

Preparation of Polyacrylonitrile and Cellulose Acetate Blend Fibers through Wet-Spinning

H. Barani,¹ S. H. Bahrami²

¹Department of Textile Engineering, Islamic Azad University-Birjand Branch, Birjand, Iran

²Department of Textile Engineering, Amir Kabir University of Technology, Tehran, Iran

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ABSTRACT: Fibers containing both polyacrylonitrile (PAN) and cellulose acetate (CA) were prepared through wet-spinning by using *N,N*-dimethylformamide (DMF) as a solvent. Compatibility of PAN and cellulose acetate blend (PCB) fibers was investigated by means of scanning electron microscopy (SEM), differential scanning calorimetry (DSC), and infrared (IR) spectrophotometry. The absorptive capacity and mechanical properties of the fibers were measured. It was observed that the surface and the cross section of PAN fibers were quite

smooth and free from voids and microcracks, whereas cracks and voids were present on the surface and cross section of blend fibers, which increased with the incorporation of CA in the blend. Moisture regains of blend fibers were quite high while their tensile properties showed a partial decrease. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 103: 2000–2005, 2007

Key words: polyacrylonitrile; cellulose acetate; poly blend fiber; wet-spinning; properties

INTRODUCTION

Polymer blend fiber spinning is a method to achieve specific improvement in the properties of synthetic fibers. Polymer blend refers to the process in which two or more different polymers are mechanically blended together without chemical reaction. The properties of polymer mixtures largely depend on the effect of the components on one another, i.e., on their compatibility. Mixtures of incompatible polymers have poor mechanical properties. On the other hand, if it is somehow possible to obtain a highly dispersed mixture from incompatible polymer mixtures, the fabricated articles may combine the properties of the miscible component so that the mechanical properties will be superior to those of component polymers.^{1–12}

It is well known that the hydrophilic properties of synthetic fibers will be greatly modified if they contain numerous microvoids inside. Polyacrylonitrile (PAN) and cellulose acetate (CA) are incompatible in crystal region.¹³ Incompatibility and phase separation are important requisites for producing high water-retentive microporous fibers.¹⁴ Microporous fibers may be developed by conjugate spinning, i.e., by spinning PAN with another polymer of lower molecular weight.¹⁵ Cates and White reported several years ago the preparation of polyblend fibers through dry spinning of PAN and CA.¹⁶

As a continuation of modification of the PAN, in this experiment we prepared wet-spinning poly blend fiber of PAN and CA. The cross-sectional, the size and shape of void and physical properties of poly blend fiber have been studied.

EXPERIMENTAL

Materials

The PAN sample was synthesized in our laboratory with aqueous solution polymerization system using AIBN as an initiator.¹⁷ The viscosity average molecular weight (\bar{M}_v) of PAN was established from intrinsic viscosity measurement,¹⁸ and was found to be 0.93×10^5 for PAN. CA purchased from Aldrich with degree of polymerization and substitution of 160 and 2.4, respectively, was used. *N,N*-Dimethylformamide (DMF) solvent was acquired from Fluka Chemika and was used after slow distillation.

Fiber preparation

The spinning dopes were prepared by dissolving CA and PAN in DMF separately and then mixed together and filtered. The solid content of the spinning dope was 20 wt %. The spinning solutions were extruded through spinneret into a precipitation bath that contained a coagulating solution (Table I). Then fibers were washed in a second bath containing distilled water and were finally taken up on roller. Figure 1 displays the schematic of wet-spinning line.

Correspondence to: H. Barani (Barani_aut@yahoo.com).

TABLE I
Process Data for Filament Formation

| | |
|---|---------|
| Take up speed (m/min) | 6 |
| Washing bath temperature (°C) | 20 |
| Coagulation bath temperature (°C) | 10 |
| Spinneret diameter (mm) | 0.4 |
| Coagulation solution (DMF : H ₂ O) | 25 : 75 |
| Dopes concentrations (wt %) | 20 |

Infrared spectroscopy

Infrared (IR) spectroscopy of PAN and cellulose acetate blend (PCB) fibers was recorded by using a Nicolet nexus 670-USA FTIR. An equal amount of sample along with KBR was used for making pellets of equal weight.

Differential scanning calorimetry

A Perkin-Elmer differential scanning calorimeter (Model DSC 2010, USA) was used to record differential scanning calorimetry (DSC) curves, by heating from 20°C to 140°C in nitrogen atmosphere at a heating rate of 10°C min⁻¹. Powdered samples (10 mg each) were weighed and encapsulated in pans.

Scanning electron microscopy

The morphology of the prepared fibers was studied from the cryogenically fractured surface of the samples. They were coated with gold in a sputter coating unit for 2 min and observed in a (JEOL, Jxa-840, England) electronic microscope. The microporous areas on the fibers were measured by using image analysis of Matlab 6.5 software.

Moisture regain

To evaluate the moisture regain value, PAN and PCB fibers were conditioned at 20.0°C ± 0.1°C with a relative humidity of 65% for 24 h. The moisture regain capacities of fibers were calculated from the weight gain.

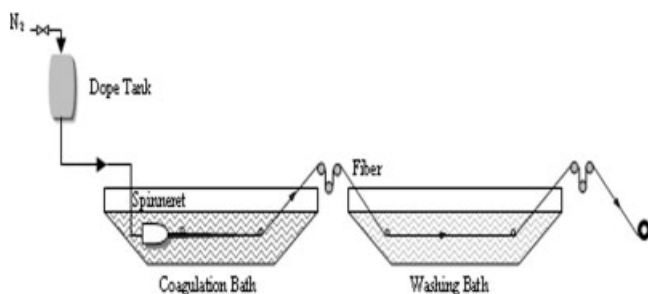


Figure 1 Schematic of wet-spinning fiber formation.

Linear density determination

Vibromat M (Textechno, Germany), according to ASTM D 1577-96, was used to measure the linear density of fibers. Linear density measurements were essential to calculate the necessary tensile properties. Each linear density value was the average of 10 samples.

Tensile testing individual fibers

The tensile properties of fibers were measured by Favigraph M (Textechno, Germany). Gage length was 20 mm and crosshead speed was 1 mm/min, according to ASTM D 3822. The samples were chosen randomly by 10 readings for each specimen.

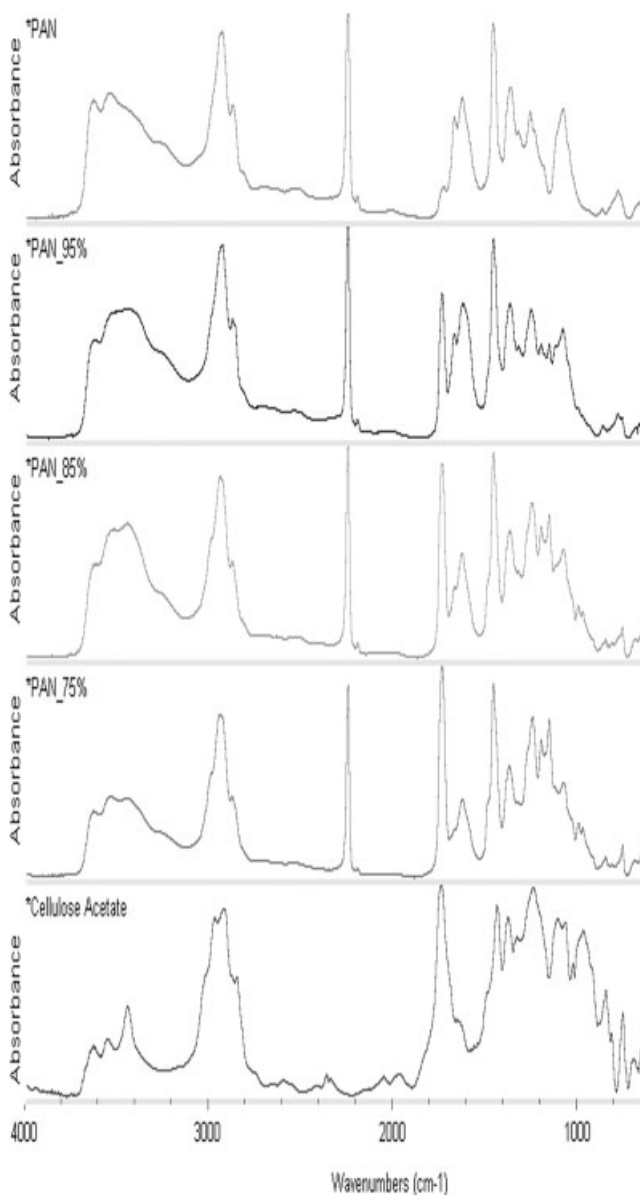


Figure 2 Infrared spectra of PAN, CA, and PCB fibers.

RESULTS AND DISCUSSION

IR spectroscopy analysis

IR spectra of CA, PAN, and PCB fibers are shown in Figure 2. The positions of the CA and PAN absorption bands indicate good agreement between IR spectra of this work and literature data.^{19–24} PAN IR spectrogram shows band absorption at 2243 cm^{-1} , which is attributed to the shrinking vibration of nitrile groups. The absorption bands at 1452 and 1364 cm^{-1} are characteristic of hydrocarbon, while an absorption band of 2925 cm^{-1} was assigned to C–H stretching vibration. In the IR spectra of CA, an ester carbonyl band with a strong intensity of 1734 cm^{-1} (C–O) and medium intensity band of 1372 cm^{-1} (related to angular distortion of C–H in the ester methyl group), and C–O–C of 1103 cm^{-1} was seen. Features above 2000 cm^{-1} were both intense and composition-sensitive. They appeared at 2916 cm^{-1} (–CH₂) and 3441 cm^{-1} (OH). Absorption bands, due to OH group, for all PCB fibers appeared in the same area.

Special focus was made on change in the intensity of nitrile and carbonyl groups. It can be seen from Figure 3 that the nitrile group of PAN fibers shows higher intensity compared with PCB fiber samples. Increasing the amount of CA in PCB fibers, increases

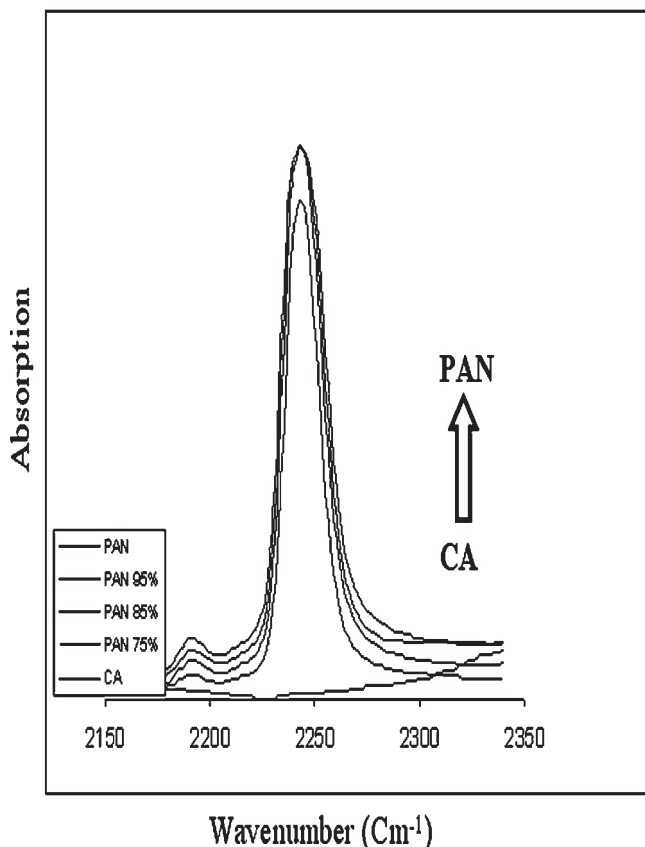


Figure 3 Infrared spectra of samples at the region of CN absorption.

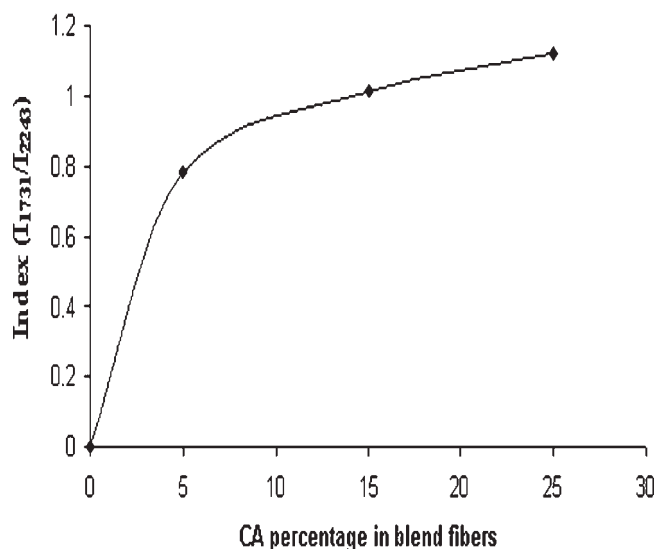


Figure 4 Carbonyl index versus CA percentage in PCB fibers.

the intensity of carbonyl group. Figure 3 shows the IR absorption, due to nitrile group, for all samples. Their positions do not change while the highest and lowest peaks belong to pure PAN and CA samples, respectively.

The intensity ratios of $1731\text{ cm}^{-1}/2243\text{ cm}^{-1}$ absorption bands can be taken as an appearance characteristic of carbonyl group in the blend fibers. It can be seen from Figure 4 that as the amount of CA in blends increases, the ratio index also increases which indicates growth in the concentration of CA in the PCB fibers and the samples containing 25% by weight of CA had the highest ratio index.

DSC analysis

DSC curves of all fibers are shown in Figure 5. With an increase in CA content the T_g of blend fibers shifts partially to higher temperature (Table II). The T_g of CA fiber is higher than its decomposition tempera-

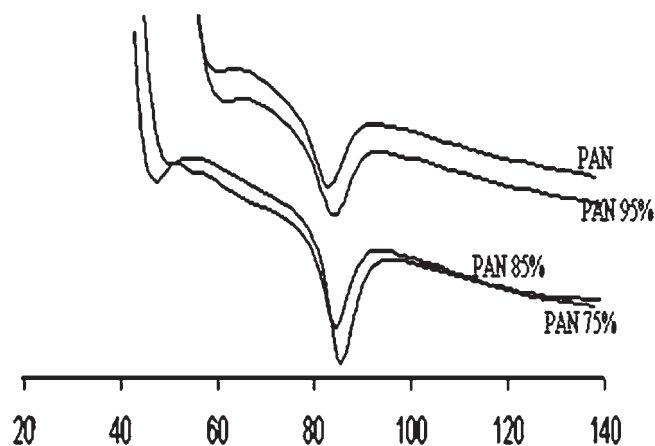


Figure 5 DSC thermograms of the fibers.

TABLE II
Glass-Transition Temperature of the Fibers

| Sample | PAN/CA ratio | T_g (°C) |
|--------|--------------|------------|
| 1 | 100/0 | 76.8 |
| 2 | 95/5 | 77.2 |
| 3 | 85/15 | 79.3 |
| 4 | 75/25 | 81.6 |

ture.¹ The glass-transition temperature (T_g) is directly related to the mixing at the molecular level in a polyblend. If two polymers can mix at molecular level, the polyblend presents only one T_g which depends on both the T_g and the volume fraction of the two polymers. When the amount of CA in the blend fibers increased, a slight increase in T_g was seen. However,

partial increase of the T_g of blend fibers indicates that the two polymers are compatible in amorphous regions, and that there was partial mixing of two polymers at molecular level only in the amorphous region and are incompatible in crystal regions.

Scanning electron microscopy micrograph analysis

Figure 6 shows cross-section scanning electron microscopy (SEM) photographs of PAN and PCB fibers. SEM is the evidence of porosity in blend fibers. Pores are formed because of the high interfacial energy barrier, the low intermolecular adhesive force, phase separation, and immiscibility of two polymers. The cross section of PAN fiber does not show evidence of large macrovoids, while blend fibers have macrovoids that indicate that phase separation occurs in PCB fibers. SEM photographs of the PCB samples show that the cross sections are divided into three sections: the thin layer surface, which is the part of fibers at first formed in the coagulation bath, the middle transition layer, which contains macrovoid and acts as a limitation tensile property, and the symmetric central core, which is spongy like. The porous areas are measured at various CA percentages in blend fibers and the results are shown in Figure 7.

The surfaces of fibers are shown in Figure 8. PCB fibers surface show some cracks on their surface and an increase in the sizes of voids with an increase in CA content.

Moisture regain analysis

The change in moisture regain with blending percentage is given in Table III. Moisture regain values of fibers

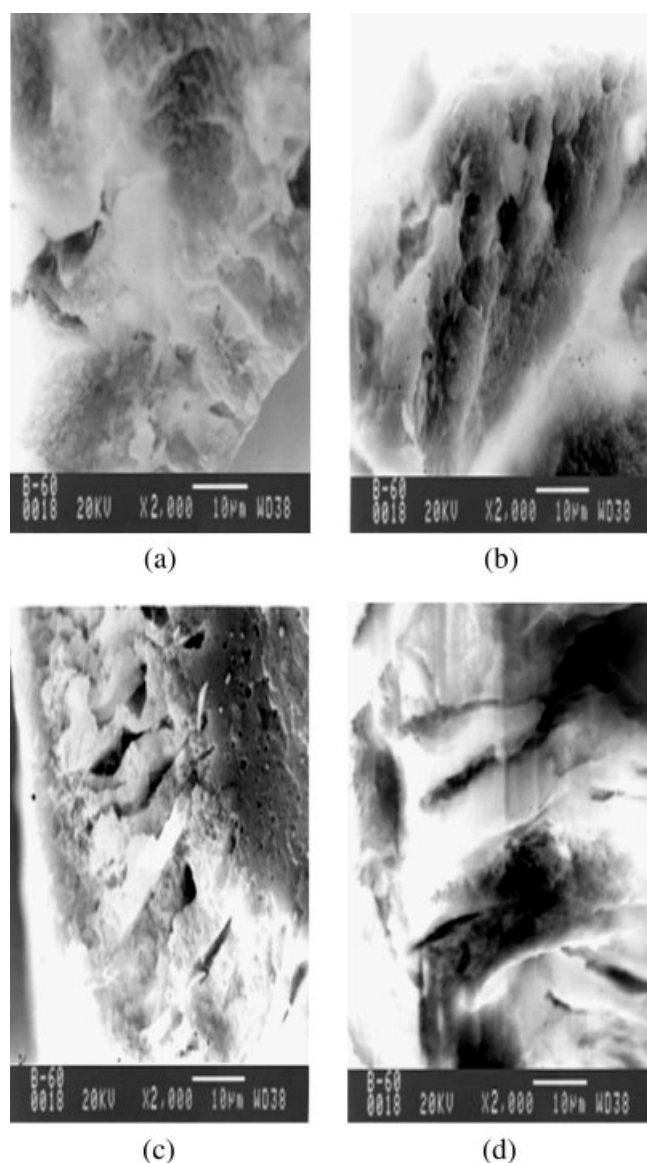


Figure 6 Scanning electron micrograph of a cross section of PCB fibers: (a) PAN, (b) PAN/CA (95/5), (c) PAN/CA (85/15), and (d) PAN/CA (75/25).

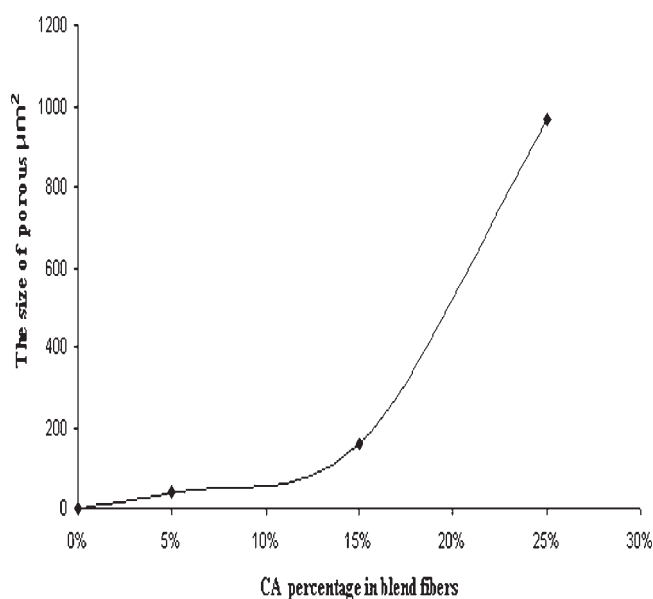


Figure 7 The increasing porous trend versus CA percentage in PCB fibers.

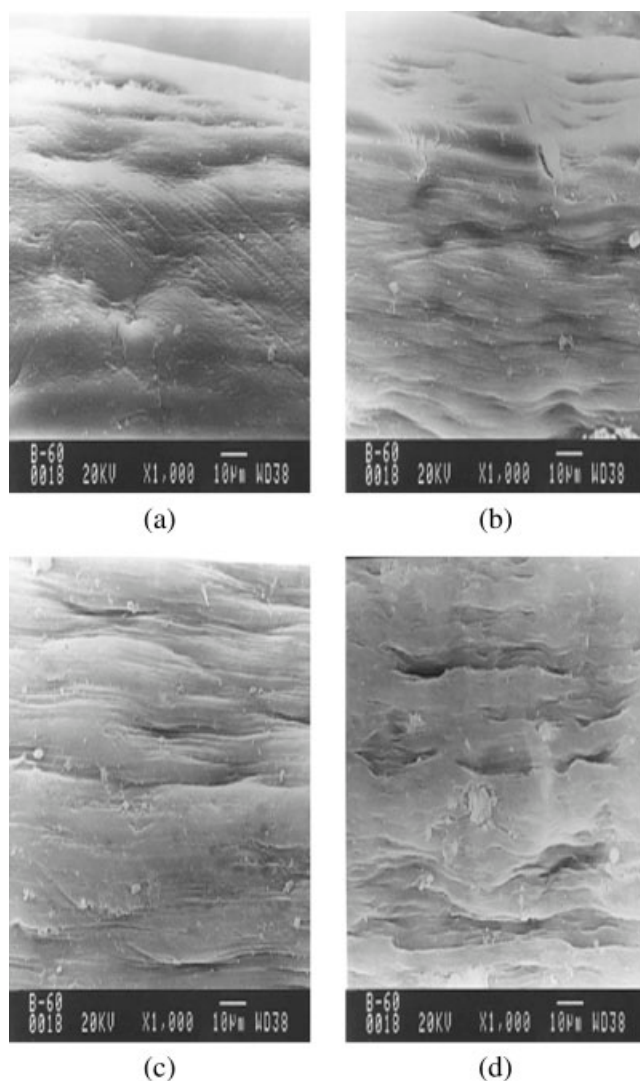


Figure 8 Scanning electron micrograph of a surface of PCB fibers: (a) PAN, (b) PAN/CA (95/5), (c) PAN/CA (85/15), and (d) PAN/CA (75/25).

increased from 1.8 to 2.9, while the blending percentage of CA increased to 25%. These increases in the moisture regain values of the blend fibers can be attributed to the existence of cracks and voids in blend fibers.

Tensile properties

The mechanical properties of fibers are presented in Table IV. As expected, PAN fibers are shown with

TABLE III
Moisture Regains Results

| PAN/CA percentage | Moisture regain (%) at 65% RH |
|-------------------|-------------------------------|
| 100/0 | 1.8 |
| 95/5 | 2.1 |
| 85/15 | 2.5 |
| 75/25 | 2.9 |

TABLE IV
Mechanical Properties of Blend Fibers

| PAN% | Tex | Load at break (cN) | Tenacity (N/Tex) | Work of rupture (N cm) |
|------|------|--------------------|------------------|------------------------|
| 100 | 10.2 | 53.48 | 6.67 | 0.5 |
| 95 | 10.1 | 46.01 | 5.76 | 0.38 |
| 85 | 10.1 | 38.81 | 4.86 | 0.18 |
| 75 | 10 | 32.24 | 4.18 | 0.08 |

comparatively better tensile strength (6.67 N/Tex), elongation at break (46.63%), and work of rupture (0.5 N cm).

The mechanical properties of PCB fibers were strongly influenced by the amount of each polymer in the blend fibers, their structure, and the interaction between each polymer. The poor mechanical properties exhibited by CA may be attributed mainly to the void formation in blend fibers, in which polyblend fibers with a higher CA content had a greater degree of phase separation, and so fibers with higher CA contents had further void in their structures. The PCB fibers were broken when the maximum amount of tensile stress was applied to them. After adding the CA component, the mechanical properties of blend fibers largely decreased. With an increase of up to 25% in the ratio of CA, the tenacity of fibers decreased from 6.67 to 4.18 N/Tex. The fiber sample that had 25% (wt %) CA showed poorer tensile properties than the other samples because its macrovoid at the surface and in the cross section was very large. In blend samples, the presence of CA produced weak points, and stress concentrations decreased tensile strength during tensile testing that in turn caused fibers to break untimely and under low tension.²⁵

CONCLUSIONS

CA that has a low molecular weight was used as a blending polymer to modify PAN fiber properties. The blend fibers of the two polymers were incompatible, which is evident by the characteristic peaks of PAN and CA in the spectrogram and DSC curves.

The SEM micrograph showed that phase inversion occurred in blend fibers and caused voids to appear in them. The tensile properties and macrovoid formation directly correspond to the composition of component. It was observed that when CA was blended, the tensile properties and work of rupture of PCB fibers decreased. Blend fibers containing a CA showed an increasing tendency to moisture regain, which reached a maximum at 25% CA.

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