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HOMOGENEOUS MODIFICATION OF SUGARCANE BAGASSE TO CELLULOSE AND GRAFTED WITH 2-HYDROXYETHYLACRYLATE USING CERIC AMMONIUM NITRATE AS AN INITIATOR.

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ABSTRACT

This work deals with an approach of synthesizing cellulose-graft- 2-hydroxyethylacrylate copolymer using ceric ammonium nitrate as an initiator. Initially the cellulose fiber was extracted from sugarcane bagasse by utilizing steam explosion method. The 2-hydroethylacrylate monomer was then grafted onto cellulose backbone in a homogeneous solution using water as solvent. The structure of extracted cellulose and graft copolymer was characterized by FTIR spectra, XRD and TGA analysis and in addition the effects of various reaction conditions such as monomer concentration on the percentage of conversion (PC %), graft and graft efficiency (GE %) were studied and the results were investigated.

KEYWORDS: Cellulose fiber, 2-hydroethylacrylate, CAN and NaOH.

INTRODUCTION

Agricultural activities all over the world generate enormous volumes of agricultural wastes that contain cellulose fibre. The production of large-scale wastewater is unavoidable consequence of modern-day societies. Maize stem and cobs, banana and plantain pseudostem, raffia from Raphia hooker; orange mesocarp, coconut shell, groundnut husk, sugar cane bagasses, soybean, oath, wheat and rice hull are common examples for agricultural wastes.[1] Recently there has been increased in developing techniques to convert the lignocellulosic materials into environmental friendly chemical biomaterials. A great deal of attention has been given to the production of bio-adsorbents from lignocellulosic byproducts such as wood pulp[2] sugarcane bagasse.[3,4]

Sugar cane bagasse contains cellulose content as high as 62% based on the oven dry weight.[5] Cellulose is the most abundant, renewable biopolymer and a very promising raw material available for the preparation of various functional the modifications deal with chemical grafting of pre-polymers.[6] In addition, it is one of the most promising raw materials due to its abundance, easy availability, and low cost. It is a linear polysaccharide with long chains which consists of β-D-glucopyranose units joined by β-1,4 glycosidic linkages.[7,9] In one repeating unit of cellulose molecule, there are one methylol and two hydroxyl groups as functional groups.[10] Although cellulose has good properties, it has some undesirable ones such as low tensile strength, high moisture regain and low strength against microbial attack. Grafting of synthetic polymers onto cellulose eliminates these drawbacks and allows the acquisition of additional properties of grafted polymers without destroying its own properties.[11] The pretreatment method plays an important part in the lignocellulose modification process. It can damage the cellulose fiber structure through hydrolysis of hemicelluloses and partial removal of lignin. There are a variety of existing pretreatment methods include chemical methods, such as strong/weak acid and alkali treatments. Also the physical and mechanical combination methods, such as ball milling, as well as physical and chemical combination methods, steam explosion.[12] Among them steam explosion is one of the most effective pretreatment methods for improving the specific area of the bagasse surface.

Steam explosion was introduced and patented as a biomass pre-treatment process in 1926.[13] Steam explosion of biomass is a pre-treatment process that opens up the fibers and makes the biomass polymers more accessible for subsequent processes, i.e. fermentation, hydrolysis or densification processes. The major components are cellulose, embedded in a matrix of lignin and hemicelluloses.[14] Together they form tightly packed cellular structures (fibers). Grafting of other monomers onto cellulose is an important tool for the modification of cellulose. In this process, side chain grafts are covalently attached to a main chain of a polymer backbone to form a branched copolymer.

Grafting techniques is simple method to active the functional group on the backbone of the polymer for different purposes. It leads a physical change onto different structural characteristics in raw materials.[15] CAN in presence of nitric acid is an efficient initiator for graft copolymerization of monomer on to cellulose[16,17] in heterogeneous medium but in homogeneous conditions this will produce gel confirming the regeneration of cellulose and also monomer from the solution. The present paper deals with the study of effect of grafting conditions on grafting - 2-hydroxyethylacrylate onto cellulose.

In this present investigation, the effect of steam explosion pretreatment conditions on the sugarcane bagasse was determined. The graft copolymerization of 2-hydroxy ethylacryalte 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. Thermal degradation can be investigated by TGA analysis.

MATERIALSAND METHODS

MATERIALS

The materials used for the study includes sugarcane bagasse (collected from local forms), NaOH (commercial grade), acetic acid (commercial grade), sodium Hypo chlorite (commercial grade), oxalic acid (commercial grade). Analytical grade 2-Hydroxyl ethylacetate, ceric ammonium nitrate and nitric acid were used.

PREPARATION OF STEAM EXPLODED FIBERS

About 40 gm of sugar cane bagasse were chopped into uniform size of approximately10 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 auto- clave 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 78.8g, 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%) were 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 were 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 KMnO4 solution to make sure that the washings were free from acid.[18,19] Mechanical treatment of the processed fibers The acidically treated fibers was suspended in water and then stirred well using a mechanical stirrer of C°type RQ ñ 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 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 homogeneous suspension. 1ml of 2-hydroxy ethylacrylate monomer dissolved in 20ml of water was then added to that homogenous solution. The initiator ceric ammonium nitrate (0.5 g of CAN in 10ml of 1N HNO_3) was added in the above mixture to initiate the polymerization process. After all the addition was C. Simultaneously the stirring of that mixture was performed using a over, the above mixture was heated to 70 magnetic stirrer. It was then stirred for a period of approximately 30 minutes. After a time period of 30minutes the above solution was poured into excess sodium hydroxide (2N) solution. Finally, the obtained graft co- polymer precipitate was then filtered, dried and weighed. The grafting parameters including the grafting efficiency (GE) and grafting percentage (GP) were systematically evaluated as a function of various monomer concentration.[20] The grafting parameters can be represented in equations (1)-(2).

GE(%) =Wt of graft polymer/Wt of graft polymer +Wt of homopolymer x100 (1)

GP(%) =Wpa/Wa x 100 (2)

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 sugar cane bagasse fiber and graft copolymer were recorded by Fourier transform infra-red spectrophotometer (FTIR) using the Perkin Elmer 200 FTIR Spectrophotometer. 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 oC/min. The X-ray diffraction patterns were tested by an X-ray scattering SHIMADUZ XD-

DI Diffractometer using Nifilter CuK· radiation source (Î=0.154nm), set at scan rate = 10 o /min, using a voltage of 40kV and a current of 30 mA.

RESULTSAND DISCUSSION

Effect of monomer concentration

Fig.1 shows the effect of the ratio of 2-hydroxy ethylacrylate to sugarcane bagasse cellulose on the different parameters of grafting. Results show that as the monomer ratio was increased, there is a significant increase in graft % and graft efficiency %. Similar trends were observed by other investigators[21] with further increase of monomer concentration however, these values decrease. This is mainly due to the formation of homopolymer of 2-hydroxy ethylacrylate at the higher concentration as well as due to restricted movement of free radicals onto polymer backbone because of increased viscosity. These homopolymers successfully hinders the rate of penetration of monomer molecules to the cellulosic material, resulting in the low percentage of grafting. Furthermore as the monomer concentration increases, the rate of homo polymerization increases thereby decreasing the formation of graft copolymer.[21,22]

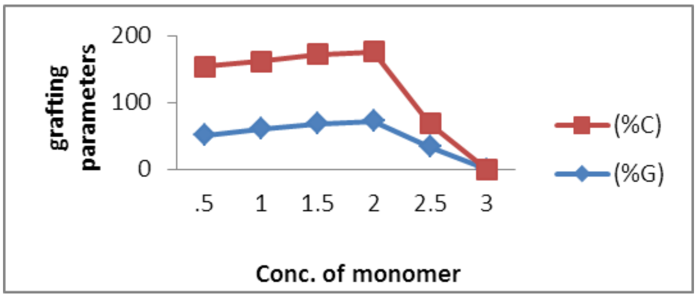

Figure-1 Effect of Monomer.

FT-IR

FTIR Spectra shows the four treatment stages of bagasse fibre and grafted copolymer Fig 2 (a-e). Fig 2(a) shows the prominent peak at 3440.81 cm^{-1} corresponding to OH stretching. Corresponding peak at 2920.85 cm-1 is due to CH2 stretching.[23] The peak obtained at 1628.20 cm-1 is due to C=O stretching. The peaks at 1168.18 cm-1, 1115.18 cm-1 and 1058.61 cm -1 are attributed to C-O stretching, C-H in plane bending and C-O-C stretching, respectively. Similar the peaks were obtained in fig 2(b-d). On comparing the FTIR Spectra of steam exploded fibres of four stages, it shows the area of the peak at 1620.32cm^{-1} (due to bonded acetyl group) increased effectively.[24] 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. And also grafted copolymers were characterized by FTIR spectra. The FTIR spectra of graft copolymer (cellulose-g-2-hydroxyethylacrylate) Figure 2(e) showed the peaks corresponding to the groups present in the four stages. In addition to the above peaks, it was observed that some additional strong peaks was observed at nearly 1670.19 cm -1 and 844.71cm -1 corresponding to the C=C stretching vibration of ethylacrylate and deformation in of CH_2. These above observed additional peaks confirm that the grafting had taken place effectively between the cellulose and the 2-hydroxyethylacrylate.

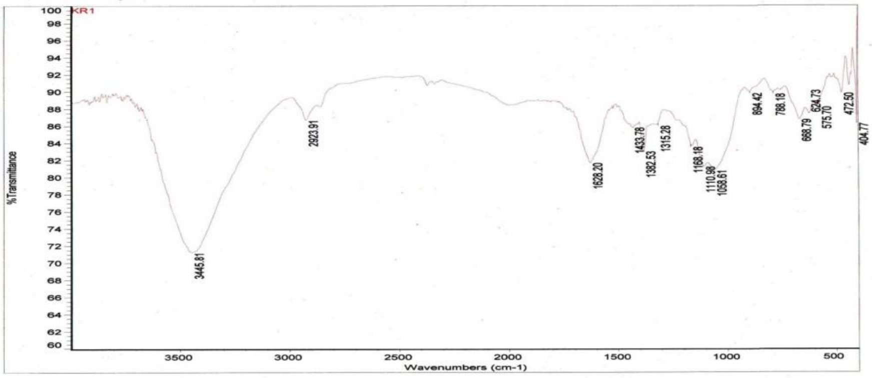

Figure-2(A) Ftir Studies of Steam Exploded Fiber (Stage- I).

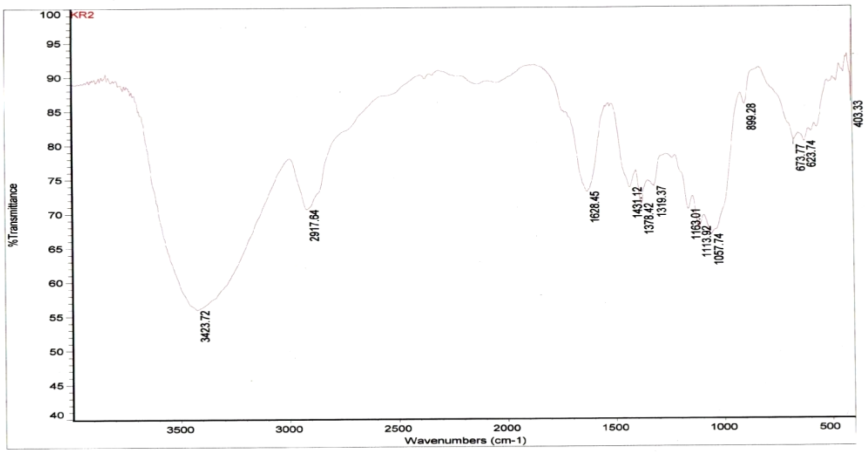

Figure-2 (B) Ftir Studies of Steam Exploded Fiber (Stage- Ii).

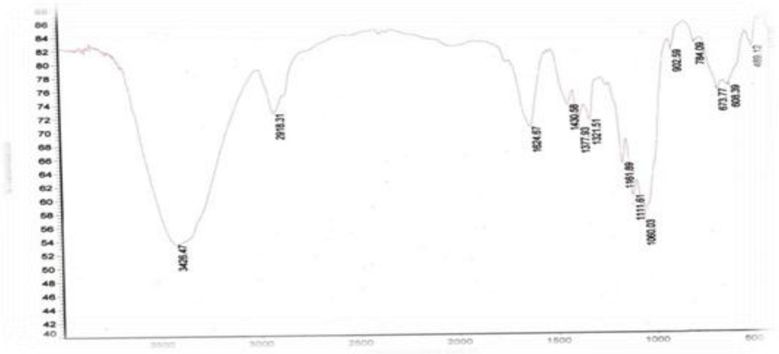

Figure-2(C) Ftir Studies Of Steam Exploded Fiber (Stage- Iii).

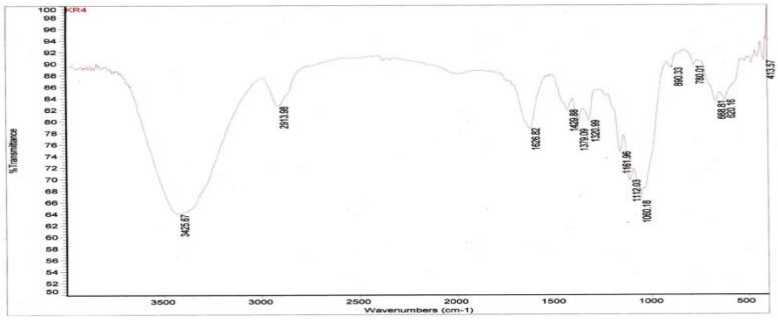

Figure-2(D) FTIR Studies of Steam Exploded Fiber (Stage- Iv).

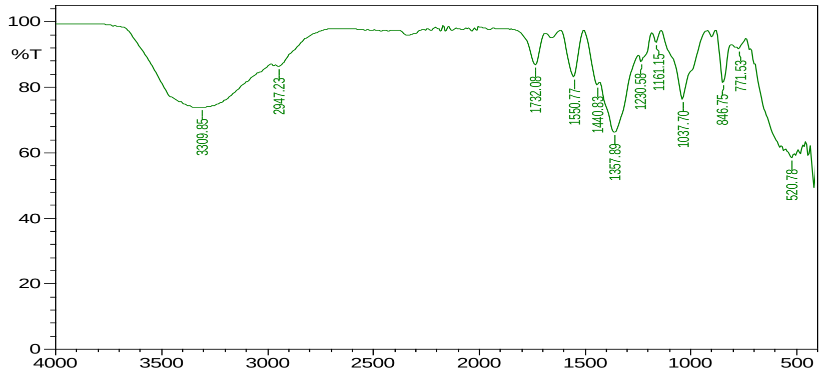

Figure-2(e) FTIR Studies of Cellulose Graft Copolymer.

XRD Diffraction Studies

The XRD spectra 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) mechanically treated processed fibers(stage-4) and 4(e) graft copolymer(cellulose-g-2-hydroxyethylacrylate) was shown in the Figure. The XRD of steam exploded fibers shows three distinct sharp peaks at around 15˚, 22˚, 40˚. 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˚ and 23˚ when it was subjected to further treatments such as bleaching, fiber in acidic medium and mechanical treatment which was shown in Figure 4(b), Figure4 (c), Figure 4(d). These results indicate that the bleached fiber, acid treated fiber and mechanically treated fiber are more crystalline 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.[25,26] The XRD of the grafted cellulose with 2-hydroxyethylacrylate shows sharp peak at around 35˚c which indicate that a change in more crystallite nature was observed in the grafted copolymers which was shown in Figure 4(e).

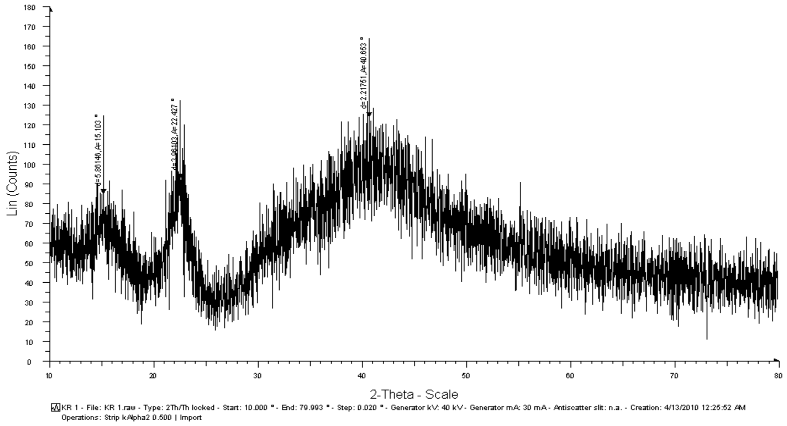

Figure-4(a) XRD spectra of Steam Exploded Cellulose Fiber (Stage-I).

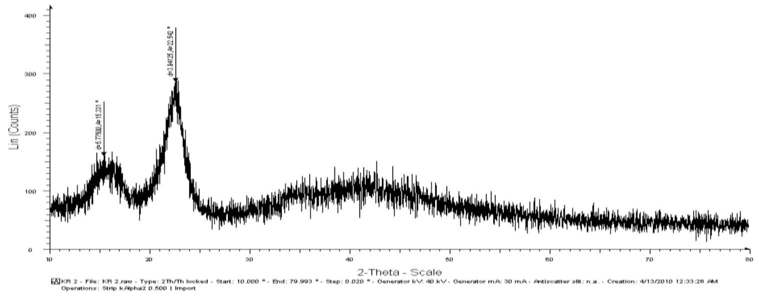

Figure-4(b) XRD spectra of Steam Exploded Cellulose Fiber (Stage-II).

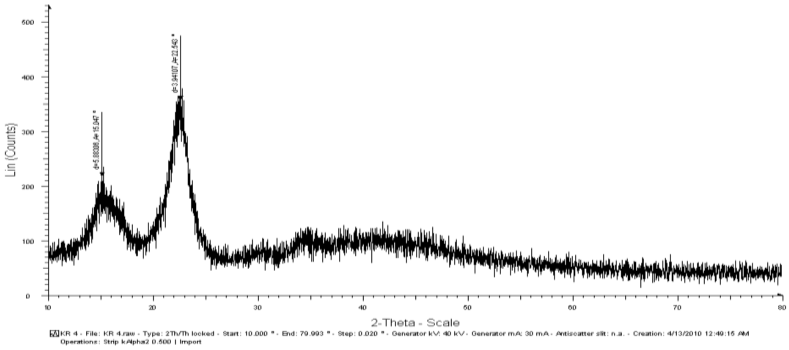

Figure-4(c) XRD spectra of Steam Exploded Cellulose Fiber (Stage-III).

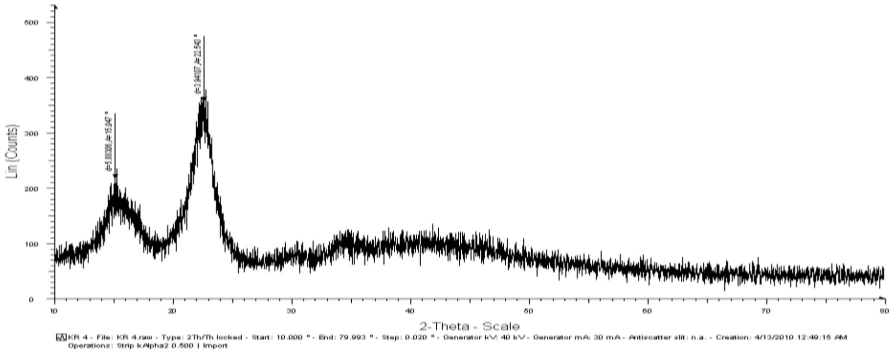

Figure-4(d) XRD spectra of Steam Exploded Cellulose Fiber (Stage-VI).

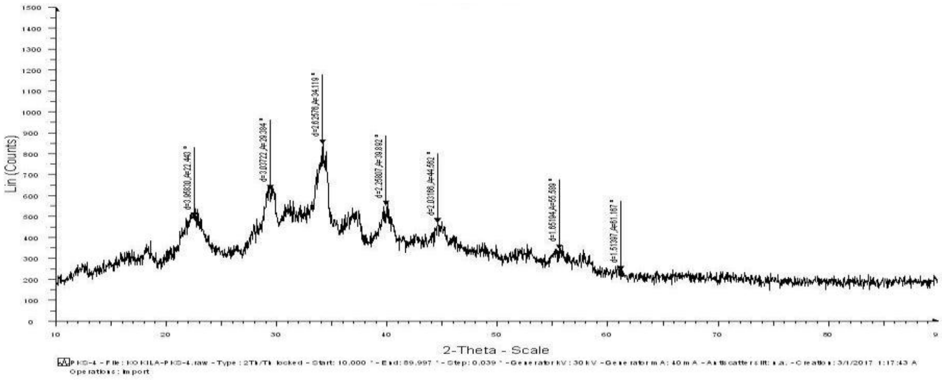

Figure-4(e) XRD spectra of Cellulose-g-2-hydroxyethylacrylate.

Thermo Gravimetric Analysis

The TGA thermogram details of 3(a) steam exploded fibers (stage-1), 3(b) steam exploded bleached fibers (stage-2), 3(c) steam exploded fibers in acidic medium (stage-3), 3(d) mechanical treatment of the processed fibers (stage-4), 3(e) graft copolymer (cellulose-g-2-hydroxyethylacrylate) was shown in the Figure- 3. 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 indicates in the fibers after chemo-mechanical treatment maybe the result of removal of non cellulosic materials during these treatments.[27] The TGA thermogram of the graft copolymer (Cellulose-g-2-hydroxyethylacrylate) Figure 3(e) shows that the maximum weight loss occurs at the temperature range of 200˚ C to 450 ˚C. Around 43.73% of the sample was disintegrated in 760˚C leaving behind 56.27% of the sample as a residue. On comparing Figure-3(e) with Figure 4(a), these observations have clearly indicated that grafting of cellulose –g-2-hydroxylethylacrylate copolymer has improved the thermal stability of cellulose.[28]

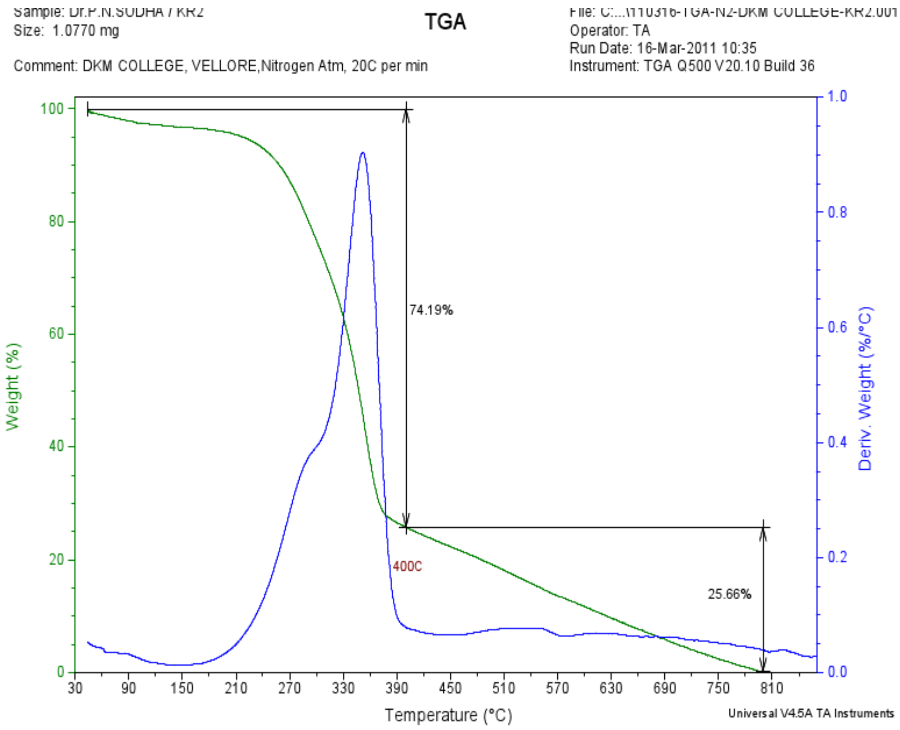

Figure-3(A) Tga Of Steam Exploded Cellulose Fiber (Stage-I).

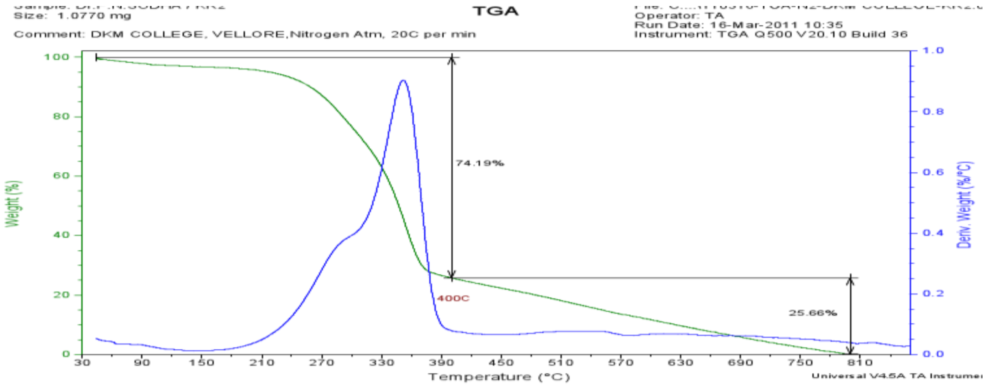

Figure-3(b) TGA of Steam Exploded Cellulose Fiber (Stage-II).

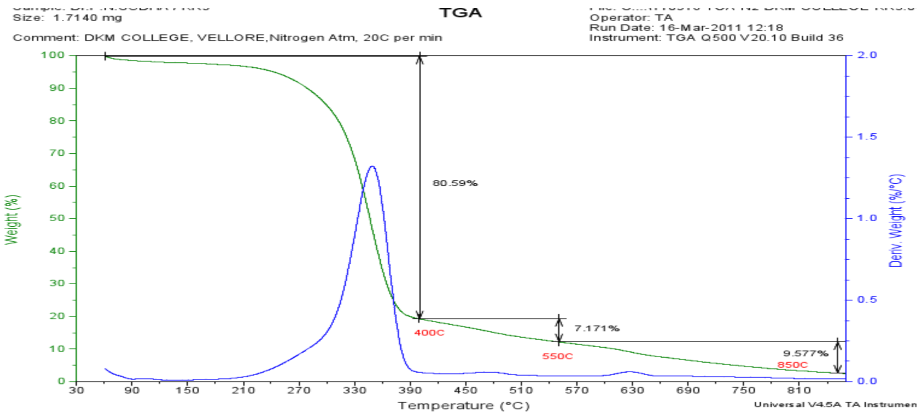

Figure-3(c) TGA of Steam Exploded Cellulose Fiber (Stage-III).

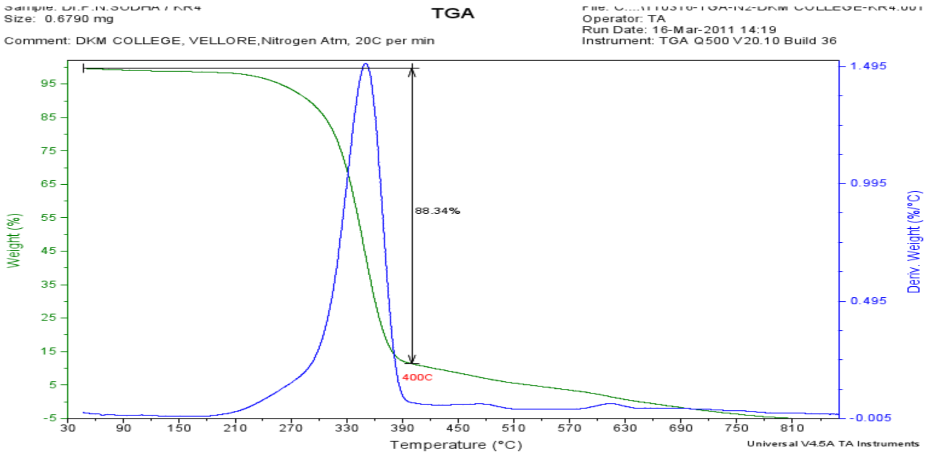

Figure-3(d) TGA of Steam Exploded Cellulose Fiber (Stage-IV).

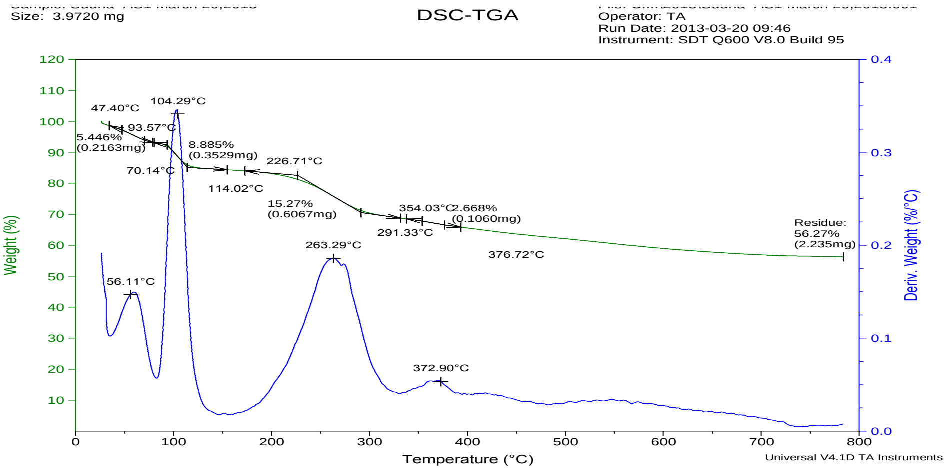

Figure-3(e) TGA of Cellulose-g-2-hydroxyethylacrylate.

CONCLUSION

Cellulose was extracted Sugar cane Bagasse by steam explosion method and it was successfully grafted by 2-hydroxyethylacrylate monomer in the presence of ceric ammonium nitrate. Based on this observation 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 results respectively. Cellulose grafted 2-hydroxyethylacrylate have many applications.

REFERENCES

1. Israel, AU, Obot, IB, Umoren, SA, MkepenieV, & Asuquo, JE. Production Cellulosic Polymers from Agricultural wastes. E-Journal of Chemistry, 2005; 5(1): 81-85.
2. Sokker, HH. Grafted wood pulp containing quaternary ammonium group and its application in the removal of different anions from aqueous solution. Delivered at the 8th Arab International Conference on Polymer Science & Technology, (2005), Cairo-Sharm El-Shiekh, Egypt.
3. Chung, S., Sudan, MT., & Venosa, A D. Partially acetylated sugarcane bagasse for wicking oil from contaminated wetlands. U.S. Environmental Protection Agency Papers, (2011); Paper 118.
4. Werkneh, AA., Abay, A K., & Senbeta, A M. Removal of water hardness causing constituents using alkali modified sugarcane bagasse and coffee husk at Jijiga city, Ethiopia: A comparative study. International Journal of Environmental Monitoring and Analysis. 2015; 3(1): 7-16.
5. Wilke, CR. Cellulose as a chemical and energy resource, Biotechnology and bioengineering symposium, 1994; 27-42.
6. Mohammad Sadeghi, Nahid Ghasemi and Fatemeh Soliemani.,Graft Copolymerization Methacrylamide Monomer onto Carboxymethyl Cellulose in Homogeneous Solution and Optimization of Effective Parameters. World Applied Sciences Journal, 2012; 16(1): 119-125.
7. Bikales NM, Segal L Cellulose and cellulose derivatives. Wiley Interscience, New York, NY. (1971).
8. Qin C, Soykeabkaew N, Xiuyuan N, Peijs T The effect of fiber volume fraction and mercerization on the properties of all-cellulose composites. Carbohydr Polym, 2008; 71: 458–467.
9. Gurgel LVA, Junior OK, Gil RPDF, Gil LFAdsorption of Cu(II), Cd(II) and Pb(II) from aqueous single metal solutions by cellulose and mercerized cellulose chemically modified with succinic anhydride. Biores Technol, 2008; (99): 3077–3083.
10. Wojna´rovits L, Fo¨ldva´ry CM, Taka´cs E) Radiation-induced grafting of cellulose for adsorption of hazardous water pollutants: a review. Radiat Phys Chem., 2010; (79): 848–862.
11. Gupta KC, Sahoo S. Khandekar, K. “Graft copolymerization of ethyl acrylate onto cellulose using ceric ammonium nitrate as initiator in aqueous medium”, Biomacromol., 2002; 3: 1087-1094.

12. Ellison. A, Wilson, RD, Wellner, N, Collins, R.S, Roberts N. Effect of steam explosion on waster copier paper alone and a mixed lignocellulosic substrate on saccharification, Biroresource technology, 2015; 187: 136-143. DOI: 10.1016/j.biortech.2015.03.089.
13. Mason WH, Process and apparatus for disintegration of wood and the like. (1926) US Patent: 1578609.
14. Fengel D, Wegner G. Wood – Chemistry, Ultrastructure, Reactions. De Gruiter, Berlin, 1983.
15. Onigbinde, M O, Adu, DO and Osuide, MO. sau Grafting of Acrylamide Monomer on Sugarcane Bagasse Sci-Tech. J, 2016; 1(1): ISSN: 2536 – 6866.
16. Reveley. A, Cellulose and its derivatives, chemistry, biochemistry and applications-1 cellulose edited by J.F Kennedy (Ellis Horwood Limited, Chichester), 1985.
17. Brewer R J & Bogan RT Encyclopedia of polymer science and engineering, Vol3 2nd edn, edited by mrk HF & Bikles Nm (wiley Interscience, New york), 1995.
18. Juan Morain, Vera Alvarez, Viviana Cyras; Extraction of cellulose and preparation of nanocellulose from sisal fibers, Cellulose, 2008; (15): 149-159.
19. Susheel Kalia, LucAverous, James Njuguna, Alain Dufresne, Bibin Mathew Cherian; Natural Fibers, Bio- and Nanocomposites, InternationalJournal of Polymer Science, Article ID 735932, 2 (2011).
20. Halil Ibrahim Unal; Graft Copolymerization of N- Vinylimidazole on Poly (Ethylene Terephthalate) fi- bersin a swellingsolvent usingazobisisobutyronitrile as initiator, Turk. J. Chem., 2003; (27): 403-415.
21. Nada, MA A., Alkady, MY., & Fekry, HM. Synthesis and characterization of grafted cellulose for use in water and metal ions sorption. Bio Resources, 2007; 3(1): 46-59.
22. Khullar, R, Varshney, V K., Naithani, S., & Soni, P L. Grafting of acrylonitrile onto cellulosic material derived from bamboo (Dendrocalamus strictus). eXPRESS Polymer Letters, 2008; 2(1): 12-18.
23. ong Ding, Frank Harris; Pure. Appl. Chem., 1995; 1997-2004.
24. Mwaikambo LY&Ansell, MP. The effect of chemical treatment on the properties of hemp, sisal, jute and kapok fibres for composite reinforcement in 2nd International Wood and Natural Fibre Composites Symposium, (1999). June 28-29.
25. Mehdi Joonobi, Jalaaudin Harun Paridah Md Tahir; Characteristics of nanofibers extracted from kenaf fiber, Bioresources. com, 2010; 5(4): 2556-2566.

26. Aboul-Fadl SM, Zeronian SH, Kamal MM,. Kim MS,. Ellison MS; Effect of mercerisation on the relation between single fibre mechanical properties and fine structure for different cotton spe- cies, Textile Research Journal, 1985; (55): 461-469.
27. Hearle, JW & Peters; Structure properties and uses, fibre structure, Butterworth, London, 1963; 621-640.
28. Athawale, VD. and Lele,V. Granular Maize Starch and its Graft Copolymers with Water-Absorbing Vinyl Monomers, Starch/Starke, 2000; (52): 205-213.