

# Graft Polymerization of Polyacrylonitrile onto Rubber (*Hevea brasiliensis*) Seed Shell-Cellulosic and its Utilization Potential for Heavy Metal Uptake from Aqueous Medium.

Lawrence O. Ekebafé, M.Sc.<sup>1\*</sup>; Joseph E. Imanah, Ph.D.<sup>1</sup>; Mariam O. Ekebafé, M.Sc.<sup>2</sup>; and Stella O. Ugbesia, M.Sc.<sup>1</sup>

<sup>1</sup>Department of Polymer Technology, Auchí Polytechnic, PMB 13, Auchí, Nigeria.

<sup>2</sup>Chemistry Division, Nigeria Institute for Oil Palm Research, PMB 1030, Benin City, Nigeria.

E-mail: [lawekebafé@gmail.com](mailto:lawekebafé@gmail.com)\*  
[lawrenceekebafé@yahoo.com](mailto:lawrenceekebafé@yahoo.com)

## ABSTRACT

Graft polymerization of polyacrylonitrile onto cellulosic material obtained from Rubber (*Hevea brasiliensis*) seed shell using ceric ammonium nitrate as initiator was investigated. The conditions of grafting (e.g. duration of soaking of cellulosic material in ceric ammonium nitrate solution, concentration of ceric ammonium nitrate solution, polymerization time, temperature of reaction, acrylonitrile concentration and saponification time) to study their influence on percent grafting yield and grafting efficiency were evaluated. The resulting cellulose –g-polyacrylonitrile (PAN) copolymers were fractionated by extraction at room temperature with N, N' dimethylformamide. Fractions were characterized by determining the % add-on, % grafting, % grafting efficiency, and the % free polymer. Saponification of the cellulose –g-polyacrylonitrile isolated with methanol precipitation on drying gave a good water absorbing properties as super slurpers. 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.

(Keywords: *rubber seed shell cellulosic, acrylonitrile, grafting, copolymers, metal ions*)

## INTRODUCTION

The development of commodities derived from petrochemical polymers has brought many

benefits to mankind. However, it is becoming more evident that the ecosystem is considerably disturbed and damaged as a result of pollution occasioned by the discharge of heavy metals and the non-degradable materials used in disposable items. Therefore, the interest in polymers from renewable resources has recently gained exponential momentum and the use of biodegradable and renewable materials to replace conventional petroleum materials for disposable and other industrial applications is becoming popular and necessary [1, 2].

Within the broad family of renewable polymers, cellulose is one of the most attractive and promising sources for biodegradable materials because of the abundant supply, low cost, renewability, biodegradability, and ease of chemical modifications [3, 4]. In recent years, graft polymerization of cellulose has attracted considerable attention and has offered an interesting alternative for pure synthetic polymers where long-term durability is not needed and degradation is an advantage [5-8].

Lignocellulosic agricultural byproducts are a copious and cheap source for cellulose fibers. Agro-based biofibers have the composition, properties and structure that make them suitable for uses such as composite, textile, pulp, paper manufacture etc. In addition, biofibers can also be used to produce fuel, chemicals, enzymes and food. Byproducts produced from the cultivation of corn, wheat, rice, sorghum, barley, sugarcane, pineapple, Bamboo, banana and coconut are the major sources of agro-based biofibers. Biomass such as agricultural crops and residues, forest resources and residues, animal and municipal

wastes is the largest source for cellulose in the world [2].

Organic agricultural wastes (agricultural byproducts) are annually renewable, available in abundance and of limited value at present. Primary lignocellulosic agricultural byproducts that are available in considerable quantity and at low cost are corn stover, wheat, rice, barley straw, sorghum stalks, coconut husks (coir), sugarcane bagasse, pineapple leaves, bamboo culms, and banana leaves. Using these crop residues for industrial applications could be an additional source of revenue for farmers, without adversely affecting soil fertility. Not all of these agricultural byproducts are commonly available across the world. Many are native to a particular region, depending on the climatic conditions required to grow the food crops.

Rubber belongs to one of the most important classes of structural materials attracting ever-growing interest. Rubber seed shells are by products of the rubber tree (*Hevea brasiliensis*), which have become a huge agricultural waste in Nigeria; ongoing research program is aimed at utilizing these materials to increase their economic value.

The present communication describes the utilization potential and optimization of the reaction conditions for grafting of polyacrylonitrile onto cellulosic material obtained from rubber seed shell 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, concentration of acrylonitrile and saponification time and studying their effects on % add-on, %G (percent grafting), %GE (percent grafting efficiency) and the water retention values of the hydrogel and sorption of metal ions. Each of these parameters was varied one by one keeping other conditions constant in the reaction.

## **MATERIALS AND METHODS**

Rubber seed shells were obtained from Otuo village, Owan west, Edo State, Nigeria. Acrylonitrile (AN) was used without further purification is a product of Sigma-Aldrich, Germany, as well as the ceric ammonium nitrate. Sodium hydroxide (M&B, England), methanol (BDH, England), ethanol (BDH, England), N,N-dimethyl formamide (DMF)(Rankem, India), acetic

acid (BDH, England), nitric acid (BDH, England), and Toluene (BDH, England) reagent grade chemicals were used without further purification.

### **Preparation of the Rubber Seed Shell Cellulosic Material**

The shells were separated from the seeds and air-dried and reduced to small sizes. The shells were small enough to be placed in a Milling machine. The material was grounded in the Mill and then placed in a shaker with sieves to pass through a 450- $\mu\text{m}$  mesh sieve yet retained on a 250- $\mu\text{m}$  mesh sieve. The resulting material was placed in glass jars labeled with appropriate designation for the analysis.

The cellulosic material was isolated using the method described by Tappi [9] by extraction with acetic acid and nitric acid for 30 minutes at 80°C, the solution was allowed to cool, inverted and shaken; and then centrifuge for 15 minutes at 1,000 rpm. Using a pipette, the supernatant were removed as much as possible from samples into waste beaker. This process was repeated with ethanol and acetone and the supernatant removed. Samples were placed in warm oven until they appear dry. Cellulose yield was determined, expressed in percentage.

### **Characterization of the Powdered Rubber Seed Shell**

The powdered rubber seed shell was characterized in terms of the lignin content, holocellulose content, ash content, hemicellulose content, and cellulose content according to standard methods; as follows: Lignin in Rubber seed shell was determined according to ASTM D1106-56(1977) as follows: A one-gram, oven-dried sample of extractive-free powdered rubber seed shell (PRSS) was placed in a 150mL beaker. 15mL of cold sulfuric acid (72%) was added slowly while stirring and mixed well. The reaction proceeded for 2hrs with frequent stirring in a water bath maintained at 20°C.

The contents of the flasks were filtered after washing with distilled water into a glass crucible of known weight. The residue was washed free of acid with 500mL of hot water and then oven-dried at 103 $\pm$ 2°C. Crucibles were then cooled in a desiccator and weighed until a constant weight was obtained.

The following formula was used to obtain the lignin content of PRSS:

$$\text{Lignin content in PRSS (percent)} = (W_4 - W_3 / 100W_2) \times (100 - W_1) \quad (1)$$

Where,

$W_1$ =alcohol-toluene extractive content (percent).

$W_2$ =weight of oven-dried extractive-free sample (grams).

$W_3$ =weight of oven-dried crucible (grams).

$W_4$ =weight of oven-dried residue and crucible (grams).

Holocellulose in PRSS was determined using the method described by ASTM 1104-56 (1978): A two-gram sample of oven-dried extractive-free PRSS was weighed and placed into a 250mL flask with a small watch glass cover. The specimen was then treated with 150mL of distilled water, 0.2mL of cold glacial acetic acid, and one gram of  $\text{NaClO}_2$  and placed into a water bath maintained between  $70^\circ\text{C}$  -  $80^\circ\text{C}$ . Every hour for 5 hrs, 0.22mL of cold glacial acetic acid and one gram of  $\text{NaClO}_2$  were added and the contents of the flask were stirred constantly. At the end of 5 hrs, the flasks were placed in an ice water bath until the temperature of the flasks was reduced to  $10^\circ\text{C}$ .

The contents of the flask were filtered into a glass crucible of known weight. The residue was washed free of  $\text{ClO}_2$  with 500mL of cold distilled water and the residue changed color from yellow to white. The crucibles were then oven-dried at  $103 \pm 2^\circ\text{C}$ , then cooled in a desiccator, and weighed until a constant weight was reached.

The following formula was used to determine the holocellulose content in PRSS:

$$\text{Holocellulose content in PRSS (percent)} = (W_4 - W_3 / 100W_2) \times (100 - W_1) [10] \quad (2)$$

Where,  $W_1$ =alcohol-toluene extractive content (percent).

$W_2$ =weight of oven-dried extractive-free sample (grams).

$W_3$ =weight of oven-dried crucible (grams).

$W_4$ =weight of oven-dried residue and crucible (grams).

Cellulose in PRSS was determined according to ASTM D1103-60 (1978): A three gram oven-dried sample of holocellulose extracted from the PRSS was placed in a 250mL Erlenmeyer flask with a small watch glass cover. The flasks were placed

into water bath that was maintained at  $20^\circ\text{C}$ . The sample was then treated with 50mL of 17.5 percent NaOH and thoroughly mixed for one minute and allowed to react for 30 minutes and 50ml distilled water added. The contents of the flask were filtered into a glass crucible of known weight. The residue was washed first with 50mL of 8.3 percent NaOH, then with 40mL of 10 percent acetic acid. The residue was washed free of acid with 1L of hot water. The crucible was oven-dried in an oven at  $103 \pm 2^\circ\text{C}$ , then cooled in a desiccator, and weighed until a constant weight was reached.

The following formula was used to obtain the cellulose content in PRSS:

$$\text{Cellulose (percent)} = (W_4 - W_3 / 100W_2) \times W_1 [11] \quad (3)$$

Where,

$W_1$ =Holocellulose content (percent).

$W_2$ =weight of oven-dried Holocellulose sample (grams).

$W_3$ =weight of oven-dried crucible (grams).

$W_4$ =weight of oven-dried residue and crucible (grams).

Ash Content in PRSS was determined as described by ASTM D1102-84 (1990): Ignite an empty crucible and cover in the muffle at  $600^\circ\text{C}$ , cool in a desiccator, and weigh to the nearest 0.1 mg. Put about 2 gram sample of air-dried PRSS in the crucible, determine the weight of crucible plus specimen, and place in the drying oven at  $103 \pm 2^\circ\text{C}$  with the crucible cover removed. Cool in a desiccator and weigh until the weight is constant. Place the crucible and contents in the muffle furnace and ignite until all the carbon is eliminated. The temperature of final ignition is  $580^\circ\text{C}$  to  $600^\circ\text{C}$ . Remove the crucible with its contents to a desiccator, replace the cover loosely, cool and weigh accurately. Repeat the heating for 30 min periods until the weight after cooling is constant to within 0.2 mg.

The following formula was used to obtain the ash content in PRSS:

$$\text{Ash content (percent)} = 100W_2 / W_1 [12] \quad (4)$$

Where,

$W_1$ =weight of ash (grams).

$W_2$ =weight of oven-dried sample (grams).

The results are given in Table 1.

## **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 cellulose was immersed in 30 ml solution of CAN (10–20 mmol/L) for a particular time (30–120 mins) 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 hrs to remove the free polymer/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 Equations (5) and (6) [3]:

$$\%G = (\text{Final cellulose wt} - \text{initial cellulose wt}) / \text{initial cellulose wt} \times 100 \quad (5)$$

$$\%GE = (\text{Final cellulose wt} - \text{initial cellulose wt}) / (\text{Total polymer wt after reaction} - \text{initial cellulose wt}) \times 100 \quad (6)$$

Results are as presented in Table 2-7

## **Characterization of Rubber Seed Shell Cellulosic-g-P (AN) Copolymers**

A dispersion of 2g of cellulosic-g-P (AN) in 150ml of 2M hydrochloric acid was heated under reflux for 1.5h. The insoluble polymer was separated by filtration, washed with water, and dried under vacuum at 60°C. "Percent add-on" in the original copolymer was determined from weight loss on acid hydrolysis. Grafting performance in terms of percentage add-on, percentage grafting yield and grafting efficiency was determined.

## **Alkaline Saponification**

A suspension of 1.0 g of cellulose –g-poly (AN) copolymer in 9mL 0.7 N NaOH was introduced in a weighing bottle and mixed well. The bottle (loosely 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 200mL 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 a Fourier transform infrared (FTIR-5300) spectrophotometer using the KBr disc technique in the range 4000–650 cm<sup>-1</sup>.

## **Absorbency or Swelling Measurement**

Absorbency of superabsorbent polymers are measured by the free swelling method 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 investigation (0.1 g) was immersed in 100mL of distilled water at room temperature for 30 min and allowed to stand to full hydration of the hydrogel was achieved. 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. Water absorbency or swelling characteristic was calculated as g/g using the following equation:

$$\text{Water retention value (g/g)} = W_2 - W_1 / W_1$$

Where,  $W_2$  and  $W_1$  are the weights of water swollen hydrogel and dry absorbent in grams, respectively.

## **Uptake of Heavy Metal Ions from Aqueous Medium**

Sorption of metals was determined by using the Atomic absorption spectrophotometer (AAS).

Sorption was carried out by stirring 0.1g of grafted and hydrolyzed grafted cellulose for 30 mins in 25ml solution containing  $20\mu\text{gml}^{-1}$  ions of (Nickel, Copper, Manganese, Chromium and Lead). 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:

Metal ions uptake % = (amount of metal in polymer/amount of the metal in the feed) x 100

Retention Capacity = (amount of metal ions in polymer/weight dry of polymer)

## RESULTS AND DISCUSSION

### Characteristics of the Powdered Rubber Seed Shell and Cellulose Yield

The characteristics of the PRSS and the extractive cellulose yield are given in Table 1.

The average percent yield is due to the experimental conditions as some of the cellulose was lost in the course of removing the supernatants.

### 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.* [13] and Hon [14].

### 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 mins after which it levels off with the exception of the free polymer which continuously increases. Soaking time allows ceric solution to diffuse into cellulose fibers prior to grafting reaction thereby allowing initiation of free radicals on cellulose sample by oxidation with ceric ions. Initial increase can be attributed to this factor [14].

**Table 1:** Characteristics of the Powdered Rubber Seed Shell and the Extractive Cellulose Yield.

	Ash (%)	Lignin (%)	Hemicellulose (%)	Cellulose (%)	Holocellulose (%)	Cellulose yield (%)
PRSS	0.82	2.98	24.56	71.64	96.20	55.52

**Table 2:** Effect of Duration of Soaking Cellulosic Material in CAN Solution.

Soaking time (mins)	FP (%)	Add-on (%)	G yield (%)	GE (%)	WRV (g/g)
30	12.1	32.5	69.4	46.6	163
60	12.9	49.4	128.3	86.9	220
90	10.5	53.4	131.1	68.2	186
120	19.7	21.1	101.2	64.8	177
150	27.7	10.2	92.3	49.7	155

The decreasing effect by prolonging this soaking time beyond 60 mins could be attributed to the decay of free radical activity of ceric ions oxidized cellulose resulting from the free radical termination by charge transfer. Similar trend was observed by Hon [14] and Kulkarni and Mehta [15].

The effect of variation in CAN concentration was studied and the results are shown in Table 3. CAN concentration was increased from 10 – 30mmol/L. It is evident that all the parameters increase with an increase in the initiator concentration, but reaches maximum value at 20mmol/L of CAN. These increasing trends of the grafting parameters indicated that ceric ions participate in the formation of active sites on the cellulose up to this concentration of ceric ions, and beyond it, no more active sites are formed on the cellulose. Further increase in CAN concentration is accompanied by a decrease. The decreasing trend beyond 20mmol/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 cellulose [15, 16].

### **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 30.50mol/AGU, there is an increase in %G, reaching a maximum value of 134.28% at 24.50mol/AGU and shows decreasing trend with further increase in monomer concentration. Similarly, at acrylonitrile concentration of 24.50mol/AGU, %GE and WRV reaches a maximum value of 88.35% and 229g/g respectively. Thereafter, there is a decrease in %GE with increase in acrylonitrile concentration. Similar trend is also revealed at acrylonitrile concentration of 24.50mol/AGU, for add-on (%) which reaches a maximum value of 58.42%.

Thereafter, there is a decrease with increase in acrylonitrile concentration. However, there is a continuous increase of the free polymers uptill 24.50mol/AGU of acrylonitrile concentration and then an increase, this is owing to the trend in %G and % GE.

**Table 3:** Effect of CAN Concentration on the Graft Yield%, %GE and wt Graft Copolymer and Water Retention Values.

<b>CAN conc.</b> (mmol/L)	<b>FP (%)</b>	<b>Add-on (%)</b>	<b>G yield (%)</b>	<b>GE (%)</b>	<b>WRV (g/g)</b>
10	9.52	30.8	58.8	82.60	134
15	10.83	41.4	67.26	92.45	151
20	10.54	62.8	144.62	94.21	187
25	12.80	48.2	112.06	88.14	151
30	16.42	40.1	89.19	62.11	142

Polymerization Condition: Soaking time: 60mins, temp.40°C for 60mins. Saponification Condition: One gram of poly (AN)-cellulose copolymer, 9mL of 0.7 N NaOH; saponification temperature, 95°C; saponification time, 3 h.

**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.

<b>AN Conc.</b> (mol/AGU)	<b>FP (%)</b>	<b>Add-on (%)</b>	<b>G yield (%)</b>	<b>GE (%)</b>	<b>WRV (g/g)</b>
12.50	16.74	35.82	70.48	70.11	143
18.50	13.06	46.46	88.95	76.44	174
24.50	10.28	58.42	134.28	88.35	229
30.50	18.24	48.23	110.37	82.82	179
36.50	21.92	38.48	81.80	74.42	162

Polymerization Condition: Soaking time: 60mins, [CAN] 20 m.mole/L; temp.40°C for 60mins. Saponification Condition: Grafted cellulose, 1 g; 9 mL of 0.7 N NaOH; saponification temp., 95°C; saponification time, 3 h.

### 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 (except FP) 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 [17, 18].

### 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 hrs. 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 [20].

Since there is a large excess of acrylonitrile monomer even after the longer reaction times, the leveling off after 4 hrs is presumably due to initiator exhaustion [19]. These observations are in accordance to those observed by Cruz *et al.* [24], and Gupta [21].

### 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 [25].

**Table 5:** Effect of Temperature on FP (%), Add-on(%), %G, %GE and WRV

Temp. (°C)	FP (%)	Add-on (%)	G yield (%)	GE (%)	WRV g/g)
20	14.88	48.11	108.48	64.80	148
30	12.43	48.50	100.26	70.55	155
40	10.48	64.21	145.85	90.23	189
50	13.81	50.10	121.46	78.22	156
60	14.40	44.49	106.52	64.82	132

Polymerization Condition: Soaking time: 60mins, monomer conc. 24.50mol/AGU, time: 60mins. Saponification Condition: One gram of poly (AN)-cellulose copolymer, 9mL of 0.7 N NaOH; saponification temperature, 95°C; saponification time, 3 h.

**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

Duration Time (min)	FP (%)	Add-on(%)	%G yield	% GE	WRV (g/g)
60	26.80	60.18	88.67	62.12	132
120	20.88	44.48	121.76	76.65	148
180	18.67	38.98	139.60	80.55	166
240	15.67	30.33	166.69	92.54	224
300	20.12	43.88	154.53	81.48	147

Polymerization Condition: soaking time: 60mins, [CAN], 20 m.mole/L ; AN molar conc, 24.50/AGU; reaction temp., 40°C  
Saponification Condition: 1g grafted cellulose; 9 mL of 0.7 N NaOH; saponification temp., 95°C; saponification time, 3 h.

**Table 7:** Effect of Saponification Time on the Water Retention Value of Hydrogel Prepared From Poly (AN)-Starch Copolymer.

Time (mins)	30	60	120	180	240
WRV (g/g)	128	142	167	224	165

Saponification Condition: Grafted cellulose 1 g; 9 mL of 0.7 N NaOH; saponification temp., 95°C.

### 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 [26] that is identical to the same as that described by Grignon and Scallman for the swelling of cellulosic gels [27].

The concentration of mobile Na<sup>+</sup> ions 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 semipermeable 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 [28].

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 behavior and the quantity of metal ions taken up depend, in addition to the attributes of metal ions, also 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 exchanger is affected by the electronegativity and hydrated values of metal ions. The sequence of metal ions sorption was as follows: Cr, Mn, Pb, 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 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].

**Table 8:** Extent of Heavy Metal uptake by Grafted Cellulosic and the Hydrogel.

Samples	Metal ions uptake (%)					Retention Capacity				
	Cr	Pb	Mn	Ni	Cu	Cr	Pb	Mn	Ni	Cu
Grafted cop	94.5	90	92.5	82	84	189	180	185	165	170
Hydrogel	97	92	95	90	91	194	185	190	180	185



## IR Characterization

The FTIR spectra of the cellulosic material derived from rubber (*Hevea brasiliensis*) seed shell 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 ( $\nu_{\text{OH}}$  3414  $\text{cm}^{-1}$ ,  $\nu_{\text{CH}}$  1431  $\text{cm}^{-1}$ ,  $\nu_{\text{COC}}$  1059  $\text{cm}^{-1}$ ,  $\nu_{\beta}$ -linkage 890  $\text{cm}^{-1}$ ), the characteristic absorption bands at 2245  $\text{cm}^{-1}$ , for the nitrile group ( $-\text{CN}$ ) introduced and 2926  $\text{cm}^{-1}$  (characteristic for  $-\text{CH}_2$  group) with increased intensity were observed, furnishing thereby the evidence that grafting of acrylonitrile has occurred.

## CONCLUSION

- Graft copolymerization of acrylonitrile onto cellulosic material derived from Rubber seed shell 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 0.5h CAN concentration 20 mmol/l, acrylonitrile concentration 24.50 mol/AGU, temperature of reaction 40°C, polymerization time 4 h and saponification time 3h.
- The %G for optimized samples is 167.89%, %GE is 93.52 and WRV is 389g/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.

## REFERENCES

1. Reddy and Yiqi Yang. 2005. "Biofibers from Agricultural byproducts for Industrial Applications". *TRENDS in Biotechnology*. 23(1).

2. Van Wyk, J.P.H. 2001. "Biotechnology and the Utilization of Biowaste as a Resource for Bioproduct Development". *Trends BioTechnol.* 19(5):172–177.
3. Barkalow, D.G. and Young, R.A. 1985. "Cellulose Derivatives Derived from Pulp and Paper Mill Sludge". *Journal of Wood Chemistry and Technology*. 5:293–312.
4. Mohanty, A.K. et al. 2000. "Biofibres, Biodegradable Polymers and Biocomposites: An Overview". *Macromol. Mater. Eng.* 276/277, 1–24
5. Ogbeifun, D.E. and Okieimen F.E. 2004. "Synthesis, Characterisation, and Flocculation Properties of Carboxymethyl Cellulose-g-Acrylamide". *Journal of Sciences, Islamic Republic of Iran*. 15(1): 53-57
6. Okieimen, F.E. and Ogbeifun, D.E. 1996. "Graft Copolymerizations of Modified Cellulose: Grafting of Methyl Acrylate, Ethyl Acrylate, and Ethyl Methacrylate on Carboxy Methyl Cellulose". *Eur. Polym J.* 32: 311.
7. Okieimen, F.E. and Ogbeifun, D.E. 1996. "Synthesis, Characterization, and Flocculation Properties of Carboxyl Methyl Cellulose-g-Acrylamide". *J. Appl. Polym. Sci.* 59: 981.
8. Okieimen, F.E., Ogbeifun, D.E., and Jideonwo. 1996. "Grafting Characteristics of Acrylamide on Carboxymethyl Cellulose using Ceric Ion Initiator". *J. Macromol. Sci. Macromolecular Reports.* A33: 391.
9. Brendel, O., Iannetta, P.P.M., and Stewart, D. 2000. "A Rapid and Simple Method to Isolate Pure-Cellulose". *Phytochemical Analysis*. 11:7–10.
10. Adams, G.A. 1965. *Methods Carbohydr. Chem.* 5:171.
11. Bagby, M.O., G.H. Nelson, E.G. Helman, and T.F. Clark. 1971. "Determination of Lignin in Non-wood Plant Fiber Sources". *Tappi*. 54:1876-1878.
12. Fengel, D. and G. Wegener. 1976. *Wood: Chemistry, Ultrastructure, Reactions*. Walter de Gruyter Publishers: Berlin, Germany. 613(1984).
13. Gangneux, A., Watteiz, D., and Marechal, E. 1976. "Synthese et Etude de Celluloses Echangeuses d'ions. Leur Employ dans l'epuration des Eaux Residuaire de l'industrie Textile-1: Synthese d'une Cellulose Greffee par des Chaines Poly (Acide Acrylique) et d'une Cellulose Renfermant des Fonctions Ammonium Quaternaire". *European Polymer Journal*. 12:535–541.

14. Hon, D.N.S. 1982. *Graft Copolymerization of Lignocellulosic Fibers*. ACS Symposium Series: Washington, D.C.
15. Kulkarni, A.Y. and Mehta P. C.1986. "Ceric Ion-Induced Redox Polymerization of Acrylonitrile on Cellulose". *Journal of Applied Polymer Science*. 12:1321–1342.
16. Gupta, S. 2005. "Chemical Modification of *Cassia occidentalis* Seed Gum". Ph.D. Thesis, Forest Research Institute: Dehra Dun. 181–191.
17. Sharma, B.R., Kumar, V., and Soni, P.L. 2003. "Graft Copolymerization of Acrylonitrile onto *Cassia tora* Gum with Ceric Ammonium Nitrate-Nitric Acid as Redox Mixture". *Journal of Applied Polymer Science*. 90:129–136.
18. Heikal, S.O. and El-Kalyubi, S.F. 1982. "Graft Copolymerization of Acrylonitrile onto Bagasse and Wood Pulp". *Journal of Applied Polymer Science*. 27:3027–3041.
19. Cruz, R.A., Mendoza, A.M., Vieira, M.C., and Heinze T. 1999. "Studies on Grafting of Cellulosic Materials Isolated from *Agave lechuguilla* and *Fourcroydes*". *Die Angewandte Makromolekulare Chemie*. 273:86–90.
20. Vera-Pacheco, M., H. Vazquez- Torres, and G. Canche- Escamilia. 1993. "Preparation and Characterization of Hydrogels obtained by Grafting of Acrylonitrile onto Cassava Starch by Ceric Ion Initiation". *J. Appl. Polym. Sci*. 47:53.
21. Ziderman, I.J. and Belayche, J. 1986. "Role of Polyacrylate Starch Copolymer in Water Sorption". *J. Appl. Polym. Sci*. 32. 5791-5798.
22. Grignon, J. and Scallman, A.M. 1980. "Effect of pH and Neutral Salts upon the Swelling of Cellulose Gels". *J. Appl. Polym. Sci*. 25:2829-2843.
23. Okieimen, F.E. and Ebhoaye, J.E. 1986. "Grafting Acrylic Acid Monomer on Cellulosic Materials". *J. Macrom Sci. Chem*. 23(2):349-353.
24. Okieimen, F.E., C.E. Sogbaike, and J.E. Ebhoaye. 2005. "Removal of Cadmium and Copper Ions from Aqueous Solution with Cellulose Graft Copolymers". *J. Haz. Mat. B*. 97:219.

## ABOUT THE AUTHORS

**Lawrence Ekebafé** is a Lecturer at the Auchi Polytechnic, Department of Polymer Technology. He is a registered chartered Chemist and is a member of the Polymer Institute of Nigeria, Chemical Society of Nigeria, Institute of Chartered Chemists of Nigeria, and a student member of the Institute of Public Analysts of Nigeria. He is presently undertaking his doctorate studies at the University of Benin, Nigeria, where he obtained Master of Science degree in Industrial Chemistry. His areas of research interest include: filler-polymer matrix interactions, graft polymerization of cellulosic fibers, hydrogels, and interpenetrating networks in agricultural applications.

**Joseph E. Imanah** is a Chief Lecturer at the Department of Polymer Technology; Auchi Polytechnic. He is a registered chartered Chemist and Fellow of the Polymer institute of Nigeria, and Chemical Society of Nigeria, Member, Institute of Chartered Chemists of Nigeria and Institute of Public Analysts of Nigeria. He holds a Ph.D. degree in Industrial Chemistry. His research interests are in latex adhesives and processing, fillers from agricultural wastes, and biomaterial interactions with polymers.

**Mariam O. Ekebafé** is a Research Officer with the Nigerian Institute for Oil Palm Research. She is a registered chartered Chemist and a member of the Chemical Society of Nigeria and the Institute of Chartered Chemists of Nigeria. She is presently undertaking her doctorate degree studies at the University of Benin, Nigeria, where she obtained a Master of Science degree in Analytical and Environmental Chemistry. Her areas of research interest include: graft polymerization of oil palm fibers with polymers for agricultural applications and Soil and plant fertility.

**Stella Ugbesia** is a Lecturer with the Polymer Technology Department, Auchi Polytechnic, Nigeria. She is registered chartered Chemist and member of the Chemical Society of Nigeria, and the Institute of Chartered Chemists of Nigeria. She holds a Master of Science degree in Polymer Industrial Chemistry of the Federal University of Technology, Akure, Nigeria. Her area of research interest is in filler–polymer matrix interactions.

## SUGGESTED CITATION

Ekebafé, L.O., J.E. Imanah, M.O. Ekebafé, and S.O. Ugbesia. 2010. "Graft Polymerization of Polyacrylonitrile onto Rubber (*Hevea brasiliensis*) Seed Shell-Cellulosic and its Utilization Potential for Heavy Metal Uptake from Aqueous Medium". *Pacific Journal of Science and Technology*. 11(2):488-498.

 [Pacific Journal of Science and Technology](http://www.akamaiuniversity.us/PJST.htm)