Thermoregulating and hydrophobic nanofibers

Nuray Kizildag* and Nuray Ucar

Istanbul Technical University, Department of Textile Engineering, Gumussuyu, Istanbul, Turkey

E-mail: kizildagn@itu.edu.tr

Abstract. Phase changing materials are widely investigated in many different aspects due to the increasing interest in energy storage applications, thermal insulation and thermal comfort. Electrospinning is a simple technique for producing ultrafine (sub-micron) fibers from a wide variety of polymers. With PCMs, it is generally used as a method to obtain shape stabilized PCMs. In this study, microencapsulated phase change materials (MPCM) are incorporated into nanofiber structure. Morphology, chemical structure, thermal properties and water absorbency of the composite nanofibers are investigated. Uniform nanofibers displaying both thermoregulatory properties and hydrophobicity were obtained.

1. Introduction

Phase changing materials (PCMs), which include inorganic materials, organic materials and their blends, have the capability to absorb and release latent heat during a phase transition process over a narrow temperature range [1-2]. The storage or release of latent heat (thermal regulation) is based on the transition of a material (PCM) between phases. When a PCM is heated to its melting point, it absorbs heat as it changes from solid to liquid state and a temporary cooling effect is obtained. Conversely, when a PCM goes from liquid phase to a solid phase, it releases the latent heat to the environment and a temporary heating effect is obtained [3]. Paraffin waxes [4], polyethylene glycols [5], fatty acids and fatty acid derivatives [6] are types of PCMs which are very often used in research studies. Phase changing materials are widely investigated in many different aspects due to the increasing interest in energy storage applications, thermal insulation and thermal comfort [1-2]. Due to their high heat storage capacities, PCMs are applied to textiles in a variety of processes to improve thermal comfort of the products [7].

Electrospinning is a simple technique for producing ultrafine (sub-micron) fibers from a wide variety of polymers. It uses electrostatic forces to draw nanofibers. It provides a straightforward and cost-effective method to produce fibers with diameters ranging from nanometers to submicrons. The electrospinning setup consists of a high voltage power supply, a pump, and a grounded collector. The polymer solution, which is filled into a syringe, is fed by a pump through a needle. A high voltage power supply is used to form an electrostatic field between the droplet of polymer solution at the tip of a needle and the collector. As the voltage applied is increased, a force is built on the pendant drop and the drop is elongated forming a conical shape known as Taylor cone. When the voltage is further increased, the electrostatic force overcomes the surface tension of the solution droplet and a continuous jet forms, which is attracted by the grounded collector. During its fly from the tip of the needle to the collector, the jet undergoes instabilities (bending and whipping motions) during which the solvent evaporates and

the jet diameter reduces. The jet rapidly thins and dries. Finally the nanofibers are collected on the collector in nanoweb form with random nanofiber orientation [8]. It is a widely used technique to obtain shape stabilized PCMs with the elimination of the need for the encapsulation process [1].

Chen et al. [1,9,10] conducted a series of studies on the incorporation of PCMs into nanofiber structure. They successfully produced ultrafine fibers of lauric acid/polyethylene terephthalate (LA/PET, 1:1, w/w) which showed smooth surfaces with acceptable tensile strength. The latent heat of fusion of the fibers was about 70.76 J/g. The composite nanofibers were suggested as suitable for the applications such as solar energy storage and thermo-regulating textiles [1]. They also produced composite nanofibers using stearyl stearate as additive. Increase was observed in average nanofiber diameter with addition of the additives. The morphology of the composite fibers had no obvious variation after thermal treatments, which confirmed that the developed material showed form stable phase changing property. DSC showed that the enthalpy of the composite fibers increased with the increase in additive content. The thermal performances of the fibers could be maintained after 100 heating–cooling thermal cycles, which indicated that the composite fibers had good thermal stability and reliability [9]. In another study, they produced composite PET nanofibers using a series of fatty acids such as lauric acid (LA), myristic acid (MA), palmitic acid (PA), and stearic acid (SA). The average diameter and morphology of the nanofibers was found to be affected by the amount of the fatty acid. While the latent heat of the composite fibers increased with the increase in the additive amount, the phase transition temperature of the fibers didn't varied compared to that of the fatty acid. The latent heat and phase transition temperature of composite fibers were dependent on the type of the fatty acids [10]. Producing composite PET nanofibers with a series of different fatty acid eutectics, Cai et al. [11] also reported that the latent heat and phase transition temperature of composite fibers were dependent on the type of the fatty acids and suggested that the composite nanofibers could be used in the field of building energy conservation. Ke et al. [12] electrospun composite PET nanofibers using a series of fatty acid eutectics for thermal energy storage. The composite nanofibers, which possessed smooth and cylindrical morphological structure with diameters of about 100-300 nm, showed different enthalpy depending on the content and the type of binary fatty acid eutectics. Chen et al. [5] produced cellulose acetate/ polyethylene glycol nanofibers, in which PEG acted as PCM. The heat capacities of the composite fibers with 10–70 wt% PEG content varied between 3.8 kJ/kg and 120.2 kJ/kg in DSC analyses. Cai et al. [6] electrospun composite nanofibers of polyethylene terephthalate (PET)/lauric acid (LA)/silica nanoparticles and investigated morphology, thermal storage, thermal stability, and combustion properties of the composite nanofibers. T. McCann et al. [4] used melt coaxial electrospinning for producing nanofibers consisting of n-octadecane and n-eicosane cores as phase change materials.

In this study, microencapsulated phase change materials (MPCM) are incorporated into nanofiber structure. The composite nanofibers are characterized in terms of morphology, chemical structure, thermal properties and water repellency.

2. Experimental

2.1. Materials
Polyacrylonitrile (PAN) (Sigma Aldrich, 181315, average Mw: 150.000g/mol), microencapsulated phase change materials (MPCM) (Microtek Laboratories, Inc., MPCM28D, Tm = 28□C), dimethylformamide (DMF) were used as received.

2.2. Solution Preparation
The required amount of MPCM (25 and 50 wt%) was added to the required amount of DMF and homogenized with ultrasonic tip for 10 minutes and with ultrasonic bath for 45 min. Then PAN was added to this dispersion and dissolved by stirring with a magnetic stirrer at 40°C, 300 rpm for 3 hours. Composite electrospinning solutions containing 25 and 50 wt% MPCM were prepared. The

concentration of PAN was 7 wt%. PAN/DMF solution was prepared for the production of the reference nanofibers.

2.3. Electrospinning

The nanofibers were produced using a horizontal electrospinning setup, the schematic of which is shown in figure 1. It contained a high voltage power supply (Matsusada, 0-50 kV), a precisely-controlled syringe pump (SINO MDT, SN-50C6), and a grounded rotating collector covered by aluminum foil and nonwoven. The nanofibers were collected on nonwoven to be able to easily peel off the nanowebs produced. Electrospinning solutions were filled into a syringe of 10 mL and fed through a needle (Ultradent Products Inc.) with a outer diameter of 1.25 mm. The flow rate of the electrospinning solution was set as 1 mL/h. The distance between the tip of the needle and the collector was 10 cm. The applied voltage was changed in order to obtain stable electrospinning.
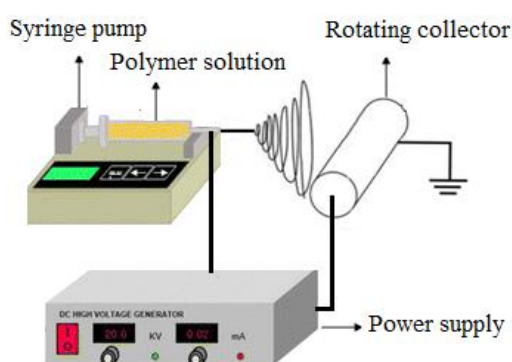
**Figure 1.** Schematic of the electrospinning setup.

2.4. Characterization

Composite nanofibers with MPCM were characterized in terms of morphology, chemical structure, thermal properties and hydrophobicity. The morphology of the nanofibers were analysed using scanning electron microscope (SEM, Jeol Quanta 200 FESEM). SEM images were taken at an accelerating voltage of 20 kV. Before SEM analysis, the samples were coated with gold using a sputter coater. The fiber diameters were measured using Image J. The average nanofiber diameters and the standard deviations were based 50 measurements per sample. Average nanofiber diameters were expressed as the mean±standard deviation. A Fourier transform infrared (FTIR) spectrophotometer from Perkin Elmer (Spectrum Two) was used to record absorption spectra of composite nanofibers in a range from 4000 to 400 cm^{-1} with a resolution of 4 cm^{-1}. 32 scans were taken for each experiment. The spectrum of MPCM was normalized to the largest peak observed, namely the –CH$_3$ stretchings observed at 2915 cm^{-1} and the spectrum of 100% PAN and composite nanofibers were normalized to the characteristic C≡N stretching band of PAN which appears around 2242 cm^{-1} to be able to compare them. Thermal properties were evaluated using differential scanning calorimetry (DSC, PerkinElmer DSC4000) in a temperature range from 0ºC to 60ºC, at a heating rate of 5ºC/min in nitrogen environment. Hydrophobicity of the composite nanofibers were evaluated by water contact angle measurements.

3. Results and Discussion

3.1. Morphology

The reference and composite nanowebs were white in color. The SEM images taken with 25kX magnification and the average nanofiber diameters are presented in figure 2. The fibers were uniform in structure even at the MPCM content of 50 wt%. They were free of any beads. The average nanofiber diameter increased as a result of MPCM addition, likely due to the increased viscosity of the electrospinning solutions [13].
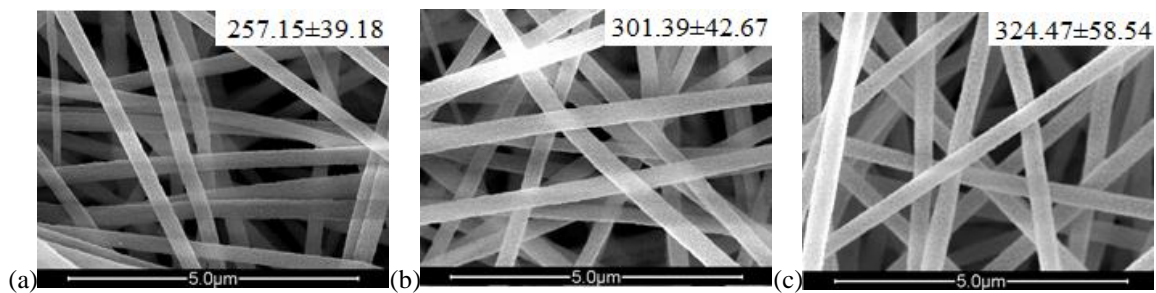
Figure 2. SEM images of reference and composite nanofibers: (a)100%PAN; (b)PAN/25%MPCM; (c)PAN/50%MPCM.

3.2. Fourier Transform Infrared Spectroscopy (FTIR)

FTIR spectroscopy analysis was performed to confirm the presence of MPCM in the composite fiber structure, and compare the spectral differences between the composite nanowebs and the reference 100% PAN nanoweb. The FTIR spectra obtained from MPCMs, 100% PAN nanoweb and composite nanowebs with MPCMs are shown in figure 3.
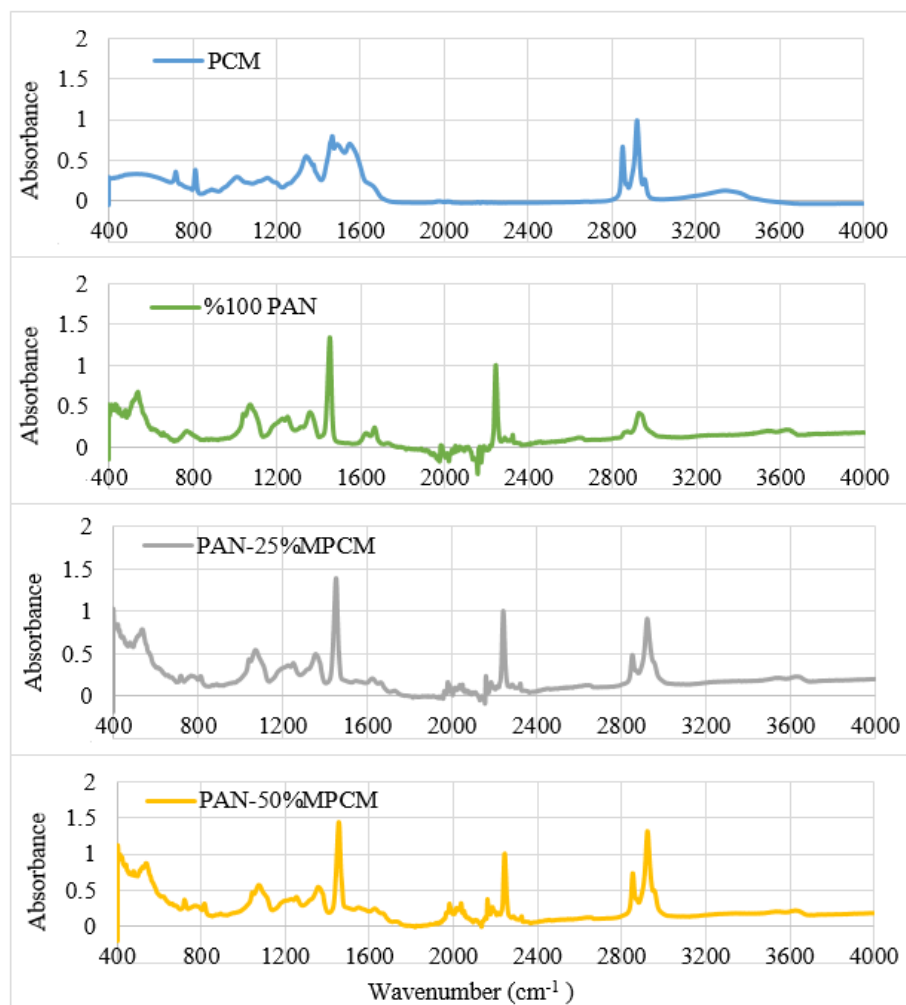

Figure 3. FTIR spectra of (a)MPCMs and (b)100%PAN; (c)PAN-25%PCM; (d)PAN-50%PCM nanowebs.

In the spectra of MPCMs (figure 3(a)), the bands located at 2915 cm^{-1} and 2849 cm^{-1} represented the stretching vibrations of –CH$_3$ and –CH$_2$ groups. The peak at 1470 cm^{-1} represented the –CH$_2$ bending vibration [14]. In the spectra of PAN nanofibers (figure 3(b)), the peaks are as follows: 3626 cm^{-1} (OH stretching), 2922 and 2870 cm^{-1} (C–H asymmetric and symmetric stretchings in CH, CH$_2$, and CH$_3$ groups), 2242 cm^{-1} (C≡N stretching), 1622 cm^{-1} (C=C stretching), 1452 cm^{-1} (CH$_3$ bending and CH$_2$ scissor vibration), 1356 cm^{-1} (CH$_3$ symmetric bending vibration in C-CH$_3$), and 1252 cm^{-1} (C–N stretching), 1070-1040 cm^{-1} (C=N bending), and 778 cm^{-1} (-C-CN-stretching) [15-19]. The FTIR spectra of composite nanowebs (figure 3(c) and 3(d)) showed characteristic peaks of MPCMs in addition to the characteristic peaks of PAN, which showed the successful incorporation of MPCMs into the PAN nanofiber structure. With the increase in the MPCM content, the intensities of the peaks related with MPCM (located between 1400 and 1600 cm^{-1}, 2915 and 2849 cm^{-1}) increased.

3.3. Differential Scanning Calorimetry Analysis (DSC)

DSC thermograms of 100% PAN nanoweb and composite samples are presented in figure 4. While 100% PAN nanoweb displayed no phase transitions between 0 and 60°C, composite samples showed phase transitions due to the presence of MPCMs in the nanofiber structure. The corresponding thermal properties of composite nanowebs are summarized in Table 1. Melting took place between the onset temperature of about 23°C and 28°C and crystallization occurred between 24°C and 13°C. Both melting and crystallization enthalpies increased as the MPCM content in the nanofibers increased. The melting enthalpy increased from 11.42 to 24.71 J/g as the MPCM content increased from 25% to 50%.
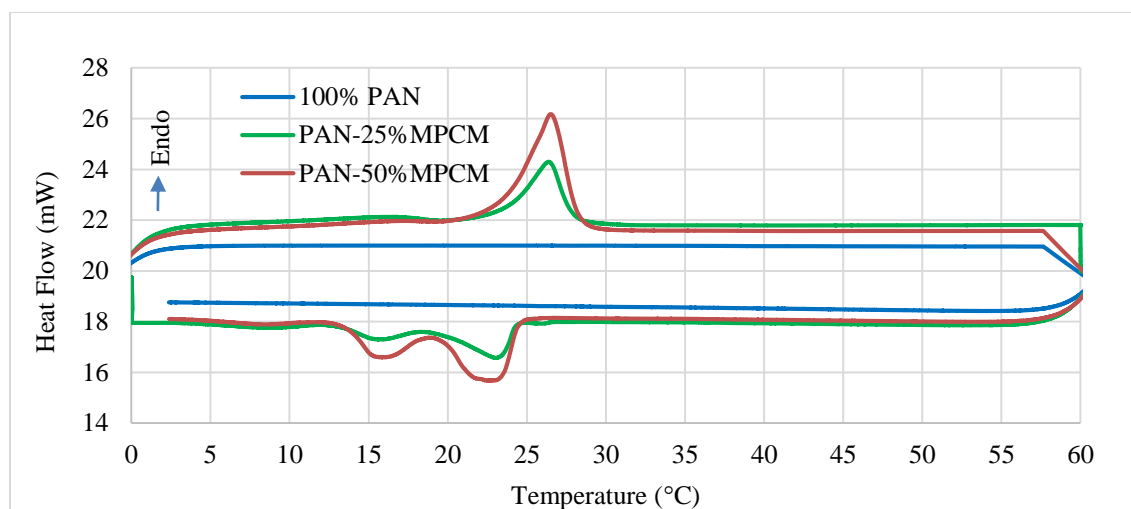
Figure 4. DSC thermograms of 100%PAN and composite nanowebs containing MPCMs.

**Table 1.** Thermal properties of composite nanowebs containing MPCMs.

Sample	Onset of melting (°C)	End of melting (°C)	Latent heat of melting (ΔH) (J/g)	Onset of crystallization (°C)	End of crystallization (°C)	Latent heat of crystallization (ΔH) (J/g)
PAN-25%PCM	23.53	27.81	11.42	24.26	13.38	11.53
PAN-50%PCM	23.85	28.13	24.71	24.45	13.58	26.45

3.4. Hydrophobicity

Water contact angle measurements were performed in order to be able to evaluate the hydrophobicity of the composite nanowebs. The basis of the contact angle measurement is to instill a drop of a liquid onto the surface and then record the drop using a camera. The video image is evaluated in order to

determine the contact angle after a certain time. The larger the contact angle, the more hydrophobic the surface is considered. A surface is called "hydrophobic" if the water drop contact angle is higher than 90° and "hydrophilic" if the contact angle is smaller than 30°.

The images of drops taken by the camera are presented in figure 5. The composite nanofibers gained hydrophobic properties with the addition of MPCMs. While the water droplet was absorbed by 100% PAN nanoweb in less than a second, the water contact angle was measured as 107° for PAN nanoweb containing 25% MPCM.
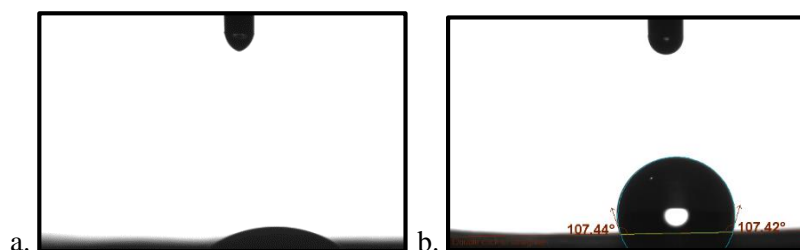
Figure 5. Contact angles obtained for a.100% PAN and b.PAN-25%MPCM.

4. Conclusions

This study showed the possibility of producing thermoregulating and hydrophobic nanofibers with the addition of phase change materials into the structure of nanofibers. Uniform nanofibers were produced which displayed thermoregulating and hydrophobic properties. The composite nanofibers with phase changing nanoparticles are suggested for use in active wear, undergarments, bedding, packaging materials, and insulation materials, etc.

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