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Sunn hemp cellulose graft copolymers polyhydroxybutyrate composites: morphological and mechanical studies

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ABSTRACT

For the synthesis of biocomposite materials for useful applications, it becomes necessary to modify the surface of natural fibers through chemical treatments. Morphology, structure and properties of natural fibers have an obvious effect on the mechanical properties of the biocomposite materials. It is thus necessary to know the morphology, thermal stability and crystalline behavior of original and modified fibers. In present paper, sunn hemp fibers (SHF) were chemically modified with ethyl acrylate and binary monomers (EA+MMA, EA+AA) through microwave radiations induced graft copolymerization. Various reaction parameters were optimized to get maximum grafting (91.8%). Morphology, thermal stability and crystalline behavior of original and modified fibers were investigated. Morphological and thermal studies showed that surface of sunn hemp fibers becomes rough and amorphous through graft copolymerization and thermal stability has been found to be increased. Microwave radiation induced grafting showed a diminutive effect on the crystalline behavior of the sunn hemp fibers as optimum time to get maximum grafting is very less (40 min) in comparison to conventional grafting. Synthesized graft copolymers were used as reinforcing material in preparation of polyhydroxybutyrate biocomposites. It has been observed that graft copolymers improved the interface between fiber and matrix and enhanced the mechanical strength of composites. Copyright © 2011 VBRI press.

Keywords: Sunn hemp fibers; morphology; thermal stability; crystallinity; mechanical properties.



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Introduction

Graft copolymerization is a technique used to transform the properties of natural polymers. Modifying the properties of natural polymers through graft copolymerization has been reported by Sabaa and Mokhtar [1] and various other prominent workers [2-5]. In view of the fact that the prospect of fabrication of newer monomers at low cost is very uninviting, so the modification of a wide array of existing synthetic and natural polymer through graft copolymerization technique for incorporating highly specific properties is of great importance. Graft copolymerized fibers are better in dyeing, printing, chemical resistance, water repellency, fiber strength, abrasion resistance, crease resistance etc. Studies of different workers shown that the monomer reactivity ratios for the grafting procedure are completely different from the values observed for conventional solution polymerization, for example, binary mixtures of monomers: ethyl acrylate/acrylic, acid acrylonitrile/styrene and acrylamide/ styrene. Thermal stability, crystallinity and morphology of the graft copolymers were too studied [3-4]. Methyl methacrylate has been reported to polymerize under microwave irradiation using very low concentration of initiator [6]. In a recent report, grafting of acrylamide [7] and acrylonitrile [8] onto chitosan and acrylonitrile onto guar gum [9] was done under microwave conditions, in very short reaction time and in absence of any redox initiator.

Mechanical properties of thermoplastic composites reinforced with acrylate grafted henequen cellulose fibers were studied. It has been found that best results could be obtained with polymethyl methacrylate (PMMA) grafted cellulose fibers because of better fiber-matrix adhesion. The modulus of polyvinyl chloride composites is increased when grafted or ungrafted cellulose are used as reinforcement but the composites with PMMA grafted cellulose present the higher modulus [10]. Green composites reinforced with S. spontaneum fiber and its different graft copolymers were fully biodegradable and environment friendly. Mechanical properties including tensile strength, compressive strength and wear resistance of different reinforced samples were significantly improved in comparison to pure corn starch matrix. Maximum compressive strength and wear resistance was found in case of fibers grafted with MMA [11]. Agave fiber reinforced polystyrene composites were prepared by compression molding technique in which good interfacial adhesion is generated by fiber surface modification. The agave fibers were modified through graft copolymerization with methyl methacrylate. The short grafted fibers were then spread between the alternate layers of polystyrene resin by hand lay-up method to obtain the thermoplastic composites. Polystyrene composites reinforced with graft copolymers of agave fibers showed better mechanical properties [12].

Since grafting on to SH fibers under microwave radiations is not enough reported in literature, so in this chapter we report the grafting of ethyl acrylate and its binary monomers onto SH fibers and graft copolymers were used as reinforcing material for the synthesis of biocomposites.

Experimental

Materials and Methods

Sunn hemp fiber an extensively distributed and commonly cultivated herb in northern India was obtained from the farmers of Mohindergrh district of Haryana, India. Ceric ammonium nitrate (Qualigens Fine Chemicals) was used as initiator. Nitric acid, NaOH and acetone of 99.5% purity were supplied by E. Merck. Methyl methacrylate (Spectrochem Mumbai), acrylic acid (Merck) and ethyl acrylate (Merck) were used as received. PHB (Biomer P226) purchased from Biomer, was Krailling, Germany. Composites were prepared in compression molding machine (Santec India Ltd.). Tensile and compressive strength test were carried on Universal Testing Machine as per ASTM methods.

Purification of sunn hemp fibers

Sunn hemp fibers (*Crotalaria juncea* L) were washed with detergent in order to remove impurities and then Soxhlet extracted with acetone for 72 h in order to remove waxes, lignin and other impurities.

Graft copolymerization

Sunn hemp fiber (500 mg) were immersed in 100 mL of distilled water for 24 h prior to its grafting under the influence of microwave radiation. A definite ratio of CAN-HNO₃ and a known amount of monomer were added to the reaction mixture. The reaction mixture was stirred and transferred to the microwave equipment operating at 210W microwave powers for a specific time interval. The different reaction parameters such as monomer concentration, reaction time, CAN concentration etc. were optimized and the homopolymer was separated from the grafted fiber by soxhlet extraction in order to obtain maximum graft yield. The graft copolymer obtained was dried in the hot air oven at 50°C until a constant weight was obtained. The percent graft yield (%G) and percent grafting efficiency (%GE) were calculated as follows [3]:

$$%G = \frac{\text{Final weight of SH fiber - Initial weight of SH fiber}}{\text{Initial weight of SH fiber}}$$

$$%GE = \frac{\text{Final weight of SH fiber - Initial weight of SH fiber}}{\text{Weight of monomer}}$$
(2)

Preparation of composites

PHB matrix based composite were prepared by mixing a particular ratio (10:0.5) of resin with fiber. The matrix (PHB) was melted and mixed with fiber and then placed in

the mold of a particular dimension (length 40-80 mm and cross section 5×5 mm). Degasification of sample was carried out in compression molding machine and the samples were put for curing at 120° for 10 minutes under 400 kg cm⁻³ pressure. Composites thus prepared were subjected for different mechanical studies. The number of specimen used for the determination of mechanical properties was three in each case. Tests were conducted at ambient laboratory condition (temperature: 35° C and RH: 50).

Characterizations

Infra red spectroscopy (IR): IR spectra of the ungrafted and grafted Sunn hemp fiber were taken with KBr pallets on Perkin Elmer Spectrophotometer. IR spectra of ungrafted and grafted natural fiber are useful in explaining the grafting of a particular monomer on to the fiber. The presence of a new peak in spectra of grafted fiber confirms grafting on to natural fibers.

Scanning electron microscopy (SEM): Scanning electron microscopic studies of were carried out on Electron Microscopy Machine (LEO 435 VP).

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.

X-ray diffraction studies (XRD): 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 20 angle close to 22° and 18°. The counter reading at peak intensity at 22° is said to represent the crystalline material and the peak intensity at 18° corresponds to the amorphous material in cellulose. Percentage crystallinity (%Cr) and crystalline index (C.I.) were calculated as follow [**4**]:

$$\% Cr = \frac{I_{22}}{I_{22} + I_{18}} \times 100 \qquad ------(3)$$
$$C.I. = \frac{I_{22} - I_{18}}{I_{22}} \times 100 \qquad ------(4)$$

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

Results and discussion

Grafting yield of sunn hemp fiber directly immersed in monomer in the presence of initiator is very low. This is because of the fact that sunn hemp being a cellulosic fiber is highly hydrogen bonded polymer and vinyl monomers are not in a position to penetrate beyond the surface of the cellulose substrate. In order to overcome this barrier fiber has been immersed in water for 24 h so as to open the active sites of the cellulosic back bone and grafting has been carried-out by using solvent-monomer mixtures rather than pure monomer which enhances the deep penetration of monomer inside the polymer matrix and considerably increases the graft yield. The success of this method is due to the combination of two effects: (i) reduction in viscosity of the reaction medium which helps in the easy movement of the free radicals towards the active site and (ii) easy and greater accessibility of the swollen polymer matrix to the monomer. Modification of the sunn hemp fibers has been carried out under MWR induced grafting in aqueous medium using CAN-HNO₃ as initiator as per following mechanism.

Mechanism

In polymeric materials containing cellulose (**Fig. 1**) as a building block, C_2 , C_3 and C_6 hydroxyl groups and C—H sites are the active centers for grafting of polymeric chain onto polymeric backbone. Ceric ammonium nitrate takes part in redox reaction with Ce⁴⁺. Ceric(IV) ion induce active center in cellulose polymeric chain by oxidizing the basic glucose molecule. It oxidizes and produces the free radical of cellulose polymeric chain. Ceric ions form the chelate complex with cellulose molecule through C₂ and C₃ hydroxyl group of glucose unit. Ce⁴⁺ ion is reduced to Ce³⁺ by transfer of electron from cellulose molecule.



Fig. 1. Structure of cellulose.

The breaking of bonds at C_2 and C_3 carbon of glucose molecule of cellulose results in the formation of free radical sites. The grafting of ethyl acrylate onto sunn hemp cellulose (SHC) is supposed to follow the following mechanism (**Fig. 2**).

Ceric ions forms complexes with carbon chain of polymer back bone as well as from monomer chains and generate free radicals (equation 1 & 2). Free radicals then combine at reactive sites on the polymer backbone (equation 3 & 4) to form graft copolymer [SHC-g-poly(EA)]. On other hand different monomer free radicals combines to form homopolymer [poly(EA)] free radical (equation 5). The homopolymer free radical thus formed by the combination of monomers combines with the cellulose chain and forms homopolymer and SH free radical (equation 6). On the other hand the ceric ion combines with the free radical to form a stable poly(EA) (equation 8) chain as well as SHC-g-poly(EA) (equation 7) and terminates the polymerization. Another termination step is the combination of homopolymer free radical and EA free radical (equation 8).

Optimization of different reaction parameters for grafting of ethyl acrylate on to sunn hemp

Grafting of different vinyl monomer on to the sunn hemp fibers may be influenced by the presence of the number of active sites on to the fiber surface. The reaction parameters such as reaction time, Initiator ratio (CAN - HNO₃), amount of monomer concentration used to carry out graft copolymerization of ethyl acrylate were optimized. The optimized reaction parameters for grafting of EA on to SHF are given below in **Table 1**.

Step I: Initiation



Step II Propagation



Fig. 2. Probable mechanism for graft copolymerization of ethyl acrylate onto sunn hemp cellulose.

Poly(EA)

Effect of monomer concentration

In Sunn hemp fiber grafting increases with increase in monomer concentration which become maximum (65.8%) at 0.369 mol dm^{-3} and then decreases with further increase in

concentration (**Table 1**). This may be due to excessive formation of homopolymer at higher concentration of monomer.

Effect of Reaction Time

The optimum reaction time is found by varying reaction time between 35 to 55 minutes. The optimized time of polymerization on to SHF is found to be 40 min (**Table 1**). With further increase in time a decline in percentage grafting has been observed, which may be due to hydrogen attraction reaction along with some other side chain reaction as well as due to homopolymerization. With homopolymerization the system becomes heterogeneous and creates obstacle in path of the free radicals in reaching the active sites present on the back-bone polymer. Hence, a decreased graft yields.

Effect of CAN Concentration

The effect of variation in CAN concentration was studied and the results are shown in **Table 1**. CAN concentration was increased from 3.85 to 7.26×10^{-3} mol dm⁻³. It is evident that %G increases with an increase in the CAN concentration, and reaches maximum value of 91.8%, at 6.41 $\times 10^{-3}$ mol dm⁻³ of CAN. These increasing trends of the grafting parameters indicated that ceric ions exclusively participate in the formation of active sites on the cellulose up to this concentration of ceric ions, and beyond it, no more active sites are formed on the cellulose. Further increase in CAN concentration is accompanied by a decrease in the %G .The decreasing trend in %G beyond 6.41 $\times 10^{-3}$ mol dm⁻³ concentration of ceric ions may be assumed to be due to its participation in the termination reactions with growing homopolymer and propagating chains on the cellulose.

Effect of HNO₃ concentration

With increase in nitric acid concentration there is a decrease in percentage grafting. This is due to the reason that at higher concentration of acid causes a degradation of backbone chains of cellulose and graft chains. Higher acid concentration also causes an oxidation of the free radicals formed which results in an increased homopolymerization (**Table 1**).

About 0.5 g sunn hemp fibers were immersed in 100 mL of water for 24 h prior to their grafting under microwave radiations. The fiber was then mixed with known amount of binary monomer mixture and definite amount of CAN – HNO₃ (6.41×10^{-3} mol dm⁻³ + 0.313 mol dm⁻³) at optimum reaction time and monomer (EA) concentration. **Table 2** shows that in case of binary vinyl monomer mixture of EA+MMA the percentage grafting increases with increase in conc. of MMA, becomes maximum (135.2%) at 0.329 mol dm⁻³ and then decreases with further increase up to 40% with 0.219 mol dm⁻³ and then decreases beyond this conc. of AA.

 Table 1. Optimization of different reaction parameters for grafting of ethyl acrylate on to sunn hemp.

SI. No.	Monomer (mol dm ⁻³)	Time (min)	Initiator ratio (×10-3 mol dm-3 + mol dm-3)	Grafting (%)	GE (%)
1	0.092	45	4.81+0.235	23.2	24.7
2	0.184	45	4.81+0.235	29.9	15.9
3	0.276	45	4.81+0.235	46.4	16.4
4	0.369	45	4.81+0.235	65.8	17.5
5	0.461	45	4.81+0.235	32.8	6.98
6	0.369	35	4.81+0.235	65.0	17.3
7	0.369	40	4.81+0.235	81.8	21.8
8	0.369	50	4.81+0.235	50.2	13.3
9	0.369	55	4.81+0.235	47.2	12.5
10	0.369	40	3.85+0.235	47.0	12.5
11	0.369	40	5.55+0.235	87.4	26.6
12	0.369	40	6.41+0.235	91.8	30.0
13	0.369	40	7.26+0.235	74.6	19.8
14	0.369	40	6.41+0.157	58.4	15.5
15	0.369	40	6.41+0.313	88.8	23.6
16	0.369	40	6.41+0.392	79.8	21.2
17	0.369	40	6.41+0.470	42.4	11.3

Table 2. Optimization of concentration of binary vinyl monomer on %grafting.

EA (0.	EA (0.369 mol dm ⁻³) + Methyl Methacrylate				EA (0.369 mol dm ^{.3}) + Acrylic Acid			
SI. No.	MMA Conc. (mol dm ⁻³)	Grafting (%)	GE (%)	AA Conc. (mol dm ⁻³)	Grafting (%)	GE (%)		
1	0.235	106.2	45.2	0.146	26.2	24.95		
2	0.282	118.4	42.0	0.219	40.6	25.85		
3	0.329	135.2	36.0	0.292	35.8	17.0		
4	0.375	82.8	22.0	0.365	25.0	9.5		

Effect of Concentration of Binary Monomer mixtures on percentage grafting

High percent graft yield in case of EA+MMA is due to the presence of strong acceptor monomer in the binary mixture EA+MMA and less association of MMA with water, which result in generation more free radical sites. In case of EA+AA binary mixture, low percent grafting is due to miscibility of acrylic acid with water and thereby resulting in generation of less number of free radical sites on the backbone polymer.



Fig. 3. FT-IR of (a) sunn hemp fiber, (b) SHF-g-poly(EA), (c) SHF-g-poly(EA+AA), (d) SHF-g-poly(EA+MMA)

Characterization of graft copolymers

FT-IR spectroscopy: The IR spectra of C. juncea fiber showed a broad peak at 3413.27cm⁻¹ with relative absorbance of 81.9% due to bonded OH groups in cellulose and at 2922.64 with relative absorbance of 81.6% due to -CH stretching in cellulose and hemicelluloses. Another peak at 1644.81 may be due to C-C bond. The carbon-oxygen single bond also has an absorption in the fingerprint region, varying between 1000 and 1350 cm⁻¹ depending on the molecule in it. The wave number in finger print region at 1067.72 cm⁻¹ may be due to C-O stretching. Because C-H bond is found in almost all organic compounds, so it is not much important. What it means is that a trough just under 3000 cm⁻¹ can be ignored, because it is probably just due to C-H bond (Fig. 3a). The carbon-oxygen double bond C=O, is one of the really useful absorption, found in the range 1670-1760 cm⁻¹. Its position varies slightly depending on what sort of compound it is in. In raw sunn hemp fibers (Crotalaria juncea L) a trough in region 1670-1760 cm⁻¹ is absent which shows the absence of C=O in it.

In case of SH-g-poly(EA) a peak at 1733.56 cm⁻¹ with relative absorbance of 96.5% shows high absorbance in this region is due presence of C=O group. This group presents in

ethyl acrylate () molecule which confirms the grafting of it on to sunn hemp fiber (Fig. 3b). Other peaks at 3433.90 cm⁻¹ due O-H stretching, 2981.32 cm⁻¹ due to C-H stretching and 1111.64 cm⁻¹ may be due to C-O group are similar to the raw fiber. SH-g-poly (EA+AA) shows absorbance at 1733.63 cm⁻¹ due to C=O stretching with relative absorbance of 88.2% due to presence of C=O in both molecules i.e. in ethyl group acrylate) as well as in acrylic acid (он). The presence of this peak supports grafting of EA+AA on to sunn hemp fiber. Other peak at 3434.55 cm⁻¹ is due to O-H group is broader than in raw fiber which indicates the presence of alcoholic as well as carboxylic O-H group in the fiber. The peaks other then C=O groups are not much informative, these are 2922.64 cm⁻¹ due to C-H stretching,

Table 3. FT-IR data of raw and grafted sunn hemp fiber.

1160.3 due C-O stretching etc (Fig. 3c).

			Relative % absorbance		
Wave Number (cm ⁻¹)	Group	Raw fiber	SHF-g- poly(EA)	SHF-g- poly(EA+AA)	SHF-g- poly(EA+MMA)
3600-3200	-OH stretching	81.9	92.5	85.2	91.5
2962-2850	-CH stretching	81.6	91.7	84.8	90.6
1760-1670	-C=O aldehyde,	-	96.5	88.2	90.5
1470-1350	-CH bending	77.6	91.5	84.2	88.1
1350-1000	C-O stretch	80.2	95.0	87.1	89.8

In this spectra of SH-g- poly (EA+MMA), the peak at 3430.06 cm^{-1} with relative absorbance 85.2% is due to O-H

(\checkmark) molecule, the high absorbance supports the good graft yield (**Fig. 3d**). A peak at 2986.61 cm⁻¹ due to C-H stretching and at 1159.15 cm⁻¹ may be due to C-O stretching, these peaks do not give much information. All these results confirm the grafting of ethyl acrylate and binary vinyl monomers on to sunn hemp fiber (**Table 3**).

Morphological studies

Scanning electron microscopic provides an excellent technique for the study of surface morphology of original and chemically modified sunn hemp (SH) fibers. It has been observed that surface morphology of original SH fibers differs in smoothness and roughness than grafted SH fibers. **Fig. 4a–d** show the SEM of original and grafted SH fibers. These micrographs clearly showed the difference in their surface morphology. The original fiber (**Fig. 4a**) is free from any deposition of polymer chain and surface is very smooth in comparison to modified fibers. Modified SH fibers (**Fig. 4b-d**) showed that considerable amount of polymer chains are grafted and their surface becomes rough [**13**].



Fig. 4. SEM of (a) SHF (b) SHF-g-poly(EA), (c) SHF-g-poly(EA+MMA) and (d) SHF-g-poly(EA+AA).

Thermal analysis (TGA/DTG)

Thermal gravimetric analysis: Thermal transition for a polymer often changes because even a pure polymer is a mixture of homolog and not a single chemical entity. TGA of hemp fiber and SH-g-poly(EA), sunn SH-g-poly (EA+MMA) and SH-g-poly(EA+AA) was carried out at a rate of 10°C/min in nitrogen as a function of percentage weight loss versus temperature. In TGA of raw fiber, two stage decomposition has been observed, with maximum weight loss between 100 and 300°C (16.6%) and 300 to 374°C (59.5%). The first stage decomposition may be due to loss of moisture and second stage decomposition is due to cellulosic and lignin degradation. The initial and final

decomposition temperatures of raw fiber are 100 and 300°C respectively. The TGA of sunn hemp-g-poly (EA) also shows two stages decomposition. The first stage at 100 to 300°C may be due to breakdown of hemicellulose and glycosidic linkage of cellulose whereas the second stage of decomposition at 300 to 400°C may be related to the degradation of grafted poly (EA) chains on to the fiber surface. In case of sunn hemp-g-poly (EA), initial and final decomposition temperatures are 100 and 300°C respectively. On the other hand in SH-g-poly(EA+MMA), there is decrease in weight loss in first stage decomposition. The first stage decomposition is in between 100 to 300°C (8.3%) and second stage decomposition is 300 to 413°C (75.2%). There is increase in second stage decomposition temperature in case of grafted fiber which confirms the strengthening of fiber due to grafting. Where as in SH-g-poly(EA+AA) the decompositions start at 100°C and is 13.2% up to 300°C while second stage decomposition is 64.2% from 300 to 450°C. The increase in second stage decomposition in grafted fiber may be due to initial strengthening of the crystal structure of the fiber under microwave radiations. From the above result it is clear that there has been increase in the thermal stability of fiber upon grafting.

Differential thermogravimetric: In case of SHF, decompositions at 60 and 350 °C were found at the rate of 0.172 and 1.188 mg/min weight loss respectively. However in case of SH-g-poly(EA) decomposition at 61, 356 and 393 °C occurred with 0.136, 1.142 and 0.651 mg/min weight loss respectively, and in SH-g-poly(EA+MMA) decomposition was observed at 54, 362 and 397 °C with 0.096, 0.970 and 1.555 mg/min weight losses, respectively. In another grafted fiber SH-g-poly(EA+AA) the weight loss at 54, 355 and 399 °C was found to be 0.075, 0.981 and 0.994 mg/min (Table 4). Thus it could be concluded from DTG studies that the rate of thermal decomposition was higher in case of SH fiber then grafted fibers. The better thermal resistance of grafted copolymer were due to incorporation of more covalent bonding through inclusion of poly(EA), poly(EA+MMA) and poly(EA+AA) chains onto back-bone polymer.

Table 4. DTG showing rate of weight loss per minute at different temperatures.

SI. No.	Sample	Temp. (°C)	Rate of wt. loss (mg/min)	Temp. (°C)	Rate of wt. loss (mg/min)	Temp. (°C)	Rate of wt. loss (mg/min)
1	SHF	60	0.172	350	1.188	-	-
2	SHF-g-poly(EA)	61	0.136	356	1.142	393	0.651
3	SHF-g-poly(EA+MMA	54	0.096	362	0.970	397	1.555
4	SHF-g-poly(EA+AA)	54	0.075	355	0.981	399	0.994

X-Ray diffraction studies (XRD)

The degree of crystallinity in polymers is commonly known to significantly affect their mechanical properties and X-ray diffraction provides significant structural information for polymers and composites. Therefore, it is important that the degree of crystallinity in modified fibers be precisely determined. X-ray diffraction studies were performed on Xray diffractometer (Philips 1140/90). It is evident from **Table 5** that raw fiber at 2θ scale showed peaks at 22.56 and 18.83 with relative intensities of 2772 and 639, respectively.

Similarly SH-g-poly(EA), showed peaks at 22.66° and 18.74° with relative intensities of 1114 and 482, respectively. The percentage crystallinity of SH and SH-g-poly(EA) fiber comes out to be 81.26 and 69.79 while crystallinity index is 0.7695 and 0.5673. It has been observed that there is a slight decrease in percent crystallinity of the fiber on graft copolymerization, which results in increase in randomness or disorder in the crystal lattice of cellulose fiber. This is due to incorporation of poly(EA) chains on the active sites of backbone during grafting.

SH-g-poly(EA+MMA) shows 20 scale intensities at 1541 and 552, the percent crystallinity of the fiber decreases to 73.62 and crystallinity index to 0.6418. While in case of SH-g-poly(EA+AA) the peaks at 20 scale are at 22.75° and 18.83° with relative intensities 1390 and 480, respectively (**Fig. 5**). The percentage crystallinity and crystallinity index of SH-g-poly(EA+AA) fiber comes out to be 74.33 and 0.6547, respectively. Results showed that % Cr & C.I. has been found to decrease on grafting of binary vinyl monomer on to SHF (**Table 5**). Due to grafting of EA and binary vinyl monomer fiber becomes more amorphous and results in impaired crystalline structure.



Fig. 5. XRD of sunn hemp fiber and its graft copolymers.

 Table 5. X-Ray diffraction data of sunn hemp fiber and graft copolymers.

SI. No.	Sample	I ₂₂ (at 2θ scale)	I ₁₈ (at 2θ scale)	% Cr.	C.I.
1.	SHF	2772	639	81.26	0.7695
2.	SHF-g-poly(EA)	1114	482	69.79	0.5673
3.	SHF-g-poly (EA+MMA)	1541	552	73.62	0.6418
4.	SHF-g-poly(EA+AA)	1390	480	74.33	0.6547

Morphological study of graft copolymers reinforced PHB composites

Scanning electron microscopic (SEM) provide an excellent technique for the study of surface morphology of original and chemically modified sunn hemp (SH) fiber reinforced composites. It has been observed that surface morphology of PHB matrix differs in smoothness and roughness from grafted SH fiber reinforced composites. Fig. 6a-c show the SEM of smooth area of pure PHB matrix, SH fiber reinforced composites and grafted SH reinforced composites. Fig. 6d-f show the SEM of fracture area of pure PHB matrix, SH fiber reinforced composites and grafted SH reinforced composites. These micrographs clearly showed the difference in their surface morphology. The pure matrix (Fig. 6a and d) is free from any fiber and surface is very smooth in comparison to SH fiber reinforced composites. SH fiber reinforced composites (Fig. 6b and e) showed that considerable amount of binding of fiber bundles and matrix. It has been found that graft copolymers showed better binding with matrix as there surface is amorphous and rough (Fig. 6c and f) in comparison to original SH fiber. Fig. 6f showed the strong binding of fiber and matrix in fracture surface of graft copolymer reinforced PHB composites.



Fig. 4. SEM of (a) PHB (b) SHF-PHB (c) SHF-g-copolymer-PHB smooth surface of composites and (d) PHB (e) SHF-PHB (f) SHF-g-copolymer-PHB fracture surface of composites.

Mechanical properties of graft copolymers reinforced PHB composites

Tensile properties of PHB matrix and composite reinforced with sunn hemp fiber have been found to 56 and 199 Newton force, respectively. In case of reinforcement with SH-gpoly(EA), SH-g-ploy(EA+MMA), SH-g-poly(EA+AA), tensile strength of composites was 315, 318, and 295 Newton force, respectively. It is evident that applied load at breaking point in case of composites reinforced with graft copolymer is more in comparison to reinforcement with SH fiber. It is found that composites reinforced with SH-gpoly(EA+AA) breaks at lower tensile load as compared to

SH-g-poly(EA+MMA) SH-g-poly(EA). reinforced composites also breaks at lower tensile load. Compressive strength of polyhydroxybutyrate and composite reinforced with sunn hemp fiber has been found to 73 and 325 Newton force, respectively. Compressive strength of composites reinforced with SH-g-poly(EA), SH-g-ploy(EA+MMA), SHg-poly(EA+AA) was 625, 567 and 478 Newton force, respectively. It has been resulted that composites reinforced with graft copolymers shows enhanced mechanical strength in comparison to pure matrix and reinforcement with SH fiber. This is because; surface of fiber becomes rough during grafting, which results in better binding between fiber and matrix. Moreover, microwave radiation induced grafting results in enhanced strength of fiber.

Conclusion

Graft copolymerization is preeminent method for the surface modification of cellulose fibers. Through graft copolymerization, surface of sunn hemp fibers becomes rough and amorphous and thermal stability has been found to be increased. Microwave radiation induced grafting showed a diminutive effect on the crystalline behavior of the sunn hemp fibers. Graft copolymers reinforced composites showed enhanced mechanical properties, thermal stability and they improved the interface between sunn hemp fibers and polyhydroxybutyrate.

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