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Studies on Graft Copolymerization of Acrylic Acid onto Acetylated Cellulose from Maize Cob

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Abstract: Acrylic acid was grafted onto cellulose acetate using ceric ammonium nitrate (CAN) initiator at varying temperatures (30, 40, 50, 60, 70, and 80 °C) and reaction period of 2-6 hours. Grafting parameters like grafting yield (GY), grafting efficiency (GE) and total conversion of monomer to polymer (TC) were evaluated at different reaction conditions such as temperature, time, monomer and initiator concentration. The homopolymer was removed from the reaction mixture using Soxhlet extraction. The graft copolymer of cellulose acetate produced at 70°C after 3 hours had the highest GY of 85%. The products were characterized by Fourier-transform infrared spectroscopy (FTIR), Scanning electron microscopy (SEM) and X-ray diffraction (XRD) analyses.

Keywords: Acrylic acid, cellulose, graft copolymerization, grafting yield, maize cob,

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INTRODUCTION

Cellulose is the most abundant naturally occurring and renewable biopolymer in the world. It is also one of the most promising raw materials due to its availability and low cost. It is a linear polysaccharide which consists of β-D-glucopyranose units joined by β-1, 4 glycosidic linkages (1,2,3). In one repeating unit of the cellulose molecule, there is one methylol and two hydroxyl groups as functional groups (4,5).

Graft copolymerization is a commonly used method for the modification of polymer surfaces and is a vital technique employed in improving the physical and chemical properties of polymers. Chemical modification of natural polymers is normally carried out so as to produce materials with properties that are not found in starting material. In other words, it aims to produce materials with improved properties (6).

The idea of chemical modification of cellulose is to introduce functional groups into the cellulose backbone, usually achieved by substituting the protons in the hydroxyl groups of cellulose to a varying extent. In which we can have mono, di, and tri-substituted products as shown in Figure 1.

Cellulose grafted with acrylic acid or acrylamide are hydrophilic in nature. Thus, they have a high water absorption capacity. These properties have made them suitably used as body fluid absorbents as well as in medical applications (7). The grafting of water soluble vinyl monomers onto amine-treated cotton fiber produces a graft copolymer with enhanced moisture sorption ability that can be used in athletic wear. Cellulose graft copolymers obtained by grafting vinyl monomers with functional groups such as acrylamide, acrylic acid, and acrylonitrile have been used in the adsorption of hazardous pollutants such as dyes or heavy metals from aqueous solution (8,9,10).

Depending on the chemical structure of the monomer grafted onto cellulose, graft copolymers gain new properties such as water absorption, improved elasticity, hydrophilic or hydrophobic character, ion-exchange and dye adsorption capabilities, heat resistance, thermosensitivity, pH sensitivity, antibacterial effect, resistance to microbiological attack, etc. (11,12).

Gurdag *et al*. (1997) (13) reported the grafting of acrylic acid onto cellulose using ceric ammonium nitrate (CAN) initiator in aqueous nitric acid solution at 30, 50, 70, and 90 °C, respectively. During the reaction period of 30-180 minutes, about 45% of the AA was polymerized at 90 °C. After 180 minutes, the maximum grafting yield was obtained at 30˚C, which has the highest water retention capacity. Hiltunen *et al*. (2011) (14) have reported the preparation of cellulose-graft-polyacrylamide and cellulose-graft-poly (N,N-dimethylacrylamide) copolymers by single-electron transfer living radical polymerization (SET-LRP) using DMSO as solvent.

According to some reports, maize is one of the world's most widely planted crops, which accounts for around 800 million tons every year, and for every 100 kg of maize grain, 18 kg is the cob (15). Ordinarily, maize cobs are often discarded after harvest as unwanted residues in the environment.

In this work, however, extracted cellulose from the residual waste (maize cob) is acetylated before grafting with acrylic acid. The grafting parameters of the copolymerization reaction are studied. Acetylation of polysaccharides before graft copolymerization produces a copolymer with a comb-like structure that is able to retain aqueous substances several times their weight (16). Chemical modification of such materials could find applications in waste water treatment, superabsorbents, etc (16). The samples being used in this work are abundant waste from the plant's harvest in different parts of the world. The environmental concern over hazardous and toxic materials in waste water treatment would suitably encourage the use of ecofriendly materials made from cellulose for important applications.

EXPERIMENTAL

Materials and Methods

The maize cob is an agricultural waste obtained from farms in Katsina State, Nigeria. Acrylic acid, ceric ammonium nitrate, sodium hydroxide, sodium hypochlorite, hydroquinone, potassium hydroxide, pyridine, and acetic anhydride were obtained from Sigma Aldrich.

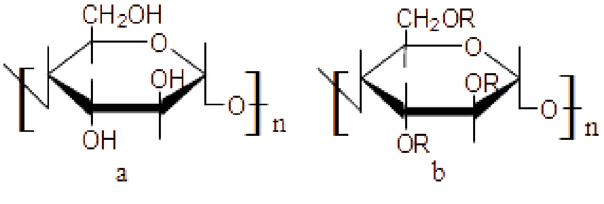

Figure 1: (a) Cellulose and **(b)** Substituted cellulose.

Delignification and Extraction of Cellulose from Maize Cob

The procedure reported by Azubuike and Okhimifen (16) was used with little modification. The maize cob was crushed to a finer size and 25 g was treated with an aqueous solution of sodium hydroxide (250 cm^3, 2% w/v) in a stainless steel vessel immersed in a water bath at 100˚C for 3h. Further digestion was carried out with an aqueous solution of sodium hydroxide (200 cm^3, 17.5 %w/v) for 1 h at 80 °C. After washing with distilled water, the remaining solid was filtered and dried in an oven at 60 °C for 16 h.

Bleaching of Extracted Cellulose

The extracted cellulose was bleached with an aqueous solution of sodium hypochlorite (62 cm^3, 3.2 %w/v) in a stainless steel vessel at 40 °C for 1.5 h. The bleached sample was thoroughly washed with distilled water until a neutral pH was obtained. The sample was then filtered and dried in an oven at 60 °C for 16 h. The dried product was milled and sieved through a mesh (500 µm) and further dried at 60 °C for 1 h. It was then stored in a tightly closed container.

Acetylation of Extracted Cellulose

Cellulose (5 g) was dried in an oven for 24 h at 50 °C and mixed with pyridine (40 g). After stirring for 5 minutes, acetic anhydride (20 g) was added to the mixture, and the temperature was increased to 100 °C within 15 minutes and held for 150 minutes. The final product was precipitated in ethanol and the white acetylated product was dried and ground to a finer size before testing (15). Equation (1) was used to determine the degree of substitution of the samples (17).

$$Ds=\frac{162(Db)}{4300-42-(Db)} \quad \text{(Eq. 1)}$$

Where *Db* is the percentage of acetyl group =
(value for blank – value for sample)
DS= degree of substitution

Grafting of Acrylic Acid onto Acetylated Cellulose

The cellulose acetate (1.25 g) was poured into 150 mL distilled water in a 250 cm^3 three-necked round-bottom flask equipped with magnetic stirrer, temperature controlled oil bath, reflux condenser, and nitrogen inlet. Different amounts of CAN (0.3–0.8 g), followed by addition of acrylic acid (AA) (1.25–2.0 cm^3) were used. The reaction was carried out in a nitrogen atmosphere for 2–6 h at varying temperatures of 30–80 °C and terminated by the addition of hydroquinone. The product was poured into cold distilled water with stirring and kept overnight at ambient temperature. It was then filtered, washed with distilled water, dried at 50 °C and weighed. The product was extracted with acetone using soxhlet extraction technique to remove the homopolymer. The grafted sample was dried at 60 °C to a constant weight. Grafting Yield (%GY), Grafting Efficiency (%GE) and Total Conversion (%TC) were obtained as follows: (18).

$$GY\% = \frac{W3 - W1}{W1 \times 100} \quad \text{(Eq. 2)}$$

$$GE\% = \frac{W2 - W1}{W4 \times 100} \quad \text{(Eq. 3)}$$

$$TC\% = \frac{W3 - W1}{W2 - W1 \times 100} \quad \text{(Eq. 4)}$$

Where W1 is the weight of original cellulose acetate (CA) before reaction; W2 is the weight of grafted CA before extraction; W3 is the weight of grafted product after extraction, and W4 is the weight of monomer charged.

RESULTS AND DISCUSSION

The crude biomass, apart from cellulose, contains other components. Table 1 shows the composition of each component in the crude biomass.

Acetyl content

Equation (1) was used to determine the acetyl content of the modified cellulose and was found to be 28.24% as indicated in Table 1 (3).

Table 1: Chemical Composition of Maize Cob.

Component	**wt (%)**
Hemicellulose	40.44
Cellulose	25.56
Lignin	34.00
Acetyl content	28.24

Grafting Parameters

Effect of Time

Table 2 shows that the grafting parameters (% GY, %GE, and %TC) increase with reaction time and then decrease at higher reaction times. This is due to an increase in the number of free radicals on the CA backbone, resulting in high number of reactive sites that interact with monomers there by increasing the grafting parameters. At longer reaction times, however, the three parameters decrease because of the high tendency of free radical coupling, leading to an increase in the rate of termination (16).

Effect of Temperature

Grafting reaction was carried out by varying the temperature from 30 to 80 °C, and the result is given in Table 2. It was observed that %GY of the AA grafted product increases with an increase in temperature. However, at 70 °C and above, the increase in temperature causes a decrease in the % GY. The trend could be due to a higher rate of free radical chain termination at higher temperatures and times. The grafting efficiency comparatively increases with rise in temperature, the trend, however, changes after 60 °C; an increase in temperature at a shorter reaction time favors high GE, but decreases at longer time of reaction. This may be due to the high tendency to increase the chain length of the graft copolymers over a longer time rather than increasing the reaction sites. A similar trend is observed in total conversion yield (16).

Homopolymer Formation

The variation of homopolymer formation was also investigated at different reaction times and temperatures and the results are given in Table 2. Graft copolymerization via free radical technique basically leads to homopolymerization as a side reaction. From the results, it can be observed that homopolymers are being formed along with the copolymers. Homopolymer formation is reported at higher reaction time and reaction temperature to some extent. The highest amount of homopolymer (0.54 g) is obtained at 60°C, at a 2 h reaction time. However, at higher temperatures, the homopolymer amount decreases even at a longer time of reaction.

Table 2: Effect of time and temperature on the grafting parameters.

SN	Temp (°C)	Sample Code	Time (h)	Wt of HP(g)	%GY	%GE	%TC
1	30	CA-g-PAA-01	2	0.09	12.80	64.00	12.08
2		CA-g-PAA-02	3	0.10	15.20	65.52	14.01
3		CA-g-PAA-03	4	0.11	16.00	64.52	14.98
4		CA-g-PAA-04	5	0.06	21.60	81.82	15.94
5		CA-g-PAA-05	6	0.05	24.00	85.71	16.91
6	40	CA-g-PAA-06	2	0.25	12.00	37.50	19.32
7		CA-g-PAA-07	3	0.26	15.20	42.22	21.74
8		CA-g-PAA-08	4	0.22	20.00	53.19	22.71
9		CA-g-PAA-09	5	0.20	24.00	60.00	24.15
10		CA-g-PAA-10	6	0.15	32.00	72.73	26.57
11	50	CA-g-PAA-11	2	0.15	22.40	65.12	20.77
12		CA-g-PAA-12	3	0.14	23.60	66.84	24.98
13		CA-g-PAA-13	4	0.31	25.80	69.04	25.71
14		CA-g-PAA-14	5	0.34	26.00	71.04	26.09
15		CA-g-PAA-15	6	0.30	29.00	75.45	26.57
16	60	CA-g-PAA-16	2	0.54	3.20	6.90	28.02
17		CA-g-PAA-17	3	0.05	36.00	90.00	24.15
18		CA-g-PAA-18	4	0.10	60.00	88.24	41.06
19		CA-g-PAA-19	5	0.17	58.40	81.11	43.48
20		CA-g-PAA-20	6	0.33	59.20	69.16	51.69
21	70	CA-g-PAA-21	2	0.19	85.60	84.92	24.12
22		CA-g-PAA-22	3	0.12	77.60	88.99	47.66
23		CA-g-PAA-23	4	0.08	72.80	91.92	54.83
24		CA-g-PAA-24	5	0.40	24.80	43.66	58.30
25		CA-g-PAA-25	6	0.20	24.00	60.00	60.87
26	80	CA-g-PAA-26	2	0.11	11.20	56.00	12.08
27		CA-g-PAA-27	3	0.06	11.20	57.00	13.66
28		CA-g-PAA-28	4	0.18	10.60	28.00	17.08
29		CA-g-PAA-29	5	0.40	7.00	27.27	26.57
30		CA-g-PAA-30	6	0.30	6.00	21.00	36.23

Effect of Initiator Concentration

The effect of initiator concentration was also investigated and is presented in Table 3. The initiator concentration is varied from 0.55 to 0.918 mmolL^{-1} at constant AA conc. (11.72 mmolL^{-1}), at 30 °C and a varied time of 2-6 h.

The rate of reaction increases with an increase in initiator concentration because of the increase in the number of free radicals generated on the CA backbone. This results in the increase in the rate of monomer conversion. The rate of reaction rises and then decreases at higher initiator concentration due to initial homopolymerization which occurs at longer reaction time and also decreases the mobility of monomer in the viscous grafted polymer solution (19).

At higher reaction time, however, the monomers tend to decompose, which decreases the number of reactive sites created and, therefore, the percentage grafting and grafting efficiency fall. The termination of growing copolymer radicals was dominated over propagation with CAN concentration, leading to a decrease in %GY. This is due to the difficulty in hydrogen abstraction from the substrate. The decrease in grafting parameters (%GY and %GE) at high CAN concentration could be due to the formation of more initiating radicals and consequently increase their changes to participate in either primary or secondary recombination with each other, or may react with the propagating polymer radicals, which could contribute to termination (20).

Table 3: Variation of CAN concentration at constant temperature 30 °C and AA concentration 11.72 mmol.

SN	CAN Conc. (mmol)	Time (h)	Wt of HP(g)	%GY	%GE	%TC
1	0.55	2	0.15	20.00	62.50	19.32
2		3	0.06	18.40	79.31	14.01
3		4	0.10	16.80	67.74	14.98
4		5	0.14	15.20	57.58	15.94
5		6	0.26	7.20	25.71	16.91
6	0.916	2	0.50	0.00	0.00	24.15
7		3	0.46	14.40	28.13	30.92
8		4	0.10	28.00	77.78	21.74
9		5	0.07	28.00	83.33	20.29
10		6	0.04	19.20	85.71	13.53

CHARACTERIZATION

FTIR Analysis

Figure 2 shows the FTIR spectra of the extracted cellulose, acetylated cellulose and grafted cellulose acetate. Stretching vibration at 3324 cm^{-1} is due to OH stretching vibration in the cellulose molecules; C-H stretching vibration is observed at 2908 cm^{-1} while the C-O-C stretching band is observed at 1029 cm^{-1}.

The acetylated cellulose was observed to have the following absorption peaks; absorption peak at 1741 cm^{-1} due to C=O stretching vibration of the acetyl group present on the cellulose backbone.

In the grafted product, however, there is an observed shift of OH stretching mode from 3324 to 3342 cm^{-1} and a shift in the C=O stretching peaks from 1741 cm^{-1} of the acetylated product to 1718 cm^{-1} of the graft copolymer. The changes above have shown that cellulose has been successfully transformed from its native form to an acetylated product and then to a graft copolymer with acrylic acid.

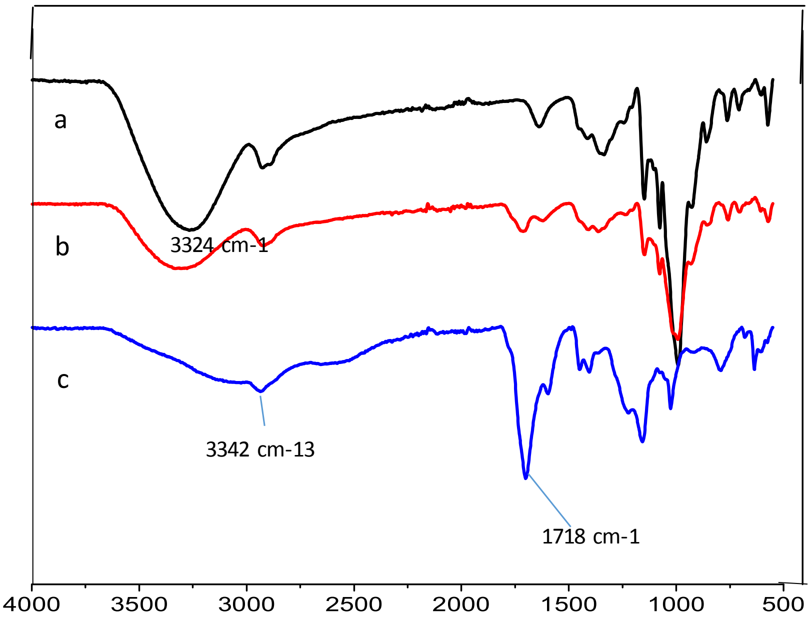

Figure 2: FTIR spectral data of **(a)** extracted cellulose, **(b)** acetylated cellulose and **(c)** CA-g-PAA.

Scanning Electron Microscopy (SEM) Analysis

The surface morphologies of extracted cellulose, CA, and CA-g-PAA are shown in Figure 3 (a-c). The surface morphology showed some variations due to chemical modifications. Pure cellulose in Figure 3 (a) showed a rough surface and irregular shapes of varied particles. The cellulose ester in Figure 4 (b) showed a varied morphology with small pores and a relatively rough surface. However, in the graft copolymer, Figure 3 (c), the surface morphology showed many pores and thick-coated rough surface, which confirmed the grafting of AA onto acetylated cellulose.

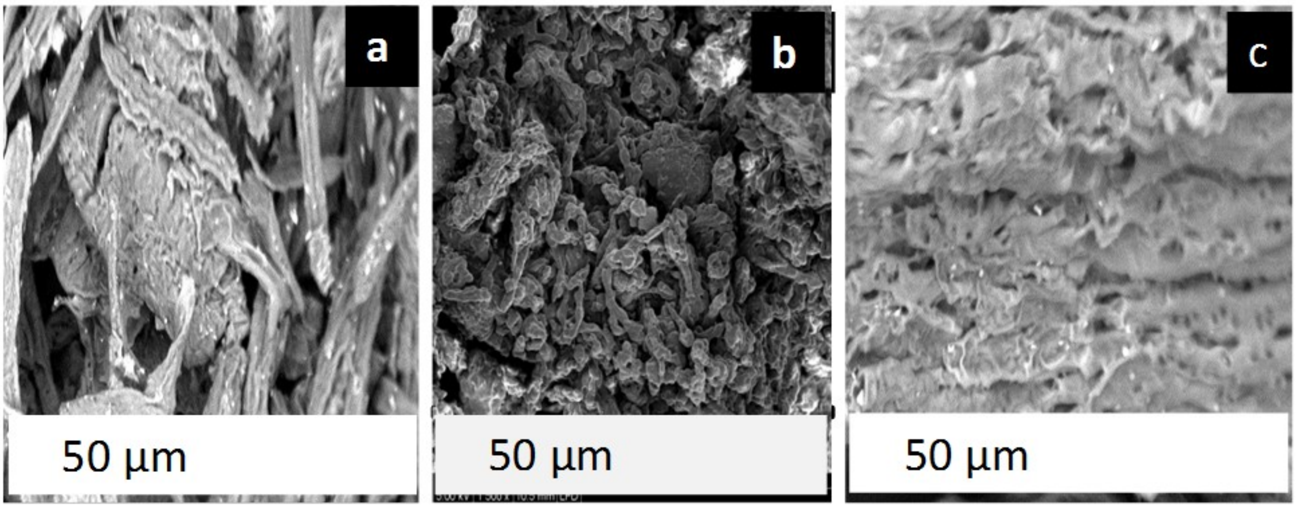

Figure 3: SEM image of **(a)** extracted cellulose **(b)** acetylated cellulose, and **(c)** CA-g-PAA.

X-ray diffraction (XRD) analysis

Structural changes were studied in the cellulose and the modified cellulose samples using X-ray diffraction technique. Figure 4 shows the XRD results of the samples; in the extracted cellulose, two responses were noticed at 2Θ=15.7° or 22° and 30°. These indicate that the cellulose is a semi-crystalline material (17). Other responses at 18° and 21° in the modified samples, and with disappearance of intensive peak at 30°, showing that the crystallinity of the cellulose decreases after chemical modification (17). On grafting the acetate fiber, a new response was observed with different intensities and was accompanied by a decrease in the relative degree of crystallinity (Figure 4). This could be explained on the basis that grafting causes disturbance in the crystalline region of the cellulose and increases the intensity of the amorphous region. As the degree of grafting increases, the amorphous regions become predominant and overshadow the crystalline feature on the cellulose material. This is evidence of the formation of a new material.

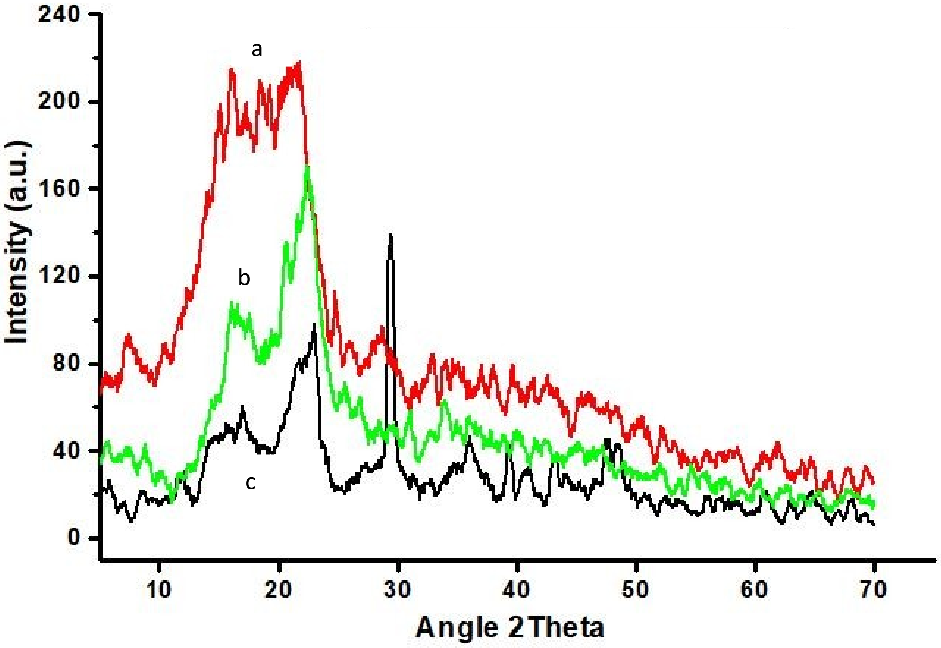

Figure 4: XRD Spectra of **(a)** cellulose, **(b)** CA, and **(c)** CA-g-PAA.

CONCLUSION

Cellulose extracts have been successfully modified through acetylation and grafting by free radical polymerization. The optimum condition for the maximum degree of grafting obtained at 70 °C after 180 min is (85%). Monomer conversion increases as reaction temperature increases, and grafting yield decreases as reaction temperature decreases, and higher temperature favour grafting more than homopolymerization. Samples' characterization using FTIR, SEM and XRD confirmed a successful modification of the starting material. The characterization of the samples has shown that there are structural changes of cellulose molecules after the modification.

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