Comparative Study on the Optimization of Graft Copolymerization of Acrylic Acid and Acrylonitrile onto Cellulose Prepared From Sisal Fibre

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ABSTRACT

Using the combination of chemical and mechanical treatments, the cellulose was extracted from the sisal fiber. Chemical modification of the extracted cellulose was done using grafting technique. The grafting of acrylic acid and acrylonitrile monomer onto the extracted cellulose was carried out separately in a homogeneous aqueous phase by using ceric ammonium nitrate as the initiator. The effect of initiator concentration and monomer concentration on grafting parameters (GE\%, GY (\%), GP\%) were studied. FTIR, TGA, SEM and XRD methods are used to characterize the treated fibers and the graft copolymer. The results of FT-IR studies clearly indicate that acrylic acid and the acrylonitrile monomer were effectively grafted onto cellulose obtained from sisal fiber. From the results of the XRD pattern, the change in crystallinity of the graft copolymeric samples was elucidated. The increase of the thermal stability of the polymer upon grafting was concluded from the TGA and DSC studies.

Keywords: Acrylic acid, Acrylonitrile, Cellulose, Graft copolymerization, grafting parameters, Sisal fiber, Steam explosion.

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Introduction

One of the most important cheapest and the common renewable resource in many developing countries of the world was the natural fibers. It provide a solution to environmental pollution by finding new uses for waste materials without introducing health hazards\textsuperscript{1,2}. Every year around 35 million tons of natural fibers was harvested by the farmers.
from a wide range of plants and animals\textsuperscript{3}. The most common reinforced natural fibers are the flax, hemp, sisal, nettle and jute. Among the various natural fibers, since the sisal fiber is fairly coarse, inflexible, renewable, nonabrasive and biodegradable, it possesses moderately high specific strength and stiffness, durability, ability to stretch, and resistance to deterioration in saltwater\textsuperscript{4,5}. Our study is focused on sisal plant fiber, which is a local product in the countries of Mediterranean rim. Especially the mechanical properties of natural fibers depend on their cellulose type.

The field of natural fiber research has experienced an explosion of interest\textsuperscript{6} within the last two decades. Steam explosion technology has become a well known method for separating the lingo-cellulose materials into its main components cellulose, lignin and hemicelluloses\textsuperscript{7}. Using the various treatments such as chemical or physical treatments the compatibility of natural fibers was improved. These treatments was mainly done with the goal of modifying the surfaces of the fibers\textsuperscript{8}. Among the various treatments applied to the natural fibers, the most commonly used one is alkaline treatment which was also named as mercerization. The alkaline treatment was done to the natural fibers mainly to promote the removal of partially amorphous constituents such as hemicelluloses, lignin, and waxes. As a result of this the level of fiber aggregation making the surface rougher becomes reduced\textsuperscript{9}. Steam explosion technology has become a well known method for separating the lignocellulosic materials into its main components cellulose, lignin and hemicelluloses.

It is essential to modify the properties of a polymer according to tailor-made specifications designed for target applications. Grafting is one of the promising methods for modifying the properties of polymer. A challenging field of research with unlimited future prospects is the grafting of vinyl monomers onto natural and synthetic polymers. Using various initiators such as hexavalent chromium, tetravalent cerium, trivalent manganese, peroxydisulphate and peroxydiphosphate ions the graft copolymerization of several monomers was done onto a multitude of natural and synthetic polymers like wool, silk, cellulose, nylon and PET, rubber during the last decades. These studies was carried out by Nayak, 2001 and his co-workers which was done mainly to enhance their properties\textsuperscript{10,11,12,13,14}.

The aim of this work was to isolate cellulose from the sisal fiber, using chemical and mechanical treatments. The graft copolymerization of acrylic acid and acrylonitrile monomer onto the extracted cellulose was carried out using CAN as an initiator. Chemical
modifications in the samples after the various extraction and purification treatments were analyzed using Fourier transform infrared spectroscopy (FTIR) whereas the crystallinity of cellulose was evaluated by X-ray diffraction.

**MATERIALS AND METHODS**

**Materials**

The materials used for the study includes fibers (collected from local farms), NaOH (commercial grade), acetic acid (commercial grade), sodium hypochlorite, oxalic acid (commercial grade). Analytical grade ceric ammonium nitrate, acrylic acid and nitric acid were used.

**Preparation of Steam Exploded Fibers**

About 30 g of sisal fiber having uniform size of approximately 10 cm was taken in a beaker. It was then treated with 2% NaOH (fiber to liquor ratio 1:10) solution. Then the above treated fiber was placed in an autoclave and kept under 20 lb pressure for a period of 1 h. 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 solutions. This bleaching process was repeated six times. After bleaching process is over, the fibers were thoroughly washed in distilled water and then it was allowed to dry.

**Preparation of Steam Exploded Fibers in Acidic Medium**

The steam exploded bleached fibers were treated with oxalic acid of varying concentrations (5%, 7%, 9%, and 11%) in an autoclave till it attained a pressure of 20 lb. The pressure was released immediately. 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 KMnO₄ solution to make sure that the washings were free from acid.
Mechanical Treatment of the Processed Fibers

The acid treated fibers suspended in water was continuously stirred with a mechanical stirrer of type RQ – 1.27 A at 8000 R.P.M. for 4 h. After 4 hours, the suspension was kept in an oven at 90°C till it was dry.

Preparation of grafted co-polymer

Graft copolymerization of acrylonitrile onto cellulose extracted from the sisal fiber was carried out using various amounts of the monomer and ceric ions and a constant amount of cellulose (1 g) dispersed in 100 ml of distilled water at 70°C. In a typical experiment, 1 g of cellulose was dispersed in 100 ml of distilled water in a 250 ml beaker. A given amount of acrylonitrile monomer (1 ml) was added to the beaker and the mixture was stirred for 10 min. Then the initiator solution was added to the mixture and continuously stirred for a period of 30 minutes. The above mixture was then poured into large excess of 2N sodium hydroxide solution with stirring to precipitate the polymer. Finally the graft co-polymeric product obtained was filtered, air dried and weighed. A similar procedure was carried out to prepare the cellulose graft acrylic acid copolymer. The grafting percentage, grafting efficiency, grafting yield and the degree of grafting was calculated by weighing the extracted cellulose and the grafted product. The grafting parameters can be represented in equations (1)-(3) 17

\[
GE(\%) = \frac{\text{Wt of graft polymer}}{\text{Wt of graft polymer} + \text{Wt of homopolymer}} \times 100 - (1)
\]

\[
GY(\%) = \frac{Wg-Wi}{Wi} \times 100 - (2)
\]

\[
GP(\%) = \frac{Wpa}{Wa} \times 100 -- (3)
\]

Where Wi =Wt of ungrafted polymer, Wpa or Wg = Wt of graft polymer, Wa- Weight of monomer.

Characterization

The FT-IR spectra of chemically and mechanically treated sisal fibers and graft copolymer were recorded using the Perkin Elmer 200 FTIR Spectrophotometer. DSC thermograms of processed sisal fiber and graft copolymer were measured with a DSC Q200 V24.4 build instrument. The temperature range was changed from 30°C to 350°C with the heating rate of 10°C/min. The samples prepared under different conditions were tested in a TGA Q500 V20.10 Build 36 instrument. While recording the TGA, the temperature range
was varied 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 Cu Kα radiation source (λ=0.154nm), set at scan rate = 10°/min, using a voltage of 40kV and a current of 30 mA.

Results and Discussion

The grafting of acrylic acid (AA) and acrylonitrile (AN) monomer onto extracted cellulose was carried out separately at various initiator concentration and monomer concentration separately by keeping the other variables (temperature, time, cellulose) as constant.

Effect of initiator concentration

At first graft copolymerization was carried out at various cerium-ammonium-nitrate concentration (0.3-1.2g) at constant temperature, time and monomer concentration.

Figure 1: Effect of initiator on cellulose graft acrylic acid

![Effect of initiator](image1.png)

Figure 2: Effect of initiator on cellulose graft acrylonitrile

![Effect of initiator](image2.png)
Figure 1 and Figure 2 shows the changes observed in the grafting parameters of cellulose-g-acrylic acid and cellulose-g-acrylonitrile as a function of the change in the ceric ammonium nitrate concentration respectively. The results presented in the above figures indicate that the grafting parameters (GE%,GP% and GY%) increases with increase in the initiator concentration up to 0.8g in the case of acrylonitrile and 1.0 g in the case of acrylic acid beyond which it decreases. The initial increase may be attributed to the increased free radical concentration in the system. The retarding effect of grafting parameters with initiator concentration beyond 0.8g in the case of acrylonitrile and 1.0 g in the case of acrylic acid may be due to predominance of homo polymerization over grafting. In addition to this the decrease in the grafting parameters beyond the optimum CAN concentration was also due to the termination of growing grafted chains by excess of primary radicals formed from the initiator\textsuperscript{19,20}. From these results, 0.8g and 1.0 g cerium-ammonium-nitrate can be proposed for the optimal grafting efficiency for cellulose-graft acrylonitrile and cellulose-graft acrylic acid graft copolymers.

**Effect of monomer concentration**

The effects of monomer concentration on the level of conversion and quantities of grafted acrylonitrile and acrylic acid onto extracted cellulose were investigated. Experiments were performed in the monomer concentration ranges of 0.3-1.2 ml. The observed results were shown in the figure-3 and figure-4 respectively.

Figure 3: Effect of monomer on cellulose graft acrylic acid

![Effect of monomer(AA)](image-url)
From the above graphical results it was inferred that the the grafting parameters increased initially with increase in monomer concentration. But after reaching a certain optimum monomer concentration it shows a decrease. The extent of graft copolymer formation mainly depends on the amount of monomer complexed. Due to increasing supply of monomers to cellulose macro radicals and the nonexistence of homopolymer on acrylonitrile the grafting parameters shows an initial increase. Maximum values of 65.5% and 190.60% were obtained for grafting efficiency and percentage grafting respectively at 0.8 ml monomer concentration in the case of acrylonitrile and maximum values of 64.6% and 181.00% were obtained for grafting efficiency and percentage grafting at 0.7ml monomer concentration in case of acrylic acid monomer. At higher monomer concentration (>0.7 and 0.8 ml), the decrease in grafting parameters was observed. This decrease was due to the increase in the chain transfer reactions to excess molecules in the vicinity of growing ends of grafted chains. Inspite of this, the way of monomer molecules to the cellulose macroradicals was also blocked by the large amounts of homopolymer deposits resulting in decrease of the grafting parameters. Therefore 0.7 ml in case of acrylic acid and 0.8ml in case of acrylonitrile was taken as the maximum concentration at which monomer can be complexed.

**FT-IR spectral analysis**

The grafted copolymer and the four stages of chemically treated fibers were characterized by IR spectrophotometer. The FT-IR spectra of four stages of fibers such as steam exploded fibers(stage-1), steam exploded bleached fibers(stage-2), steam exploded fibers in acidic medium(stage-3),mechanically treated processed fibers (stage-4), graft...
copolymers (cellulose-g-acrylic acid) and graft copolymer (cellulose-g-acrylonitrile) was shown in Figure 5(a)-(f). The spectra of the grafted copolymer showed the existence of a moderate peak at 2120 cm\(^{-1}\) and at 2500 cm\(^{-1}\) as observed in Figure 5(e) and Figure 5(f) which is an evidence of grafting. This absorption band arises from the stretching vibration mode of the nitrile groups (Figure 5(e)) and of the acid group (Figure 5(f)). These above observed peaks confirms that the grafting had taken place effectively. Most of the other peaks are related to the polymer backbone (cellulose)\(^{24}\).

Figure 5(a): FT-IR spectra of steam exploded fibre

![Figure 5(a): FT-IR spectra of steam exploded fibre](image1)

Figure 5(b): FT-IR spectra of steam exploded bleached fibre

![Figure 5(b): FT-IR spectra of steam exploded bleached fibre](image2)
Figure 5(c): FT-IR spectra of steam exploded bleached fibre in acidic medium

Figure 5(d): FT-IR spectra of mechanical treatment of fibre

Figure 5(e): FT-IR spectra of cellulose graft acrylic acid.
Figure 5(f): FT-IR spectra of cellulose graft acrylonitrile

Thermo gravimetric analysis

The TGA thermogram details of steam exploded fibers, steam exploded bleached fibers, acidically treated fiber, mechanically treated fibers, graft copolymer (cellulose-g-Acrylic acid) and graft copolymer (cellulose-g-acrylonitrile) was shown in the Figure 6(a)-(f).

Figure 6(a): TGA thermogram of steam exploded fibre
Figure 6(b): TGA thermogram of steam exploded bleached fibre.

Figure 6(c): TGA thermogram of steam exploded bleached fibre in acidic medium
Figure 6(d): TGA thermogram of mechanical treatment of fiber.

Figure 6(e): TGA thermogram of cellulose graft acrylic acid.
Figure 6(f): TGA thermogram of cellulose graft acrylonitrile.

The TGA thermogram details of steam exploded fibers shows that around 94.83% of the sample had decomposed at 850˚C leaving behind 5.169% of the sample as a residue. The smaller amount of remaining residual fibers at the end of the experiment was mainly due to the removal of non-cellulosic materials during the chemo-mechanical treatments of the sisal fiber\(^2\). It can be noticed that the steam exploded fibers show major weight loss of 61.03% takes place in the range of 200°–400° C at Tmax = 400°C derived from derivatogram, whereas cellulose-g-acrylonitrile shows major weight loss of 32.25% in the range of 150°–390° C at Tmax = 350° C and cellulose-g-acrylic acid shows major weight loss of 13.02% in the range of 250°–400° C at Tmax = 350° C. Around 67.822% of the cellulose-g-acrylic acid copolymer sample was disintegrated in 850°C leaving behind 32.178% of the sample as a residue whereas in case of cellulose-g-acrylonitrile copolymer sample around 40.477% of the sample was disintegrated in 840°C leaving behind 59.553% of the sample as a residue.

The difference in degradation temperature confirms that upon grafting of acrylic acid and acrylonitrile onto cellulose, some chemical changes in the structure of cellulose takes place. With the help of comparison of results of thermogram details of cellulose-g-acrylic acid and cellulose-g-acrylonitrile with steam exploded fiber, it was finally concluded that the graft copolymer was found to be thermally more stable. In addition to this on comparing the
thermogram details of cellulose-g-acrylic acid with cellulose-g-acrylonitrile it was concluded that the cellulose-g-acrylonitrile copolymer was found to be thermally more stable than cellulose-g-acrylic acid respectively. 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**

Figure 7 represents the DSC curve of four stages of fibers, graft copolymer (cellulose-g-acrylic acid) and graft copolymer(cellulose-g-acrylonitrile) respectively. Broad endothermic peaks are observed at various temperatures indicating the crystallization of processed sisal fiber and graft copolymer. The DSC curve of steam exploded fibers Figure 7(a) shows that the glass transition temperature was observed at 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 was found to be 180°C in the case of graft copolymer prepared using the extracted cellulose and acrylic acid monomer. A broad endothermic peak was observed at 76.05°C.A similar type of result is observed in the case of (cellulose-g-acrylonitrile) copolymer. In the case of cellulose-g-acrylonitrile copolymer the glass transition temperature was found to be 200°C and a broad endothermic peak was observed at 93.05°C. On comparing the DSC curve of both graft copolymers 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 the thermal stability. In addition to this on comparing the DSC curve details of cellulose-g-acrylic acid with cellulose-g-acrylonitrile it was concluded that the cellulose-g-acrylonitrile copolymer was found to be thermally more stable than cellulose-g-acrylic acid respectively. The higher the Tg, the better will be the long term thermal stability of a material.
Figure 7(a): DSC Curve of steam exploded fibre.

![DSC Curve of steam exploded fibre](image1)

Figure 7(b): DSC Curve of steam exploded bleached fibre.

![DSC Curve of steam exploded bleached fibre](image2)
Figure 7(c): DSC Curve of steam exploded bleached fibre in acidic medium

Figure 7(d): DSC Curve of mechanical treatment of processed fibre
XRD diffraction studies

The X-ray diffraction patterns of steam exploded fibers, steam exploded bleached fibers, steam exploded fibers in acidic medium, mechanically treated processed fibers, graft...
copolymer (cellulose-g-Acrylic acid) and graft copolymer(cellulose-g-acrylonitrile) are shown in Figures 8(a)–(f). It could be seen that there were some differences of peak height, width and position between them. Several researchers reported that the proportion of crystalline material present in plant fibers was reduced by the alkali treatment. The XRD of steam exploded fibers shows three distinct sharp peaks at 15°, 22°, 40° which indicates three crystalline forms are present in fiber. When it is subjected to further treatments such as bleaching, fiber in acidic medium and mechanical treatment only two crystalline forms were observed at around 16° and 23°. This indicates that the bleached fiber, acid treated fiber and mechanically treated fiber are more amorphous than raw fiber. The XRD of the grafted cellulose with acrylic acid shows two sharp distinct peaks at around 21°, 42° indicating that two crystalline forms are obtained on grafted copolymers. The appearance of peak again around 20°, 40° indicates that the processed fiber (cellulose) undergoes grafting with the monomer acrylic acid. The XRD of the grafted cellulose with acrylonitrile shows broad peak at around 40° which indicate that a change in crystallinity (amorphous nature) was observed in the cellulose-g-acrylonitrile copolymer.

Figure 8(a): XRD of steam exploded fibre
Figure 8(b): XRD of steam exploded bleached fibre

Figure 8(c): XRD of steam exploded bleached fibre in acidic medium.
Figure 8(d): XRD of mechanical treatment of fibre.

Figure 8(e): XRD of cellulose graft acrylonitrile
Conclusion

Grafting parameters such as conversion of monomer to polymer, graft yield can be varied substantially by varying the concentration ratio of initiator (Ce$^{4+}$) to cellulose and monomer to cellulose. The optimum synthetic conditions may be given as follows: CAN concentration-1.0g; acrylic acid -0.7 ml for cellulose-g-AA and CANconcentration-0.8g; acrylonitrile-0.8ml for cellulose-g-AN. From the results it was observed that the calculated grafting parameters were different for grafting of AA than for AN. These results confirm that the grafting parameter slightly depends upon on the functional group present in the monomer. The proof of grafting was obtained from the FT-IR results. 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. From the TGA and DSC results it was concluded that the cellulose-g-acrylonitrile was found to be highly thermally stable. This type of work could encourage the synthesis of new grafted polymers, where some functionality is required, for specific purposes.

References


