

Recycling the Cellulosic Biomass to Competent Advanced Material

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Abstract

Sereni is a common plant found in abundance through-out the world. Its stem fiber is rich in cellulose that was graft copolymerized with different vinyl monomers. Variable graft yield was obtained depending on properties of the monomers, reaction conditions and other physico-chemical factors. The graft copolymers were characterized by SEM & FTIR and studied for change in properties like swelling and dye-uptake behavior. These modified fibers were then used as reinforcement in the composites. These composites were then evaluated for physico-chemico-mechanical properties. The modified fiber and the composites could be useful for various industrial and scientific applications.

Keywords: Polymer; Mechanical; Grafting; Swelling; Dye

Introduction

Natural fibers have been used by the man since ancient times. As they are renewable resource so they can also be utilized for various secondary needs. Many attempts have been made to explore their potential yet a lot remains undiscovered. The natural fibers suffer from various draw-backs such as low weather-stability, fast-decaying and low chemical resistance. Amongst various methods prevalent to improve these properties, graft copolymerization of vinyl monomers onto natural backbones has been an interesting tool to reduce the ageing in textiles, enhancing the mechanical properties and modifying the texture. Graft copolymerization of various vinyl monomers onto cellulose has been extensively studied. Numerous scientists have explored the potential of this chemical technique on different natural fibers and used latest advanced means of characterization like FTIR, XRD, SEM, TGA, DTA, DSC and evaluated the properties for their variable applications. It modifies the properties of polymer back-bone and incorporates the desired features without drastically affecting the basic traits of the substrate [1-6].

Use of natural fiber in textile and advanced engineering products has focused the attention of many scientists in the new era. The present paper deals with the graft copolymerization of methyl acrylate (MA) as principal monomer while acrylic acid (AA), acrylamide (Aam) and 4-vinyl pyridine (4-VP) as secondary monomer onto virgin Sereni (*Hibiscus sabdariffa*, Family: Malvaceae) stem fiber, rich in cellulose content (73.9%) [7,8]. The evaluation of the swelling and dye-uptake behavior and the use of grafted fiber as reinforcement in composite still remains unexplored. This paper attempts to find the applicability of the modified fiber for textile and advanced engineering material.

Experimental

Materials

H. sabdariffa fiber was obtained from the Department of Agronomy, Chaudhary Sarwan Kumar Himachal Krishi Vishwavidyalaya, Palampur (H.P.) India. Monomers (Merck) and ceric ammonium nitrate (s. d. fine-Chem, Pvt. Ltd, Mumbai, India) were used as received. *H. sabdariffa* fiber was purified through soxlet extraction in acetone for 72 h.

Graft copolymerization

Graft copolymerization of the monomer onto *H. sabdariffa* was carried-out for optimization of different reaction conditions

like reaction time, reaction temperature, monomer concentration, concentration of initiator system and pH in order to obtain maximum graft yield. The fiber (0.5g) was activated by swelling in 100 ml of the distilled water for 24 hrs. Mixture of ceric ammonium nitrate (CAN) and conc. HNO₃ mixture was slowly added to the reaction medium with continuous stirring followed by the drop by drop addition of a definite ratio of binary vinyl monomeric mixture. The reaction was carried-out at a definite temperature for a particular time interval. On completion of the reaction, poly(MA), poly(MA-co-AA), poly(MA-co-Aam) and poly(MA-co-4-VP) were removed on extraction with acetone, methanol chloroform and water. The graft co-polymer was dried at 50°C, till a constant weight was obtained. The percent grafting (P_g) was calculated as per the reported method [9]:

$$P_g = \frac{W_f - W_i}{W_i} \times 100 \quad (1)$$

where, W_f = final weight of the fiber, W_i = initial weight of the fiber.

Characterization

IR spectra of the *H. sabdariffa* and its graft copolymers were recorded with Perkin Elmer Fourier Transform Infrared (FTIR) spectrophotometer using KBr pellets (Sigma Aldrich). Scanning Electron Micrographs (SEM) of *H. sabdariffa* and its graft copolymers were obtained by using Electron Microscopy Machine (LEO 435-25-20).

Synthesis of phenol-formaldehyde resin

Phenol-formaldehyde resin was prepared in a resin kettle by taking specific molar ratio of phenol and formalin. Phenol and formalin were mixed with the help of mechanical stirrer. Sodium hydroxide solution (50% aqueous solution of sodium hydroxide prepared on the basis of

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5% relative weight of sodium hydroxide to the weight of phenol taken) was added to the reaction mixture with constant stirring and heating. Since, the reaction was exothermic, so the reaction temperature was maintained between 50°-60°C by circulating the cold water around the resin kettle initially for two hours. Thereafter, reaction temperature was raised to 80-90°C and setting of resinification was checked on appearance of turbidity by adding a drop of condensing resin to the cold water. Condensing resin was further heated at this temperature for another two and half hour and afterwards the resin was cooled to room temperature [4].

Preparation of the bio-composites

Phenol-formaldehyde matrix based bio-composites were prepared by mixing fiber to resin (12.7 : 87.3). The mixture was then placed in the mold of a particular dimension : 40-80 mm (length), 5 x 5 mm (cross section). Degasification of sample was carried-out in Compression Molding Machine and the samples were kept for curing at 120°C for 10 minutes under 400 kg/cm² pressure. Composites thus prepared by reinforcing the raw fiber and its graft copolymers In each case, the number of specimen used for the determination of mechanical properties were three. Tests were conducted under ambient laboratory conditions [4].

Physico-Chemical Evaluation

Swelling behavior in different solvents

250 mg. of each grafted and raw sample was immersed in a definite volume (100 ml) of water, methanol, n-butanol and dimethyl-formamide under ambient conditions for a period of 24 hours. Samples were removed from the solvent and excess solvent was removed quickly with filter papers. Final weight of the sample was taken and the percent swelling was calculated as follows [1-3]:

$$\text{Percent swelling } (P_s) = \frac{W_2 - W_1}{W_1} \times 100 \quad (2)$$

Where, W_1 and W_2 are the initial and final weights of samples, respectively.

Dye uptake behavior

0.1% Gentian violet solution was prepared in distilled water. 10% NaCl and a few drops of acetic acid were added to this solution. Dye uptake of raw fiber and its graft copolymers was carried-out by immersing the known weight of each sample in 100 ml of Gentian violet dye. Optical densities of test solutions were noted down using Digital Photo Colorimeter after particular time intervals till constant readings were obtained for seven consecutive hours and the concentrations of test solution were calculated as [1-3]:

$$\text{Conc. of test solutn } (C_t) = \frac{I_t}{I_o} C_o \text{ molL}^{-1} \quad (3)$$

Where, I_o , I_t and C_o are optical density of standard solution, optical density of test solution and concentration of standard solution, respectively.

Mechanical Evaluation

Modulus of rupture (MOR)

MOR was determined according to ASTM D 790 standard and was calculated using the Eq. 4 [4]:

$$\text{MOR} = \frac{3PL}{2bd^2} \text{ N / mm}^2 \quad (4)$$

where, P = peak load, L = length of the sample, b = width of the sample and d = thickness of the sample.

Modulus of elasticity (MOE)

MOE was determined according to ASTM D 790 standard and was calculated using the following equation 5 [4]:

$$\text{MOE} = \frac{P_1 L^3}{4bd^3 y} \text{ N / mm}^2 \quad (5)$$

where, P_1 = load at the limit of proportionality and y = rate of bending.

Stress at the limit of proportionality (SP)

Stress at the limit of proportionality was calculated by using the equation 6 [4]:

$$\text{SP} = \frac{3P_1 L}{2bd^2} \text{ N / mm}^2 \quad (6)$$

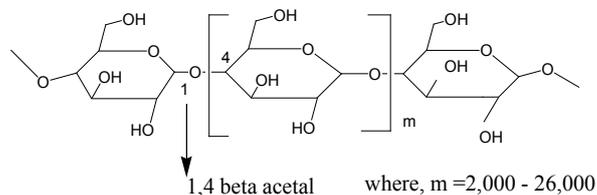
Hardness

Hardness of the composites was tested using Rockwell Hardness tester (Balancing Instrument and Equipments Miraj Pvt. Ltd., Model-TSM) following ASTM D785 standard, using B-scale, 100 Kg as a major load and 10 Kg as a minor load with 1.58mm indenter steel ball and was measured in HRB.

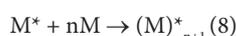
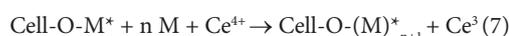
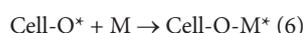
Results and Discussion

Mechanism

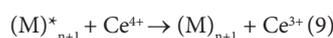
Ceric ion forms complex with the cellulose through C-2 and C-3 hydroxyl groups of the anhydro glucose unit. Transfer of the electron from the cellulose molecule to Ce (IV) would follow, leading to its reduction to Ce (III), breakage of -OH bonds at C-2 and C-3 and the formation of the free radical sites where the monomeric chains get grafted. Graft yield and homo-polymer formation have been found to be the functions of both the monomer and initiator concentration [10,11].



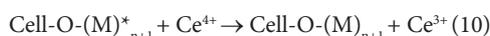
Cellulose



(active homopolymer moiety)



(homopolymer)



(graft copolymer)

where, Cell-OH = *H. sabdariffa* backbone and M = monomer

Characterization

Fourier transformer infrared spectroscopy (ftir) : FTIR spectrum of the *H. sabdariffa* showed a broad peak at 3424.0 cm^{-1} (-OH group) and peaks at 2924.7 cm^{-1} , 1246.9 cm^{-1} and 1032.0 cm^{-1} were observed due to -CH₂, C-C and C-O stretching, respectively. However, in case of *Hs-g-poly(MA)* peak due to >C=O groups appeared at 1738.0 cm^{-1} whereas, in case of 1639.4 cm^{-1} (vinyl group) in *Hs-g-poly(MA-co-4VP)*; 3369.7 cm^{-1} (N-H stretch) of amide in *Hs-g-poly(MA-co-AAm)*; 1649.7 cm^{-1} (>C=O of acid) in *Hs-g-poly(MA-co-AA)* [11].

Scanning electron microscopy (sem): In SEM, the cellulose was gold plated to have an impact. It is quite evident from the Figures 1-3 that there has been a sufficient deposition of polyvinyl monomers onto fiber. Comparison of the scanning electron micrographs of the raw *H. sabdariffa* fiber with the graft copolymers reveals the distinction between the ungrafted and grafted samples, depending upon the Pg [11].

Effect of binary vinyl monomers on percentage grafting

The optimized parameters for the graft copolymerization of MA (as a principal monomer) onto *H. sabdariffa* fiber, to obtain the maximum graft yield (60.24 %) were: temperature (°C), 35; time (minute), 120; CAN (mol L⁻¹), 1.49×10^{-4} ; HNO₃ (mol L⁻¹), 3.36×10^{-3} ; MA (mol L⁻¹), 2.21×10^{-3} and pH, 7.0 [11].

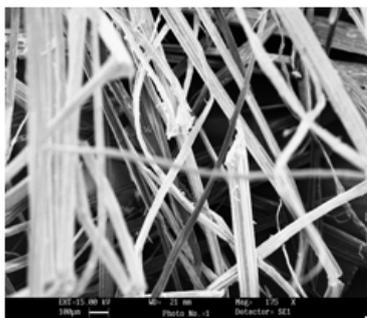


Figure 1: SEM of *H. sabdariffa*.



Figure 2: 2 SEM of *Hs-g-poly(MA)*.

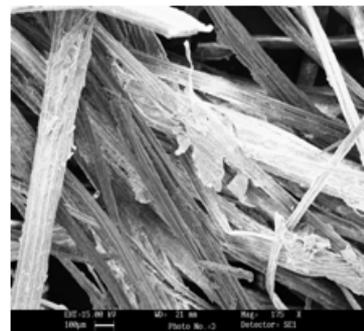


Figure 3: SEM of *Hs-g-poly(MA-co-AA)*.

Since, it is hard to justify the results merely on the basis of concentration of binary vinyl mixtures, therefore, it is important to consider the reactivity, nature and behavior of monomer species. From the literature review it is clear that the reactivity of the acrylate monomers in reference to styrene radicals is normally higher. Since, the carboalkoxy group is highly electronegative; therefore, it causes the acrylate double bond to be positive in character. Methyl acrylate radical has hyper conjugative resonance with methyl hydrogen as well as with the carboxy group. The polar character of the acrylates results in the penultimate group effects in both propagation and the termination reactions [11-14].

In case of MA+AA binary mixture, r_1 ; r_2 ratio (0.98 + 0.02: 0.42 + 0.02 at 45°C) is quite satisfactory but due to more association of AA with water, low free radical transfer to the backbone (due to low C_M) results in low Pg (74.14). In case of acrylamide, a low graft yield (23.75%) was observed as in this case Kp value is higher but C_M value is low which results in more homo-polymerization. 4-VP on the other hand, causes steric hindrance that reduces the reactivity and causes a marked decrease in Pg with increase in its concentration (11.50) by its antagonistic effect [11-14].

However, many other factors also determine the graft yield like the type of fiber, swelling, number of active sites, the nature and amount of the solvent and temperature of polymerization strongly influence the reactivity ratios. In absence of monomer rich phase, the diluents will compete with the monomers for adsorption sites. The amount of adsorption will depend upon the total amount of surface area present and this in turn, is dependent upon the rate of stirring. Physical factors like mixing efficiency determines the melt temperature, the pressure, the rheological properties, solubility of the initiator and the monomer. Elevated temperature favors the degradation, reduces the initiator half life, modifies the rate or specificity of the reaction, influences the solubility and rheological parameters (Table 1) [11].

Physico-chemical evaluation

Swelling behavior in different solvents: The swelling behavior studies were carried-out in different solvents like Water, MeOH, BuOH and DMF. It has been observed that *H. sabdariffa* fiber showed maximum swelling in Water (59%) followed by MeOH (46%), BuOH (38%) and DMF (30%). However, the swelling behavior of the highest graft copolymers followed the pattern: DMF > BuOH > Water > MeOH and the trend obtained has a direct correlation with the solubility parameters like solvent basicity, the molar ratio, hydrogen bond formation and the percentage grafting. Depending on the chemical nature and the property, the pendent groups of the grafted polymers

such as $-\text{COOCH}_3$, $-\text{COOH}$, $-\text{CH}=\text{CH}_2$ and $-\text{CONH}_2$ have different interactions with the solvents. Higher percentage swelling in DMF and BuOH is due to better interaction with such pendent groups that increases with increase in Pg. However, a reverse trend has been found in the case of raw *H. sabdariffa*. Since a crystalline polar polymer is soluble in solvent is capable of hydrogen bond formation therefore, the raw fiber has more swelling in water and MeOH followed by DMF and BuOH. Presence of $-\text{OH}$ and $-\text{CH}_2\text{OH}$ groups in cellulosic fibers further supports the deep penetration of the polar solvents into the polymer backbone thereby, resulting in higher swelling. Whereas, in case of DMF and BuOH, the affinity of these solvents towards $-\text{OH}$ groups is less and ultimately a decreased swelling takes place. Moreover, other factors like the fiber size, steric hindrance and temperature also influence the percentage of swelling [1-3,6,11,15-17] (Table 2).

Dye-uptake behavior: The dye uptake behavior of the graft copolymers vis-à-vis raw fiber, was studied for seven consecutive hours to find out the effect of grafting on dye uptake (Table 3). Graft copolymers were found to exhibit less dye uptake as compared to the backbone and was found to be a function of Pg. It was observed that dye uptake decreases with increase in Pg. Cellulose is semi crystalline polymer that easily swells due to competitive processes of adsorption through hydrogen bonding and the scission of the internal hydrogen bonds between the amorphous molecules. Presence of free reactive sites like $-\text{OH}$ and $-\text{CH}_2\text{OH}$ in raw fiber helps in the absorption of the dye. But these sites get occupied with poly(vinyl monomer) chains and poly(binary vinyl monomer) chains in the backbone that restrain dye uptake and is Pg dependent. Therefore, with increase in Pg, dye uptake has been found to decrease [1-3,11,15,16,18].

Mechanical evaluation

The results obtained after the mechanical evaluation of phenoplast, fiber reinforced composites and grafted fiber reinforced bio-composites

Sample	Binary mixture (x 10 ⁻³ mole L ⁻¹)	Mean Pg	±SD	±SE
<i>Hs-g-poly</i> (MA+AA)	2.21+0.72	18.00	±4.47	±2.58
	2.21+1.45	74.14	±2.68	±1.54
	2.21+2.17	42.35	±3.53	±2.04
	2.21+2.91	10.28	±4.40	±2.55
<i>Hs-g-poly</i> (MA+Aam)	2.21+0.70	20.22	±1.78	±1.02
	2.21+1.05	23.75	±4.42	±2.55
	2.21+1.40	15.54	±3.44	±1.98
	2.21+1.75	14.00	±3.57	±2.06
<i>Hs-g-poly</i> (MA+4VP)	2.21+2.10	12.38	±1.96	±1.13
	2.21+0.92	11.50	±0.98	±0.50
	2.21+1.38	11.30	±1.87	±1.08
	2.21+1.85	7.70	±1.70	±0.98
	2.21+2.30	5.00	±1.71	±0.98

Table 1: Effect of the binary mixtures on Pg using MA as a principal monomer.

Sample	Pg	% Swelling			
		Water	MeOH	BuOH	DMF
<i>H. sabdariffa</i>	-	59.00	46.00	38.00	40.00
<i>Hs-g-poly</i> (MA)	60.24	29.00	26.00	44.00	60.00
<i>Hs-g-poly</i> (MA-co-4VP)	11.50	52.00	42.00	33.00	45.00
<i>Hs-g-poly</i> (MA-co-Aam)	23.75	46.00	36.00	30.00	49.00
<i>Hs-g-poly</i> (MA-co-AA)	74.14	20.00	15.00	49.00	66.00

Table 2: Effect of solvents on swelling behavior of graft copolymers vis-à-vis backbone.

Sample <i>Hs-g-poly-</i>	Pg	Dye concentration of the test solution at different time intervals (x 10 ⁻⁴ mol L ⁻¹)						
		1 h	2 h	3 h	4 h	5 h	6 h	7 h
<i>H. sabdariffa</i>	raw	4.96	4.38	4.08	4.08	3.79	3.21	3.21
(MA)	60.24	5.25	5.25	4.96	4.96	4.67	4.67	4.67
(MA-co-4VP)	11.50	4.96	4.67	4.67	4.67	4.38	3.21	3.21
(MA-co-Aam)	23.75	5.84	5.84	5.84	4.38	3.79	3.79	3.79
(MA-co-AA)	74.14	5.84	5.84	4.96	4.96	4.96	4.96	4.96

Table 3: Dye uptake studies of the graft copolymers vis-à-vis back bone.

Composite	Strength Test			
	MOR (N/mm ²)	MOE (N/mm ²)	SP (N/mm ²)	Hardness (HRB)
Phenol-formaldehyde	43.20	496.12	38.40	Brittle
<i>H. sabdariffa-r-PF</i>	69.99	614.40	57.60	67.00
<i>Hs-g-poly</i> (MA)-r-PF	74.00	753.00	62.36	70.00
<i>Hs-g-poly</i> (MA-co-4VP)-r-PF	70.80	630.99	54.70	68.00
<i>Hs-g-poly</i> (MA-co-Aam)-r-PF	72.40	696.96	60.84	70.00
<i>Hs-g-poly</i> (MA-co-AA)-r-PF	77.96	780.00	66.66	75.00

where, -r-PF refers to reinforced Phenol-formaldehyde.

Table 4: MOR, MOE, SP and Hardness studies of graft copolymers reinforced P-F composite vis-à-vis P-F resin.

are given in Table 4. It is evident from the results, that *H. sabdariffa* fiber as reinforcement has improved the mechanical properties of the P-F composites. In most of the cases, graft copolymers of methyl acrylate and its binary mixtures were found to exhibit better mechanical behavior as compared to composites reinforced with the raw fiber and the phenoplast. The better mechanical behavior could be accounted by the functioning of the monomer as a coupling agent, fiber size, nature of the fiber, better fiber matrix interaction, compatibility and orientation of the fiber. However, some deviation in the results could be justified by other governing factors for overall mechanical performance like nature and amount of matrix and fiber, orientation, distribution of the fiber with respect to the matrix axis, form of reinforcement used (woven or non-woven, grafted or ungrafted), strength of the interfacial bond between the fiber and matrix, length of the fiber (continuous or discontinuous), aspect ratio that on mere imbalance may lead to debonding and cracking [11,16-18].

Conclusions

Grafting of poly (MA) (Pg: 60), poly (MA-co-4VP) (Pg: 11.50), poly (MA-co-Aam) (Pg: 23.75) and poly (MA-co-AA) (Pg: 74.14) onto *H. sabdariffa* stem fiber in the presence of ceric ion initiator yielded novel regenerated graft copolymers. It is evident from the characterization and evaluation studies of the graft copolymers through different technique that grafting resulted in the morphological transformation that improved the various physico-chemical properties of the fiber and the mechanical strength of the composites when used as reinforcement. Physico-chemical resistance, hydrophobicity and miscibility with the organic solvents acquired by the fiber after graft copolymerization innovates to utilize the renewable waste biomass in various scientific and industrial applications like in aerospace, transportation, packaging and insulators.

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