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Physico-chemico-thermal assessment of *H. sabdariffa*-graft-copolymers

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ABSTRACT

The reaction parameters for the graft copolymerization of Ethyl acrylate (EA) onto Hibiscus sabdariffa (Roselle) stem fiber were optimized and used to explore the additive effect of secondary monomer on percentage grafting, change in the properties, behavior of the fiber. The graft co-polymers were characterized by advanced techniques and evaluated for the changes. With increase in percentage grafting there was increase in physico-chemico-thermal resistance, hydrophobicity and miscibility in organic solvents but decrease in percentage crystallinity and crystallinity index. However, cellulose form I remained unchanged. These modified graft copolymer procured from renewable waste biomass can have numerous scientific and industrial applications.

Keywords*: Cellulose, crystallinity, polymer, thermal resistance.*
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INTRODUCTION

Graft copolymerization is a versatile technique for incorporating the desired properties into raw fiber without drastically affecting its basic traits. It imparts additional features such as thermal and chemical resistance to the naturally existing back-bone for their use in various fields. Natural fibers are cost-effective, biodegradable and efficacious to be used in technological processes like water treatment, controlled drug delivery, membrane technologies, removal of hazardous metal ions from effluent and as flocculants. They are mostly fragile and are sensitive towards moisture and chemicals but these properties could be improved by versatile means like graft-copolymerization. Modification of the properties in natural fibers by graft copolymerization has been reported by various scientist using modern method, new monomers and advanced analytical techniques. X-ray powder diffraction and thermal analysis are the principal tools to study thermodynamic changes in the solid state materials. *Hibiscus sabdariffa* is a rich source of cellulose found in abundance through-out the world and has attained prominence as a jute substitute. Attempts are being made to extend its cultivation in areas which are not favorable for

jute cultivation. It shows better mechanical properties when studied but still remain unexplored for its viability as substrate to grafting by vinyl monomers [1-6].

The versatility of graft copolymerization inspired the thought to use the *Hibiscus sabdariffa* stem fiber as backbone for grafting effective ethyl acrylate (EA) as a principal monomer and its binary mixtures with vinyl acetate (VA), 2-vinyl pyridine (2-VP) and styrene (Sty). The change in percentage grafting and properties of the fiber were then characterized by IR, SEM, XRD, TGA and DTA and evaluated for change in physico-chemical thermal behavior.

MATERIALS AND METHODS

H. sabdariffa was refluxed with acetone for 72 hrs. Monomers (Merck- Schuchardt, Germany) and ceric ammonium nitrate (S. d. fine-Chem. Pvt. Ltd, India) were used as received. Weighing was carried-out on Libror AEG-220 (Shimadzu) electronic balance. LEO Electron microscope (S. No. 435-25-20) and Perkin Elmer instrument were used for SEM and IR analysis, respectively. X-ray diffraction studies were performed on Bruker-D_8 Advance. Thermo gravimetric analysis (TGA) and Differential Thermal Analysis studies (DTA) were conducted in air on Thermal Analyzer (LINSEIS, L81-11) at a heating rate of 10 ^{0}C /minute.

Synthesis of the graft copolymers
The graft copolymerization of 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 and later used these optimized reaction parameters in binary vinyl monomeric mixtures. The fiber (0.5g) was activated by swelling in 100 ml of distilled water for 24 hrs. Ceric ammonium nitrate (CAN) and conc. HNO_3 mixture were 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 pre-optimized reaction conditions. On completion of the reaction, the homo-polymers were removed on extraction with hot water, alcohol, chloroform and acetone. The graft co-polymers were dried at 50°C till a constant weight was obtained. The percent grafting (P_g) was calculated as per the reported method in Eq. 1[1-6]:

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

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

X-ray Diffraction Studies
X-ray diffraction studies were performed under ambient conditions, using Cu Kα (1.5418Å) radiation, Ni-filter and scintillation counter at 40 KV and 40 mA on rotation between 13^0 to 25^0 at 2θ-scale at 1 sec. step size and increment of 0.01 degree with 0.5^0 or 1.0 mm of divergent and anti-scattering slit and calibrated by corundum. Degree of crystallinity and crystallinity index were calculated as shown in Eq. 2 and 3[1,4,5].

$$\% \ Cr = [I_{22.68}/ (I_{22.68} + I_{15})] \times 100 \quad (2)$$

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$$C. I. = [(I_{22.68} - I_{15}) / I_{22.68}] \qquad (3)$$

where, $I_{22.68}$ and I_{15} are the crystalline and amorphous intensities at 2θ-scale close to 22.68^0 and 15^0, respectively.

Physico-Chemical Evaluation
Moisture absorption study
Moisture absorbance percentage was found by placing a known weight (W_i) of dry grafted and ungrafted samples in a humidity chamber for about twelve hours and then the final weight (W_f) of the samples exposed to different relative humidities ranging from 30 – 90 % were taken. The percentage of moisture absorbance was calculated from the increase in initial weight in the following manner [2,3,6]:

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

Acid and Base Resistance
Acid and base resistance studies were carried-out as per the method reported in Eq. 5 [2,3,6]. Acid and base resistance was studied by placing a known weight (W_i) of dry grafted and ungrafted samples in fixed volume (50 ml) of 1N HCl and 1N NaOH and the final weights (W_f) of the samples were noted down after 72 hours:

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

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 [2,3,6]:

$$\text{Percent swelling } (P_S) = \frac{W_2 - W_1}{W_1} \times 100 \qquad (6)$$

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 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 [2,3,6]:

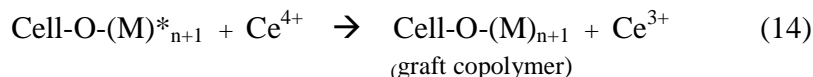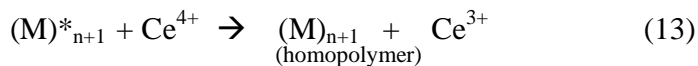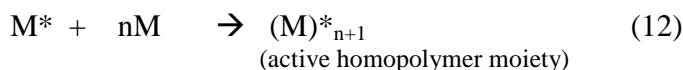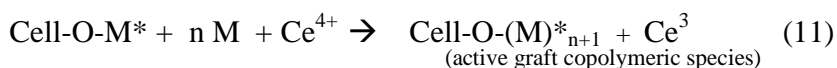$$\text{Cont. of test solution } (C_t) = \frac{I_t}{I_o} \times C_o \text{ mol L}^{-1} \qquad (7)$$
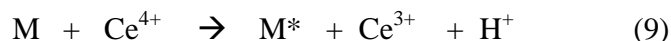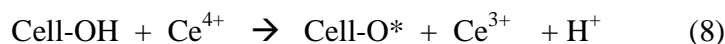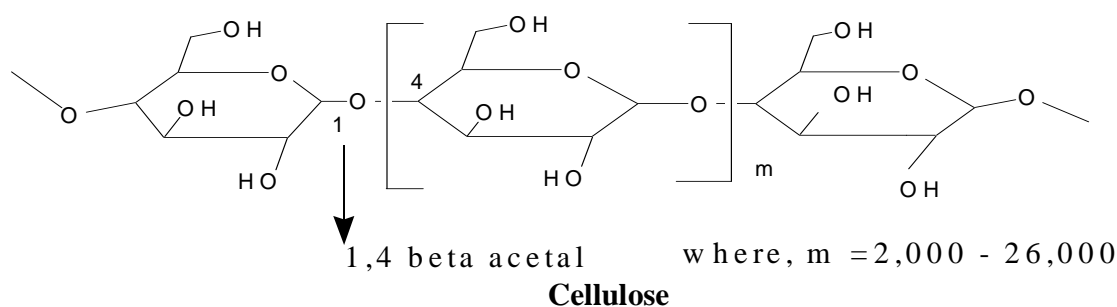
where, I_o, I_t, and C_o are optical density of standard solution, optical density of test solution and

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concentration of standard solution, respectively.

RESULTS AND DISCUSSION

Mechanism of Graft Copolymerization
Ceric ion forms complex with the cellulose through C-2 and C-3 hydroxyl groups of the anhydro glucose unit (Eq. 8). Transfer of the electron from the cellulose molecule to Ce (IV) leads 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 (Eq. 11). Graft yield and homo-polymer formation (Eq. 12) have been found to be the functions of both the monomer and initiator concentration [1,4,7].

1,4 beta acetal   where, m = 2,000 - 26,000
Cellulose

$$\text{Cell-OH} + \text{Ce}^{4+} \rightarrow \text{Cell-O*} + \text{Ce}^{3+} + \text{H}^+ \qquad (8)$$

$$\text{M} + \text{Ce}^{4+} \rightarrow \text{M*} + \text{Ce}^{3+} + \text{H}^+ \qquad (9)$$

$$\text{Cell-O*} + \text{M} \rightarrow \text{Cell-O-M*} \qquad (10)$$

$$\text{Cell-O-M*} + n\,\text{M} + \text{Ce}^{4+} \rightarrow \text{Cell-O-(M)*}_{n+1} + \text{Ce}^3 \qquad (11)$$
$$\text{(active graft copolymeric species)}$$

$$\text{M*} + n\text{M} \rightarrow \text{(M)*}_{n+1} \qquad (12)$$
$$\text{(active homopolymer moiety)}$$

$$\text{(M)*}_{n+1} + \text{Ce}^{4+} \rightarrow \text{(M)}_{n+1} + \text{Ce}^{3+} \qquad (13)$$
$$\text{(homopolymer)}$$

$$\text{Cell-O-(M)*}_{n+1} + \text{Ce}^{4+} \rightarrow \text{Cell-O-(M)}_{n+1} + \text{Ce}^{3+} \qquad (14)$$
$$\text{(graft copolymer)}$$

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

Optimization of the reaction parameters and effect of the secondary monomer
The optimized parameters for the graft copolymerization of EA (as a principal monomer) onto *H. sabdariffa* fiber, to obtain the maximum graft yield were: monomer conc.:2.26×10^{-3} mol L^{-1}; CAN: 2.41×10^{-4} mol L^{-1} ; HNO$_3$ conc.: 1.46×10^{-3} mol L^{-1}; pH of the medium : 7; time: 150

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mins. ; temperature: 35^0C that yielded Pg of 117.30 ($\pm$SD: 7.13; $\pm$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. Vinyl acetate has low reactivity (0.02), low polarity that effects its interaction with EA (Pg : 36.10). 2-VP on interaction with EA results in low graft yield (Pg : 22), because of low C_M [0.00 (25 ^{0}C)], low K_p/K_t value [5.6 x 10^6 (25^0C)], unfavorable reactivity ratio moreover, steric hindrance dominates its reactivity (1.30). Styrene in binary mixture with ethyl acrylate because of low K_p/K_t value [0.98 x 10^6 , 1.08 x 10^6 (30^0C)], low polarity, low C_M [0.16 x 10^4 , 0.2 x 10^4 (25 ^{0}C), 0.2 x 10^4 , 0.32 x 10^4 (30^0C)] and unfavorable reactivity ratio further supports low graft yield (Pg: 9.90) (Table 2). 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 [8-11].

Characterization
FTIR and SEM
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 –CH_2, C-C and C-O stretching, respectively. However, in case of *Hs*-g-poly(EA) an additional peak (due to >C=O groups) at 1734.0 cm^{-1} was witnessed whereas, a significant peak at 1651.1 cm^{-1} (vinyl group) in *Hs*-g-poly(EA-co-VA); 1651.2 cm^{-1} (vinyl group) in *Hs*-g-poly(EA-co-2VP); 1602.0 cm^{-1} (>C=C< aromatic stretch) in *Hs*-g-poly(EA-co-Sty) was observed due to secondary monomer.

The cellulosic fiber lying distant apart in raw sample started forming bundles in graft co-polymers, depending upon the Pg. Figures 1a-1c illustrates the morphological transition brought about by graft copolymerization [1-6].

X-ray Diffraction Studies
It is evident from Table 2 and Figure 2 that with increase in Pg, there has been a constant decline in % Cr and C.I. Cellulosic fiber possesses both crystalline and amorphous regions. The x-ray pattern of the crystalline polymer shows sharp peaks associated with the region of three dimensional order and the diffused features are characteristics of the molecularly disordered substances coexisting within itself. Crystallinity is correlated to the strength of the fiber. On grafting crystal lattice of the polymer is disrupted but the strength of the material may add to reinforce the structure as seen in the case of *Hs*-g-poly(EA). The X-ray spectrum of raw fiber is more complex than that of graft copolymers.

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

Sample	Binary mixture (x 10^{-3} mole L^{-1})	Mean Pg	$\pm$SD	$\pm$SE
Hs-g-poly (EA+2VP)	2.26+0.76	22.00	$\pm$3.57	$\pm$2.06
	2.26+1.53	13.00	$\pm$0.90	$\pm$0.52
	2.26+2.30	7.00	$\pm$0.46	$\pm$0.26
	2.26+3.06	2.00	$\pm$0.89	$\pm$0.51
	2.26+3.83	-	-	-
Hs-g-poly (EA+VA)	2.26+0.91	36.10	$\pm$3.58	$\pm$2.06
	2.26+1.80	28.06	$\pm$2.62	$\pm$1.51
	2.26+2.72	20.76	$\pm$2.60	$\pm$1.50
	2.26+3.60	15.06	$\pm$1.76	$\pm$1.01
	2.26+4.52	10.46	$\pm$4.39	$\pm$2.53
Hs-g-poly (EA+Sty)	2.26+ 0.71	9.90	$\pm$1.77	$\pm$1.02
	2.26+1.45	9.60	$\pm$2.60	$\pm$1.50
	2.26+2.16	9.00	$\pm$3.55	$\pm$2.05
	2.26+2.90	8.00	$\pm$0.88	$\pm$0.50
	2.26+3.61	2.00	$\pm$0.89	$\pm$0.51

where,* refers to the effective Pg.

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

Sample	Pg	2θ Scale		%Cr	C.I.
		I_{15}	$I_{22.68}$		
H. sabdariffa	-	40	136	77.20	0.70
Hs-g-poly(EA)	117.30	10	29	74.35	0.65
Hs-g-poly(EA-co-STY)	09.90	45	119	72.56	0.62
Hs-g-poly(EA-co- 2VP)	22.00	42	110	72.36	0.61
Hs-g-poly(EA-co-VA)	36.10	40	100	71.42	0.60

where, % Cr= percentage of crystallinity, C. I.= crystallinity index.
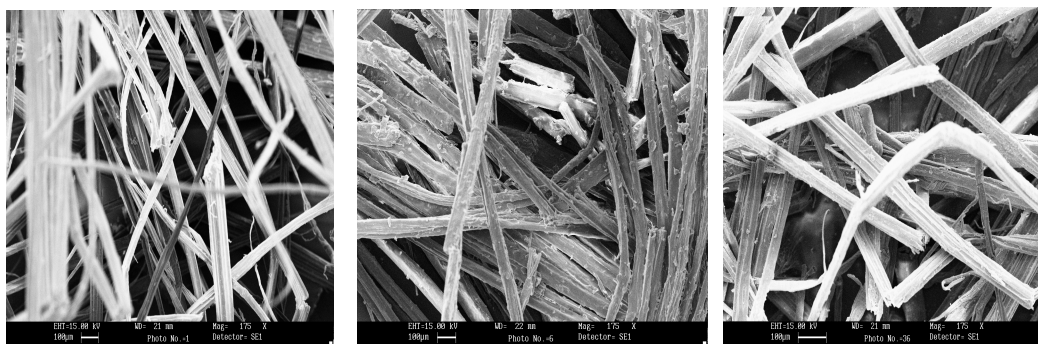

| Fig. 1a | Fig. 1b | Fig. 1c |

Fig. 1 SEM of (a) Raw *Hibiscus sabdariffa* (b) *Hs*-g-poly(EA); Pg: 117.30 *Hs*-g-poly(EA-co-VA); Pg: 36.10

In case of raw *Hibiscus sabdariffa* fiber the % Cr and C.I. are higher and the incorporation of the monomer chains to the back-bone impairs the crystallinity. Therefore, on grafting the percentage crystallinity decreases rapidly with reduction in its stiffness and hardness. Crystallinity index gives a quantitative measure of the orientation of the cellulose crystals in the fibers. A lower

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crystalline index in case of graft co-polymers means poor order of arrangement of cellulose crystals in the fiber, that is due to dis-orientation of the cellulose crystalline lattice to the fiber axis during grafting. However, the cellulosic form I remained unchanged [1, 4, 11, 12].

TG-DTA studies

6.0 mg of the each sample was taken into silica crucible for TG-DTA analysis in air with temperature range varying from 50° to $600\,^{o}C$. The heating rate of the sample was $10\,^{o}C$ per min and it was scanned for 60 minutes. Results were reported as Delta-M (mg) vs. temperature (^{o}C) in case of TGA while DTA signal (μV) vs. temperature (^{o}C) in case of DTA studies.

The degradation occurs in various forms like dehydration, decarboxylation and chain scissions. In case of raw fiber, both initial decomposition temperature (IDT) and final decomposition temperature (FDT) are lower (225.7 ^{0}C and 463.0 ^{0}C, respectively) as compared to those of graft copolymers. In case of *H. sabdariffa*, two-stage decomposition has been found, the former stage is attributed to loss by dehydration, volatilization whereas, the later stage is attributed to loss by depolymerization, delignification and oxidation of the char. Graft copolymers showed two stage decomposition. The first stage refers to the loss of moisture, decarboxylation and chain scissions while the second stage pertains to the breaking up of covalent bonds that has raised the FDT. Thus, it is evident from the TGA data that grafted fiber is thermally more stable than the raw fibers. This may be due to the incorporation of poly(vinyl) chains on backbone polymer either through covalent bonds or mechanically, confirming the additional strength to the fiber (Table 3, Figs. 3, 4) [1, 13,14].
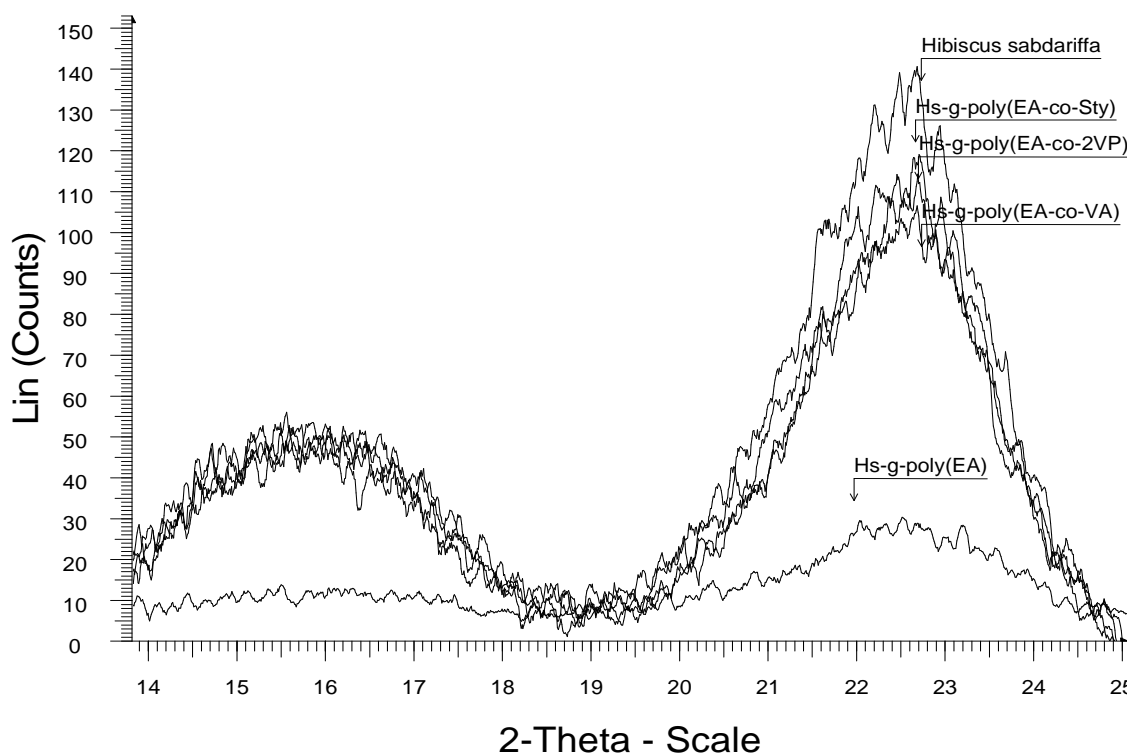

Fig. 2 The XRD overlay of *Hibiscus sabdariffa* and its graft copolymers

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Table 3 TG-DTA of *H. sabdariffa* and its graft copolymers

Graft copolymer		TGA			DTA
Hs-g-poly-	Pg	IDT	FDT	% Residue left	Peaks in ^{0}C(μV)
H. sabdariffa	-	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	361.2 (3.4), 432.5 (29)
(EA-co-Sty)	09.9	230.2	465.0	16.00	126.9(8), 340.2(12), 390.1(21.5)
(EA-co-2VP)	22.0	238.9	474.0	15.00	136.1(6), 337.0(20), 425.9(38.9)
(EA-co-VA)	36.1	246.7	482.0	11.00	140.2(5), 347.9(26), 432.9(25.0)

where, IDT = initial decomposition temperature, FDT= final decomposition temperature.
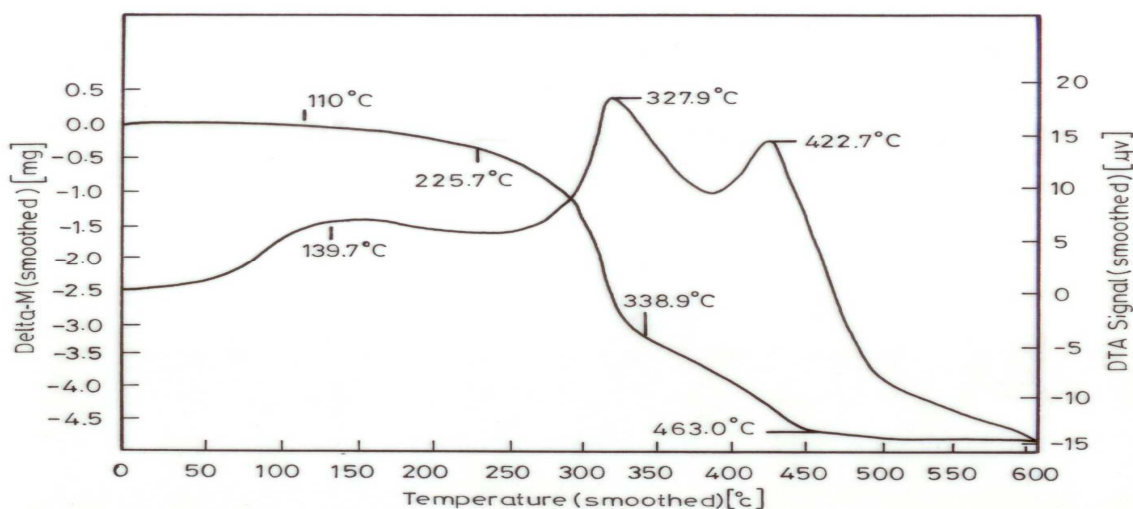
Fig.3. TG-DTA of raw *H. sabdariffa*
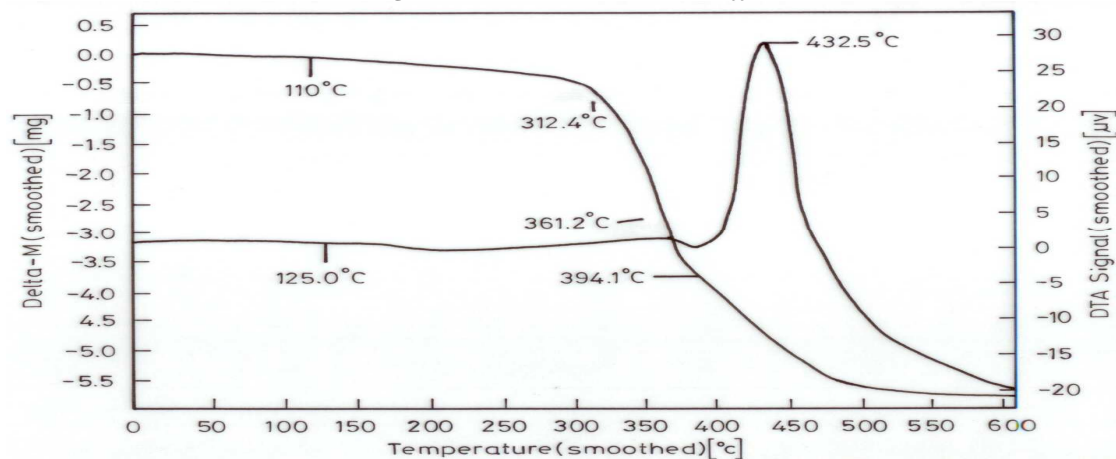
Fig. 4. TG-DTA of highest grafted *Hs*-g-poly(EA); Pg: 117.30

In DTA studies, *H. sabdariffa* has been found to exhibit two major exothermic peaks whereas, graft copolymers exhibited some minor and major exothermic peaks. The first and second transition peaks revealed the dehydration, adsorption and oxidation of the semi-crystalline host and the major peak signifies the fusion and irreversible dissociation of the crystallites. Moreover, most of the hydroxyl groups of the native form have been replaced by the covalent bonds

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resulting in increased thermal resistance (Table 3, Figure 3,4) [1, 13,14].

Physico-chemico Evaluation
Moisture absorbance behavior
It was found that graft co-polymerization of vinyl monomer onto *H. sabdarifa* had a great impact on the moisture absorbance behavior (Table 4). It was observed that with increase in graft yield, there was a decrease in percent moisture absorbance. This was due to blocking of sites vulnerable for moisture absorbance with vinyl monomer chains, thereby, converting the fiber less sensitive towards moisture [15,16].

Chemical resistance
It was observed that acid- base resistance of the fiber increased with increase in percent grafting. It was due to the fact that covalently bonded poly (vinyl) chains grafted onto *H. sabdariffa* fiber had less sensitivity for 1 N HCl and 1N NaOH as compared to hydroxyl groups present in ungrafted fiber. Therefore, the resistance of fiber towards acid-base was found to increase with the incorporation of poly (vinyl) chains on the active sites of the backbone (Table 4) [15,16].

Swelling behavior studies
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 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 $-COC_2H_5$, $-C_5H_5N$, $-C_6H_5CH=CH_2$,

$-CH_2=CH_2$ had 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 –OH and –CH_2OH 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 –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 (Table 5) [11, 15-19].

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). 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 –OH and –CH_2OH 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. Thus, grafting has helped to improve the various properties as seen by various means of characterization and evaluation [15,16, 20].

Table 4 Chemical resistance and moisture absorbance behavior of graft copolymers vis-à-vis back bone

Graft copolymers	Pg	% Chemical resistance		% Moisture absorbance				
		% wt. loss after 72 hours		at different RH after 12 hours				
Hs-g-poly-		In 1N HCl	In 1N NaOH	30-35%	50-55%		60-65%	85-90%
H. sabdariffa	-		55.0	43.0	0.5	0.8	1.8	2.5
(EA)	117.30		04.0	-	-	-	-	0.2
(EA-co-Sty)	09.90		53.0	40.0	0.3	0.7	1.8	2.5
(EA-co-2VP)	22.00		38.0	28.0	-	0.3	1.2	2.0
(EA-co-VA)	36.10		05.0	02.0	-	-	0.5	1.7

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

Sample	Pg	% Swelling			
		Water	MeOH	BuOH	DMF
H. sabdariffa	-	59.00	46.00	38.00	40.00
Hs-g-poly(EA)	66.80	14.00	10.00	62.00	78.00
Hs-g-poly(EA-co-Sty)	09.90	55.00	44.00	39.00	40.00
Hs-g-poly(EA-co-2VP)	22.00	49.00	39.00	43.00	45.00
Hs-g-poly(EA-co-VA)	36.10	39.00	28.00	48.00	50.00

Table 6 Dye uptake studies of the graft copolymers vis-à-vis back bone

Sample	Pg	Dye concentration of the test solution at different time intervals (x 10^{-4} mol L^{-1})						
Hs-g-poly-		1 hr	2 hr	3 hr	4 hr	5 hr	6 hr	7 hr
H. sabdariffa	00.00	4.96	4.38	4.08	4.08	3.79	3.21	3.21
(EA)	117.30	5.84	5.84	5.54	5.54	5.54	5.54	45.54
(EA-co-Sty)	09.90	4.96	4.38	4.08	4.08	3.79	3.79	3.21
(EA-co-2VP)	22.00	4.96	4.38	4.38	4.38	3.79	3.79	3.79
(EA-co-VA)	36.10	5.54	5.25	5.25	4.96	4.38	4.08	4.08

CONCLUSION

Grafting of poly (EA) and its graft copolymers formed in presence of ceric ion initiator yielded reformed graft copolymers. It is evident from the characterization and evaluation of the graft copolymers through different advanced technique that grafting resulted in the morphological transformation of the renewable waste biomass to advanced materials. It improved the properties of the fiber. These graft copolymers were found to be physico-chemico-thermally resistant, miscible in organic solvent and hydrophobic. These reformed bio-polymers obtained by economic and judicious means from renewable resource could be utilized in various scientific applications and for the advancement of technology.

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