

INVESTIGATION OF THE CHEMICAL STRUCTURE OF CARBOXYLATED AND CARBOXYMETHYLATED FIBERS FROM WASTE PAPER VIA XRD AND FTIR ANALYSIS

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This paper describes preparation of carboxymethylated and carboxylated cellulosic fibers from waste paper. Chemical properties of the product were distinguished by Fourier-transform infrared (FTIR) spectroscopy and X-ray diffraction (XRD) spectral analysis. To produce carboxylated and crosslinked fibers and also to increase the anionic surface charge of the fibers, maleic anhydride was used in three different batches; 0, 1%, and 5%. The treatment condition for producing carboxymethylated fibers also involved the use of isopropanol, sodium hydroxide solution, and monochloroacetic acid. The product was purified with 70/30 methanol/water. Then one sample was neutralized with acetic acid and the other was considered as a sample without having been neutralized. Effects of these treatments were evaluated by FTIR and XRD analysis. The results of FTIR analysis indicated that the carboxyl and methyl functional groups had increased in the carboxymethylated fibers and that just carboxyl groups had increased in carboxylated fibers. The results of XRD analysis showed that the crystallinity of cellulose had decreased in both the carboxymethylated and carboxylated fibers.

Key words: Ether cellulose; Carboxymethylated fiber; Carboxylated fibers; Crystallinity index; XRD; FTIR

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INTRODUCTION

Our purpose in this research was to increase the number of carboxyl groups of cellulosic fiber and thereby increase its capacity to bond to cationic materials and its ability to retain those materials. The charged nature of a cellulosic fiber surface is expected to play major roles in such phenomena as fiber dispersion, flocculation, adhesion, and adsorption of polyelectrolytes (Hubbe 2006). Several studies concerned with the production of carboxymethyl cellulose from different fibers and chemical surface modification of cellulose fibres have been published, and the effect of these treatments on the properties of cellulose fibers have been considered by different analyses. Carboxymethyl cellulose (CMC) and alkali cellulose are the most important cellulose derivatives. Cellulose is a linear and high molecular weight polymer that can be described as natural, renewable, and biodegradable (Heydarzadeh et al. 2009). Due to hydrogen bonds that are associated with the structure of the molecular cellulose, it neither melts nor dissolves readily in common solvents (Adinugraha and Marseno 2005). The most important and most widely used cellulose ether is carboxymethyl cellulose (CMC),

having an annual worldwide production of about 300,000 tons (Jardeby et al. 2005). CMC is used in the detergent, food, textile, pharmaceutical, and paint industries. High purity grades are employed as food additives (Pushpamalar et al. 2004). CMC is often used for improvement of paper quality, as it can participate in the development of bonds between the cellulosic fibers. A film coated on the fibers by CMC gel tends to enhance the physical properties of paper for printing purposes (He et al. 2009). Due to the importance of its multiple applications, CMC and its sodium salt (NA-CMC) are commercially produced in much higher amounts than any other cellulose ether. These products are prepared by the reaction of monochloroacetic acid or sodium monochloroacetate with alkali cellulose (Luo and Neogi 2006; Heydarzadeh et al. 2009). CMC has been synthesized from raw cellulose, wood, paper sludge, cotton-linter fibers, banana plants, and sago pulp (He et al. 2009; Heydarzadeh et al. 2009; Jardeby et al. 2005). In pulp samples, by virtue of its hydroxyl groups, cellulose is a polar molecule that can form hydrogen bonds with other polar molecules, such as other cellulose molecules. Wood pulp fibers also contain hemicelluloses, a component that has a moderate number of carboxyl groups, providing the fibers with an overall negative charge. Accordingly, cellulosic fibers have some natural tendency to retain certain other materials by charge interactions. The addition of fixed anionic sites (carboxyl groups) to cellulose fibers provides the fibers with additional positions through which bonding to cationic species can occur. The number of carboxyl groups added to a fiber is particularly critical and can be controlled to provide fibers having the desired capacity to retain certain materials. The more highly anionic fibers would be expected to interact more strongly with cationic additives such as cationic starch, wet-strength resins, and cationic retention aids.

In general, as used herein, the term “bond” refers to the electrostatic attractive force between oppositely charged materials, such as the anionic sites of a cellulose fiber and a cationic retention aid or positively charged filler particle. Stenstad et al. (2008) used succinic and maleic anhydrides coupled to the (MFC) microfibrillated cellulose through reaction with the surface hydroxyls under water-free conditions. In studies of the effects of fibre surface chemistry on the properties of cellulose fibre see Isogai (2001), as well as Lindström and Wagberg (2002), and for modified cellulose fibres by silanization see (Joseph et al. 1996). The negatively charged cellulose microfibrils resulting from surface modification with anhydrides may have application in nanoscale electronic and optoelectronic devices (Li and Xia 2004).

EXPERIMENTAL

Carboxylation Process

White paper produced from recycled fibers was used as raw material. This was obtained from a local market with Copimax brand name, with basis weight 80 g/m², produced by the Sepahan Company. In this research the experimental treatments were conducted based on earlier work (Hubbe 1999). In the first experiment the entire waste paper was pulped at 4% consistency in a laboratory mixer; then the pulp was dried under ambient conditions to about 95% solids content. The pulp was treated with 1% by weight maleic anhydride (MAH) powder, based on dried fibers, with a purity of 99% (Merck,

Germany), and the mixture was tumbled to uniformly distribute the powder in the pulp. The pulp samples were placed in foil and cured for 10 minutes at 115 °C in a conventional oven (Memmert oven). After curing, the pulp was rinsed with distilled water. The pH of the samples was measured in 3 stages with a pH meter (Metrohm, Switzerland). The pH of samples before treatment was 9, after curing in the oven it was 8.5, and after rinsing with distilled water it was 8. In the second experiment the procedure of experiment 1 was repeated, except that the pulp was treated with 5% by weight maleic anhydride (MAH) powder (Merck, Germany). In the second experiment, the pH of the samples again was measured in 3 stages, with the following results: before treatment pH=9, after oven curing pH=8, and after rinsing with distilled water pH=7.5.

Carboxymethylation Process

Recycled paper from the same source was used in a second set of experiments. The experimental procedure for the treatment process was as described by Luo (2006). In the first experiment the entire waste paper batch was pulped at 4% consistency in a laboratory mixer then dewatered to about 40% consistency, after which it was mixed with 11 mL isopropanol with purity of 99.5% (Merck, Germany), and 25% sodium hydroxide with purity of 98% (Merck, Germany). The mixture was diluted with distilled water with 50% weight of sodium hydroxide. The excess sodium hydroxide from the pretreated fibers was removed with a filter press. Then 46% monochloroacetic acid was added, and the mixture heated at 70 °C in a conventional oven (Memmert oven) for 3.5 hours. The product carboxymethylated cellulose was purified by washing with a solution containing 70% methanol with purity of 99.9% (Merck, Germany) and 30% water. The solution pH was measured (Metrohm, Switzerland). In the second experiment the procedure of experiment 1 was repeated, except that the pH of the pulp was neutralized by acetic acid with purity of 98% (Romil-SA, England).

Fourier Transform Infrared analysis

To determine the content of carboxyl groups in carboxylated fibers and carboxyl, methyl groups in carboxymethylated cellulose fibers, the dried powder of samples was analyzed by Fourier Transform Infrared (FTIR, Thermo Nicolet, USA) spectroscopy. A KBR disc technique was used. The range of wavenumber was calculated from 4000 to 400 cm^{-1} . Carboxymethylated fibers were compared with a CMC reference powder (Aldrich Chemical Industry Co., Ltd., USA). It has a viscosity 3000 to about 6000 cp at 25°C (see Fig 4).

X-ray Diffraction Analysis

The measurement of crystallinity in cellulose fibers was carried out by powder X-Ray Diffractometry (XRD, Philips xpert, Netherlands) as described by Segal et al. (1959). Crystallinity (%) was defined as $(I_{002} - I_{am}) / I_{002} \times 100$, where I_{002} is the crystalline peak of the maximum intensity at 2θ between 22° and 23° for cellulose I, and I_{am} is the minimum intensity at 2θ between 18° and 19° for cellulose I. The average size of crystallites was calculated by the Scherrer equation, Eq. 1. This is a method based on the width of the diffraction patterns in the X-ray reflected crystalline region. In this study,

the crystallites size were determined by using the diffraction pattern obtained from 002 lattice planes of pulp samples,

$$D_{hkl} = k\lambda / (B_{hkl} \cos \theta) \quad (1)$$

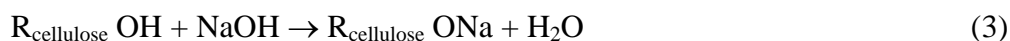
where D_{hkl} is the size of crystallite, k is the Scherrer constant (0.84), λ is the X-ray wavelength, and B_{hkl} is the FWHM (full width half maximum) of the reflection hkl measured at 2θ , the corresponding Bragg angle (Gumuskeya et al. 2003).

RESULTS AND DISCUSSION

The mechanism of polycarboxylic acid crosslinking of papers has been shown to occur in four stages: (1) formation of a 5- or 6-membered anhydride ring from polycarboxylic acid; (2) reaction of the anhydride with a cellulose hydroxyl group to form an ester and link the polycarboxylic acid to cellulose; (3) formation of an additional 5- or 6-membered ring anhydride from polycarboxylic acids pendant carboxyl groups; and (4) reaction of the anhydride with other cellulose hydroxyl groups to form ester crosslinks. These relationships can be expressed by the following equation (Jewell et al. 2003):



Two reactions are necessary for the production of CMC to occur. These are (a) preparation of alkali cellulose, and (b) formation of ether links in which the hydroxyl group of anhydrous glucose is replaced by the carboxymethyl group of monochloroacetic acid. These steps are shown below as Equations (3) and (4) (Feller and Wilt 1990; He et al. 2009; Heydarzadeh et al. 2009).



The main step in the carboxymethylation reaction is the formation of alkali cellulose, which increases the accessibility of fibers to chemicals by swelling. The role of organic solvent in the carboxymethyl cellulose reaction is to provide the accessibility of the reactants in the etherification of the cellulose chain. The polarity of the organic solvent assists the carboxymethylation of cellulose molecule. The polarity of isopropanol is less than that of water. As the polarity of the aqueous media is decreased, the efficiency of the methylation reaction is expected to increase (Heydarzadeh et al. 2009).

FTIR Analysis

FT-IR spectroscopy was used to identify the organic compounds. According to Heydarzadeh et al. (2009), carboxyl, methyl, and hydroxyl functional groups yield bands at wavelengths of 1618, 1426, and 1300 cm^{-1} . The absorbance peaks in the 3300-3400 cm^{-1} region were attributed to the stretching of O-H groups, whereas those around 2800-

2900 cm^{-1} were due to the stretching of C-H (Khalil et al. 2001). Carboxylation of cotton linters was investigated relative to its use in ion exchange, and the effect of these treatments in cotton-linter fibers was considered in relation to the FTIR spectrum (Nada et al. 2009). Modified microfibrillated cellulose (MFC) also was characterized by FTIR (Stenstad et al. 2008). In one study, birch and aspen woods had a thermal treatment and then both their chemical composition and mechanical properties were investigated, and the former was then analyzed by Fourier transform infrared spectroscopy (FTIR) (Kocaefe et al. 2008). FT-IR spectrum has been used for analysis of CMC made from paper sludge (He et al. 2009). According to reported data, the peaks at wavelength of 1620 and 1423 cm^{-1} represent two different functional groups in CMC (Adinugraha and Marseno 2005). In a study characterizing carboxymethyl cellulose and polyacrylamide graft copolymer, a peak at 1603 cm^{-1} was attributed to the presence of carboxyl group and peaks at of 1325 and 1423 cm^{-1} were allocated to methyl and hydroxyl groups (Biswal et al. 2004). Nada et al. 2009 showed that carboxylated crosslinked cotton linters treated with LiCl had higher relative absorbance of COOH at 1720 cm^{-1} and CH_2 at 2920 cm^{-1} , than other treated cotton linters.

The treated samples (carboxylated and carboxymethylated fibers), untreated sample (blank sample), and CMC reference were analyzed by FTIR. Table (1) shows the different infrared data of untreated and carboxylated fibers (see Figs. 1 to 3). Table (2) shows the different infrared data of untreated, carboxymethylated fibers, and CMC reference (see Figs. 1, 4-6). It is obvious that the broad absorption band around 3400 cm^{-1} is due to the stretching frequency of the hydroxyl group ($-\text{OH}$). From Table 3 it is clear that the crystallinity index of carboxymethylated fibers was decreased. This can be confirmed by the shift that occurred for OH group at 3418 to 3443 cm^{-1} in carboxymethylated fibers with neutral pH due to the decrease in hydrogen bonds by breakage of hydrogen bonds in the crystalline part of cellulose chains. Also, from the table, the crystallinity index of MAH treated fibers and carboxymethylated fibers without neutral pH was decreased. This may mean that the wave number of OH groups at 3418 cm^{-1} was decreased by increasing MAH due to the decrease in the amorphous region. The band around 2900 cm^{-1} is due to the carbon-hydrogen bond (C-H) stretching vibration. The presence of a strong absorption band around 1500 to 1700 cm^{-1} confirmed the presence of the carboxyl group ($-\text{COO}$). The bands around 1300 and 1400 cm^{-1} are assigned to methyl ($-\text{CH}_2$) scissoring and hydroxyl group ($-\text{OH}$) bending vibration, respectively. The band around 1050 to 1100 cm^{-1} is due to $>\text{CH}-\text{O}-\text{CH}$ stretching. Tables 3 and 4 show the relative absorbance (ratio of intensity of any band to intensity of band at 1325 cm^{-1} ; Nada et al. 2009) of COOH at 1720 cm^{-1} , OH 3439 and CH_2 at 2920. These tables show that treated fibers had higher relative absorbance of COOH and OH. This is attributed to the increase of swelling of cellulose chains. This result showed the penetration of chemicals through cellulose chains and consequently increases the incorporation of carboxylic groups onto cellulose. As shown in Figs. 1 to 6, there were distinct increases in both the carboxyl groups in pulp samples treated with maleic anhydride, and carboxyl, methyl groups in carboxymethylated fibers. As shown in Fig. 6, for carboxymethylated fibers that had been treated by 46% MCA, 25% NaOH with neutral pH, the percent transmittance at 1614 cm^{-1} was reduced. This is due to the cleavage of ether linkage in treated fibers during neutralization with acetic acid.

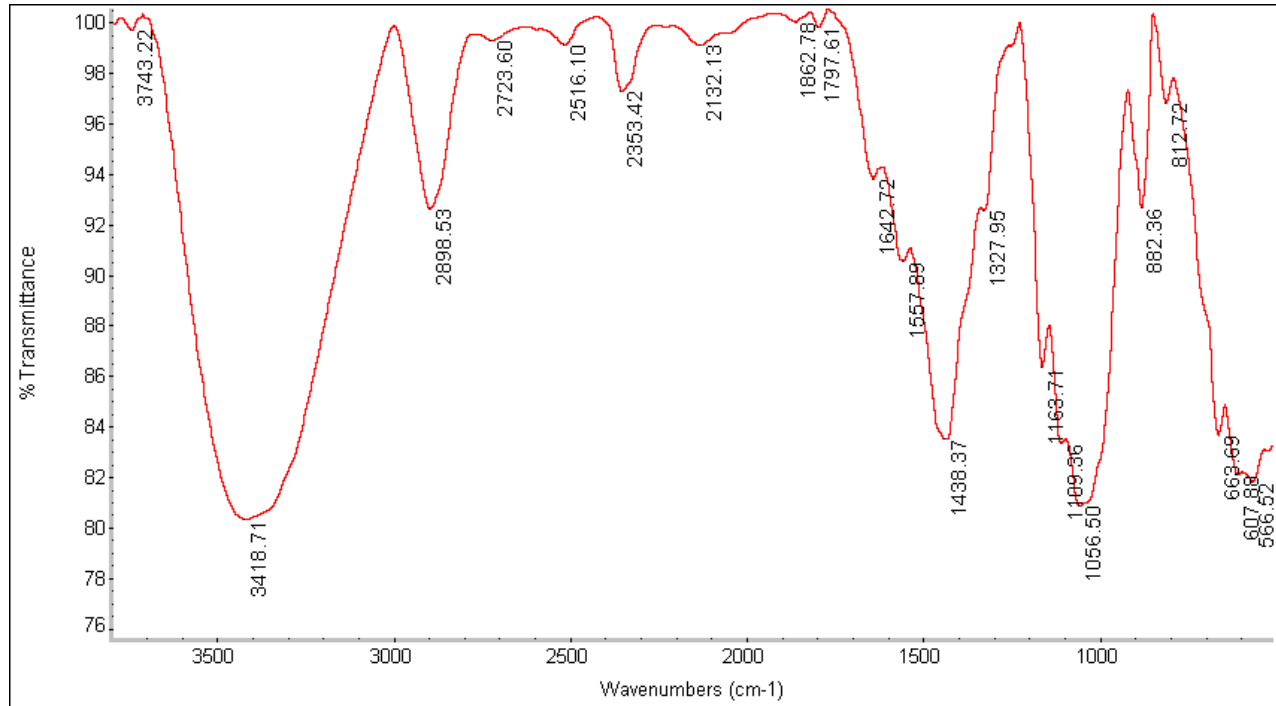


Figure 1. FTIR of blank sample

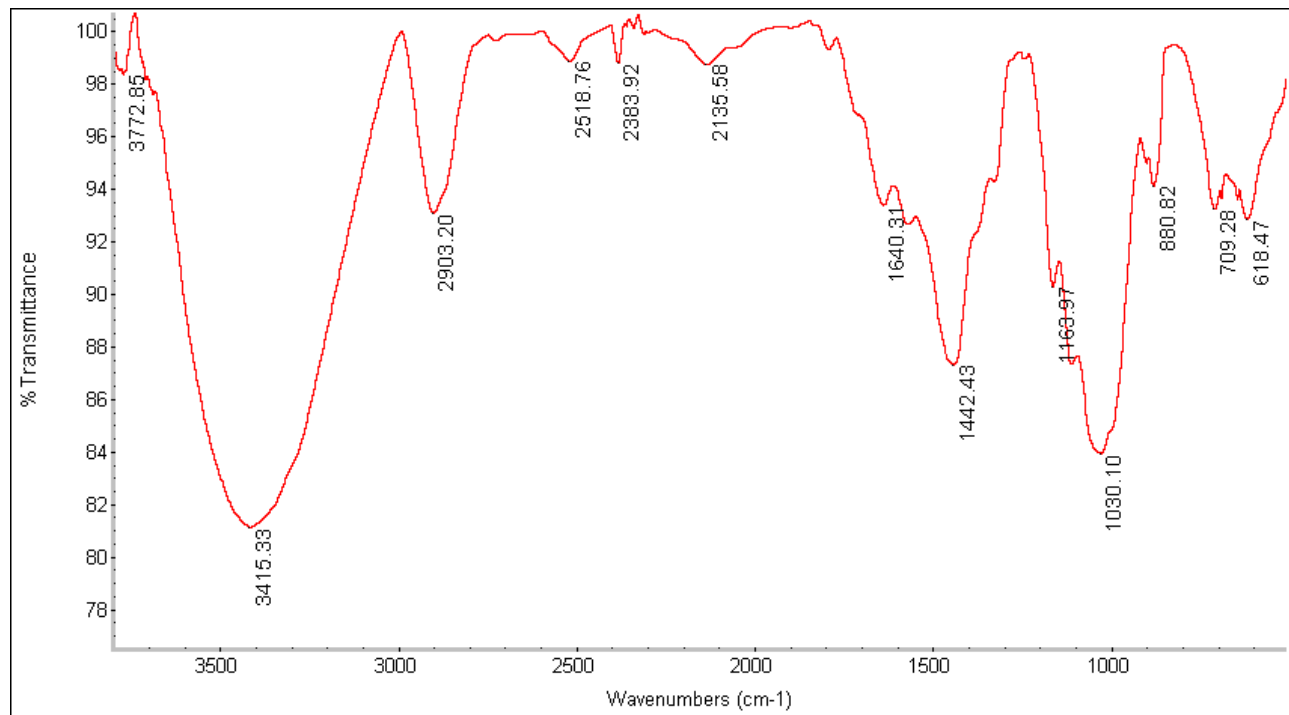
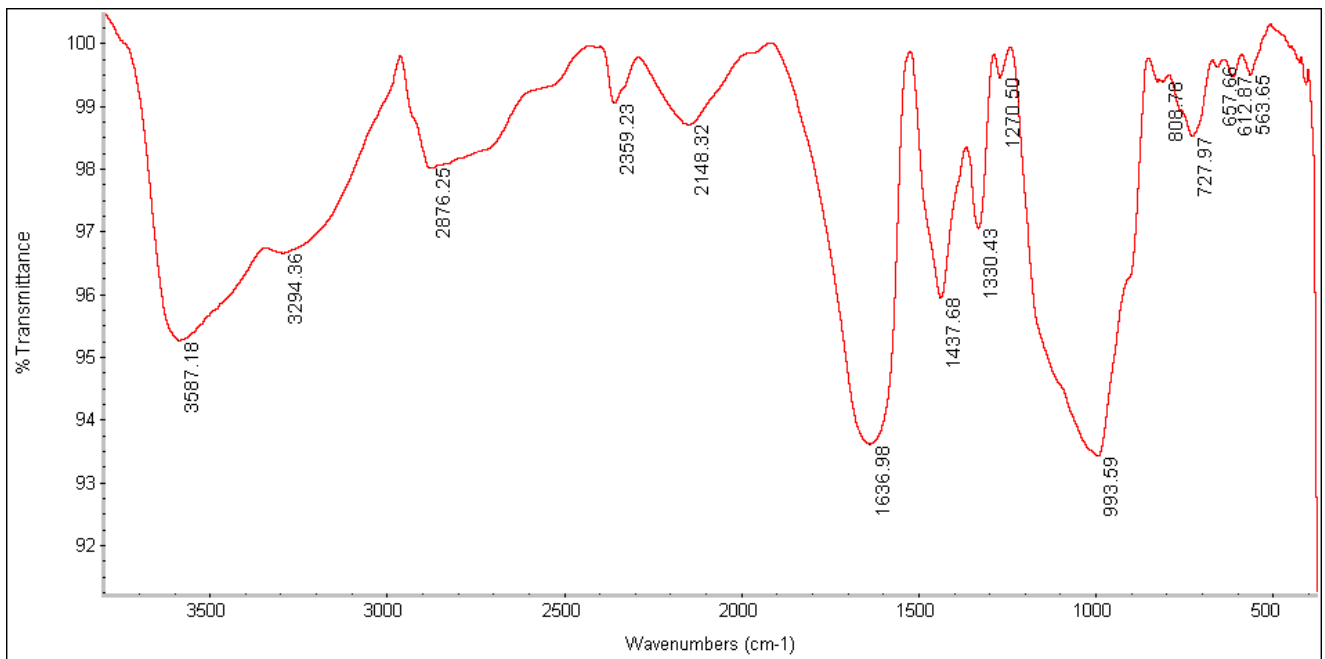
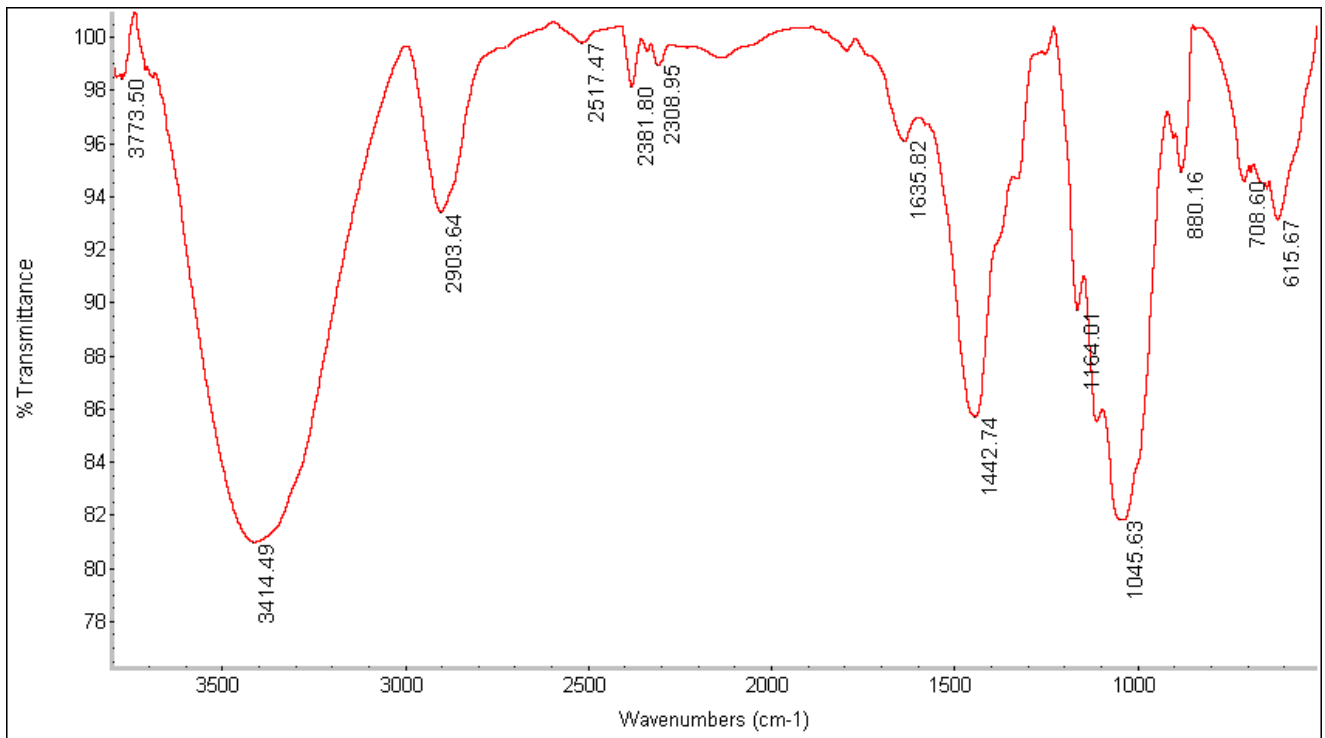


Figure 2. FTIR of sample treated by 1% maleic anhydride



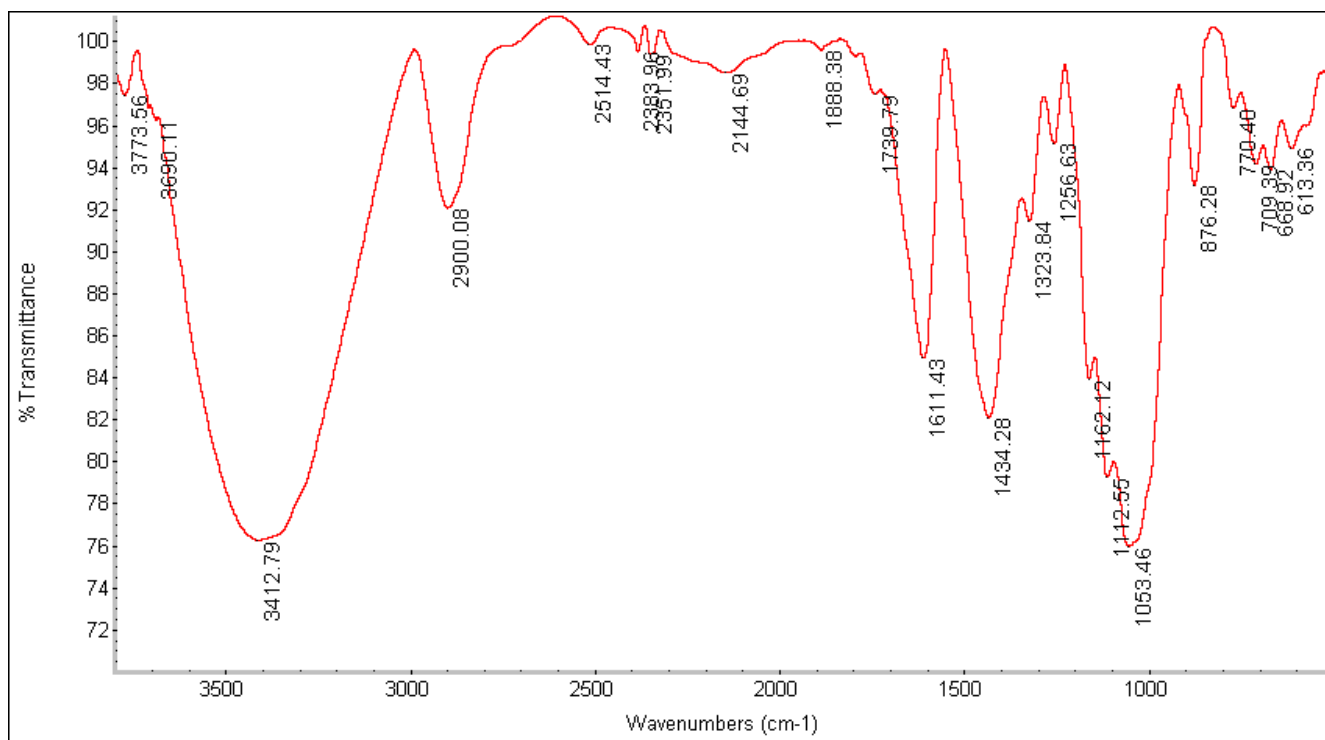


Figure 5. FTIR of sample treated by %46 MCA, %25 NaOH without neutral pH

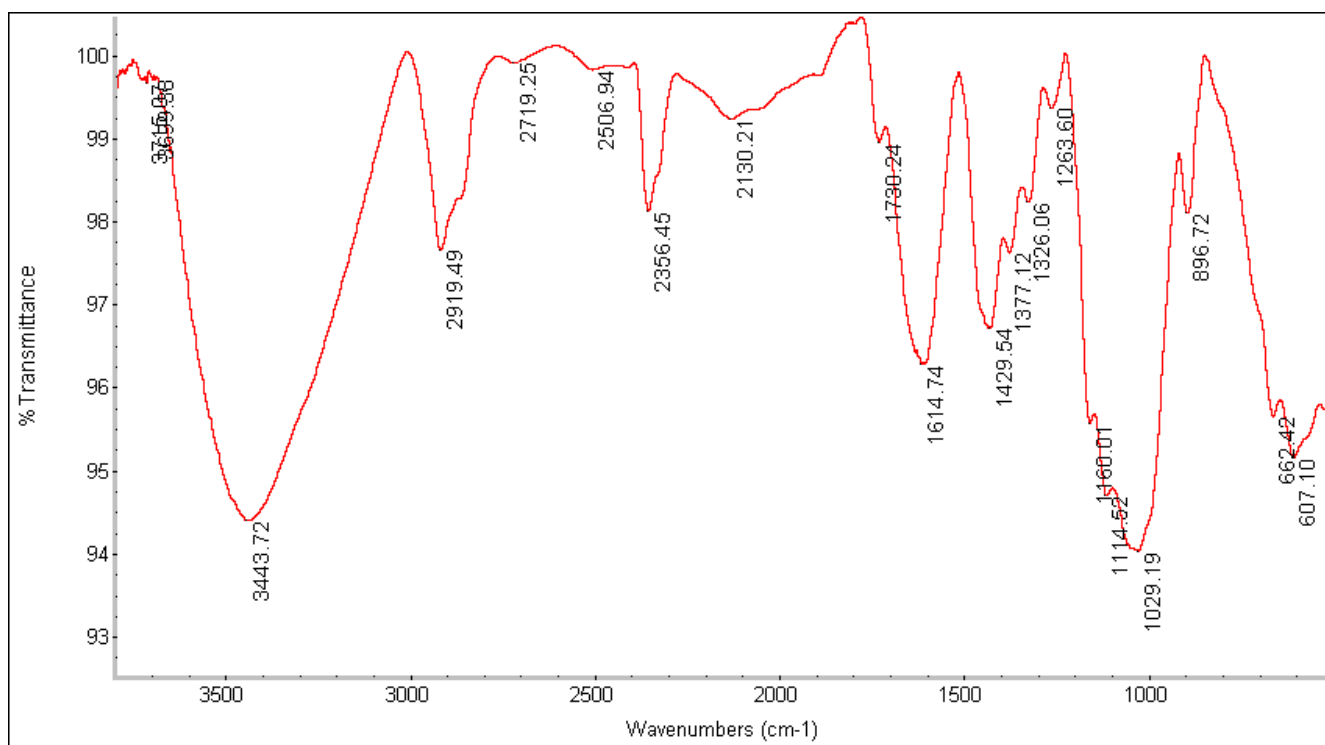


Figure 6. FTIR of sample treated by %46 MCA, %25 NaOH with neutral pH

Table 1. Infrared Spectra of Blank Sample and Carboxylated Fibres

Material	Wavenumber (-COO) (cm ⁻¹)	Wavenumber (-OH) (cm ⁻¹)
Blank sample	1642	3418
Sample treated by 1% maleic anhydride	1640	3415
Sample treated by 5% maleic anhydride	1635	3414

Table 2. Infrared Spectra of Blank Sample, CMC Reference and Carboxymethylated Fibres

Material	Wavenumber (-COO) (cm ⁻¹)	Wavenumber (-CH ₂) (cm ⁻¹)	Wavenumber (-OH) (cm ⁻¹)	
Blank sample	1642	1438	–	3418
CMC reference (Aldrich)	1636	1437	1330	3587
Sample treated by 46% MCA, 25% NaOH without neutral pH	1611 1739	1434	1323	3412
Sample treated by 46% MCA, 25% NaOH with neutral pH	1614 1730	1429	1326 1377	3443

Table 3. Relative Absorbance of Infrared Spectra from CMC Reference and Carboxymethylated Fibers

Material	Relative absorbance of COOH	Relative absorbance of OH	Relative absorbance of CH ₂
Blank sample	0.19	2.37	0.75
CMC reference (Aldrich)	1.5	1.3	0.46
Sample treated by 46% MCA, 25% NaOH without neutral pH	0.56	2.74	0.89
Sample treated by 46% MCA, 25% NaOH with neutral pH	0.57	3.57	1.42

Table 4. Relative Absorbance of Infrared Spectra from Carboxylated Fibers

Material	Relative absorbance of COOH	Relative absorbance of OH
Blank sample	0.19	2.37
Sample treated by 1% maleic anhydride	0.37	2.83
Sample treated by 5% maleic anhydride	0.53	3.87

XRD Analysis

The crystallinity and crystallite size of cellulose fibers in treated samples (carboxylated and carboxymethylated fibers) and untreated sample (blank sample) were analyzed by X-ray diffraction. Table (3) shows the crystallinity and crystallite size of cellulose in pulp samples (see Figs. 7 to 11). The result of XRD analysis showed that crystallinity was decreased in treated fibers. In pulp treatment there was breakage of hydrogen bonds in the crystalline part of cellulose chains, resulting in reduced crystallinity. The proportional crystallinity of cellulose fibers was increased by degradation of hydrogen bonds in the amorphous part of cellulose chains. Crystallinity of cellulose treated with 5% maleic anhydride was higher than pulp samples treated with 1% maleic anhydride; such results might also be attributed to the removal of lignin and hemicelluloses, because of their amorphous nature or more degradation of hydrogen bond in the amorphous part of cellulose chains than the other one. In carboxymethylated fibers consumption of NaOH due to breakage of hydrogen bonds in the crystalline part of cellulose chains and results to reduce the crystallinity. Therefore, NaOH can cause cleavage of the hydrogen bonds in pulp during alkali treatment. It also showed that there was a conversion of cellulose I to cellulose II in treated pulp samples. This can be confirmed by the shift that occurred for OH group at 3418 cm^{-1} to high wave number of caroxymethylated fibers without neutral pH (alkali treated fibers) due to the decrease in hydrogen bond and to low wave number In carboxylated fibers and caroxymethylated fibers with neutral pH (acid treated fibers) due to the increase in the hydrogen bonds by degradation of amorphous parts in cellulose chains (see 1 and 2 tables) according to Nada et al. 2009. This conversion also resulted in peak broadening due to the increase in distance between pulp polymer molecules, thus facilitating the substitution of NaMCA molecules to the pulp polymers.

The higher DS of CMC resulted in a broader crystallinity peak and decrease of the crystallinity. In samples that treated with maleic anhydride (anhydride of carboxylic acid) this resulted in growth crystallite size of cellulose caused by consumption of acid that reason to increase the hydrogen bonds by degradation of hydrogen bond in the crystalline part of cellulose chains. As the results of XRD analysis in this research such as reduce the crystallinity demonstrated that degree of substitution (DS) was increased in carboxylated and carboxymethylated fibers.

The crystallinity of cellulose has been reported in various studies. In a series of native celluloses, wood pulp has about 65%, valonia 65 to 70%, and bacterial cellulose about 40% crystallinity (Hermans and Weidinger 2003). X-ray diffraction has been used for evaluation of the percentage crystallinity in CMC made from paper sludge; this analyses indicated that the product has characteristics of high degree of substitution (DS) and low crystallinity (He et al. 2009). X-ray diffraction has been used for evaluation of the percent crystallinity in CMC made from cavendish banana (Adinugraha and Marseno 2005). The same method also has been used for investigated crystallinity index in carboxylated cellulose for metal ions absorption; in that investigation Nada et al. (2009) explained that consumption of acid causes an increase in the hydrogen bonds by degradation of hydrogen bond in the amorphous part of cellulose chains and also chemical treatment cause to increase crystallinity of cellulose. According to Alemdar and Sain (2007), such an increase in the crystallinity index was expected after chemical

treatment. Nonetheless, it might also be due to the removal of lignin and hemicelluloses, because of their amorphous nature (Joonobi et al. 2009). Adinugraha and Marseno (2005) made this point: “reduce the crystallinity demonstrated that degree of substitution (DS) was increased in carboxymethylated fiber, and the higher DS of CMC resulted in broader crystallinity peak and decrease of the crystallinity”.

Table 5. Crystallinity Index and Crystallite Size of Cellulose in Blank Sample and Treated Fibers

Material	% Crystallinity index	Crystallite size (nm)
Blank sample	49	4
Sample treated by 1% maleic anhydride	36	4.5
Sample treated by 5% maleic anhydride	38	4.8
Sample treated by %46 MCA, %25 NaOH without neutral pH	27	3.6
Sample treated by %46 MCA, %25 NaOH with neutral pH	21	2.5

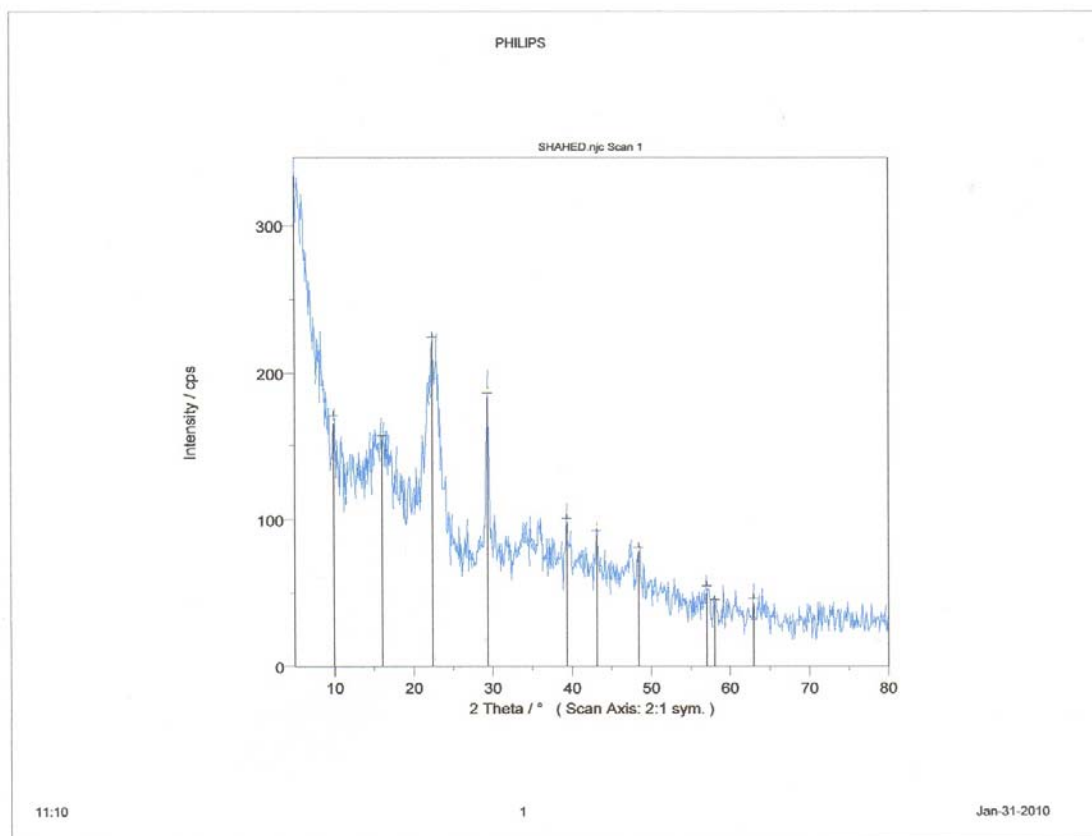
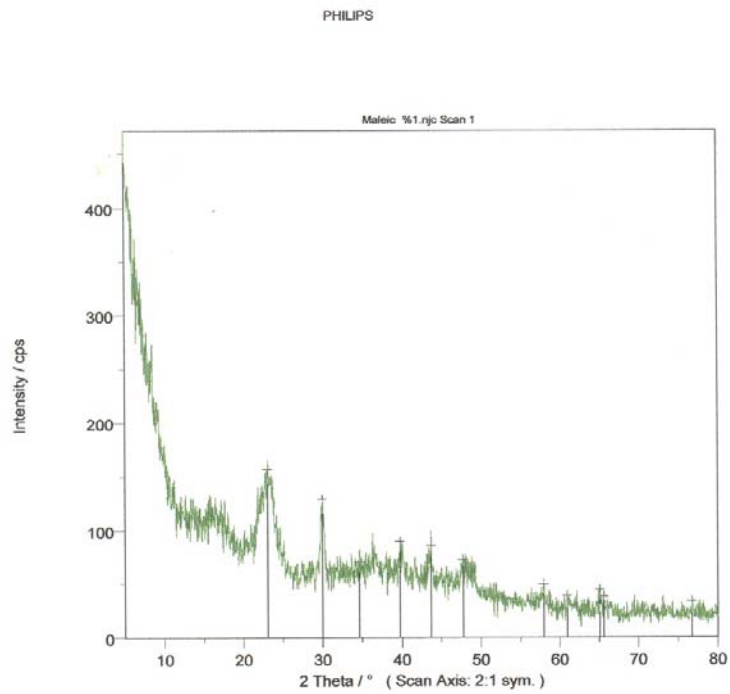


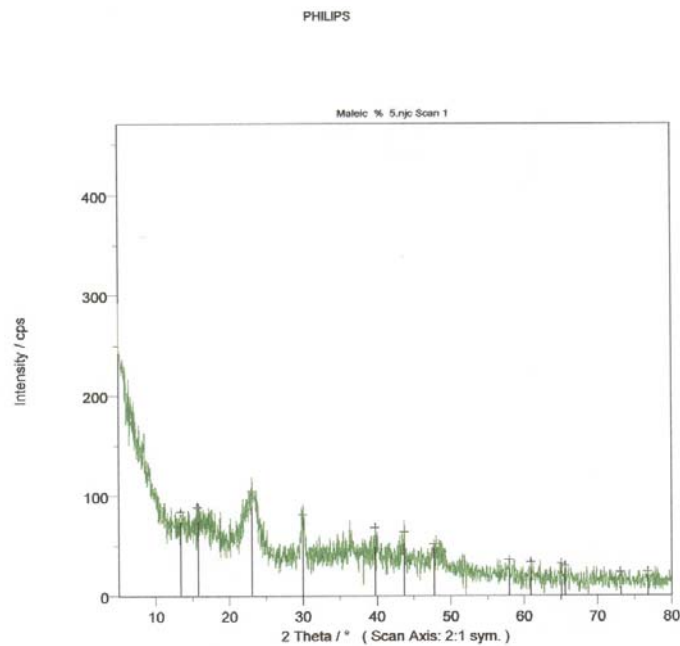
Figure 7. XRD of blank sample



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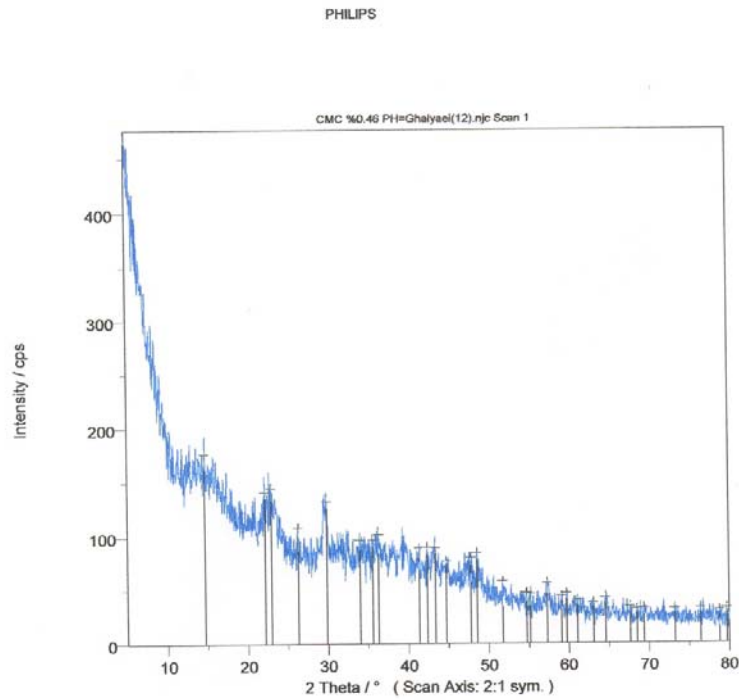
Figure 8. XRD of sample treated with 1% maleic anhydride

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Figure 9. XRD of sample treated with 5% maleic anhydride

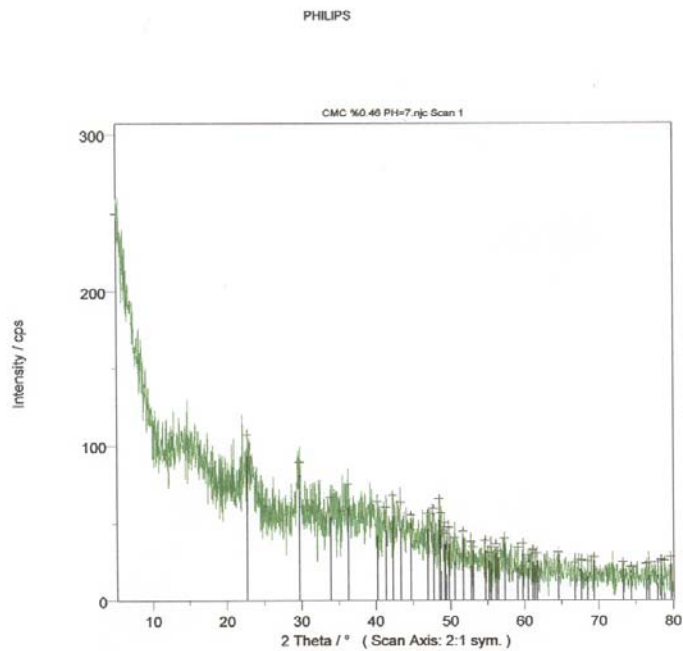


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Figure 10. XRD of sample treated by %46 MCA, %25 NaOH without neutral pH



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Figure 11. XRD of sample treated by %46 MCA, %25 NaOH with neutral pH

CONCLUSIONS

1. Carboxylated cellulose was successfully synthesized using waste paper fibers in the presence of maleic anhydride under suitable conditions.
2. Carboxymethylated cellulose also were successfully synthesized using waste paper fibers with the presence of sodium hydroxide, monochloroacetic acid, and isopropanol as solvent.
3. The results of FTIR analysis indicated that functional groups of carboxyl in carboxylated fibers and carboxymethyl functional groups in carboxymethylated fibers had increased. The presence of a strong absorption band around 1500 to 1700 cm^{-1} was confirmed the presence of carboxyl group ($-\text{COO}$).
4. The results of XRD analysis show that the crystallinity of cellulose was decreased in carboxymethylated fibers.
5. The carboxymethylation of the fibers resulted in a decrease in the crystallinity of cellulose. This is due to the cleavage of the hydrogen bonds in pulp during alkali treatment with NaOH. The decrease in crystallinity was confirmed by the results of XRD analysis.

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