Hindawi Publishing Corporation
International Journal of Polymer Science
Volume 2014, Article ID 605938, 6 pages
http://dx.doi.org/10.1155/2014/605938

Research Article

Post-Heat Treatment and Mechanical Assessment of Polyvinyl Alcohol Nanofiber Sheet Fabricated by Electrospinning Technique

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Received 7 October 2013; Revised 3 February 2014; Accepted 3 February 2014; Published 1 April 2014

Academic Editor: Yulin Deng

Polyvinyl alcohol (PVA) sheets based nanofibers were produced by electrospinning technique. Postheat treatment of the produced PVA sheets with temperatures both below and above Tg to improve the mechanical properties of this material is conducted. The morphology, microstructures, and thermal degradation of the nanofibers sheets produced were investigated using scanning electron microscopy (SEM), transmission electron microscope (TEM), and thermal gravimetric analysis (TGA). Produced nanofibers are compact, and entangled with each other, with diameters from around 150 to 210. Some mechanical characteristics of the successfully produced PVA sheets, and heat-treated, are then conducted and assessed employing uniaxial tensile tests at different speeds ranging from 1 mm/min to 100 mm/min. The tensile test results obtained show that the PVA sheets are strain rate sensitive with increasing strength as the speed (i.e., strain rate) increases. The yield tensile stress ranges from 2.411 to 6.981 MPa, the ductility (i.e., elongation percent) from ~21 to 60%, and Young modulus ranges from 103 to 0.137 KPa. However, for heat-treated samples, it is found that the yield strength increases almost by ~35–40% more than the values of untreated cases with values reaching up to about 3.627–9.63 MPa.

1. Introduction

Electrospinning is a simple technique to produce nonwoven polymeric fibrous structures with diameters ranging from tens of nanometers to microns [1–3]. The outstanding properties of produced fibers opened many potential applications based on such fibers specifically their use as wound dressing, drug delivery, and a support in catalysis has been realized [4, 5].

In the last few years, polyvinyl alcohol (PVA) presents an important material which received huge attention by many investigators due to its interesting properties such as film forming properties, nontoxic, and high mechanical properties [6, 7]. PVA is widely used for industrial products such as adhesive, coatings, surfactant, films useful for packaging, and in hygiene products as a biodegradable plastic backing sheet [6]. In addition to that, PVA has been widely used in different areas of the biomedical field [8, 9]. PVA besides its high density, crystallinity, relatively high tensile, and bending strength has many physical cross-linking points, and the surface is brittle and rigid; thus, PVA has some disadvantages, such as (i) the melting temperature is higher than its thermal decomposition temperature; (ii) its viscosity in the melting process is high, which makes its molding a very difficult process; (iii) it has bad water solubility properties; (iv) PVA has a lower breaking elongation [6, 10]. In this context, most of the PVA fibers investigations were concentrated on the fiber production, physical, thermal, and chemical characterization [11–13]. On the other hand, we have reported the coating of PVA electrospun nanofibers on aluminum surface for anticorrosion applications [14]. Very few works address postsheet production process of

PVA. This is important in order to assess the behavior of these sheets under mass-production and loading conditions in an ever-increasing industrial production rates; thus, the postthermal and mechanical treatments assessments of the produced sheets and films are essential. As the production rate is increased, the handling of these materials and products requires special understanding to cope with the strain rates encountered in the production processing. This necessitated intensive and systematic investigation on the strain rate and thermal effects on the final products. As mentioned before, we have deposited PVA electrospun fibers on the surface of aluminum substrate [14]. In this work, multilayer electrospun nanofibers films have been prepared, and then we investigate the effect of strain rate and thermal effects on PVA electrospun nanofibers sheets.

2. Experimental Details

2.1. Electrospinning of Polymers. Nanofibers were prepared using an electrospinning apparatus. In atypical experiment, "the electrospinning apparatus comprised a 20 mL Syringe with a 0.6 mm innerdiameter, a graphite electrode, an aluminum collecting drum covered by aluminum foil sheet, and a high voltage supply. An aqueous solution of 10 wt% PVA was used, and flow rate of 0.3 mL/hour was maintained by connecting a syringe pump to the hypodermic syringe. Produced multilayers electrospun nanofibers films were detached from aluminum sheet, and then dried in vacuum" [14, 15].

2.2. Nanofibers Morphological Characterization. Surface morphology of produced and heat-treated electrospun nanofibers at the various temperatures was examined using scanning electron microscopy (SEM), (JEOL JSM-7800F), and Transition Electron Microscopy (TEM). Fibers size distribution was measured from five frames of randomly selected SEM micrograph using software [14, 15].

2.3. Tensile Test. Standard tensile tests were carried out according to the ASTM_D 882-2002 standard on tensile samples made of PVA sheets, using Instron bench universal testing machine [16]. A total of 60 standard tensile tests were conducted, covering four loading speeds (i.e., strain rates) of 1, 5, 10, and 100 mm/min on three group samples produced at room temperature, and postheat-treated samples at T_g (85°C, which is ~0.5 of the melting temperature, T_m) and ~1.65 T_g (140°C, which is ~0.7 T_m). For accuracy and result consistency, each test was repeated five times and an average value was taken. These temperatures were selected based on previous experience and some reported tests [17, 18]. On the other hand, these temperatures were selected to be below the decomposition temperature of PVA, which should be at least 30–40°C below the melting temperature of PVA.

3. Results and Discussion

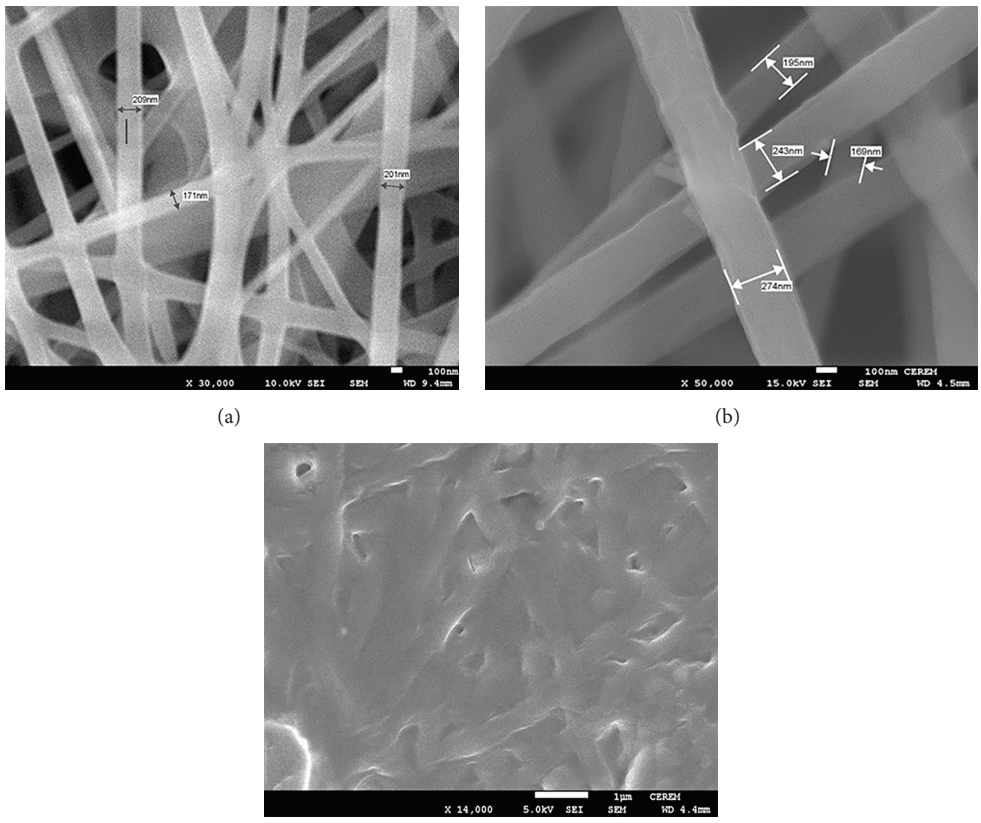
3.1. Morphology. The SEM photographs of as prepared and heat-treated PVA nanofibers samples at T_g (85°C, which is ~0.5 T_m) and ~1.65 T_g (140°C, which is ~0.7 T_m) are shown in Figure 1. Figure 1(a), shows a web of random oriented fiber with abroad distribution from around 150 to 210 nm. Meanwhile, Figures 1(b) and 1(c) display the fibers merging, partial melting, and fusion features at T_g (85°C) and ~1.65 T_g (140°C), respectively. As the treatment temperature increased, full melting of some of the fibers has been observed. This in turn causes some changes in the fibers structure including merging and fusion among fibers as well as some surface texture changes particularly during the heating process which resulted in dynamic crystallization and recrystallization, at the melted regions, as shown in the TEM photographs shown in Figures 2(a) and 2(b).

3.2. Thermal Characteristics and Degradation Analysis. Figure 3 shows both the (DSC) and Differential Thermal Analysis (TGA) thermogram in a nitrogen atmosphere for electrospun PVA nanofibers where data came in agreement with our previous published data [14, 15]. The data reveals that PVA electrospun nanofibers decompose in three stages. The loss of moisture content is the main reason for weight loss at around 30.00–210.00°C in the first stage. The weight loss at the second stage at around 210–350°C is due to degradation of a polymer structure. By increasing the heating temperature, polymer backbone will break down and lead to complete cracking of PVA [19, 20]. Affirmatively, the third step was the predominant degradation process. Finally, the weight loss at the third stage above around 350°C may be due to decomposition to carbon oxide and volatile hydrocarbons [14, 15].

3.3. The Tensile Tests Analysis. Standard uniaxial tensile tests, according to the ASTM standard, are carried out on five standard samples cut from the successfully fabricated PVA electrospun nanofibers films, as prepared, at constant tensile test speeds of 1, 5, 10, and 100 mm/min. The load displacement results are obtained and then converted to stress-strain curves. An average representative curve for the samples of PVA tested at each speed is obtained. A typical average representative curve at the different speeds is displayed in Figure 4. From these representative average curves the tensile yield stress is found to be from 2.411 to 6.981 MPa and the average Young's modulus is from 103 to 128 kPa; meanwhile, the average elongation percentage found is from 35.02 to 59.81%. The same procedure is repeated for the samples heat-treated at temperatures of ~0.5 T_m (~85°C) and at ~0.7 T_m (~140°C); see Figure 5. Again, from these representative average curves the tensile yield stress is found to be from 3.627 to 9.630 MPa and 4.11 to 6.298 MPa, also, the average Young's modulus is from 110 to 137 KPa and 109 to 137 KPa; meanwhile, the average elongation percentage found is from 28.82 to 31.26% and 21.47 to 29.71% for the other two groups of samples heat-treated at 85°C and 140°C, respectively.

However, Figure 6 summarizes the complete mechanical results of all the samples tested and displays the variation of the tensile strength, elongation percentage, and Young's modulus values with the testing speed (i.e., strain rate).

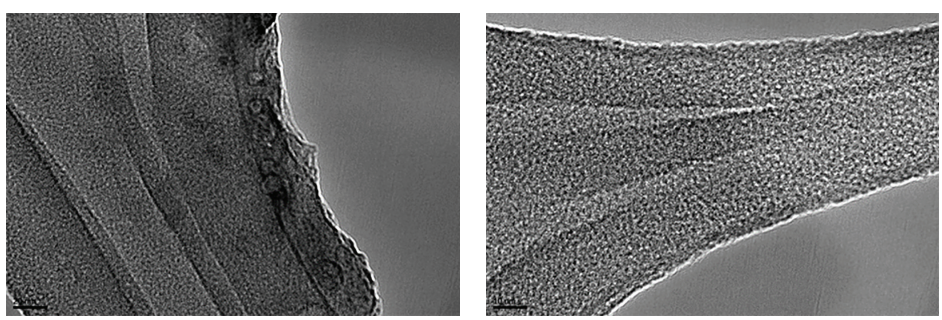
It is clearly shown that PVA is strain sensitive material with varying degrees. The results show that as the strain



(a) (b)

(c)

Figure 1: Typical SEM micrographs of the PVA electrospun nanofibers: (a) as spun; (b) heat treated at T_g (85°C, which is ~0.5 T_m); and (c) heat treated at ~1.65 T_g (140°C, which is ~0.7 T_m).



(a) (b)

Figure 2: (a), (b) Typical TEM micrographs of some PVA heat-treated nanofibers.

rate (speed) increases the values of the yield strength (flow stress) are increased, while the elongation % and Young's modulus are mostly decreased in a nonlinear manner for all tested temperatures. Figures 4 and 6(a) show increasing load resistance and higher values of yield strength as the speed of testing is increased for the whole range of temperature tested. Meanwhile, the ductility (i.e., elongation percentage) is decreased as the speed increasing Figures 5 and 6(b), except for the sample tested at room temperature (i.e., at 25°C). Also, the Young's modulus is noticed to increase at lower speeds with little or no variation in the values at higher speeds, as shown in Figures 4, 5 and 6(c).

Generally, the material tends to display more rigid and brittle behavior at higher temperatures and rates due to the dynamic crystallization changes taking place during the loading and cooling after heat treatment; see Figure 2. These variations, as reported by many investigators [21–25], "can be attributed to a change either from ductile to brittle behavior or a reduction in the amount of plastic deformation due to the time dependent nature of the plastic

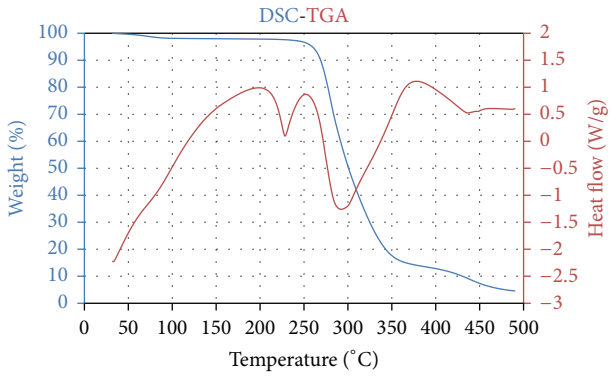


Figure 3: The DSC-TGA thermogram in nitrogen atmosphere for PVA electrospun nanofibers.

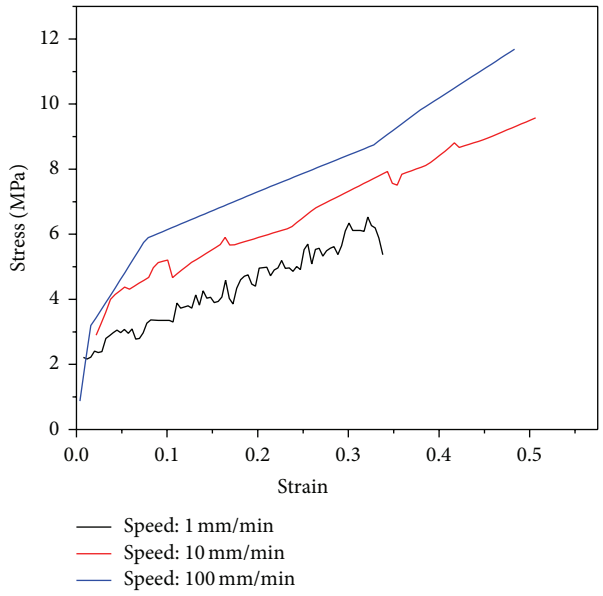


Figure 4: Typical representative stress strain curves for PVA samples at different constant speeds.

flow (i.e., the viscoelastic-plastic behavior of the polymer nature of PVA material)." This, however, can be explained in terms of dislocation and diffusion processes responsible for plastic deformation mechanisms during the tensile loading process [26]. At low speeds, where adequate time is available, the dislocation mechanisms are dominant and the plastic deformation is believed to be manifested by the dislocation mechanisms (slip, glide, climb, etc.), soon replaced by some form of diffusion process at higher speeds and rates (i.e., shorter time duration) and temperatures (i.e., high crystallization and brittleness). For the samples tested, the brittle crystalline heat-treated samples at about 140°C, see Figure 2, are found to be the least strain sensitive, while those samples of nontreated PVA are found to be the reverse. Actually, the higher the heat treatment temperature is the more melting and recrystallization are involved in the process and the material becomes more brittle; see Figure 2 and Figures 4–6. This consolidates our selection of the heat treatment

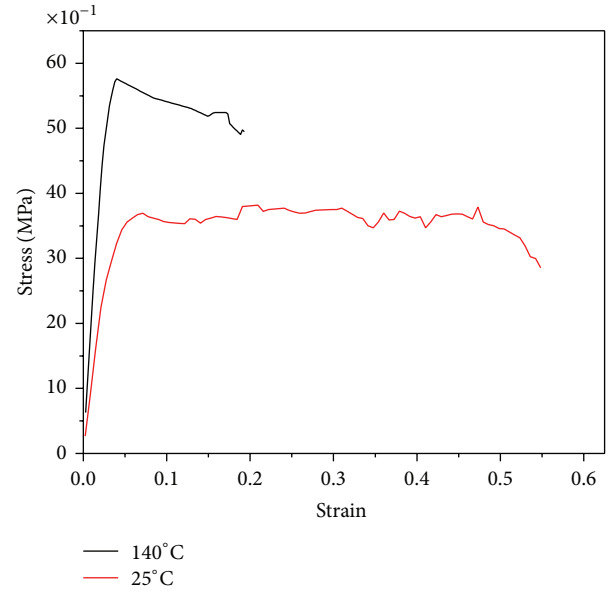


Figure 5: Typical representative stress strain curves for PVA samples heat-treated at two different temperatures and tested at constant speed of 5 mm/min.

temperatures to be above T_g (i.e., ~0.5 T_m, ~85°C) and below T_m (i.e., ~0.7 T_m, ~140°C) to avoid excessive melting and thus dynamic crystallization and brittleness which decrease mechanical ductility and handling properties. As stated above [18, 19], these temperatures are selected to be well below the decomposition temperature of PVA, which should be at least 30–40°C below the melting temperature, T_m of PVA, fount to be ~200°C.

Our results show that Young's modulus values are in the range of 103 kPa to 137 kPa compared with the values given in [27] (30 kPa to 100 kPa), where Young's modulus is obtained from pressure column and from elastogram at low temperatures. However, due to the different testing (temperature and speed) conditions used in this investigation, a maximum difference of ~37% in the values is observed. But in general a good agreement in results is observed [27]. Young's modulus calculated is in the range of 103 to 137 kPa, which is around the same range as arterial tissues described in the literature, 10 to 100 kPa [27].

4. Conclusion

In this work, PVA electrospun nanofibers films are successfully prepared. The morphologies and the microstructures of the PVA electrospun nanofibers films are characterized and assessed using scanning electron microscopy (SEM), transmission electron microscope (TEM), and thermal characteristic and degradation analysis (DSC-TGA). The measurements obtained from the tensile tests on the PVA films indicated that the material is ductile with maximum elongation percentage of about 67%, and Young's modulus of up to 140 KPa and maximum yield strength of 5.76 MPa. Postheat treatment of PVA sheets, to temperatures up to 0.7

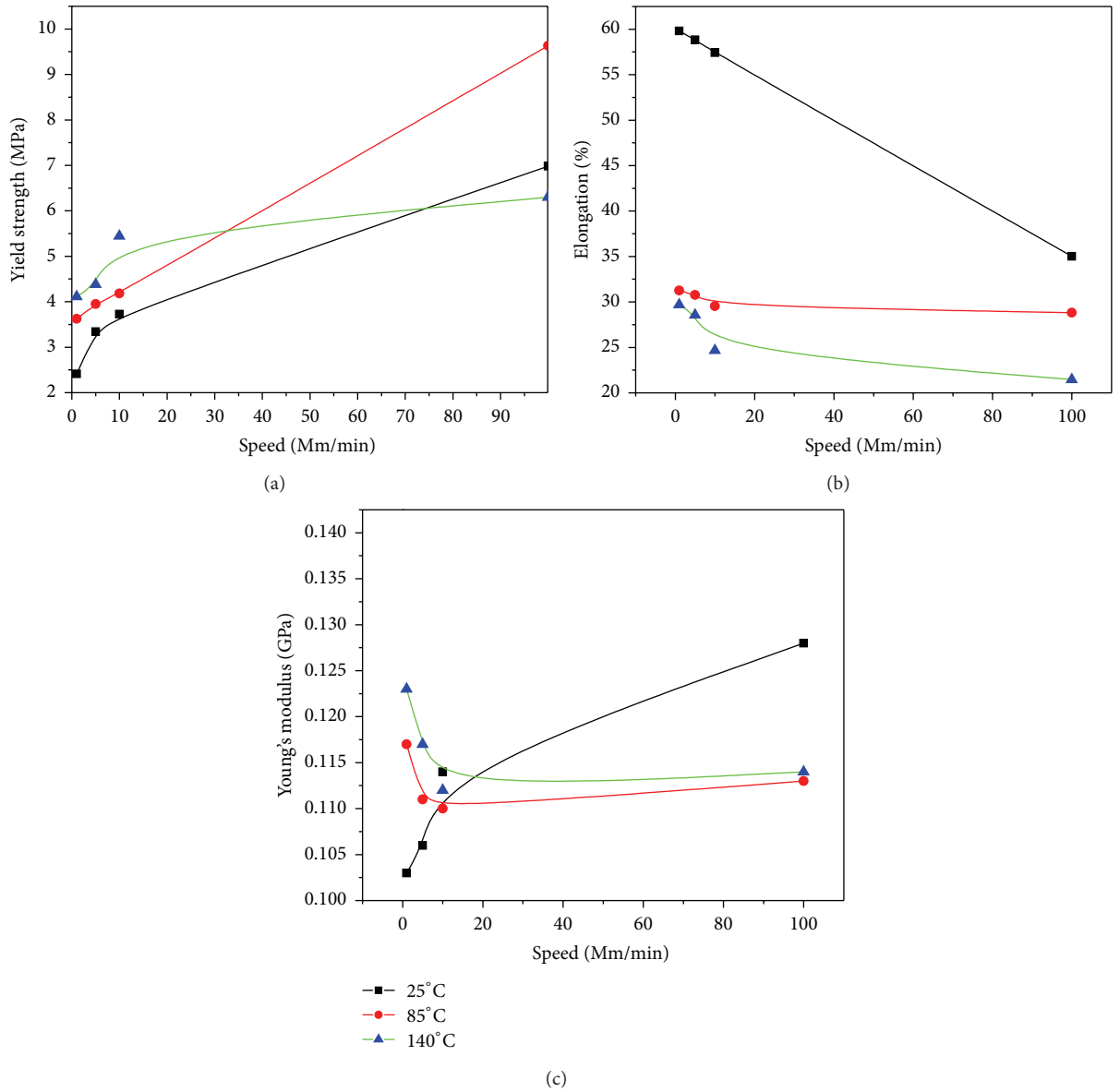


Figure 6: (a) The variation of the mechanical properties; yield strength of the PVA films with the speed at different temperatures. (b) The variation of the mechanical properties; elongation % of the PVA films with the speed at different temperatures. (c) The variation of the mechanical properties; Young's modulus of the PVA films with the speed at different temperatures.

of the melting temperature, T_m, can improve the mechanical properties. Also, the PVA is found to be strain rate sensitive. It displays high resistance to loading as the speed of production (i.e., strain rate) increases. All measurements were in good agreement with published data and confirmed that the PVA electrospun nanofibers films can, to a great extent, withstand mechanical handling and further industrial processing.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

Acknowledgment

The authors extend their appreciation to the Deanship of Scientific Research at King Saud University for funding the work through the research group project no. RGP-VPP-036.

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