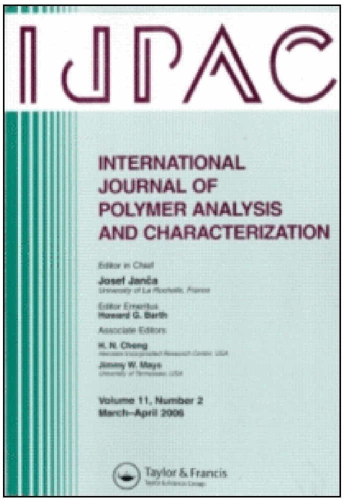

International Journal of Polymer Analysis and Characterization
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713646643

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To cite this Article Kaith, B. S. , Chauhan, Aashish , Singha, A. S. and Pathania, D.(2009) 'Induction of Morphological Changes in *Hibiscus sabdariffa* Fiber on Graft Copolymerization with Binary Vinyl Monomer Mixtures', International Journal of Polymer Analysis and Characterization, 14: 3, 246 — 258

To link to this Article: DOI: 10.1080/10236660802663506

URL: http://dx.doi.org/10.1080/10236660802663506

International Journal of Polymer Anal. Charact., 14: 246–258, 2009

ISSN 1023-666X print
DOI: 10.1080/10236660802663506

Induction of Morphological Changes in *Hibiscus sabdariffa* Fiber on Graft Copolymerization with Binary Vinyl Monomer Mixtures

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Abstract: Various reaction parameters of the graft copolymerization of *Hibiscus sabdariffa* fiber with methyl acrylate as principal monomer and its binary mixture with acrylonitrile, acrylic acid, and acrylamide were optimized. The graft copolymers obtained were characterized by XRD, TGA-DTA, SEM, and FT-IR techniques and were evaluated for different physicochemical changes like moisture absorption and chemical resistance against 1 N NaOH and 1 N HCl. The percentage crystallinity and crystallinity index were found to decrease with increase in grafting, while there was reduction in moisture absorption and increase in chemical and thermal resistance of the graft copolymers.

Keywords: Acrylamide; Acrylic acid; Acrylonitrile; Binary mixture; Graft copolymerization; *Hibiscus sabdariffa*; Methyl acrylate

Submitted 14 October 2008; accepted 21 November 2008.

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INTRODUCTION

Graft copolymerization is a convenient method for the incorporation of new and desired properties into textile fibers without drastically affecting the basic properties of the substrate.[1] It imparts additional properties such as thermal and chemical resistance to the naturally existing backbone for their use in various fields.[2,3] Natural fibers such as flax, jute, ramie, and pine needles are principally suitable as reinforcement materials in industries such as automobile, packaging, and construction materials[4] because of their relatively high strength and stiffness to satisfy economic and environmental demands.

Various polysaccharides such as cellulose,[5] starch,[6] chitosan,[7] guar gum,[8] and psylium[9] have been modified for their use in metal ion sorbtion,[10] drug delivery,[11] and water absorption studies.[12] Moreover, these polymeric materials have been extensively used in agricultural and membrane technology.[13] These studies have shown that the natural polymers are very efficient and are of great significance in water treatment processes due to biodegradability and cost effectiveness.[14]

Roselle (*H. sabdariffa*) has attained prominence as a jute substitute, and attempts are being made to extend its cultivation in areas that are not favorable for jute cultivation.[15] It shows better mechanical properties when studied for injection-molded isotactic polypropylene/roselle fiber composites[16] but still remains unexplored for its viability as substrate to grafting by many vinyl monomers. The versatility of this useful chemical technique inspired thoughts to implement it and screen it onto this fiber by using methyl acrylate (MA) as principal monomer and its binary mixtures with acrylonitrile (AN), acrylic acid (AA), and acrylamide (AAm).

EXPERIMENTAL SECTION

Materials

H. sabdariffa was refluxed with acetone for 72 h. Monomers were used as received (Merck-Schuchardt, Germany). Fresh ceric ammonium nitrate (S. D. Fine-Chem. Pvt. Ltd, India) was used as initiator. Weighing was carried out on a Libror AEG-220 (Shimadzu) electronic balance. A LEO electron microscope (S. No. 435-25-20) and Perkin Elmer instrument were used for the scanning electron microscopy (SEM) and IR analysis. X-ray diffraction (XRD) studies were performed on a Bruker-D_8 Advance. Thermogravimetric analysis (TGA) and differential thermal analysis studies (DTA) were conducted in air on a thermal analyzer (Linseis, L81-11) at a heating rate of 10°C/min.

Methods

Graft copolymerization of binary vinyl monomer mixtures onto *H. sabdariffa* fiber was carried out using methyl acrylate as principal monomer in combination with the secondary monomers under the optimized conditions as per the method reported earlier.[1–3] *H. sabdariffa* fiber (0.5 g) was activated by swelling in 100 mL of distilled water for 24 h. Ceric ammonium nitrate (CAN) and HNO_3 mixture was slowly added to the reaction flask with continuous stirring, followed by the addition of monomer under the optimized conditions. Homo-polymers were removed by solvent extraction. The graft copolymers were dried at 50°C until a constant weight was obtained (Table I). The percentage grafting (Pg) was calculated as follows:

$$Pg = \frac{W_2 - W_1}{W_1} \times 100$$

where W_2 and W_1 are the weights of the functionalized and original samples, respectively.

Table I. Graft copolymerization of different binary vinyl monomeric mixtures onto *H. sabdariffa* fiber

Sample no.	Sample ($\times 10^{-3}$ mol L^{-1})	Binary mixture	Pg
1.	*Hs*-g-poly(MA–co–AN)	2.20 + 1.51	47.30
		2.20 + 2.27	62.40
		2.20 + 3.03	68.08
		2.20 + 3.79	100.12
		2.20 + 4.56	100.64
		2.20 + 5.31	57.06
		2.20 + 6.07	52.73
2.	*Hs*-g-poly(MA–co–AA)	2.20 + 0.72	26.00
		2.20 + 1.45	74.14
		2.20 + 2.17	42.14
		2.20 + 2.91	10.28
		2.20 + 3.62	10.00
3.	*Hs*-g-poly(MA–co–AAm)	2.20 + 0.74	20.22
		2.20 + 1.05	23.75
		2.20 + 1.40	17.40
		2.20 + 1.76	16.00
		2.20 + 2.11	12.00

Infrared Spectroscopy (IR)

IR spectra of the ungrafted and the grafted samples were taken with KBr pellets on a Perkin Elmer spectrophotometer.

Scanning Electron Microscopy (SEM)

Since the cellulose exhibits nonconducting behavior, it was gold plated to have an impact. The scanning was synchronized with microscopic beam in order to maintain the small size over a large distance relative to the specimen. The resulting images have a great depth of the field. A remarkable three-dimensional appearance with high resolution was obtained on the LEO electron microscope (S. No. 435-25-20).

X-ray Diffraction Studies of Graft Copolymers (XRD)

X-ray diffraction studies were performed under ambient conditions, on a Bruker D_8 Advance model using Cu Kα (1.5418 Å) radiation, Ni filter, and scintillation counter 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 anti-scattering slit and was calibrated by corundum. The small particle size of each grafted and ungrafted fiber was determined. Each sample was homogeneously mixed prior to subjecting it to X-ray diffractometry. The sample holder was made of poly(methyl methacrylate) (PMMA) and consisted of a round central cavity.

The randomly oriented powdered sample with a uniform surface was exposed to X-rays from all possible planes of the sample and then by measuring the scattering angle of the diffracted X-rays with respect to the angle of the incident beam, continuous scans were taken and different *d*-spacings (Å) and relative intensities (I) were obtained. The counter reading of highest peak intensity near 22.68° represents crystalline material, and the peak near 15.0° in the halo pattern corresponds to the amorphous material[17] in cellulose. Degree of crystallinity (%Cr) and crystallinity index (C.I.) were calculated as per the following method[18]:

$$\%\mathrm{Cr} = \frac{I_{22.68}}{I_{22.68} + I_{15.00}} \times 100$$

$$\mathrm{C.I.} = \frac{I_{22.68} - I_{15.00}}{I_{22.68}}$$

where %Cr = percentage of crystallinity, C.I. = crystallinity index, and $I_{22.60}$, $I_{15.00}$ = peak intensities of crystalline and amorphous content at 2θ scale close to 22.68 and 15.46°, respectively.

Thermogravimetric and Differential Thermal Analysis of Graft Copolymers (TGA/DTA)

Thermogravimetric analysis studies were carried out as per the method reported earlier.[18]

Moisture Absorbance and Chemical Resistance

Moisture absorbance and chemical resistance studies were carried out as per the methods reported earlier.[2,3]

RESULTS AND DISCUSSION

Ceric ion forms a complex with the cellulose through C-2 and C-3 hydroxyl groups of the anhydro-glucose units. 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 bond, 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 functions of both the monomer and initiator concentration.[2]

Optimization of the Reaction Parameters

During the graft copolymerization of MA (as a principal monomer) onto *H. sabdariffa* fiber, the optimized reaction parameters to obtain the maximum graft yield (60%) were: temperature (°C), 35; time (min), 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.

Effect of the Binary Monomer Mixtures on Percentage Grafting

Graft copolymerization of different binary mixtures, MA + AN, MA + AA, and MA + AAm, using MA as a principal monomer under optimized reaction conditions showed 100.64%, 74.14%, and 23.75% grafting, respectively. High Pg of MA + AN and MA + AA are due to high monomer reactivity of MA and an effective reactivity ratio with both the binary vinyl monomer, under the optimized conditions. Moreover, AN and AA are the strong acceptor monomers and many free radical sites are produced, which result in the higher graft yield.[19] On the other hand, acrylamide showed a decreased percent yield as its reactivity is determined by the solubility, nature, composition, rate, and change in

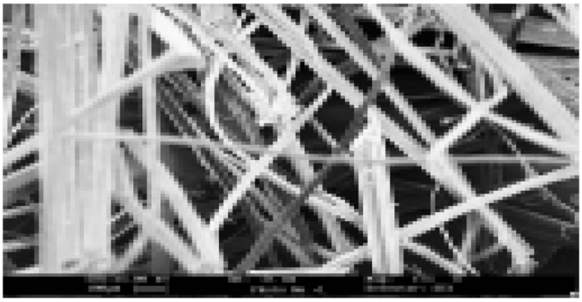

Figure 1. SEM of *Hibiscus sabdariffa* fiber.

overall concentration of the initial monomer, which greatly affects the flocculation property of acrylamide, effecting its copolymerization.

Characterization of Graft Copolymers

Fourier Transform-Infrared Spectroscopy (FT-IR)

H. sabdariffa fiber showed a broad peak at 3420 cm^{-1} (-OH groups) and peaks at 2924.8, 1654, and 1055 cm^{-1} (-CH_2, C-C, and C-O stretching, respectively). However, in the case of *H. sabdariffa*-g-poly(MA–co–AA), sharp peaks at 1740 and 1638.7 cm^{-1} due to $>C{=}O$ stretching of methyl acrylate and acrylic acid, respectively, were observed. A peak at 2926 cm^{-1} (due to OH stretching of -COOH) was observed. *H. sabdariffa*-g-poly(MA–co–AN) exhibited peaks at 1735 cm^{-1} ($>C{=}O$ stretching, methyl acrylate) and 2240 cm^{-1} (-CN stretching, acylonitrile). *H. sabdariffa*-g-poly(MA–co–AAm) showed peaks at 1733 cm^{-1} ($>C{=}O$ of methyl acrylate) and 1604.5 cm^{-1} ($>C{=}O$ stretching, amide group).

Figure 2. SEM of *Hs*-g-poly(MA–co–AN).

Figure 3. SEM of *Hs*-g-poly(MA–co–AA).

Scanning Electron Microscopy (SEM)

The cellulosic fibers lying at a distance in raw sample started forming bundles in graft copolymers *Hs*-g-poly(MA–co–AN), *Hs*-g-poly(MA–co–AA), and *Hs*-g-poly(MA–co–AAm) and are quite conspicuous from Figures 1–4. SEM studies could distinguish between the grafted and ungrafted fibers, as a great deal of morphological modification took place in the *H. sabdariffa* fiber after graft copolymerization.

X-ray Diffraction Studies of Graft Copolymers (XRD)

It is evident from Table II that with increase in Pg, there is a decline in %Cr and C.I. Crystallinity index gives a quantitative measure of the orientation of the cellulose crystals in the fibers. A lower crystalline index in the case of graft copolymers means poor order of arrangement of cellulose crystals in the fiber. This is due to misorientation of the cellulose crystalline lattice to the fiber axis during grafting process (Fig. 5).[18]

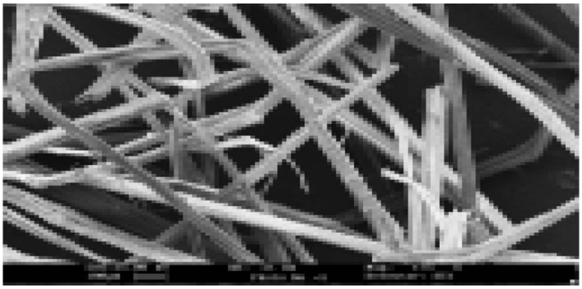

Figure 4. SEM of *Hs*-g-poly(MA–co–AAm).

Table II. Percentage crystallinity (%Cr) and crystallinity index (C.I.) of the grafted and raw *H. sabdariffa* fiber

		2θ scale			
Sample	Pg	$I_{15.00}$	$I_{22.68}$	%Cr	C.I.
Hs raw	00.00	40.00	136.0	77.20	0.70
Hs-g-poly(MA–co–Am)	23.75	39.00	78.00	66.66	0.50
Hs-g-poly(MA–co–AA)	74.14	15.00	26.00	63.41	0.42
Hs-g-poly(MA–co–AN)	100.64	10.20	17.00	62.50	0.40

Thermogravimetric and Differential Thermal Analysis (TGA-DTA) of Graft Copolymers

The samples were scanned at the heating rate of 10°C per minute up to 600°C. Thermogravimetric analysis of raw *H. sabdariffa* fiber and of its graft copolymers was carried out as a function of weight loss versus temperature. The degradation occurred in various forms like deacetylation, dehydration, decarboxylation, and chain scissions. The thermograms of grafted fibers depicted two-phase decomposition. The first stage signifies the breakdown of cellulose and is shifted to higher

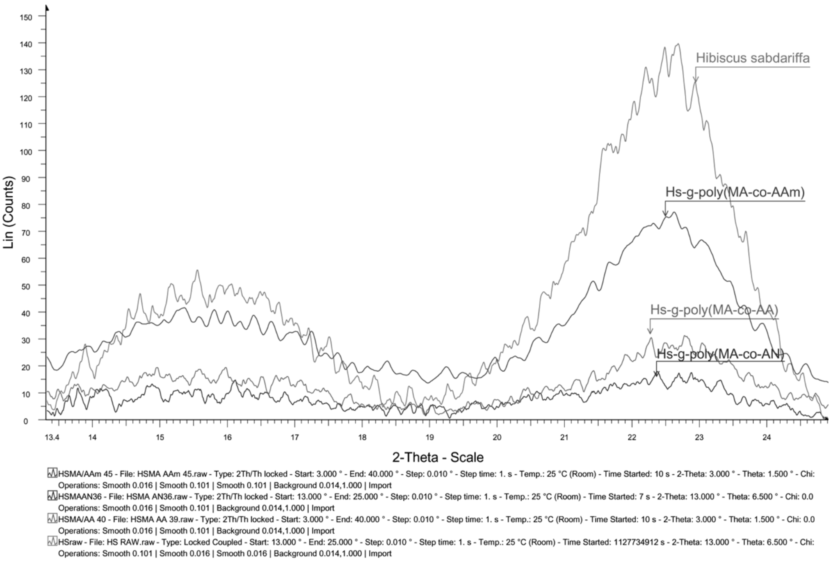

Figure 5. XRD overlay pattern of the raw *H. sabdariffa* and its graft copolymers with binary vinyl monomeric mixtures.

Table III. Thermogravimetric and differential thermal analysis of *Hibiscus sabdariffa* and its graft copolymers

		TGA		DTA
Sample	Pg	IDT (°C)	FDT(°C)	Observed peaks °C [μV]
Raw *Hs*	00.00	225.7	463.0	139.7 (6), 314.4 (18.0), 422.7 (14.0)
Hs-g-poly (MA–co–Am)	23.75	238.8	552.3	133.6 (13.8), 331.1 (22.3), 424.9 (28.1)
Hs-g-poly (MA–co–AA)	74.14	244.4	483.5	151 (14.5), 342.3 (25.6), 399.5 (34.3)
Hs-g-poly (MA–co–AN)	100.6	265.3	500.0	156.3 (7), 372.6 (19.0), 478.6 (6.4)

temperature as compared to raw fiber while the second stage is related to the degradation of the grafted polyvinyl chains. The shift to higher temperature could be due to an increase in the covalent bonds in the graft copolymers varying with Pg. In the case of *H. sabdariffa* fiber, the major weight loss occurred in the first stage due to cellulosic decomposition followed by the oxidation of the char.[20] In the case of raw fiber, both initial decomposition temperature (IDT) and final decomposition temperature (FDT) are lower, i.e., 225.7°C and 463.0°C, respectively, than those of graft copolymers and, therefore, graft copolymerization has resulted in increased thermal resistance[18] (Table III).

Further, TGA studies have been strongly supported by the DTA evaluation pattern (Table III). The thermogram of *H. sabdariffa* fiber shows two exothermic peaks at 314.4°C (18 [μV]) and 422.7 (14 [μV]).

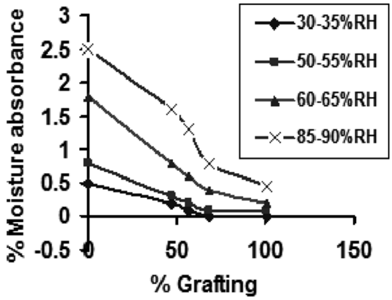

Figure 6. Moisture absorbance behavior of *Hs*-g-poly(MA–co–AN) at different RH.

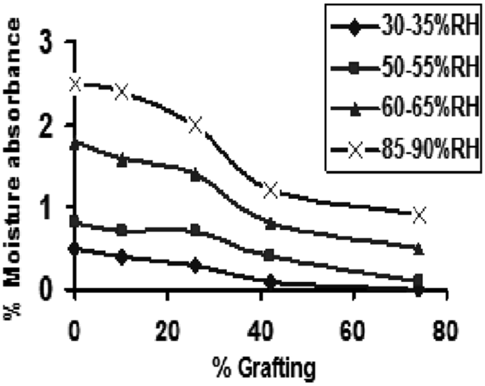

Figure 7. Moisture absorbance behavior of *Hs*-g-poly(MA–co–AA) at different RH.

However, in the case of *Hs*-g-poly(MA–co–AN), *Hs*-g-poly(MA–co–AA), and *Hs*-g-poly(MA–co–AAm), the exothermic peaks were observed at elevated temperatures along with higher energy release, and this again endorses higher thermal stability of the graft copolymers than the raw *H. sabdariffa*. The first transition peak revealed the dehydration, adsorption, and oxidation from the semicrystalline host, and the second 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 covalent bonding with polyvinyl chains.

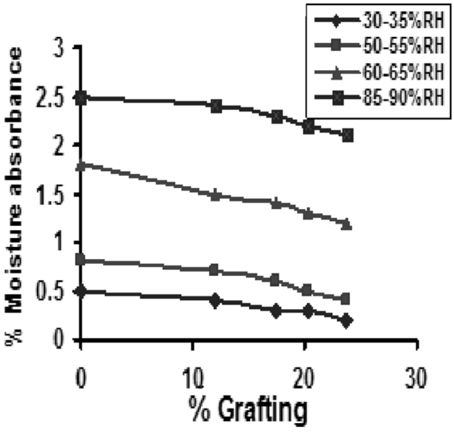

Figure 8. Moisture absorbance behavior of *Hs*-g-poly(MA–co–AAm) at different RH.

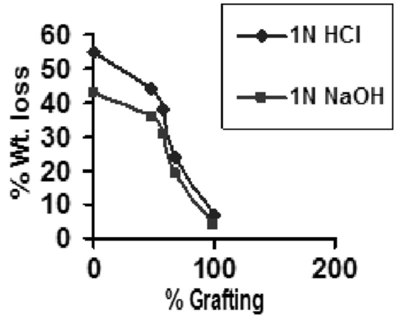

Figure 9. Chemical resistance behavior of *Hs*-g-poly(MA–co–AN) against 1 N HCl and 1 N NaOH.

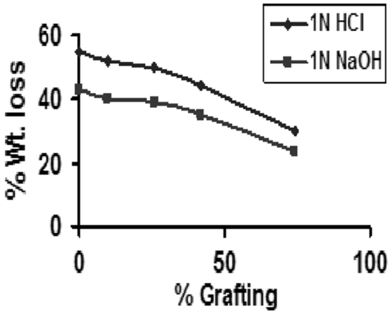

Figure 10. Chemical resistance behavior of *Hs*-g- poly(MA–co–AA) against 1 N HCl and 1 N NaOH.

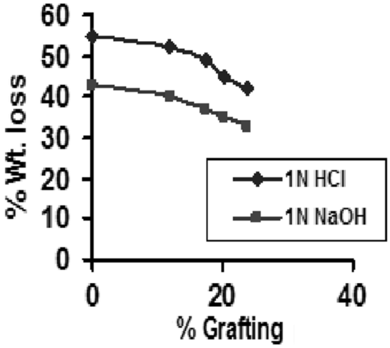

Figure 11. Chemical resistance behavior of *Hs*-g-poly(MA–co–AAm) against 1 N HCL and 1 N NaOH.

Physical and Chemical Properties of Graft Copolymers

Moisture Absorbance Behavior

It is evident from Figures 6–8 that the graft copolymerization has greatly affected the moisture absorbance behavior of *H. sabdariffa* fiber through incorporation of the hydrophobic organic moieties replacing the free hydroxyl groups at C-2, C-3, and C-6. Thus, with increase in Pg, there was a decrease in percent moisture absorbance.

Chemical Resistance

It was observed that with an increase in Pg there was an increase in chemical resistance against 1 N HCl and 1 N NaOH. This could be due to the fact that the incorporation of polyvinyl chains, which are highly hydrophobic in nature, through graft copolymerization in natural backbone decreased the chemical sensitivity, and the grafted sample becomes more resistant towards acids and bases (Figures 9–11).

CONCLUSION

Graft copolymerization is an efficient mean to incorporate desired features into the natural fiber while sustaining its inherent characteristics. It is evident from the characterization of the graft copolymers that the grafting resulted in the modification of the physical and chemical properties by incorporating moisture, chemical, and thermal resistance into *H. sabdariffa* fiber.

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