Synthesis, Characterization, and Evaluation of Novel *Hibiscus sabdariffa*-g-poly(EA) Copolymer

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ABSTRACT: In this article, the morphologic transformation of *Hibiscus sabdariffa*, a natural fiber through graft copolymerization with ethyl acrylate 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 get maximum graft yield (117.3%). The graft copolymer thus formed was characterized by Fourier transform infrared, scanning electron micrographs, X-ray diffraction, thermogravimetric analysis, and differential thermogravimetric analysis techniques. The graft copolymer was found to be moisture, chemical, and thermal resistant. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 123: 448–454, 2012

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

INTRODUCTION

Natural fibers have been widely screened for the graft copolymerization with different vinyl monomers to explore the maximum utilization of this renewable resource. These fibers are generally moisture sensitive and have least chemical resistance. Graft copolymerization is one of the versatile chemical techniques that incorporates 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. Because natural fibers occur in abundance in nature and are renewable resource, various workers have focused on the graft copolymerization of different cellulosic backbones using vinyl monomers through various chemical and radiation techniques.[1–10] Misra and co workers[11,12] have extensively studied the modification of natural and synthetic fibers such as wool, gelatin,[13,14] poly(vinyl alcohol),[15,16] rayon, and polyamide-6.[17] The potential applications of graft copolymerization could be immensely increased by selecting various initiators such as ceric ammonium nitrate (CAN), potassium per sulfate, and ammonium per sulfate.[18] Researchers have used different vinyl monomers with varied backbones such as poly butyl acrylate,[19] poly methyl acrylate,[20] poly acrylic acid, poly vilidene fluoride,[21] glycol polymers,[22] and cellulose[23] to get increased graft yield, hydrophobicity, chemical resistance, and physical strength. Literature review reveals that graft copolymerization of vinyl monomers such as ethyl acrylate (EA) onto *Hibiscus sabdariffa* (*Hs*) fiber still remains unexplored; therefore, it was considered worthwhile to screen the effect and study the behavioral and morphologic transformations.

EXPERIMENTAL

Materials and methods

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

Characterization

FTIR and SEM

Infrared (IR) spectra of the *H. sabdariffa* and *Hs*-g-poly(EA) were recorded with Perkin–Elmer Fourier transform infrared (FTIR) spectrophotometer using KBr pellets (Sigma Aldrich-Chemie GmbH, Riedstrasse, Steinheim, Germany). Scanning electron micrographs (SEM) of *H. sabdariffa* and its graft copolymers were obtained by using Electron Microscopy Machine (LEO 435-25-20).

Thermogravimetric–differential thermogravimetric Analyses

Thermogravimetric and differential thermal analyses (TG–DTA) were performed on thermal analyzer

(LINSEIS, L-81 11). Thermogravimetric analysis (TGA) of ungrafted and grafted *H. sabdariffa* has been studied as a function of wt % loss versus temperature.

X-ray diffraction

X-ray diffraction (XRD) studies were performed on X-ray diffractometer (Bruker D8 Advance) under ambient conditions using CuKα (1.5418 Å) radiation, Ni-filter, and scintillation counter as detector at 40 kV and 40 mA on rotation between 13° and 25° at 2θ scale at 1 s. step size and increment of 0.01° with 0.5° or 1.0 mm of divergent and antiscattering slit. Each sample was homogenously mixed before subjecting for analysis. Corundum and quartz were the reference to verify and calibrate the instrument.

The randomly oriented powdered sample with a uniform surface was exposed to X-rays from all the possible planes of the sample and then measuring the scattering angle of the diffracted X-rays with respect to the angle of the incident beam. The continuous scans were taken, and different d-spacings and relative intensities (I) were obtained. Crystallinity index (CI), which measures the orientation of the cellulose crystals with respect to fiber axis, was determined by using the wide-angle XRD counts at 2θ scale close to 22.68° and 15°. The counter reading at the peak intensity at 22.68° represents the crystalline material, and the peak intensity at 15° corresponds to the amorphous material in cellulose.[24] Percentage crystallinity (% Cr) and CI were calculated as follows[25,26]:

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

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

Graft copolymerization

Graft copolymerization of the monomer (EA) onto *H. sabdariffa* was performed for optimization of different reaction conditions such as reaction time, reaction temperature, monomer concentration, concentration of initiator system, and pH to obtain maximum graft yield. The fiber (0.5 g) was activated by swelling in 100 mL of distilled water for 24 h. Mixture of CAN and concentrated nitric acid mixture was slowly added to the reaction medium with continuous stirring followed by the addition of monomer. The reaction was performed at a definite temperature for a particular time interval under optimized conditions. On completion of the reaction, poly(EA) was extracted with acetone and alcohol.

The graft copolymer was dried at 50°C, till a constant weight. The percent grafting (P_g) was calculated as per the reported method[26]:

$$P_g = W_f - W_i \times 100$$
$$W_i$$

where W_f is the final weight of the fiber and W_i is the initial weight of the fiber.

Moisture absorption study

Moisture absorbance studies at various relative humidity levels were performed as per the method reported.[27] 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 h 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 percent moisture absorbance was calculated from the increase in initial weight in the following manner[27]:

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

Acid and base resistance

Acid and base resistance studies were performed as per the method reported earlier.[28] Acid and base resistance was studied by placing a known weight (W_i) of dry grafted and ungrafted samples in fixed volume of 1N HCl and 1N NaOH, and the final weights (W_f) of the samples were noted after 72 h.
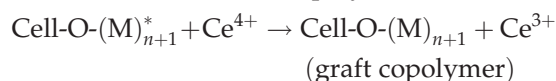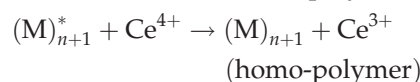
$$\text{Weight loss}(\%) = [(W_i - W_f)/W_i] \times 100$$

RESULTS AND DISCUSSION

Mechanism

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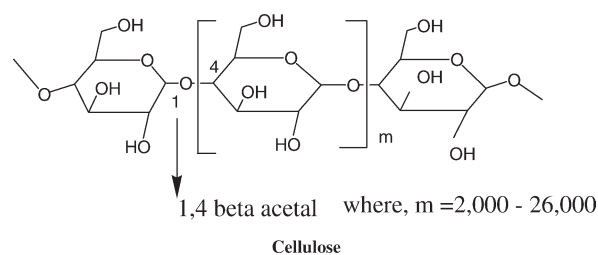
Cellulose

C_2, C_3, and C_6 hydroxyls and C—H groups are the active sites for the incorporation of polymeric chains through grafting onto cellulosics. CAN was used as a source of ceric ion, and the presence of concentrated nitric acid played an important role during

graft copolymerization because in the aqueous medium ceric ion exists as $[Ce-O-Ce]^{6+}$. Because of the large size, $[Ce-O-Ce]^{6+}$ ion is unable to form a complex with the fiber, whereas in the presence of HNO_3, more of Ce^{4+} and $[Ce(OH)_3]^{3+}$ ions were formed, and these ions easily undergo complex formation. Ceric ion forms the chelate complex with the cellulose molecule 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 the bonds at C-2 and C-3, resulting in the formation of the free radical sites. Grafting of vinyl monomer onto polymeric backbone occurs as follows[3,24]:

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

$$M + Ce^{4+} \rightarrow M^* + Ce^{3+} + H^+$$

$$Cell\text{-}O^* + M \rightarrow Cell\text{-}O\text{——}M^*$$

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

(active graft copolymeric species)

$$M^* + nM \rightarrow (M)^*_{n+1}$$

(active homo-polymer moiety)

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

(homo-polymer)

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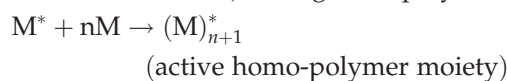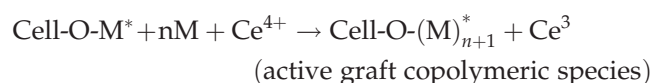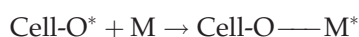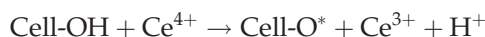
(graft copolymer)

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

The use of EA as 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 that transformed the property and morphology of the fiber (Table I).[29–31]

Optimization of different reaction parameters

Effect of reaction temperature

Reaction temperature was found to play a significant role to achieve the maximum graft yield (Table II). The effect of temperature was studied from 25 to 65°C while keeping the other reaction conditions constant. P_g increased with increase in reaction temperature, and the maximum grafting was found at 35°C (62.40%). This was due to higher diffusion rate of monomer from the reaction medium to cellulose. However, further increase in temperature decreased the graft yield. This could be due to various hydrogen abstraction reactions and homopolymerization. Moreover, increase in the temperature resulted in

TABLE I
Percentage Crystallinity (% Cr) and Crystallinity Index (CI) of the Grafted and Raw *Hibiscus sabdariffa* Fiber

Sample	P_g	At 2θ scale		% Cr	CI
		$I_{15.0}$	$I_{22.68}$		
H. sabdariffa	—	40.0	136.0	77.20	0.70
Hs-g-poly(EA)	117.30	10.0	29.0	74.35	0.65

$I_{15.0}$ and $I_{22.68}$ = peak intensities at 2θ scale.

the loss of weight due to dissolution of water-soluble constituents of the fiber that affected the overall graft yield.[32]

Effect of reaction time

As the reaction time increased, P_g was found to increase gradually and reached maximum value (83.90%) at 150-min time interval (Table II). The increase in graft yield with time could be explained on the basis that with increase in time interaction between Ce^{4+} and *H. sabdariffa* backbone increased. As a result, there was generation of free radical sites on the backbone and on growing poly(EA) chains. However, further increase in time interval resulted in decreased graft yield. This could be due to dominance of homopolymerization over graft copolymerization and disintegration of poly(EA) chains grafted on backbone polymers beyond optimum reaction time.[33]

Effect of pH of reaction medium

The pH of the reaction medium played an important role in grafting. Maximum graft yield was found at pH 7 (Table II). Further decrease or increase in pH resulted in decreased graft yield. This could be due to termination of polymerization with increase in pH. Moreover, free radicals like OH^* generated in the medium combined with the chain-propagating species and acted as reaction terminator. There were chances that cellulose might be converted to sodium salt, and therefore it did not effectively interact with ceric ion to form the complex and generate the free radical sites. A pH below 7 might affect the redox initiator system.[34]

$$Hs\text{-}(M)^*_{n+1} + OH^* \rightarrow Hs\text{-}(M)_{n+1}\text{——}OH$$
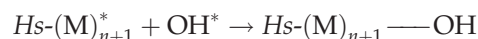
Effect of nitric acid concentration

Ceric ion in water reacts in the following manner:

$$Ce^{4+} + H_2O \rightarrow [Ce(OH)^{3+}]$$

$$2[Ce(OH)^{3+}] \rightarrow [Ce\text{——}O\text{——}Ce]^{6+} + H_2O$$

Optimization of Different Reaction Parameters for Graft Copolymerization of EA onto *Hibiscus sabdariffa* Fiber

Sample: *Hs*-g-poly(EA)				
Optimization of different reaction conditions				
Fixed parameters	Variable parameters	Mean P_g	±SE	±SD
Time (min): 150	Monomer ($\times 10^{-4}$ mol L^{-1})			
pH: 7.0	1.35	79.83	±2.54	±4.42
CAN ($\times 10^{-4}$ mol L^{-1}): 2.41	1.81	147.2	±3.61	±6.26
Temp. (°C): 35	2.26	188.0	±4.12	±7.13
Nitric acid ($\times 10^{-3}$ mol L^{-1}): 1.46	2.71	118.0	±2.55	±4.40
	3.18	114.0	±2.51	±4.35
Temp. (°C): 35	Time (min)			
pH: 7.0	60	25.30	±0.50	±0.88
CAN ($\times 10^{-4}$ mol L^{-1}): 2.26	90	59.90	±0.51	±0.89
Nitric acid ($\times 10^{-3}$ mol L^{-1}): 1.46	120	78.50	±2.06	±3.56
EA ($\times 10^{-3}$ mol L^{-1}): 2.41	150	83.90	±1.50	±2.59
	180	73.15	±1.02	±1.77
Time (min): 150	Temp. (°C)			
pH: 7.0	25	26.20	±1.01	±1.76
CAN ($\times 10^{-4}$ mol L^{-1}): 2.26	35	62.40	±2.54	±4.39
Nitric acid ($\times 10^{-3}$ mol L^{-1}): 1.46	45	50.00	±2.06	±3.57
EA ($\times 10^{-3}$ mol L^{-1}): 2.41	55	32.00	±3.51	±6.07
	65	27.00	±1.50	±2.59
Time (min): 150	CAN ($\times 10^{-4}$ mol L^{-1})			
pH: 7.0	1.20	58.70	±2.06	±3.56
Temp. (°C): 35	1.81	89.23	±1.01	±1.75
Nitric acid ($\times 10^{-3}$ mol L^{-1}): 1.46	2.41	105.4	±1.50	±2.59
EA ($\times 10^{-3}$ mol L^{-1}): 2.41	3.03	96.70	±2.06	±3.57
	3.63	80.6	±0.51	±0.90
Time (min): 150	Nitric acid ($\times 10^{-3}$ mol L^{-1})			
pH: 7.0	0.73	47.40	±1.50	±3.58
CAN ($\times 10^{-4}$ mol L^{-1}): 2.41	1.46	88.76	±3.51	±6.08
Temp. (°C): 35	2.19	79.66	±2.52	±4.37
EA ($\times 10^{-3}$ mol L^{-1}): 2.41	2.92	56.16	±2.54	±4.40
	3.66	50.11	±2.08	±3.54
Time (min): 150	pH			
Temp. (°C): 35	2.5	73.06	±3.51	±6.07
CAN ($\times 10^{-4}$ mol L^{-1}): 2.41	5.0	54.93	±2.08	±3.60
Nitric acid ($\times 10^{-3}$ mol L^{-1}): 1.46	7.0	117.30	±4.12	±7.13
EA ($\times 10^{-3}$ mol L^{-1}): 2.41	8.0	81.56	±3.51	±6.06
	12.0	73.36	±2.50	±4.34

CAN, ceric ammonium nitrate; SD, standard deviation; SE, standard error.

In aqueous medium, ceric ion exists as Ce^{4+}, [Ce(OH)]$^{3+}$, and [Ce—O—Ce]$^{6+}$, and because of its large ion size, grafting onto backbone is not possible in the absence of nitric acid as it is not able to form the complex. But in its presence, the equilibrium shifted more toward Ce^{4+} and [Ce(OH)$^{3+}$] formation that easily formed the complex. However, on increasing the acid concentration, the graft efficiency decreased because of reduction in the free radical species.[35]

Effect of initiator concentration

CAN is an efficacious initiator that helped in the formation of C—C bond, cleavage of C—H bond, rearrangement, and oxidative fragmentation. It is a powerful one-electron oxidant. P_g increased with increase in initiator concentration. The active sites were generated by the formation of complex with cellulose. Maximum P_g (105.4%) was observed at 2.41×10^{-4} mol/L CAN concentration. However, further increase in initiator concentration led to premature decay, thereby decreased the P_g.[36]

Effect of monomer concentration

With increase in concentration of EA, P_g was found to increase continuously and reached maximum value (188.0%) at 2.26×10^{-3} mol/L. However, further increase in monomer concentration resulted in decreased graft yield. Poly(EA), the homopolymer, is insoluble in water. It might be that increased homopolymer formation being insoluble made the system heterogeneous that inhibited the movement of the growing polymeric chains to active sites leading to decrease in percentage grafting.[32,33]
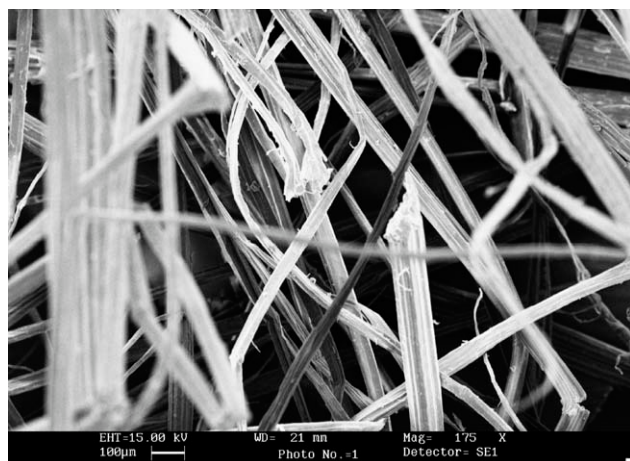
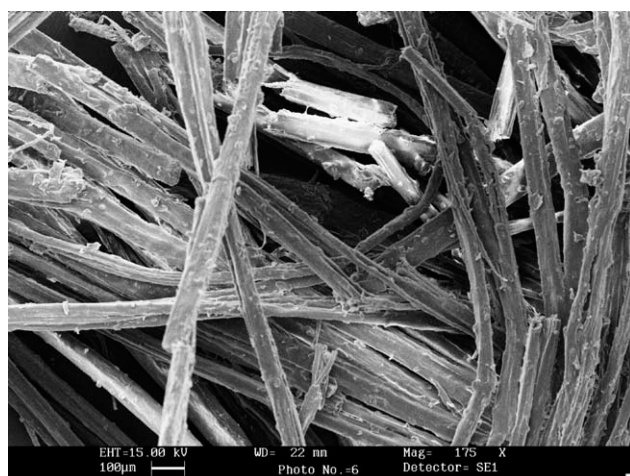**Figure 1** Scanning electron micrograph of *Hibiscus sabdariffa* fiber.

Characterization

FTIR

IR spectrum of the *H. sabdariffa* showed a broad peak at 3424.0 cm^{-1} (—OH group), and peaks at 2924.7, 1246.9, and 1032.0 cm^{-1} were observed as a result of —CH$_2$, C—C, and C—O stretching, respectively. However, in case of *Hs*-g-poly(EA), an additional peak as a result of >C=O groups was witnessed at 1734.0 cm^{-1} that confirms the incorporation of the functional group in the graft copolymer formed.

Scanning electron microscopy

Because cellulose has nonconducting behavior, it was gold plated to have an impact. Scanning was synchronized with microscopic beam to maintain the small size over the large distance relative to the specimen. The resulting images had a greater depth of the field. A remarkable three-dimensional appear-

**Figure 2** Scanning electron micrograph of *Hibiscus sabdariffa*-g-poly(EA).
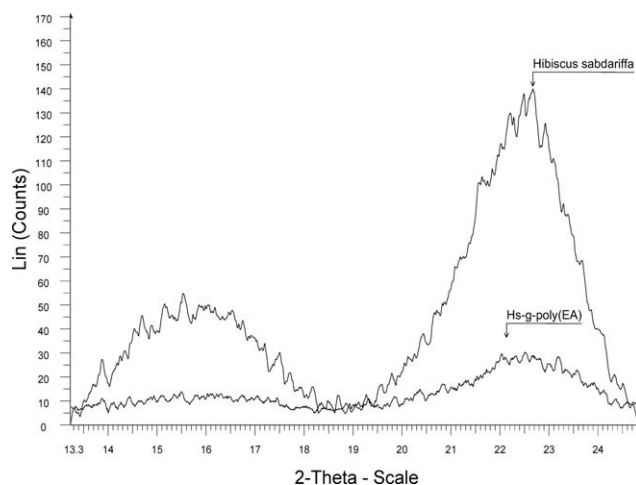
**Figure 3** XRD overlay pattern of the raw and grafted *Hibiscus sabdariffa* fiber.

ance with high resolution was obtained. The scans could easily verify the fact that cellulosic fibers lying apart in raw sample started forming bundles in the graft copolymers. It is evident from Figures 1 and 2 that there has been a sufficient deposition of polyvinyl monomers onto fiber. Comparison of the SEM of raw *H. sabdariffa* fiber with the graft copolymers obtained revealed the distinction between the ungrafted and grafted samples.[25,26]

XRD studies

As is evident from Figure 3, percentage crystallinity and CI were found to decrease with increase in percentage grafting of EA onto *H. sabdariffa* fiber. Because the incorporation of monomer moiety in the backbone disturbed the natural crystallinity of the fiber, the graft copolymerization of EA onto *H. sabdariffa* fiber resulted in impaired crystallinity and increased the amorphous region of the fiber (Table I). Thus, with increase in percentage grafting, the
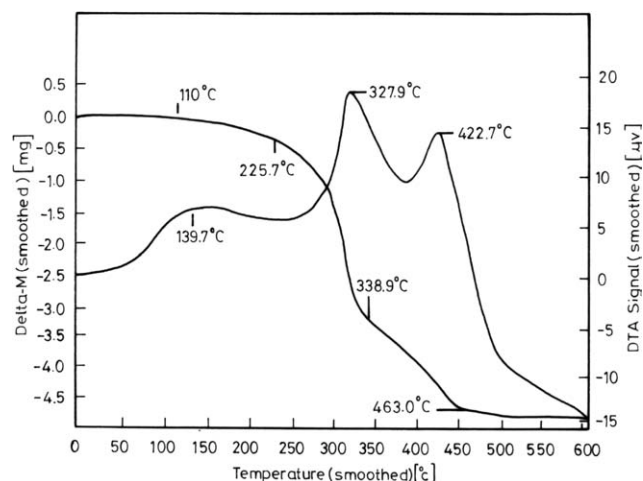
Figure 4 TGA and DTA curves of *Hibiscus sabdariffa* fiber.
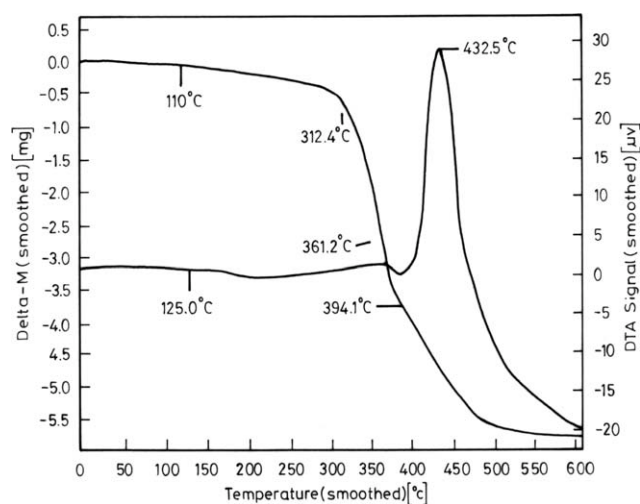
Figure 5 TGA and DTA curves of *Hibiscus sabdariffa*-g-poly(EA).

percentage crystallinity and CI decreased along with the reduction in stiffness and hardness. CI is the quantitative measure of the orientation of the crystal lattice to the fiber axis; therefore, lower CI in case of graft copolymers stands for poor order of crystal lattice in the fiber. The disorientation of the crystal lattice to the fiber axis during grafting resulted in graft copolymer with low crystallinity and CI. It clearly indicates that the cellulose crystals are better oriented in *H. sabdariffa* fiber rather than in *Hs*-g-poly(EA).[26]

TG-DTA studies

Cellulose 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 from 225.7 to 338.9°C with 54.0 wt % loss and 338.9 to 463.0°C with 26.00 wt % loss. The former stage is attributed to loss by dehydration and volatilization processes, whereas the later stage is attributed to loss by depolymerization, delignification and oxidation of the char.[26] *Hs*-g-poly(EA) showed two-stage decomposition. The first stage refers to loss of moisture and de-

carboxylation ranging from 312.4 to 394.1°C with 64.0 wt % loss, and the second stage pertains to breaking up of covalent bonds in the vinyl monomer in the range of 394.1–500.0°C with a weight loss of 29.3%. Thus, it is evident from the TGA data that grafted fiber is thermally stable than the raw fibers. It may be due to the incorporation of poly(EA) chains onto backbone polymer through strong covalent bonding or mechanically due to surface grafting that confirms the additional strength and stability to the fiber.[26]

In case of differential thermogravimetric analysis (DTA) studies, *H. sabdariffa* has been found to exhibit two exothermic peaks at 327.9°C (18 μV) and 422.7°C (14 μV). The exothermic peak at 327.9°C corresponds to decomposition stage between 225.7 and 338.9°C, whereas the exothermic peak at 422.7°C corresponds to second decomposition stage (338.9–463.0°C) in TGA. However, *Hs*-g-poly(EA) exhibited a minor exothermic peak at 361.2°C (1.5 μV) that refers to decomposition stage between 312.4 and 394.1°C, corresponding to the onset of degradation reactions of *Hs*-g-poly(EA) chains, whereas a major peak at 432.5°C (29.0 μV) corresponds to the decomposition between 394.1 and 500°C. 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 (Figs. 4 and 5).

Moisture absorbance study

It was found that graft copolymerization of EA onto *H. sabdariffa* had an impact on the moisture absorbance behavior (Table III). It has been observed that with increase in graft yield, there was a decline in percent moisture absorbance. It was due to blocking of sites vulnerable to moisture absorbance with hydrophobic poly(EA) chains, thereby converting the fiber less sensitive toward moisture.[26,27,32–34]

Acid–base resistance study

It has been observed that acid–base resistance of the fiber increased with increase in percent grafting.

TABLE III
Chemical and Moisture Resistance Studies of Graft Copolymers vis-à-vis Back Bone

Graft copolymers *Hs*-g-poly(EA)	P_g	% Chemical resistance		% Moisture absorbance			
		wt % loss after 72 h		At different RH after 12 h			
		In 1*N* HCl	In 1*N* NaOH	30–35%	50–55%	60–65%	85–90%
Hibiscus sabdariffa	—	55.0	43.0	0.5	0.8	1.8	2.5
Hs-g-poly(EA)	25.30	43.0	36.0	0.2	0.5	1.5	2.1
	47.40	36.0	29.0	0.1	0.3	0.8	1.8
	78.50	18.0	09.0	—	0.1	0.4	1.4
	96.70	08.0	—	—	—	0.1	0.5
	117.30	04.0	—	—	—	—	0.2

This is due to the fact that covalently bonded poly(EA) chains grafted onto *H. sabdariffa* fiber had less sensitivity for 1*N* HCl and 1*N* NaOH compared with hydroxyl and other functional groups present in ungrafted fiber. Therefore, the resistance of fiber toward acid and base was found to increase with the incorporation of poly(EA) chains on the active sites of the backbone (Table III).[28,32–34]

CONCLUSIONS

Grafting of EA onto *H. sabdariffa* fiber in presence of ceric ion initiator was found to have physicochemical and morphologic impact. Different reaction conditions such as reaction time and temperature, pH and concentration of nitric acid, initiator, and monomer were found to have a significant effect on the fiber after graft copolymerization. Although with increase in grafting, % Cr and CI decreased, but incorporation of poly(EA) chains on backbone polymer resulted in higher acid–base and thermal resistance and an increase in moisture repellence. Moreover, on grafting, the morphologic changes with respect to surface topography in graft copolymer improved physical, chemical, and thermal properties of the polymer.

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