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Synthesis and characterization of graft copolymerized acrylic acid onto cellulose prepared from sisal fibre

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ABSTRACT

The extraction of cellulose from sisal fiber was done using the steam explosion technique. Four different stages of fiber such as steam exploded fiber, bleached fiber, acid treated fiber and mechanically treated fiber were prepared from sisal fiber to convert it into cellulose. The graft copolymer of the cellulose extracted from sisal fiber with acrylic acid was synthesized in aqueous solution using ceric ammonium ion as the initiator. The prepared extracted cellulose-g-acrylic acid monomer was characterized with the help of analytical techniques such as FTIR, XRD, TGA and DSC studies. The grafting phenomenon taking place between cellulose and the acrylic acid was proved by Fourier transform infrared spectroscopy (FTIR). The XRD pattern elucidates the change in crystallinity of the grafted polymeric samples. The results of TGA and DSC studies indicate the enhancement of thermal stability of the polymer upon grafting. © 2013 Trade Science Inc. - INDIA

INTRODUCTION

Around 35 million tons of natural fibers was harvested by the farmers each year from a variety of plants and animals. This was reported by the food and agricultural organization (FAO)^[1]. The fibers which are obtained naturally from the plants, animals and minerals was termed as natural fibers^[2]. The basic components which was present in the natural fibers are the cellulose, lignin and hemicelluloses. Since the natural fibers mainly consist of cellulosic components the natural fibers was also termed as cellulosic or lignocellulosic fibers. In order to remove lignin-containing materials such as pectin, waxy substances and natural oils covering the external surface of

KEYWORDS

Sisal fiber; Steam explosion; Cellulose; Acrylic acid; Graft copolymerization; Grafting parameters.

the fibre cell wall, chemical treatment was done with the natural fibers. The factors which mainly influence the properties of the cellulosic fibers are chemical composition, internal fiber structure, microfibril angle, cell dimensions and defects, which differ from different parts of a plant as well as from different plants^[3].

Depending on the part of the plant from which cellulose was extracted, the fibers were classified into three categories. They are the fruit fibers (cotton, coir, oil palm etc.), stem fibers (jute, banana) and leaf fiber (sisal, pineapple etc.). The natural fibers have better mechanical performance and advantages than the synthetic fibers. The main advantages are the low cost, better renewability, biodegradability and as well as more abundance.

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 gms of fibers were chopped into uniform size of approximately 10 cm. The fibers were treated with 2% NaOH (fiber to liquor ratio 1:10) 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 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. The bleaching process was repeated six times. After bleaching, the fibers were thoroughly washed in distilled water and dried.

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^[13,14].

Mechanical treatment of the processed fibers

The fibers were suspended in water and under continuous stirring with a mechanical stirrer of type RQ - 1.27 A and 8000 R.P.M. for 4 h. The suspension was kept in an oven at 90°C till it was dry.

Preparation of grafted co-polymer

A required amount of cellulose (1g) was added

Most of the plant fibres such as coir, sisal, jute, banana and pineapple are used as a resource for industrial materials^[4]. The plant fibers have been recognized as an important source of fibre for composites^[5,6]. Among the various natural fibres, the most important fiber which is of particular interest was the sisal fiber. A sisal fiber (SF), an environmental friendly crop which belongs to the Agave family (Agave Sisalina) was a strong, stable and versatile material having high specific strength and stiffness, durability, ability to stretch, and resistance to deterioration in saltwater^[7,8].

The superior mechanical properties were found in the fibers having high crystallinity and cellulose content. The mechanical properties of the natural fibers were determined with the help of type of cellulose present in it. This is because each type of cellulose has its own crystalline organization. When sisal fibers were modified with surface treatment, the mechanical properties was found to be improved^[9]. The most commonly used chemical for bleaching and cleaning the surface of plant fibres was the sodium hydroxide. Due to this bleaching treatment the fine structure of the native cellulose I (native cellulose) was changed into cellulose II (regenerated cellulose). The native cellulose was termed as the crystalline cellulose whereas the cellulose (II) was termed as the regenerated cellulose. The cellulose II refer to cellulose precipitated out of solutions, generally alkali solutions^[10].

The most unstable form of cellulose was the cellulose (I) and the thermodynamically stable form was the cellulose (II). An additional hydrogen bond per glucose residue in cellulose II makes this allomorph the most thermodynamically stable form^[11]. The modification of properties of the polymers was done in the polymeric age to get the targeted applications^[12]. Among the many methods of modification of polymers, grafting is one of the promising methods. The main aim of this study was to evaluate the extraction of cellulose from sisal fiber (cellulose-II) using chemical and mechanical process. The four different stages of fibers were prepared such as steam exploded sisal fiber, bleached fiber, acid treated fiber and mechanically treated fiber. The graft copolymerization of acrylic acid onto the extracted cellulose was carried out using CAN as an initiator and the prepared materials are characterized.



MMAIJ, 9(1) 2013

Full Paper

to100ml of water with constant stirring to form a homogeneous suspension. 1ml of monomer dissolved in 20 ml of water was then added to that homogenous solution. The initiator ceric ammonium nitrate (10 ml) was then added to the above mixture to initiate the polymerization process. After all the addition was over, the mixture was heated to 70°C. The stirring of the prepared hot mixture was performed using a magnetic stirrer simultaneously. This solution was then poured into excess sodium hydroxide solution to precipitate the graft copolymer. It was then filtered, dried and weighed. The grafting parameters, such as the grafting percentage, grafting efficiency, grafting yield were defined and calculated as follows.

GE(%) = Wt of graft polymer/	
Wt of graft polymer + Wt of homopolymer x100	(1)
GY(%) = Wg-Wi/Wi x100	(2)
GP(%) = Wpa/Wa x 100	(3)
With a weight of the stand of t	

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

CHARACTERIZATION

FT-IR analysis

The four stages of sisal fiber and graft copolymer were recorded by Fourier transform infra-red spectrophotometer (FT-IR) using KBr pelleted samples with Perkin Elmer 200 FTIR Spectrophotmeter.

Differential scanning calorimetry

DSC thermograms of processed sisal fiber and graft copolymer were measured using a DSC Q200 V24.4 build instrument. The temperature range was varied from 30°C to 350°C with the heating rate of 10°C/min.

Thermal gravimetric analysis

The samples prepared under different conditions were tested in a TGA Q500 V20.10 Build 36 instrument. The temperature range was varied from room temperature to 850°C with the heating rate of 10°C/min.

X-ray diffraction

The X-ray diffraction patterns were tested by an X-ray scattering SHIMADUZ XD-DI Diffractometer using Ni filter Cu K α radiation source (λ =0.154nm), set at scan rate = 10° /min, using a voltage of 40kV and a current of 30 mA.

Macromolecules

An Indian Journal

RESULTS AND DISCUSSION

Effect of initiator and monomer concentration

Figure 1 and Figure 2 shows the effect of ceric ammonium nitrate concentration and acrylic acid concentration on the grafting parameters of cellulose-g-acrylic acid respectively. From the Figure 1, it is evident that when the total volume, reaction temperature, time and





Figure 1 : Effect of ceric ammonium nitrate concentration.

Effect of monomer(AA)



Figure 2 : Effect of acrylic acid concentration.

pH are kept constant, by varying the CAN concentrations, the grafting parameters initially increases significantly reaching a maximum value, and then decrease slightly^[15].

In a grafting point of view, the initial increasing trend may be due to the fact that in a certain CAN concentration range, the CAN attacks the characteristic group (OH) of cellulose backbone directly, and creates a great deal of grafting sites, which will initiate the grafting^[16]. But when the CAN concentration exceeds a certain value, increased free radical concentration results in serious homopolymerization. In addition to this, an excess of CAN will accelerate the oxidation of radicals by CAN and the propagating chain will be terminated. These will lead to the decrease in the grafting param-

31

eters^[17]. The decline of grafting parameters may also be due to the enhanced chance of the transfer reaction to monomer. Also a similar type of results was observed by changing the monomer (AA) concentration. At first it shows an increase with increase in acrylic acid concentration but thereafter decreases. 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^[18].

FT-IR spectral analysis

Figure 3(a-e) shows the FT-IR spectra of four stages of fibers and graft copolymer. The IR spectra of the steam exploded fibers (Figure 3(a)) shows a prominent peak at 3445.81 cm⁻¹ corresponding to OH stretching. A peak at 2923.91 cm⁻¹ corresponds to CH₂ stretching^[19]. The peak obtained at 1628.20cm-1 was

due to C = O stretching. The peaks at 1168.18 cm⁻ ¹,1110.98 cm⁻¹ and 1058.61 cm⁻¹ corresponds to C-O stretching, C-H in plane bending and C-O-C stretching respectively. A similar type of results was observed in stage-2, stage-3 and stage-4(Figure 3(b-d)). On comparing the FTIR spectral results of steam exploded fibers with the other stages it was found that the area of the peak at 1628.45 cm⁻¹ was found to increase successively. The increase in peak intensity at 1628.45 cm⁻ ¹ in sisal fiber is due to the bonded acetyl group^[20]. 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; hemicelluloses etc., The grafted co polymers thus prepared were characterized by FTIR spectral studies. The FTIR spectra of graft copolymer (Figure 3(e)) (cellulose-g-acrylic acid) showed the peaks corresponding to the groups present in the four stages of fiber and acrylic acid monomer. These additional peaks confirm that the grafting had taken place effectively.

Thermo gravimetric analysis

The TGA thermal behavior of (a) steam exploded

Macromolecules

An Indian Journal







An Indian Journal







An Indian Journal









Figure 4(e) : TGA of graft copolymer.

fibers (stage -1), (b) steam exploded bleached fibers (stage - 2), (c) steam exploded fibers in acidic medium (stage-3), (d) mechanical treatment of the processed fibers (stage-4), (e) graft copolymer (cellulose-g-Acrylic acid) were represented in the Figure 4. The four stages of fibers shows three decomposition stages with the major weight loss of 88% takes place in the range of 240° -420° C at Tmax = 400°C derived from derivatogram, whereas graft copolymer (Figure 4(e) shows two stages of decomposition with major weight loss of 35.25% in the range of 200° - 390° C at Tmax = 350° C. The Tmax of chitosan have appeared to be around 400° C in the pure form and at 350° C in the grafted form. The difference in degradation temperature confirms that upon grafting of AA onto cellulose some chemical changes in the structure of chitosan takes place^[21]. The TGA thermogram of steam exploded fibers (Figure 4-a) shows that 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 cellulosic materials during these

Macromolecules An Indian Journal treatments^[22]. The TGA thermogram of the graft copolymer (cellulose-g-Acrylic acid) shows that the maximum weight loss occurs at the temperature range of 200°C to 350°C. Around 67.822% of the sample was disintegrated in 850°C leaving behind 32.178 % 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

Figure 5 represents the DSC curve of (a) steam exploded fibers (stage –1), (b) steam exploded bleached fibers (stage-2), (c) steam exploded fibers in acidic medium (stage-3), (d) mechanical treatment (stage-4) of the processed fibers, (e) graft copolymer (cellulose-g-Acrylic acid) 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 5-a) shows





Figure 5(c)(d) : DSC curve of Steam Exploded bleached Fibers (c) in acidic medium Stage-3; (d) in mechanical treatment stage -4.

Macromolecules An Indian Journal





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. On comparing the DSC curve of graft copolymer (Figure5(e)) (cellulose-g-Acrylic acid) 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. The higher the Tg 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), (e) graft copolymer (cellulose-g-Acrylic acid) was shown in the Figure 6. 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. Alkali treatment is reported to reduce the proportion of crystalline material present in plant fibres, as observed by several researchers^[23,24]. 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. In the XRD spectrum of graft copolymer, it's observed that diffraction intensity of the broad peak at around 42° was obviously weak-

> Macromolecules An Indian Journal



Macromolecules An Indian Journal



Figure 6(c)(d) : XRD spectra of steam exploded bleached fibers in (c) acidic medium (stage-3); (d) in mechanical treatment (stage-4).



Figure 6(e) : XRD spectra of graft copolymer.

ened indicating that the crystallinity of the chitosan decreased after modification.

CONCLUSION

Graft copolymerization is one of the most attractive technique which is used to widen its applications. Moreover, graft copolymerization is used to attach various functional groups and to control hydrophobic, cationic and anionic properties of grafted chitosan. The effect of monomer and initiator on grafting parameters has been reported. With increasing the concentration of the monomer as well as the initiator the graft yield decreases due to the formation of homolpolymer formation. The evidence of grafting has been ascertained from the FTIR spectra. 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. This type of work could encourage the synthesis of new grafted polymers, where some functionality is required, for specific purposes.

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