69 °C. These results indicated that the overall crystallinity of composite fibers was significantly lower than that of neat PEO powder. The crystallinity of composite fibers is significantly impaired by the introduction of

Ac. WP. Moreover, it is possible that the network of intermolecular bond is either deformed or ruptured during the electrospinning process which results in lower melting point of the electrospun composite fibers.

The thermal degradation patterns of composite fiber and neat PEO powder are illustrated in Fig. 5. Both samples demonstrated endothermic reactions. The degradation temperature onsets at 320 °C for neat PEO powder whereas the decomposition temperature for composite fibers was noticed above 200 °C.

A significant thermal behavior in the composite fibers and PEO powder was observed between 200 and 364 °C. These results are possibly due to the addition of Ac. WP in polymer because the Ac. WP will be decomposed between the aforementioned temperatures. In other words, the electrospun fibers became less crystalline due to addition of Ac. WP. As a result, the composite fibers were less thermally stable than PEO powder. The thermal stability of both samples was entirely identical after 364 °C.

FTIR spectroscopic analysis

FTIR analysis was used to investigate the functional groups in the samples and the interactions between polymer and

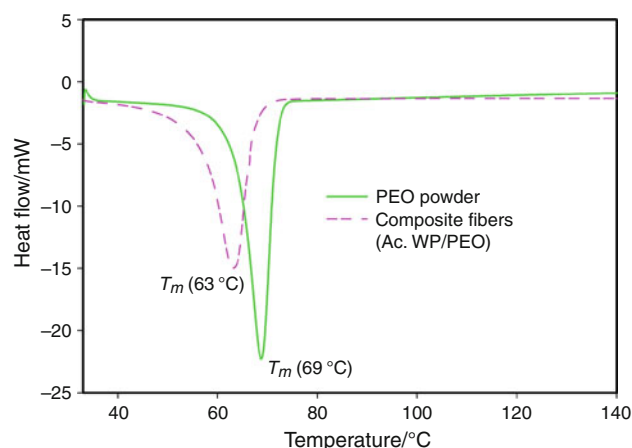


Fig. 4 DSC curves of the composite fibers (5% Ac. WP/95% PEO) and neat PEO powder

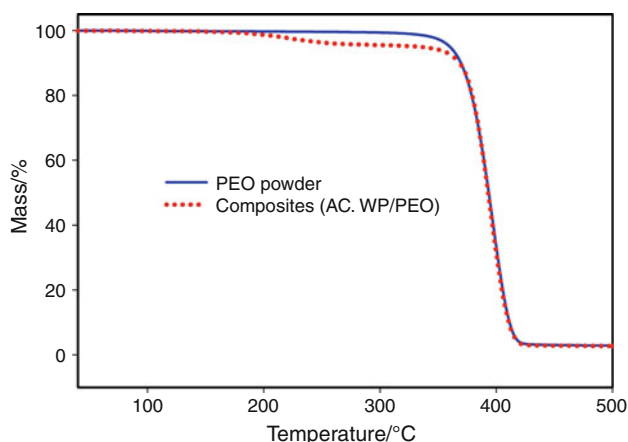


Fig. 5 TG results of electrospun composite fibers and neat PEO powder

wood pulp. The proof of acetylation was verified by FTIR spectra. FTIR results revealed the presence of acetyl groups in the wood fibers. Figure 6 shows the FTIR spectra of unmodified wood pulp and Ac. WP. The characteristic peaks observed in the samples are summarized in Table 2.

Due to acetylation of wood pulp, the FTIR spectra was increased in the three major bands, i.e., the carbonyl (C=O) stretching region (1746 cm^{-1}), the carbon–hydrogen (C–H), or C–CH₃ stretching region (1366 cm^{-1}), and the carbon–hydrogen or C–O band stretching (1233 cm^{-1}). The broad peak at 3326 cm^{-1} is the characteristic band for O–H stretching, and the peak at 2893 cm^{-1} is the characteristic band for C–H stretching. The absorption peak at 3326 cm^{-1} may be associated with hydroxyl groups. The shoulder near the OH stretching vibrations may be due to CH stretching vibrations. Upon acetylation of wood pulp, the OH peak did not change significantly. The peak intensity of modified wood pulp was appeared at 1746 cm^{-1} due to grafting of acetyl groups. The main

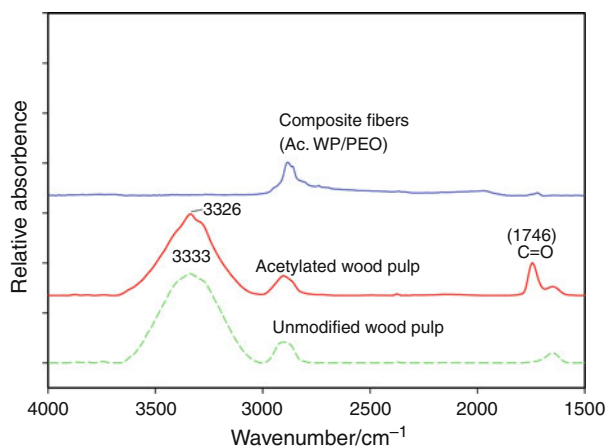


Fig. 6 FTIR spectra of composite fibers, treated, and untreated wood pulp

Table 2 FTIR results of acetylated wood pulp with respect to untreated wood pulp

Wavenumber of untreated wood pulp/ cm^{-1}	Wavenumber of acetylated wood pulp/ cm^{-1}	Bond type
3333	3326	Strong band of –OH group
2893	2893	C–H stretching
–	1746	C=O (Carbon double bond)
1646	1646	C=O
1366, weak peak	1366, strong peak	C–H bending
1032	1032	C–C stretching

differences between modified and unmodified wood pulp samples can be seen in the region $960\text{--}1746\text{ cm}^{-1}$. A considerable amount of absorbency was viewed between $1000\text{--}1500\text{ cm}^{-1}$ bands in modified wood pulp owing to the escalating of O–H stretching and C–O stretching which also indicates ester formation (i.e., introduction of acetyl groups). A broad peak was observed at 3333 cm^{-1} in the wood pulp. The results are in well agreement with the results obtained by other researchers [28–31]. No –OH peak was appeared in the composite fibers (Ac. WP/PEO). Only 5% of Ac. WP was added in the composite system this is why no characteristic peak was appeared due to modified wood pulp. Due to less incorporation of Ac. WP, the prominent peak of modified wood was merged in the composite fibers. This is why, the carbonyl peak in composites were disappeared compared to Ac. WP. As a result, the composite fibers were provided only characteristic of PEO due to the major component. Since PEO is the major component in the composite fibers, therefore the absorption peak at 2886 and 1459 cm^{-1} which corresponds to the molecular stretching of the CH₂ group and CH₂ bending, respectively, whereas peaks at 1100 and 960 cm^{-1} were due to the stretching of the C–O–C group [32]. The acetylation of wood pulp may increase the hydrophobicity of fibers because hydroxyls group of fibers are replaced by acetyl groups. It is expected that Ac. WP would assist to improve fiber–polymer adhesion which would, in turn, increase the mechanical properties of the composite fibers (as compared to WP/PEO).

Conclusions

The developed nano-composite fibers were aligned through the electrostatic interactions between two collector disks. The composite fibers (Ac. WP/PEO) revealed lower fiber diameters due to addition of Ac. WP compared to unmodified wood pulp. The surface of both composite

fibers appeared identical. The poor development of crystalline structure in the composite fibers and Ac. WP were observed by DSC studies. TG results showed that the composite fibers were relatively less thermally stable than PEO powder. The hydrophobicity of Ac. WP was observed by FTIR studies. The peak intensity of Ac. WP was appeared at 1746 cm^{-1} due to grafting of acetyl groups. Remarkable differences between modified and unmodified wood pulp samples can be seen in the region $960\text{--}1746\text{ cm}^{-1}$. Since the wood pulp became hydrophobic, the compatibility between fibers and PEO will be increased. Characteristic peak of PEO was observed in the composite fibers because the wood pulp was the minor component there. The Ac. WP could increase fiber–matrix adhesion compared to unmodified wood pulp in composite fibers. Therefore, the mechanical properties of composite fibers could increase.

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