

Synthesis and characterization of methyl methacrylate and 4-vinylpyridine grafted silk fiber for dye uptake studies

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ABSTRACT

Graft copolymerization of binary monomer mixture of methyl methacrylate (MMA) and 4-vinylpyridine (VP) onto silk fiber was carried out by using ceric ammonium nitrate (CAN) as initiator in aqueous medium. Characterization of graft copolymers were done by various chemical and physical techniques like FTIR, TGA, SEM, moisture absorbance and chemical resistance in acidic and alkaline medium. Swelling properties of graft copolymers were studied in various solvents like water, methanol, dimethyl formamide and butanol. Gentian violet, dye uptake studies of graft copolymer was performed photo-calorimetrically.

Key words: Binary monomers, grafting, moisture absorbance, dye uptake

INTRODUCTION

Graft copolymerization is one of the promising techniques to add a variety of functional groups to a polymer of biological origin for their utilization in diverse applications [1-5]. Silk is one such biopolymer on which grafting of vinyl monomers [6-14] were reported to improve its intrinsic properties like solvent resistance, moisture repellency, dye uptake and chemical resistance. Literature study reveals that grafting can be done onto silk fiber by use of various types of initiators like benzoyl peroxide (BPO) [16], KMnO_4 -oxalic acid redox initiator [17,18], potassium peroxydiphosphate-cysteine redox initiator [19], acetylacetonate oxovanadium (IV) complex [20] and ceric ammonium nitrate (CAN) [15]. In present work we have graft copolymerized mulberry silk fibers with binary vinyl monomers methyl methacrylate (MMA) and 4-vinylpyridine (VP). The changes in physical and chemical properties of silk fibers were studied by different physical-chemical methods. Graft copolymers were also investigated for Gentian violet dye uptake.

MATERIALS AND METHODS

Materials

Mulberry silk (origin Assam, India) was procured from market. MMA (Merck, Germany), VP (Merck, Germany), ceric ammonium nitrate (CAN) (S.D. fine Chemicals, India), HNO_3 (S.D. fine Chemicals, India) and Gentian violet (Nice Co., India), were used as received. All chemicals used were of analytical grade.

Graft Copolymerization

In our earlier publication we have reported graft copolymerization of MMA onto silk [21]. In that paper we have discussed that optimization of grafting conditions for grafting of MMA onto silk fiber in distilled water. One of

reaction conditions like amount of (initiator) ceric ammonium nitrate, nitric acid and monomer MMA were varied keeping other conditions constant at a time to evaluate optimum grafting conditions. Homopolymer was separated from the graft copolymer in soxhlet using acetone. The graft copolymers were dried at 50 °C till constant weight was obtained. At these optimum reaction conditions for unitary monomer system (MMA) onto silk, binary monomer mixtures of MMA were co-grafted with five different concentrations of VP. Results have been presented in Table 1. The percent grafting (P_g) and percent grafting efficiency (%GE) were calculated as follows [15].

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

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

Characterization

Graft copolymers were characterized by FTIR, SEM and TGA. FTIR spectra of the silk fiber and graft copolymers were recorded in KBr pellets in Thermo Nicolet 6700 spectrometer. SEM was 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, Chemical Resistance and Swelling studies:

Moisture absorbance was determined by the method reported in the earlier work [21, 15]. 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 [15]:

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

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 1N NaOH and 1N HCl. The loss in weights was studied at different time intervals and the % chemical resistance (%CR) was calculated as [15]:

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

Where, W_f and W_{ft} are total weight of fiber and weight after certain intervals, respectively. Swelling of the grafted and ungrafted fibers was determined in different solvents i.e. DMF, water, methanol and *n*-butanol.

Dyeing behavior

For 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 fiber was immersed and the fiber 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 at different time interval of 1, 2, 3, 4 and 5hrs, respectively. The concentration of each solution after dye uptake by the fiber and % transmittance (%T) was calculated as [15]:

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

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

Where, I_i & I_o are optical density of rejected dye solution and standard solution, respectively [15].

RESULTS AND DISCUSSION

Silk contains several functional groups which act as active sites for the grafting of vinyl monomers. The mechanism of grafting and optimum grafting conditions for MMA onto silk fiber in the presence of CAN was reported earlier [21]. The maximum P_g (74.4) of MMA onto silk fibers alone was observed at 2.94×10^{-3} mol/L of MMA, 1.75×10^{-4} mol/L of CAN at 55°C temperature and at reaction time of 120 min. At these optimum reaction conditions comonomer VP 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 $\times 10^{-3}$ (mol/L)	[CAN] $\times 10^{-4}$ (mol/L)	[HNO ₃] $\times 10^{-3}$ (mol/L)	Time (min)	Temp. (°C)	P_g	% GE
(MMA + VP)							
1.	2.94+0.463	1.75	5.13	120	55	90.5	7.83
2.	2.94+0.927	1.75	5.13	120	55	151.0	11.57
3.	2.94+1.390	1.75	5.13	120	55	171.6	11.69
4.	2.94+1.854	1.75	5.13	120	55	190.53	11.69
5.	2.94+2.318	1.75	5.13	120	55	199.93	11.15
6.	2.94+2.781	1.75	5.13	120	55	116.8	5.97

^aSilk fiber = 0.5g

Effect of concentration of binary monomers onto P_g & %GE

Binary mixtures of MMA with VP were grafted onto silk fiber, keeping concentration of MMA constant i.e. 2.94×10^{-3} mol/L and varying concentration of VP from 0.463×10^{-3} mol/L to 2.781×10^{-3} mol/L. P_g increased from 90.5 to 199.93 with increase in concentration of 4-VP from 0.463×10^{-3} mol/L to 2.318×10^{-3} mol/L and then decreases with further increase of VP concentration (Table 1).

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 1644.5cm^{-1} , 1553.3cm^{-1} , 1220.6cm^{-1} and 1043.2cm^{-1} , which are assigned to β -sheet structure. Figure 1b shows clear absorbance at 1725.4cm^{-1} , which is attributed to the carbonyl group of the side chain of the MMA polymer present in the silk fibre and absorbance at 1561.1cm^{-1} is because of C=N of VP, another sharp absorbance peak at 990.7cm^{-1} is because of ring structure of VP.

Scanning electron microscopy

Scanning electron micrographs (SEM) of silk and its graft copolymers are presented in figures 2a–2b. SEM of the silk-g-poly (MMA-co-VP) (figures 2b) showed clear deposits of the graft copolymers on the silk fibre when compared with SEM of un-grafted silk of fig. 2a.

Thermogravimetric analysis

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 of silk and its graft copolymers. 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°C to 377.6°C . Figure 3b represent the thermal degradation of silk grafted with MMA-co-VP in which 76.1% weight loss is observed from 258.2°C to 394.8°C , that may be because of degradation of grafted side chain. Ungrafted silk show one exothermic peak at 316.4°C in DTA (figure 3a), where as grafted sample shows exothermic peak at 371.4°C 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 Figure 4. 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 occupancy of the active site of the silk fiber.

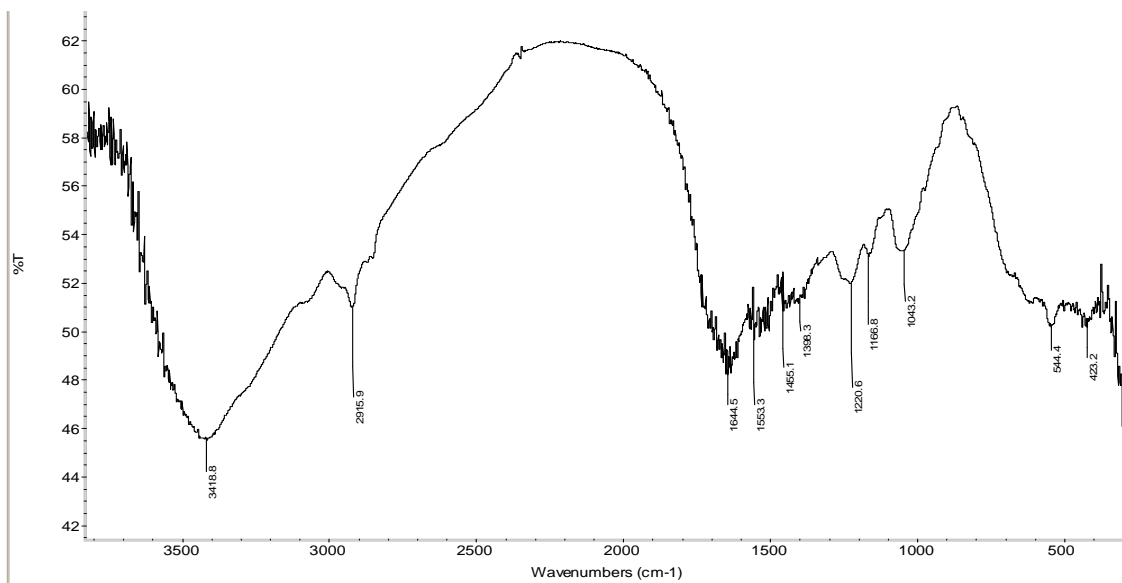


Figure 1a: FTIR of ungrafted silk

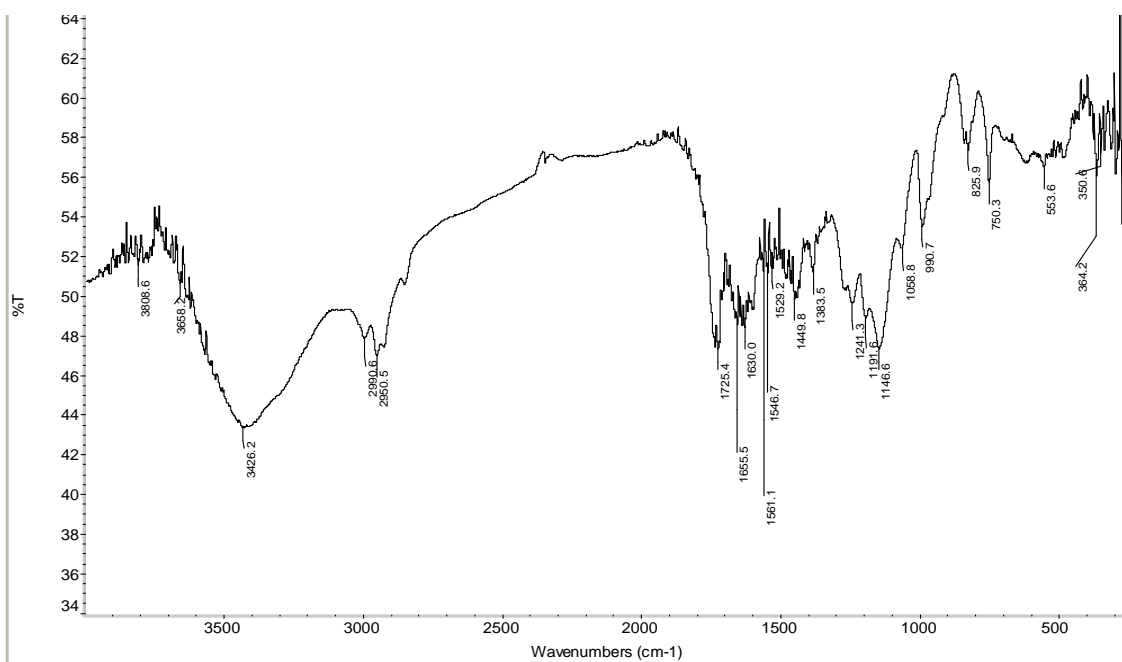


Figure 1b: FTIR of silk-g-poly(MMA-co-VP)

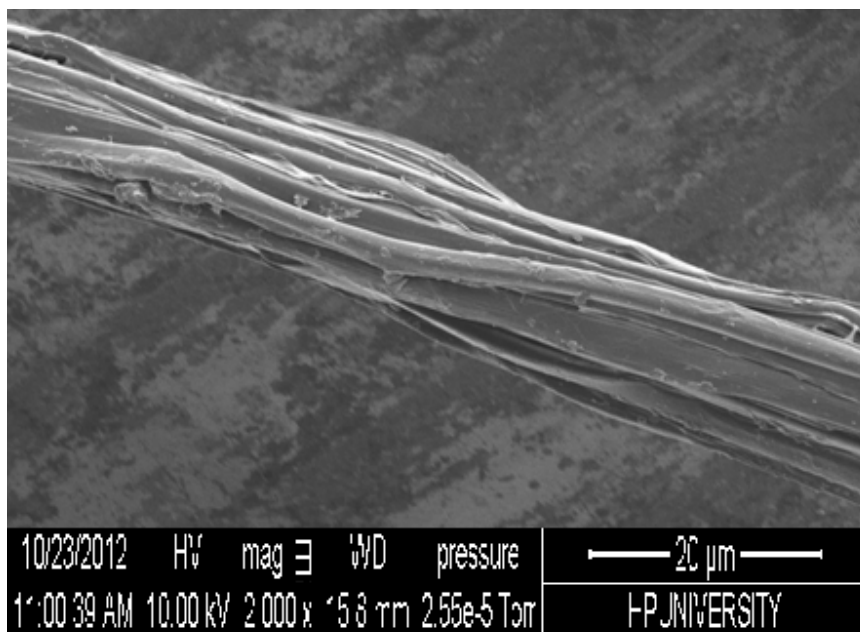


Figure 2a: SEM of ungrafted silk

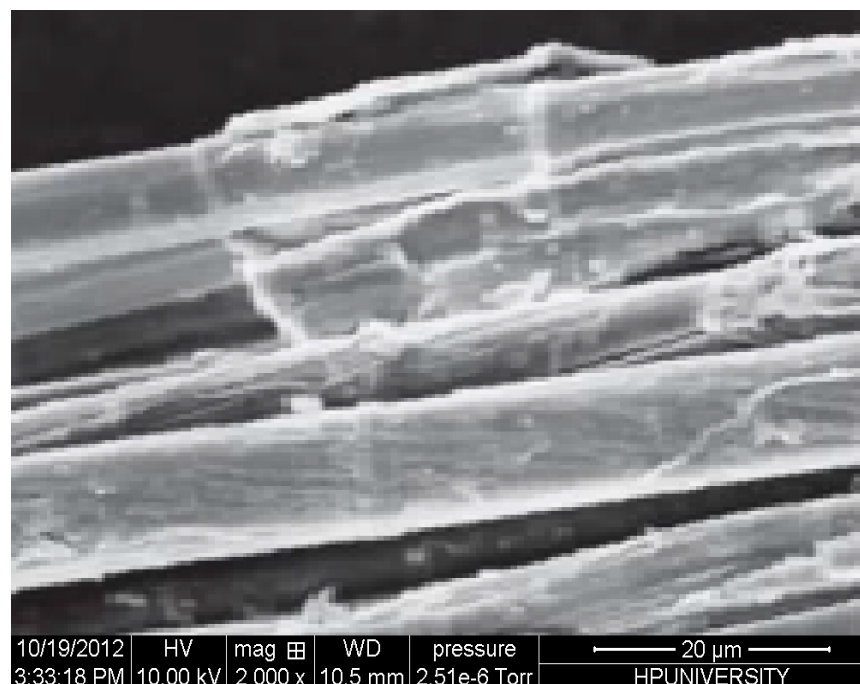


Figure 2b: SEM of silk-g-poly(MMA-co-VP)

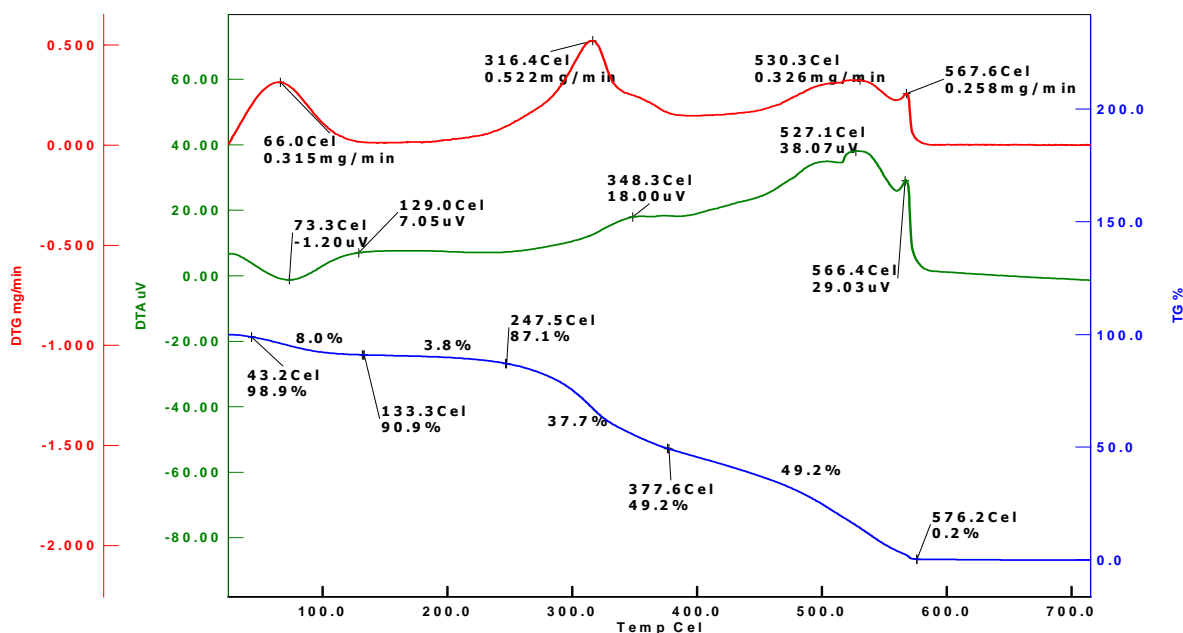


Figure 3a: Thermogravimetric analysis of ungrafted silk

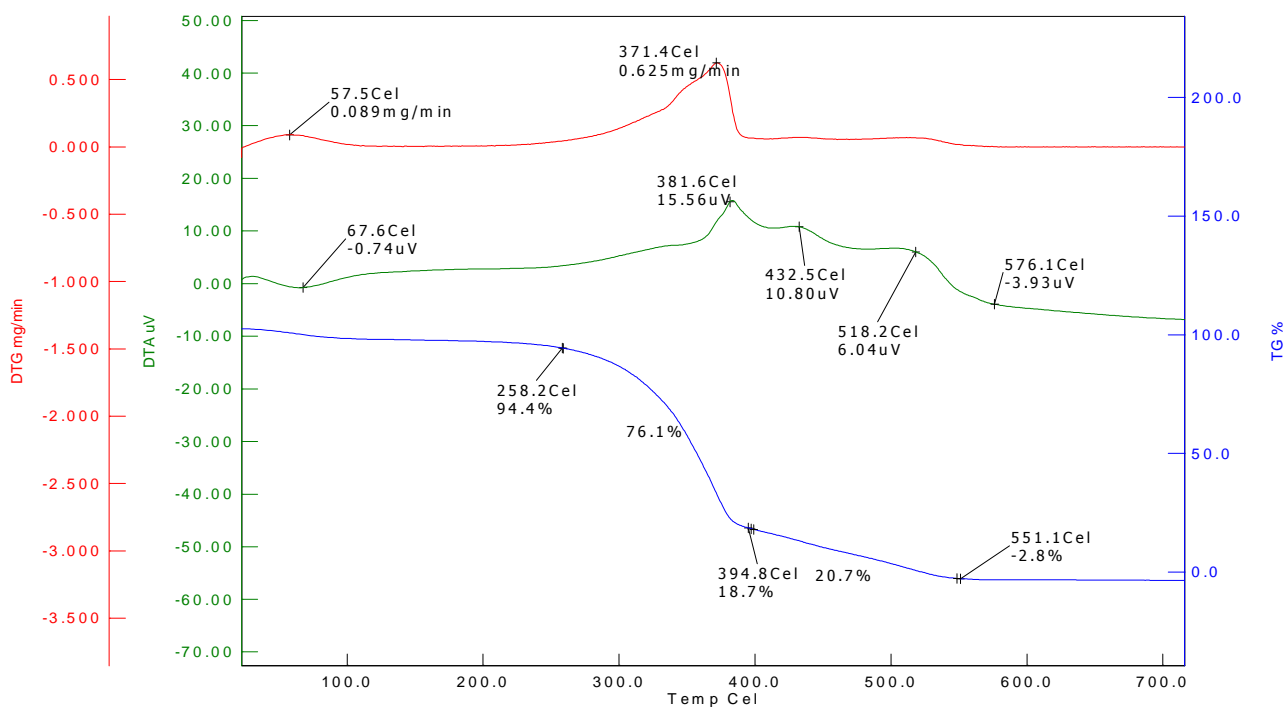


Figure 3b: Thermogravimetric analysis of silk-g-poly(MMA-co-VP)

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]. The graft copolymers exhibited good stability in the acidic medium, while most of these readily degraded in the alkaline medium (Figure 5). Further, the degradation behavior was also specific to the graft copolymers as one of the components is more stable to the acidic hydrolysis, and the later readily hydrolyzes in the presence of alkali.

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 fiber is of hydrophilic nature, hence in different media the swelling of the native fiber was observed to follow the order: $H_2O > MeOH > n-BuOH > DMF$. In this case the swelling order is explained by the presence of polar groups on the native silk fiber. These groups interact with the water molecules, hence maximum swelling was observed in water. Water can swell the native fiber 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 fiber. However, in the case of graft copolymers, the reverse trend was observed as the swelling order can be put as: $DMF > n-BuOH > MeOH > H_2O$ (Figure 6). Such trend can be explained by the fact that the grafting of MMA-co-VP consumed many functional groups on the backbone polymer that otherwise act as active sites for the water absorption. Further, the incorporation of hydrophobic polymers like poly(MMA) or poly(MMA-co-VP) or poly(VP) 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: $DMF > n-BuOH > MeOH > H_2O$.

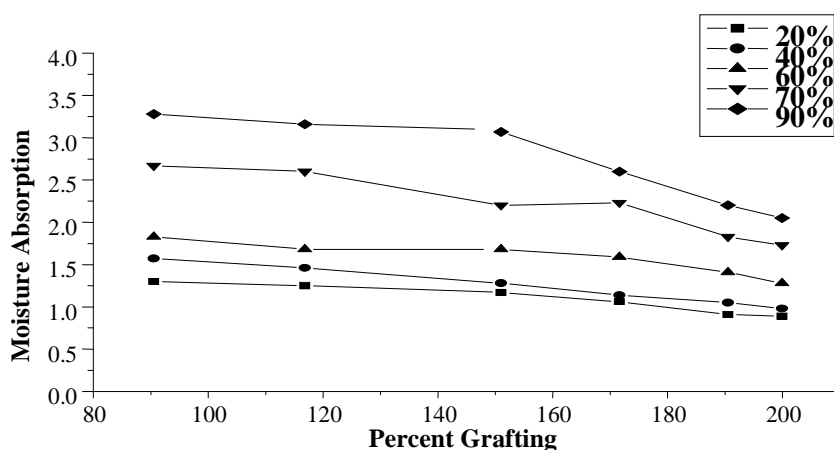


Figure 4: Moisture Absorbance of silk-g-poly(MMA-co-VP)

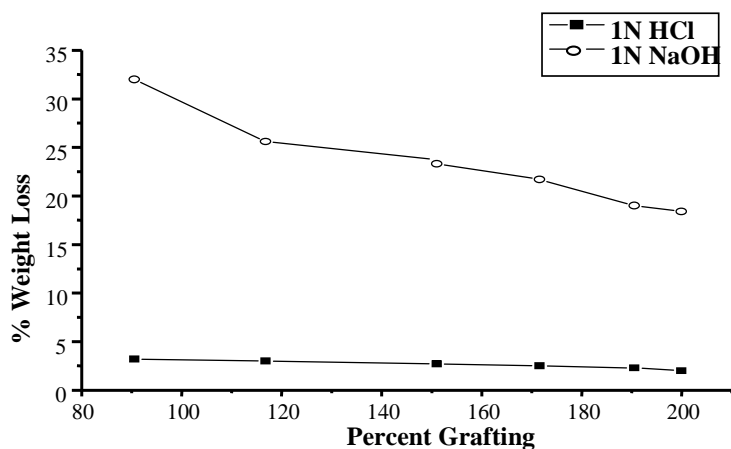


Figure 5: Chemical Resistance of silk-g-poly(MMA-co-VP)

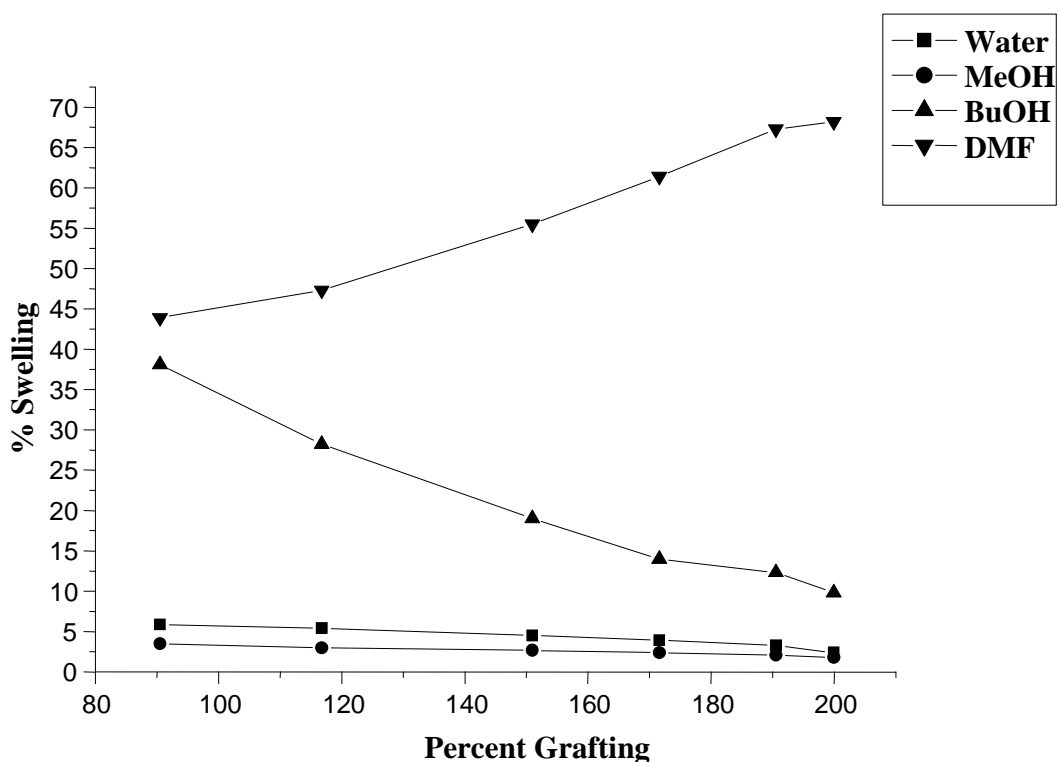


Figure 6: Swelling of silk-g-poly(MMA-co-VP)

Dyeing Studies of Mulberry Silk and Its Graft Copolymers

The dyeing capability of mulberry silk fiber not improved by grafting. The absorption of Gentian violet by the ungrafted and grafted silk fibers has been depicted in Table 2. The graft copolymerization of the binary mixture of vinyl monomers on to mulberry silk fiber shows that dyeing ability decreases with increase in P_g . This may be because of hydrophobic nature of both the monomers.

Table 2: Dye up-take by Silk-g-poly (MMA-co-VP)

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	00.00	0.16 [4.48]	0.13 [3.64]	0.12 [3.36]	0.12 [3.36]	0.12 [3.36]	76.19	61.19	57.14	57.14	57.14
2	90.50	0.19 [5.32]	0.18 [5.04]	0.18 [5.04]	0.18 [5.04]	0.18 [5.04]	90.48	85.71	85.71	85.71	85.71
3	116.80	0.20 [5.60]	0.19 [5.32]	0.19 [5.32]	0.19 [5.32]	0.19 [5.32]	95.24	90.48	90.48	90.48	90.48
4	151.00	0.20 [5.60]	0.19 [5.32]	0.19 [5.32]	0.19 [5.32]	0.19 [5.32]	95.24	90.48	90.48	90.48	90.48
5	171.60	0.20 [5.60]	0.18 [5.04]	0.18 [5.04]	0.18 [5.04]	0.18 [5.04]	95.24	85.71	85.71	85.71	85.71
6	190.53	0.20 [5.60]	0.19 [5.32]	0.19 [5.32]	0.19 [5.32]	0.19 [5.32]	95.24	90.48	90.48	90.48	90.48
7	199.93	0.20 [5.60]	0.19 [5.32]	0.19 [5.32]	0.19 [5.32]	0.19 [5.32]	95.24	90.48	90.48	90.48	90.48

CONCLUSION

The graft copolymerization of the binary mixture of methyl methacrylate and 4-vinyl pyridine 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 for both monomers monomers (MMA & VP). 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 onto silk fiber improved its chemical resistance towards alkali and acids but decrease its dyeing ability. 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 applications.

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