

Bioremediation of Natural Fiber by Graft Copolymerization

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Abstract

In this research paper, the Sorrel stem fiber was graft copolymerized by vinyl monomeric mixtures that lead to an increase in the percentage grafting with a significant change in physico-chemico-thermal resistance. Miscibility in organic solvents, hydrophobicity was found to increase whereas crystallinity, crystallinity index, dye-uptake and hydrophilicity decreased after graft copolymerization. These graft copolymers were reinforced in polymer matrix (Phenol-Formaldehyde) to procure green composite. These bio-composites were subjected to characterized and evaluated and were found to be advanced material.

Keywords: *Hibiscus sabdariffa*; Modulus; Stress; Strength

Introduction

The diverse metabolic capabilities of microorganisms and their interactions with hazardous organic and inorganic compounds have long been recognized. Microbial processes are environmentally compatible and can be integrated with non-biological processes to detoxify, degrade and immobilize environmental contaminants. Bioremediation, the application of biological methods, has been used successfully for soil remediation yet a lot remains to be done. Natural fibers and polymer are of immense importance to mankind. The whole world has laid stress to bioremediation and judicious use of renewable and sustainable resources because of environment and health concerns. The development of new biodegradable polymer from renewable raw materials in comparison to artificial fibers has increased during last few years. Natural fibers are the most suitable reinforcement materials because of their relatively high strength and stiffness in industries such as automobile, packaging and construction materials, to match their economic and ecological aspects [1-4]. Low cost, easy availability and attractive properties like low density, high mechanical strength makes them lucrative in place of glass, carbon and other synthetic fibers. The constituents of natural fibers are cellulose, hemicelluloses, lignin and pectins with a small quantity of the extractives. The properties of bio-fibers mainly depend upon their origin, age, climatic conditions and extraction techniques. The presence of hydroxyl groups (polar group) in various constituents of lingo-cellulosic fiber reduces the utilities in many applications [5-12]. In order to improve its adhesion, various techniques like graft copolymerization, chemical treatment like mercerization, acetylation, benzoylation and treatment with various coupling agent can be used. It also helps in easy decay of the products.

Graft copolymerization is a significant technique to endow desirable properties to backbone polymers. It is a versatile chemical technique that incorporates the desired features in natural fiber without affecting their inherent traits. Various workers have carried out the graft copolymerization onto different cellulosic backbone using vinyl monomers through various chemical while using wide range of initiator, oxidizer, monomers, binary vinyl monomeric mixtures and radiation techniques and achieved fruitful results [13-22].

Literature reveals that Sorrel lacks therapeutic potential but its low weight, high tensile strength and rich cellulose content (73.9%) promotes its use as backbone for graft copolymerization. Therefore, it was worthwhile to screen the graft copolymerization of effective vinyl monomer like Ethyl acrylate (EA) onto *Hibiscus sabdariffa* (Hs) stem fiber and its binary vinyl monomeric mixture with butyl acrylate (BA) and vinyl acetate (VA), that still remains unexplored. To present the

cumulative effect of these binary vinyl monomers on the behavioral, morphological transformations in the fiber after graft copolymerization and explore the potential of the graft copolymers as reinforcement in phenoplast (phenol-formaldehyde: P-F) polymer matrix based green composite to explore the change in mechanical strength such as flexural strength/modulus of rupture (MOR), young's modulus/modulus of elasticity (MOE), stress at the limit of proportionality (SP) and hardness using advanced analytical and evaluation techniques that remains unnoticed [23,24].

Experimental

Material and methods

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, Phenol (s. d. fine-Chem, Pvt. Ltd, Mumbai, India) and formaldehyde (CDH, India) were used as received. Composites were prepared in Compression Molding Machine (SANTEC India Ltd.). Libror AEG-220 (Shimadzu) electronic balance was used for weighing. Compressive/Tensile strength, MOR, MOE and SP of the samples were tested on the Universal Testing Machine (HOUNSFIELD, H25KS). Curing and degasification were done on Compression Molding Machine (Santech India Ltd).

Characterization

Fourier Transform Infra Red Spectroscopy (FTIR) and Scanning Electron Microscopy (SEM): IR spectra of the *H. sabdariffa* and its graft copolymers were recorded on Perkin Elmer Fourier Transform Infrared (FTIR) spectrophotometer using anhydrous KBr (Sigma Aldrich). Scanning Electron Micrographs (SEM) of *H. sabdariffa* and its graft copolymers were obtained by using Electron Microscopy Machine (LEO 435-25-20), under ambient conditions.

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Thermogravimetric-Differential Thermogravimetric Analysis (TG-DTA): Thermogravimetric and differential thermal analysis were performed on thermal analyzer (LINSEIS, L-81 11). TGA of raw and grafted fiber has been studied as a function of percentage wt. loss vs. temperature.

X-ray powder diffraction (XRD): X-ray diffraction studies were performed on X-ray diffractometer (Bruker D8 Advance) under ambient conditions using Cu K α (1.5418 Å) radiation, Ni-filter and scintillation counter as detector at 40 KV and 40 mA on rotation between 13° (2 theta) to 25° (2 theta) at 1s accumulation time and step size of 0.01 degree with 0.5° or 1.0 mm of divergent and anti-scattering slit. Corundum and quartz were used as the reference to verify and calibrate the instrument. Percentage Crystallinity (% Cr) and Crystallinity index (C. I.) were calculated by Eq. 1 and 2 as reported before [15, 25-27]:

$$\%Cr = \left[\frac{I_{22.68}}{(I_{22.68} + I_{15})} \right] \times 100 \quad (1)$$

$$C.I. = \left[\frac{(I_{22.68} - I_{15})}{I_{22.68}} \right] \quad (2)$$

Graft copolymerization

Graft copolymerization of the monomer (EA) onto *H. sabdariffa* was carried-out for the optimization of different reaction conditions like reaction time, reaction temperature, monomer concentration, concentration of initiator system and pH in order to obtain the maximum graft yield as per the method reported before [15,25-27]. On completion of the reaction, poly(EA), poly(BA) and poly(VA) were removed on extraction with acetone, methanol, chloroform and water. The graft co-polymers were dried at 50°C, till a constant weight. The percent grafting (P_g) was calculated by Eq. 3 [15,25-27]:

$$P_g = \frac{W_f - W_i}{W_i} \times 100 \quad (3)$$

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

Preparation of the Polymer matrix resin and Bio-composites

Phenol-formaldehyde resin (P:F ratio of 0.75:1.0) was prepared as per the method reported earlier to optimum better mechanical properties [25,26]. Phenol-formaldehyde matrix based bio-composites were prepared by mixing ratio of phenol: formaldehyde (0.75:1.0) and fiber to resin (12.7:87.3), respectively. The mixture was then placed in the mold of a specific dimension:40-80 mm (length), 5 x 5 mm (cross section). Degasification of samples 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 [25,26].

Physico-chemical evaluation

Moisture absorption study: Moisture absorbance studies were carried-out at various relative humidity levels ranging from 30-90 % as per the method mentioned before and given in Eq. 4 [1-3]:

$$\text{Moisture absorbance (\%)} = [(W_f - W_i) / W_i] \times 100 \quad (4)$$

Acid and base resistance: Acid and base resistance studies were carried-out as shown in Eq. 5 [1-3] and the final weights (W_f) of the samples was observed after 72 hours, under ambient conditions.

$$\text{Weight loss (\%)} = [(W_i - W_f) / W_i] \times 100 \quad (5)$$

Swelling behavior in different solvents: 250 mg. of 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 as per the method studied before and final weight of the sample was taken and the percentage of swelling was calculated as follows [1-3]:

$$\text{Swelling (\%)} = \frac{W_2 - W_1}{W_1} \times 100 \quad (6)$$

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 solution and a few drops of acetic acid were added to this solution. Dye uptake of the samples were carried-out for seven consecutive hours and the concentrations of the test solution were calculated [1-3,25]: Cont. of test solution

$$(C_t) = \frac{I_t}{I_o} \times C_o \text{ molL}^{-1} \quad (7)$$

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 (flexural strength): MOR was determined according to ASTM D 790 standard and was calculated using the Eq. 8 [25,26]:

$$MOR = \frac{3PL}{2bd^2} \text{ N / mm}^2 \quad (8)$$

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

Modulus of elasticity (young's modulus): MOE was determined according to ASTM D 790 standard and was calculated using the following equation 9 [25,26]:

$$MOE = \frac{PL^3}{4bd^3y} \text{ N / mm}^2 \quad (9)$$

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

Stress at the limit of proportionality: Stress at the limit of proportionality was calculated by using the equation 10 [25,26]:

$$SP = \frac{3PL}{2bd^2} \text{ N / mm}^2 \quad (10)$$

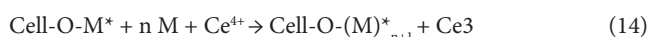
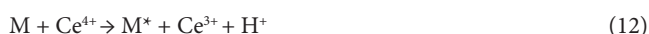
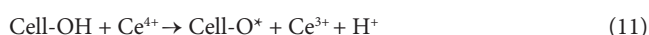
Hardness: Hardness of the composites was tested using Rockwell Hardness tester (Balancing Instrument and Equipments Miraj Pvt. Ltd., Model-TSM) following ASTM D785 standard, using B-scale, 100 Kg as a major load and 10 Kg as a minor load with 1/16 inch indenter steel ball and was measured in HRB [25,26].

Results and Discussion

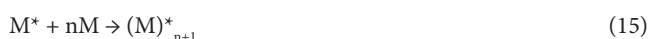
Mechanism

The graft copolymerization of poly(EA) as principal monomer onto *H. sabdariffa* fiber was effective (P_g : 117.30). Use of ethyl acrylate as principal monomer in binary vinyl monomeric mixture with secondary monomers like butyl acrylate and vinyl acetate resulted in *Hs-g-poly(EA-co-BA)* and *Hs-g-poly(EA-co-VA)*, respectively. C_2 , C_3 , and C_6 hydroxyls and C-H groups were the active sites for the incorporation of polymeric chains through grafting onto cellulose (Eq. 14 and 17). Ceric ammonium nitrate was used as a source of ceric ion and the presence of concentrated nitric acid played an important role during

graft copolymerization. In aqueous medium, ceric ion existed as $[\text{Ce-O-Ce}]^{6+}$. Since, the large size $[\text{Ce-O-Ce}]^{6+}$ ions were unable to form complex with the fiber so, due to the presence of nitric acid, more Ce^{4+} and $[\text{Ce}(\text{OH})_3]^{3+}$ ions were formed. Then these ions easily underwent complex formation with the fiber. Ceric ion formed the chelate complex with the cellulose through C-2 and C-3 hydroxyl groups of the anhydrous glucose unit. Transfer of the electron from the cellulose molecule to Ce (IV) followed, leading to its reduction to Ce (III), breakage of the bonds at C-2 and C-3 that resulted in the formation of the free radical sites. Grafting of vinyl monomer onto polymeric backbone occurred as follows [15,25]:



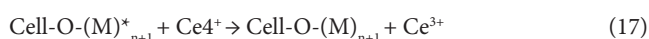
(Active graft copolymeric species)



(Active homo-polymer moiety)



(Homo-polymer)



Graft copolymer)

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

The optimized reaction conditions using EA as principal monomer onto the fiber were: monomer conc.: $2.26 \times 10^{-3} \text{ mol L}^{-1}$; CAN: $2.41 \times 10^{-4} \text{ mol L}^{-1}$; HNO_3 conc.: $1.46 \times 10^{-3} \text{ mol L}^{-1}$; pH of the medium: 7; time: 150 mins. ; temperature: 35°C that yielded Pg of 117.30 ($\pm\text{SD}$: 7.13; $\pm\text{SE}$: 4.12). The use of ethyl acrylate as principal monomer for graft copolymerization onto *H. sabdariffa* fiber yielded a high Pg. It was due to high rate of propagation (K_p), low rate of termination (K_t), higher transfer rate constant (C_m) and higher reactivity of the monomer. Butyl acrylate as comonomer with ethyl acrylate yields high Pg on graft copolymerization over *H. sabdariffa* backbone, but the relatively bulky group encounters steric hindrance that affects Pg (112.20). Vinyl acetate has low reactivity (0.02), low polarity, that effects its interaction with EA (Pg : 36.10) (Table 1). However, many other factors also influence the graft yield like the type of fiber, swelling, and number of active sites, the nature and amount of the solvent, temperature of polymerization, reactivity ratios. [28-31].

Sample	Binary mixture ($\times 10^{-3} \text{ mole L}^{-1}$)	Mean Pg	$\pm\text{SD}$	$\pm\text{SE}$
<i>Hs-g-poly</i> (EA+BA)	2.26+0.58	90.40	± 4.37	± 2.52
	2.26+1.17	112.2	± 6.06	± 3.50
	2.26+1.75	88.16	± 3.56	± 2.06
	2.26+2.33	53.40	± 2.60	± 1.50
	2.26+2.91	44.80	± 1.75	± 1.01
<i>Hs-g-poly</i> (EA+VA)	2.26+0.91	36.10	± 3.58	± 2.06
	2.26+1.80	28.06	± 2.62	± 1.51
	2.26+2.72	20.76	± 2.60	± 1.50
	2.26+3.60	15.06	± 1.76	± 1.01
	2.26+4.52	10.46	± 4.39	± 2.53

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

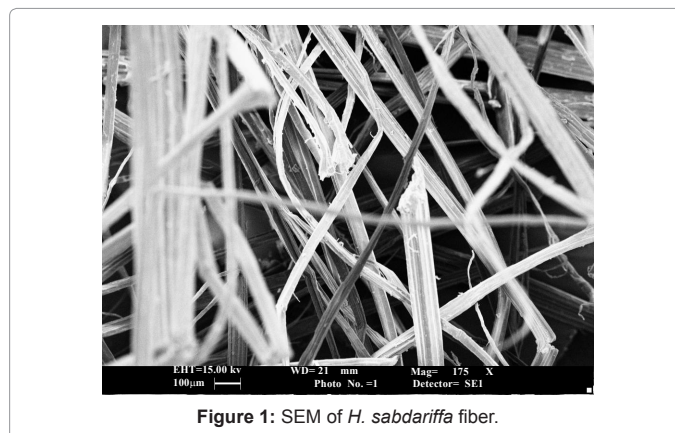


Figure 1: SEM of *H. sabdariffa* fiber.

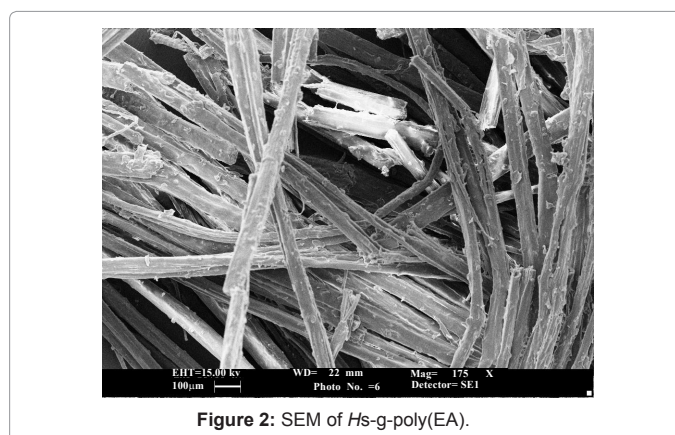


Figure 2: SEM of *Hs-g-poly*(EA).

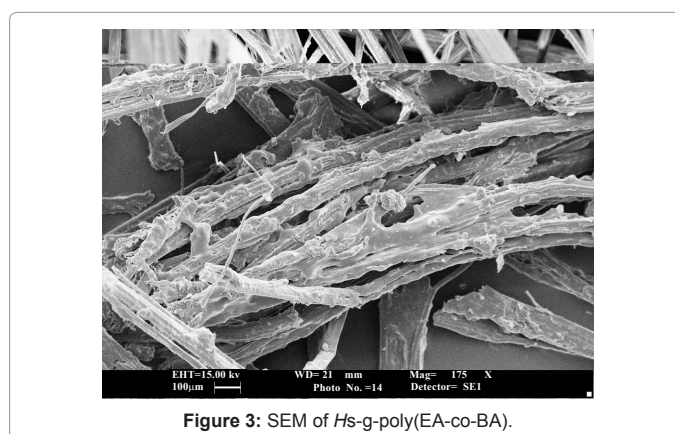


Figure 3: SEM of *Hs-g-poly*(EA-co-BA).

Characterization

FT-IR: IR spectrum of the *H. sabdariffa* showed the prominent broad peak at 3424.0 cm^{-1} ($-\text{OH}$ group) and peaks at 2924.7 cm^{-1} , 1246.9 cm^{-1} , 1032.0 cm^{-1} were observed due to $-\text{CH}_2$, C-C and C-O stretching, respectively. However, in case of *Hs-g-poly*(EA) an additional peak due to $>\text{C}=\text{O}$ groups of the EA was witnessed at 1734.0 cm^{-1} whereas a peak at 1732.8 cm^{-1} ($>\text{C}=\text{O}$ group) in *Hs-g-poly*(EA-co-BA), 1651.1 cm^{-1} (vinyl group) in *Hs-g-poly*(EA-co-VA); confirms the incorporation of the secondary monomers in these graft copolymers.

Scanning electron microscopy: The cellulose and P-F matrix had non-conducting behavior hence they were gold plated prior to analysis. It is quite evident from the figures 1-4, that there has been

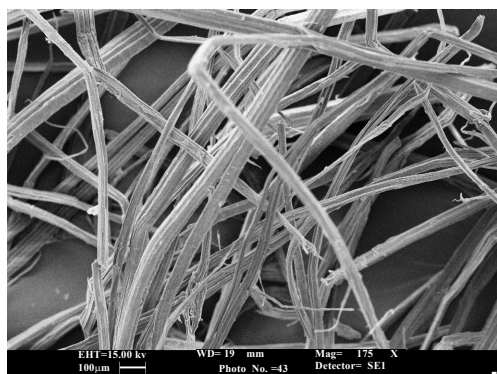


Figure 4: SEM of Hs-g-poly(EA-co-VA).

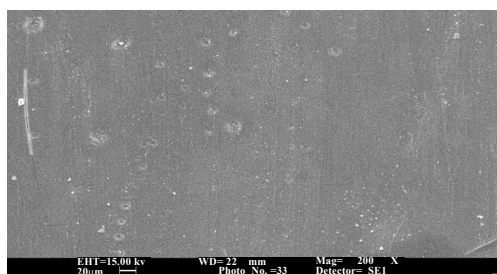


Figure 5: SEM of Phenoplast.

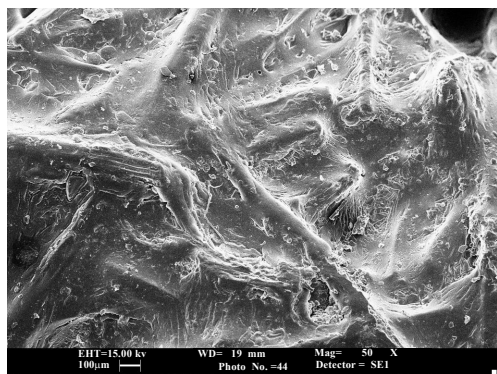


Figure 6: SEM of fiber reinforced composite.

a sufficient deposition of polyvinyl monomers onto fiber. Comparison of the scanning electron micrographs of raw *H. sabdariffa* fiber with the graft copolymers reveals the clear distinction between the randomly distributed ungrafted fiber and the grafted samples that started forming the bundles in close packing, depending upon the Pg [26]. Similarly, the phenoplast when embedded with fiber and graft copolymers completely changed the surface (Figure 5,6).

X-RD studies: It is evident from the figure 7 and table 2 that the percentage crystallinity and crystallinity index were found to decrease with increase in percentage grafting of EA and its co-monomer onto *H. Sabdariffa* fiber. With increase in percentage grafting, the percentage crystallinity and crystallinity index decreased. Lower crystallinity index in case of graft copolymers stands for the poor order of crystal lattice in the fiber. The dis-orientation of the crystal lattice to the fiber axis during grafting resulted in graft copolymer with low crystallinity and

crystallinity index. This clearly indicates that the cellulose crystals are better oriented in raw *H. sabdariffa* fiber rather than in Hs-g-poly(EA) and other graft copolymers. The PF resin gave a halo pattern while there was further increase in amorphous content with increase in fiber and grafted fiber content in the composite [15,25,27].

TG-DTA studies: Cellulosic in *H. sabdariffa* degrades by dehydration, glycogen formation and depolymerization. In case of *H. sabdariffa*, two-stage thermal degradation has been found in the temperature range of 225.7-338.9°C with 54.0 % weight loss and between 338.9-463.0°C with 26.00 % weight loss (Table 3 and Figure 8). The former stage is attributed to the loss by dehydration, volatilization processes whereas the later stage is referred to loss by depolymerization, delignification and oxidation of the char. Hs-g-poly(EA) and Hs-g-poly(EA-co-vinyl monomer) showed two major stages of decomposition (Table 3 and Figure 9). The first stage refers to loss of moisture and decarboxylation ranging from 240.6-312.4°C and the second stage pertains to the breaking up of crystallites and covalent bonds in vinyl monomer in the range of 475.0-520.0°C. Thus, it is evident from the TGA data that grafted fibers are thermally more stable than the raw fibers. It could be due to the incorporation of poly(EA) and poly(vinyl) monomer chains on backbone polymer through strong covalent bonding or mechanically due to surface grafting, confirming the additional strength and stability to the fiber [25,32].

In case of DTA studies, *H. sabdariffa* has been found to exhibit two exothermic peaks at 327.9°C (18 μV) and 422.7°C (14 μV). Exothermic peak at 327.9°C corresponds to decomposition stage between 225.7-338.9°C while the exothermic peak at 422.7°C corresponds to second decomposition stage (338.9 - 463.0°C) in TGA (Table 3 and Figure 7). In case of graft copolymers, the first and second transition peaks revealed the dehydration, adsorption and oxidation of the semi-crystalline host

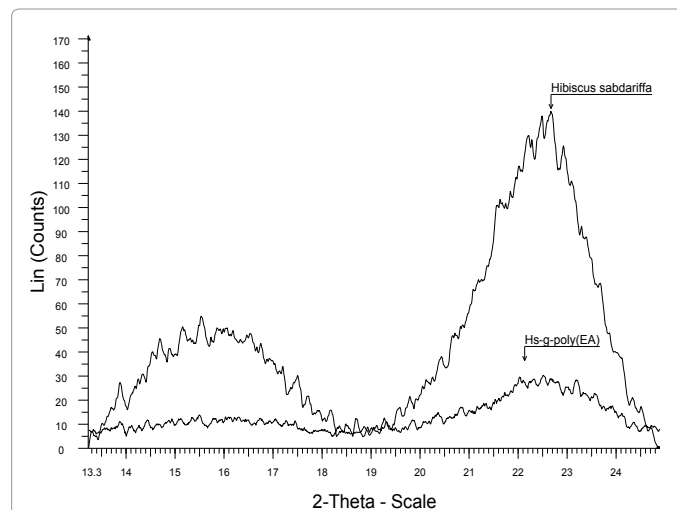


Figure 7: The XRD overlay pattern of highest grafted copolymer vise-a-vise raw fiber.

Sample	Pg	2θ Scale		%Cr	C.I.
		I ₁₅	I _{22.68}		
<i>H. sabdariffa</i>	-	40	136	77.20	0.70
Hs-g-poly(EA)	117.30	10	29	74.34	0.65
Hs-g-poly(EA-co-BA)	112.20	15	28	65.11	0.46
Hs-g-poly(EA-co-VA)	36.10	40	100	71.42	0.60

Table 2: The % Cr and C.I. of the *H. sabdariffa* fiber and its graft copolymers.

and the major peak signifies the fusion and irreversible dissociation of the crystallites (Table 3 and Figure 8) [25,32].

Physicochemical Evaluation

Moisture absorbance study: It was observed that graft copolymerization of poly(EA) and other poly(vinyl) monomer chain onto *H. sabdariffa* had a great impact on the moisture absorbance behavior of the fiber (Table 4). It has been observed that with increase in graft yield, there was significant decrease in the percentage of

moisture absorbed due to blocking of the sites vulnerable for moisture absorbance with hydrophobic poly (EA), poly (vinyl) monomer chains, thereby, transforming the fiber less sensitive to moisture. Similarly, the graft fiber reinforced composite complex showed a marked decrease in moisture absorbance due to intricate three dimension bonds in the resin that formed strong fiber matrix complex moreover, the monomer acted as a coupling agent to reinforce the strength in comparison to the phenoplast [1-3,25,32].

Acid –base resistance study: It has been observed that acid- base resistance of the fiber increased with the increase in percent grafting. It could be accounted by the fact that poly (EA) and poly (vinyl) monomer chains grafted and covalently bound onto *H. sabdariffa* fiber had lesser reactivity for 1 N HCl and 1N NaOH as compared to the free hydroxyl groups present in the ungrafted fiber. Therefore, the resistance in the fiber for strong acid and base was found to increase by the incorporation of poly (vinyl) chains on the active sites of the backbone after graft copolymerization (Table 4). Similarly, the graft fiber reinforced composite showed a marked increase in chemical resistance due to strong fiber matrix complex formation in comparison to the phenoplast [1-3,25,32].

Swelling behavior study: 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 graft copolymers followed the pattern: DMF > BuOH > Water > MeOH and the trend obtained had a correlation with the solubility parameters like solvent basicity, the molar ratio, hydrogen bond formation and the percentage grafting. The differential swelling behavior of the fibers could be justified depending upon the chemical nature and the property of the pendent groups (-COC₃H₇ and -CH=CH₂) that had different interactions with the solvent. Higher swelling in DMF and BuOH in grafted copolymers could be due to better interaction with the pendent groups that increases with increase in Pg. However, a reverse trend was found in the case of raw *H. sabdariffa*. The cellulose is semi crystalline, polar polymer and miscible with in polar solvent due to hydrogen bond formation [32] and imbibitions therefore, the raw fiber had higher swelling in water and MeOH followed by DMF and BuOH. Other factors like the fiber size, steric hindrance and temperature also played a key role in the percentage of swelling [1-3,25,32] (Table 5).

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 6). The graft copolymers exhibited less dye uptake as compared to the raw fiber as it 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

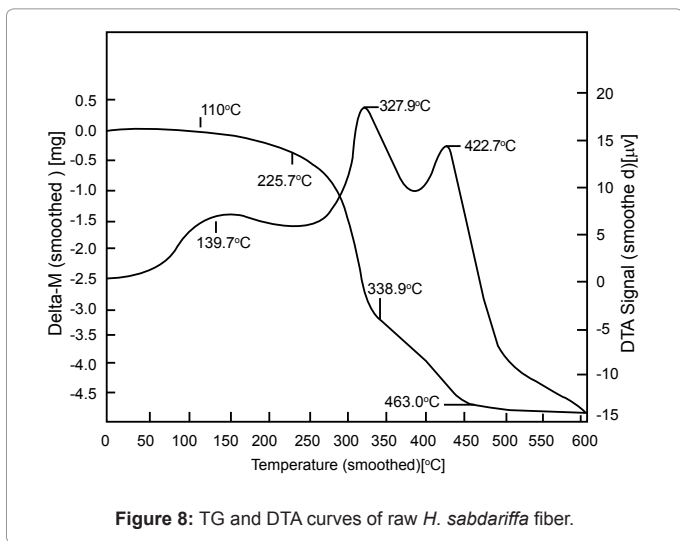


Figure 8: TG and DTA curves of raw *H. sabdariffa* fiber.

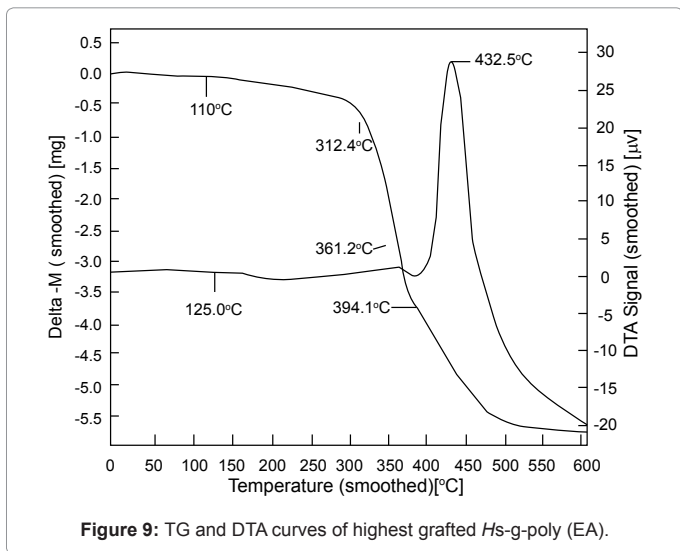


Figure 9: TG and DTA curves of highest grafted *Hs-g-poly* (EA).

Sample	Pg	TGA			DTA	
		IDT	FDT	% Residue	Peaks in °C(μV)	
<i>H. sabdariffa</i>	-	225.7	463.0	20.00	139.7 (6), 327.9 (18.0), 422.7 (14)	
(EA)	117.3	312.4	500.0	06.70	125.0 (2), 361.2 (1.2), 432.5 (29)	
(EA-co-BA)	112.2	300.6	486.0	08.00	159.0 (1.8), 357.8 (3.9), 385.3 (19)	
(EA-co-VA)	36.1	268.0	470.0	13.30	178.4 (19.1), 348.0(23), 424.0 (23.7)	
Phenoplast	-	500.0	600.0	-	551.0 (150)	
<i>Hs-r-PF-C</i>	-	540.0	680.0	10.0	610.0 (164)	

where, C= composite, IDT = initial decomposition temperature, FDT= final decomposition temperature.

Table 3: TG-DTA of *H. sabdariffa*, graft copolymers and composite.

Graft copolymer	Pg	% Chemical resistance % wt. loss after 72hour		% Moisture absorbance at different RH after 12 hours			
		1N HCl	1N NaOH	30-35%	50-55%	60-65%	85-90%_
<i>Hs-g-poly-</i>							
<i>H. sabdariffa</i>	-	55.0	43.0	0.5	0.8	1.8	2.5
(EA)	117.30	04.0	-	-	-	-	0.2
(EA-co-BA)	112.20	04.0	-	-	-	-	0.1
(EA-co-VA)	36.10	40.0	30.0	-	0.2	1.0	1.8
Phenoplast	-	04.0	02.0	-	-	3.0	5.0
<i>Hs-r-PF-C</i>	-	01.0	-	-	-	-	3.0

where, C= composite.

Table 4: Chemical resistance and moisture absorbance studies of composite, graft copolymers vis-à-vis back bone.

Sample	Pg	% Swelling			
		Water	MeOH	BuOH	DMF
<i>H. sabdariffa</i>	raw	59.00	46.00	38.00	40.00
<i>Hs-g-poly</i> (EA)	117.30	14.00	10.00	62.00	78.00
<i>Hs-g-poly</i> (EA-co-BA)	112.20	16.00	10.00	60.00	72.00
<i>Hs-g-poly</i> (EA-co-VA)	36.10	53.00	42.00	46.00	59.00

Table 5: Effect of solvents on swelling behavior of graft copolymers vis-à-vis backbone.

Sample	Pg	Dye concentration of the test solution at different time intervals ($\times 10^{-4}$ 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
<i>Hs-g-poly</i> (EA)	117.3	5.84	5.84	5.54	5.54	5.54	5.54	5.54
<i>H-g-ply</i> (EA-co-BA)	112.2	5.84	5.54	5.54	5.54	5.54	5.54	5.54
<i>Hs-g-ply</i> (EA-co-VA)	36.1	5.84	5.54	3.79	3.79	3.79	3.79	3.79

Table 6: 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> (EA)-r-PF	82.04	898.56	74.24	75.00
<i>Hs-g-poly</i> (EA-co-BA)-r-PF	79.90	875.99	74.08	74.00
<i>Hs-g-poly</i> (EA-co-VA)-r-PF	71.96	689.80	60.56	70.00

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

Table 7: MOR, MOE, SP and Hardness studies of graft copolymers reinforced P-F composite vis-à-vis P-F resin.

between the amorphous molecules. Presence of free reactive sites like -OH and -CH₂OH in raw fiber helped in the absorption of the dye. But, these sites were occupied with poly(EA) chains and poly(EA-co-BA) and poly(EA-co-VA) chains in the backbone that restrain dye uptake depending upon the Pg [1-3,25,32].

Mechanical assessment

Hs-r-PF composites with phenol:formaldehyde of 0.75:1.0 and fiber to matrix ratio of 12.7:87.3, depicted better mechanical behavior when subjected for the evaluation of different mechanical properties as compared to the P-F resin. Inadequate amount of fiber within the polymer matrix did not support the composite under continuous stress and strain whereas, the excess of the fiber led to debonding. Loading of the matrix beyond optimum ratio decreased the stiffness and impaired the needed fiber matrix interaction [29]. The results obtained for MOR, MOE, SP and Hardness testing (Table 7), clearly magnify the difference in mechanical strength brought about to the phenoplast after reinforcement with Sorrel and its graft copolymers. It is evident from the results, that *H. sabdariffa* fiber as reinforcement has improved the mechanical properties of the P-F composites. The graft copolymers reinforced bio-composites had better mechanical behavior MOR, MOE, SP and hardness as compared to raw fiber as reinforcement

and phenoplast. The better mechanical behavior could be accounted due to monomer incorporated onto the fiber that acts as coupling agent, compatible fiber-matrix interaction 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 un-grafted), 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 [25,26,31].

Conclusions

Hs-g-poly(EA) Pg: 117.30, *Hs-g-poly*(EA-co-BA) Pg: 112.20 and *Hs-g-poly*(EA-co-VA) Pg: 36.10 were found to have undergone tremendous physico-chemico-thermal changes. The higher graft yield obtained could be accounted by the efficient physico-chemical behavior and interaction between the monomers and the fiber. With increase in graft yield, undesired features like dye uptake, hydrophylicity, percentage of crystallinity and crystallinity index decreased whereas desired traits like physico-chemico-thermal resistance and miscibility in organic solvents improved. The use of these graft copolymers as reinforcement

in phenoplast matrix based composite improved the physico-chemico-thermo-mechanical competence, eased the degradation, sustained the availability and served as an alternate to glass fiber as reinforcement. These novel graft copolymer and green composites could be used in insulator, transportation, packaging, aerospace and enhance the credibility of bioremediation.

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