PREPARATION AND CHARACTERIZATION OF THE CARBON NANOFIBER MAT PRODUCED FROM ELECTROSPUN PAN/LIGNIN PRECURSORS BY ELECTRON BEAM IRRADIATION

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Abstract. In this study, polyacrylonitrile (PAN)/lignin nanofiber mats were fabricated from PAN and lignin using an electrospinning method. The nanofiber mats were irradiated with an electron beam to induce structural crosslinking. Subsequently, the crosslinked PAN/lignin nanofiber mats were carbonized to produce the carbon nanofiber mats. The PAN/lignin nanofiber mats were characterized by SEM, ARES, XRD, and UTM analysis, respectively. The thermal stability of the PAN/lignin nanofiber mats was studied using a thermogravimetric analyzer (TGA).

1. INTRODUCTION

Carbon fibers have been widely used for numerous applications because of their unique chemical, electrical, and mechanical properties. However, the cost of carbon fiber production limits their widespread use. Lignin is the second most abundant polymer in nature, after cellulose. It is a high molecular weight, polyaromatic macromolecule, with a reported total worldwide production of approximately 26 million tons/year. The use of lignin as a precursor to carbonaceous materials has gained interest due to its low cost and high availability [1-3].

Electrospinning is a simple and inexpensive technique for producing continuous submicron- to nanosized polymeric fibers. The produced fibers exhibit high continuous surface areas. Ionizing radiation may induce several changes in the structure of polymers, with crosslinking, bond and chain scission, gas desorption, changes in crystallinity and unsaturation being the main effects [4-6]. Curing was an essential step in the preparation of the PAN/lignin nanofiber mat; it prevents the mats from melting during the carbonization process. The chemical structure change in PAN/lignin nanofiber mat caused by E-beam irradiation was probably due to the formation of conjugated carbon-nitrogen double bonds at the expense of the pendant nitrile groups [7]. The fiber mats were irradiated with an electron beam (E-beam) to induce structural crosslinking.

In this study, we fabricated PAN/lignin nanofiber mats using the electrospinning technique. The electrospun PAN/lignin nanofiber mats were cured using E-beam irradiation and then carbonized in a tube furnace at atmospheric pressure, in the presence of nitrogen, and at a temperature of 1000 °C for 1 h. The PAN/lignin nanofiber mats were characterized by SEM, ARES, XRD, and UTM analysis, respectively.

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2. EXPERIMENTAL

2.1. Materials

Polyacrylonitrile (PAN, M.W. = 150,000 g/mol) was used as a matrix polymer for the PAN/lignin nanofiber mats. Lignin alkali (low sulfonate content, M.W. = 60,000 g/mol) was purchased from Aldrich (USA). N.N-dimethylformamide (DMF) was purchased from Showa (Japan) and used as a solvent without any further purification.

2.2. Preparation of PAN/lignin nanofiber mats

The weight ratio of PAN to lignin in the composite solutions were 100:0, 50:50, 60:40, 70:30, and 80:20, respectively. Homogenous solutions were obtained by heating at 60 °C for 4 hour with constant stirring. During the electrospinning, a high electric potential was applied to a droplet of the polymer solution at the tip (ID 0.36 mm) of a syringe needle. The solution was then ejected through the syringe using a syringe flow pump at a feed rate of 0.02 mL/min while a voltage of 15 kV was applied at a tip-target distance of 100 mm.

The electrospun PAN/lignin nanofiber mats were cured by E-beam irradiation. The mats were placed on a water-cooled stainless-steel bed to prevent the temperature of the PAN/lignin nanofiber mats from increasing during the irradiation, which occurred in a nitrogen-filled chamber. The E-beam was generated using a 1.14 MeV acceleration voltage, a 4 mA of current, and a 2,000 kGy absorbed dose. Finally, the PAN/lignin fiber mats were heat-treated in a tube furnace in which the temperature was increased at a rate of 10 °C/min to a maximum temperature of 1000 °C in the presence of nitrogen for 1 h.

2.3. Characterization

Solution viscosity measurements were performed using an Advanced Rheometric Expansion System (ARES, TA instruments, USA). Electrical conductivity was measured with a HD 2156.2 conductivity meter at room temperature. The microstructure of the PAN/lignin nanofiber mats were observed with a
field emission scanning electron microscope (Sirion, FEI, Netherlands). The tensile strength of PAN/lignin nanofiber mat according to ASTM D638 was measured by Instron 5569 universal test machine. The machine was operated under a displacement control mode at the crosshead speed of 5 mm/min. The crystal phase of the PAN/lignin nanofiber mat was analyzed by XRD, and the thermal stability was assessed using a TA instrument equipped with a TGA (Q600). The runs were performed in the presence of nitrogen, at a heating rate of 10 °C /min, and at temperatures ranging from room temperature to 1000 °C.

3. RESULTS AND DISCUSSION

The viscosities and conductivities of the polymer solutions with different concentrations of lignin (0, 50, 60, 70, and 80 wt.%) are presented in Fig. 1. It was observed that the viscosity of the polymer solutions decreased with increasing lignin concentration. Also, It was observed that the variations in the lignin concentrations lead to variations solution conductivities of polymer solutions. The conductivity of the polymer solutions decreased with increasing lignin concentration. The decrease in conductivity of the solution results in the production of beads and thicker fibers because the polymer solution is subjected to more stretching under the high electric field [8,9].

Fig. 2 presents the SEM images of the electrospun PAN/lignin nanofiber mats prepared with various lignin concentrations. These data indicate that a 3D woven mat was created. In the process of electrospinning process, the addition of lignin significantly influenced the diameter and surface. The SEM images indicate that uniform, circular fibers with an average diameter of 300 nm were produced when the lignin contents was 50 wt.%. The uniform morphology shifted to a beaded morphology, when the concentration of lignin was 60 wt.%. In addition at a lignin concentration of 80 wt.% electrospinning dots that rarely interconnected with the fibrous structure were observed rather than fibers, along with debris.

The tensile properties of the control and PAN/lignin nanofiber mats prepared with various E-beam absorption doses are provided in Fig. 3. The tensile strength of the irradiated PAN/lignin nanofiber mats gradually increased to 480% relative to that of the non-irradiated PAN/lignin nanofiber mats. The increase in the tensile strength could be attributed to the stabilization of PAN during the E-beam irradiation.

XRD was used to investigate the transformation in the phase structure of the PAN/lignin nanofiber mats (Fig. 4). The PAN/lignin nanofiber mat can be
seen that the diffraction peak at 2θ of 16.8° and 28.8° were assigned to (100) and (110) crystallographic planes of PAN. After E-beam irradiation, the (100) peak was decreased due to the formation of ladder-like polymeric structures in the stabilized PAN. The diffraction peak around the 2θ of 25° ~ 26° was attributed to the (002) crystallographic planes of graphite crystallites [10]. These results indicated that the PAN/lignin nanofiber mats were converted to carbon nanofiber mats.

The thermal stability of the fabricated mats was investigated with TGA (Fig. 5). The runs were performed in the presence of nitrogen which causes hydrogen cyanide, ammonia, water and other gases to separate without addition reaction. The weight percent of the residue of electrospun PAN/lignin nanofiber mat, E-beam irradiated PAN/lignin nanofiber mat and carbon nanofiber mat up to 1000 °C were 62.6, 82.5, 99.7%, respectively. This fact means that the E-beam cured PAN/lignin nanofiber mat was thermodynamically more stable than the electrospun PAN/lignin nanofiber mat. This high weight percent of residue of E-beam irradiated PAN/lignin nanofiber mats are mainly attributed to the formation of large numbers of cyclic structure in PAN [11].

4. CONCLUSIONS

PAN/lignin nanofiber of 300 nm diameter with uniform, circular fibers were fabricated using the electrospinning technique when the lignin contents was 50 wt.%. The PAN/lignin nanofiber mats were crosslinked by E-beam irradiation, which could have a significant effect on the mechanical and thermal properties of the PAN/lignin nanofiber mats. XRD data indicated that the PAN/lignin nanofiber mats were converted to carbon nanofiber mats.

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