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Effects of Blend Ratio and Heat Treatment on the Properties of the Electrospun Poly(ethylene terephthlate) Nonwovens

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Abstract: Semicrystalline poly(ethylene terephthalate) (cPET)/amorphous poly(ethylene terephthalate) with isophthalic acid (aPET) blends with 100/0, 75/25, 50/50, 25/75, and 0/100 by weight ratios were dissolved in a mixture of trifluoroacetic acid (TFA)/methylene chloride (MC) (50/50, v/v) and electrospun via the electrospinning technique. Solution properties such as solution viscosity, surface tension and electric conductivity were determined. The solution viscosity slightly decreased as aPET content increased, while there was no difference in surface tension with respect to aPET composition. The characteristics of the electrospun cPET/aPET blend nonwovens were investigated in terms of their morphology, pore size and gas permeability. All these measurements were carried out before and after heat treatment for various blend weight ratios. The average diameter of the fibers decreased with increasing aPET composition due to the decrease in viscosity. Also, the morphology of the electrospun cPET/aPET blend nonwovens was changed by heat treatment. The pore size and pore size distribution varied greatly from a few nanometers to a few microns. The gas permeability after heat treatment was lower than that before heat treatment because of the change of the morphology.

Keywords: Electrospinning, Morphology, Pore size, Gas transport properties, Mechanical properties

Introduction

The electrospinning technique has attracted great attention in the past few years owing to its ability to produce fibers with sub-micron to nanoscale diameters from the polymer solution or melt [1,2]. Electrospinning also has the advantage of being simple, inexpensive and convenient. Doshi and Reneker [3] reported the effect of the solution properties including the viscosity, conductivity, and surface tension on the process of electrospinning. By appropriately varying one or more of the above parameters, fibers were successfully electrospun from water soluble polymers, biopolymer and liquid crystalline polymers. The electrospun fibers can have an unusually small diameter, a high surface area to volume ratio, and a high length to diameter ratio [4]. These characteristics are useful in a variety of applications, such as separation membranes, wound dressing materials, artificial blood vessels, reinforcements in nano-composites, nonwoven fabrics, and many others [5-11].

Poly(ethylene terephthalate) (PET) is one of versatile polymers with excellent thermal and chemical resistance and mechanical properties [12]. Although it has high melting and glass transition temperatures, its drawback lies in the brittleness of its final products [13], which make it necessary to modify its properties for it to be used in practical applications. One of the most common ways of varying the properties of polymeric materials is copolymerization. In the past, a series of random poly (buthylene isophthalate/terephthalate) copolymer prepared by the bulk polymerization were studied in terms of their solution behavior and thermal and mechanical properties [13,14]. Though a number of studies were published on the mechanical properties of various copolymers, until now no papers have appeared in the literature regarding the effects of the blend ratio and thermal treatment on the mechanical properties of the electrospun crystalline PET (cPET) with amorphous PET (aPET) nonwovens.

In this study, we report on the effect of aPET ratio and the heat treatment on the mechanical behaviors of the electrospun cPET/aPET blend nonwovens.

Experimental

cPET and aPET (copolymer containing 35 mol% of isophthalic acid) chips with intrinsic viscosity of 0.64 and 0.61, respectively, were obtained from Huvis of South Korea and used as such. Trifluoroacetic acid (TFA) and methylene chloride (MC) as a solvent for PET were purchased from Showa Chemical of Japan and used without further purification.

15 wt% polymer solutions containing cPET/aPET in the ratios of 100/0, 75/25, 50/50, 25/75 and 0/100 (w/w) were prepared in a mixture of TFA/MC (50//50, v/v) solvent system. Then, a 5 m*l* syringe tip with a diameter of 0.6 mm was filled with the polymer solution. To induce an electric force between tip and collector, a copper wire electrode was immersed into the polymer solution. And the negative electrode was attached to a metal collector covered by aluminium foil. The tip of the syringe was placed at a fixed distance (13 cm) form metal drum collector and the applied voltage was 15 kV. In order

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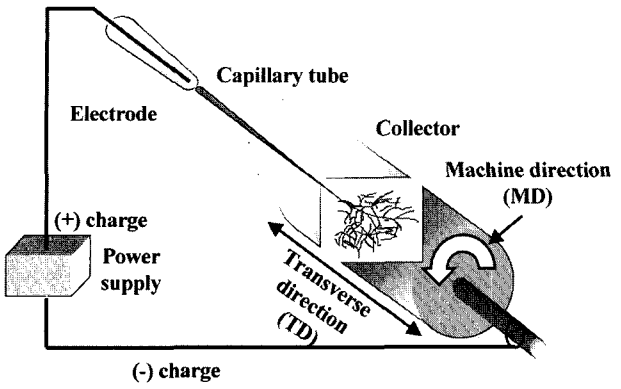

Figure 1. Electrospinning devices used in this study.

for the drops of the solution coming out of the syringe to be small, the tip of the syringe was clamped at an angle of 10 ° to the horizontal. The electrospinning devices used in this study are shown in Figure 1.

The surface tension and the viscosity of the polymer solution were measured at 20 °C by tensiometer (K10ST, Krüss Co., Germany) of the Wilhelmy plate type and DV III viscometer (Brookfield Co., USA), respectively. An electrical conductivity meter (G series, CM-40G, TOA Electronics Ltd., Japan) was used to check the conductivity of the polymer solutions at 25 °C.

Morphology was obtained using Scanning electron microscope (SEM) (GSM-5900, Jeol. Co., Japan). Average fiber diameters were obtained using Image-proplus image analyzer (Media Cybernetics Co. USA).

The pore size and porosity of the electrospun blend nonwovens were investigated by Autopore IV 9500 porosimeter (Micromeritics, Co., USA). The pore diameter was calculated by applying the Washburn equation and the cylindrical pore method.

The gas permeability was determined with a model GPA-2001 Gas Permeation Analyzer (B. S. Chem. Inc., South Korea).

The contact angle measurement was carried out by the sessile drop technique [15,16] and performed on the contact angle micrometer. A 1 μl drop of distilled water was fallen down on the samples. The contact angle, θ, was captured electronically and measured.

The mechanical behaviors were tested with a universal test machine (UTM) (AG-5000, Shimadzu, Japan) on the basis of ASTM D 638 with an extension rate of 10 mm/min at room temperature.

Results and Discussion

Solution Properties

The effect of aPET on the solution viscosity, surface tension and electrical conductivity of the cPET/aPET blend solutions dissolved in TFA/MC (50/50, v/v) is shown in Figure 2. From this observation, we found that the solution viscosity

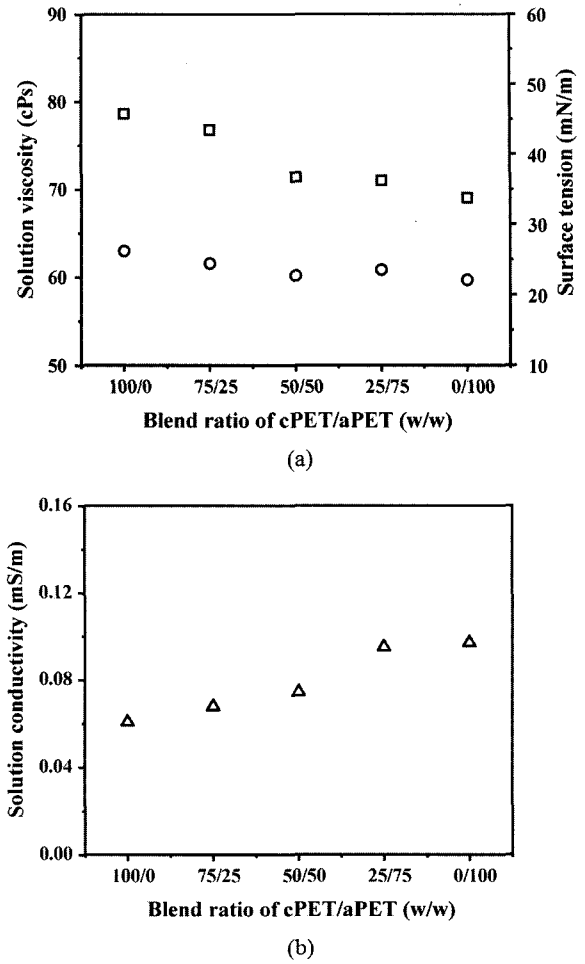

Figure 2. Polymer solution properties as a function of blend ratio: (a) solution viscosity (□), surface tension (○), and (b) solution conductivity (△).

of the cPET/aPET blend was decreased notably in the initial stages of blending when the proportion of aPET was low. Also, the surface tension of the polymer solutions with different cPET/aPET ratios did not vary greatly. The electrical conductivity of the various polymer solutions, which is presented in Figure 2(b), shows that the electrical conductivity of the polymer blend solutions increased as the aPET content increased.

Scanning Electron Microscopic (SEM) Studies

The surface morphology of the electrospun cPET/aPET blend nonwovens was studied by SEM. Figure 3 shows the appearance of the electrospun cPET/aPET blend nonwovens before and after heat treatment. At a blend ratio of 0/100, the nonwovens lost their shape after heat treatment. Nonwovens with other blend ratio kept their appearance. The fiber diameter of the electrospun cPET/aPET blend nonwovens decreased only slightly following the addition of aPET, however, an increased number of beads appeared in the

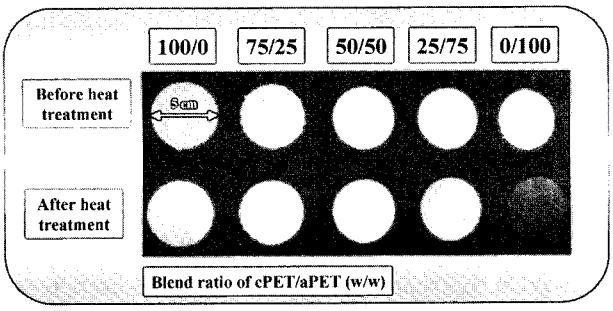

Figure 3. Photographs of the electrospun cPET/aPET blend nonwovens as a function of blend ratio before heat treatment and after heat treatment.

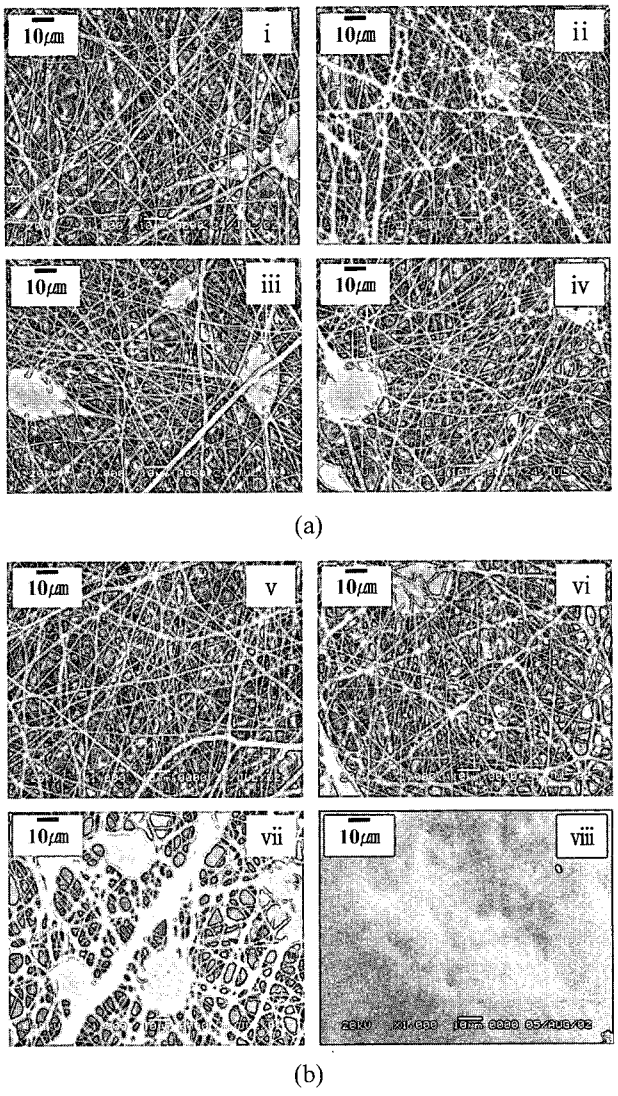

Figure 4. SEM images of the electrospun cPET/aPET blend nonwovens as a function of blend ratio before and after heat treatment: (a) before heat treatment ((i) 75/27, (ii) 50/50, (iii) 25/75, (iv) 0/100) and (b) after heat treatment ((iv) 0/100, (v) 75/25, (vi) 50/50, (vii) 25/75, and (viii) 0/100).

SEM images (Figure 4(a)). The presence of this increased number of beads is due to the low viscosity of the polymer solutions having a high aPET content. In order to observe the effect of heat treatment on the structure of the blend nonwovens, they were heated at 120 °C for 1 h in atmospheric conditions. From the SEM images of the electrospun cPET/aPET blend nonwovens after heat treatment, which are shown in Figure 4(b), we found that many small fibers were interwined with large fibers following the addition of aPET, which is less thermally stable than cPET. Also, the fibers were fused together at certain crossing points due to the heat treatment. Increasing aPET content of cPET/aPET blend caused the fibers within blend nonwovens to change into a membrane-like structure at 25/75 (Figure 4(b)). But, at blend ratio of 0/100, the fibers were not found. Therefore, it is clear that the surface morphology of the cPET/aPET blend could be changed into a membrane-like structure by thermal treatment. This change of morphology had an impact on the pore size and gas permeability of the blend nonwovens.

Transport Properties

A mercury porosimeter was used to determine the pore size distribution, total pore areas, and porosity. The functioning of mercury porosimeter is based on the capillary law governing liquid penetration into small pores. This law is expressed by the Washburn equation [17];

$$D = -4\alpha\cos\theta/P$$

where D is the pore diameter, P the applied pressure, α the surface tension, and θ the contact angle, all of which should be in consistent units. V, the volume of mercury penetration is measured directly as a function of the applied pressure. Thus, this value was used to investigate the pore size, total pore area, and porosity of the electrospun cPET/aPET blend

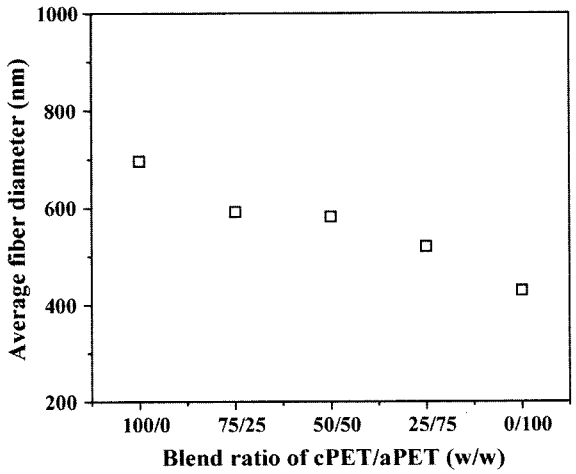

Figure 5. Average fiber diameter of the electrospun cPET/aPET blend nonwovens before heat treatment as a function of blend ratio.

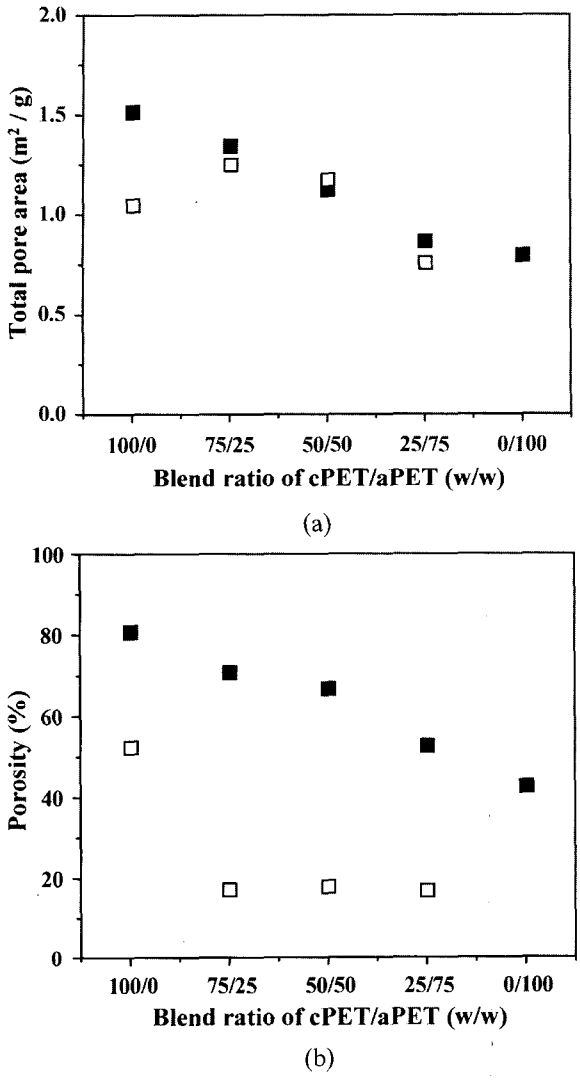

Figure 6. Total pore area and porosity of the electrospun cPET/aPET blend nonwovens: (a) total pore area, and (b) porosity ((■) before heat treatment, (□) after heat treatment).

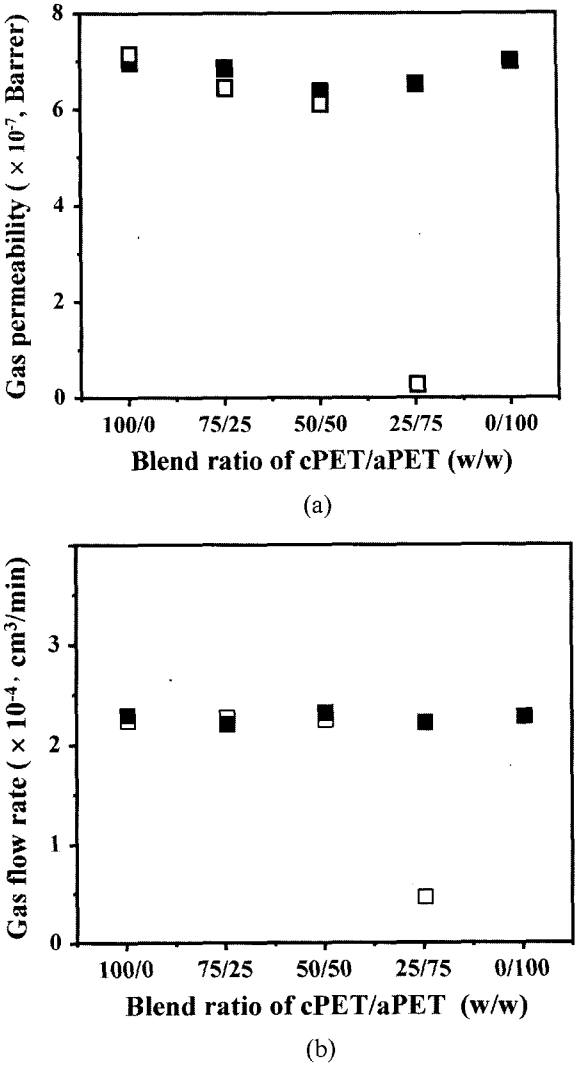

Figure 7. N_2 transport properties of the electrospun cPET/aPET blend nonwovens: (a) gas permeability, and (b) gas flow rate ((■) before heat treatment, (□) after heat treatment).

nonwovens. In the case of the electrospun cPET/aPET blend nonwovens, more the number of pores were found than that found in bulk film, because during electrospinning the fibers were deposited randomly on the collector surface. Figure 6 shows the variation of the total pore area as a function of the blend ratio. As the amount of aPET increased, the total pore area and porosity decreased slightly, because the finer fibers had a large surface area per unit volume [6]. These results corresponded to the data obtained for the average fiber diameter before heat treatment as shown in Figure 5. After heat treatment, the total pore areas and porosity of the electrospun cPET/aPET blend nonwovens decreased. This decrease is related to the change of surface morphology of the electrospun cPET/aPET blend nonwovens as shown in Figure 4.

To measure the gas transport efficiency of the electrospun cPET/aPET blend nonwovens, we performed an experiment by passing N_2 gas through the electrospun cPET/aPET blend nonwovens with different cPET/aPET ratios. Figure 7 shows the N_2 transport properties of the cPET/aPET blend nonwovens before and after heat treatment. From Figure 7, it was found that the gas permeability and the flow rate of the cPET/aPET blend nonwovens were almost similar compared to those before heat treatment. However, after heat treatment, neither the gas permeability nor the gas flow rate was changed until a blend ratio of 50/50 was attained. It is noted that at a blend ratio of 25/75, the gas permeability and gas flow rate drastically decreased. This result is correlated to the change in the pore structure of the cPET/aPET blend nonwovens resulting from the heat treatment. At a blend ratio of 0/100, the gas permeability and gas flow rate could not be measured after heat treatment due to the absence of fibers.

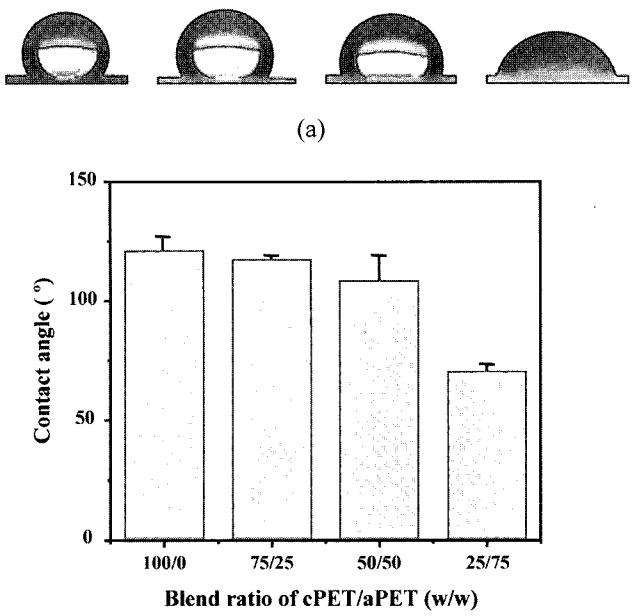

Figure 8. Contact angle of the electrospun cPET/aPET nonwovens as a function of blend ratio: (a) images of contact angle, and (b) average contact angle.

Contact Angle Measurement

Contact angle measurement is the simplest surface analysis technique to determine the hydrophilicity and hydrophobicity of polymer. Until now, the water contact angle of bulk PET, fabric, and modified PET fabric were reported [15,16]. In this study we investigated the contact angle of the electrospun cPET/aPET blend nonwovens with water before and after heat treatment. The contact angles between the water and the electrospun cPET/aPET blend nonwovens with the different blend ratio before heat treatment were found to be in the range of 120~130 ° (Figure not shown in the article). These values were higher than those of bulk or modified PET because the fiber diameters of the electrospun cPET/aPET blend nonwovens was thin and smooth. After heat treatment, however, the electrospun cPET/aPET blend nonwovens showed a decrease in contact angle as a function of the blend ratio and 30 minutes as shown in Figure 8. The decrease in the contact angle of electrospun cPET/aPET blend nonwovens after heat treatment is due to the fact that fiber diameters were increased considerably resulting into a membrane like structure. Their surface morphology was also affected by heat treatment.

Mechanical Properties

. We determined the effects of the blend ratio and heat treatment on the mechanical properties of the electrospun cPET/aPET blend nonwovens. The mechanical properties of the electrospun cPET/aPET blend nonwovens are measured in both the machine direction (MD) and the transverse direction (TD). From the results in Figure 9, it is clear that were higher

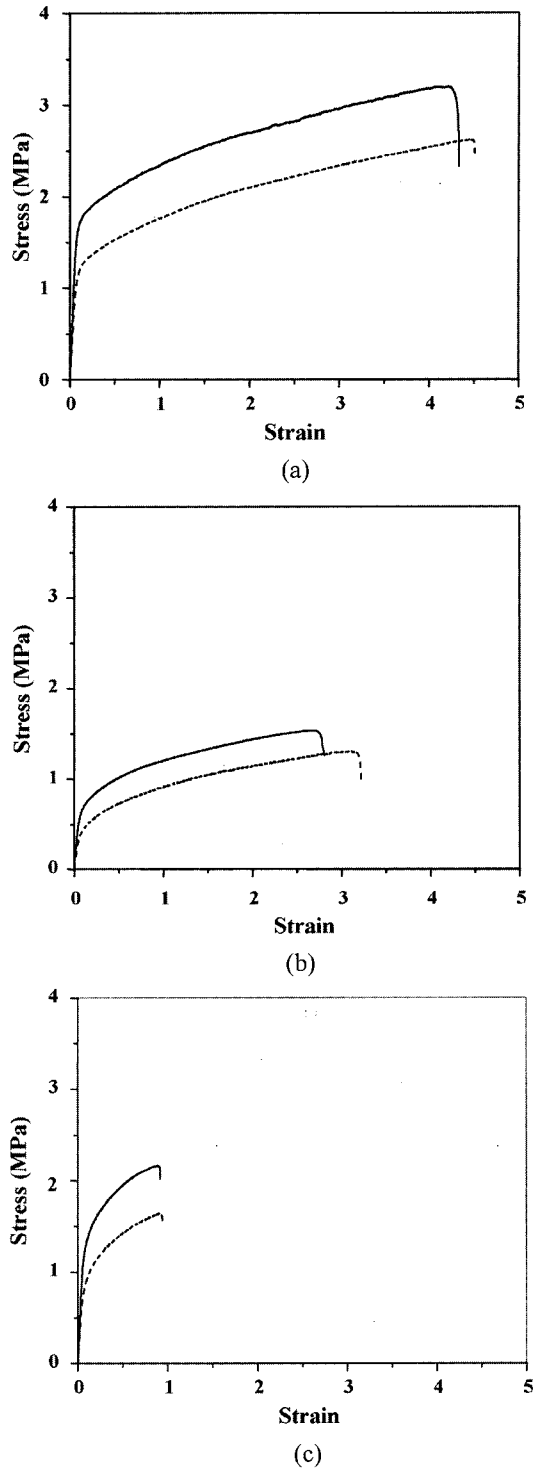

Figure 9. Mechanical properties of the electrospun cPET/aPET nonwovens as a function of blend ratio: (a) 100/0 before heat treatment, (b) 50/50 before heat treatment, (c) 50/50 after heat treatment (solid line = TD, dashed line = MD).

in TD than MD. From our earlier reports [18,19] we found that the arrangement of fibers in the nonwovens was determined by linear velocity of drum surface in both the TD and MD. The results of stress-strain curves for the electrospun cPET/aPET blend nonwovens with blend ratios of 100/0 and 50/50 before heat treatment are shown in Figure 9(a) and (b). From these figures, a little decrease in the value of young's modulus, yield stress, tensile strength and elongation at break was observed in the blend nonwovens. Young's modulus, yield stress and tensile strength for the electrospun cPET/aPET blend with 50/50 after heat treatment at 120 °C for 1h showed an increase, on the other hand, the value of elongation at break was decreased after heat treatment (Figure 9(c)). Hence, from this study, we concluded that the addition of aPET deteriorated the mechanical properties of the electrospun cPET/aPET blend nonwovens. Further, young's modulus, yield stress, and tensile strength of the electrospun cPET/aPET nonwovens with a blend ratio of 50/50 were higher for the blend nonwovens after heat treatment that before heat treatment, whereas for the same nonwovens, the elongation at break after heat treatment was less than that before heat treatment.

Conclusion

The effect of the blend ratio and the heat treatment on the solution properties, morphology, gas transport property and mechanical properties of the electrospun cPET/aPET nonwovens was investigated. From this study, it was found that the addition of aPET changed the surface morphology of the nonwovens. The nonwovens were transformed into membrane-like materials after heat treatment at 120 °C for 1 h. The gas transport properties of cPET/aPET nonwovens before heat treatment varied very little for various blend ratios, but varied considerably after the heat treatment. Young's modulus, yield stress, tensile strength and elongation at break of the electrospun cPET/aPET blend nonwovens with a blend ratio of 100/0 were higher than those of the nonwovens with a blend ratio of 50/50 both before and after heat treatment. Moreover, young's modulus, yield stress and tensile strength of the cPET/aPET blend nonwovens with a blend ratio of 50/50 were found to be higher after heat treatment than before heat treatment. The elongation at break of the cPET/aPET blend nonwovens with a blend ratio of 50/50 was higher before heat treatment than after heat treatment. The reason for this is that the aPET causes the fibers to become intertwined during heat treatment.

Acknowledgements

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