THE EFFECT OF SEPIOLITE CLAY ON THE PROPERTIES OF POLYACRYLONITRILE COMPOSITE NANOFIBERS

Nergis DEMİREL GÜLTEKİN[1], Nuray UÇAR[1]

[1]*İstanbul Technical University, Department of Textile Engineering, İstanbul, Turkey,*
demirelgultekin@itu.edu.tr

Abstract

In this study, polyacrylonitrile (PAN) nanofibers containing sepiolite needle-like nanoparticles were produced with electrospinning method. PAN polymer solution concentration was fixed at 12 wt% and sepiolite nanoparticle concentration was varied. Electrospinning solutions were prepared with sepiolite nanoparticles concentrations of 0, 1, 3 and 10 % of the mass of the PAN polymer. The effect of the sepiolite nanoparticle concentration on thermal, morphological and mechanical properties of nanofibers were studied.

Keywords: nanofiber, PAN, sepiolite, clay, composite

1. INTRODUCTION

Polymer composites are widely used in applications such as transportation, construction, electronics and consumer products. In order to modify and improve mechanical, thermal and chemical properties, the methods such as blending polymers with each other and the introduction of inorganic fillers into polymer matrix are used. Among these methods, inorganic nanofiller-organic composite nanofibers due to their nanometer size, high specific surface area, easy dispersion in polymer matrix and the high thermal stability are used extensively. The properties of particle-reinforced polymer composites are strongly influenced by the particle content, particle shape and size, surface characteristics and degree of dispersion. Recently, there has been a growing interest in the development of polymer-clay nanocomposites [1-3].

Sepiolite clay is a naturally occurring layered fibrous hydrated magnesium silicate with a large specific surface area (more than 200 m^2/g) and characterized by a needle-like morphology and it has good mechanical strength and thermal stability [4-6]. Sepiolite as a kind of porous mineral material has many nanometer level micropores and mesopores, which can play an active role as an additive for composite materials in thermal insulation [7]. Electrospinning is a simple method for the production of micro and nanocomposite fibers [8, 9]. Electrospun nanofibers are used in protective clothing, nanocomposites [10], membranes, thin films, filtration, etc [11].

The choice of the proper insulation materials type and form depends on the type of application as well as the desired materials physical, thermal and other properties. Some typical properties of insulating materials are mechanical, physical, and thermal properties such as low thermal conductivity, ease of handling and machining, durability and light weight, and safe/healthy use [12].

The objective of the present work was to study the influence of the addition of sepiolite nanoparticles upon thermal conductivity and heat retention capability of the electrospun PAN nanofibers. In this study, polyacrylonitrile (PAN) nanofibers containing sepiolite needle-like nanoparticles were produced with electrospinning method. PAN polymer solution concentration was fixed at 12 wt% and sepiolite nanoparticle concentration was varied. Electrospinning solutions were prepared with sepiolite nanoparticles concentrations of 0, 1, 3 and 10 % of the mass of the PAN polymer. The effect of the sepiolite nanoparticle concentration on thermal, morphological and mechanical properties of nanofibers were studied.

2. EXPERIMENTAL

2.1 Sample Preparation

The PAN was dissolved in DMF (Merck, used as solvent) at 60°C and stirred at 300 rpm for 2 h and the concentration was fixed at 12 wt%. Then, PAN solutions with commercial sepiolite nanoparticles were prepared. First, to obtain well dispersed nanoparticles in solution, probe sonication technique for 10 minutes, then bath sonication technique for 45 minutes were applied. The PAN polymer was, then, added to the solution, stirred at 60°C for 2 h. The concentrations of nanoparticles in electrospinning solution were 0, 1, 3 and 10% with reference to the PAN polymer mass, respectively. For electrospinning, 10 ml of each kind of PAN/Sepiolite solution was loaded in a syringe and injected through a stainless steel capillary metal needle at an injection rate of 1 ml/h using an infusion pump. The positive electrode of the high voltage power supply was connected to the needle tip. The grounded electrode was connected to a metallic collector wrapped with aluminum foil. The tip to collector distance and applied voltage was fixed at 10 cm and 15 kV, respectively.

2.2 Characterization

The morphology and structure of PAN and PAN/Sepiolite nanofibers were investigated by SEM Carl Zeiss EVO MA10. The SEM tests were applied at 5 kV voltage. The mechanical behavior was determined by a tensile testing machine under a crosshead speed 3 mm/min at room temperature. At least seven specimens were tested for tensile behavior and the average values were reported. Three parameters were determined from each stress–strain curves: Elastic modulus, tensile strength, and elongation at break. The examine the heat preservation ability of the PAN composite nanofibers, Testo® 880 thermal camera and TestoIRSoft® software program were used. The set heat source was 77W halogen light. The heat source distance was 25 cm. The thermal images were taken at 5 minute intervals and the total illumination time was 40 min. The each average value was obtained from the results of 5 analysis. The heat conduction apparatus was used to measure the thermal conductivity of the PAN composite nanofibers according to the TS 4512 Standard.

3. RESULTS AND DISCUSSION

3.1 Morphological Analyses

Surface morphology of the nanofibers were examined with SEM images and presented in Figure 1. The figure indicates that the PAN/Sepiolite composite nanofibers were successfully spun by electrospinning at 15 kV. SEM images of nanofibers show smooth, defect-free structure. Also the nanofibers obtained had cylindrical morphology and non-beaded structure. From the morphological images of nanofibers, we can say that the tip-to-collector distance was adequate for evaporation of the solvent. Fig. 1(a) presents the SEM image of the 100 wt% PAN nanofibers showing that the nanofibers were continuous and oriented randomly. Also, it is obvious from the figure that the morphology of the composite nanofibers were very smooth and defect-free. The average diameters of neat PAN and PAN/Sepiolite nanofibers containing 3 wt% sepiolite nanoparticles were 475±146 nm and 345±58 nm, respectively. The diameter of neat PAN nanofiber is higher than that of PAN/Sepiolite nanofibers containing 3 wt% sepiolite nanoparticles.

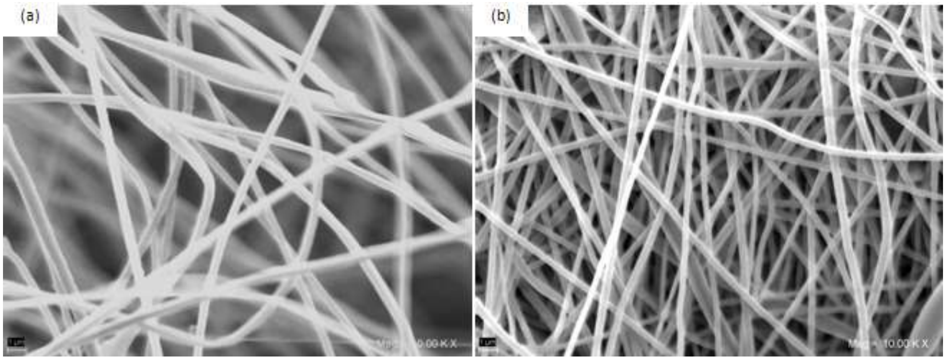

Fig. 1 SEM micrographs of (a) 100% PAN nanofibers, (b) PAN nanofibers containing 3 wt% sepiolite nanoparticles.

3.2 Mechanical Properties

Tensile strength, elongation at break and elastic modulus of PAN and PAN/Sepiolite composite nanofibers are given in Table 1 as a function of sepiolite nanoparticle concentration. As it can be seen from this table, PAN nanofiber containing 1 wt% sepiolite nanoparticles has the highest mechanical properties. The addition of small amount of sepiolite nanoparticles (1 wt%) improves the mechanical properties of composite nanofibers when compared to the neat PAN nanofibers. But, at the 3 and 10 wt% sepiolite nanoparticle concentration, the mechanical properties of PAN composite nanofibers worsen when compared to the neat PAN nanofibers. This may be due to an increase of agglomeration tendency of nanoparticles with an increase of the amount of nanoparticles.

Table 1. Mechanical properties of PAN and PAN/Sepiolite composite nanofibers

	Tensile Strength (MPa)	CV%	Elongation at Break (%)	CV%	E- Modulus (MPa)	CV%
100 wt% PAN	44.95±10.92	24.30	44.53±5.38	12.08	52.27±15.05	28.79
1 wt% Sep	55.31±19.12	34.57	42.69±13.18	30.87	66.89±21.03	31.44
3 wt% Sep	41.19±12.69	30.81	35.40±11.88	33.58	21.70±4.69	21.64
10 wt% Sep	21.91±4.71	21.48	28.63±5.05	17.66	20.04±5.91	29.48

3.3 Thermal Conductivity

Thermal conductivity of polymers is an important property. Polymers have typically intrinsic thermal conductivity much lower than those for metals and ceramics, therefore polymers are good thermal insulators compared to most of metals and ceramics. Generally, polymers have low thermal conductivities, ranging from 0.1 to 0.6 W/mK. In the literature, the thermal conductivity of PAN polymer is given as 0.26 W/mK [13]. The type of clay and moisture content affect the thermal conductivity of clay which has generally high water absorbancy. In the literature, for conventional clay, the thermal conductivity is 0.25 W/mK for no moisture and about 2.0 W/mK at 50% moisture [14]. Thus it can be said that its thermal conductivity is higher than PAN polymer if it contains any moisture.

The thermal conductivity of 100 wt% PAN nanofiber was measured as 0.304 W/mK. Table 2 presents the thermal conductivity values of PAN/Sepiolite composite nanofibers as a function of sepiolite nanoparticle concentration. It can be seen from the table that the thermal conductivity of neat PAN nanofiber has the highest value of all. With the addition of sepiolite nanoparticles to the nanofiber structure, thermal conductivity values show a decreasing trend. At the highest nanoparticle concentration, thermal conductivity starts to increase; however, it is still lower than the neat PAN nanofiber. The thermal conductivity of a material depends on the conductivity of the phases within its microstructure. Among them, the pore (voids) phase plays an important role. Bigger pores (voids) within the structure act like barriers to heat conduction. The decrease in thermal conductivity at 3 wt% sepiolite nanoparticle concentration can be due to probable voids within the composite structure. The increase in thermal conductivity at 10 wt% sepiolite nanoparticle concentration which is still lower than the neat PAN nanofiber can be due to higher thermal conductivity of clay which may contain any moisture due to solvents Therefore, the thermal conductivity of PAN composite nanofibers containing 10 wt% sepiolite nanoparticles increases with the increase of nanoparticle concentration, because moisture within the sepiolite nanoparticles become more effective.

Table 2. Heat Preservation and Thermal Conductivity Values of PAN/Sepiolite Composite Nanofibers

		Sepiolite Concentration (wt %)			
		0	1	3	10
Heat Preservation Value (°C)	Before	28.3	27	27.4	27.6
	After	32.1	31.6	30.8	30.8
	Temp.Difference (°C)	3.8	4.6	3.4	3.2
Thermal Conductivity (W/mK)		0.304	0.242	0.233	0.284

3.4. Heat Preservation Analyses

Atoms or molecules inside of a material have a certain vibration frequency produced by electromagnetic waves which keeps them constantly moving. When this frequency is in the same as that of molecules in another material, the material will absorb the energy from the electromagnetic waves and further transform it into heat . Energy from the sun light emits in an electromagnetic form to the fabric and the fabric absorbs the energy, then emits to human body also in the electromagnetic form. Then it emits to human body also in the electromagnetic style. After the human body absorbs the energy, the water molecules generate resonance and promote the blood circulation, in order to achieve the effect of the heat preservation of human body. Human body can also release energy and fabric absorbs the energy. Energy can also be radiated by the human body, the fabric with function of far infrared ray absorbs the energy and then releases it back to the human body in the form of far infrared ray, so that it can repeatedly reach the effect of the heat preservation of human body [15].

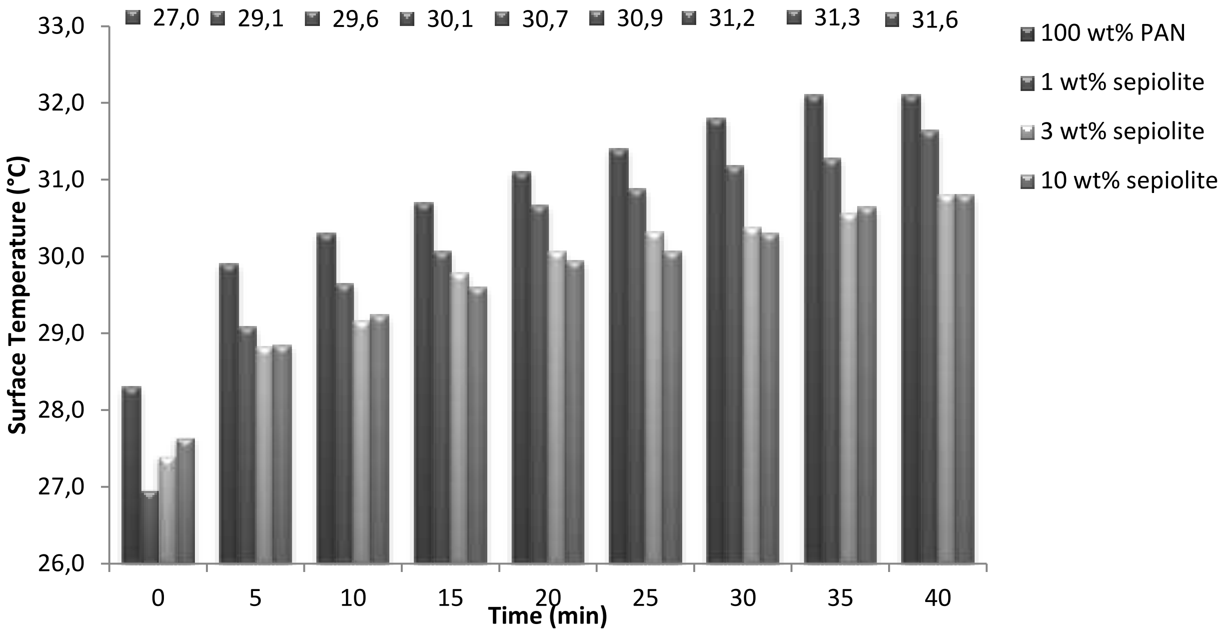

Fig. 2 The heat preservation test result of PAN/Sepiolite nanofibers by halogen light emission method.

As can be seen in Fig. 2, the surface temperatures of the specimens before exposure to the halogen lamp for 40 minutes range from 27 °C to 28.3 °C. After halogen lamp exposure for 40 minutes, the surface temperature of the PAN nanofibers containing 3 and 10 wt% sepiolite nanoparticles are the lowest (30.8 °C). After the nanofibers are exposed to halogen light for 40 minutes, the surface temperature of the neat PAN nanofiber only increases 3.8 °C, while that of PAN nanofiber containing 1wt% sepiolite nanoparticles increases 4.6 °C. PAN nanofibers containing 3 and 10 wt% sepiolite nanoparticles have the lowest temperature difference, 3.4 and 3.2 °C, respectively. From the results, we can say that after PAN nanofiber with 1 wt% sepiolite nanoparticles absorbs energy, it releases far infrared rays and generates a thermal effect. Thus, when compared to the neat PAN nanofiber, the addition of 1 wt% sepiolite nanoparticles to the polymer structure, the composite nanofiber absorbs more heat and generates a thermal effect. As can be seen from Table 2, although PAN composite nanofiber containing 10wt% sepiolite nanoparticles has higher amount of nanoparticle, its heat preservation is the least one, this may be explained by its higher thermal conductivity.

4. CONCLUSIONS

In this study, PAN nanofibers containing different amount of sepiolite nanoparticles were successfully produced without the occurrence of bead defects using electrospinning process. The highest mechanical properties and the heat preservation value were obtained from the PAN nanofiber containing 1 wt% sepiolite nanoparticles. PAN composite nanofiber containing 1 wt% sepiolite nanoparticles has approximately 25% improvement in breaking strength together with 0.8˚C higher temperature increase comparing to neat PAN nanofiber. The heat preservation effect was decreased with the increase of the concentration of sepiolite nanoparticles (3 and 10 wt%) when compared to the neat PAN nanofibers.

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