# Morphological and Grafting Modification of Natural Cellulose Fibers

**S. Ouajai, A. Hodzic,* R. A. Shanks**

*Applied Chemistry, RMIT University, GPO Box 2476V, Melbourne 3001, Australia*

**ABSTRACT:** Crystal structure and mechanical properties of cellulose fibers were studied to investigate the effect of chemical treatment on the fiber. Pretreatment by acetone extraction, mercerization with 3–20% wt/v sodium hydroxide (NaOH), and acrylonitrile (AN) grafting initiated by azo-bis-isobutylonitrile were performed. From Fourier transform infrared spectroscopy and wide-angle X-ray diffraction quantitative measurements, the pretreated fibers showed an induced slight decrease of crystallinity index. The structural transformation of the fibers from cellulose I to cellulose II was observed at high NaOH concentration of 10–20% wt/v. The amount of grafting, 1.56, 2.94, 6.04, 8.34, or 10.46%, was dependent upon the initiator concentration and the volume of monomer in the reactor. The AN grafted fibers had no transformation of crystalline structure as observed after mercerization. Only a variation of X-ray crystallinity index with grafting amount was observed. Moisture regain of pretreated and modified fibers depended on the structure of the fiber and the amount of grafting. The mechanical properties performed by a single fiber test method were strongly influenced by the cellulose structure, lateral index of crystallinity, and fraction of grafting. Scanning electron microscopy was used for analysis of surface morphologies of treated fibers. © 2004 Wiley Periodicals, Inc. J Appl Polym Sci 94: 2456–2465, 2004

**Key words:** cellulose; fiber; biofiber; crystal structure; graft copolymer; mechanical properties

## INTRODUCTION

Natural cellulose fibers provide a wide range of applications in composite materials such as materials for construction,[1] automotive parts,[2] and food packaging.[3] The strongest potential for cellulose products originates from the combination of their low cost, biodegradability, renewability, and high specific strength, especially in the bast fibers of hemp and flax. It is very likely that they will be a major chemical resource for the future.[4] Numerous chemical treatments and modifications have been employed on cellulose fibers before incorporation into finished products. The most common pretreatment processes are extraction with solvent and mercerization. A cleaner surface and better adhesion with a polymer matrix were obtained.[5] Sodium hydroxide (NaOH) treatment, however, caused either total or partial crystalline structure transformation of native cellulose from cellulose I to cellulose II. The treated fibers exhibit different properties such as oxidative degradation.[6]

Further modification by chemical derivatization such as acetylation[7] and esterification[8] resulted in structural change of cellulose fibers. The solvent system and conditions of modification seem to be the major factors affecting the structural change. Fortunately, it was reported that a grafting technique for acrylic monomers at low pressure had no effect on the cellulose structure and also increased the penetration depth of monomer and minimized the formation of homopolymer.[9] The combination of a solvent-free grafting system and a low-pressure technique was used to protect degradation of the properties of the fibers.

As a vinyl monomer, acrylonitrile has the potential to graft onto cellulose fiber using different initiating systems, such as ionic[10] and radical initiators.[11] The graft copolymerization can take place in heterogeneous or homogeneous reactions,[12] with or without solvent inclusion. Concerning the introduction of hydrophobic groups onto cellulose and the further modification to hydrophilic character after grafting,[13] the solvent-free system initiated by free radicals from azo-bis-isobutylonitrile (AIBN) for grafting cellulose at low grafting levels was studied in this research.

The aim of this research was to modify natural cellulosic fibers to improve and increase the consistency of their performance in biodegradable materials. Fiber modification consisted of solvent extraction and NaOH treatment to remove wax and lignin before

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*Correspondence to:* R. A. Shanks (robert.shanks@rmit. edu.au).

*\*Current address:* School of Engineering, James Cook University, Townsville, Queensland, Australia.

grafting with acrylonitrile. The mechanical properties, moisture regain, and pore structures were investigated. Finally, an analysis of crystalline structure was performed using quantitative Fourier transform infrared spectroscopy (FTIR) and wide-angle X-ray diffraction (WAXRD) to assess the relationship between structure and properties after modification. Morphologies of cellulose fibers were investigated by scanning electron microscopy (SEM).

## EXPERIMENTAL

### Materials

Hemp (*Cannabis sativa*) was obtained from Australian Hemp Resource and Manufacture and Flax (Durafibre Grade I, 1.95% purity) was obtained from Cargill, Canada. Arylonitrile monomer (AN) purchased from Aldrich Chemical Co. was washed with 8% NaOH followed by distilled water and dried over anhydrous sodium sulfate. AIBN (Eastman) was used as the initiator. The treatment and characterization were applied mainly on hemp fiber for the entire work. Only the solvent extraction and mercerization were carried out for flax fiber. That is because the flax fiber shrunk after alkalization and was not suitable for the single fiber mechanical property testing and the further grafting procedure.

### Pretreatment

#### Dewaxing

The fibers were subjected to Soxhlet extraction with acetone for 3 h to remove any waxes present and then air-dried.

#### Alkalization

Dried fibers (2.5 g) were treated with various concentrations of NaOH solution (100 mL) and placed in an oven at 30°C for 1 h to remove lignin associated with the fibers. The concentrations of NaOH solutions were 3, 5, 8, 10, 12, 15, and 20% wt/v. The alkaline-treated fibers were subsequently washed with running tap water followed by distilled water until no alkali was present in the wash water.

### Grafting reaction

The 8% NaOH treated hemp fibers were dried under vacuum at 60°C for 3 h and weighed and then introduced into a glass reaction vessel. The reactor was connected with a dropping funnel and a vacuum pump. Once the pressure reached 0.5 mbar, an acrylonitrile–AIBN solution was slowly added. The concentration of initiator varied from 2 to 5% w/v. After 2 h the excess monomer solution was removed from the fiber surfaces. Nitrogen gas was then purged through the reactor to obtain atmospheric pressure and also to release the air.

The vessel was heated and held at 60°C for 4 h by surrounding it with hot water from a circulating bath to control the temperature of the reaction. The reaction was left overnight at room temperature to complete the grafting. The fibers were heated to 100°C for 30 min and vacuum dried at 60°C for 3 h before being washed with acetone to eliminate any residual monomer. The grafting yield of acrylonitrile into hemp fibers was estimated using the equation

% grafting yields = 100 × (dry weight of grafted hemp − dry weight of original hemp)/(dry weight of original hemp).

### Characterization methods

#### Surface and pore structure analysis

Nitrogen adsorption isotherms were measured for each grafted hemp fiber using a Micromeritics ASAP 2000 apparatus. The specific surface area and pore size distributions of hemp fibers were calculated from approximately 1 g of sample after they were vacuum dried at 105°C.

#### FT-IR measurements

The measurements were performed using a Perkin-Elmer 2000 spectrometer. A total of 100 scans were taken with a resolution of 2 cm$^{-1}$ for each sample. The fibers were cut in an IKA MF10 cutting mill and sieved to provide a size range between 106 and 212 $\mu$m. A mixture of 5.0 mg of dried fibers and 200 mg of KBr was pressed into a disk for FTIR measurement. The lateral crystallinity index of samples was evaluated as the intensity ratio between IR absorptions at 1430 and 898 cm$^{-1}$ assigned to the CH$_2$ symmetric bending mode and C$_1$ group frequency, respectively.

#### Wide angle X-ray diffraction measurements

The fibers (70 mg) were cut and pressed into a disk using a cylindrical steel mold ($\phi$= 1.3 cm) with applied pressure of about 7000 kg/cm$^2$ in a laboratory press. Ni-filtered CuK$\alpha$ radiation ($\lambda$ = 0.1542 nm) was generated at 40 kV and 35 mA using a Bruker AXS D8 WAXRDS. The X-ray diffractograms were recorded from 5 to 60° of 2$\theta$ (Bragg angle) by a goniometer equipped with a scintillation counter at a scanning speed of 0.02°/s and sampling rate of 2 data/s.

#### Single fiber mechanical properties

The mechanical properties of alkaline and AN-grafted hemp were determined by a single fiber measurement.

**TABLE I**
**Effect of Initiator Concentration and Monomer-Fibre Ratio on Grafting and Pore Structure Characteristic of Acrylonitrile Grafted Hemp Fibre**

| Grafting (%) | Initiator (AIBN) concentration (%wt/v) | Monomer/Fibre (ml/g) | BET surface area ($m^2/g$) | Cumulative pore volume ($cm^3/g$) | Adsorption pore diameter (angstrom) |
|---|---|---|---|---|---|
| 0 | — | — | 0.257 | 0.00004 | 28.9 |
| 1.56 | 3 | 0.99 | 0.296 | 0.00019 | 21.7 |
| 2.94 | 2 | 4.45 | 1.235 | 0.00163 | 88.1 |
| 6.04 | 4 | 1.70 | 1.286 | 0.00137 | 48.1 |
| 8.34 | 5 | 3.25 | 0.731 | 0.00045 | 537.4 |
| 10.46 | 5 | 6.59 | 3.231 | 0.00557 | 125.9 |

Gauge length of the fiber was set at 10 mm and each end of a single fiber was fastened with adhesive between two small pieces of paper for gripping. The tests were carried out on a Rheometric DMTA IV at a speed of 0.03 mm/min. The fiber was assumed to have a cylindrical shape. Two values of diameter were measured perpendicular to each other at the middle of specimen using a Mitutoyo micrometer. This aimed to minimize mechanical damage to the fiber from micrometer squashing. The average diameter was then used to calculate the cross-section area of fibers. The average mechanical measurements were taken from at least five specimens of each sample. The fibers were supported by a paper frame during sample loading to avoid bending or breaking and the frame was cut prior to the stress–strain scan.

### Moisture regain measurements

The moisture regain of alkaline-treated and AN-grafted hemp fibers at a relative humidity (RH) of 0, 65, and 93% was obtained by placing 1 g of sample over phosphorus pentoxide or saturated aqueous solutions of magnesium acetate and ammonium phosphate, respectively, at 25°C for 1 week. A desiccator-weighing procedure was performed to control the relative humidity of the sample during the measurement. The amount of moisture regain was based on the calculation using the dry weight of fibers at 0% RH.

### Fractographic analysis

SEM was used to observe the microstructure and the surface morphology of treated and untreated cellulose fibers. The instrument was a Phillips XL 30 Oxford 6650 SEM with an acceleration voltage of 142 eV. The samples were coated with gold to provide about a 200-Å gold layer thickness using a vacuum sputter coater.

## RESULTS AND DISCUSSION

### Acrylonitrile grafting yield

#### Effect of the concentration of AIBN

The effect of concentration of AIBN on the grafting yield is shown in Table I. With an increase of AIBN concentration from 2 to 5% wt/v, the grafting yield increased gradually from 1.56 to 10.46%. This result suggests that AIBN was mostly responsible for the generation of free radicals on the cellulose backbone for the initiation of the graft copolymerization. The active sites may be increased on the cellulose backbone for grafting at higher concentrations of the initiator.

#### Effect of the ratio of an monomer to hemp fiber

Grafting yields were increased with AN monomer to hemp fiber ratio as presented in Table I. The best explanation for this effect can be seen with the use of 5% AIBN, which provided a dissimilar amount of grafting. The higher ratio provided a better yield because of the adsorption ability of AN into the fiber; conversely when the ratio of AN to fiber was low, the available AN molecules in the fiber was less so that the grafting yield was lower too.

### Fourier transform infrared spectroscopy

Infrared spectra of flax and hemp fibers after acetone extraction and the alkalization by NaOH are shown in Fig. 1. The acetone-extracted hemp fiber spectrum is similar to that of the untreated hemp, although a light green extract was observed during Soxhlet extraction. However, the adsorption band at 1730 cm$^{-1}$ attributed to the C = O stretching vibration disappeared after NaOH treatment. This is due to the removal of the carboxyl or carbonyl groups present in the fiber as a trace of fatty acid present in absorbed oils.[14] The main spectral changes were an increase of the 898 cm$^{-1}$ band, attributed to the symmetric in-phase ring-stretching mode, and a decrease in the 1430 cm$^{-1}$ band
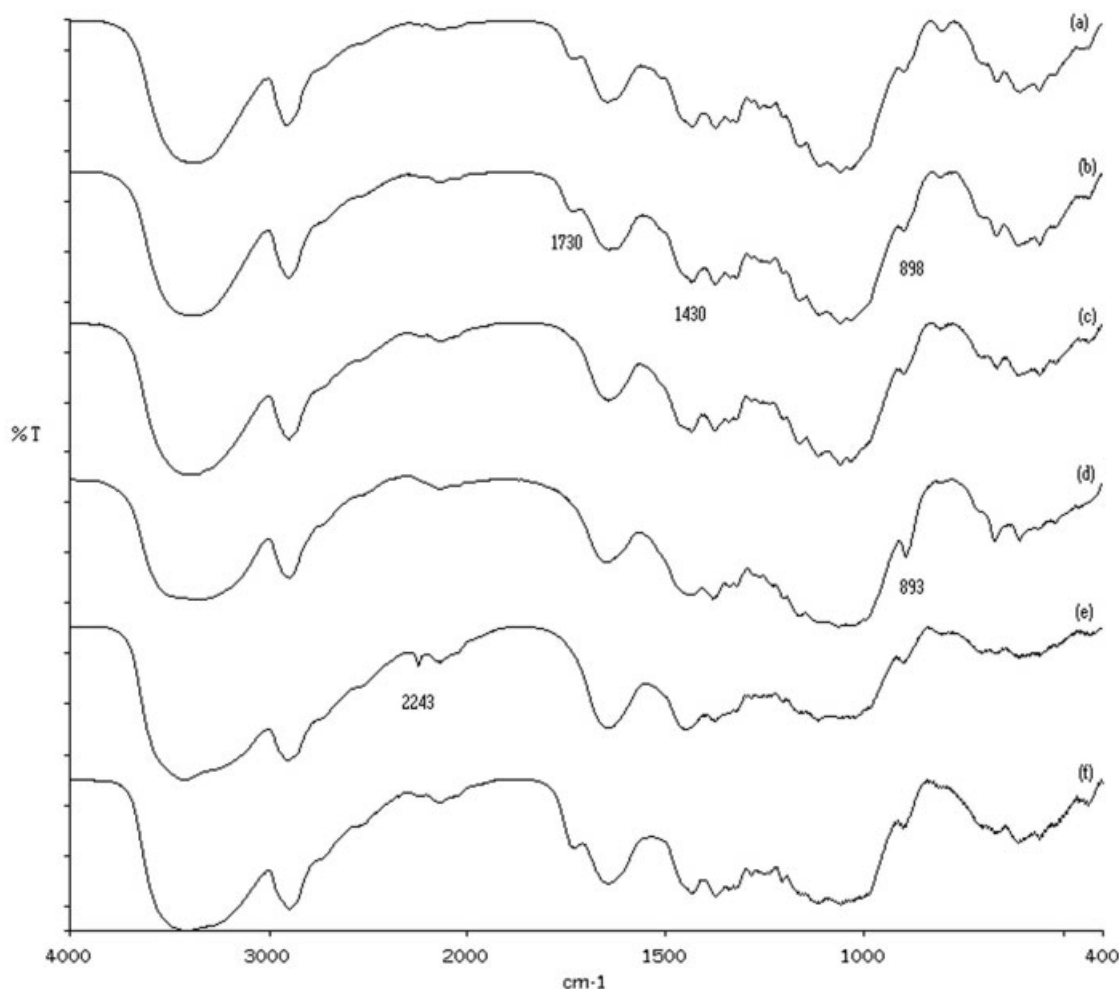
**Figure 1** Infrared spectra of hemp and flax fibers for measurements of lateral crystallinity. (a) Untreated hemp; (b) acetone-extracted hemp; (c) 8% NaOH-treated hemp; (d) 20% NaOH-treated hemp; (e) 2.94% acrylonitrile-grafted hemp; and (f) untreated flax.

attributed to $CH_2$ bending. This observation shows that the crystalline structure of the fibers was changed from cellulose I to cellulose II after NaOH treatment. The IR crystallinity (or lateral order) index was calculated from the absorption ratio at 1430 and 898 cm$^{-1}$.[15] The intensity of the 1430 cm$^{-1}$ band was reduced while the 898 cm$^{-1}$ band was increased and shifted to 893 cm$^{-1}$ with an increase of NaOH concentration. This suggests that the formation of amorphous cellulose and cellulose II took place after mercerization. The crystallinity index showed a quite stable value at low NaOH concentration, 3–8% (Fig. 5a), and then a dramatic drop occurred and it reached a stable value of 15%. Variation in this ratio showed that the transition took place over the range of NaOH concentration from 8 to 12% for flax and 8 to 15% for hemp. The significant drop of crystallinity index and the earlier transformation to cellulose II of flax were an indication of a lower alkalinity resistance compared with hemp.

An infrared spectrum of acrylonitrile grafted hemp fibers is shown in Fig. 1f. The band at 2243 cm$^{-1}$ arising from the stretching vibration of $C \equiv N$ was used for characterization of the modified hemp. The intensity of this band cannot be used for quantitative determination of the degree of grafting because internal grafting of the fibers may result in an underestimated intensity.

## Wide angle X-ray diffraction

Figures 2 and 3 show X-ray diffractograms of hemp fiber and flax, respectively. Untreated fiber shows the characteristics of cellulose I. As the concentration of NaOH increased, the crystalline transformation to cellulose II can be seen. The major diffraction planes of cellulose, namely 101, 10$\bar{1}$, 021, and 002, are present at 14.8, 16.7, 20.7, and 22.5 2$\theta$ angles.[16] Alkaline treatment caused a decreasing intensity of the 002 plane and an increasing intensity of the 10$\bar{1}$ and 021 planes.

A separation of the peak due to each diffraction plane was achieved through curve fitting using a set of pseudo-Voigt curves to fit the experimental data. This operation resulted in the disappearance of the amorphous diffraction for calculation of the crystallinity index using the equations[5,17]
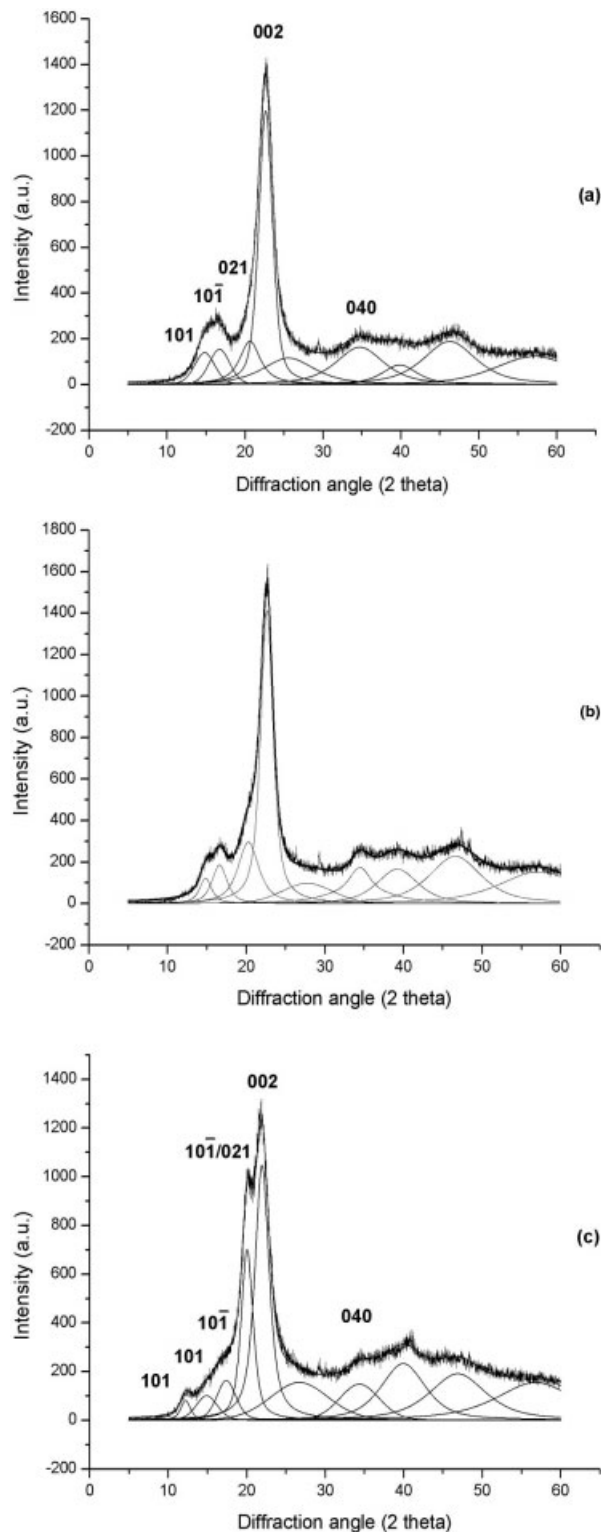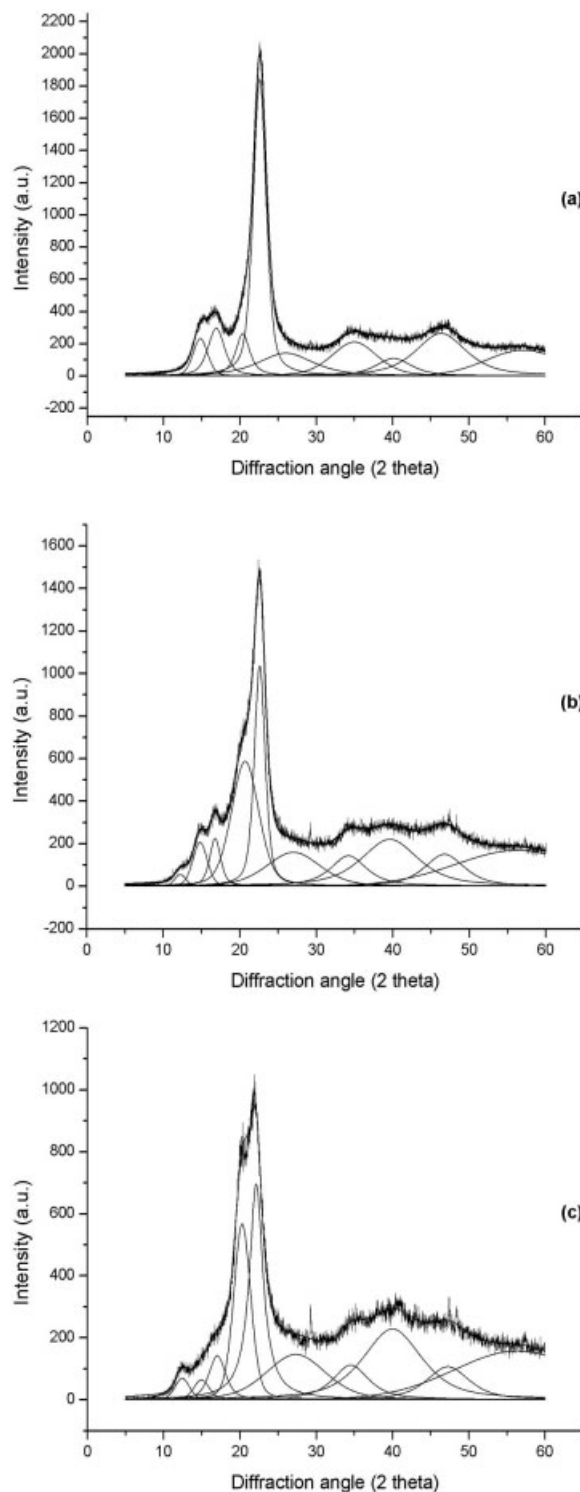


**Figure 2** Wide angle X-ray diffractogram and fitted data for hemp fibers: (a) acetone-treated hemp;(b) 12% NaOH-treated hemp; (c) 20% NaOH-treated hemp.

A new 101 diffraction plane at the lowest 2θ (Fig. 2c) represented the introduction of cellulose II after treatment.



**Figure 3** Wide angle X-ray diffractogram and fitted data for flax fibers: (a) acetone-treated flax; (b) 12% NaOH-treated flax; (c) 20% NaOH-treated flax.

$$CrI = 100\frac{I_{002} - I_{Amorph}}{I_{002}}, \qquad (1)$$

where $CrI$ is the degree of crystallinity, $I_{002}$ is the maximum intensity of the (002) lattice diffraction, and $I_{Amorph}$ is the intensity diffraction at 18° $2\theta$ degrees, and

$$Cryst(\%) = \frac{A_{cryst} \times 100}{A_{total}}, \qquad (2)$$

where Cryst (%) is the percentage of crystallinity, $A_{cryst}$ is the area from the (002) plane, peak at $2\theta$ = 22.6°, and from the (101) and (10$\bar{1}$) plane, peak at 13–18°, and $A_{total}$ is the area below the whole region.

These two methods used the amorphous fraction in terms of intensity and area to calculate the crystallinity index. The selected position that was assigned to the amorphous fraction was the diffraction angle at around 18° $2\theta$. A disadvantage of these two methods was the difficulty in defining the exact amount of amorphous fraction. Hence, performing the calculation without using an amorphous and crystalline standard would yield a result not representative of absolute sample crystallinity.

From the X-ray results, there was an increased intensity at 16.7 and 20.7° $2\theta$ that represented the 10$\bar{1}$ and 021 planes. The appearance of these nonparallel fiber axis diffraction planes occurred while there was a decline of the 002 fiber diffraction plane. This seemed to indicate that the degree of perfection of the best ordered fraction, 002, in the fiber was changed. It is important to note that the crystallinity index is used to indicate the order of crystallinity rather than the absolute crystallinity of crystalline regions.[14]

Therefore, the calculation of the X-ray crystalline order index was performed to represent the degree of crystalline order in the fibers. The crystalline order index was determined from the fraction of the ratio of the 002 to the sum of 10$\bar{1}$, 021, and 002 refraction areas:

$$CrI = 100 \frac{A_{002}}{A_{10\bar{1}} + A_{021} + A_{002}}. \qquad (3)$$

The variation of X-ray crystalline order index with NaOH concentration is illustrated in Fig. 5b. The high crystallinity index value, 82+%, of hemp fiber is comparable with the use of diffraction intensity for calculation,[5] although this differed in methodology. Moreover, the X-ray crystalline order index is in good agreement with the IR crystalline index. Figure 4 shows the X-ray diffractogram of AN-grafted fibers. There is no crystalline transformation of the crystalline structure as was observed in other kinds of grafting reactions.[7,8] Only the variation of crystallinity index with grafting amount was found. Figure 5c shows the
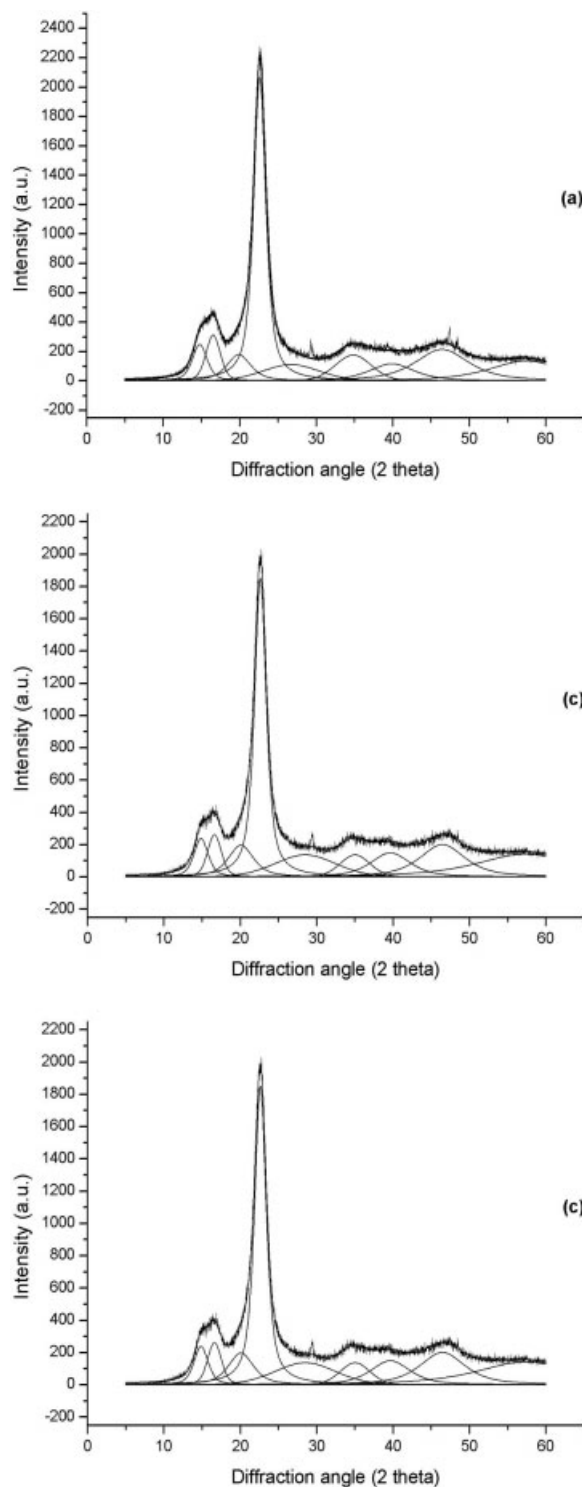


**Figure 4** Wide angle X-ray diffractogram and fitted data for acrylonitrile-treated hemp fibers: (a) 1.56% AN-grafted hemp;(b) 8.34% AN-grafted hemp; (c) 10.46% AN-grafted hemp.

X-ray crystalline order index of treated hemp. The crystalline index increased with grafting content up to 2.94% and then decreased as the grafting content increased. This result suggests that a low grafting
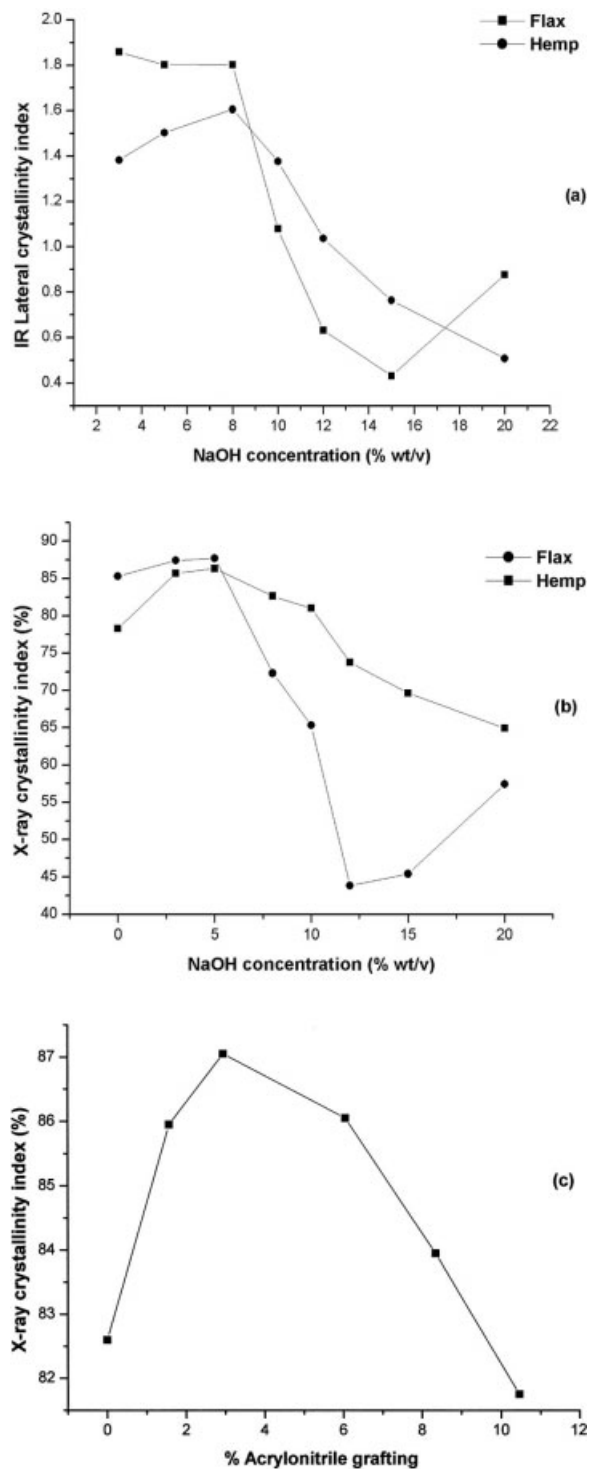
**Figure 5** Crystallinity index dependence on NaOH concentration and grafting amount (a) IR crystallinity index of NaOH-treated hemp and flax fiber; (b) X-ray crystallinity index of NaOH-treated hemp and flax fiber; (c) X-ray crystallinity index of AN-grafted hemp.

amount may create an orderly arrangement of PAN units, resulting in the increase of X-ray crystallinity index.[18]

## Mechanical properties

The mechanical properties of alkaline-treated and AN-grafted hemp are shown in Figs. 6 and 7 respectively. The average values are presented with 95% confidence
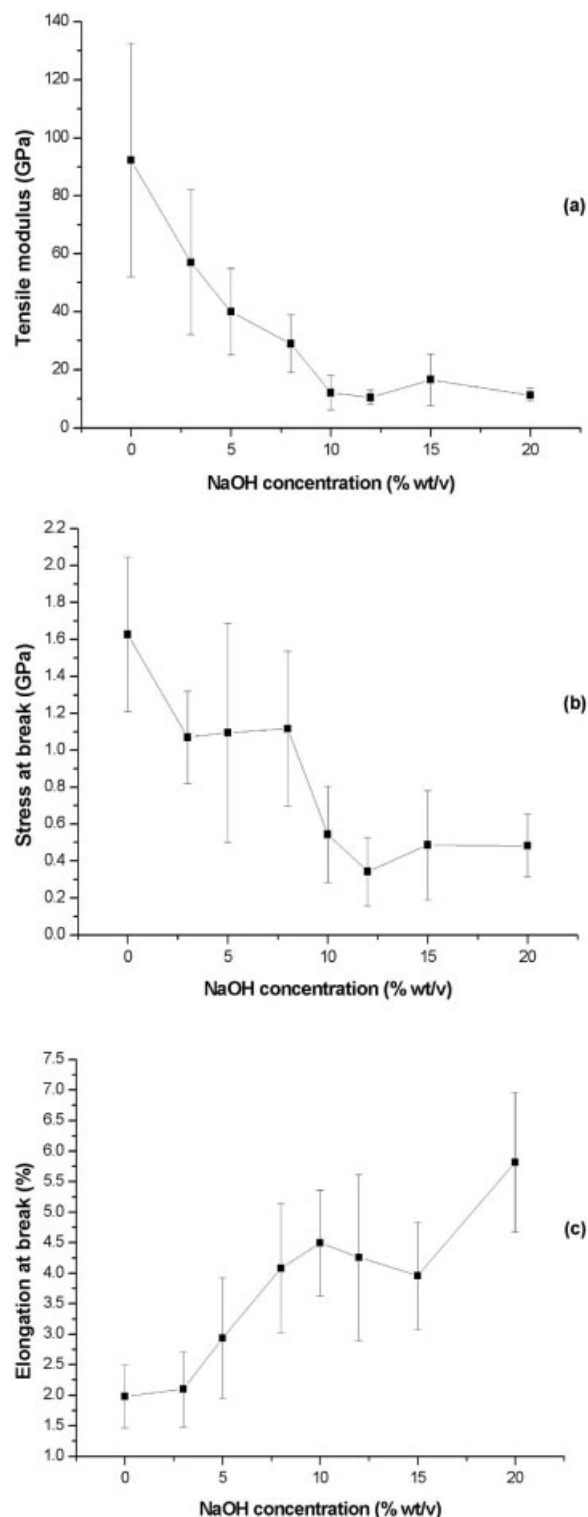


**Figure 6** Mechanical properties of alkaline-treated hemp single fiber: (a) Tensile modulus; (b) tensile stress at break; (c) elongation.
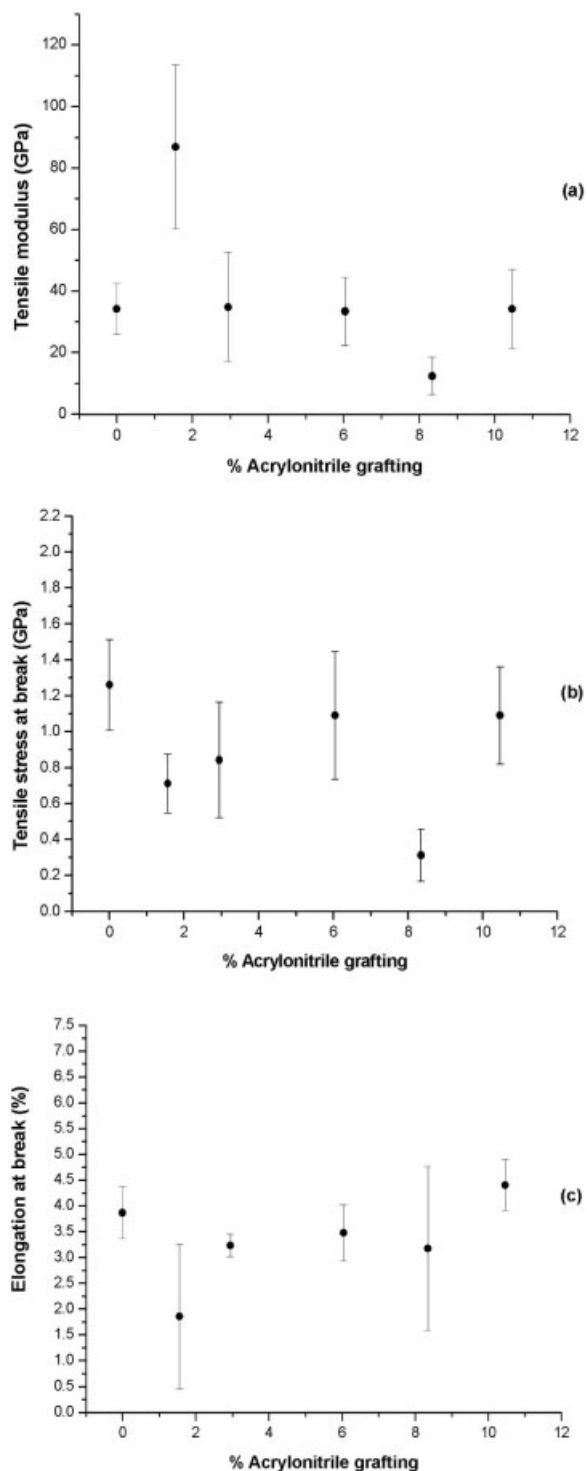
**Figure 7** Mechanical properties of acrylonitrile-grafted hemp single fibers: (a) tensile modulus; (b) tensile stress at break; (c) elongation.

showed a sudden decrease after treatment with 10% NaOH where the transition to cellulose II started to take place. The elongation at break increased with NaOH concentration. The values are in a typical range of hemp mechanical properties reported elsewhere.[19] The mechanical properties of AN-grafted hemp (Fig. 7) show a variation with graft amount. The grafting, however, produced little degradation effect on the mechanical properties.

## Moisture regain

The moisture regains of alkaline-treated and AN-grafted hemp fiber at 65 and 93% RH are presented in Fig. 8. Moisture can be adsorbed at high relative humidity. The difference is about 6% for the entire range of modifications. The increase of NaOH concentration gave slight increases in moisture regain (Fig. 8a), indicating that the higher concentration alkaline-treated
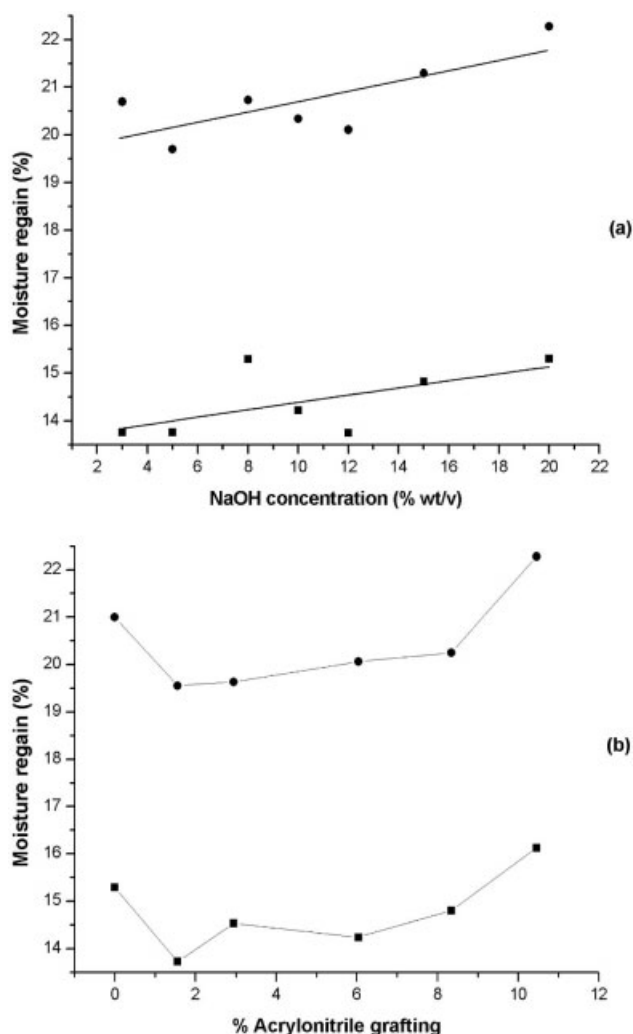


**Figure 8** Moisture regain of hemp fibers with humidity variation, (■) 65% RH, (●) 93% RH: (a) after NaOH treatment; (b) after acrylonitrile grafting.

interval variation. The modulus of the fibers decreased gradually with NaOH concentration and remained constant after 10% NaOH treatment. This is probably due to the reduction of lignin content that will bind the cellulose fibers together. The tensile properties
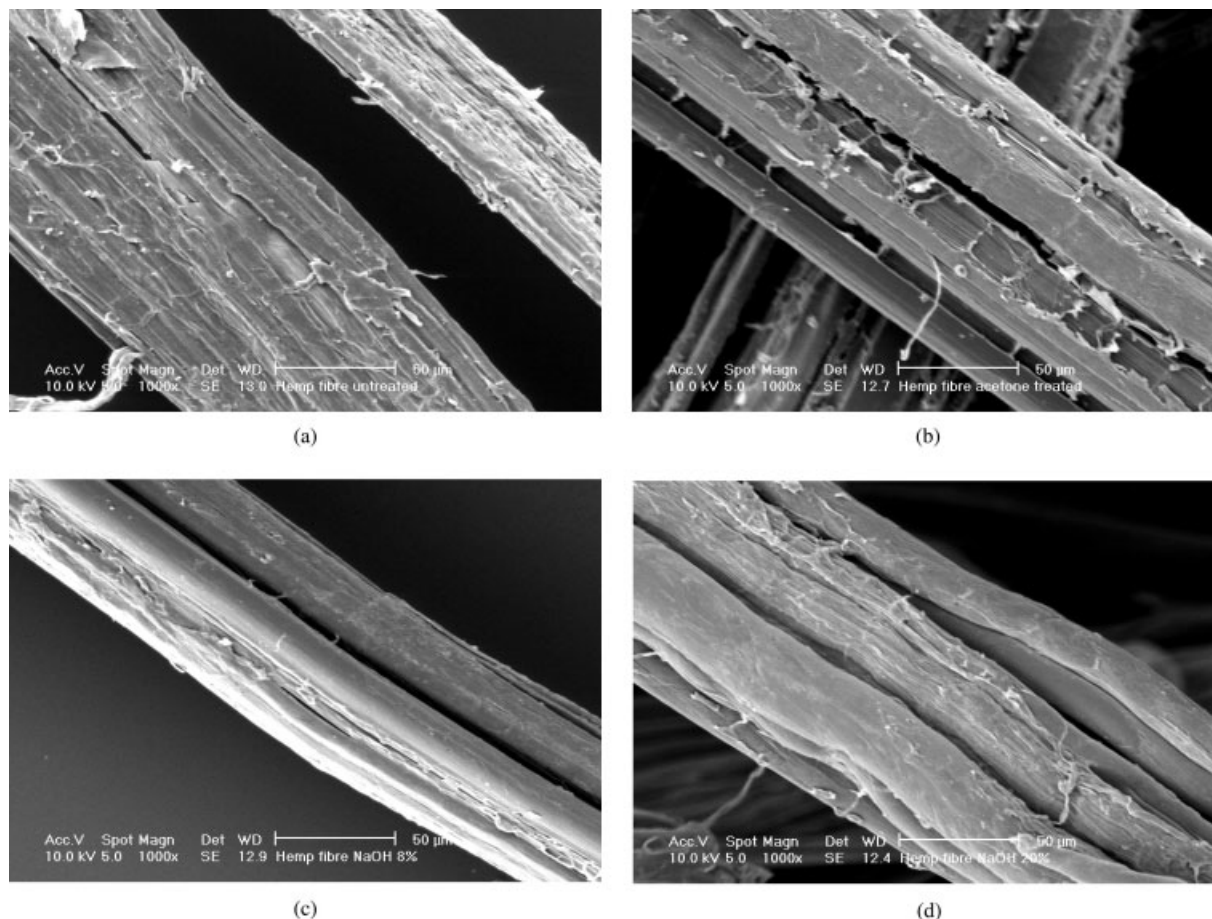
**Figure 9**    SEM photomicrographs of hemp: (a) untreated hemp; (b) acetone-treated hemp; (c) 8% NaOH-treated hemp; (d) 20% NaOH-treated hemp.

fibers are more accessible to water vapor than the lower concentration treated fibers. This result agrees with the reduction of lateral crystalline index observed from IR and WAXRD measurements.

Figure 8b shows a small reduction of about 1% of moisture regain for AN-grafted fiber compared with untreated fiber. However, the degree of reduction was lower than that of the AN-grafted cellulose using UV radiation.[12] This probably arises from the difference in the location of the grafted molecules. The grafted molecules of UV-irradiated fibers were limited to near the surface of the cellulose fibers. Nevertheless, the observed value was comparable with grafting using a ceric salt-initiated grafting system.[20] Instead of reducing moisture regain with increased amount of grafting, the grafted fiber showed quite stable values and even a slight increase when there was an increased amount of grafting. Especially the moisture regain at 10.46% grafting was significantly higher than that of ungrafted fiber. This behavior may be explained by the physical change of the fiber on grafting. The existence of polyacrylonitrile seemed to have a pronounced effect on the pore structure of the grafted fibers. The BET surface area, cumulative pore volume, and adsorption pore diameter were

found to dramatically expand, as shown in Table I. This fiber characteristic enhanced the penetration of water into the fibers, resulting in a smaller reduction of moisture with increased amount of grafting than expected, particularly in the case of the large surface area obtained with 10.46% grafting.

### Fractographic analysis

#### Hemp fiber treatment

SEM images at magnifications between 500 and 2000 were obtained for untreated and treated fibers under all conditions reported in this work. Figure 9a–d shows the transformation of hemp fiber with acetone and NaOH treatments. The surface of untreated raw hemp fiber shows considerable roughness due to the presence of lignin and waxes (Fig. 9a), which are partially removed with acetone (Fig. 9b) and further removed with NaOH treatment (Fig. 9c), resulting in a smooth surface, suitable for polymer grafting. The treatment of hemp fiber with 20% NaOH damaged the fiber and caused separation of individual segments, as shown in Fig. 9d. These results correspond well with the investigation of the mechanical properties.
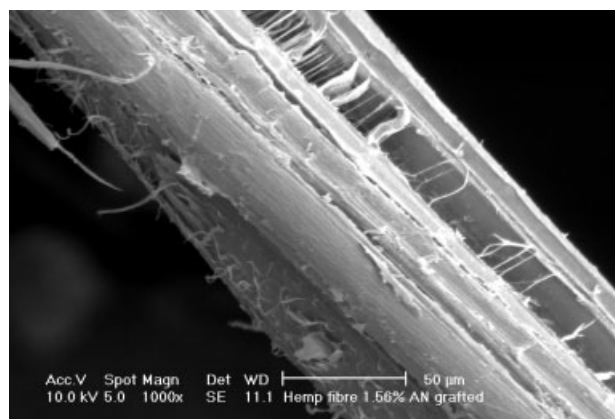
(a)
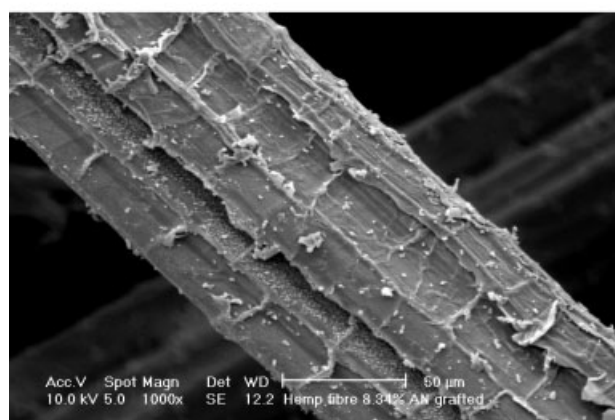


(b)
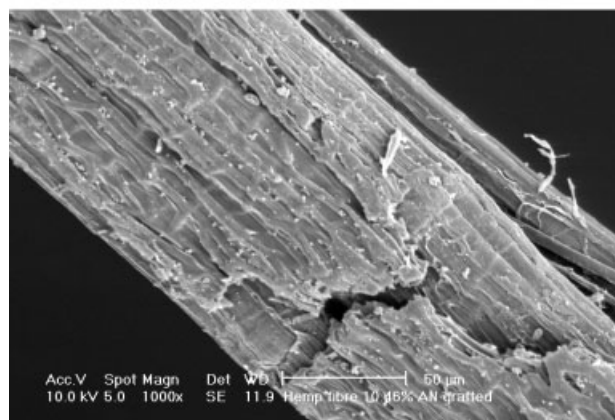


(c)

**Figure 10** SEM photomicrographs of acrylonitrile-grafted hemp: (a) 1.56% grafted; (b) 8.34% grafted; (c) 10.46% grafted.

AN–AIBN grafting of hemp fibers

Figure 10a–c shows hemp fibers initially treated with acetone and 8% NaOH subjected to AN grafting with 1.56, 8.34, and 10.46%. The amount of grafting is directly correlated with the thickness of the AN-grafted layer on the fiber, providing more structure, and increased surface area for adhesion with a polymer matrix and improved environmental resistance of the fiber.

## CONCLUSION

Modification of hemp and flax fibers by solvent extraction, alkalization, and AN grafting of hemp fibers wewasre carried out in this study to obtain better surface properties of hemp fibers, while maintaining good inherent mechanical properties. The amount of grafting was controlled by initiator concentration and monomer/fiber ratio. Moreover, a low-pressure solvent-free grafting technique prevented the fiber from undergoing crystalline transformation. The morphology changed after treatment from cellulose I crystalline structure to cellulose II. The internal pore structure was changed after grafting. A combination of WAXRD and FTIR techniques was used to investigate the crystalline development. The results showed a good correlation and resulted in a new method for the calculation of crystalline order index. Finally, a large increase of surface area after modification may be suitable for composite application to obtain better fiber–matrix adhesion.

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