

L.O. EKEBAFE¹
M.O. EKEBAFE²
F.A.O. AKPA¹
G. ERHUANGA¹
B.W. ETIOBHIO¹

¹Department of Polymer Technology, Auchu Polytechnic, Auchu, Edo State, Nigeria

²Chemistry Division, Nigerian Institute for Oil Palm Research, Benin City, Nigeria

SCIENTIFIC PAPER

UDC 66.095.26-922:678.744:676.1

DOI 10.2298/CICEQ101021063E

GRAFT COPOLYMERIZATION OF ACRYLONITRILE ONTO DELIGNIFIED NATIVE BAMBOO (*Bambusa vulgaris*) CELLULOSIC AND ITS UTILIZATION POTENTIAL FOR HEAVY METAL UPTAKE FROM AQUEOUS MEDIUM

Graft polymerization of acrylonitrile onto delignified cellulosic material obtained from Nigeria grown bamboo (Bambusa vulgaris) could be initiated by a ceric ammonium nitrate redox system. Optimization of grafting of acrylonitrile onto cellulosic material was performed by varying the reaction conditions, such as the duration of soaking of cellulosic material in ceric ammonium nitrate solution, concentration of ceric ammonium nitrate solution, polymerization time, temperature of reaction, and acrylonitrile concentration and saponification time, in order to study their influence on percent grafting yield and grafting efficiency. The resulting cellulosic-g-polyacrylonitrile (PAN) copolymers were fractionated by extraction at 33 °C with N,N'-dimethylformamide. Fractions were characterized by determining both the % add-on and the free polymer. Saponification of grafted copolymer was done by reaction with sodium hydroxide followed by methanol precipitation. The absorbent polymer so produced gave fair water retention values. The optimum reaction conditions obtained were: 20 mmol/L ceric ammonium nitrate solution in 1% nitric acid, soaking duration of 0.5 h at 40 °C for a polymerization time of 2 h and saponification time of 3 h. The percent grafting was 167.89%, grafting efficiency was 93.52% and water retention value was 389 g/g. The grafting was confirmed using FTIR. Sorption of different metal ions in the mixture, e.g. Cr, Mn, Ni, Cu and Pb, by grafted cellulosic and the hydrogel was also investigated. Hydrolysis increases the sorption affinity of grafted cellulose toward water and metal ions.

Key words: bamboo cellulosic; acrylonitrile; grafting and copolymers.

Renewable raw materials, are gaining considerable relevance in view of the global need for environmental conservation. In this regard, cellulose rich biomass acquires enormous significance as chemical feedstock, since it consists of cellulose, hemicellulose and lignin, which are renewable raw materials containing many functional groups suitable to chemical derivatization [1,2].

Graft copolymerization of cellulose is a process in which attempts have been made to combine synthetic polymers with cellulose, to produce materials

with the best properties of both. This grafting process is usually done by modifying the cellulose molecules through creation of branches of synthetic monomers that confer certain desirable properties on the cellulose without destroying its intrinsic properties [3]. Depending on the chemical structure of the monomer grafted onto cellulose, graft copolymers gain new properties such as hydrophilic and hydrophobic character, improved elasticity, water absorption, ion-exchange capability and heat resistance. These copolymers are finding applications in water treatment for textile industry, reclaiming ions of precious metals, water absorption and personal care products such as diapers, etc. [4].

Bamboo plants are identified as species of sub-family Bambusoideae, family Gramineae. They are distributed in many parts of the world. Bamboo is a

Corresponding author: L.O. Ekebafé, Department of Polymer Technology, Auchu Polytechnic, P.M.B. 13, Auchu, Edo State, Nigeria.

E-mail: lawekebafé@gmail.com; lawrenceekebafé@yahoo.com

Paper received: 21 October, 2010

Paper revised: 16 December, 2010

Paper accepted: 18 December, 2010

naturally occurring composite material which grows abundantly in most of the tropical countries. It is considered a composite material because it consists of cellulose fibers embedded in a lignin matrix. Cellulose fibers are aligned along the length of the bamboo providing maximum tensile flexural strength and rigidity in that direction [5]. Over 1200 bamboo species have been identified globally [6]. Bamboo is also one of the oldest building materials used by mankind [7]. It has been used widely for household products and extended to industrial applications due to advances in processing technology and increased market demand.

As a cheap and fast-grown resource with superior physical and mechanical properties compared to most wood species, bamboo offers great potential as an alternative to wood. Since bamboo species are invasive and spread very fast, uncared bamboo species also cause environmental problems. Increased research during the recent years has considerably contributed to the understanding of bamboo as well as to improved processing technologies for broader uses. Bamboo is presently super abundant in Nigeria with so much untapped potentials. Some of the common species of bamboo in Nigeria include the wide spread *Bambusa vulgaris*, commonly found in south Nigeria, *B. arundinacea*, *B. tulda*, *Dendrocalamus giganteus*, and *Oxytenanotteria Abyssinia*.

We were interested in studying the derivatization of bamboo cellulose from this native species through substitution and grafting reactions. The present work describes the swelling behaviour, utilization potential for heavy metal uptake from aqueous medium and optimization of the reaction conditions for grafting of acrylonitrile onto cellulosic material obtained from bamboo (*B. vulgaris*) by varying the reaction parameters such as the duration of soaking cellulosic material in ceric ammonium nitrate, concentration of ceric ammonium nitrate, polymerization time, temperature and concentration of acrylonitrile and saponification time, studying their effects on free polymer (%), add-on (%), %G (percent grafting), %GE (percent grafting efficiency) and water retention values (*WRV*).

MATERIALS AND METHODS

Bamboo culms were obtained from Igieduma village, along the Benin-Auchi Expressway, Edo State, Nigeria. Acrylonitrile (AN) was supplied by B.D.H. as reagent grade and was distilled under reduced pressure and stored in the dark at 5 °C before use; ceric ammonium nitrate and other reagents used were of analytical grade.

Preparation of the bamboo cellulosic material

Matured bamboo culms were harvested and cut into small strips with a saw blade. The strip material was grounded in the mill. The material was then placed in a shaker with sieves to pass through a 425 µm mesh sieve yet retained on a 250 µm mesh sieve. The resulting material was placed in glass jars labeled with appropriate designation for the analysis.

The delignified cellulosic was isolated using the method described by Brendel *et al.* [8].

Characterization of the bamboo culms

The bamboo culms were characterized in terms of the lignin content, determined according to ASTM D1106-56 [9] holocellulose content, determined using the method described by ASTM 1104-56 [10], ash content, determined as described by ASTM D1102-84 [11], hemicellulose content and cellulose content, determined according to ASTM D1103-60 [12]. The results are as presented in Table 1.

Table 1. Characteristics of the bamboo culms and the extractive cellulose yield (in %)

| Ash | Lignin | Hemi-cellulose | Cellulose | Holo-cellulose | Cellulose yield |
|------|--------|----------------|-----------|----------------|-----------------|
| 1.95 | 21.26 | 24.44 | 47.51 | 71.95 | 62.46 |

Graft copolymerization

The grafting reaction was carried out under nitrogen atmosphere in a flask equipped with a nitrogen inlet immersed in a constant temperature water bath. Solution of ceric ammonium nitrate (CAN) of varied concentrations were prepared by dissolving the required molar concentration of CAN salt in 1% nitric acid. In a typical reaction, 1 g cellulosic was immersed in 30 mL solution of CAN (10-20 mmol/L) for a particular time (30-120 min) followed by addition of a mixture of toluene (20 mL) and acrylonitrile (12.5-30.5 mol/AGU). The reaction mixture was stirred. A continuous supply of nitrogen was maintained throughout the reaction period. The grafting reaction was carried out for varying periods of time (2-5 h) at varied temperatures (20-50 °C) under stirring. At the end of reaction, mixture was washed with distilled water, subsequently with methanol, filtered and the product was dried in the vacuum oven at 60 °C for 4 days. The dried product was extracted with dimethylformamide for 48 h to remove the free polymer (FP)/homopolymer (polyacrylonitrile). The grafted cellulose was dried for 4 days to obtain a constant weight. The percent graft yield (%G) and percent grafting efficiency (%GE) were calculated on an oven dry weight of cellulose from the increased weight of cellulose after grafting by using the Eqs. (1) and (2):

$$\%G = \frac{\text{Final cellulose mass} - \text{Initial cellulose mass}}{\text{Initial cellulose mass}} \times 100 \quad (1)$$

$$\%GE = \frac{\text{Final cellulose mass} - \text{Initial cellulose mass}}{\text{Total polymer mass after reaction} - \text{Initial cellulose mass}} \times 100 \quad (2)$$

Results are presented in Tables 2 and 3.

Characterization of bamboo cellulosic-g-P(AN) copolymers

A dispersion of 2 g of cellulosic-g-P(AN) in 150 mL of 2 M hydrochloric acid was heated under reflux for 1.5 h. The insoluble polymer was separated by filtration, washed with water, and dried under vacuum at 60 °C. “% add-on” in the original copolymer was

determined from weight loss on acid hydrolysis. Grafting performance in terms of % add-on, % grafting yield and grafting efficiency was determined. Results are as presented in Tables 4-6.

Alkaline saponification

A suspension of 1.0 g of cellulose-g-poly(AN) copolymer in 9 mL, 0.7 M NaOH was introduced in a weighing bottle and mixed well. The bottle (loosely

Table 2. Effect of duration of soaking cellulosic material in CAN solution

| Soaking time, min | FP, % | Add-on, % | G Yield, % | GE, % | WRV, g/g |
|-------------------|-------|-----------|------------|-------|----------|
| 30 | 16.9 | 47.4 | 89.6 | 64.5 | 263 |
| 60 | 14.1 | 51.1 | 163.2 | 86.6 | 300 |
| 90 | 20.0 | 33.0 | 144.8 | 78.5 | 286 |
| 120 | 29.5 | 15.5 | 132.8 | 72.2 | 277 |
| 150 | 37.3 | 12.6 | 112.1 | 58.4 | 255 |

Table 3. Effect of CAN concentration on the graft yield%, %GE and gravimetric graft copolymer and water retention values (polymerization conditions: soaking time: 60 min, temperature: 40 °C for 60 min. Saponification conditions: 1 g of poly(AN)-cellulose copolymer, 9 mL of 0.7 M NaOH; saponification temperature: 95 °C; saponification time: 3 h)

| CAN concentration, mmol/L | FP, % | Add-on, % | G Yield, % | GE, % | WRV, g/g |
|---------------------------|-------|-----------|------------|-------|----------|
| 10 | 10.64 | 33.0 | 62.4 | 88.35 | 236 |
| 15 | 11.08 | 40.2 | 66.56 | 90.12 | 251 |
| 20 | 11.59 | 50.3 | 140.28 | 92.15 | 387 |
| 25 | 12.20 | 48.9 | 102.56 | 90.44 | 351 |
| 30 | 15.47 | 41.8 | 87.98 | 78.61 | 242 |

Table 4. Effect of acrylonitrile concentration on the graft yield% of poly(AN)-cellulose graft copolymer, the % add-on, along with the onset of this on water retention value (polymerization conditions: soaking time: 60 min, [CAN]: 20 mmol/L; temperature: 40 °C for 60 min. Saponification conditions: grafted cellulose, 1 g; 9 mL of 0.7 M NaOH; saponification temperature: 95 °C; saponification time: 3 h)

| AN Concentration, mol/AGU | FP, % | Add-on, % | G Yield, % | GE, % | WRV, g/g |
|---------------------------|-------|-----------|------------|-------|----------|
| 12.50 | 16.90 | 25.78 | 68.11 | 82.30 | 245 |
| 18.50 | 18.90 | 40.26 | 98.35 | 84.4 | 264 |
| 24.50 | 20.11 | 58.54 | 136.34 | 88.38 | 379 |
| 30.50 | 25.08 | 39.80 | 74.57 | 82.12 | 349 |
| 36.50 | 30.19 | 34.11 | 61.23 | 74.72 | 232 |

Table 5. Effect of temperature on FP, Add-on, %G, %GE and WRV (polymerization conditions: soaking time: 60 min, monomer concentration: 24.50 mol/AGU, time: 60 min. Saponification conditions: 1 g of poly(AN)-cellulose copolymer, 9 mL of 0.7 M NaOH; saponification temperature: 95 °C; saponification time: 3 h)

| Temperature, °C | FP, % | Add-on, % | G Yield, % | GE, % | WRV, g/g |
|-----------------|-------|-----------|------------|-------|----------|
| 20 | 12.82 | 47.21 | 110.11 | 64.80 | 248 |
| 30 | 13.73 | 48.56 | 130.56 | 79.45 | 265 |
| 40 | 14.97 | 54.98 | 145.43 | 90.23 | 381 |
| 50 | 13.11 | 48.79 | 121.46 | 72.12 | 355 |
| 60 | 11.45 | 40.43 | 108.52 | 60.22 | 232 |

Table 6. Effect of duration of polymerization on the graft yield% of poly(AN)-cellulose graft copolymers, the free polymer (%), % add-on and along with the onset of this on water retention value (polymerization conditions: soaking time: 60 min, [CAN]: 20 mmol/L; AN molar concentration: 24.50/AGU; reaction temperature: 40 °C. Saponification conditions: 1 g grafted cellulose; 9 mL of 0.7 M NaOH; saponification temperature: 95 °C; saponification time: 3 h)

| Duration time, min | FP, % | Add-on, % | G Yield, % | GE, % | WRV, g/g |
|--------------------|-------|-----------|------------|-------|----------|
| 60 | 17.67 | 50.18 | 98.67 | 62.12 | 232 |
| 120 | 26.78 | 54.48 | 121.76 | 76.65 | 248 |
| 180 | 29.77 | 58.98 | 149.63 | 80.55 | 366 |
| 240 | 15.67 | 60.33 | 167.89 | 93.52 | 379 |
| 300 | 20.12 | 53.88 | 155.23 | 84.88 | 247 |

stoppered to permit escape of ammonia) was then placed in an electric oven at 95 °C for desired time to complete the saponification. The mixture was dispersed in 200 mL methanol using electric blender for 5 min and then poured into an excess of ethanol. The precipitate was washed with slightly acidified ethanol (ethanol with few drops of acetic acid) until pH 8, then filtered and dried at 60 °C for 3 h.

Infrared analysis

IR spectra of ungrafted and grafted cellulose were recorded on an ABB Bomem MB-100 FTIR spectrophotometer and as presented in the spectral sheet in Figure 1.

Swelling measurement

Swelling of superabsorbent polymers was measured by the free swelling method [15] and expressed as a water retention value (WRV) calculated in grams of water per grams of dry polymer. Thus, an accurately weighed quantity of the hydrogel under inves-

tigation (0.1 g) was immersed in 100 mL of distilled water for 30 min and allowed to stand. The swollen hydrogel was then separated from unabsorbed water by screening through a tared 100 to 150 mesh sieve. The hydrogel was allowed to drain on the sieve for 10 min and the sieve was then weighed to determine the weight of water which caused swelling of the hydrogel. The swelling characteristic was calculated as Water retention value, g/g, using the following equation:

$$(g/g) = \frac{(W_2 - W_1)}{W_1} \quad (3)$$

where W_2 and W_1 are the weights of water swollen hydrogel and dry absorbent in grams, respectively. Results are presented in Table 7.

Uptake of heavy metal ions from aqueous medium

Sorption of metals was determined by using the Perkin-Elmer (Analyst 200) atomic absorption spectrophotometer (AAS). Sorption was carried out by stir-

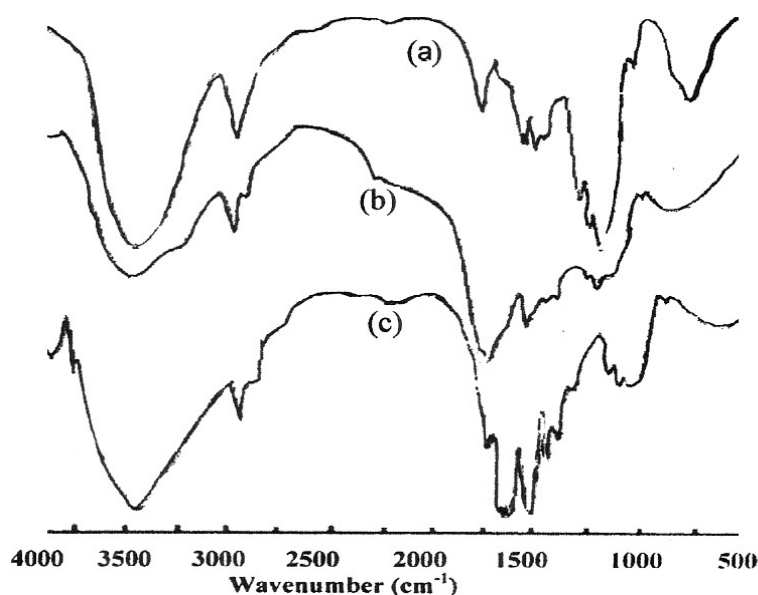


Figure 1. IR spectra of ungrafted (a), grafted (b) and hydrolyzed grafted (c) bamboo cellulosic.

ring 0.1 g of grafted and hydrolyzed grafted cellulose for 30 min in 25 mL solution containing 20 $\mu\text{g mL}^{-1}$ ions of nickel, copper, manganese, chromium and lead, respectively. After filtration, the remaining metal ions in the filtrate were determined using the AAS. The extent of uptake and retention capacity of the grafted copolymer and hydrogel are expressed in percentage as follows:

$$\text{Metal ion uptake \%} = \frac{\text{Amount of metal in polymer}}{\text{Amount of the metal in the feed}} \times 100 \quad (4)$$

$$\text{Metal ion uptake \%} = \frac{\text{Amount of metal ion in polymer}}{\text{Mass of dry polymer}} \quad (5)$$

Results are presented in Table 8.

Table 7. Effect of saponification time on the water retention value of hydrogel prepared from poly(AN)-bamboo cellulosic (saponification conditions: grafted cellulose, 1 g; 9 mL of 0.7 M NaOH; saponification temperature: 95 °C)

| Time, min | 30 | 60 | 120 | 180 | 240 |
|-----------|-----|-----|-----|-----|-----|
| WRV, g/g | 228 | 242 | 367 | 389 | 265 |

RESULTS AND DISCUSSION

Characteristics of the bamboo culms and cellulose yield

Table 1 shows the characteristics of the bamboo culms and the extractive cellulose yield. In general, the alpha-cellulose content in bamboo is 40-50%, which is consistent with the reported cellulose content of softwoods (40-52%) and hardwoods (38-56%). Alpha-cellulose is the main source of the mechanical properties of bamboo and wood [13]. Hemicellulose include alpha-cellulose and hemicellulose. Approximately 40-55% of the dry substance in bamboo is alpha-cellulose.

Hemicelluloses are heterogeneous polysaccharides. Like cellulose, most hemicelluloses function as supporting materials in the cell walls [14]. Bamboo lignin is built up from three phenyl-propane units, p-coumaryl, coniferyl and sinapyl alcohols interconnected through biosynthetic pathways [15].

The lignin present in bamboos is unique. The lignification process undergoes changes during the elongation of the culms, the full lignification of the bamboo culm is completed within one growing sea-

son, the lignin values of 20-23% place bamboo at the high end of the normal range or 11-27% reported for non-woody biomass [16] and closely resemble the ranges reported for softwoods (24-37%) and hardwoods (17-30%) [17,18]. The high lignin content of bamboo contributes to its high heating value of bamboo, and its structural rigidity makes it a valuable building material [14]. Ash is a term generally used to

refer to inorganic substances such as silicates, sulfates, carbonates, or metal ions [19].

Grafting characteristics

Previous reports have dealt with grafting of acrylonitrile to cellulose and to a great extent unveiled the advantageous use of non-aqueous medium (toluene). In the current study a two-phase system (aqueous initiator-toluene mixture) was used, which afforded high graft yields. Use of toluene inhibits diffusion of CAN out of the fiber, thus lessening homopolymer formation in the solution, and increases the availability of acrylonitrile, as reported by Gangnuex *et al.* [20] and Hon [21].

Effect of cellulosic soaking time

The effect of soaking time on Add-on (%), free polymer (FP), %G, %GE and water retention value (WRV) is shown in Table 2. It revealed that the parameters as stated increase rapidly with increase in time up to 60 min after which they level off, with the exception of the free polymer, which continuously increases. The soaking time allows the ceric solution to diffuse into the cellulose fibers prior to grafting reaction, thereby allowing initiation of free radicals on the cellulose sample by oxidation with ceric ions. The initial increase can be attributed to this factor [21]. The decreasing effect by prolonging this soaking time beyond 60 min could be attributed to the decay of free radical activity of ceric ions oxidized cellulose resulting from the free radical termination by charge transfer. A similar trend was observed by Hon [21] and Kulkarni and Mehta [22].

Table 8. Extent of heavy metal uptake by grafted cellulosic and the hydrogel

| Samples | Metal ion uptake, % | | | | | Retention capacity | | | | |
|-------------|---------------------|------|------|------|------|--------------------|-----|-----|-----|-----|
| | Cr | Pb | Mn | Ni | Cu | Cr | Pb | Mn | Ni | Cu |
| Grafted cop | 96.5 | 93.3 | 94.5 | 85.5 | 86.2 | 192 | 189 | 184 | 178 | 174 |
| Hydrogel | 98.1 | 94.4 | 97.6 | 93.8 | 94.4 | 199 | 189 | 196 | 185 | 189 |

Effect of ceric ammonium nitrate concentration

The effect of variation in CAN concentration was studied and the results are shown in Table 3. CAN concentration was increased from 10-30 mmol/L. It is evident that all the parameters increase with an increase in the initiator concentration, but reaches maximum value at 20 mol/L of CAN. These increasing trends of the grafting parameters indicated that ceric ions participate in the formation of active sites on the cellulosic up to this concentration of ceric ions, and beyond it, no more active sites are formed on the cellulosic. Further increase in CAN concentration is accompanied by a decrease. The decreasing trend beyond 20 mmol/L concentration of ceric ions may be assumed to be due to its participation in the termination reactions with growing free polymer/homopolymer and propagating chains on the cellulosic [23,24].

Effect of acrylonitrile concentration

The effect of variation of monomer concentration was studied and the results are shown in Table 4. The results show that as the monomer concentration increases from 12.50 to 30.50 mol/AGU, there is an increase in %G, reaching a maximum value of 136.34% at 24.50 mol/AGU and exhibiting a decreasing trend with further increase in monomer concentration. Similarly, at acrylonitrile concentration of 24.50 mol/AGU, %GE and WRV reaches a maximum value of 88.38% and 379 g/g, respectively. Thereafter, there is a decrease in %GE with increase in acrylonitrile concentration. Similar trend is also revealed at acrylonitrile concentration of 24.50 mol/AGU, for add-on (%) which reaches a maximum value of 58.54%. Thereafter, there is a decrease with increase in acrylonitrile concentration. However, there is a continuous increase of the free polymers.

Effect of temperature

The grafting reactions were carried out at different temperatures (20-60 °C), keeping the other variables constant. The effect of temperature on the parameters is shown in Table 5. Results show that maximum on all parameters is obtained at 40 °C and decreases with further increase in temperature. The dependence of the parameters on temperature can be ascribed to higher rate of dissociation of ceric ammonium nitrate-nitric acid initiator as well as the diffusion and mobility of acrylonitrile from the aqueous phase to cellulose phase, resulting in considerable improvement in the grafting yield [24,25].

Effect of duration of polymerization

The effect of polymerization time on the parameters was studied and the results are shown in

Table 6. It can be seen from the Table that the parameters increase rapidly with increase in time up to 4 h. The increase is accounted for by the increase in number of grafting sites in the initial stages of reaction due to high rate of ceric ion participation in the formation of reactive sites at the cellulose backbone [23].

Since there is a large excess of acrylonitrile monomer even after the longer reaction times, the leveling off after 4 h is presumably due to initiator exhaustion [21]. These observations are in accordance to those observed by Cruz *et al.* [26] and Gupta [14].

Effect of saponification time

Table 7 shows the effect of saponification time on the water retention value of hydrogels derived from poly(AN)-cellulose copolymers. It is clear (Table 7) that the water retention value increases by increasing the time of saponification within the range 120-180 min to reach a maximum of 389 g water per 1 g hydrogel. Further increase in the saponification time leads to a decrease in water retention value. This could be interpreted in terms of greater conversion of the amide groups to carboxylate groups at longer saponification time. That is, the carboxylate groups increases as the time of saponification increases and the water retention values are only due to insoluble graft copolymer. This behavior has been reported for similar experiments with different cellulose [27].

Water absorption

Water absorption values of the cellulosic-g-polyacrylonitrile increased with the acrylonitrile contents, Tables 2-7. Water absorption values of the copolymer were in the same trend as the percent add-on and grafting efficiency. These results correlate quite well with the mechanistic model of the enhanced water absorbency of acrylate-grafted polysaccharides [28] that is identical to the same as that described by Grignon and Scallman for the swelling of cellulosic gels [29].

A careful study of the reaction schemes indicated that grafting is associated with the homopolymer formation and cellulosic oxidation and that saponification converts the same grafted poly(AN) chain and homopoly(AN) chain with cyano group (-C=N) as the main group to both amide (-CONH₂) and carboxylate (-COONa) groups. The nitrile groups of PAN were converted to a mixture of hydrophilic carboxamide and carboxylate groups during alkaline hydrolysis, followed by in situ cross-linking of the grafted PAN chains. More PAN led to more carboxamide and carboxylate groups being generated from the alkaline hydrolysis of PAN; however, the decrease in value with higher amounts of PAN can be explained by the formation of a higher cross-linked, rigid structure.

The concentration of mobile Na^+ in the polymer gel, resulting from the saponification step is higher than those in distilled water used which comprises only hydrogen and oxygen atoms. As the ionic groups cannot move out of the gel, the solution within the gel is regarded as separated from the external solution by a semi permeable membrane which confines to the sodium carboxylate and carboxamide groups, but gives free passage of water. The gel swells as a result of the entry of water in an attempt to reduce the osmotic pressure differential due to the difference in ion concentrations. Swelling continues until the osmotic pressure differential is equal to the resistance to further expansion. That is, when the ion concentration between inside and outside the gel has reached equilibrium. The water absorption properties of cellulosic materials are thought to result from interaction through hydrogen bonding of the hydroxyl groups on the cellulose with water molecules [30].

IR Characterization

The FTIR spectra of the cellulosic material derived from bamboo (*Bambusa vulgaris*) and the optimized grafted sample (%G 167.3, %GE 93) were recorded. In the FTIR spectra of the optimized sample of grafted cellulose, besides the typical signals of cellulose backbone (νOH 3414 cm^{-1} , νCH 1431 cm^{-1} , νCOC 1059 cm^{-1} , $\nu\beta$ -linkage 890 cm^{-1}), the characteristic absorption bands at 2245 cm^{-1} , for the nitrile group ($-\text{CN}$) introduced and 2926 cm^{-1} (characteristic for $-\text{CH}_2$ group) with increased intensity were observed, furnishing thereby the evidence that grafting of acrylonitrile has occurred.

METAL IONS UPTAKE FROM AQUEOUS MEDIUM

Structural aspects of the polymeric backbone are important factors affecting metal ions sorption. The prepared grafted cellulose copolymer removes metal ions both by adsorption on nitrogen of the amide groups and also by sorption in the bulk of grafted copolymer hydrogel. Therefore, the structure of a polymeric hydrogel affects the level of polymer interaction with water and the provision of active sites to absorb or coordinate metal ions. Hence, the sorption behaviour and the quantity of metal ions taken up depend, in addition to the attributes of metal ions, on different structural aspects of the polymer. It is clear from Table 8, that the metal ions uptake percentage and retention capacity of Cr were higher than Mn, Cu, and Ni. This can be attributed to the fact that the Cr ion has a lower atomic radius than other metal ions and consequently its adsorption by polymer is high. In general, the amount of metal ions uptake by ion ex-

changer is affected by the electronegativity and hydrated values of metal ions. The sequence of metal ions sorption was as follows: Cr, Mn, Pb, Cu, Ni.

Hydrolysis of the hydrogel affected the metal ions uptake percentage and retention capacity by activation of functional groups of grafting chains by opening up the hydrogel network and activating amide groups into more active ions. Partial hydrolysis of amide groups increased the water uptake of hydrogel and increased the tendency of functionalized hydrogel, leading to enhanced metal ions sorption. So from Table 8, it is seen that the metal ions uptake percentage and retention capacity of hydrolyzed grafted cellulosic was higher than the grafted cellulosic [29].

CONCLUSION

Graft copolymerization of acrylonitrile onto cellulosic material derived from bamboo can be initiated effectively with CAN.

The optimum reaction conditions obtained for grafting of acrylonitrile onto cellulosic material were: duration of dipping cellulosic material in CAN solution 0.5 h, CAN concentration 20 mmol/L, acrylonitrile concentration 24.50 mol/AGU, temperature of reaction: $40\text{ }^\circ\text{C}$, polymerization time 4 h and saponification time 3h.

The %G for optimized samples is 167.89%, %GE is 93.52 and WRV is 389 g/g.

The characterization of the grafted products by means of FTIR furnished the evidence of grafting of acrylonitrile onto the cellulosic material.

The effect of water absorption depends on the frequency of interposition of the grafted polymer chains on the cellulosic backbone, and the nature of the grafted polymer. In other words, the amount of grafting chain or acrylonitrile is one of the determining factors.

Grafting enhances metal ions uptake from aqueous medium, and the extent of uptake is influenced by the sizes of the ions.

REFERENCES

- [1] R. Khullar, V.K. Varsgney, S. Naithani, P.L. Soni, *Express Polym. Lett.* **2** (2008) 12-18
- [2] D.G. Barkalow, R.A. Young, *J. Wood Chem. Technol.* **5** (1985) 293-312
- [3] A. Hebeish, J.T. Guthrei, *The chemistry and technology of cellulosic copolymers*, Springer-Verlag, Berlin, 1981
- [4] G. Gürdag, G. Güclü, S. Ozgümüş, *J. Appl. Poly. Sci.* **80** (2001) 2267-2272
- [5] S.C. Lakkad, J.M. Patel, *Fiber Sci. Technol.* **14** (1980) 319-322

- [6] D. Wang, S.J. Shen, *Bamboos of China*, Timber Press, Portland, Oregon, 1987, pp. 428
- [7] M. Abd Latif, W.A.W. Tarmeze, A. Fauzidah. *J. Trop. Forest. Sci.* **2**(3) (1990) 227-234
- [8] O. Brendel, P.P.M Iannetta, D. Stewart, *Phytochem. Anal.* **11** (2000) 7-10
- [9] G.A. Adams, *Methods Carbohydr. Chem.* **5** (1965) 171-175
- [10] E. Sjostrom, *Wood Chemistry*, Academic Press, Inc. London, 1981, pp. 223
- [11] Y.D Chen, W.L. Qin, *Proceedings of the International Bamboo Workshop*, Hangzhou, China, Chinese Academy of Forestry, Beijing China, International Development Research Center, Ottawa, Canada, 1985, pp. 110-113
- [12] W.Y.Feng, Zh. Wang, W.J. Guo, *Chinese academy of pulp and paper making*, 2002
- [13] J.J.A. Janssen, *Building with bamboo*, 2nd ed., Intermediate Technology Publication Limited, London, 1995, pp. 65
- [14] J.M.O. Scurlock, D.C. Dayton, B. Hames, *Biomass Bioenerg.* **19** (2000) 229-244
- [15] W. Liese, *Anatomy and properties of bamboo*, in: *Recent Research on Bamboos*. Chinese Academy of Forestry, A.N. Rao, G. Dhanarajan, C.B. Sastry Eds., China and International Development Research Centre, Canada, 1987, pp. 196-208
- [16] M.O. Bagby, G.H. Nelson, E.G. Helman, T.F. Clark, *TAPPI J.* **54** (1971) 1876-1878
- [17] D. Fengel, G. Wegener, *Wood: chemistry, ultrastructure, reactions*, Walter de Gruyter Publishers, Berlin, 1984, pp. 613
- [18] C.W. Dence, *Methods in lignin chemistry*, Springer-Verlag, Heidelberg, 1992, pp. 33-61
- [19] S.A. Rydholm, *Pulping Processes*, Interscience Publications, New York, 1965, pp. 1049
- [20] A., Gangneux, D. Watteiz, E. Marechal, *Euro. Poly. J.* **12** (1976) 535-541
- [21] D.N.S. Hon, *ACS Symposium Series*, Washington, 1982
- [22] A.Y. Kulkarni, P.C. Mehta, *J. Appl. Poly. Sci.* **12** (1968) 1321-1342
- [23] S. Gupta, Ph.D. Thesis, Forest Research Institute, Dehra Dun, 2005, pp. 181-191
- [24] B.R. Sharma, V. Kumar, P.L. Soni, *J. Appl. Poly. Sci.* **90** (2003) 129-136
- [25] S.O. Heikal, S.F. El-Kalyubi, *J. Appl. Poly. Sci.* **27** (1982) 3027-3041
- [26] R.A. Cruz, A.M. Mendoza, M.C. Vieira, T. Heinze, *Makro. Chem.* **273** (1999) 86-90
- [27] M. Vera-Pacheco, H. Vazquez-Torres, G. Canche-Escamilla, *J. Appl. Polym. Sci.* **47** (1993) 53
- [28] I.J. Ziderman, J. Belayche, *J. Appl. Poly. Sci.* **32** (1986) 5791-5798
- [29] J. Grignon, A.M. Scallman, *J. Appl. Polym. Sci.* **25** (1980) 2829-2843
- [30] F.E. Okieimen, J.E. Ebhoaye, *J. Macromol. Sci. Chem.* **23**(2) (1986) 349-353.

L.O. EKEBAFE¹
M.O. EKEBAFE²
F.O. AKPA¹
G. ERHUANGA¹
B.W. ETIOBHIO¹

¹Department of Polymer Technology, Auchi Polytechnic, Auchi, Edo State, Nigeria

²Chemistry Division, Nigerian Institute for Oil Palm Research, Benin City, Nigeria

NAUČNI RAD

GRAFT POLIMERIZACIJA AKRILONITRILA NA DELIGNIFIKOVANIM CELULOZNIM MATERIJALIMA DOBIJENIM IZ BAMBUSA (*Bambusa vulgaris*) I NJIHOVA PRIMENA ZA UKLANJANJE TEŠKIH METALA IZ VODENIH RASTVORA

*Graft polimerizacija akrilonitrila na delignifikovanim celuloznim materijalima dobijenim iz bambusa uzgajanog u Nigeriji (*Bambusa vulgaris*) može biti inicirana pomoću amonijum-cerijum(IV)-nitrata. Optimizacija graftovanja akrilonitrila na celuloznom materijalu je izvršena variranjem reakcionih uslova, kao što su: dužina natapanja celuloznih materijala u amonijum-cerijum(IV)-nitratu, koncentracija rastvora amonijum-cerijum(IV)-nitrata, vreme polimerizacije, temperatura reakcije, koncentracija akrilonitrila i vreme saponifikacije, kako bi se ispitaio njihov uticaj na prinos i efikasnost graftovanja. Celulozni-g-poliakrilonitrilni (PAN) kopolimeri su dobijeni ekstrakcijom na 33 °C sa N,N'-dimetilformamidom. Frakcije su okarakterisane određivanjem svake ponaosob i slobodnog polimera. Saponifikacija graftovanog kopolimera je izvršena u reakciji sa natrijum-hidroksidom, nakon čega je sledila precipitacija metanolom. Ovako dobijeni polimer je pokazao zavidne vrednosti zadržavanja vode. Dobijeni su sledeći optimalni uslovi reakcije: 20 mmol·dm⁻³ amonijum-cerijum(IV)-nitrata u 1% rastvoru azotne kiseline, vreme upijanjaja 0,5 h na 40 °C u vremenu polimerizacije od 2 h i vremena saponifikacije 3 h. Procent graftovanja iznosi 167,89%, efikasnost graftovanja je 93,52%, a vrednost zadržavanja vode je 389 g/g. Graftovanje je potvrđeno pomoću FTIR. Takođe je ispitivana sorpcija različitih metalnih jona u mešavini, npr. Cr, Mn, Ni, Cu i Pb pomoću graftovane celuloze i hidrogelova. Hidroliza povećava afinitet sorpcije premea graftovanoj celulozi u odnosu na vodu i metalne jone.*

Ključne reči: celuloza iz bambusa; akrilonitril; graftovanje i kopolimeri.