

# Development and Assessment of the Advanced Graft Copolymers Obtained from *Hibiscus sabdariffa* Biomass

Ashish Chauhan, Balbir Kaith

Department of Chemistry, Dr. B. R. A. National Institute of Technology, Jalandhar, Punjab 144 011, India

Received 24 January 2011; accepted 25 March 2011

DOI 10.1002/app.34635

Published online 19 August 2011 in Wiley Online Library (wileyonlinelibrary.com).

**ABSTRACT:** In this article, the morphological transformation in *Hibiscus sabdariffa* stem fiber through graft copolymerization with effective ethyl acrylate (EA) and its binary vinyl monomeric mixtures using ceric ammonium nitrate—nitric acid initiator system has been reported. Different reaction parameters such as temperature, time, initiator concentration, monomer concentration, and pH were optimized to obtain the maximum graft yield (117.3%). The optimized reaction parameters were then used to screen the additive effect of EA with *n*-butyl acrylate (BA), acrylic acid (AA), and 4-vinyl pyridine (4-VP) in binary vinyl monomer mixtures on percentage grafting, properties, and the behavior of

the fiber. The graft copolymers were characterized by FTIR, SEM, XRD, TGA, and DTA techniques and evaluated for physico-chemical changes. With increase in the  $P_g$ , a significant physico-chemico-thermal resistance, miscibility in organic solvents, hydrophobicity were found to increase, whereas crystallinity, crystallinity index, dye-uptake, and hydrophylicity decreased, however, the cellulose form I remained unchanged. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 123: 1650–1657, 2012

**Key words:** *Hibiscus sabdariffa*; graft copolymerization; chemical resistance; thermal resistance

## INTRODUCTION

Natural fibers have been extensively screened for the graft copolymerization with different vinyl monomers to explore the maximum potential of these renewable resources. These fibers are generally moisture sensitive and have least chemical resistance. Graft copolymerization is one of the versatile chemical techniques that incorporate the desired features in natural fiber without affecting their inherent traits. Modification of cellulosic fibers through graft copolymerization provides a significant means to alter the physical and chemical properties of the fiber. As natural fibers occur in abundance in nature and are renewable resource so various workers have focused onto the graft copolymerization of different cellulosic back-bones using vinyl monomers through various chemical and radiation techniques.<sup>1–10</sup> Misra et al have extensively studied the modification of natural and synthetic fibers such as wool,<sup>11,12</sup> gelatin,<sup>13,14</sup> poly(vinyl alcohol),<sup>15,16</sup> rayon, and polyamide-6.<sup>17</sup> The potential applications of graft copolymerization could be immensely increased by selecting various initiators like ceric ammonium nitrate (CAN), potassium per sulphate (KPS), and ammonium per sulphate (APS).<sup>18</sup> Researchers have

used different vinyl monomers with varied backbones such as poly(butyl acrylate),<sup>19</sup> poly(methyl acrylate),<sup>20</sup> poly(acrylic acid), poly(vinylidene fluoride),<sup>21</sup> glycol polymers,<sup>22</sup> and cellulose<sup>23</sup> to get increased graft yield, hydrophobicity, chemical resistance, and physical strength.

Literature reveals that graft copolymerization of effective vinyl monomer like EA onto *Hibiscus sabdariffa* stem fiber and its binary vinyl monomeric mixture with *n*-BA, AA, and 4-VP, still remains unexplored. Therefore, it was worthwhile to screen the cumulative effect of the binary vinyl monomers on the behavioral and morphological transformations in the fiber after graft copolymerization.

## EXPERIMENTAL

### Material and methods

*H. sabdariffa* fiber was obtained from the Department of Agronomy, Chaudhary Sarwan Kumar Himachal Krishi Vishwavidyalaya, Palampur (HP), India. Ethyl acrylate, *n*-butyl acrylate, acrylic acid and 4-vinyl pyridine (Merck), and CAN (s.d. fine-Chem, Mumbai, India) were used as received.

### Characterization

FTIR and SEM

IR spectra of the *H. sabdariffa* and its graft copolymers were recorded on Perkin–Elmer Fourier transform infrared (FTIR) spectrophotometer using

Correspondence to: A. Chauhan (aashishchauhan26@gmail.com).

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.

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 % 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 $\alpha$  (1.5418 Å) radiation, Ni-filter and scintillation counter as detector at 40 KV and 40 mA on rotation between 13° (2 $\theta$ ) and 25° (2 $\theta$ ) at 1s accumulation time and step size of 0.01° with 0.5° or 1.0 mm of divergent and antiscattering slit. Each sample was homogeneously mixed and mounted on PMMA holder. Corundum and quartz were used as the reference to verify and calibrate the instrument.

The continuous scan between 22.68° (2 $\theta$ ) and 15° (2 $\theta$ ) were taken. The counter reading at the peak intensity at 22.68° (2 $\theta$ ) represents the crystalline material and the peak intensity at 15° (2 $\theta$ ) corresponds to the amorphous material in the cellulose. 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 while crystallinity index is the quantitative measure of the orientation of the crystal lattice to the fiber axis. Percentage crystallinity (% Cr) and crystallinity index (C. I.) were calculated by eqs. (1) and (2):<sup>24–28</sup>

$$\% \text{Cr} = [I_{22.68}/(I_{22.68} + I_{15})] \times 100 \quad (1)$$

$$\text{C.I.} = [(I_{22.68} - I_{15})/I_{22.68}] \quad (2)$$

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 to obtain the maximum graft yield. The raw fiber (0.5 g) was activated by swelling in 100 mL of distilled water for 24 hrs. Mixture of CAN and conc. nitric acid was slowly added to the reaction medium under continuous stirring followed by addition of the monomer. The reaction was carried-out under ambient and preoptimized reaction conditions. On completion of the reaction, poly(EA), poly(BA), poly(AA), and poly(4-

VP) were removed on extraction with acetone, methanol, chloroform and water. The graft copolymers were dried at 50°C, till a constant weight. The percent grafting ( $P_g$ ) was calculated by eq. (3):<sup>26–28</sup>

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

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

### Moisture absorption study

Moisture absorbance studies were carried-out at various relative humidity levels. Moisture absorbance percentage was found by placing a known weight ( $W_i$ ) of dry grafted and ungrafted samples in a humidity chamber for about 12 hrs and then the final weight ( $W_f$ ) of the samples exposed to different relative humidities ranging from 30 to 90% were taken at ambient temperature. The moisture absorbance was calculated by the eq. (4):<sup>26–28</sup>

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

### Acid and base resistance

Acid and base resistance studies were carried-out as shown in eq. (5).<sup>26–28</sup> A known weight ( $W_i$ ) of dry grafted and ungrafted samples in fixed volume of 1N HCl and 1N NaOH was kept 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

Two-hundred and fifty milligram 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. Samples were removed from the solvent and excess solvent was removed with filter paper. Final weight of the sample was taken and the percentage of swelling was calculated as follows:<sup>26–28</sup>

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

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

### Dye uptake behavior

Gentian violet solution (0.1%) was prepared in distilled water. Ten percent NaCl solution and a few

drops of acetic acid were added to this solution. Dye uptake of the raw fiber and its graft copolymers were carried-out by immersing the known weight of the sample in 100 mL of Gentian violet dye. Optical densities of the test solutions were observed using digital photo colorimeter for seven consecutive hours and the concentrations of test solution were calculated as:<sup>26–28</sup>

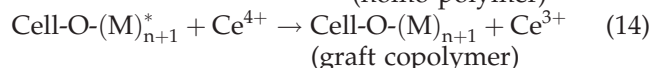
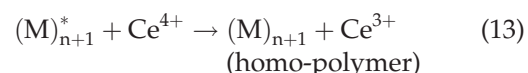
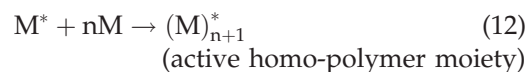
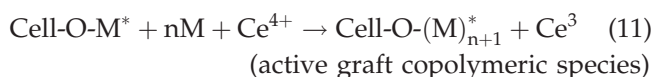
$$\text{Cont. of test solution } (C_t) = \frac{I_t}{I_o} \times C_o \text{ mol L}^{-1} \quad (7)$$

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.

## RESULTS AND DISCUSSION

### Mechanism

The graft copolymerization of EA as principal monomer onto *H. sabdariffa* fiber was effective ( $P_g$ : 117.30). Use of EA as principal monomer in binary vinyl monomeric mixture with secondary monomers like acrylic acid, butyl acrylate and 4-vinyl pyridine resulted in *H. sabdariffa*-g-poly(EA-co-AA), *H. sabdariffa*-g-poly(EA-co-BA) and *H. sabdariffa*-g-poly(EA-co-4-VP), 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 celluloses [eqs. (11) and (14)]. CAN 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  $[\text{Ce}-\text{O}-\text{Ce}]^{6+}$ . As, the large size  $[\text{Ce}-\text{O}-\text{Ce}]^{6+}$  ions were unable to form complex with the fiber so, due to the presence of nitric acid, more  $\text{Ce}^{4+}$  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 anhydro 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:<sup>28,29</sup>



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

The optimized reaction conditions using EA as principal monomer onto the fiber were: monomer conc.:  $2.26 \times 10^{-3}$  mol L<sup>-1</sup>; CAN:  $2.41 \times 10^{-4}$  mol L<sup>-1</sup>; HNO<sub>3</sub> conc.:  $1.46 \times 10^{-3}$  mol L<sup>-1</sup>; pH of the medium: 7; time: 150 mins.; temperature: 35°C that yielded  $P_g$  of 117.30 ( $\pm$ SD: 7.13;  $\pm$ SE: 4.12). The use of EA as principal monomer for graft copolymerization onto *H. sabdariffa* fiber yielded a high  $P_g$ . 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 EA yielded high  $P_g$  but the relatively bulky group of BA encountered steric hindrance that effected  $P_g$  (112.20). Acrylic acid as comonomer had very high reactivity but high solubility in the reaction medium could not maintain the balance in hydrophobic–hydrophilic monomeric interaction and decreased the  $P_g$  (94.23). 4-VP had high  $C_M$  [ $6.7 \times 10^4$  (25°C)], high  $K_p/K_t$  value [ $19 \times 10^6$  (25°C)], but the presence of bulky group deteriorated the monomeric interaction ( $P_g$ : 63.90) in binary mixture (Table I).<sup>30–32</sup> 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.<sup>28</sup>

### Characterization

#### FTIR

IR spectrum of the *H. sabdariffa* showed a broad peak at 3424.0 cm<sup>-1</sup> (–OH group) and peaks at 2924.7 cm<sup>-1</sup>, 1246.9 cm<sup>-1</sup>, and 1032.0 cm<sup>-1</sup> were observed due to –CH<sub>2</sub>, C–C and C–O stretching,



**TABLE I**  
Effect of the Binary Mixtures on  $P_g$  Using EA as a Principal Monomer

Sample	Binary mixture ( $\times 10^{-3}$ mol L $^{-1}$ )	Mean $P_g$	$\pm$ SD	$\pm$ SE
<i>H. sabdariffa</i> -g-poly(EA+AA)	2.26 + 1.21	94.23	$\pm$ 3.50	$\pm$ 2.02
	2.26 + 2.41	86.30	$\pm$ 3.62	$\pm$ 2.09
	2.26 + 3.63	78.00	$\pm$ 3.57	$\pm$ 2.06
	2.26 + 4.83	59.70	$\pm$ 7.11	$\pm$ 4.10
<i>H. sabdariffa</i> -g-poly(EA+BA)	2.26 + 6.03	37.76	$\pm$ 4.19	$\pm$ 2.42
	2.26 + 0.58	90.40	$\pm$ 4.37	$\pm$ 2.52
	2.26 + 1.17	112.2	$\pm$ 6.06	$\pm$ 3.50
	2.26 + 1.75	88.16	$\pm$ 3.56	$\pm$ 2.06
<i>H. sabdariffa</i> -g-poly(EA+4VP)	2.26 + 2.33	53.40	$\pm$ 2.60	$\pm$ 1.50
	2.26 + 2.91	44.80	$\pm$ 1.75	$\pm$ 1.01
	2.26 + 0.76	63.90	$\pm$ 2.57	$\pm$ 1.48
	2.26 + 1.53	44.20	$\pm$ 3.57	$\pm$ 2.06
	2.26 + 2.30	35.63	$\pm$ 4.47	$\pm$ 2.58
	2.26 + 3.06	30.50	$\pm$ 7.13	$\pm$ 4.12
	2.26 + 3.83	08.13	$\pm$ 0.89	$\pm$ 0.51

respectively. However, in case of *H. sabdariffa*-g-poly(EA) an additional peak due to  $>C=O$  groups of the EA was witnessed at  $1734.0\text{ cm}^{-1}$  whereas a peak at  $1732.8\text{ cm}^{-1}$  (due to  $>C=O$  groups) in *H. sabdariffa*-g-poly(EA-co-BA), at  $1710\text{ cm}^{-1}$  (due to  $>C=O$  groups) in *H. sabdariffa*-g-poly(EA-co-AA) and at  $1635.4\text{ cm}^{-1}$  (vinyl group) in *H. sabdariffa*-g-poly(EA-co-4VP) confirms the incorporation of the secondary monomers in these graft copolymers.

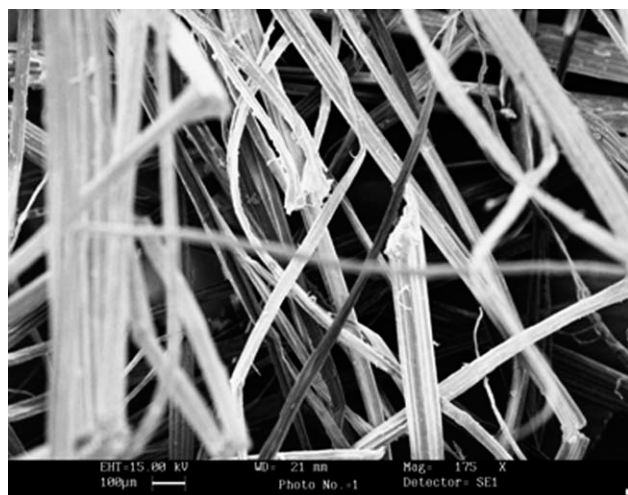
#### Scanning electron microscopy

As, cellulose has nonconducting behavior so it was gold plated to have an impact. It is quite evident from the Figures 1–5, that there has been 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 distinction between the isolated and randomly distributed ungrafted fiber and the grafted samples that started forming the bundles in close packing, depending upon the  $P_g$ .<sup>26</sup>

#### X-RD studies

It is evident from the Figure 6 and Table II that the % Cr and crystallinity index were found to decrease with increase in  $P_g$  of EA and its comonomer onto *H. sabdariffa* fiber. Since, the incorporation of monomer in the backbone impairs the natural crystallinity of the fiber, therefore, the graft copolymerization of EA onto *H. sabdariffa* fiber resulted in impaired crystallinity and increased the amorphous content in the fiber. Thus, with increase in  $P_g$ , the % Cr and crystallinity index decreased along-with reduction in stiffness and hardness. However, the cellulose form



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



**Figure 2** SEM of *H. sabdariffa*-g-poly(EA).

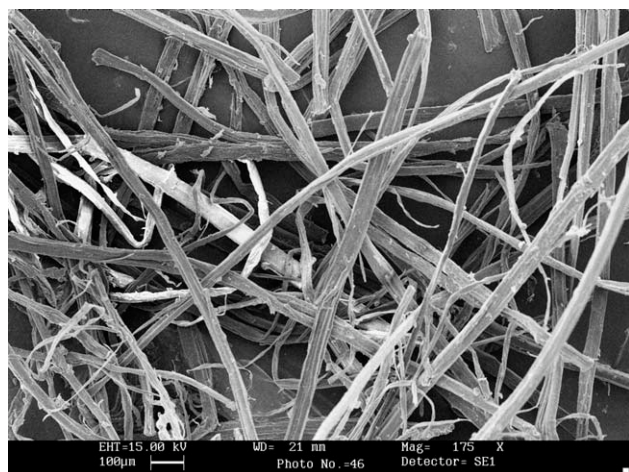


Figure 3 SEM of *H. sabdariffa*-g-poly(EA-co-4VP).

I remained unchanged. 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 *H. sabdariffa*-g-poly(EA) and other graft copolymers.<sup>28</sup>

#### 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 and 463.0°C with 26.00% weight loss (Table III and Fig. 7). The former stage is attributed to the loss by dehydration, volatilization processes whereas the later stage is referred to loss by depolymerization,



Figure 4 SEM of *H. sabdariffa*-g-poly(EA-co-BA).

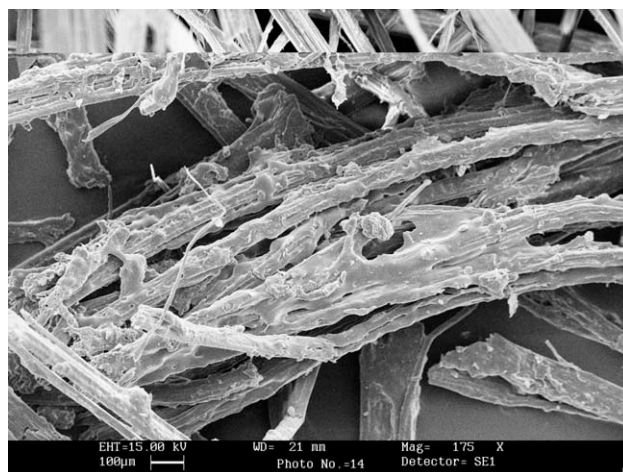


Figure 5 SEM of *H. sabdariffa*-g-poly(EA-co-AA).

delignification and oxidation of the char. *H. sabdariffa*-g-poly(EA) and *H. sabdariffa*-g-poly(EA-co-vinyl monomer) showed two stage decomposition (Table III and Fig. 8). The first stage refers to loss of moisture and decarboxylation ranging from 290.0 to 312.4°C and the second stage pertains to the breaking up of crystallites and covalent bonds in vinyl monomer in the range of 480.5–500.0°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.<sup>26–28</sup>

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 and 338.9°C while the exothermic peak at 422.7°C corresponds to second decomposition stage (338.9–463.0°C) in TGA. However, *H. sabdariffa*-g-poly(EA) and poly(vinyl) exhibited a minor exothermic peak

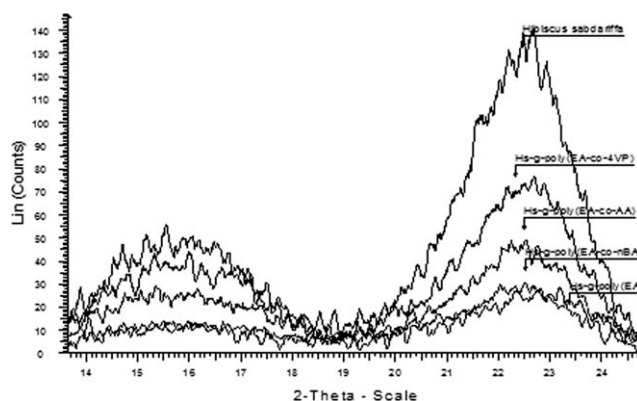


Figure 6 XRPD overlay pattern of the raw and grafted *H. sabdariffa* fiber.



**TABLE II**  
Percentage Crystallinity (% Cr) and Crystallinity Index (C.I.) of the Grafted and Raw *H. sabdariffa* Fiber

Sample	$P_g$	2 $\theta$ scale		%Cr	C.I.
		$I_{15}$	$I_{22.68}$		
<i>H. sabdariffa</i>	–	40	136	77.20	0.70
<i>H. sabdariffa</i> -g-poly(EA)	117.30	10	29	74.34	0.65
<i>H. sabdariffa</i> -g-poly(EA-co-4VP)	63.90	28	74	72.54	0.62
<i>H. sabdariffa</i> -g-poly(EA-co-AA)	94.23	18	45	71.42	0.60
<i>H. sabdariffa</i> -g-poly(EA-co-nBA)	112.20	15	28	65.11	0.46

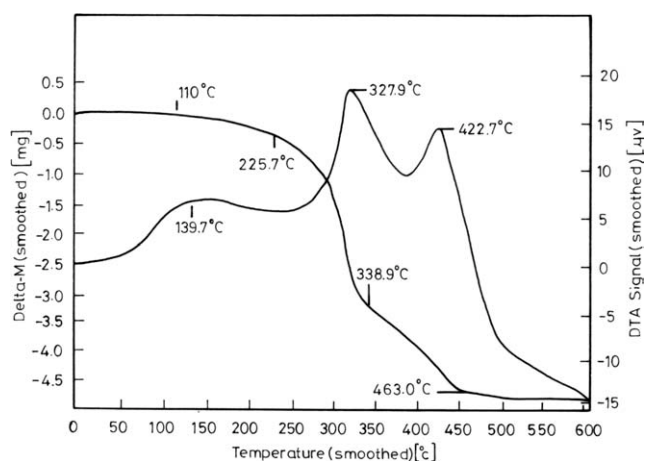
at 361.2°C (1.5  $\mu$ V) that refers to decomposition stage between 312.4 and 394.1°C, corresponding to the onset of degradation reactions of *H. sabdariffa*-g-poly(EA) chains whereas a major peak at 432.5°C (29.0  $\mu$ V) corresponds to the decomposition between 394.1 and 500°C (Table III and Fig. 8). Similarly, the other graft copolymers. The first and second transition peaks revealed the dehydration, adsorption and oxidation of the semicrystalline host and the major peak signifies the fusion and irreversible dissociation of the crystallites (Table III).<sup>26–28</sup>

### Moisture absorbance study

It was found 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 IV). It has been observed that with increase in graft yield, there was significant decrease in the percentage of moisture absorbed. It was 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.<sup>28,33–36</sup>

### Acid-base resistance study

It has been observed that acid-base resistance of the fiber increased with the increase in  $P_g$ . 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 1N HCl and 1N NaOH as compared to the free hydroxyl groups present in the ungrafted fiber. Therefore, the



**Figure 7** TG and DTA curves of raw *H. sabdariffa* fiber.

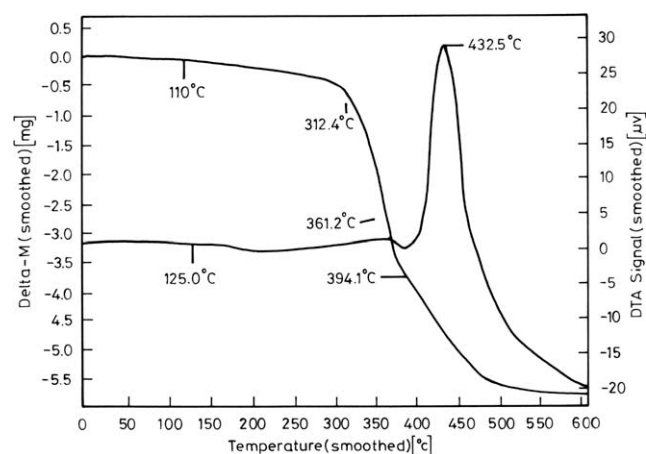
resistance in the fiber for strong acid and base was found to increase by the incorporation of poly(vinyl) chains on the active sites of the backbone after graft copolymerization (Table IV).<sup>27,33–36</sup>

### 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 direct correlation with the solubility parameters like solvent basicity, the molar ratio, hydrogen bond formation and the  $P_g$ . The differential swelling behavior of the fibers could be justified depending upon the chemical nature and the property of the pendent groups ( $-\text{COC}_4\text{H}_9$ ,  $-\text{COC}_2\text{H}_5$ ,  $-\text{COOH}$ ,  $-\text{CH}_2=\text{CH}_2$ , and  $-\text{C}_6\text{H}_6\text{N}$ ) 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  $P_g$ . Whereas, in case of poly(AA) strong intramolecular hydrogen bonding occurs.<sup>36</sup> However, a reverse trend was found in the case of raw *H. sabdariffa*.

**TABLE III**  
TG-DTA of *H. sabdariffa* and its Graft Copolymers

Graft copolymer	$P_g$	TGA			DTA
		IDT	FDT	% Residue left	Peaks in °C( $\mu$ V)
<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	6.7	361.2 (1.2), 432.5 (29)
(EA-co-4VP)	63.90	301.5	480.5	13.9	368.9(8), 391.8(12)
(EA-co-AA)	94.23	290.0	481.0	13.00	346.8 (18),389.8 (38)
(EA-co-BA)	112.2	305.0	490.0	8.7	369.2(3), 430.8 (21)



**Figure 8** TG and DTA curves of highest grafted *H. sabdariffa*-g-poly (EA).

Since, the cellulose is semi crystalline, polar polymer and miscible with in polar solvent due to hydrogen bond formation<sup>37</sup> and imbibitions therefore, the raw fiber had higher swelling in water and MeOH followed by DMF and BuOH.<sup>38,39</sup> Moreover, other factors like the fiber size, steric hindrance and temperature also influence the percentage of swelling<sup>40–42</sup> (Table V).

### 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 VI).

The graft copolymers exhibited less dye uptake as compared to the raw fiber as it was found to be a function of  $P_g$ . It was observed that dye uptake decreases with increase in  $P_g$ . 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 helped in the absorption of the dye. But, these sites get occupied with poly(EA) chains and poly(EA-co-BA), poly(EA-co-AA), and poly(EA-co-4-VP) chains in the backbone that restrain dye uptake depending upon the  $P_g$ .<sup>36,43</sup>

## CONCLUSIONS

*H. sabdariffa*-g-poly(EA)  $P_g$ : 117.3 and *H. sabdariffa*-g-poly(EA-co-BA)  $P_g$ : 112.2 obtained by using ceric ion–nitric acid initiator system were found to have undergone tremendous physico-chemico-thermal and morphological changes. The higher graft yield obtained could be accounted by the efficient physico-chemical behavior and interaction between the monomers. Whereas, poly(EA-co-AA) ( $P_g$ : 94.23) and poly(EA-co-4-VP) ( $P_g$ : 63.90) due to ineffective chemical properties and interaction with the principal monomer, under optimized reaction conditions did not improve the  $P_g$ . With increase in grafting, dye uptake, hydrophylicity, percentage of crystallinity and crystallinity index decreased, but incorporation of poly(vinyl) chains onto the backbone increased

**TABLE IV**  
Chemical Resistance and Moisture Absorbance Studies of Graft Copolymers Vis-à-Vis Back Bone

Graft copolymer	$P_g$	% Chemical resistance % wt. loss after 72 hour		% Moisture absorbance at different RH after 12 hours			
		1N HCl	1N NaOH	30–35%	50–55%	60–65%	85–90%
<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-4VP)	63.90	40.0	28.0	–	–	0.3	1.1
(EA-co-AA)	94.23	8.0	5.0	–	–	–	0.8
(EA-co-BA)	112.2	3.0	–	–	–	–	0.4

**TABLE V**  
Effect of Solvents on Swelling Behavior of Graft Copolymers Vis-à-Vis Backbone

Sample	$P_g$	% Swelling			
		Water	MeOH	BuOH	DMF
<i>H. sabdariffa</i>	raw	59.00	46.00	38.00	40.00
<i>H. sabdariffa</i> -g-poly(EA)	117.3	14.00	10.00	62.00	78.00
<i>H. sabdariffa</i> -g-poly(EA-co-4VP)	63.90	25.00	22.00	46.00	62.00
<i>H. sabdariffa</i> -g-poly(EA-co-AA)	94.23	18.00	16.00	60.00	67.00
<i>H. sabdariffa</i> -g-poly(EA-co-BA)	112.2	15.00	12.00	62.00	75.00

TABLE VI  
Dye Uptake Studies of the Graft Copolymers Vis-à-Vis Back bone

Sample	$P_g$	Dye concentration of the test solution at different time intervals ( $\times 10^{-4}$ mol L $^{-1}$ )						
		1 hr	2 hr	3 hr	4 hr	5 hr	6 hr	7 hr
<i>H. sabdariffa</i>	Raw	4.96	4.38	4.08	4.08	3.79	3.21	3.21
<i>H. sabdariffa-g-poly(EA)</i>	117.3	5.84	5.84	5.54	5.54	5.54	5.54	5.54
<i>H-g-ply(EA-co-4VP)</i>	63.90	5.25	5.25	4.96	4.67	4.38	4.38	4.38
<i>H. sabdariffa-g-poly(EA-co-AA)</i>	94.23	5.25	4.38	4.38	4.38	4.38	4.38	4.38
<i>H. sabdariffa-g-poly(EA-co-BA)</i>	112.20	5.84	5.84	5.84	5.84	5.54	5.54	5.54

the physico-chemico-thermal resistance and miscibility in organic solvents. The synthesis of such novel graft copolymers is judicious, economic, fruitful means to utilize the renewable biomass for various scientific applications and the development of technology.

## References

- Kurita, K. Prog Polym Sci 2001, 26, 1921.
- Hebeish, A.; Guthrie, J. T. The Chemistry and Technology of Cellulosic Copolymers; Springer: Berlin, 1981.
- Mino, G.; Kaizerman, S. J Polym Sci 1958, 3, 242.
- Geacintoc, N.; Stanett, V.; Abrahamson, E. W.; Hermans, J. J. J Appl Polym Sci 1960, 3, 54.
- Richards, G. N. J Appl Polym Sci 1961, 5, 539.
- Epstein, J. A.; Bar-Nun, A. J Polym Sci 1964, 2, 27.
- Ranga Rao, S.; Kapur, S. L. J Appl Polym Sci 1969, 13, 2619.
- Fazila, F.; Rostamie, S. H. J Macromol Sci Chem 1979, A13, 1203.
- Schigeno, Y.; Konda, K.; Takemoto, K. J Macromol Sci Chem 1982, 7, 571.
- Ange, C. H.; Garnett, J. L.; Levot, R.; Mervyn Long, A. J Appl Polym Sci 1982, 27, 4893.
- Sharma, R. K.; Misra, B. N. Polym Bull 1981, 6, 183.
- Misra, B. N.; Rawat, B. R. J Polym Sci Polym Chem Ed 1985, 23, 307.
- Kaur, I.; Barsola, R.; Gupta, A.; Misra, B. N. J Appl Polym Sci 1994, 54, 1131.
- Kaur, I.; Misra, B. N.; Chauhan, S.; Chauhan, M. S.; Gupta, A. J Appl Polym Sci 1996, 59, 389.
- Misra, B. N.; Kishore, J.; Kanthwal, M.; Mehta, I. K. J Polym Sci Polym Chem Ed 1986, 24, 2209.
- Kaur, I.; Maheshwari, S.; Misra, B. N. J Appl Polym Sci 1995, 58, 835.
- Kaur, I.; Misra, B. N.; Barsola, R. Ange Macromol Chem 1996, 234, 1.
- Joshi, J. M.; Sinha, V. K. Polymer 2006, 47, 2198.
- Valette, L.; Massardier, V.; Pascault, J. P.; Magny, B. J Appl Polym Sci 2002, 86, 756.
- Zabotin, K. P.; Dudorov, V. V.; Ryabov, S. A.; Khim, Tr. Chem Abstr 1972, 77, 189.
- Gallagher, G. A.; Jakeways, R.; Ward, I. M. J Polym Sci 1991, 29, 1147.
- Haddleton, D. M.; Ohno, K. Biomacromolecules 2000, 1, 152.
- Dawa, S.; Yong, H. Polymer 2004, 45, 21.
- Mwaikambo, L. Y.; Ansell, M. P. J Appl Polym Sci 2002, 84, 2222.
- Sehgal, L. C.; Martin, A. E.; Conrad, C. M. Textile Res J 1959, 29, 786.
- Kaith, B. S.; Kalia, S. Int J Polym Anal Charact 2007, 12, 401.
- Kaith, B. S.; Chauhan, A.; Singha, A. S.; Pathania, D. Int J Polym Anal Charact 2009, 14, 246.
- Chauhan, A.; Kaith, B. Fibers Polym 2011, 12, 1.
- Mino, G.; Kaizerman, S. J Polym Sci 1958, 31, 242.
- Brandrup, J.; Immergul, E. H. Polym Hand Book; Wiley: New York, 1975, II-45.
- Baysal, B.; Tobolsky, A. V. J Polym Sci 1952, 8, 529.
- Brietenback, J. W. Z Elektrochem 1956, 60, 286.
- Kaith, B. S.; Singha, A. S.; Kumar, S.; Kalia, S. Int J Polym Mater 2008, 57, 54.
- Kaith, B. S.; Singha, A. S.; Sharma, S. K. Int J Chem Sci 2004, 2, 37.
- Kaith, B. S.; Singha, A. S.; Kumar, S.; Misra, B. N. J Polym Mater 2005, 22, 4, 425.
- Kalia, S. PhD thesis, Development of Polymer Matrix Based Composites using Grafted Flax Cellulose as Reinforcing Agent and Evaluation of some Mechanical and Chemical Properties. Punjab Technical University, India, Chapter 4th, 2007.
- Chawala, S. A Text Book of Engineering Chemistry; Dhanpat Rai & Co.; Educational and Technical Publishers: New Delhi, 2002, 22.32.
- Kaith, B. S.; Singha, A. S.; Kumar, S. Int J Chem Sci 2005, 3, 587.
- Kaith, B. S.; Singha, A. S.; Kumar, S.; Int J Chem Sci 2006, 4, 195.
- Stammand, A. J.; Tarkow, H. J Phys Colloid Chem 1950, 54, 745.
- Nayer, N.; Hossfeld, R. L. J Am Chem Soc 1949, 71, 2852.
- West, H.; Banks, W. B. In Proceedings of the 10th Cellulose Conference; Scheurch, C., Ed.; Wiley: New York, 1989; p 1215.
- Hebeish, A.; Waly, A.; Abdel Mohdy, F. A. Die Angew Makromol Chem 2003, 95, 55.