Thermal Analysis of PVA Nanofibrous Membranes

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Abstract Thermal behavior of electrospun PVA nanofibrous membranes was studied by thermal analysis techniques i.e., differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). For the production of nanofibrous membranes needleless (roller) electrospinning method was used. DSC graphs showed that there is a decrease in melting temperature of the PVA polymer when crosslinking agent is used. Moreover, the change in the polymer concentration doesn’t influence the Tm. Considering the TGA results, it is realized that while crosslinked PVA nanofibers have weight losses at about 240°C, pure PVA nanofibers have a weight loss at about 290°C.

Keywords—Crosslinking agent, differential scanning calorimetry, PVA nanofibrous membrane, thermogravimetric analysis.

I. INTRODUCTION

NANOFIBERS form a new field for researchers due to their outstanding nanostructure characteristics i.e., high surface area, small pore size, and the possibility of their producing three dimensional structures [1]. Their properties provide them to be used as advanced materials in the application of technical textiles. Investigation on the thermal stability of nanofibers is required in order to have safety and stability information for handling, storage, and usage of nanofiber based combined structures. Thermal analysis techniques i.e., TGA, and DSC are used for experimentally determining thermal properties of the polymers [2].

In this study, PVA nanofibrous membranes were fabricated by electrospinning method. The effects of the polymer concentration and the usage of crosslinking agent on morphology and diameter of the fibers were investigated by SEM technique. Thermal behavior of electrospun PVA nanofibrous membranes was studied by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA).

II. EXPERIMENTAL STUDY

A. Materials

Nanofibrous membranes from polyvinylalcohol (PVA) polymer were produced. The water solution of polyvinyl alcohol PVA (Mw = 80,000 -100,000 g/mol) having both concentration of 12% and 14% was used for electrospinning. Glyoxal and phosphoric acid were added to the solution as crosslinking agents. The solution containing PVA, distilled water, glyoxal, and phosphoric acid was vigorously stirred at room temperature. A water solution of polyvinyl alcohol PVA (Mw=80,000-100,000 g/mol) having a concentration 12% was also prepared without crosslinking agent addition. Non-ionic surfactant (SLOVASOL 247/9) was added to the solution to decrease the surface tension to simplify the electrospinning process and increase the productivity.

B. Nanofiber Production

For the production of nanofibrous membranes needleless (roller) electrospinning method, which has been known as Nanospider trade name, was used [3]. In roller electrospinning (Fig. 1), a slowly rotating cylinder is partially...
immersed in a polymer solution. Polymer solution is connected to a high voltage source and collector is usually grounded. In electrospinning process, polymer solution is taken to the surface of the roller because of its rotation. With suitable high voltage, many Taylor cones are simultaneously created on the roller surface and produce nanofibers. The nanofibers are then transported towards the collector [4].

Fig. 1. Schematic diagram of roller electrospinning method used for nanofibrous membrane production.

The process parameters were set as shown in Table I below.

| Process parameters         | Value |
|---------------------------|-------|
| Roller length (mm)        | 145   |
| Roller diameter (mm)      | 20    |
| Roller angular velocity (rpm) | 2     |
| Distance between electrodes (mm) | 100   |
| Source voltage (kV)       | 50    |
| Relative humidity (%)     | 34    |
| Temperature (°C)          | 19    |

C. Scanning Electron Microscopy (SEM)

The fiber morphology and fiber diameter of the electrospun nanofibers were determined using scanning electron microscopy (SEM). A small section of the fiber mat was placed on the SEM sample holder and sputter-coated with gold using Quorum Q150R Rotary-Pumped Sputter Coater. Carl Zeiss Ultra Plus Field Emission SEM was used to take the SEM photographs. The nanofiber diameter was determined by taking 100 measurements using Image J software.

D. Differential Scanning Calorimetry (DSC)

DSC analysis provide information about the amount of energy absorbed or released by a material as it is heated, cooled or held at constant temperature. The thermal properties of nanofibrous membranes were studied by DSC. Differential scanning calorimetry analysis was performed by using a DSC-6 Perkin–Elmer differential scanning calorimeter and using 8 mg of various electrospun materials. Materials were heated from 25°C to 300°C at a heating rate of 10°C /min and then, the samples were cooled to 25°C at a rate of 10°C /min. Samples wait 1 minute at 25°C and then heated to 300°C at a heating rate of 10°C /min and the samples were cooled to 25°C.

E. Thermogravimetric Analysis (TGA)

Thermogravimetric Analysis (TGA) measures weight/mass change (loss or gain) and the rate of weight change as a function of temperature, time and atmosphere. Thermal stability of the materials can be determined by measurements. The thermal property was analyzed with Mettler Toledo TGA/SDTA851e Analyzer. Nanofibers having weight between 6-7 mg were prepared and put into aluminum oxide crucibles. Then, closed crucibles put into heating tunnel and experiment was started. TGA analysis was performed at 25°C –500°C with 10°C/min in air.
III. RESULTS AND DISCUSSION

A. Morphology

Fig. 2. SEM images of a) crosslinked PVA (12%) b) crosslinked PVA (14%) c) pure PVA (12%), magnification is 10k.

Fig. 2 shows the morphology of PVA nanofibers. As can be seen in the figure, some fibers were observed to stick each other forming an interconnected fibrous structure. The formation of bonded fibrous structure was because of the insufficient solvent (water) evaporation from the polymer jets. This is a common observation for PVA membrane production when using the needleless electrospinning process that involves many jets operating simultaneously in a very limited space [5]. However, it is evident that crosslinking agent affects the morphology of PVA nanofibers as SEM images show that the beaded structure diminished when crosslinking agent was not used.

Fiber diameters of the crosslinked PVA (12%), crosslinked PVA (14%), and pure PVA (12%) are 240±30, 300±20 and 290±20, respectively.

B. Differential Scanning Calorimetry (DSC)

DSC thermograms of the PVA electrospinning fibers are shown in Figure 3. The pure PVA fibers showed a relatively large and sharp endothermic curve with a peak at 196°C. However, for crosslinked PVA nanofibers, the peak shifted toward the low temperature.

Table II lists thermal properties of the fibers. It was observed that the peaks of the endothermic curves shifted toward the high temperature from 185 to 196°C and the $\Delta H_m$ values also increased from 29 to 52 J/g without using crosslinking agent in the polymer solution. This demonstrated that presence of the crosslinking agent in the polymer solution leaded to a worse condition for crystallization of the fiber. With increasing polymer concentration, the peak of the endothermic curve remained constant at 185°C and the $\Delta H_m$ values also increased from 29 to 50 J/g.

| DSC DATA OBTAINED FROM THE ELECTROSPUN FIBERS OF PVA |
|----------------------------------|--|--|
| Tm (°C) | $\Delta H_m$ (J/g) |
| Crosslinked PVA (12%) | 185.5 | 29.82 |
| Crosslinked PVA (14%) | 185.1 | 50.77 |
| Pure PVA (12%) | 196.3 | 52.75 |

C. Thermogravimetric Analysis (TGA)

Fig. 4 to 6 show the TGA graphs of PVA nanofibers that are drawn by Mettler Toledo Software Program. Graphs show the weight change of the samples with increasing temperature. Onset temperature that is marked in the figure is the temperature where a sharp decrease of sample weight starts.
As can be seen from Fig. 4 to 6, the degradation temperature of the crosslinked PVA nanofibers is between 230°C and 245°C. On the other hand, the degradation temperature shifted to 290°C when pure PVA solution was used for membrane production. This fact shows that crosslinking agents begin to degrade at lower temperature.

![Fig. 4. TGA graph of crosslinked PVA (12%).](image1)

![Fig. 5. TGA graph of crosslinked PVA (14%).](image2)

![Fig. 6. TGA graph of pure PVA (12%).](image3)

**IV. CONCLUSION**

The effects of the use of crosslinking agent and the solution concentration on structure and morphology of the electrospun nanofibrous membrane were investigated. The result indicated that the average diameter of the fiber gradually increased with increasing polymer concentration. Moreover, pure PVA (without crosslinking agent) showed more uniform morphology and less bead formation. DSC analysis demonstrated that the peaks of the endothermic curves shifted toward the high temperature and the \( \Delta H_m \) values also increased without using crosslinking agent in the polymer solution. TGA analysis showed that with using crosslinking agents, the degradation temperature shifted to...
lower temperature.

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