



Synthesis and Characterization of Graft Co-Polymers of Sisal Fiber with Binary Vinyl Monomers

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Abstract

In this paper morphological transformation of sisal fiber by graft copolymerization with methyl acrylate and its binary mixture with acrylic acid (AAc), vinyl acetate (VA) and *n*-butyl acrylate (BuA), using FAS-KPS initiator, under influence of microwave radiations has been reported. Optimum reaction conditions for maximum graft yield were kept same as that in case of grafting of principal monomer. Maximum grafting has been observed in case of sisal-g-poly(MA+VA). The Graft copolymers thus formed were characterized with SEM, TGA and XRD techniques. Thermal stability has been found to increase and percentage crystallinity and crystallinity index decrease upon grafting.

Keywords

Sisal Fiber, Grafting, Morphology, Crystallinity, Thermal Properties

Subject Areas: Composite Material, High Polymer Chemistry

1. Introduction

Grafting of natural fibers using binary vinyl monomers were studied by various researchers under microwave radiation [1]-[6]. Grafting involves attachment of polymer chains, usually monomer, to the back-bone of polymer. It is one of the methods to increase the compatibility between synthetic polymers and cellulose. It has been observed that monomers with polar groups support the absorption of microwave radiations λ (MWR) and modification in fibrous proteins and cellulose through graft copolymerization has been reported [7].

In comparison to conventional techniques of grafting, microwave radiations induced grafting is one of the ef-

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efficient methods for modifying the properties of cellulosic fibers because it is effective and consumes less time [8]-[10]. Different researchers have studied the graft copolymerization of vinyl monomers onto cellulosic fibers [11]-[13]. Synthesis of graft copolymers under the influence of microwave radiation was studied [14] [15]. Graft copolymers have been found to be more moisture resistant and also showed enhanced chemical and thermal resistance.

MWR technique reduces the extent of physio-chemical stress to which the fibers are exposed during the conventional techniques. It has been reported that properties of fibers treated under MWR are same or even better than those of fibers modified through other conventional techniques [16]. Grafting of butylacrylate, acrylic acid and acrylonitrile onto starch, acrylamide onto natural fiber and butyl methacrylate onto wool fibers has been studied using redox initiators under microwave radiation [17]. Methyl acrylate has been reported to polymerize under microwave radiation using very low concentration of initiator. Grafting of acryl amide and acrylonitrile [18] [19] onto chitosan and acrylonitrile onto Guar gum [20] under microwave radiation in very short reaction time and in absence of any redox initiator or catalyst has been reported. In comparison to conventional techniques of grafting, microwave radiations induced grafting is one of the efficient methods for modifying the properties of cellulosic fibers because it is not time consuming and costly [21] [22]. Different researchers have studied the graft copolymerization of vinyl monomers onto cellulosic fibers [23]. Synthesis of graft copolymers under the influence of microwave radiation was studied [24].

In the present study, Sisal fiber has been modified through graft co-polymerization with mixture of binary vinyl monomers. Sisal-g-co-polymers thus prepared were characterized with Thermo gravimetric analysis (TGA), SEM, and X-ray diffraction (XRD) techniques.

2. Experimental

2.1. Materials

Sisal fibers were obtained from sisal research station, Bamra, Sambalpur, Orissa. Potassium persulphate, ferrous ammonium sulphate, NaOH and acetone (99.5% purity) were supplied by S. D. Fine, India. Methyl acrylate, acrylic acid, vinyl acetate and butyl acrylate (Merck, India) was used as received. Microwave equipment (Electrolux EC20GBSK-MMZ) was used for grafting of binary mixtures onto sisal fibers.

Graft Copolymerization of Binary Vinyl Monomer Mixtures onto Sisal Fibers under the Influence of Microwave Radiation

Before grafting sisal fibers were previously cut in definite size, washed with distilled water and dried at 60°C and purified by soxhlet extraction with acetone for 72 hours and were dried at room temperature. 0.5 g amount of Sisal fiber was immersed in 100 mL of distilled water for 24 h prior to grafting. A known amount of binary monomer mixture and a definite ratio of initiator (FAS-KPS) were added to the reaction mixture. The reaction mixture was stirred and transferred to a microwave oven at a definite temperature, for a definite time interval. Various reaction parameters were optimized. After the completion of reaction, the reaction flask was taken out and graft copolymer was soxhlet extracted with acetone for about 5 - 6 hours to remove homopolymer poly(MA). Other homopolymer, such as poly(AAc) was removed by hot water extraction and poly(VA) and poly(BuA) were removed by extraction with alcohol. Graft co-polymers obtained were dried in a hot air oven at 50°C till constant weight was obtained. Binary vinyl monomer mixtures such as acrylic acid (AAc), vinyl acetate (VA) and n-butyl acrylate (BuA) were graft copolymerized along with principal monomer (MA) onto sisal fibers under the influence of microwave radiations. The percentage grafting (Pg) is calculated as follows:

$$Pg = \frac{W_2 - W_1}{W_1} \times 100 \quad (1)$$

where W_1 and W_2 are the weight of original and grafted sisal fibers, respectively

2.2. Characterization

2.2.1. Scanning Electron Microscopy

Scanning electron microscopic studies of sisal fiber and all its grafted fibers were carried out on Electron Microscopy Machine (LEO 435 VP, UK).

2.2.2. Thermo Gravimetric Analysis

Thermo gravimetric analysis and differential thermal analysis were carried out in nitrogen atmosphere at a heating rate of 10°C/min using Perkin Elmer, (Pyris Diamond) thermal analyzer. Nitrogen is supplied at a rate of 200 ml per minute. 10.5 mg Alumina power was used as reference in reference Pan.

2.2.3. X-Ray Diffraction Studies

X-ray diffraction studies were performed under ambient condition on X-ray diffractometer (Brucker D8 Advance). Crystallinity was determined by using the wide angle X-ray diffraction counts at 2θ angle close to 22° and 18°. The counter reading at peak intensity at 22° is said to be represent the crystalline material and the peak intensity at 18° corresponds to amorphous material in cellulose. Percentage crystallinity (% Cr) and crystalline index (C.I.) were calculated as follows [19] [20].

$$\% \text{Cr} = \frac{I_{22}}{I_{22} + I_{18}} \times 100 \quad (2)$$

$$\text{C.I.} = \frac{I_{22} - I_{18}}{I_{22}} \quad (3)$$

where I_{22} and I_{18} are the crystalline and amorphous intensities at 2θ scale close to 22° and 18°, respectively.

3. Results and Discussion

In cellulosic fibers C2, C3 and C6 hydroxyls are the most active sites for the grafting. It is evident that in case of binary monomer mixtures of sisal-g-poly(MA + BuA), sisal-g-poly(MA + VA) and sisal-g-poly(MA + AA), the percentage grafting were 36%, 66% and 32% respectively. Higher grafting in case of sisal-g-poly(MA + VA) were noticed. This is due to electron donor capacity of vinyl acetate (VA) monomer, which increases the reactivity of methyl acrylate towards the grafting. While as butyl acrylate and acrylic acid are electron acceptor monomer, being soluble in water leads to increase the infusibility of the monomer, methyl acrylate to the active sites. Presence of butyl acrylate and acrylic acid along with principal monomer (MA) leads to decrease in graft copolymerization. Monomer with electron accepting ability enters chain transferring process and results in low free radical sites, thereby reducing the ability of monomers towards grafting [21].

3.1. Morphological Studies

Figures 1(a)-1(d) show the SEM of raw and graft co-polymerized sisal fibers. These micrographs clearly showed the difference in their surface morphology. It has been observed that surface morphology of original sisal fibers differs in smoothness and roughness from graft co-polymerized sisal fibers. The surface of original fiber (**Figure 1(a)**) is smooth and clear due to the presence of oil and waxy materials.

3.2. TGA of Grafted Sisal Fibers

Two stage decompositions have been observed in all samples. The first stage decomposition may be due to loss of moisture and second stage decomposition is due to cellulosic and lignin degradation. In case of graft copolymers, sisal-g-poly(MA + VA), sisal-g-poly(MA + BuA), sisal-g-poly(MA + AAc), initial decomposition temperature (IDT) are 249°C, 300°C, 300°C and 313°C respectively and the final decomposition temperature (FDT) are 370°C, 380°C, 400°C and 390°C respectively (**Table 1**).

It was observed from the results shown in **Table 1** and **Figure 2** that graft copolymerization enhances the thermal stability of the sisal fibers. Higher IDT of all the graft copolymers is due to initial strengthening of crystal structure of the fiber, which is evident from its delayed primary decomposition reaction. However, final decomposition temperature decreased in sisal-g-poly(MA + BuA), sisal-g-poly(MA + VA), sisal-g-poly(MA + AA), due to disturbance in crystal lattice. So that it becomes amorphous, there by resulting in lower FDT of the graft copolymers.

3.3. XRD of Grafted Sisal Fibers

Graft copolymers with binary monomers sisal-g-poly(MA + VA), sisal-g-poly(MA + BuA) and sisal-g-poly

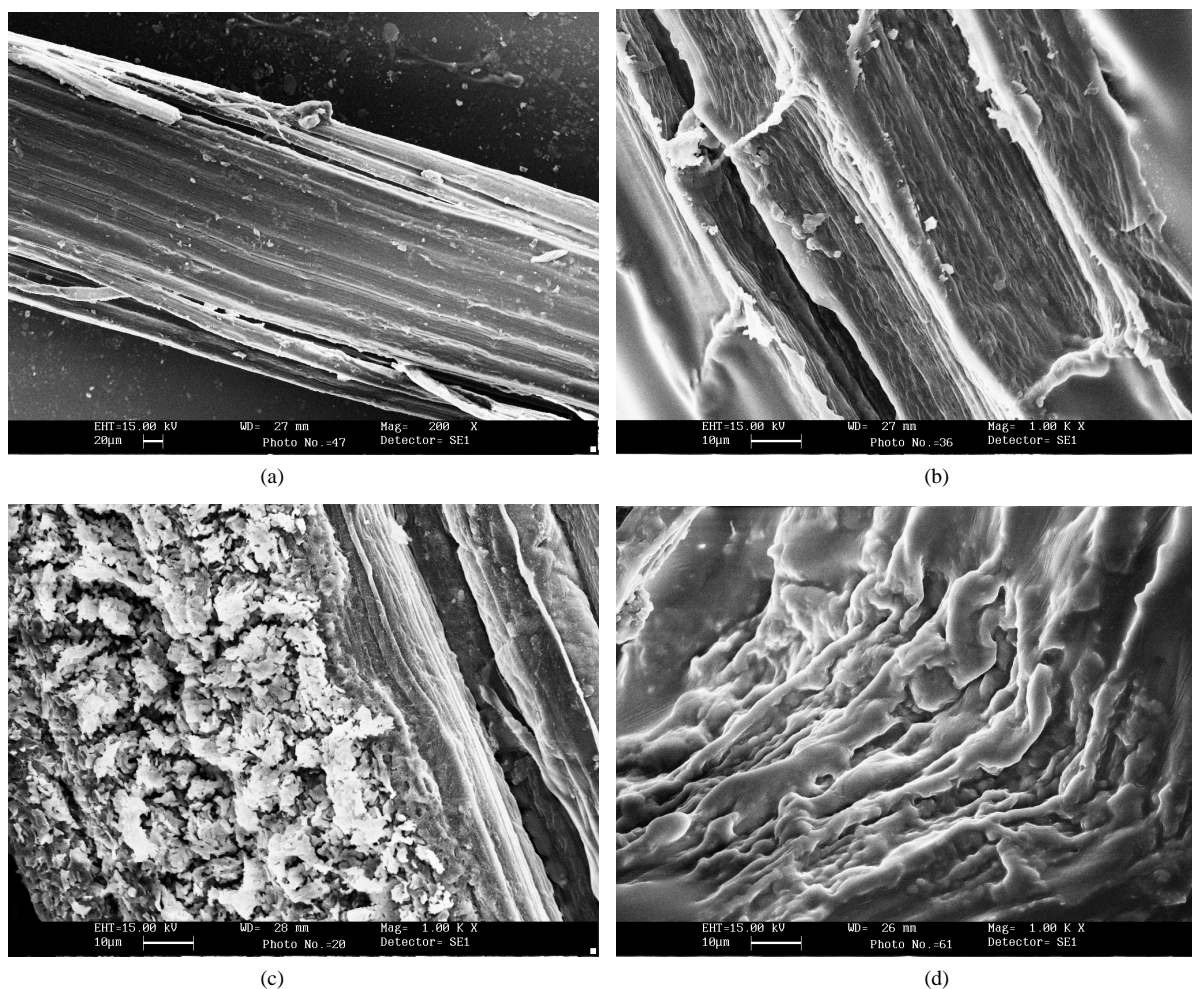


Figure 1. SEM of (a) Raw sisal fiber; (b) Sisal-g-poly(MA + AAc); (c) Sisal-g-poly(MA + BuA); (d) Sisal-g-poly(MA + VA).

Table 1. Thermal stability and crystallinity of raw and graft co-polymerized sisal fiber.

Sr. No.	Sample	TGA				XRD			
		IDT	% Wt. loss	FDT	% Wt. loss	I_{22}	I_{18}	% Cr	C.I.
1	Sisal fibers	249	9.2	370	69.2	877	346	71.7	0.60
2	Sisal-g-poly(MA + VA)	300	24.0	380	60.6	665	355	65.0	0.46
3	Sisal-g-poly(MA + BuA)	300	23.9	400	77.2	487	283	63.0	0.41
4	Sisal-g-poly(MA + AA)	313	25.5	390	72.6	827	425	66.0	0.48

(MA + AAc), I_{22} with relative intensity are 665, 487 and 827 and I_{18} were 355, 283 and 425 respectively (Table 1). The raw fiber having I_{22} with relative intensity is 877 and I_{18} with relative intensity are 346. Percentage crystallinity and crystallinity index were found to decrease in graft copolymerized fibers due to incorporation of monomer moiety on the back bone impairs the natural crystallinity of the fiber therefore graft copolymerization of binary Vinyl monomers mixtures onto sisal fiber result in impaired crystallinity and increase amorphous region of the fiber (Figure 3). Thus with increase in percentage grafting, percentage crystallinity and crystallinity index were found to decrease quickly with reduction in its stiffness and hardness [24].

4. Conclusion

The surface of sisal fiber becomes rough upon grafting by vinyl monomer mixtures in comparison with clean and

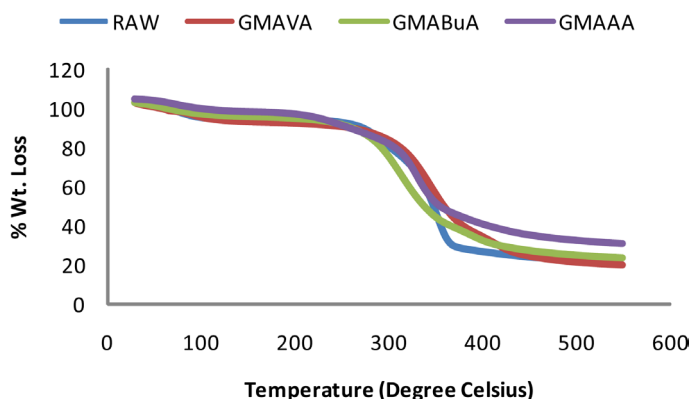


Figure 2. TGA of Raw and Graft co-polymerized Sisal fiber.

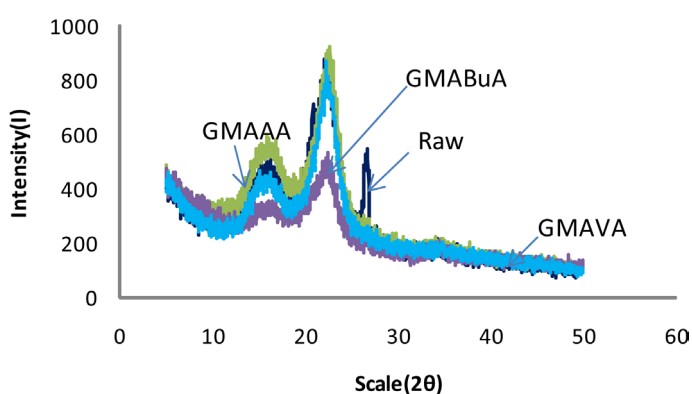


Figure 3. XRD of Raw and Graft co-polymerized Sisal fiber.

smooth surface of raw sisal fibers. It has been observed that graft copolymerization enhances the thermal stability of sisal fibers. Increase in grafting percentage, crystallinity percentage and crystallinity index was found to decrease quickly due to reduction in its stiffness and hardness.

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