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Exploring the Diversification in Grafted Copolymer

Ashish Chauhan and Balbir Kaith
Department of Chemistry, Dr. B. R. A. National Institute of Technology, Jalandhar – 144 011(Punjab) India

Abstract

Background & Aim: The paper deals with optimization of the reaction parameters, graft copolymerization, characterization and evaluation of the transformations in Roselle stem fiber on graft copolymerization with vinyl monomer, using ceric ammonium nitrate nitric acid initiator system. **Methods:** Different reaction parameters such as temperature, time, initiator concentration, monomer concentration and pH were optimized to get the maximum graft yield. The graft copolymer thus formed were characterized by advanced techniques. **Results:** The physico-chemico-thermal resistance, moisture absorbance, swelling behavior of graft copolymers and the dye uptake behavior were studied and found to have improved. **Conclusion:** Hence, this first report of novel graft copolymers is to help towards various applications.

Keywords: Roselle, graft copolymerization, chemical resistance, thermal resistance

1. Introduction

Natural fibers have been immensely used by the mankind since long. As they are renewable resource so they can also be utilized for various secondary needs. Many attempts have been made to explore their potential yet a lot remains undiscovered. The natural fibers suffer from various draw-backs such as low weather-stability, fast-decaying and low chemical resistance. Amongst various methods prevalent to improve these properties, graft copolymerization of vinyl monomers onto natural backbones has been an interesting tool to reduce the ageing in textiles, enhancing the mechanical properties and modifying the texture [1-3].

Graft copolymerization of vinyl monomers onto cellulose has been extensively studied with monomers like acrylic acid and iso-butyl acrylate. Numerous scientists have explored the potential of this chemical technique on different natural fibers and used latest advanced means of characterization like FTIR, XRD, SEM, TGA, DTA, DSC and evaluated the properties for their variable applications. It modifies the properties of polymer back-bone and incorporates the desired features without drastically affecting the basic traits of the substrate. The present paper deals with the optimization of the reaction conditions for the graft copolymerization of methyl acrylate (MA) onto *H. sabdariffa* stem fiber. The important polymeric properties like swelling, dye uptake, chemico-physico-thermal resistance, moisture absorbance have been studied that help to evaluate the acquired modification. The graft copolymers thus obtained were characterized by advanced analytical techniques and evaluated for the physico-chemico-thermal changes that improved the raw and waste biomass for better scientific application [4-24].

2.Experimental

2.1 Materials

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

2.2 Graft copolymerization

Graft copolymerization of the monomer onto *H. sabdariffa* was carried-out for optimization of different reaction conditions like reaction time, reaction temperature, monomer concentration, concentration of initiator system and pH in order to obtain maximum graft yield. The fiber (0.5g) was activated by swelling in 100 ml of the distilled water for 24 hrs. Mixture of ceric ammonium nitrate (CAN) and conc. HNO_3 mixture was slowly added to the reaction medium with continuous stirring followed by the drop by drop addition of a definite ratio of binary vinyl monomeric mixture. The reaction was carried-out at a definite temperature for a particular time interval. On completion of the reaction, poly(MA) were removed on extraction with acetone, chloroform, methanol and water. The graft co-polymer was dried at 50°C, till a constant weight was obtained. The percent grafting (P_g) was calculated as per the reported method [2,3]

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

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

2.3 Characterization

IR spectra of the *H. sabdariffa* and *its* graft copolymers were recorded with Perkin Elmer Fourier Transform Infrared (FTIR) spectrophotometer using KBr pellets (Sigma Aldrich). Scanning Electron Micrographs (SEM) of *H. sabdariffa* and its

Corresponding author
Full Address :
Department of Chemistry, Dr. B. R. A. National Institute of Technology, Jalandhar – 144 011(Punjab) India

Phone no. +91-9464616773
E-mail: aashishchauhan26@gmail.com

graft copolymers were obtained by using Electron Microscopy Machine (LEO 435-25-20). Thermogravimetric and differential thermal analysis were performed on thermal analyzer (LINSEIS, L-81 11). X-ray diffraction studies were performed on X-ray diffractometer (Bruker D8 Advance) under ambient conditions using Cu Kα (1.5418 ^{0}A) radiation.

The continuous scans were taken and different d-spacings (Å) and relative intensities (I) were obtained. Crystallinity index (C.I.) which measures the orientation of the cellulose crystals with respect to fiber axis was determined by using the wide angle X-ray diffraction counts at 2θ-scale close to 22.68^0 and 15^0. The counter reading at the peak intensity at 22.68^0 represent the crystalline material and the peak intensity at 15^0 corresponds to the amorphous material in cellulose. Percentage Crystallinity (% Cr) and Crystallinity index (C. I.) were calculated as follows [21,22]:

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

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

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.

2.4 Physico-Chemical Evaluation

2.4.1 Moisture absorption study

Moisture absorbance studies at various relative humidity levels were carried-out as per the method reported earlier. Moisture absorbance percentage was found out by placing a known weight (Wi) of dry grafted and ungrafted samples in a humidity chamber for about two hours and then the final weight (W_f) of the samples exposed to different relative humidities ranging from 30 – 90 % were taken. The % moisture absorbance was calculated from the increase in initial weight in the following manner[3,4]:

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

2.4.2 Acid and Base Resistance

Acid and base resistance studies were carried-out as per the method reported earlier[3,4]. Acid and base resistance was studied by placing a known weight (Wi) 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:

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

2.4.3 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 [3,4]:

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

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

2.4.4 Dye Uptake Behavior

0.1% Gentian violet solution was prepared in distilled water. 10% NaCl and a few drops of acetic acid were added to this solution. Dye uptake of raw fiber and its graft copolymers was carried-out by immersing the known weight of each sample in 100 ml of Gentian violet dye. Optical densities of test solutions were noted down using Digital Photo Colorimeter after particular time intervals till constant readings were obtained for seven consecutive hours and the concentrations of test solution were calculated as[3,4]:

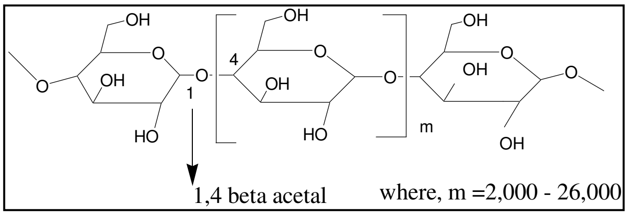
$$\text{Cont. of test solution } (C_t) = \frac{I_t}{I_o} \times C_o \text{ mol L}^{-1} \qquad (7)$$

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

3. Results and discussion

3.1 Mechanism

Ceric ion forms complex with the cellulose through C-2 and C-3 hydroxyl groups of the anhydro glucose unit. Transfer of the electron from the cellulose molecule to Ce (IV) would follow, leading to its reduction to Ce (III), breakage of –OH bonds at C-2 and C-3 and the formation of the free radical sites where the monomeric chains get grafted. Graft yield and homo-polymer formation have been found to be the functions of both the monomer and initiator concentration[25].



Cellulose

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

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

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

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

(active graft copolymeric species)

$$\text{M}^* + n\text{M} \longrightarrow (\text{M})^*_{n+1}$$

(active homopolymer moiety)

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

(homopolymer)

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

(graft copolymer)

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

3.2 Optimization of the reaction parameters

The optimized parameters for the graft copolymerization of MA (as a principal monomer) onto *H. sabdariffa* fiber, to obtain the maximum graft yield (60.24 %) were: temperature (^{o}C), 35; time (minute), 120; CAN (mol L^{-1}), 1.49×10^{-4}; HNO_3 (mol L^{-1}), 3.36×10^{-3}; MA (mol L^{-1}), 2.21×10^{-3} and pH, 7.0 (Table I). The effective graft yield of 60.24% could be accounted on the basis of chemical reactivity, nature, behavior and properties (K_p, K_t, K_p/K_t and C_M) of the monomers used [17-20].

3.3 Characterization

3.3.1 Fourier Transformer Infrared Spectroscopy (FTIR)

FTIR spectrum of the *H. sabdariffa* showed a broad peak at 3424.0 cm^{-1} (–OH group) and peaks at 2924.7 cm^{-1}, 1246.9 cm^{-1} and 1032.0 cm^{-1} were observed due to $–CH_2$, C-C and C-O stretching, respectively. However, in case of *Hs*-g-poly (MA) peak due to >C=O groups appeared at 1738.0 cm^{-1} .

3.3.2 Scanning Electron Microscopy (SEM)

In SEM, the cellulose was gold plated to have an impact. It is quite evident from the Figures I-II that there has been a sufficient deposition of polyvinyl monomers onto fiber.

Table I: Optimization of different reaction parameters for graft copolymerization of MA onto *H. sabdariffa* fiber

Sample : *Hs*-g-poly(MA)				
Optimization of different reaction conditions		Mean Pg	±SE	±SD
Fixed parameters	Variable parameters			
	Monomer			
Time (min): 120	**(x 10^{-3} mol L^{-1})**			
pH : 7.0	1.11	25.06	±1.51	±2.62
CAN (x 10^{-4}mol L^{-1}) : 1.50	2.21	60.00	±2.54	±4.41
Temp. (^{0}C): 35	3.31	45.12	±3.51	±6.08
Nitric acid (x 10 $^{-3}$mol L^{-1}): 3.66	4.41	20.30	±1.50	±2.59
	5.51	10.00	±1.01	±1.76
	Time			
	(min)			
Temp. (^{0}C): 35	60	7.50	±1.02	±1.76
pH : 7.0,	90	9.00	±0.50	±0.98
CAN (x 10^{-4} mol L^{-1}): 1.50,	120	16.58	±1.49	±2.58
Nitric acid (x 10^{-3} mol L^{-1}): 3.66	150	13.00	±1.02	±1.77
MA (x 10^{-3} mol L^{-1}) : 2.21	180	10.00	±1.01	±1.76
	Temp.(^{0}C)			
Time (min) : 120	25	15.88	±1.48	±2.57
pH : 7.0	35	17.80	±1.00	±1.75
CAN (x 10^{-4} mol L^{-1}) : 1.50	45	15.00	±1.03	±1.78
Nitric acid (x 10^{-3} mol L^{-1}): 3.66	55	04.00	±0.51	±0.89
MA (x 10^{-3} mol L^{-1}) : 2.21	65	03.00	±0.50	±0.88
	CAN			
Time (min): 120	**(x 10^{-4}mol L^{-1})**			
pH : 7.0	0.77	10.40	±0.50	±0.89
Temp. (^{0}C): 35	1.13	15.84	±1.02	±1.77
Nitric acid (x 10^{-3} mol L^{-1}): 3.66	1.50	35.16	±1.49	±2.58
MA (x 10^{-3} mol L^{-1}): 2.21	1.86	33.54	±2.05	±3.56
	2.22	30.00	±0.51	±0.89
	Nitric acid			
Time (min): 120	**(x 10^{-3} mol L^{-1})**			
pH : 7.0,	2.44	18.60	±1.50	±2.60
CAN (x 10^{-4} mol L^{-1}): 1.50	3.66	34.50	±2.54	±4.39
Temp. (^{0}C): 35	4.88	17.20	±2.05	±3.55
MA (x 10^{-3} mol L^{-1}): 2.21	6.10	14.00	±1.02	±1.77
	7.32	12.84	±0.52	±0.90
	pH			
Time (min): 120	2.5	25.00	±1.02	±1.78
Temp.(^{0}C): 35	5.0	19.64	±1.00	±1.75
CAN (x 10^{-4} mol L^{-1}): 1.50	7.0	60.24	±2.06	±3.57
MA (x 10^{-3} mol L^{-1}): 2.21	8.0	27.64	±2.53	±4.37
Nitric acid (x 10 $^{-3}$mol L^{-1}): 3.66	12.0	-	-	-

where, CAN= ceric ammonium nitrate, SD = standard deviation, SE = standard error

Comparison of the scanning electron micrographs of the raw *H. sabdariffa* fiber with the graft copolymers reveals the distinction between the ungrafted and grafted samples depending upon the Pg.

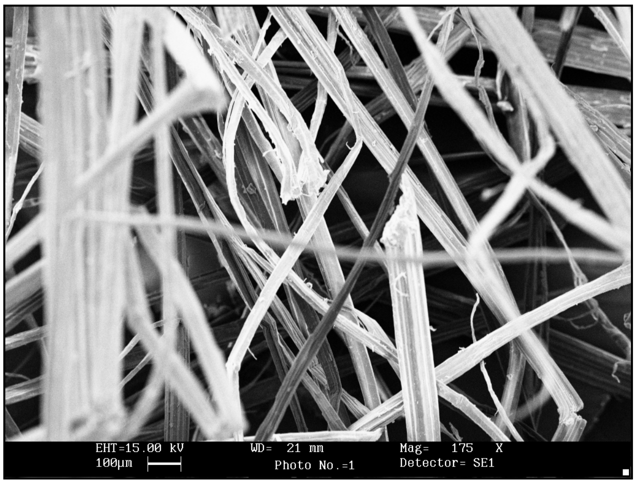


Figure I: SEM of *Hibiscus sabdariffa*

3.3.3 X -ray Diffraction Studies of Graft copolymers (XRD)

The XRD result in Table II clearly shows that the percentage crystallinity and crystallinity index were found to

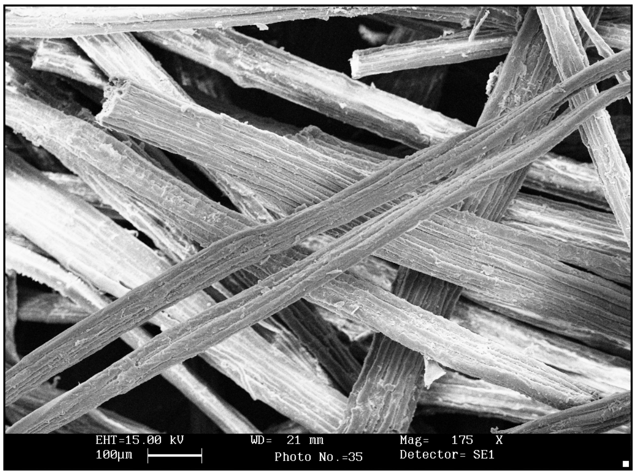


Figure II: SEM of *Hs*-g-poly(MA)

decrease with increase in percentage grafting of MA onto *H. sabdariffa* stem fiber. Since incorporation of monomer moiety in the backbone impairs the natural crystalinity of the fiber, therefore, graft copolymerization of vinyl monomers onto *H. sabdariffa* fiber resulted in impaired crystallinity and increased the amorphous region of the fiber. Thus, with increase in percentage grafting, the percentage crystallinity (68.68) and crystallinity index (0.54) decreased along-with reduction in stiffness and hardness. Crystallinity index (C. I.) is the quantitative measure of the orientation of the crystal lattice to the fiber axis, therefore, lower crystallinity index in case of graft copolymers stands for 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 *H. sabdariffa* fiber rather than graft copolymers [21,22,25].

Table II: Percentage Crystallinity (% Cr) and Crystallinity Index (C.I.) of the grafted and raw *H. sabdariffa* fiber

Sample	Pg	at 2θ Scale		% Cr	%C.I
		$I_{15.0}$	$I_{22.68}$		
H. sabdariffa	-	40.0	136.0	77.20	0.70
Hs-g-poly (MA)	60.24	31.0	68.0	68.68	0.54

where, $I_{15.0}$, $I_{22.68}$= Peak intensities at 2θ-Scale

3.3.4 Thermogravimetric and Differential Thermal Analysis (TG-DTA)

TGA of ungrafted and grafted *H. sabdariffa* have been studied as a function of % wt. loss vs. temperature (Table III). Cellulosic in *H. sabdariffa* degrades by dehydration, glycogen formation and depolymerization. In case of *H. sabdariffa*, two-stage decomposition has been found the former stage is attributed to loss by dehydration, volatilization processes, 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 loss of moisture, decarboxylation and chain scissions while the second stage pertains to breaking up of covalent bonds that has raised the FDT (480°C). 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 [23,24].

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 (Table III, Figure III,IV) [23,24].

Table III Thermogravimetric-Differential Thermal Analysis of *H. sabdariffa* and its graft copolymers

Graft copolymer *Hs*-g-poly-		TGA			DTA
		IDT	FDT	% Residue left	Peaks in ^{0}C(μV)
H. sabdariffa	-	225.7	463.0	20.0	139.7 (6), 327.9 (18.0), 422.7 (14)
(MA)	60.24	294.5	480.0	01.0	150.2 (9), 409.6(37.9)

where, IDT = initial decomposition temperature, FDT= final decomposition temperature

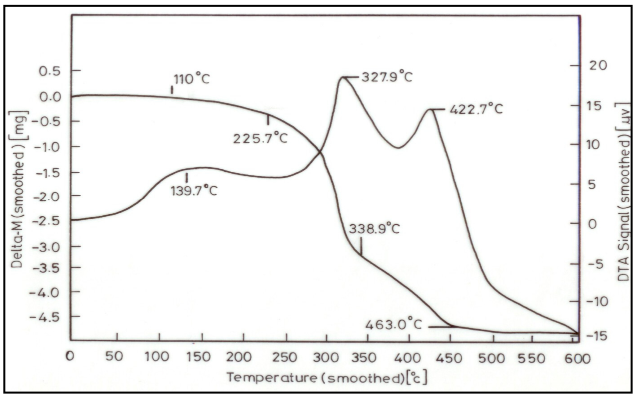


Figure III: TG-DTA of *H. sabdariffa*

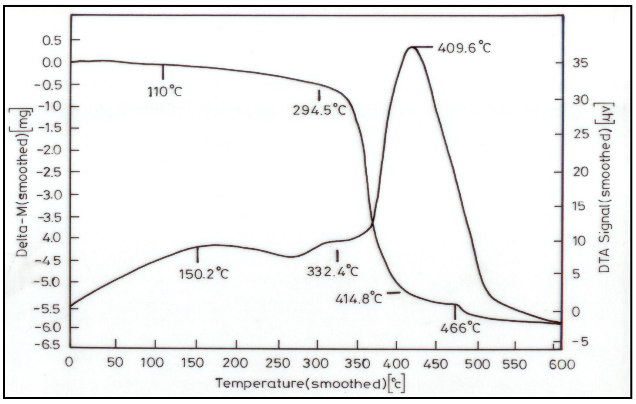


Figure IV: TG-DTA of highest graft *Hs-g*-poly(MA)

3.4 Physico-chemical Evaluation

3.4.1 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 IV). 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.

3.4.2 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 poly (vinyl) chains grafted onto *H. sabdariffa* fiber had less affinity for 1 N HCl and 1N NaOH as compared to hydroxyl and other functional 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 IV) that is clear from percentage weight loss to 39 and 27 after 72h in 1N HCl and 1N NaOH, respectively.

3.4.3 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

Table IV Chemical resistance and moisture absorbance studies of graft copolymers vis-à-vis back bone

Graft copolymer *Hs*-g-poly-	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%
H. sabdariffa	-	55.0	43.0	0.5	0.8	1.8	2.5
(MA)	60.24	39.0	27.0	-	0.1	1.4	1.8

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 $-COCH_3$ have different interactions with the solvents. Higher percentage swelling in DMF and BuOH is due to better interaction with such pendent groups that increases with increase in Pg. However, a reverse trend has been found in the case of raw *H. sabdariffa*. Since a crystalline polar polymer is soluble in solvent is capable of hydrogen bond formation therefore, the raw fiber has more swelling in water and MeOH followed by DMF and BuOH. Presence of –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[17-20] (Table V).

Table V 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 (MA)	60.24	29.00	26.00	44.00	60.00

3.4.4 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). 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[17-20,25]. Therefore, with increase in Pg, dye uptake has been found to decrease.

4. Conclusion

Grafting of poly(MA) onto *H. sabdariffa* stem fiber in presence of ceric ion initiator has yielded novel regenerated graft copolymers i.e. *Hs*-g-poly(MA) with Pg 60.24. It is evident from the characterization and chemical studies of the graft copolymers through different technique that grafting resulted in the morphological transformation that improved the physico-chemico-thermal properties of the *H. sabdariffa* fiber. The increase in Pg decreased the hydrophilicity and dye uptake but increased its chemical and thermal resistance. The graft copolymers thus obtained are the better means for the utilization of the waste biomass in the advancement of technology.

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Table VI 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})						
		1 h	2 h	3 h	4 h	5 h	6 h	7 h
H. sabdariffa	-	4.96	4.38	4.08	4.08	3.79	3.21	3.21
Hs-g-poly(MA)	60.24	5.25	5.25	4.96	4.96	4.67	4.67	4.67

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