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Advances in Applied Science Research, 2013, 4(6):41-51

ISSN: 0976-8610
CODEN (USA): AASRFC

Synthesis and characterization of graft copolymers of mulberry silk fiber with vinyl binary monomers

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ABSTRACT

Binary monomer mixtures of Acrylamide (AAm) and Vinyl acetate (VAc) with methyl methacrylate (MMA) as the principal monomer were grafted onto Mulberry silk fiber in an aqueous medium by using ceric ammonium nitrate (CAN) as redox initiator. The binary vinyl monomer were graft copolymerized by using the optimum grafting conditions as reported earlier for MMA alone onto the same backbone. The evidence of grafting was obtained from FTIR, TGA and SEM. Moisture absorbance and chemical resistance in acidic and alkaline medium were studied for graft copolymers.

Key words: Binary monomers, Grafting, moisture absorbance

INTRODUCTION

Among the methods of modification of polymers, grafting is one of the promising methods to impart a variety of functional groups to a polymer. Chemical modification of natural fibers through graft copolymerization is an effective method to incorporate useful properties to the main polymer backbone, and these are useful in many applications in diverse fields [1-5]. Silk is one of the most ubiquitous natural polymers. Graft copolymerization of vinyl monomers [6-14] onto the polymeric backbones improves their chemical resistance, moisture repellency, solvent resistance and dye uptake. In literature a number of initiators like ceric ammonium nitrate (CAN) [15], benzoyl peroxide (BPO) [16], $KMnO_4$-oxalic acid redox initiator [17,18], potassium peroxydiphosphate-cysteine (PP-Cys) redox initiator [19] and acetylacetonate oxovanadium (IV) complex [20] were reported for graft copolymerization of methyl methacrylate (MMA) onto silk fibers.

In the present study we modify mulberry silk fibers through grafting of binary vinyl monomers of MMA to impart different physical and chemical properties.

MATERIALS AND METHODS

Materials

Mulberry silk (origin Assam, India) was purchased from market. Methyl methacrylate (Merck) was purified by washing with 5% NaOH and subsequent drying over anhydrous Na_2SO_4 followed by distillation. AAm and VAc (Merck) and ceric ammonium nitrate (CAN) and HNO_3 (S.D. fine Chemicals, India), Gentian violet (Nice Co., India), were used as received.

Graft Copolymerization

Graft copolymerization of MMA onto silk was reported earlier [21]. 0.5 g of silk fiber was immersed in 100 mL distilled water for 24 h prior to graft copolymerization in air. To this known amount of (initiator) ceric ammonium nitrate, nitric acid and MMA were added. The reaction was stirred constantly for 120 min. Each reaction condition was varied keeping other conditions constant at a time to get optimum grafting conditions. The graft copolymer was separated from the homopolymer or the ungrafted copolymer by the extraction in a soxhlet using acetone. The graft copolymers were dried at 50°C to a constant weight. At these optimum reaction conditions for unitary monomer system (MMA) onto silk, binary monomer mixtures of MMA were co-grafted with MMA at five different concentrations of the comonomers (CM) AAm and VAc. Results have been depicted in Table 1. The percent grafting (P_g) and percent grafting efficiency (% GE) were calculated as follows [22].

$$P_g = \frac{\text{Weight of graft copolymer - weight of polymer backbone}}{\text{Weight of polymer backbone}} \times 100$$

$$\%\,GE = \frac{\text{Weight of graft copolymer - weight of polymer backbone}}{\text{Weight of monomer charged}} \times 100$$

Characterization:

Graft copolymers were characterized by FTIR, SEM and TGA. IR spectra of the silk fiber and graft copolymers were recorded in KBr pellets in Thermo Nicolet 6700 spectrometer. SEM were taken on Jeol, JSM-6100 at an accelerating voltage of 20 kV. Thermal analysis was done on Shimadzu DTG-60; simultaneous TG/DT model.

Moisture Absorbance, Wet-ability and Chemical Resistance

Moisture absorbance was determined by the method reported in the earlier work [21,23]. Small wicks of the grafted and ungrafted fibers of diameter 5 mm were prepared and initial mark with ink pen was put on the thread and then dipped in to a beaker containing water through capillary action in each fiber wick was noted down at different time intervals and then percent wet-ability (%W) was calculated as [23]:

$$\%W = \frac{L_f - D_w}{L_f} \times 100,$$

Where L_f and D_w are total length of fiber and distance traveled by the water, respectively. To study the chemical resistance, 100 mg of the grafted and ungrafted fiber were put in 100 mL of 1*N* NaOH and 1*N* HCl. The loss in weights was studied at different time intervals and the % chemical resistance (%CR) was calculated as [23]:

$$\%CR = \frac{W_f - W_{ft}}{W_{f0}} \times 100,$$

Where, W_f and W_{ft} are total weight of fiber and weight after certain intervals, respectively.

RESULTS AND DISCUSSION

Silk contains several functional groups. These groups act as active sites for the graft copolymerization of vinyl monomers. The mechanism of grafting onto silk fiber in the presence of CAN with MMA as monomer is reported earlier [23].

$$\sim\text{HN}-\text{Silk}-\text{CO}\sim + \text{Ce}^{4+} \rightarrow \text{Complex} \rightarrow \sim\text{HN}-\text{Silk}^{*}-\text{CO}\sim + \text{Ce}^{3+} + \text{H}^{+} \qquad (1)$$

$$\sim\text{HN}-\text{Silk}^{*}-\text{CO}\sim + \text{M} \rightarrow \sim\text{HN}-\text{Silk}-\text{CO(M)}^{*} \qquad (2)$$

$$\sim\text{HN}-\text{Silk}-\text{CO(M)}^{*} + \text{nM} \rightarrow \sim\text{HN}-\text{Silk}-\text{CO(M)}_n-\text{M}^{*} \qquad (3)$$

$$\sim HN{-}Silk{-}CO(M)_n{-}M^* + Ce^{4+} \rightarrow \sim HN{-}Silk{-}CO(M)_{n+1} + Ce^{3+} \quad (4)$$

Graft Copolymer

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

$$M^* + nM \rightarrow (M)^*_{n+1} \quad (6)$$

$$(M)^*_{n+1} + (M)^*_{n+1} \rightarrow 2(M)_{n+1} \quad (7)$$

Homopolymer

where, Silk is presented as polypeptide and M = monomer. In the case of grafting of binary monomer mixture, the M in the radicals or homopolymer or graft copolymers can be substituted by $(M_1)_m(M_2)_n$, where M_1 is MMA and M_2 is AAm or VAc and m or n is the amount of resepctive component which varies as per the monomer reactivity ratio of M_1 or M_2.

Optimization of different reaction parameters

The maximum P_g (74.4) in the case of MMA onto silk fibers alone was observed [21] at the optimum reaction conditions at 2.94 × 10^{-3} mol/L of MMA, 1.75 × 10^{-4} mol/L of CAN, and at 55°C and 120 min. At the optimum reaction conditions evaluated for the grafting of MMA alone, comonomers AAm and VAc were incorporated along with MMA onto silk backbone polymer at five concentrations of the comonomers.

Table 1: Grafting of binary vinyl monomers onto silk fiber

S. No.	Binary Monomer Mixture × 10^{-3} (mol/L)	[CAN] × 10^{-4} (mol/L)	[HNO_3] × 10^{-3} (mol/L)	Time (min)	Temp. (°C)	P_g	% GE
	(MMA + AAm)						
1.	2.94+0.79	1.75	5.13	120	55	73.93	6.45
2.	2.94+1.19	1.75	5.13	120	55	78.37	6.37
3.	2.94+1.58	1.75	5.13	120	55	53.03	4.04
4.	2.94+1.98	1.75	5.13	120	55	50.17	3.59
5.	2.94+2.37	1.75	5.13	120	55	46.17	3.12
	(MMA + VAc)						
1.	2.94+0.54	1.75	5.13	120	55	66.17	5.83
2.	2.94+1.08	1.75	5.13	120	55	76.47	5.92
3.	2.94+1.62	1.75	5.13	120	55	102.67	7.10
4.	2.94+2.16	1.75	5.13	120	55	77.80	4.86
5.	2.94+2.70	1.75	5.13	120	55	52.90	3.01

[a]*Silk fiber = 0.5g*

Effect of concentration of binary monomers onto P_g & %GE

Binary mixtures of MMA with three other vinyl monomers, AAm, VAc or 4-VPy were separately grafted onto silk fiber. In the case of co-grafting of AAm, P_g increased from 73.93 to 78.37 with increase in concentration of AAm from 0.79 × 10^{-3} mol/L to 1.19 × 10^{-3} mol/L and then decreases with further increase of AAm concentration upto 2.37 × 10^{-3} mol/L (Table 1). In case of grafting of VAc with MMA concentration of VAc was varied from 0.54 to 2.70 × 10^{-3} mol/L. Maximum P_g (102.67) and %GE (7.10) was observed at 1.62 × 10^{-3} mol/L of VAc (Table 1). But with further increase in concentration of VAc up to 2.70 × 10^{-3} both P_g and %GE decreases. From the perusal of the results presented in Table 1, it is apparent that VAc proved to be the better compatible monomer with MMA, as the maximum P_g as well as % GE were obtained.

Characterization:

Fourier transform infrared spectroscopy:

FTIR of silk is characterized by absorption bands at 3418.8cm^{-1} for N-H stretching. Figure 1a shows characteristic absorption bands at 1644.5 cm^{-1}, 1553.3 cm^{-1}, 1220.6 cm^{-1} and 1043.2 cm^{-1}, which are assigned to β-sheet structure. Figure 1b shows clear absorbance at 1736 cm^{-1}, which is attributed to the carbonyl group of the side chain of the

MMA polymer present in the silk fibre and absorbance at 1147 cm^{-1} is because of C-N of AAm. Absorbance at 1449.8 cm^{-1}, 1383.5 cm^{-1} and 1058.8 cm^{-1} are because of VAc (Figure 1c).

Scanning electron microscopy:

Scanning electron micrographs (SEM) of silk and different graft copolymers are presented in figures 2a–2c. SEM of un-grafted silk is presented in fig. 2a. SEM of the silk-g-poly(MMA) alone and its binary monomer systems with AAm and VAc (figures 2b-2c) showed clear deposits of the graft copolymers on the silk fibre.

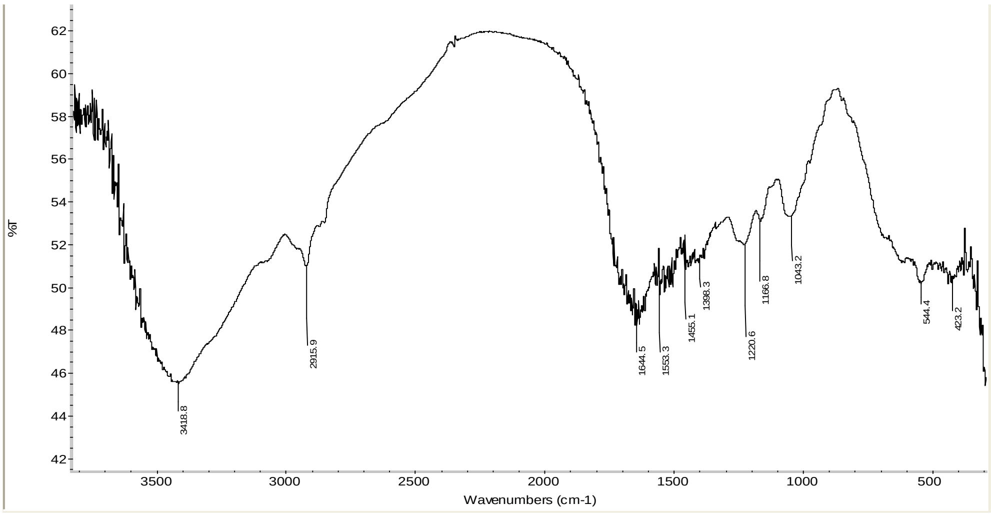

Figure 1a: FTIR of ungrafted silk

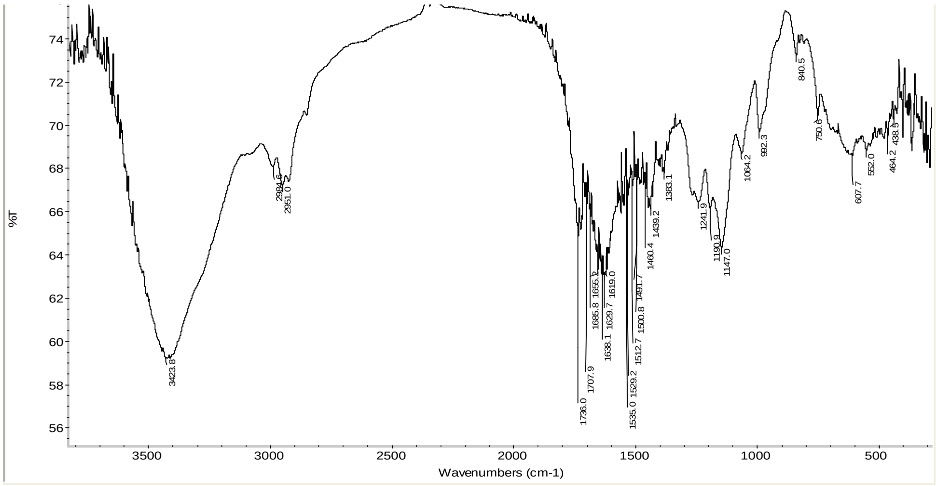

Figure 1b: FTIR of silk-g-poly(MMA-co-AAm)

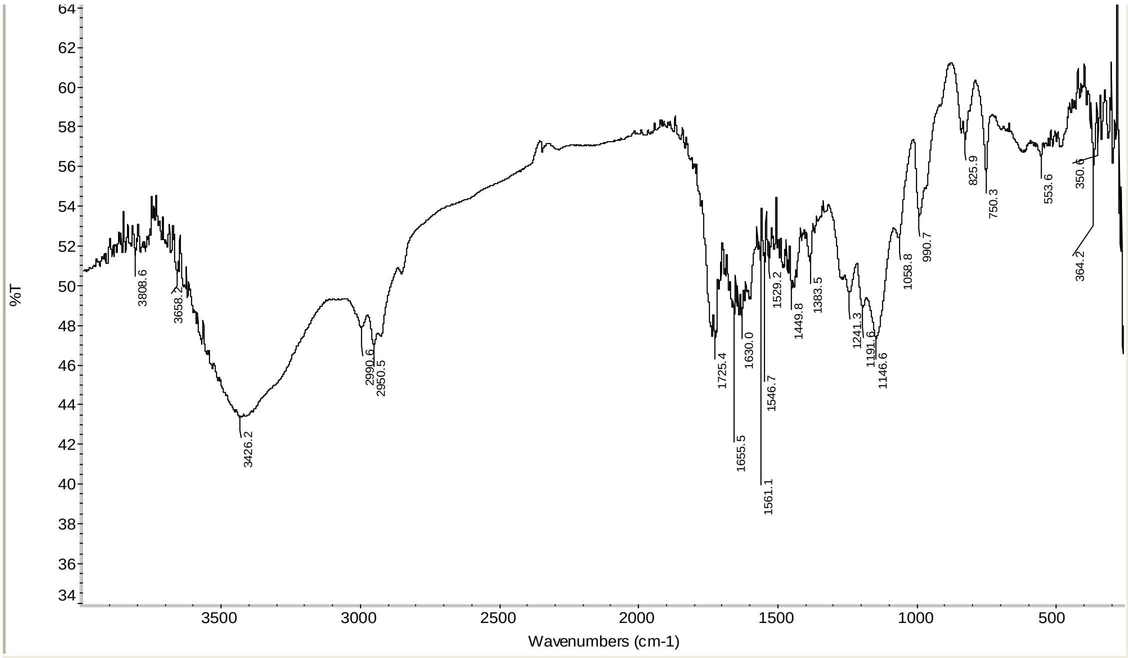

Figure 1c: FTIR of silk-g-poly(MMA-co-VAc)

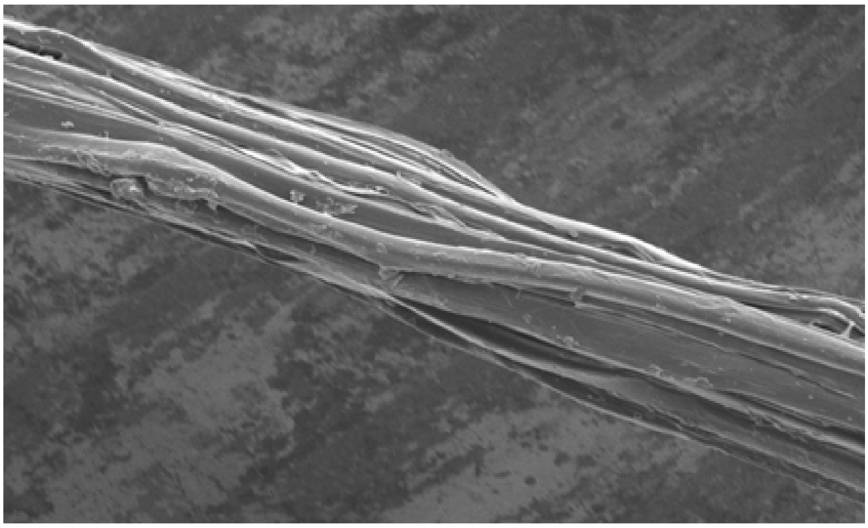

Figure 2a: SEM of ungrafted silk

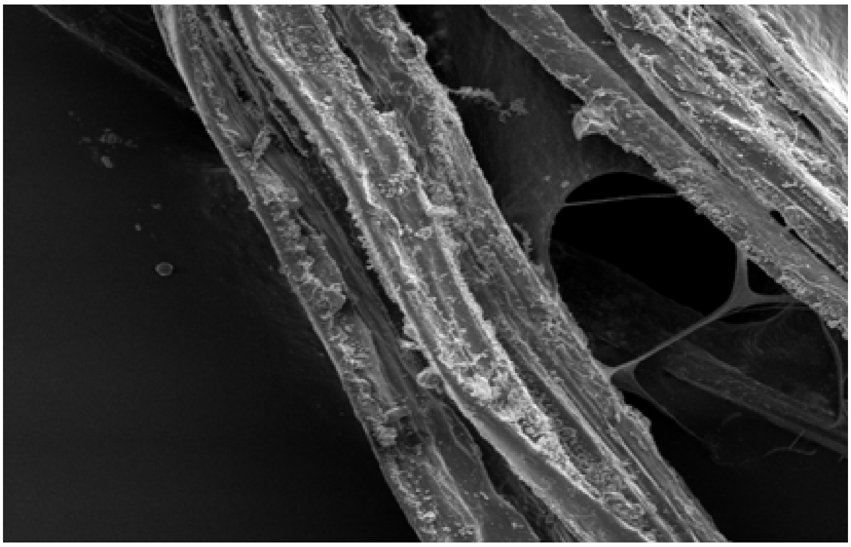

Figure 2b: SEM of silk-g-poly(MMA-co-AAm)

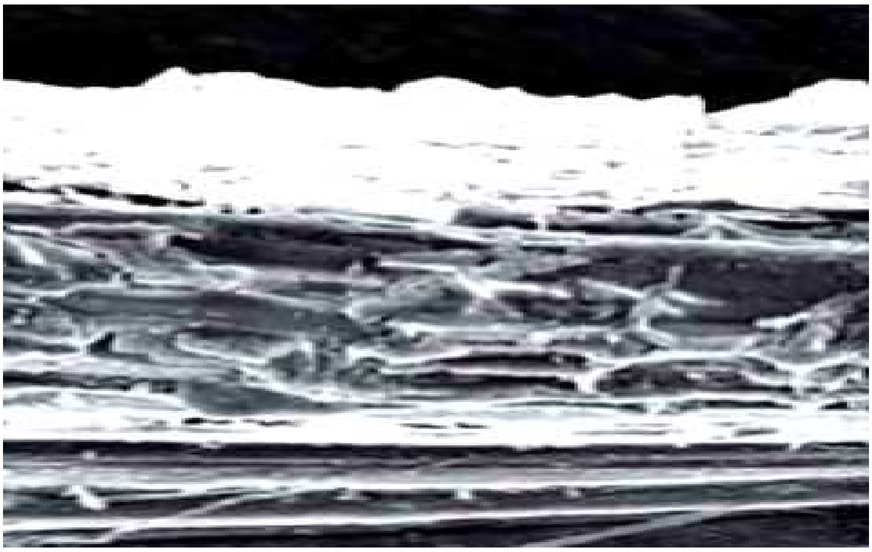

Figure 2c: SEM of silk-g-poly(MMA-co-VAc)

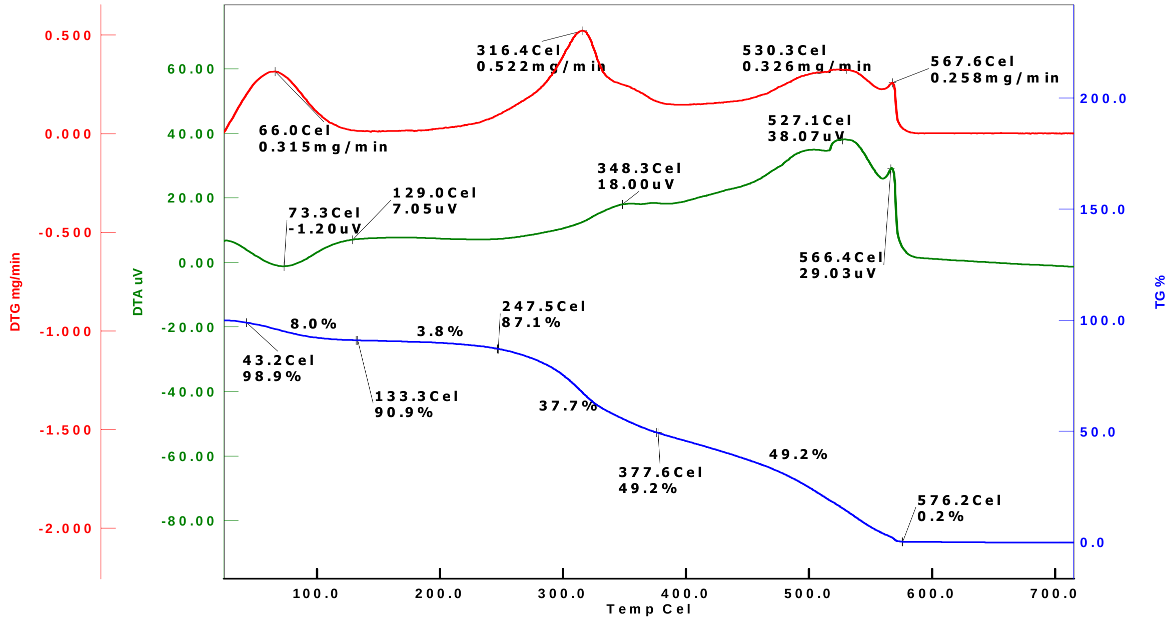

Figure 3a: Thermogravimetric analysis of ungrafted silk

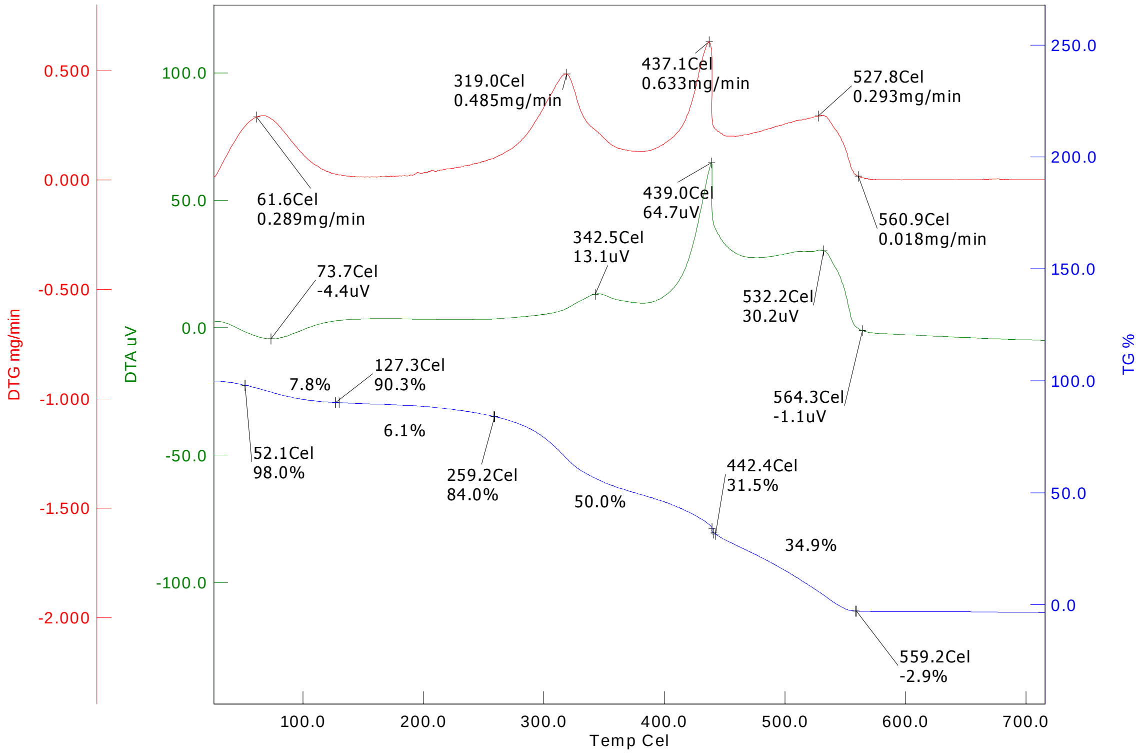

Figure 3b: Thermogravimetric analysis of silk-g-poly(MMA-co-AAm)

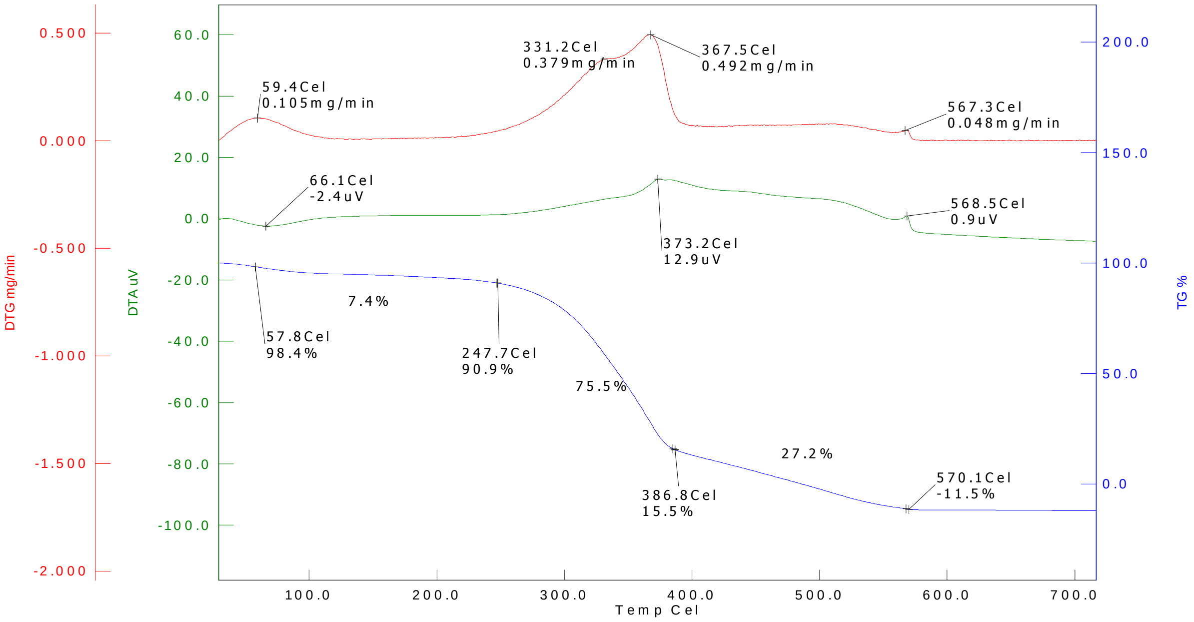

Figure 3c: Thermogravimetric analysis of silk-g-poly(MMA-co-VAc)

Thermogravimetric analysis:

In an attempt to unravel the pyrolytic behaviour of a complex material including silk fibre and graft copolymers are investigated by thermal analysis methods to show how the grafting affect the thermal properties of original silk fibre. Dynamic thermal analysis methods including differential thermal analysis (DTA) and thermogravimetric analysis (TGA) are used for detecting and measuring the sequence and extent of physical transition and chemical transformations. From figure 3a it is clear that ungrafted silk has single stage thermal degradation from 43.2°C to 576.2°C. Maximum weight loss (37.7%) was observed from 247.5^{O}C to 377.6°C. Figure 3b represent the thermal degradation of silk grafted with MMA-co-AAm in which 50% weight loss is observed from 259.2°C to 442.4°C, that may be because of degradation of grafted side chain. Maximum weight loss of 75.5% was observed from 247.7^{O}C to 386.8°C in thermogravimetric analysis of silk grafted with MMA-co-Vac which explains the thermal instability of grafted sample. Ungrafted silk show one exothermic peak at 316.4°C in DTA (figure 3a), where as grafted samples show two exothermic peaks in their DTA which clearly indicate the change in thermal behaviour of silk after grafting.

Moisture observance of Graft Copolymers

The moisture retention behavior of the graft copolymers was studied and results are presented in Figures 4a & 4b. The moisture uptake by the graft copolymers is far more than reported earlier for the graft copolymers of MMA only [21]. The moisture absorption decreased with an increase in the P_g due to the occupancy of the active site of the silk fiber. Since the moisture retention by the graft copolymers is low, hence the grafting of the binary monomer system with MMA as one of the component imparted moisture resistance to the copolymers.

Chemical Resistance of Graft Copolymers

The weight loss of the graft copolymers was less than that of the ungrafted fiber. It was also less than that of the graft copolymers of MMA alone [21]. All the graft copolymers exhibited good stability in the acidic medium, while most of these readily degraded in the alkaline medium (Figures 5a & 5b). Further, the degradation behavior was also specific to the graft copolymers as those having poly(VAc) as one of the component are more stable to the alkaline hydrolysis than those having poly(AAm), and the later readily hydrolyzes in the presence of alkali.

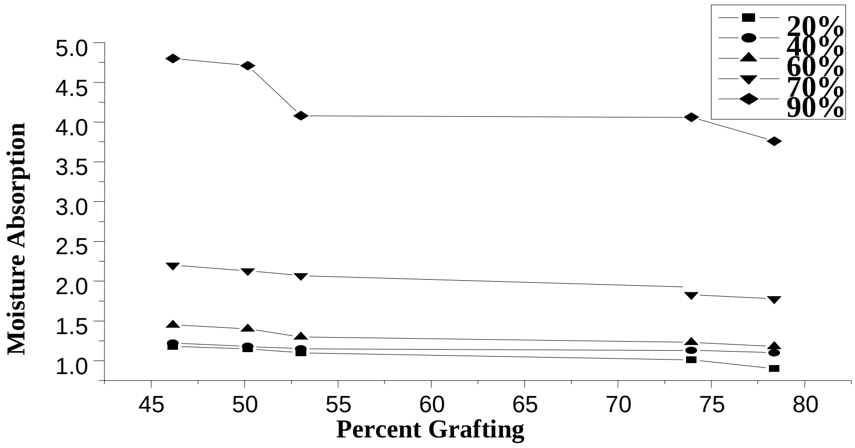

Figure 4a: Moisture Absorbance of silk-g-poly(MMA-co-AAm)

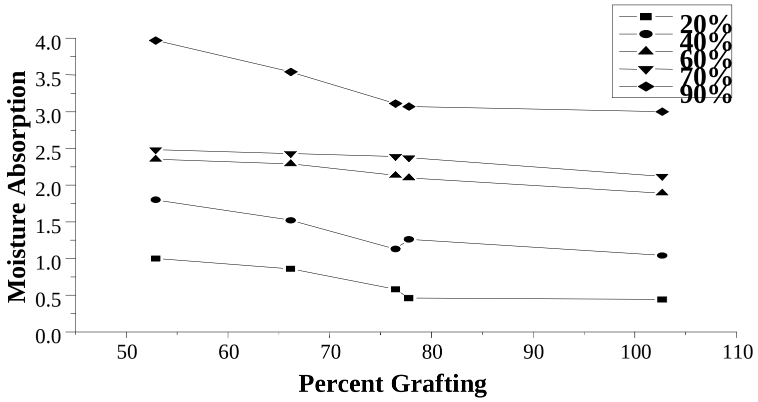

Figure 4b: Moisture Absorbance of silk-g-poly(MMA-co-VAc)

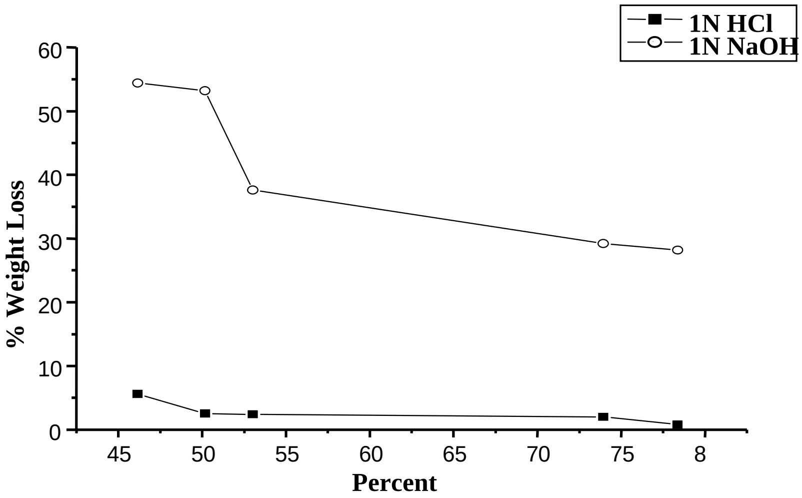

Figure 5a: Chemical Resistance of silk-g-poly(MMA-co-AAm)

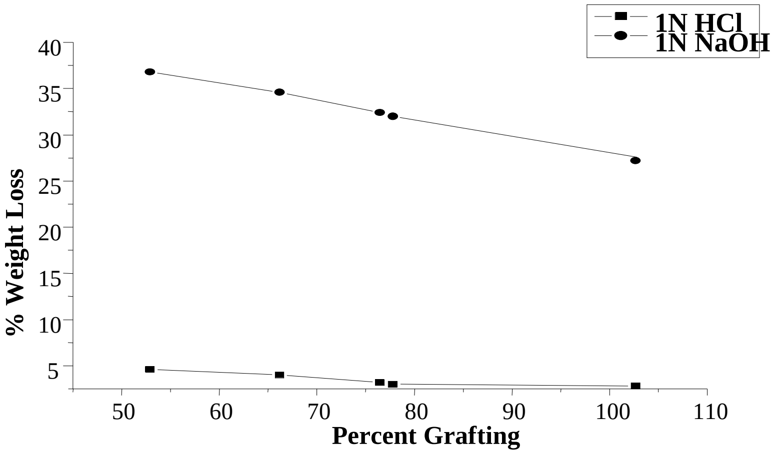

Figure 5b: Chemical Resistance of silk-g-poly(MMA-co-VAc)

CONCLUSION

The graft copolymerization of the binary mixture of two vinyl monomers separately with methyl methacrylate on to mulberry silk fiber was studied at the pre-determined optimum conditions obtained for the maximum grafting for methyl methacrylate alone. It follows from the results obtained that the nature of the monomers acts as determinant of the graft yield and grafting efficiency as both the hydrophobic monomers (VAc) exhibited more efficiency than the other monomer (AAm). Graft copolymers are characterized by physics-chemical spectroscopic methods. The properties like moisture absorption and chemical resistance was observed to vary with the graft yield or percent grafting. It was also observed that higher percent grafting of the binary mixture of vinyl monomers also improved chemical resistance towards alkali and acids. Thus, the present study was a successful attempt to improve the properties of the native silk fiber like chemical resistance and moisture absorption resistance those are useful in widening its use-spectrum in textile as well as biomedical applications.

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