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Evaluation of Morphological Transition in Advanced Materials

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ABSTRACT

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

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

INTRODUCTION

Graft copolymerization is a magnificent technique for incorporating the desired properties into raw fiber without drastically affecting its basic traits. It imparts additional features such as thermal and chemical resistance to the naturally existing back-bone for their use in various fields. Natural fibers are cost-effective, biodegradable and efficacious to be used in technological processes like water treatment, controlled drug delivery, membrane technologies, removal of hazardous metal ions from effluent and as flocculants. They are mostly fragile and are sensitive towards moisture and chemicals but these properties could be improved by versatile means like graft-copolymerization. Modification of the properties of natural fibers has been reported by various workers. X-ray powder diffraction and thermal analysis are the principal tools to study thermodynamic changes in the solid state materials. *Hibiscus sabdariffa* is a rich source of cellulose and has attained prominence as a jute substitute and attempts are being made to extend its cultivation in areas which are not favorable for jute cultivation. It shows better mechanical properties when studied but still remain unexplored for its viability as substrate to grafting by vinyl monomers [1-6].

The versatility of graft copolymerization inspired the thought to use the *Hibiscus sabdariffa* stem fiber as backbone for grafting effective methyl acrylate (MA) as a principal monomer and its binary mixtures with vinyl acetate (VA). The change in percentage grafting and properties of the fiber were then characterized by IR, SEM, XRD, TGA and DTA.

MATERIALS AND METHODS

H. sabdariffa was refluxed with acetone for 72 hrs. acrylonitrile (Merck- Schuchardt, Germany), acrylic acid (Merck-Schuchardt, Germany) 4-vinyl pyridine (Merck- Schuchardt, Germany) and ceric ammonium nitrate (S. d. fine-Chem. Pvt. Ltd, India) were used as received. Weighing was carried-out on Libror AEG-220 (Shimadzu) electronic balance. LEO Electron microscope (S. No. 435-25-20) and Perkin Elmer instrument were used for SEM and IR analysis, respectively. X-ray diffraction studies were performed on Bruker-D_8 Advance. Thermo gravimetric analysis (TGA) and Differential Thermal Analysis studies (DTA) were conducted in air on Thermal Analyzer (LINSEIS, L81-11) at a heating rate of 10 ^{0}C /minute.

Synthesis of *Hs*-g-poly(MA-co-VA)

Initially, graft copolymerization of MA onto *H. sabdariffa* was carried-out for the optimization of different reaction conditions like reaction time, reaction temperature, monomer concentration, concentration of initiator system and pH in order to obtain the maximum graft yield. The fiber (0.5g) was activated by swelling in 100 ml of distilled water for 24 hrs. Ceric ammonium nitrate (CAN) and conc. HNO_3 mixture were slowly added to the reaction medium with continuous stirring followed by the drop by drop addition of a definite ratio of binary vinyl monomeric mixture. The reaction was carried-out at pre-optimized reaction conditions. On completion of the reaction, the homo-polymers were removed on extraction with hot water, alcohol, chloroform and acetone. The graft co-polymers were dried at 50°C till a constant weight was obtained. The percent grafting (P_g) was calculated as per the reported method [1-6]:

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

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

X-ray Diffraction Studies

X-ray diffraction studies were performed under ambient conditions, using Cu Kα (1.5418Å) radiation, Ni-filter and scintillation counter at 40 KV and 40 mA on rotation between 13^0 to 25^0 at 2θ-scale at 1 sec. step size and increment of 0.01 degree with 0.5^0 or 1.0 mm of divergent and anti-scattering slit and calibrated by corundum. Each sample was homogenously mixed prior to subjecting it for analysis. The sample holder was made of PMMA and consisted of 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 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 (Å) and relative intensities (I) were obtained. The counter reading of highest peak intensity near 22.68^o represents crystalline material and the peak near 15.0^o in the halo-pattern corresponds to the amorphous material in the cellulose. Degree of crystallinity and crystallinity index were calculated [1,4,5].

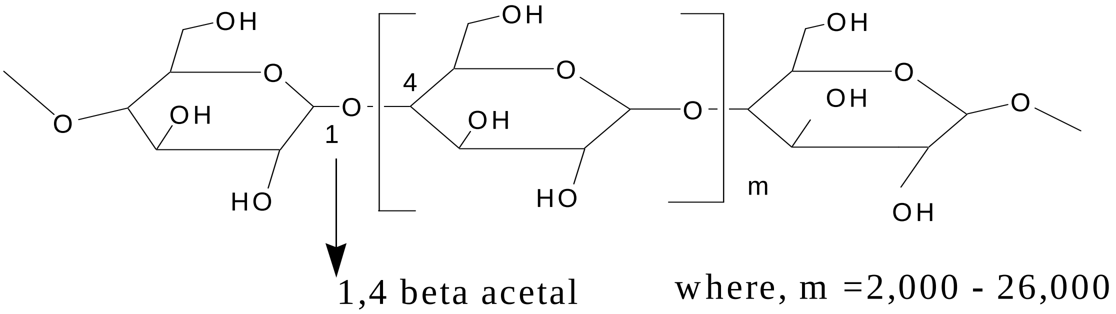
$$\% \text{ Cr} = [I_{22.68} / (I_{22.68} + I_{15})] \times 100 \qquad (2)$$

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

RESULTS AND DISCUSSION

Mechanism of Graft Copolymerization

Ceric ion forms complex with the cellulose through C-2 and C-3 hydroxyl groups of the anhydro glucose unit (Eq. 4). Transfer of the electron from the cellulose molecule to Ce (IV) leads to its reduction to Ce (III), breakage of –OH bonds at C-2 and C-3 and the formation of the free radical sites where the monomeric chains get grafted (Eq. 7). Graft yield and homo-polymer formation (Eq. 8) have been found to be the functions of both the monomer and initiator concentration [1,4,7].



where, m =2,000 - 26,000

Cellulose

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

$$\text{M} + \text{Ce}^{4+} \rightarrow \text{M*} + \text{Ce}^{3+} + \text{H}^{+} \qquad (5)$$

$$\text{Cell-O*} + \text{M} \rightarrow \text{Cell-O-M*} \qquad (6)$$

$$\text{Cell-O-M*} + n\,\text{M} + \text{Ce}^{4+} \rightarrow \underset{\text{(active graft copolymeric species)}}{\text{Cell-O-(M)*}_{n+1} + \text{Ce}^{3}} \qquad (7)$$

$$\text{M*} + n\text{M} \rightarrow \underset{\text{(active homopolymer moiety)}}{\text{(M)*}_{n+1}} \qquad (8)$$

$$\text{(M)*}_{n+1} + \text{Ce}^{4+} \rightarrow \underset{\text{(homopolymer)}}{\text{(M)}_{n+1}} + \text{Ce}^{3+} \qquad (9)$$

$$\text{Cell-O-(M)*}_{n+1} + \text{Ce}^{4+} \rightarrow \underset{\text{(graft copolymer)}}{\text{Cell-O-(M)}_{n+1} + \text{Ce}^{3+}} \qquad (10)$$

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

Optimization of the reaction parameters and effect of secondary monomer

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 x 10^{-4}; HNO_3 (mol L^{-1}), 3.36 x 10^{-3}; MA (mol L^{-1}), 2.21 x 10^{-3} and pH, 7.0 (Table 1). Methyl acrylate as a principal monomer has relative high reactivity, suitable chemical properties (Kt, K_p /K_t , C_M) needed for grafting onto *H. sabdariffa* backbone. Pg of 138.52 has been found in case of MA + VA binary mixture which is due the monomer reactivity ratio (r_1:r_2) between MA and VA of 0.8 : 0.23 therefore, it is quite evident that Pg should be higher which is further supported by high transfer rate constant of the free radical (C_M)(1.45 x 10^4, 2.4 x 10^4, 10.7 x 10^4), high propagation to termination ratio (K_p/K_t) value [37.2 x 10^6 (25^{0}C), 13.4 x 10^6 (35^{0}C), 22.6 x 10^6 (50 ^{0}C)] (Table 2). However many other factors also determine the graft yield like the type of fiber, swelling, number of active sites, the nature and amount of the solvent and temperature of polymerization strongly influence the reactivity ratios. In absence of monomer rich phase, the diluents will compete with the monomers for adsorption sites. The amount of adsorption will depend upon the total amount of surface area present and this in turn, is dependent upon the rate of stirring. Physical factors like mixing efficiency determines the melt temperature, the pressure, the rheological properties, solubility of the initiator and the monomer. Elevated temperature favors the degradation, reduces the initiator half life, modifies the rate or specificity of the reaction, influences the solubility and rheological parameters [8-11].

Characterization

FTIR and SEM

FTIR spectrum of the *H. sabdariffa* showed a broad peak at 3424.0 cm^{-1} (–OH group) and peaks at 2924.7 cm^{-1}, 1246.9 cm^{-1} and 1032.0 cm^{-1} were observed due to $–CH_2$, C-C and C-O stretching, respectively. However, in case of *Hs*-g-poly(MA) an additional peak (due to >C=O groups) at 1738.0 cm^{-1} was witnessed whereas, a significant peak at 1635.4 cm^{-1} (vinyl group) in *Hs*-g-poly(MA-co-VA) was observed [1].

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

X-ray Diffraction Studies

The raw fiber and the graft copolymers obtained during synthesis of *Hs*-g-poly(MA) and *Hs*-g-poly(MA-co-VA) with Pg: 17.80, 34.50, 60.24, 96.16 & 138.52 (Table 1,2) were analyzed under ambient condition. It is evident from Table 3 and Figure 2 that with increase in Pg, there has been a constant decline in % Cr and C.I. Cellulosic fiber possesses both crystalline and amorphous regions. The x-ray pattern of the crystalline polymer shows sharp peaks associated with the region of three dimensional order and the diffused features are characteristics of the molecularly disordered substances coexisting within itself. Lower crystallinity means higher amorphous content that may be more accessible to chemicals and water. 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. However, if crystallinity is not affected on grafting then continuous increase in strength can be obtained with Pg. The X-ray spectrum of raw fiber is more complex than that of graft copolymers. In case of raw *Hibiscus sabdariffa* fiber the % Cr and C.I. are higher and the incorporation of the monomer chains to the back-bone impairs the crystallinity. Therefore, on grafting the percentage crystallinity decreases rapidly with reduction in its stiffness and hardness (Table 3, Figure 2). Crystallinity index gives a quantitative measure of the orientation of the cellulose crystals in the fibers. A lower crystalline index in case of graft co-polymers means poor order of arrangement of cellulose crystals in the fiber, that is due to dis-orientation of the cellulose crystalline lattice to the fiber axis during grafting. However, the cellulosic form I remained unchanged [1, 5, 11, 12].

Table 1 Optimization of reaction parameters for graft copolymerization of MA onto *H. sabdariffa*

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

where, CAN= Ceric ammonium nitrate, SD = standard deviation, SE = standard error.

Table 2. Effect of the binary mixtures on Pg using MA as a principal monomer

Sample	Binary mixture (x 10^{-3}mole L^{-1})	Mean Pg	±SD	±SE
Hs-g-poly (MA+VA)	2.21+2.16	113.40	±5.36	±3.09
	2.21+2.70	120.00	±7.15	±4.13
	2.21+3.24	138.52*	±5.59	±3.23
	2.21+3.78	96.16	±5.36	±3.09
	2.21+4.32	61.04	±1.78	±1.02

where, refers to the effective Pg.*

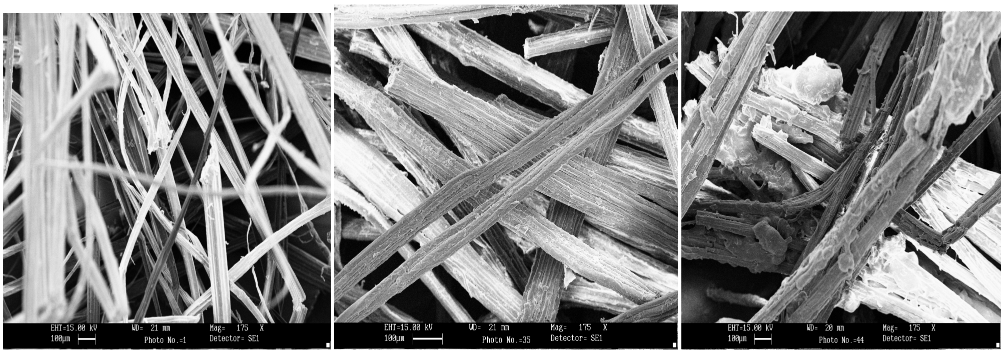


Fig. 1a **Fig. 1b** **Fig. 1c**

Fig. 1 SEM of (a) Raw *Hibiscus sabdariffa* (b) *Hs*-g-poly(MA); Pg: 60.24 (c) *Hs*-g-poly(MA-co-VA); Pg: 138.5

Table 3 The % Cr and C. I. of the *H. sabdariffa* fiber and its graft copolymers

		2θ Scale			
Sample	**Pg**	**I_{15}**	**$I_{22.68}$**	**%Cr**	**C.I.**
H. sabdariffa	-	40	136	77.20	0.70
Hs-g-poly(MA)	60.24	31	68	68.68	0.54
Hs-g-poly(MA-co-VA)	138.52	8	12	60.00	0.33

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

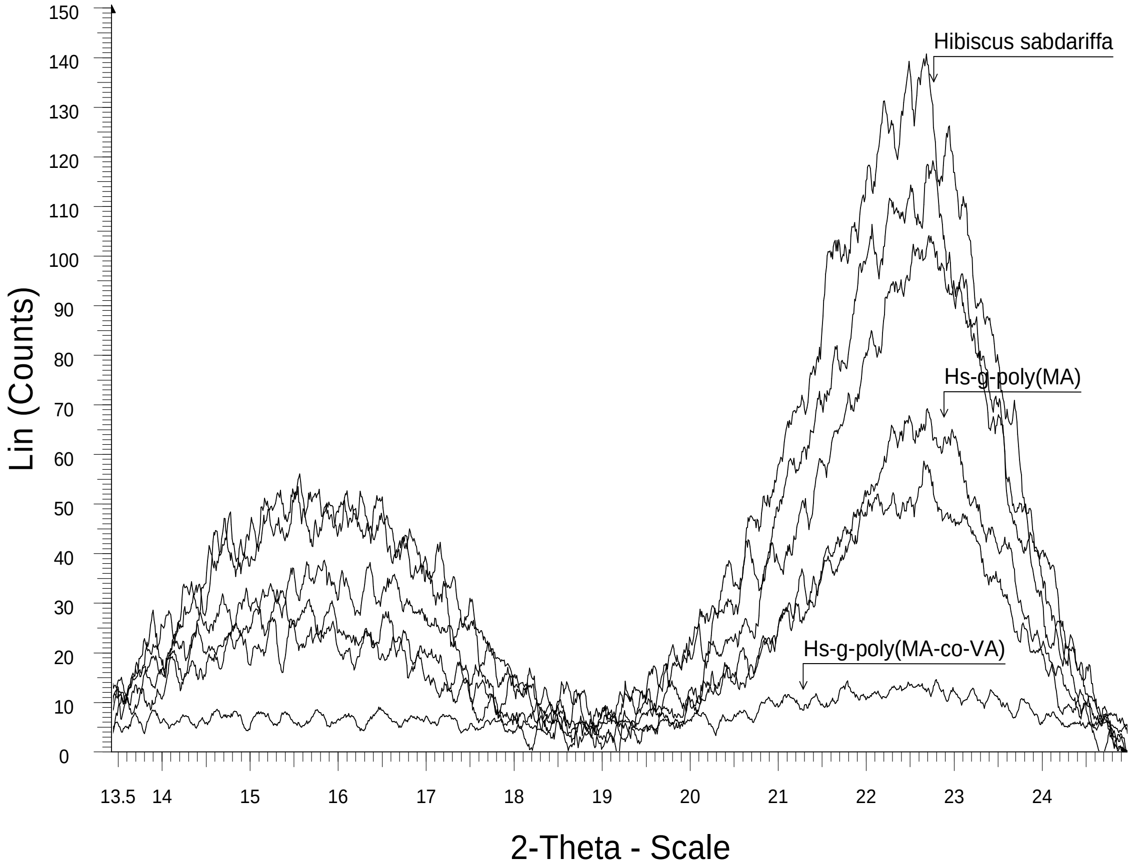


Figure 2 The XRD overlay of *Hibiscus sabdariffa* and its graft copolymers

TG-DTA studies

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

The degradation occurs in various forms like dehydration, decarboxylation and chain scissions. In case of raw fiber, both initial decomposition temperature (IDT) and final decomposition temperature (FDT) are lower (225.7 °C and 463.0 °C, respectively) as compared to those of graft copolymers. In case of *H. sabdariffa,* two-stage decomposition has been found, the former stage is attributed to loss by dehydration, volatilization whereas, the later stage is attributed to loss by depolymerization, delignification and oxidation of the char. Graft copolymers showed two stage decomposition. The first stage refers to the loss of moisture, decarboxylation and chain scissions while the second stage pertains to the breaking up of covalent bonds that has raised the FDT. Thus, it is evident from the TGA data that grafted fiber is thermally more stable than the raw fibers. This may be due to the incorporation of poly(vinyl) chains on backbone polymer either through covalent bonds or mechanically, confirming the additional strength to the fiber (Table 4, Figure 3-5) [1, 13,14].

In DTA studies, *H. sabdariffa* has been found to exhibit two major exothermic peaks whereas, graft copolymers exhibited some minor and major exothermic peaks. The first and second transition peaks revealed the dehydration, adsorption and oxidation of the semi-crystalline host and the major peak signifies the fusion and irreversible dissociation of the crystallites. Moreover, most of the hydroxyl groups of the native form have been replaced by the covalent bonds resulting in increased thermal resistance (Table 4, Figure 3-5) [1, 13,14].

Table 4 TG-DTA of *H. sabdariffa* and its graft copolymers

Graft copolymer		**TGA**			**DTA**
Hs-g-poly-	**Pg**	**IDT**	**FDT**	**% Residue left**	**Peaks in ^{0}C(μV)**
H. sabdariffa	-	225.7	463.0	20.00	139.7 (6), 327.9 (18.0), 422.7 (14)
(MA)	60.24	294.5	480.5	01.00	150.2 (8), 332.4 (9.8), 409.6 (37.9)
(MA-co-VA)	138.5	289.4	540.0	16.66	146.9(8), 347.2(22), 393.9(28.5)

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

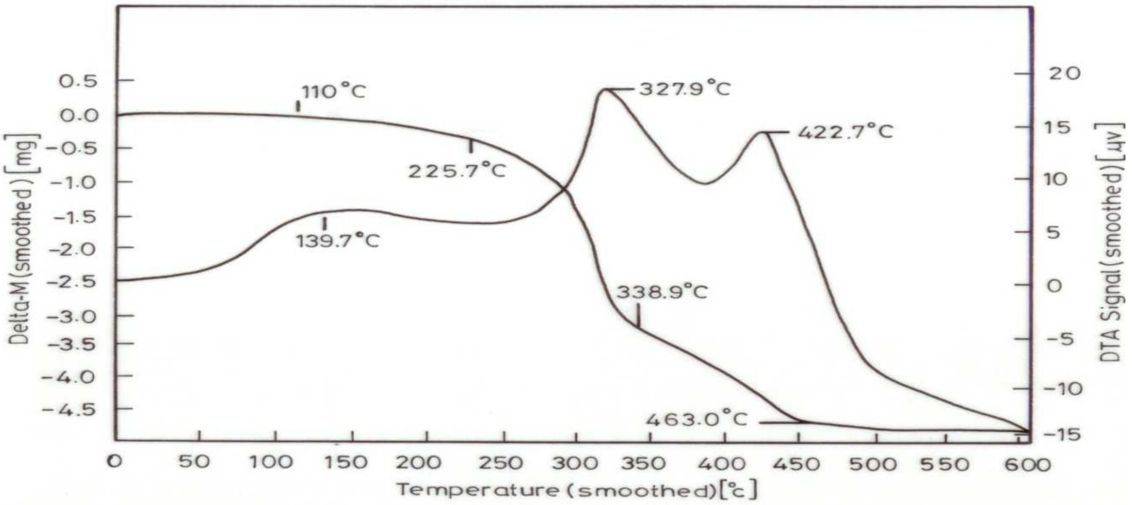


Fig.3. TG-DTA of raw *H. sabdariffa*

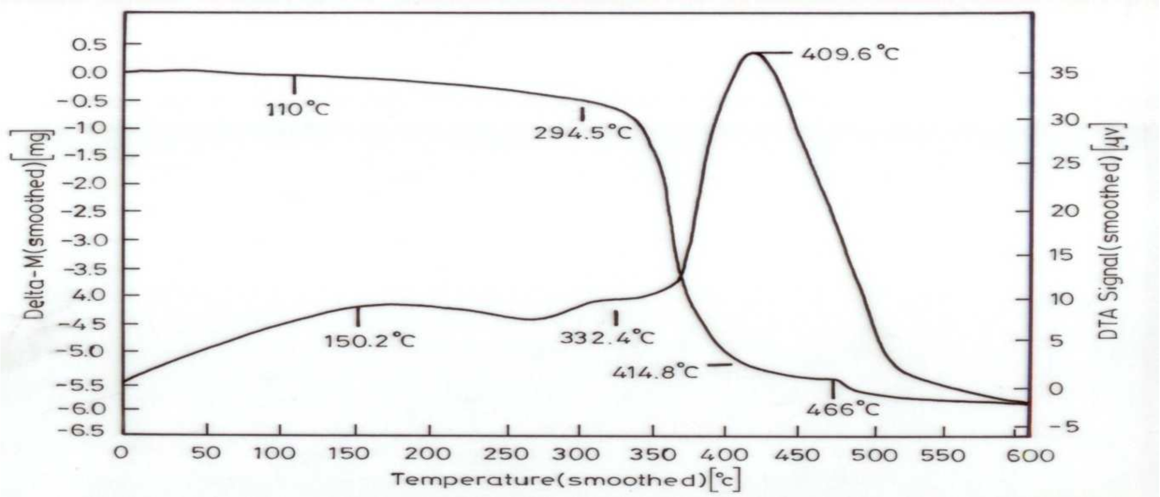


Fig. 4. TG-DTA of *Hs*-g-poly(MA); Pg: 60.24

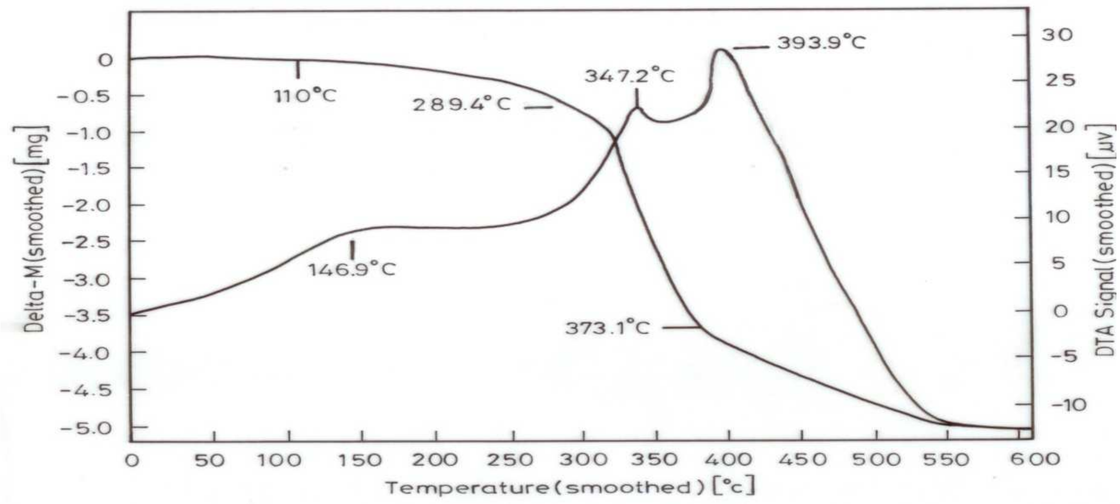


Fig. 5. TG-DTA of highest grafted *Hs*-g-poly(MA-co-VA); Pg:138.5

CONCLUSION

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

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