



## Synthesis and characterization of graft copolymerized acrylonitrile onto cellulose prepared from sisal fibre

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### ABSTRACT

Cellulose, a linear polysaccharide polymer with numerous glucose monosaccharide units is of enormous interest because of its applications in biosorption, biomedical, packaging, biofiltration and biocomposites. In this study the sisal fiber was prepared in four different stages such as the steam exploded fiber, bleached fiber, acid treated fiber and mechanically treated fiber using steam explosion method. These stages were prepared to convert it into cellulose. The graft copolymerization of acrylonitrile onto the extracted cellulose prepared from sisal fiber was done using the ceric ammonium nitrate. The grafting conditions were optimized by changing the concentration of initiator and monomer. The characterization of the processed fibers and the graft copolymer was done using FTIR, XRD, TGA and DSC studies. The FT-IR results of the graft copolymer clearly indicate that grafting had taken place between the acrylonitrile monomer and the cellulose obtained from sisal fiber. The change in crystallinity of the grafted polymeric samples was concluded from the XRD patterns. The results of TGA and DSC studies indicate the enhancement of thermal stability of the polymer upon grafting.

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### KEYWORDS

Sisal fiber;  
Acrylonitrile;  
Grafting;  
Characterization;  
Thermal analysis.

### INTRODUCTION

Natural fibers are mainly composed of cellulose, lignin and hemicelluloses components. Due to these components, natural fibers are also named as cellulosic or lignocellulosic fibers. According to their origin, these natural fibres were classified. They are grouped into *leaf*: abaca, cantala, date palm, pineapple, sisal, banana; *seed*: cotton; *bast*: flax, hemp, jute ; *fruit*: coi, oil palm. Among these various natural fibers the flax, bamboo, sisal, hemp, jute, and wood fibres are of particu-

lar interest<sup>[1]</sup>. Physical and mechanical properties mainly depends on the single fibre chemical composition (Cellulose, hemicelluloses, lignin, pectin, waxes, water content and other minors), grooving conditions (soil features, climate, aging conditions) and extraction/processing methods. Among them, the most influent parameter for the variability of mechanical properties is the grooving conditions. The main structural material present within the complex architecture of the plant cell walls is the cellulose with various contents. It is a polymer of poly-(1,4)-D-glucose having a linear structure with

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syndiotactic arrangement<sup>[2]</sup>. The parallel arrangement of cellulose chains produces the bundles. Around forty or more cellulosic macromolecules are present in the bundles which are linked by hydrogen bonds. Through the hydrogen bonded links with amorphous hemicelluloses and lignin. This will confer stiffness to the fibers called microfibrils<sup>[3]</sup>.

Crystalline microfibrils are made up of cellulose chains which are surrounded by a non-cellulosic matrix<sup>[4]</sup>. Various treatments such as the successive chemical and mechanical treatments were used to extract high-purified microfibrillated cellulose from the cell. This was done by the<sup>[5]</sup>. The bleaching agents such as the sodium chlorite or hydrogen peroxide is added mainly to the lignocellulosic fibers to degrade lignin content and the reagent sodium hydroxide is used to solubilize pectins and hemicelluloses. Mechanical treatments such as homogenization lead to homogeneous suspensions of microfibrils.

Since the cellulosic fibers are cheap, renewable, low in density, and better processing flexibility, it became so popular<sup>[6]</sup>. Farmers harvest around 35 million tons of natural fibers in each year from a wide range of plants and animals<sup>[7]</sup>. Among many natural fibers, sisal is of particular interest. Sisal fiber belongs to the Agave family (*Agave sisalina*), an environmental friendly crop. It is a strong, stable, biodegradable and versatile material which has been recognized as an important source of fiber for composites<sup>[8]</sup>. Sisal has moderately high specific strength and stiffness, durability, ability to stretch, and resistance to deterioration in saltwater<sup>[9,10]</sup>.

One of the effective technique which was used to improve the inherent properties of natural fiber was the graft copolymerization<sup>[11]</sup>. In the graft copolymerization process the branched copolymer was formed by covalently attaching the side chain grafts to the main chain of the polymer backbone. The grafting phenomenon introduces a large number of functional groups and structures onto the fiber surface<sup>[12]</sup>. Graft copolymerization of different monomers onto lignocellulosic materials has been carried out recently to enhance the properties. For example grafting of acrylonitrile onto pineapple leaf fibers was done to improve their thermal properties<sup>[13]</sup> and acrylamide onto sisal fiber was done to improve their moisture absorption<sup>[14]</sup>. One of the most frequent vinyl monomer used for grafting was the acrylonitrile

monomer. This was mainly due to its high grafting efficiency and easy hydrolysable nature to introduce varied subsequent derivatives<sup>[15]</sup>.

The current work is aiming to modify extracted cellulose using grafting phenomenon. At first the four different stages of treated fibers were prepared from the sisal fiber such as steam exploded sisal fiber, bleached fiber, acid treated fiber and mechanically treated fiber. Cellulose was extracted after the chemical and mechanical process. Then the cellulose graft acrylonitrile copolymer was synthesized using ceric ammonium nitrate (redox initiator) in nitric acid medium. The optimum conditions for the grafting was investigated by changing the amounts of initiator and acrylonitrile monomer. Finally the prepared final graft copolymeric products are characterized.

## MATERIALS AND METHODS

### Materials

The sisal fiber was collected from local farms and the chemicals such as NaOH, acetic acid, sodium hypochlorite, oxalic acid, ceric ammonium nitrate, acrylonitrile and nitric acid was obtained from Central Drug House Pvt Ltd. All the above chemicals used were of analytical grade.

### Preparation of steam exploded fibers

About 30 gm of sisal fibers were chopped into uniform size of approximately 10 cm. Then to the chopped fibers taken in a beaker, the 2% NaOH (fiber to liquor ratio 1:10) solution was added. It was then placed in an autoclave at a pressure of 20 lb for a period of 1 h. After a period of 1 hour, the pressure was released immediately. The fibers were removed from the autoclave, and then the fibers were washed in water till they were rid of alkali. The washed fibers were allowed to drain off free from water.

### Preparation of steam exploded bleached fibers

The bleaching treatment of the steam exploded fibers was done using a mixture of NaOH and acetic acid (27 and 78.8 g, respectively) and a mixture of 1:3 sodium hypochlorite solution. This treatment was then repeated for six times. After bleaching process is over, the fibers were thoroughly washed in distilled water and

dried.

### Preparation of steam exploded fibers in acidic medium

Different concentrations of oxalic acid (5%, 7%, 9%, and 11%) was added to the steam exploded bleached fibers taken in an autoclave till it attained a pressure of 20 lb. After it attains a pressure of 20 lb immediately the pressure was released. The autoclave was again set to reach a pressure of 20 lb, and the fibers were kept under that pressure for 15 min. The pressure was released and the process repeated 8 times. The fibers were taken out, washed till the washings no longer decolorized  $\text{KMnO}_4$  solution to make sure that the washings were free from acid<sup>[16,17]</sup>.

### Mechanical treatment of the processed fibers

The acidically treated fibers was suspended in water and then stirred well using a mechanical stirrer of type RQ – 1.27 A at a speed of 8000 R.P.M. for 4 h. The suspension was then finally kept in an oven at 90°C till it was dry.

### Preparation of grafted co-polymer

About 1 gram of cellulose was added to 100ml of water and stirred well to form a homogeneous suspension. 1ml of acrylonitrile monomer dissolved in 20 ml of water was then added to that homogenous solution. The initiator ceric ammonium nitrate (0.5 g of CAN in 10ml of 1N  $\text{HNO}_3$ ) was added in the above mixture to initiate the polymerization process. After all the addition was over, the above mixture was heated to 70°C. Simultaneously the stirring of that mixture was performed using a magnetic stirrer. It was then stirred for a period of approximately 30 minutes. After a time period of 30 minutes the above solution was poured into excess sodium hydroxide (2N) solution. Finally, the obtained graft copolymer precipitate was then filtered, dried and weighed. The grafting parameters including the grafting efficiency (GE), grafting yield (GY) and grafting percentage (GP) were systematically evaluated as a function of various initiator and monomer concentration<sup>[18]</sup>. The grafting parameters can be represented in equations (1)-(3)

$$\text{GE (\%)} = \frac{\text{Wt of graft polymer}}{\text{Wt of graft polymer} + \text{Wt of homopolymer}} \times 100 \quad (1)$$

$$\text{GY (\%)} = \frac{\text{Wg-Wi}}{\text{Wi}} \times 100 \quad (2)$$

$$\text{GP (\%)} = \frac{\text{Wpa}}{\text{Wa}} \times 100 \quad (3)$$

Where  $\text{Wi}$  = Wt of ungrafted polymer,  $\text{Wpa}$  or  $\text{Wg}$  = Wt of graft polymer,  $\text{Wa}$  - Weight of monomer.

### Characterization

The FT-IR spectra of chemically and mechanically treated sisal fiber and graft copolymer were recorded by Fourier transform infra-red spectrophotometer (FT-IR) using the Perkin Elmer 200 FTIR Spectrophotometer. DSC thermograms of processed sisal fiber and graft copolymer were recorded using a DSC Q200 V24.4 build instrument. The temperature range was chosen between 30°C to 350°C with the heating rate of 10°C/min. TGA analysis of the samples prepared under different conditions was done using TGA Q500 V20.10 Build 36 instruments. The temperature range was changed from room temperature to 850°C with the heating rate of 10°C/min. The X-ray diffraction patterns were tested by an X-ray scattering SHIMADUZ XD-DI Diffractometer using Ni filter  $\text{Cu K}\alpha$  radiation source ( $\lambda=0.154\text{nm}$ ), set at scan rate = 10°/min, using a voltage of 40kV and a current of 30 mA.

## RESULTS AND DISCUSSION

### Effect of initiator and monomer concentration

By keeping the other variables such as temperature, time and conc. of cellulose as constant, the grafting of acrylonitrile monomer onto extracted cellulose was done using various concentration of initiator and monomer separately<sup>[19]</sup>.

The concentration of the ceric ion, and the substrate plays an important role in the formation of average number of grafting sites per backbone molecule<sup>[20,21]</sup>. The changes observed in the grafting parameters of cellulose-g-acrylonitrile by changing the initiator and a monomer concentration separately was shown in the Figure 1 and Figure 2. From the Figure 1 it is evident that the grafting parameters sharply rises with increasing initiator concentration upto a certain value and thereafter declines. The initial increase with increase in CAN concentration was due to increase in the active free radicals on the cellulose backbone at which the monomer can be grafted. These active free radicals in the presence of monomer generate more number of graft copolymers. The decrease in grafting ratio after 0.8 g ceric

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ion concentration was mainly due to the termination of the growing grafted chains by excess of ceric ions. Also a similar type of results was observed by changing the monomer (AN) concentration which was shown in Figure 2. At first it shows an increase with increase in acrylonitrile concentration but thereafter decreases.

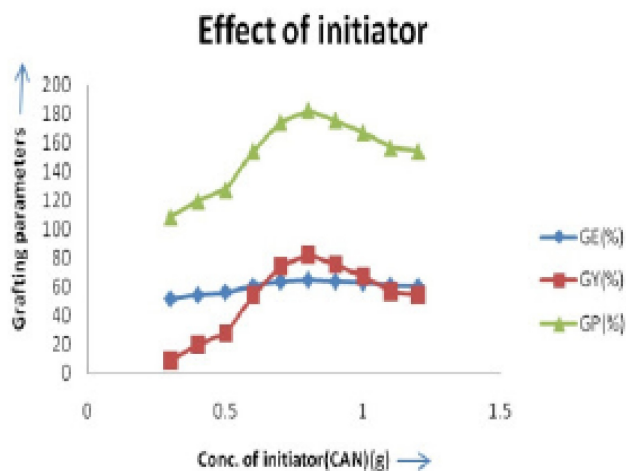


Figure 1 : Effect of initiator concentration

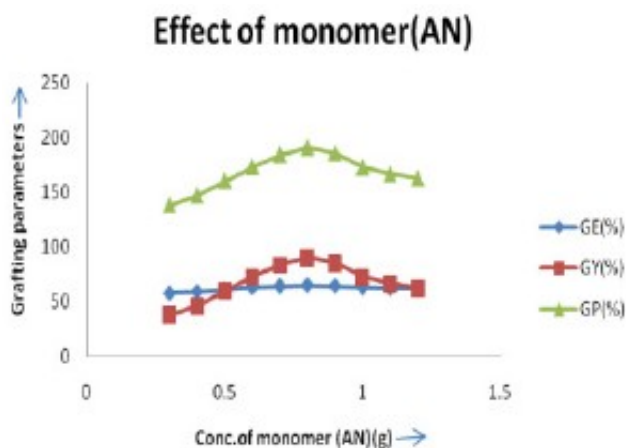


Figure 2 : Effect of monomer concentration

The initial increase in grafting may be due to the reason that most of the monomer is utilized by the available free radical. But the grafting rate does not exceed beyond the optimum monomer concentration. This may be due to the formation of more homopolymers as compared to the graft copolymer at higher monomer concentration. Moreover, due to homopolymerisation, viscosity of the reaction medium increases which creates hindrance in the movement of the free radicals towards active sites, thereby resulting in less graft yield<sup>[22]</sup>.

### FT-IR

Figure 3(a) represents the FT-IR spectra of steam

exploded fibers (stage-1), Figure 3(b) represents steam exploded bleached fibers (stage-2), Figure 3(c) represents steam exploded fibers in acidic medium (stage-3), Figure 3(d) represents mechanically treated processed fibers (stage-4), Figure 3(e) represents graft copolymer (cellulose-g-acrylonitrile). The FT-IR spectra of the steam exploded fibers (stage-1) Figure 3(a) shows a prominent peak at 3445.81  $\text{cm}^{-1}$ , 2923.91  $\text{cm}^{-1}$ , 1628.20  $\text{cm}^{-1}$ ,  $\text{cm}^{-1}$  1168.18  $\text{cm}^{-1}$ , 1110.98  $\text{cm}^{-1}$  and 1058.61  $\text{cm}^{-1}$  corresponding to OH stretching,  $\text{CH}_2$  stretching<sup>[23]</sup>, C = C stretching, C-O stretching, C-H in plane bending and C-O-C stretching respectively. A similar type of results was observed in (stage-2) Figure 3(b), (stage-3) Figure 3(c) and (stage-4) Figure 3(d). On comparing the FTIR spectral results of steam exploded fibers (stage-1) with the other stages (stage-2, stage-3, stage-4) it was found that the area of the peak at 1628.45  $\text{cm}^{-1}$  was found to increase successively which may be due to the bonded acetyl group<sup>[24]</sup>. From the successive increase in the area of peak, it was concluded that the cellulose content has been increased in mechanical treatment of processed fibers (stage-4) with the removal of lignin and hemicelluloses. The grafted copolymers thus prepared were characterized by FTIR spectral studies. The FTIR spectra of graft copolymer (cellulose-g-acrylonitrile) Figure 3(e) showed the peaks corresponding to the groups present in the four stages. In addition to the above peaks, a medium band was also observed at 2120  $\text{cm}^{-1}$  corresponding to the nitrile group (CN). These additional peaks prove that the grafting had taken place effectively.

### Thermo gravimetric analysis

The TGA thermogram details of 4(a) steam exploded fibers (stage-1), 4(b) steam exploded bleached fibers (stage-2), 4(c) steam exploded fibers in acidic medium (stage-3), 4(d) mechanical treatment of the processed fibers (stage-4), 4(e) graft copolymer (cellulose-g-acrylonitrile) were represented in the Figure-4. The TGA thermogram of steam exploded fibers shows that the residual temperature of the sample was found to be 850°C. Around 94.83% of the sample had disintegrated at the end of the experiment leaving behind 5.169 % of the sample as a residue. The small amount of residues in the fibers after chemo-mechanical treatment may be the result of removal of non cel-

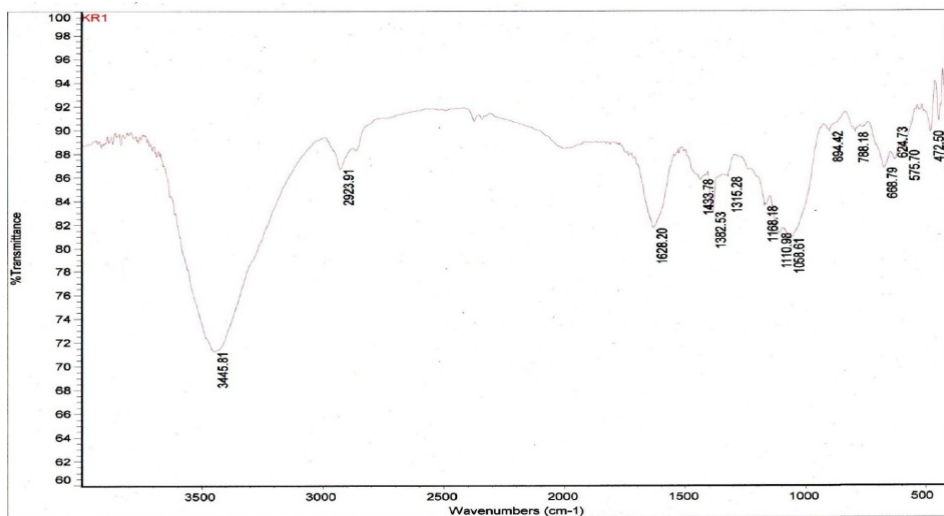


Figure 3(a) : FTIR spectra of steam exploded fiber

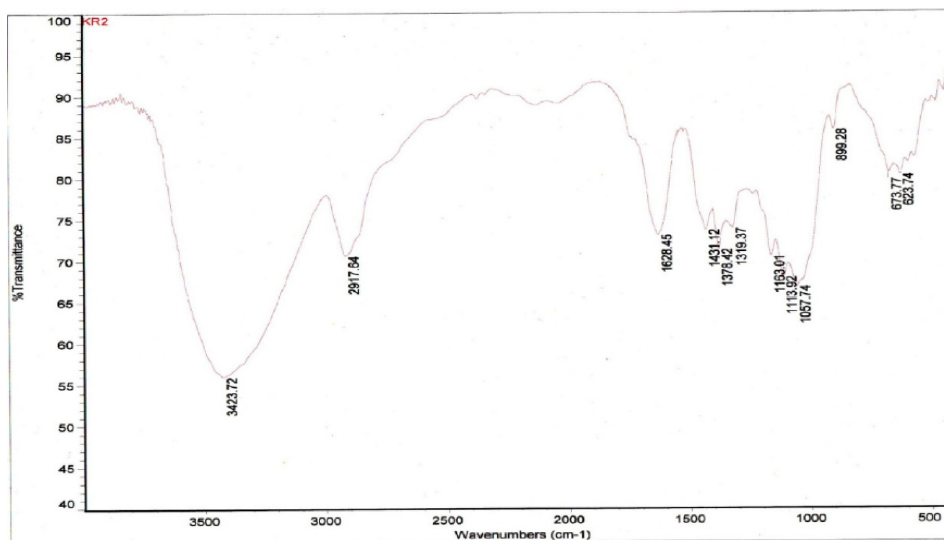


Figure 3(b) : FTIR spectra of steam exploded bleached fiber

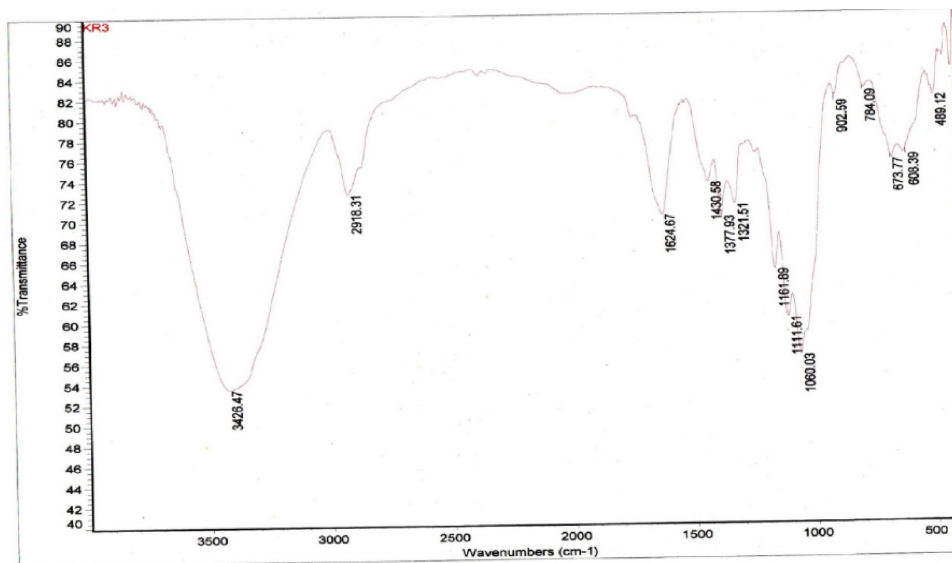


Figure 3(c) : FT-IR spectra of steam exploded fibre in acidic medium

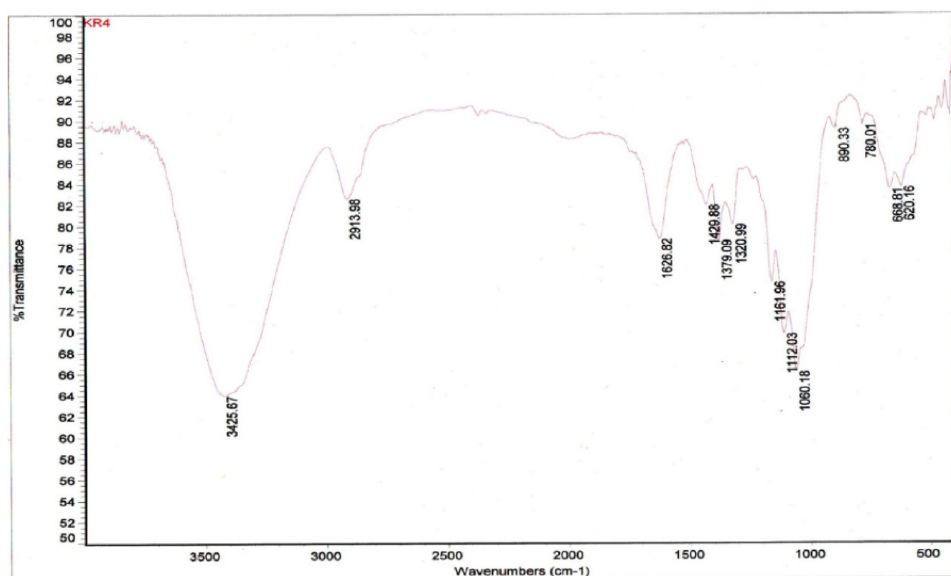


Figure 3(d) : FT-IR spectra of mechanically treated fibre

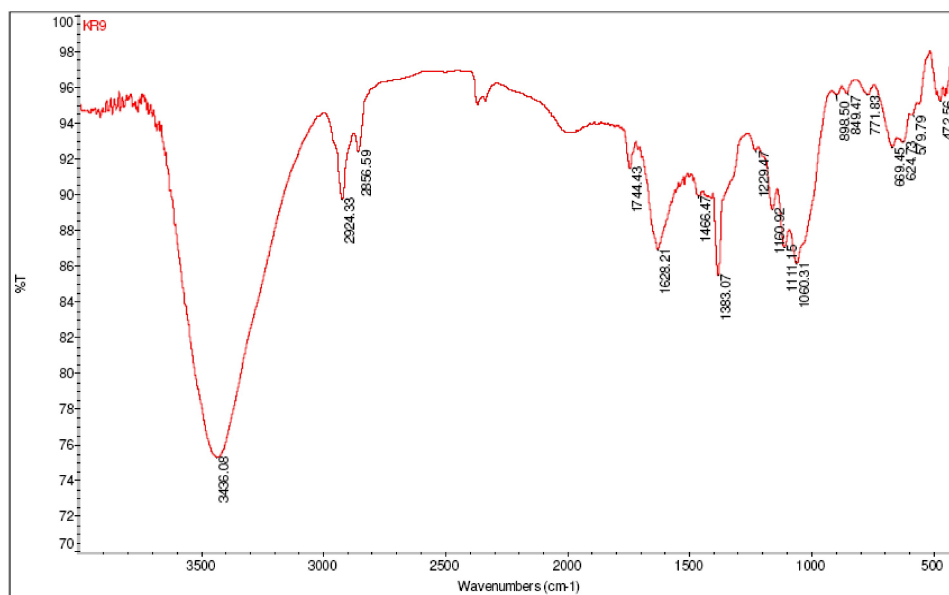


Figure 3(e) : FT-IR spectra of grafted co-polymer (cellulose-g-acrylonitrile)

lulosic materials during these treatments<sup>[25]</sup>. The TGA thermogram of the graft copolymer (Cellulose-g-acrylonitrile) Figure 4(e) shows that the maximum weight loss occurs at the temperature range of 200°C to 450°C. Around 46.447% of the sample was disintegrated in 840°C leaving behind 53.543 % of the sample as a residue. On comparing Figure-4(e) with Figure 4(a), it was concluded that the graft copolymer was found to be thermally more stable. This was confirmed from the amount of graft copolymer remained as residue at the end of the experiment, and the various decomposition temperatures.

### Differential scanning calorimetry

Figures 5(a) represents the DSC curve details of the steam exploded fibers (stage-1), and Figures 5(b) represents the DSC curve details of the steam exploded bleached fibers (stage-2), Figures 5(c) represents the DSC curve details of the steam exploded fibers in acidic medium (stage-3), Figures 5(d) represents the DSC curve details of the mechanical treatment of the processed fibers (stage-4), and Figures 5(e) represents the DSC curve details of the graft copolymer (cellulose-g-acrylonitrile) respectively. The observed results of the DSC curve of the steam exploded fiber (Figure 5a)

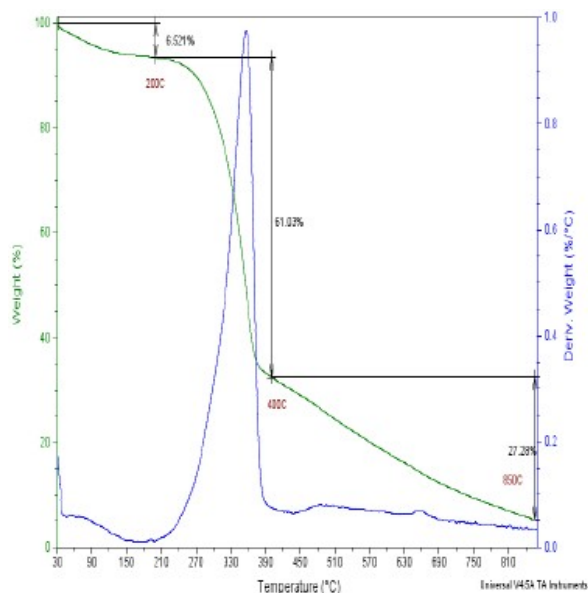


Figure 4(a) : TGA thermogram of steam exploded fibre

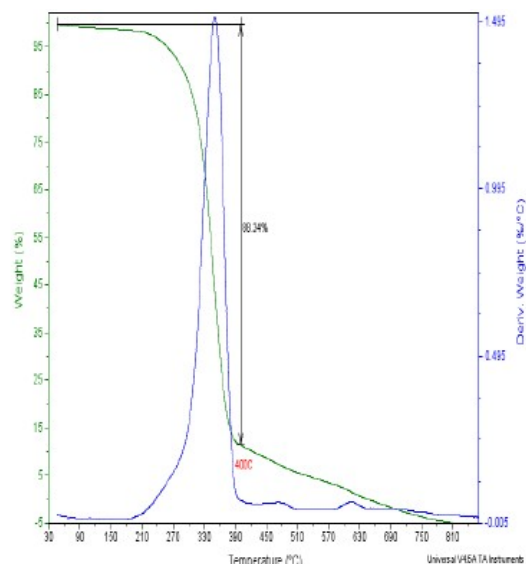


Figure 4(c) : TGA thermogram of steam exploded fibre in acidic medium

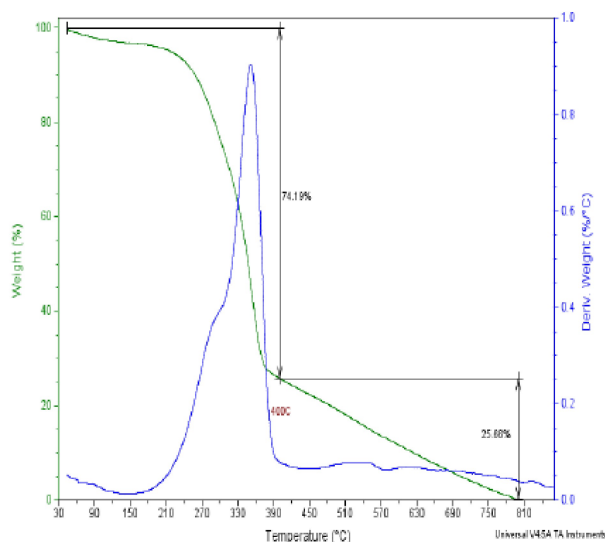


Figure 4(b) : TGA thermogram of steam exploded bleached fiber

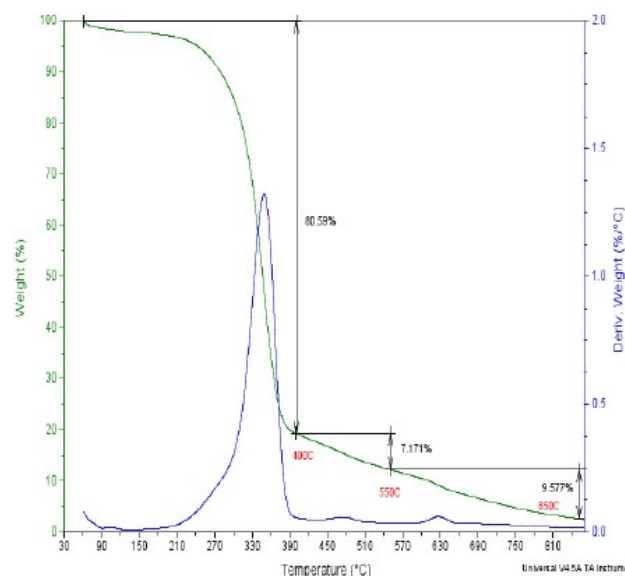


Figure 4(d) : TGA thermogram of mechanically treated fibre

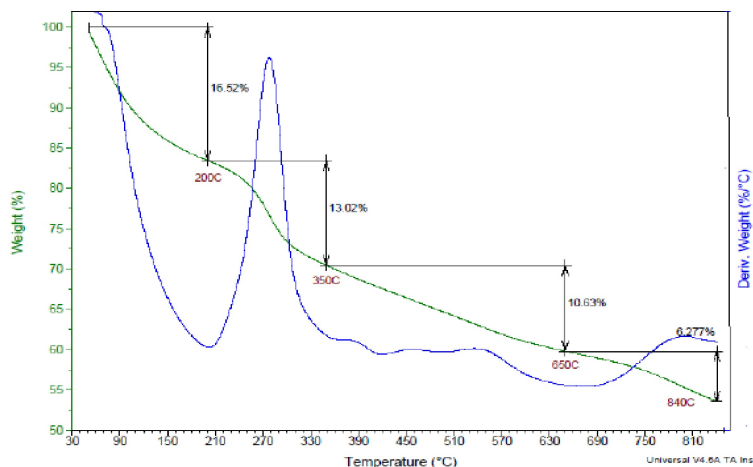


Figure 4(e) : TGA thermogram of grafted co-polymer (cellulose-g-acrylonitrile)

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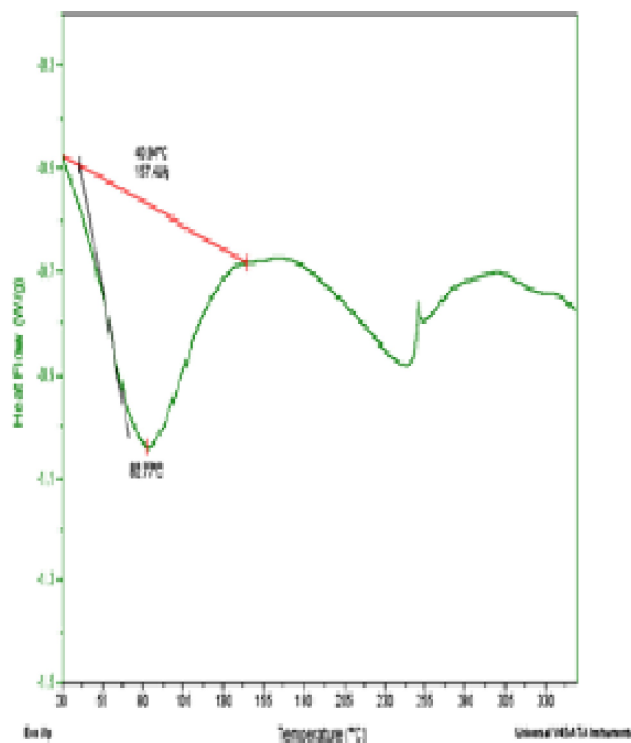


Figure 5(a) : DSC curve of steam exploded fibre

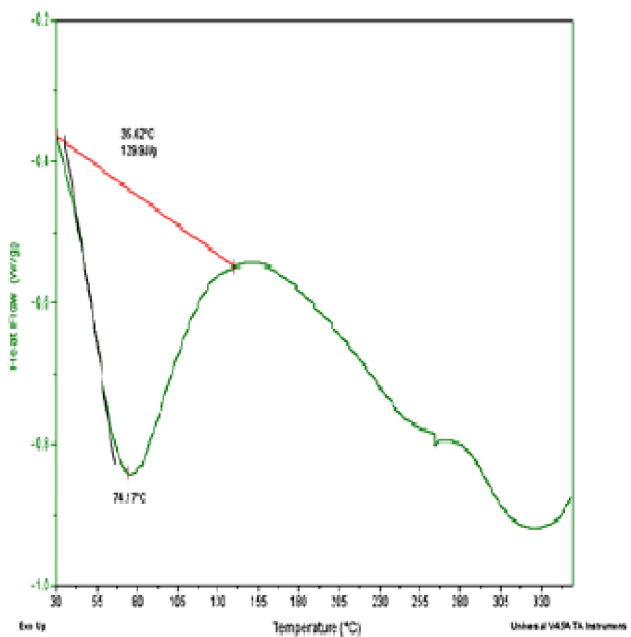


Figure 5(b) : DSC curve of steam exploded bleached fibre

indicate that the glass transition temperature was found to be 170°C. Two sharp and broad endothermic peaks are obtained at 82.77°C, 240°C showing the recrystallization process of steam exploded fiber at different temperatures. The glass transition temperature of the graft copolymer prepared using the extracted cellulose and acrylonitrile monomer was observed at

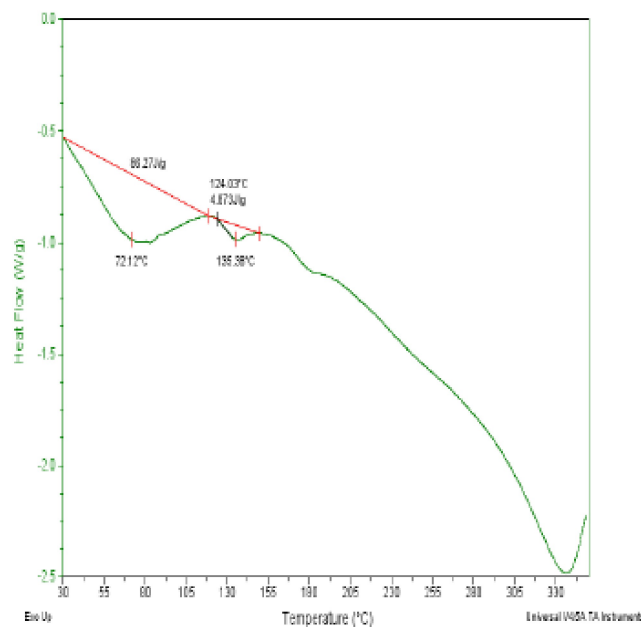


Figure 5(c) : DSC curve of steam exploded fibre in acidic medium

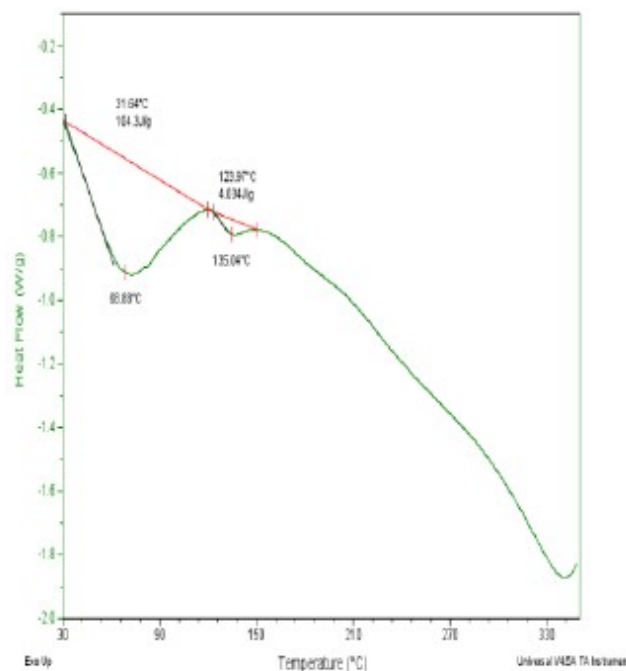
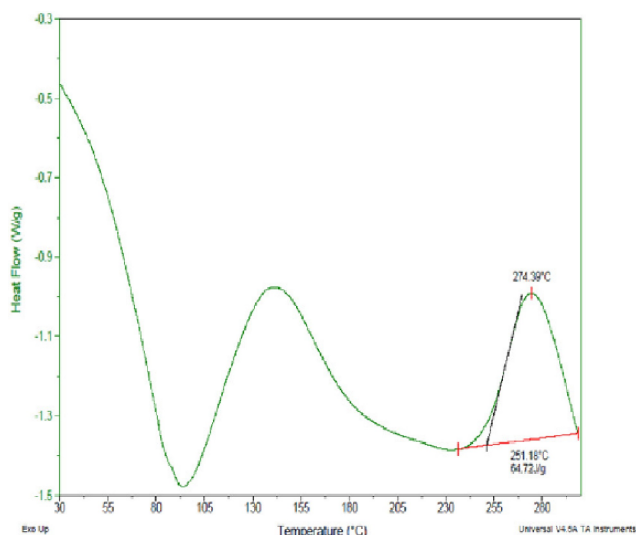


Figure 5(d) : DSC curve of mechanically treated processed fibre

200°C. A broad endothermic peak was observed at 93.05°C. On comparing the DSC curve of graft copolymer (cellulose-g-acrylonitrile) with steam exploded fibers it was observed that the glass transition temperature was shifted to a higher value for the graft copolymer. From the above results it was concluded that the addition of the monomer to extracted cellulose increases



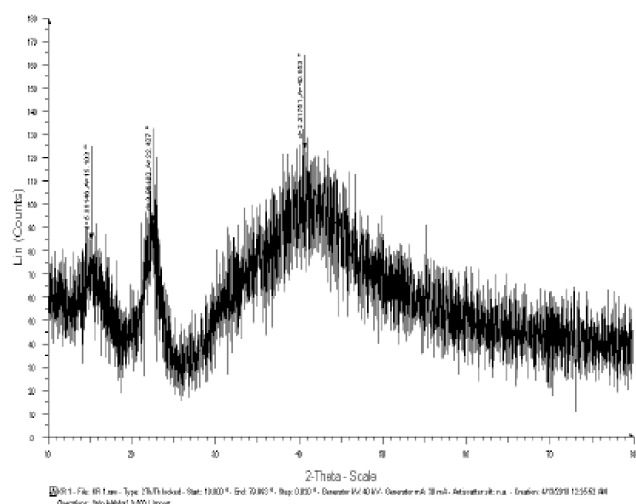


**Figure 5(e) : DSC curve of graft co-polymer (cellulose-g-acrylonitrile)**

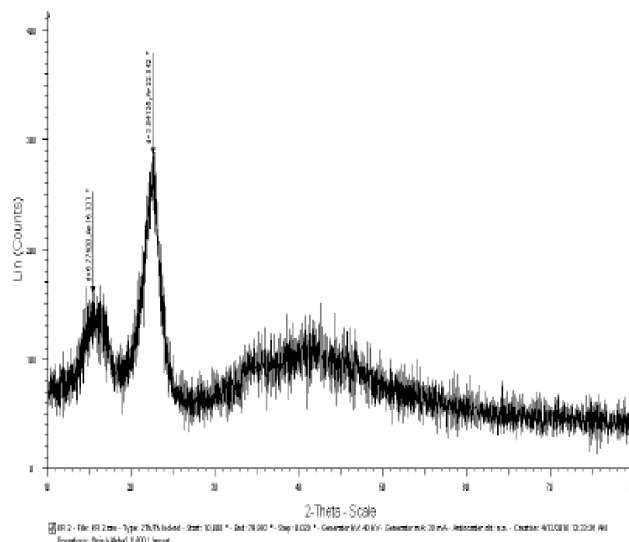
the thermal stability. The higher the  $T_g$ , the better will be the long term thermal stability of a material.

### XRD diffraction studies

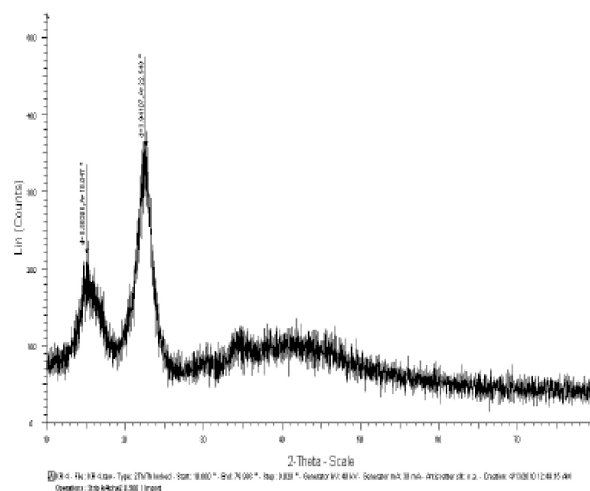
The XRD spectra of (a) steam exploded fibers (stage-1), (b) steam exploded bleached fibers (stage-2), (c) steam exploded fibers in acidic medium (stage-3), (d) mechanically treated processed fibers (stage-4) and (e) graft copolymer (cellulose-g-acrylonitrile) was shown in the Figure 6. The XRD of steam exploded fibers shows three distinct sharp peaks at around  $15^\circ$ ,  $22^\circ$ ,  $40^\circ$ . This obtained peak Figure 6(a) confirms that the three crystalline forms are present in the fiber. Only two crystalline forms were observed at  $16^\circ$  and  $23^\circ$  when it was subjected to further treatments such as bleaching, fiber in acidic medium and mechanical treat-



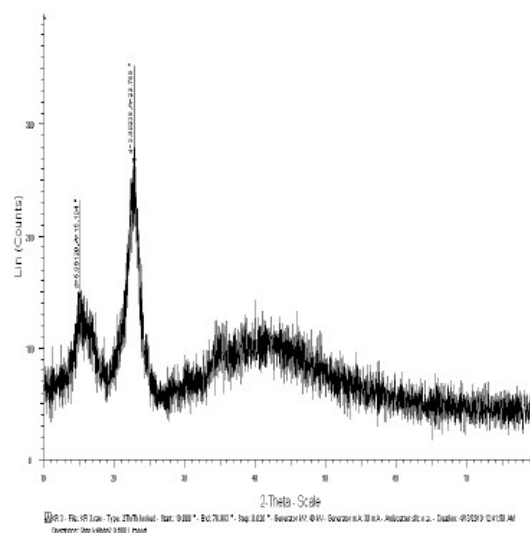
**Figure 6(a) : XRD spectra of steam exploded fiber**



**Figure 6(b) : XRD spectra of steam exploded bleached fibre**



**Figure 6(c) : XRD spectra of steam exploded fibre in acidic medium**



**Figure 6(d) : XRD spectra of mechanically treated processes fibre**

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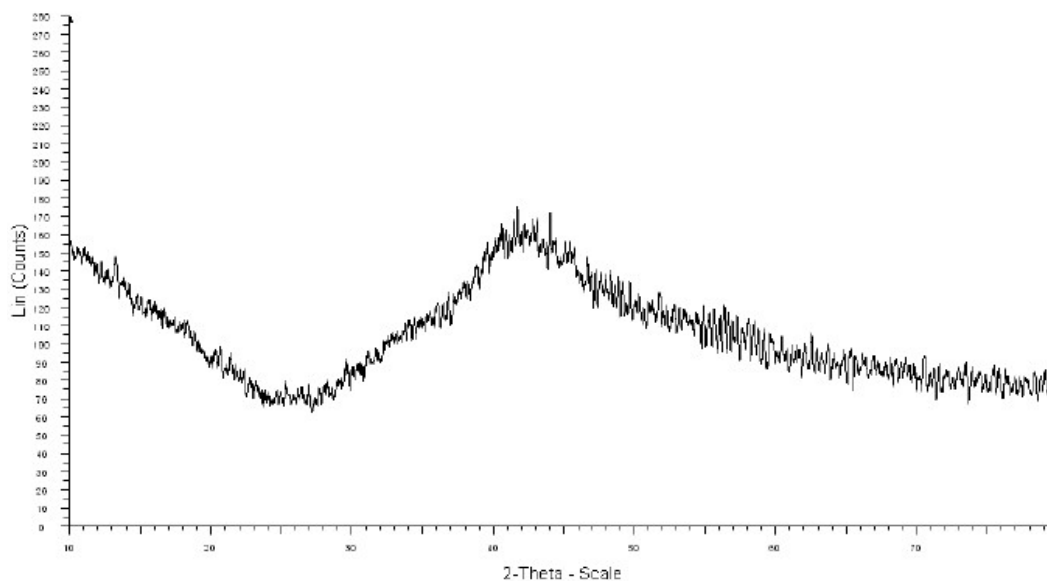


Figure 6(e) : XRD spectra of grafted copolymer (cellulose-g-acrylonitrile)

ment which was shown in Figure 6(b), Figure 6(c), Figure 6(d). These results indicate that the bleached fiber, acid treated fiber and mechanically treated fiber are more amorphous than raw fiber. Several researchers observed that the treatment by the alkali was reported to reduce the proportion of crystalline material present in plant fibers<sup>[26,27]</sup>. The XRD of the grafted cellulose with acrylonitrile shows broad peak at around  $40^\circ$  which indicate that a change in crystallinity (amorphous nature) was observed in the grafted copolymers which was shown in Figure 6(e).

### CONCLUSION

Based on the results observed in this paper, we conclude that ceric ammonium nitrate was found to be an effective initiator for grafting acrylonitrile monomer onto cellulose extracted from the sisal fiber under a wide range of experimental conditions. The results from this study also indicate that the grafting level was affected by the initiator and the monomer concentrations. The FT-IR study of the samples provides a strong evidence for grafting. The changes in crystalline nature and the increased thermal stability of the extracted cellulose due to polymerization were confirmed using X-ray diffraction patterns and TGA and DSC results respectively. Cellulose grafted acrylonitrile have many applications. Among them, heavy metal and dye removal from aqueous solutions are the prominent ones.

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