



Grafting of binary mixtures of methyl methacrylate and some vinyl monomers onto mulberry silk fibre: Synthesis, characterization and preliminary investigations into gentian violet uptake by graft copolymers

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ABSTRACT

Mulberry silk fibre was graft copolymerized with binary mixtures of acrylic acid, methyl acrylate and acrylonitrile with methyl methacrylate as the principal monomer in aqueous medium by using CAN as redox initiator. The binary vinyl monomers were graft copolymerized by using the grafting conditions like reaction time, temperature, concentration of MMA and CAN as reported earlier for optimum percent grafting (74.40) of MMA alone onto the same backbone. Graft copolymers were characterized by FTIR, SEM, swelling studies, moisture absorbance and chemical resistance in acidic and alkaline medium. Dye uptake (Gentian violet) on graft copolymers were studied photo-calorimetrically at 420 nm. The dyeing capability of the graft copolymers with binary mixture is more than the reference graft copolymer of methyl methacrylate.

Keywords: Mulberry silk fibre, Graft copolymer, CAN, FTIR, Gentian violet dye.

INTRODUCTION

Chemical modification of natural fibres 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]. The natural polymers are vulnerable to degradation by acids, bases or water, which limit their application-spectrum, especially in harsh conditions. These limitations can be improved by graft copolymerization of vinyl monomers onto the polymeric backbones, which improves their chemical resistance, moisture repellency, solvent resistance and dye uptake. Silk is one of the most ubiquitous natural polymers. It finds applications in high-end textile products and also in the surgical applications. There are reports in literature where it has been modified by the graft copolymerization of different monomers [6-13]. Various initiators like ceric ammonium nitrate (CAN)[14], benzoyl peroxide (BPO)[15], KMnO_4 -oxalic acid redox initiator[16,17], potassium peroxydiphosphate-cysteine (PP-Cys) redox initiator[18] and acetylacetonate

oxovanadium (IV) complex[19] were reported for graft copolymerization of methyl methacrylate (MMA) onto silk fibres. The modified silk has been reported in various applications such as separation technologies [20], anti-bacterial agents[21] and biomaterials[22].

In order to improve the structural limitations of silk fibres and to enhance their use-spectrum in textile industries and biomedical fields, in this article we reported modification of mulberry silk fibre by grafting of binary vinyl monomer mixtures by initiation with ceric ammonium nitrate. The later is a redox initiator capable of initiating vinyl polymerization at low temperature with minimum side reactions; hence, it is suitable for initiating grafting of vinyl monomers onto mulberry silk fibre. There is scanty information on the graft copolymerization of vinyl monomers on to mulberry silk. In the present study we designed its modification through grafting using a hydrophobic monomer (MMA) or its binary mixture with hydrophilic (acrylic acid) or hydrophobic monomers (methacrylate and acrylonitrile) to impart different physical and chemical properties to the silk backbone. The grafting was studied using the optimum grafting conditions evaluated for the grafting of MMA alone onto the same backbone[23] by Kaith and et al. Preliminary investigations were also carried into the Gentian violet uptake by the graft copolymers. Gentian violet acts a bactericide and is an effective antifungal agent used for the treatment of serious heat burns and other injuries or fungal infection of the skin and gums. These graft copolymers have potential applications in textile industry, separation technologies and biomedical applications.

MATERIALS AND METHODS

Mulberry silk (origin Assam, India) was purchased from market. Methyl methacrylate (Merck) was purified by washing with 5% NaOH and subsequent drying over anhydrous Na₂SO₄ followed by distillation. Acrylic acid (AA), methacrylate (MA), acrylonitrile (AN) (Merck, US) and ceric ammonium nitrate (CAN) and HNO₃ (S.D. fine Chemicals, India), Gentian violet (Nice Co., India), were used as received.

Graft Copolymerization

Graft copolymerization of MMA onto silk was reported in our earlier publication [23]. 0.5 g of silk fibre was immersed in 100 mL distilled water for 24 hours prior to graft copolymerization in air. A known amount of (initiator) ceric ammonium nitrate, nitric acid and methyl methacrylate were added to it. The reaction was stirred constantly for 120 min. 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 at five different concentrations of the comonomers (CM) AA, MA and AN. Results have been depicted in Table 1. The percent grafting (P_g) and percent grafting efficiency (%GE) were calculated as follows[24].

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

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

Characterization of Silk and its Graft Copolymers

FTIR spectra of the silk fibre and graft copolymers were recorded in KBr pellets in Bomem Hartmann Braun (MB-series) spectrometer and Scanning electron micrographs (SEM) are taken on Scanning Transmission Electron Microscope Model JSM6100 (Jeol).

Swelling, Moisture Absorbance and Chemical Resistance

Swelling of the grafted and ungrafted fibres was determined by treating these with DMF, water, methanol and *n*-butanol as per the method reported earlier. Moisture absorbance was determined by the method reported in the earlier work [23]. To study the chemical resistance, 100 mg of the grafted and ungrafted fibre 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 [25,26]

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

Where, W_{f0} and W_{ft} are total weight of fibre and weight after certain intervals, respectively.

Dyeing behavior

In the dyeing experiments, 0.1% Gentian violet solution was prepared in distilled water and 10% common salt and a few drops of acetic acid were added to the solution. The fibre was immersed and the fibre to liquid ratio was maintained at 1:50. The samples were kept at room temperature (35 °C) for dye absorption. The optical densities of the solution were determined by using photo-colorimeter (model 313E from Environment & Scientific Instruments Co. India) at different time interval of 1, 2, 3, 4 and 5hrs, respectively. The concentration of each solution after dye uptake by the fibre and % transmittance (%T) was calculated as:

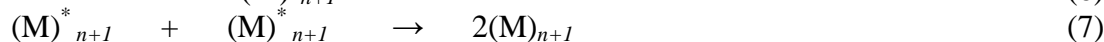
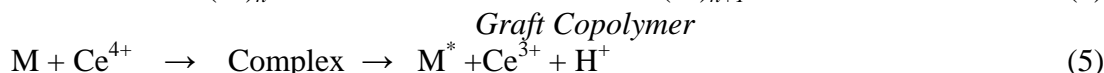
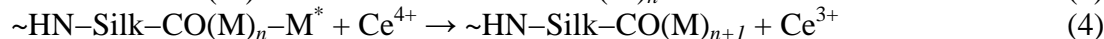
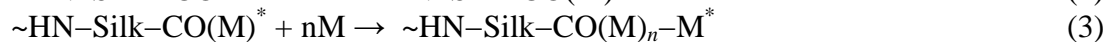
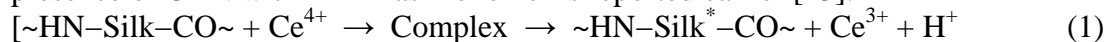
$$\text{Transmittance (T)} = \frac{I_i}{I_o} \times 100$$

$$\text{Concentration of rejected dye solution} = \frac{I_i}{I_o} \times \text{conc. of standard solution}$$

Where, I_i & I_o are optical density of rejected dye solution and standard solution, 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 fibre in the presence of CAN with MMA as monomer is reported earlier [23].



Graft Copolymer

Homopolymer

where, Silk is presented as polypeptide and M is 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 AA, MA or AN and m or n is the amount of respective component which varies as per the monomer reactivity ratio of M_1 or M_2 . Concentration of initiator and monomer, variation of time and temperature affect the graft yield as these factors determine the relative population of various radical species generated in different steps during the course of reaction.

Optimization of different reaction parameters

The maximum P_g (74.4) in the case of MMA alone onto silk was reported in our earlier publication [23], at the optimum reaction conditions i.e. 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 acrylic acid (AA), methyl acrylate (MA) and acrylonitrile (AN) are incorporated along with MMA onto silk backbone polymer at five concentrations of the comonomers.

Effect of concentration of binary monomer mixture on P_g

Binary mixtures of MMA with three other vinyl monomers, AA, MA and AN were separately grafted onto silk fibre. In the case of co-grafting of AA, P_g increased from 73.53 to 123.57 with increase in concentration of AA from 0.73×10^{-3} mol/L to 1.46×10^{-3} mol/L and then decreases with further increase of AA concentration upto 3.65×10^{-3} mol/L (Table 1). In case of grafting of MA with MMA maximum P_g (110.07) and %GE (9.66) was observed at 0.56×10^{-3} mol/L of MA (Table 1). But with further increase in concentration of MA both P_g and %GE decreases. In case of binary mixture of AN, with increase in concentration of AN from 0.76×10^{-3} mol/L to 3.04×10^{-3} mol/L maximum P_g (310.77) and %GE (20.49) were reported. But with increase in concentration of AN both P_g and %GE decreases (Table 1). From the perusal of the results presented in Table 1, it is apparent that AN proved to be the most compatible monomer with MMA, as the maximum P_g as well as % GE were obtained. These results are manifestation of the hydrophobic nature of the two monomers and formation of uniform monomer phase in the grafting system.

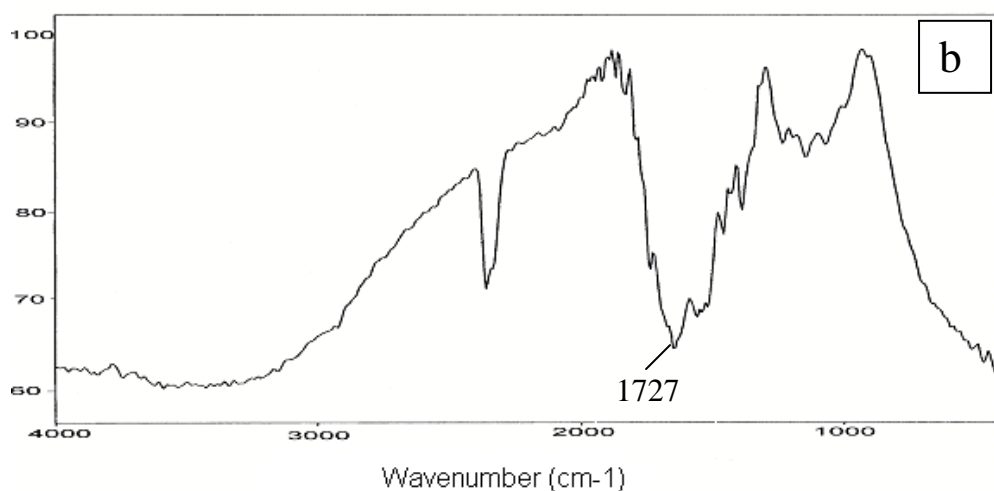
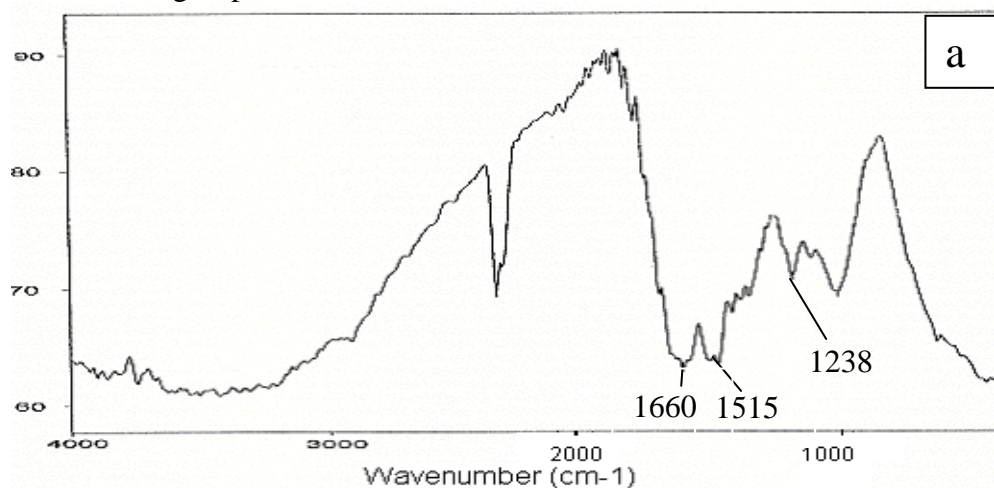
Table 1: Grafting Parameters of Graft Copolymerization of Binary Vinyl monomers onto Mulberry Silk Fibre

Sr. No.	Binary Monomer Mixture $\times 10^{-3}$ (mol/L)	[CAN] $\times 10^{-4}$ (mol/L)	[HNO ₃] $\times 10^{-3}$ (mol/L)	Time (min)	Temp. ($^\circ\text{C}$)	P_g	% GE
(MMA + AA)							
1.	2.94+0.73	1.75	5.13	120	55	73.53	6.37
2.	2.94+1.46	1.75	5.13	120	55	123.57	9.29
3.	2.94+2.19	1.75	5.13	120	55	121.4	8.07
4.	2.94+2.92	1.75	5.13	120	55	97.1	5.78
5.	2.94+3.65	1.75	5.13	120	55	96.2	5.73
(MMA + MA)							
1.	2.94+0.56	1.75	5.13	120	55	110.07	9.66
2.	2.94+1.11	1.75	5.13	120	55	65.5	5.20
3.	2.94+1.67	1.75	5.13	120	55	61.4	4.22
4.	2.94+2.22	1.75	5.13	120	55	39.6	2.45
5.	2.94+2.78	1.75	5.13	120	55	17.1	0.96
(MMA + AN)							
1.	2.94+0.76	1.75	5.13	120	55	153.57	13.78
2.	2.94+1.52	1.75	5.13	120	55	169.93	13.61
3.	2.94+2.28	1.75	5.13	120	55	179.86	13.00
4.	2.94+3.04	1.75	5.13	120	55	310.77	20.49
5.	2.94+3.80	1.75	5.13	120	55	287.36	17.41
6.	2.94+4.55	1.75	5.13	120	55	189.67	10.63

Silk fibre = 0.5 g, Temperature = 55°C and Time = 120 min.

FTIR spectroscopy

FTIR spectroscopy is useful in structural analysis of silk [27,28]. Figure 1a shows the infrared spectra of the un-grafted silk fibres. It shows characteristic absorption bands at 1660 cm^{-1} , 1515 cm^{-1} , and 1238 cm^{-1} , which are assigned to β -sheet structure. Figure 1b shows clear absorbance at 1727 cm^{-1} , which is attributed to the carbonyl group of the side chain of the MMA polymer present in the silk fibre. The band at $1350\text{--}750\text{ cm}^{-1}$ broadened as shown in figures 1b-1e that can be because of grafting onto silk fibre. The result is in accordance with Saikia's research using conventional method [17]. All these indicate the evidence that the MMA has grafted onto the silk fibre backbone. In case of FTIR of grafted binary monomer mixture of MMA-co-AN (Figure 1e) onto silk showed a peak at 2241 cm^{-1} because of $\text{--C}\equiv\text{N}$ functional group.



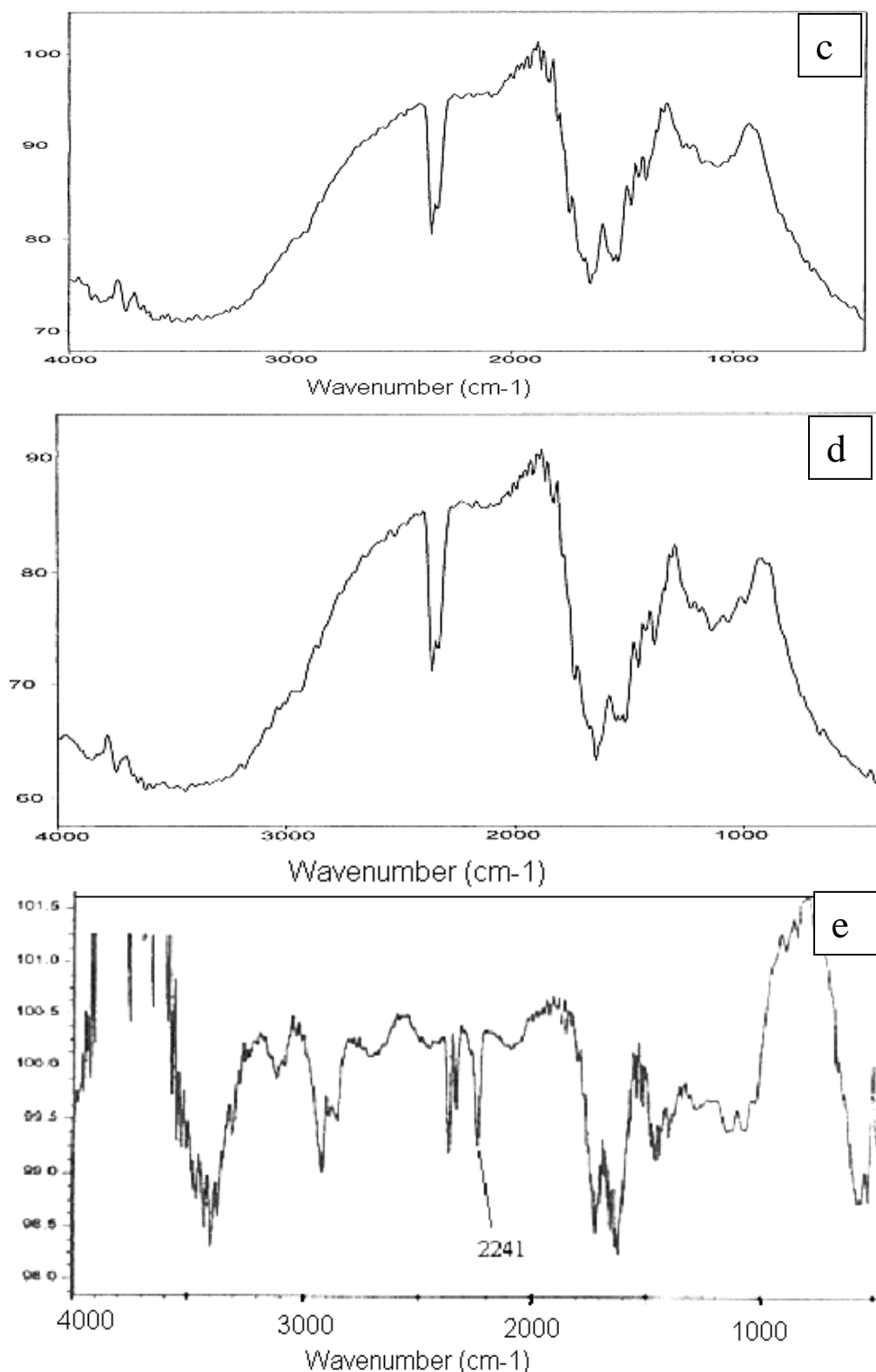
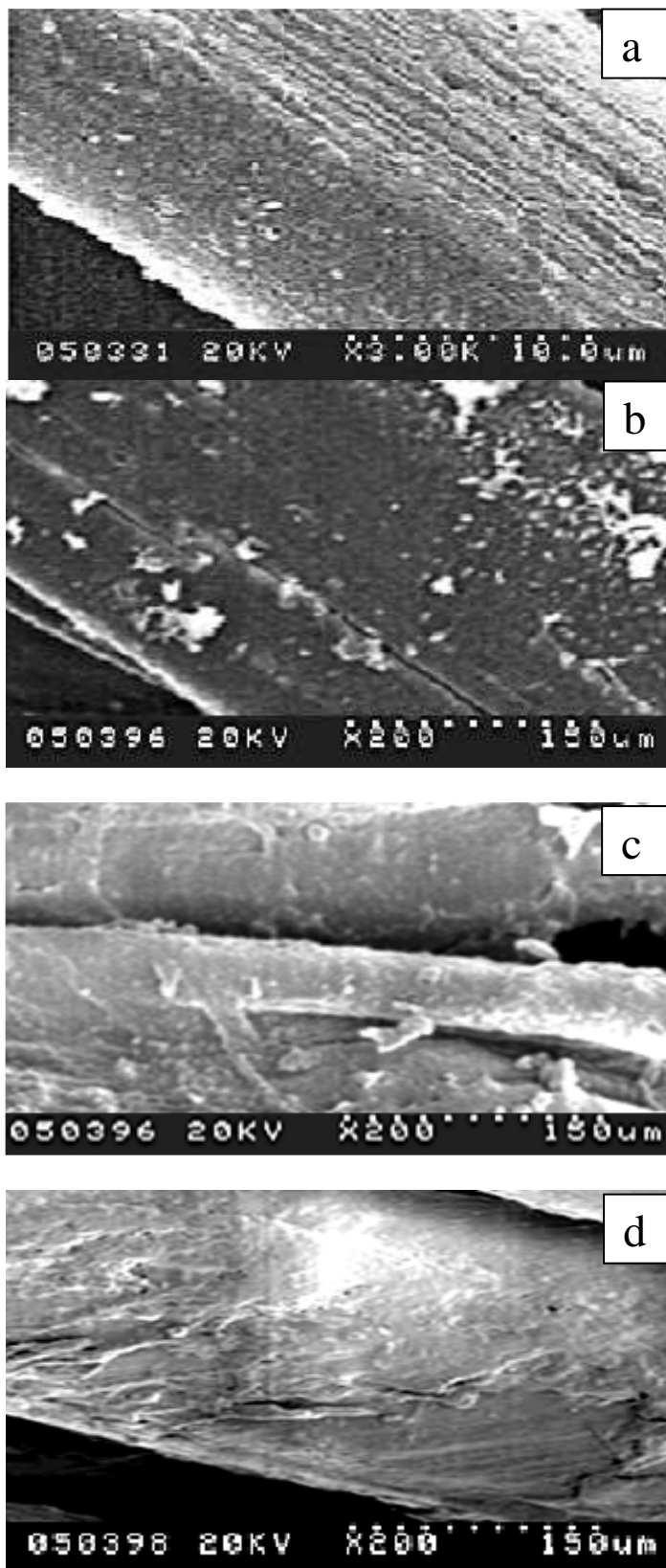


Fig. 1: FTIR spectra of a). Ungrafted Silk, b). Silk-g-MMA, c). Silk-g-MMA -co-AA d). Silk-g-MMA -co-MA, e). Silk-g-MMA -co-AN

Scanning Electron Microscopy of Silk and its Graft Copolymers

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



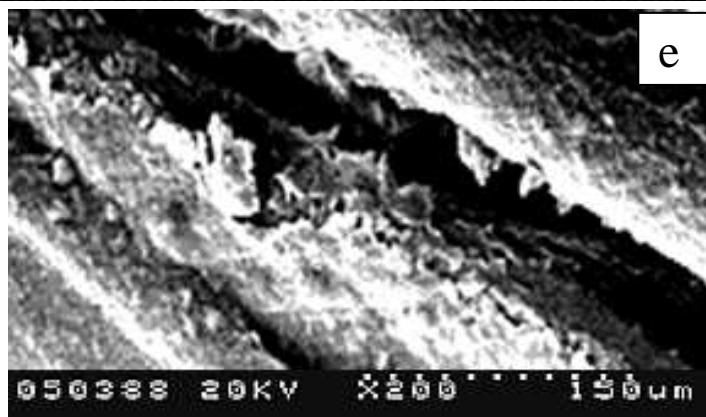


Fig. 2. Scan Electron Micrograph of a). Un-grafted Silk Fibre, b). Silk-g-MMA, c). Silk-g-MMA-co-AA, d). Silk-g-MMA-co-MA, e). Silk-g-MMA-co-AN

Swelling of Graft Copolymers

The swelling behavior of the graft copolymers was studied to define their end-uses. It was studied as a function of the nature and P_g of the graft copolymers as well as nature of the swelling medium. Silk fibre is of hydrophilic nature, hence in different media the swelling of the native fibre was observed to follow the order: $H_2O > MeOH > n\text{-BuOH} > DMF$. In this case the swelling order is explained by the presence of polar groups on the native silk fibre. These groups interact with the water molecules, hence maximum swelling was observed in water. Water can swell the native fibre by deep penetration into the polymer matrix. The same cannot be true for DMF, *n*-Butanol and methanol, as these solvents do not have enough interactions with the functional groups present on the silk fibre. However, in the case of graft copolymers, the reverse trend was observed as the swelling order in all the three types of graft copolymers can be put as: $DMF > n\text{-BuOH} > MeOH > H_2O$ (Figures 3a-3c). Such trend can be explained by the fact that the grafting of MMA or the comonomers consumed many functional groups on the backbone polymer that otherwise act as active sites for the water absorption.

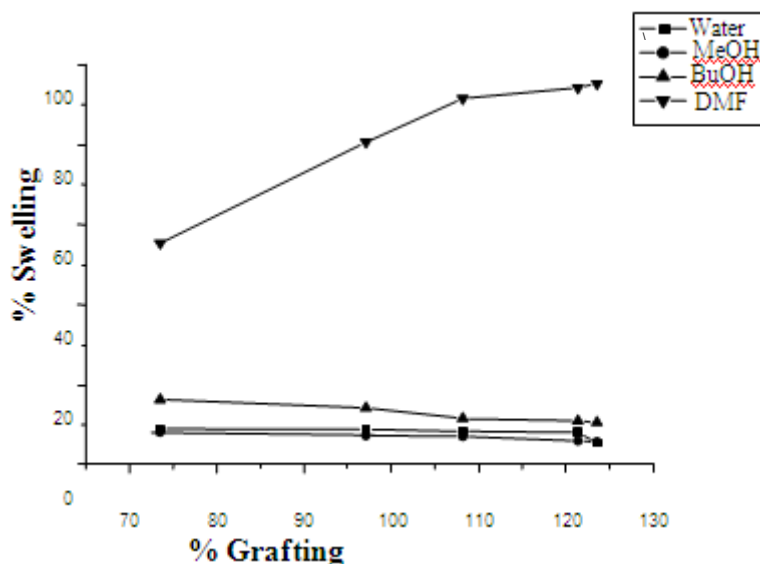


Fig. 3a. Swelling of Silk-g-poly(MMA-co-AA)

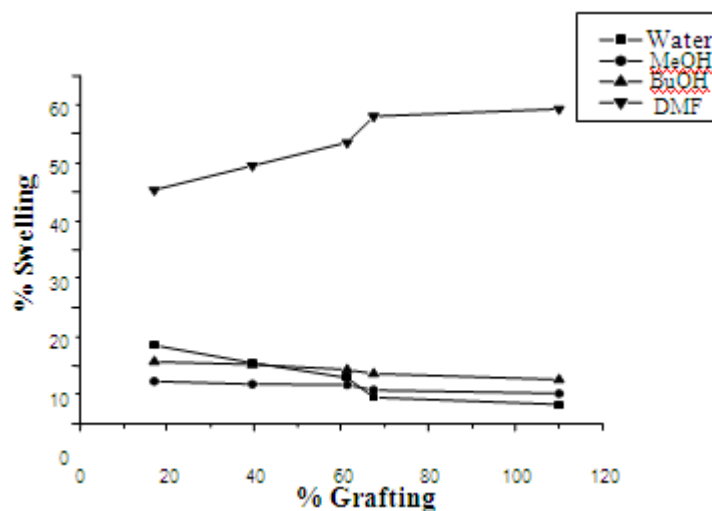


Fig. 3b. Swelling of Silk-g-poly(MMA-co-MA)

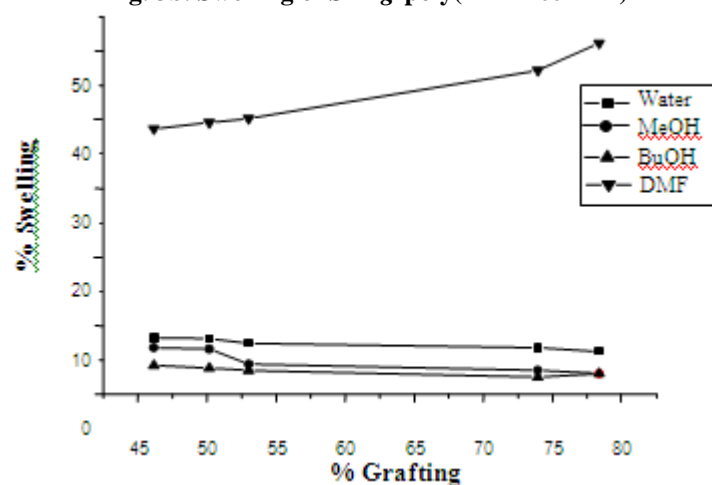


Fig. 3c. Swelling of Silk-g-poly(MMA-co-AN)

Further, the incorporation of hydrophobic polymers like poly(MMA) or poly(MA) or poly(AN) onto a hydrophilic (silk) backbone, also reduced water uptake or swelling. These grafted hydrophobic polymers are more solvated by DMF and to a lesser extent by the other solvents. Swelling behavior of the graft copolymers as the function of P_g followed the order: DMF > n-BuOH > MeOH > H₂O.

Moisture observance of Graft Copolymers

The moisture retention behavior of the graft copolymers was studied and results are presented in Figures 4a-4c. The moisture uptake by the graft copolymers is far more than reported earlier for the graft copolymers of MMA only [23]. The moisture absorption decreased with an increase in the P_g due to the occupancy of the active site of the silk fibre. 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.

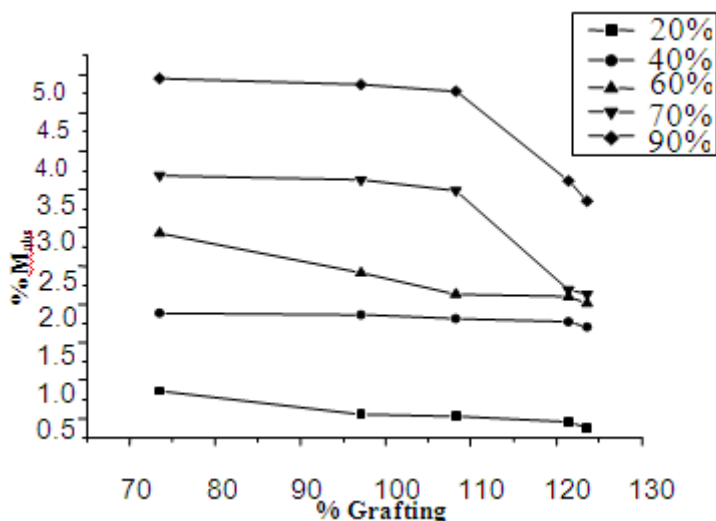


Fig. 4a. Moisture absorbance of Silk-g-poly(MMA-co-AA)

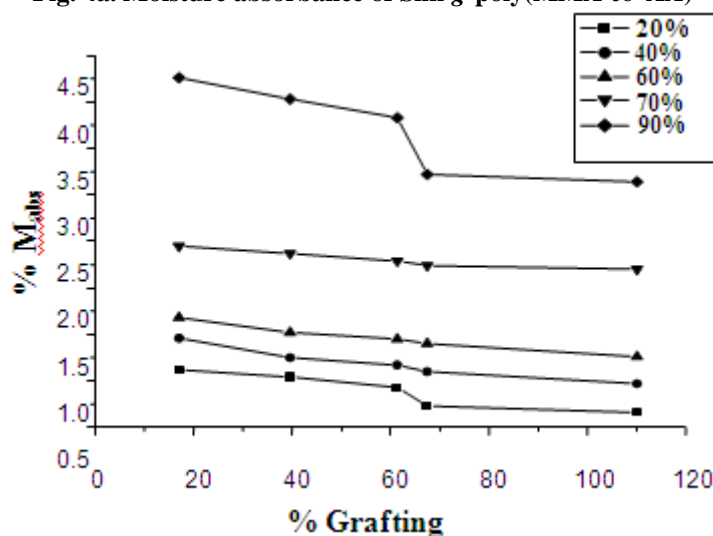


Fig. 4b. Moisture absorbance of Silk-g-poly(MMA-co-MA)

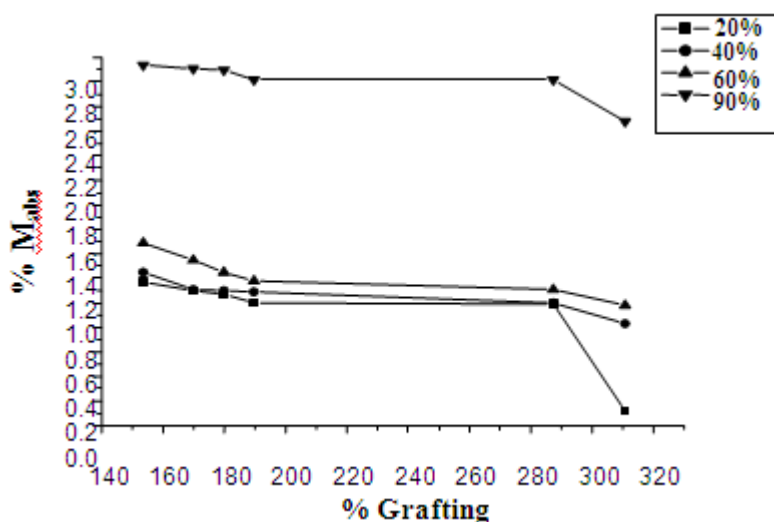


Fig. 4c. Moisture absorbance of Silk-g-poly(MMA-co-AN)

Chemical Resistance of Graft Copolymers

The weight loss of the graft copolymers was less than that of the ungrafted fibre. It was also less than that of the graft copolymers of MMA alone [23]. All the graft copolymers exhibited

good stability in the acidic medium, while all of these readily degraded in the alkaline medium (Figures 5a-5c). Further, the degradation behavior was also specific to the graft copolymers as those having poly(AA) as one of the component are more stable to the alkaline hydrolysis than those having poly(AN), and the later readily hydrolyzes in the presence of alkali. The other two series of the graft copolymers are readily susceptible to alkaline hydrolysis. In all the cases, the weight loss decreased with an increase of P_g as at the highest graft levels, the accessibility of the active agent to the active sites was reduced. The trends in the stability of the graft copolymers are thus manifestation of various factors with P_g playing the important role.

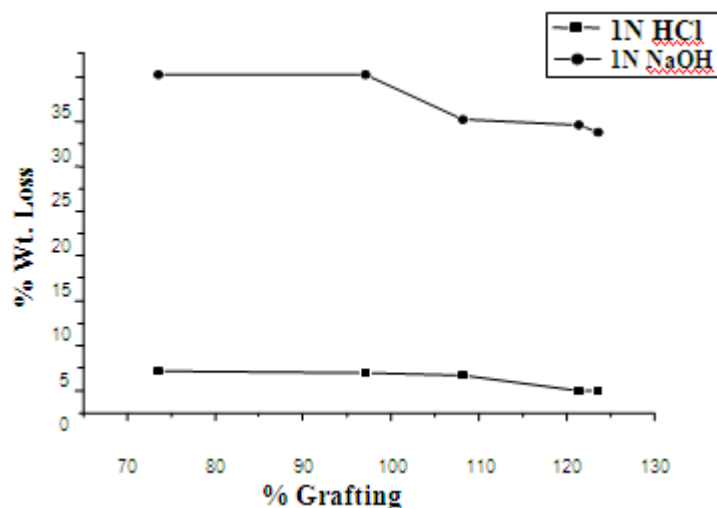


Fig. 5a. Chemical resistance of Silk-g-poly(MMA-co-AA)

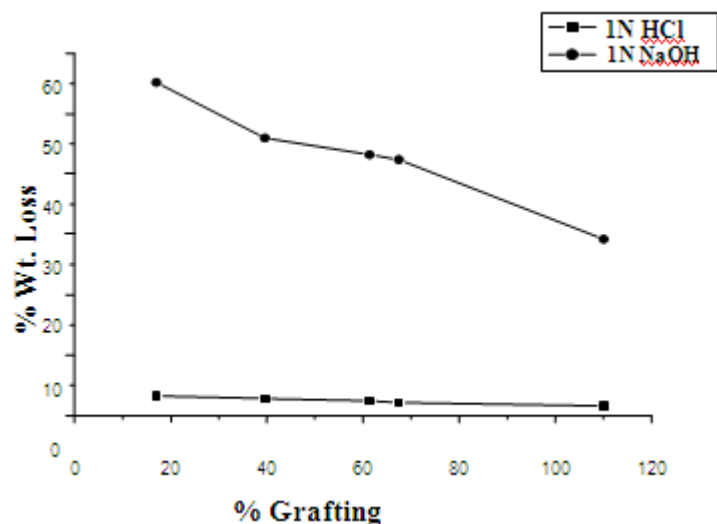


Fig. 5b. Chemical resistance of Silk-g-poly(MMA-co-MA)

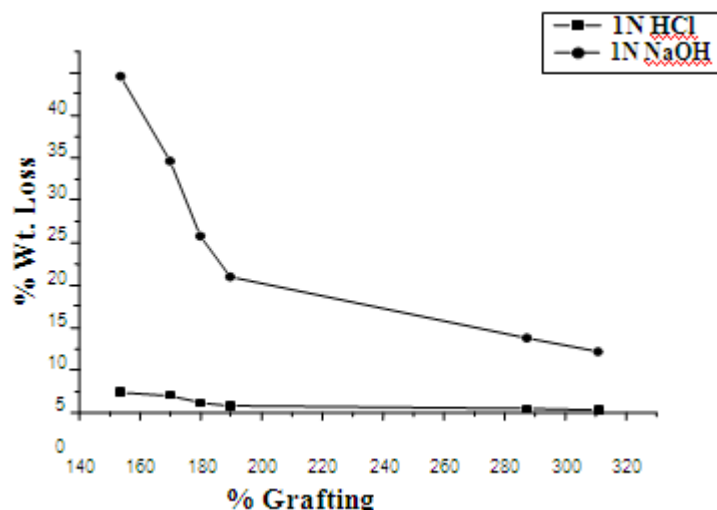


Fig. 5c. Chemical resistance of Silk-g-poly (MMA-co-AN)

Table 2: Gentian Violet Dye uptake by the silk and its Graft Copolymers Un-grafted Silk

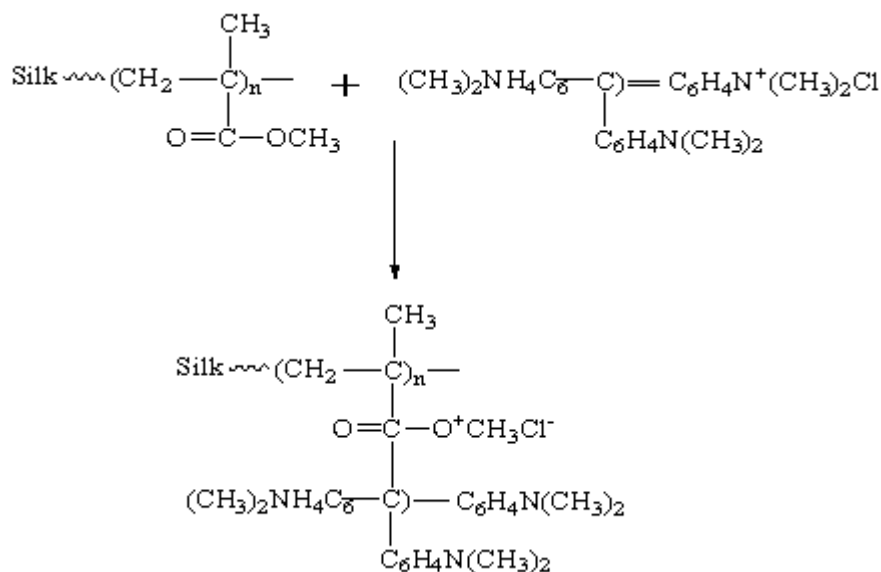
Sr. No	P_g	I_i [Conc. of test solution ($\times 10^{-4}$ mol/L)]					Transmittance (%)				
		At different time intervals (min)					At different time intervals (min)				
		60	120	180	240	300	60	120	180	240	300
1	0.0	0.17 [4.76]	0.15 [4.20]	0.15 [4.20]	0.15 [4.20]	0.15 [4.20]	80.95	71.43	71.43	71.43	71.43
Silk-g-poly(MMA-co-AA)											
Sr. No	P_g	I_i [Conc. of test solution ($\times 10^{-4}$ mol/L)]					Transmittance (%)				
		At different time intervals (min)					At different time intervals (min)				
		60	120	180	240	300	60	120	180	240	300
1	73.53	0.16 [5.04]	0.16 [4.48]	0.15 [4.20]	0.15 [4.20]	0.15 [4.20]	85.71	76.19	71.43	71.43	71.43
2	97.1	0.14 [3.92]	0.11 [3.08]	0.10 [2.80]	0.09 [2.52]	0.09 [2.52]	66.67	52.38	47.62	42.86	42.86
3	108.2	0.12 [3.36]	0.10 [2.80]	0.07 [1.96]	0.07 [1.96]	0.07 [1.96]	57.14	47.62	33.33	33.33	33.33
4	121.4	0.11 [3.08]	0.10 [2.80]	0.09 [2.52]	0.09 [2.52]	0.09 [2.52]	52.38	47.62	42.86	42.86	42.86
5	123.57	0.10 [2.80]	0.09 [2.52]	0.09 [2.52]	0.09 [2.52]	0.09 [2.52]	47.62	42.86	42.86	42.86	42.86
Silk-g-poly(MMA-co-MA)											
Sr. No	P_g	I_i [Conc. of test solution ($\times 10^{-4}$ mol/L)]					Transmittance (%)				
		At different time intervals (min)					At different time intervals (min)				
		60	120	180	240	300	60	120	180	240	300
1	17.1	0.16 [5.04]	0.15 [4.20]	0.15 [4.20]	0.15 [4.20]	0.15 [4.20]	76.19	71.43	71.43	71.43	71.43
2	39.6	0.16 [5.04]	0.16 [5.04]	0.15 [4.20]	0.15 [4.20]	0.15 [4.20]	76.19	76.19	71.43	71.43	71.43
3	61.4	0.15 [4.20]	0.15 [4.20]	0.14 [3.92]	0.14 [3.92]	0.14 [3.92]	71.43	71.43	66.67	66.67	66.67
4	67.5	0.14 [3.92]	0.14 [3.92]	0.12 [3.36]	0.12 [3.36]	0.12 [3.36]	66.67	66.67	57.14	57.14	57.14
5	110.07	0.11 [3.08]	0.11 [3.08]	0.10 [2.80]	0.10 [2.80]	0.10 [2.80]	52.38	52.38	47.62	47.62	47.62
Silk-g-poly(MMA-co-MA)											
Sr. No	P_g	I_i [Conc. of test solution ($\times 10^{-4}$ mol/L)]					Transmittance (%)				
		At different time intervals (min)					At different time intervals (min)				
		60	120	180	240	300	60	120	180	240	300

1	153.57	0.14 [3.92]	0.14 [3.92]	0.13 [3.64]	0.13 [3.64]	0.13 [3.64]	66.67	66.67	61.90	61.90	61.90
2	169.93	0.13 [3.64]	0.13 [3.64]	0.13 [3.64]	0.12 [3.36]	0.12 [3.36]	61.90	61.90	61.90	57.14	57.14
3	179.81	0.12 [3.36]	0.11 [3.08]	0.11 [3.08]	0.11 [3.08]	0.11 [3.08]	57.14	2.38	52.38	52.38	52.38
4	189.17	0.11 [3.08]	0.10 [2.80]	0.10 [2.80]	0.10 [2.80]	0.10 [2.80]	52.38	47.62	47.62	47.62	47.62
5	287.67	0.10 [2.80]	0.09 [2.52]	0.09 [2.52]	0.09 [2.52]	0.09 [2.52]	47.62	42.86	42.86	42.86	42.86
6	310.77	0.10 [2.80]	0.07 [1.96]	0.07 [1.96]	0.07 [1.96]	0.07 [1.96]	42.86	33.33	33.33	33.33	33.33

Initial concentration = 5.88×10^{-4} mol/L; wavelength = 420 nm; $I_0 = 0.21$

Dyeing Studies of Mulberry Silk and Its Graft Copolymers

The dyeing capability of mulberry silk fibre could also be improved by grafting. The absorption of Gentian violet by the un-grafted and mulberry silk fibres has been depicted in Table 2. The dyeing property of silk fibre is enhanced in each grafted binary monomer mixture, and it increases with increase in P_g . Silk-g-MMA-co-AN showed the best result of dye uptake among all graft copolymers. Hence, it has been observed that grafting with the binary mixtures of different vinyl monomers also improved the chemical resistance towards alkali and acids. The dye uptake behavior can be explained by the interaction occurring between the dye and the grafted fibre. The dyeing capability of the graft copolymers with the binary mixture was more than that of the reference silk fibre. The dye uptake is presented as follows:



CONCLUSION

The graft copolymerization of the binary mixture of three vinyl monomers separately with methyl methacrylate on to mulberry silk fibre 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 (methyl acrylate or acrylonitrile) exhibited more efficiency than the other monomer (acrylic acid). The properties like swelling behavior, moisture absorption, chemical resistance and dye uptake 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. The dye uptake behavior was also explained by the interaction occurring between the dye and the grafted fibre. The dyeing capability of the graft copolymers with binary mixture is more than the reference graft copolymer of methyl methacrylate. Thus, the present study was a successful attempt to improve the properties of the native silk fibre like chemical resistance, moisture absorption resistance and dye-ability, those are useful in widening its use-spectrum in textile as well as biomedical applications.

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