



Graft Copolymerization of Binary Monomer Mixtures onto Silk Fibre

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Abstract

In order to improve properties of Mulberry silk fibre, we have grafted binary monomer mixtures of butyl acrylate (BA) and ethyl acrylate (EA) with methyl methacrylate (MMA) in aqueous medium by using ceric ammonium nitrate (CAN) as redox initiator. The binary vinyl monomers were grafted at optimum grafting conditions as reported earlier for MMA alone onto the same backbone. Graft copolymers are characterized by Fourier transform infrared spectroscopy, Thermo-gravimetric analysis and Scanning electron microscopy studies. Moisture absorbance and chemical resistance properties of graft copolymers were studied in acidic and alkaline medium as a function of percent grafting.

Keywords: Binary monomers, grafting, moisture absorbance, chemical resistance.

Introduction

Some natural occurring as well as synthetic polymers has commercial application¹⁻³. The modification of polymers has received much attention recently. Graft copolymerization is one of the most promising techniques to impart a variety of functional groups to a polymeric back bone. Chemically modified natural fibres through graft copolymerization are useful in many applications in diverse fields⁴⁻⁸. In continuation of our earlier reported work of modification of natural polymers by grafting technique, we have grafted binary mixtures of vinyl monomers onto silk fibre. Literature survey reveals that grafting of vinyl monomers onto the polymeric fibre backbones improves their chemical resistance, moisture repellency and dye uptake⁹⁻¹⁷. In literature a number of initiators like ceric ammonium nitrate (CAN)¹⁸, benzoyl peroxide¹⁹, KMnO₄-oxalic acid redox initiator^{20,21}, potassium peroxydiphosphate-cysteine redox initiator²² and acetylacetonate oxovanadium (IV) complex²³ were reported for graft copolymerization of methyl methacrylate (MMA) onto silk fibres. In the present study we synthesize mulberry silk fibre based graft copolymers through grafting of binary vinyl monomer mixture (MMA-co-BA) and (MMA-co-EA) to impart different physical and chemical properties.

Material and Methods

Materials: Mulberry silk (origin Assam, India) was purchased from market. Methyl methacrylate (Merck) first washed with 5% NaOH and then dried over anhydrous Na₂SO₄ finally purified by distillation. BA and EA (Merck) and ceric ammonium nitrate and HNO₃ (S.D. fine Chemicals, India) were used as received.

Graft copolymerization: Graft copolymerization of MMA onto silk was reported earlier²⁴. 0.5 g of silk fibre was dipped in 100

mL distilled water for a time period of 24h prior to grafting with MMA in air. To this known amount of CAN, nitric acid and MMA were added. The reaction contents were stirred for 120 min. Grafting 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. Then 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 co-grafted with MMA at five different concentrations of the comonomers (CM) BA and EA. Results have been depicted in table 1. The percent grafting (P_g) and percent grafting efficiency (%GE) were calculated as follows²⁵.

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

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

Characterization of graft copolymers: Graft copolymers were characterized by FTIR, TGA and SEM analysis. IR spectra of the silk fibre 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. Thermo gravimetric 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^{24,26}. Small wicks of the ungrafted and grafted fibres of diameter 5 mm were prepared and with ink pen initial mark was put on the thread and then dipped in to a beaker

containing water. Water moved up through capillary action in each fibre wick was recorded at certain time intervals and then percent wet-ability (%W) was calculated as²⁶:

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

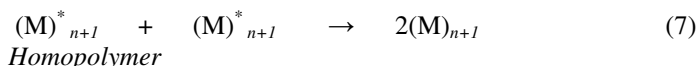
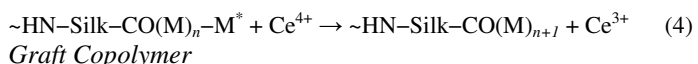
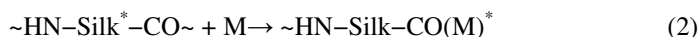
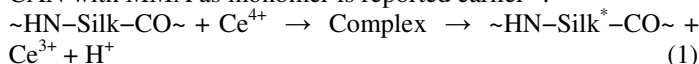
where, L_f is length of fibre and D_w is distance traveled by the water. To study the chemical resistance of ungrafted and grafted fibres, 100 mg of the ungrafted and grafted fibre were put in 100 mL of 1N NaOH and 1N HCl. The loss in weights was studied at certain time intervals and the percent chemical resistance (%CR) was calculated as²⁶:

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

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

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 earlier²⁶.



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 $(\text{M}_1)_m(\text{M}_2)_n$, where M_1 is MMA and M_2 is comonomer (BA or EA) and m or n is the amount of reselective 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 fibres alone was observed²¹ 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 reported earlier for the grafting of MMA alone, comonomers BA and EA were incorporated along with MMA onto silk backbone polymer at five concentrations of the comonomers.

Table-1
Grafting of binary vinyl monomers onto silk fibre

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)	FWT	P _g	% GE
(MMA + BA)								
1.	2.94+0.351	1.75	5.13	120	55	0.6403	113.43	10.04
2.	2.94+0.702	1.75	5.13	120	55	0.5956	98.53	7.70
3.	2.94+1.053	1.75	5.13	120	55	0.4651	55.03	3.85
4.	2.94+1.404	1.75	5.13	120	55	0.4240	41.33	2.61
5.	2.94+1.755	1.75	5.13	120	55	0.4040	34.67	2.00
(MMA + EA)								
1.	2.94+0.46	1.75	5.13	120	55	0.7016	133.87	11.81
2.	2.94+0.92	1.75	5.13	120	55	0.8433	181.10	14.07
3.	2.94+1.38	1.75	5.13	120	55	1.0203	241.77	16.78
4.	2.94+1.84	1.75	5.13	120	55	0.9903	231.00	14.44
5.	2.94+2.30	1.75	5.13	120	55	1.1399	279.96	16.02
6.	2.94+2.76	1.75	5.13	120	55	0.6578	119.30	6.27
7.	2.94+3.22	1.75	5.13	120	55	0.5773	100.0	4.50

^aSilk fibre = 0.5g

Effect of concentration of binary monomers onto P_g & %GE: Binary mixtures of MMA with two other vinyl monomers, BA and EA were separately grafted onto silk fibre. At constant concentration of MMA (2.94×10^{-3} mol/L), concentration of BA were varied from 0.351×10^{-3} mol/L to 1.755×10^{-3} mol/L. P_g and %GE both decreases with increase in BA concentration, maximum P_g (113) and %GA (10.04) was observed at minimum concentration of BA (table 1). In case of grafting of EA with MMA, concentration of EA was varied from 0.46×10^{-3} mol/L to 3.22×10^{-3} mol/L. Maximum P_g (279.96) and %GE (16.02) was observed at 2.30×10^{-3} mol/L of EA and 2.94×10^{-3} mol/L of MMA (table 1). But with further increase in concentration of EA up to 3.22×10^{-3} both P_g and %GE decreases. From the results presented in table 1, it is

apparent that EA is better compatible monomer than BA with MMA, as per results in terms of P_g as well as % GE are compared.

Characterization of graft copolymers: Fourier transform infrared spectroscopy: FTIR of silk is characterized by absorption bands at 3418.8 cm^{-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 strong absorbance peak at 1725.8 cm^{-1} , which is due to the C=O stretching of the grafted polymeric side chains of poly-MMA and poly-BA present on the silk fibre. Absorbance at 1725.6 cm^{-1} are because of C=O stretching of EA (figure 1c).

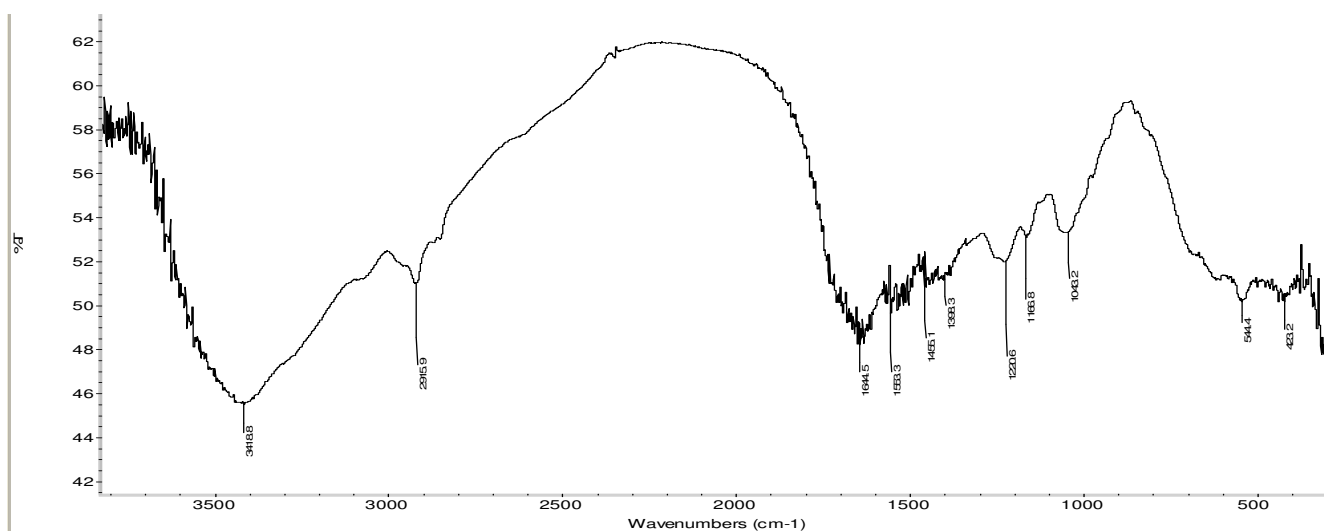


Figure-1a
FTIR of ungrafted silk

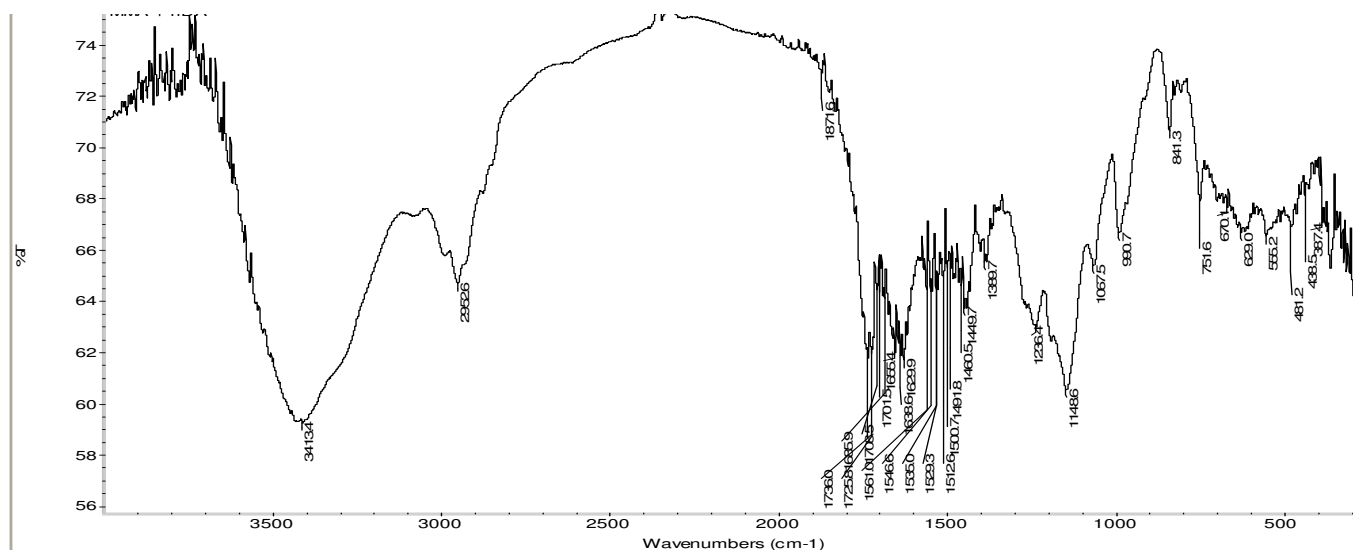


Figure-1b
FTIR of silk-g-poly(MMA-co-BAC)

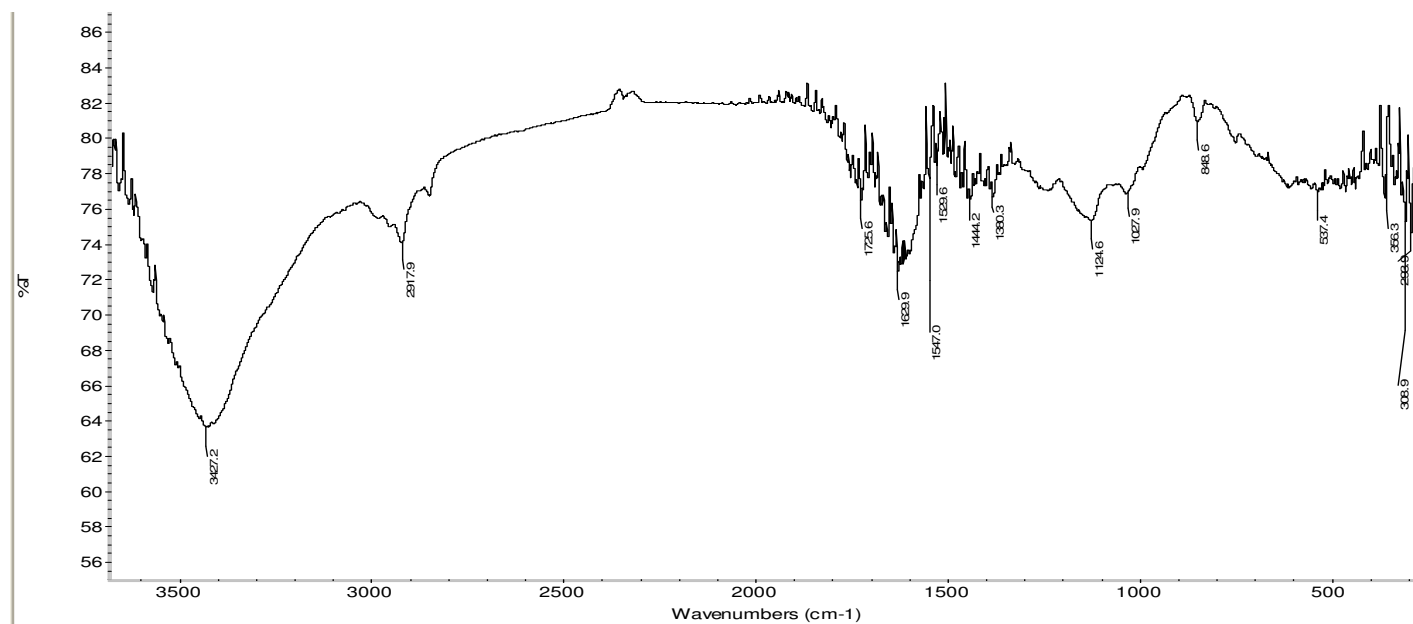


Figure-1c
FTIR of silk-g-poly(MMA-co-EA)

Scanning electron microscopy: Scanning electron micrographs of ungrafted silk and graft copolymers of silk are presented in figures 2a–2c. SEM of un-grafted silk is presented in figure 2a. SEM of the silk-g-poly (MMA-co-CM) binary monomer systems with BA and EA (figures 2b-2c) showed clear deposits of the graft copolymers on the silk fibre.

Thermogravimetric analysis: Thermo-gravimetric analysis showed how the grafting affects the thermal properties of original silk fibre. Differential thermal analysis (DTA) and thermo-gravimetric analysis (TGA) are used for detecting 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°C to 377.6°C.

Figure 3b represent the thermal degradation of silk grafted with MMA-co-BA in which 67.1% weight loss is observed from 239.2°C to 399.7°C, which may be because of degradation of grafted side chain. Maximum weight loss of 62.8% was observed from 228.2°C to 395.0°C in thermogravimetric analysis of silk grafted with MMA-co-EA (figure 3c) which explains the thermal instability of grafted sample. Ungrafted silk show one exothermic peak at 316.4°C in DTA (figure 3a), where in case of DTA of silk grafted with silk grafted with MMA-co-BA one exothermic peak at 378.9°C which clearly indicate the change in thermal behaviour of silk after grafting. Silk grafted with MMA-co-EA show two exothermic peaks at 375.9°C and 586.0°C in their DTA which clearly indicate the change in thermal behaviour of silk after grafting.

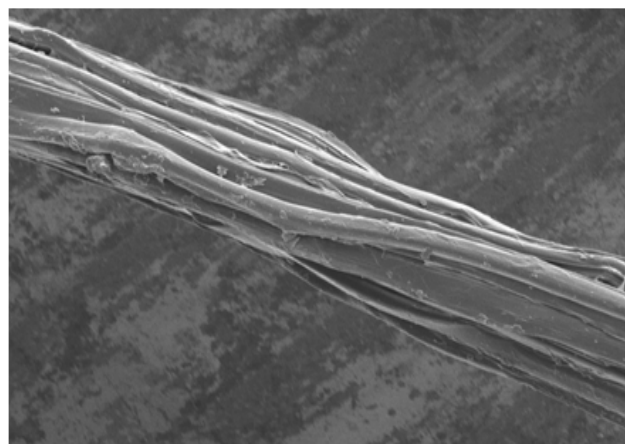


Figure-2a
SEM of ungrafted silk

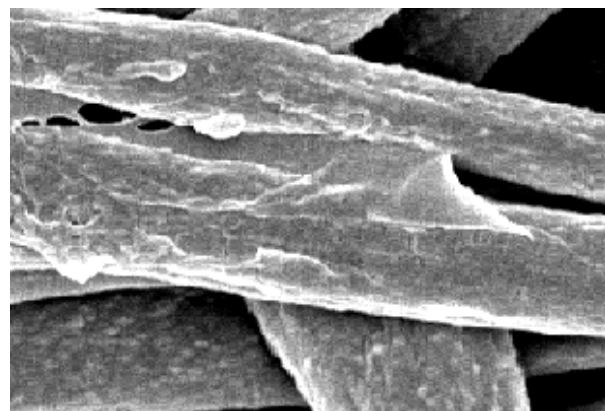


Figure-2b
SEM of silk-g-poly(MMA-co-BA)

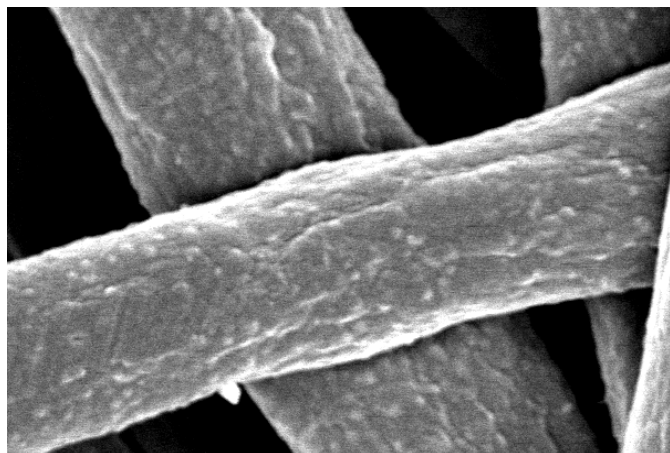


Figure-2c
 SEM of silk-g-poly(MMA-co-EA)

Moisture retention of graft copolymers: The moisture retention properties of the graft copolymers were studied and results are presented in figures 4a and 4b. The moisture uptake

by the graft copolymers is far more than reported earlier for the graft copolymers of MMA only²¹. 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.

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 alone²¹. All the graft copolymers exhibited good stability in the acidic medium, while most of these readily degraded in the alkaline medium (figures 5a and 5b). Further, the degradation behavior was also specific to the graft copolymers as those having poly (BA) as one of the component are more stable to the alkaline hydrolysis than those having poly(EA), and the later readily hydrolyzes in the presence of alkali.

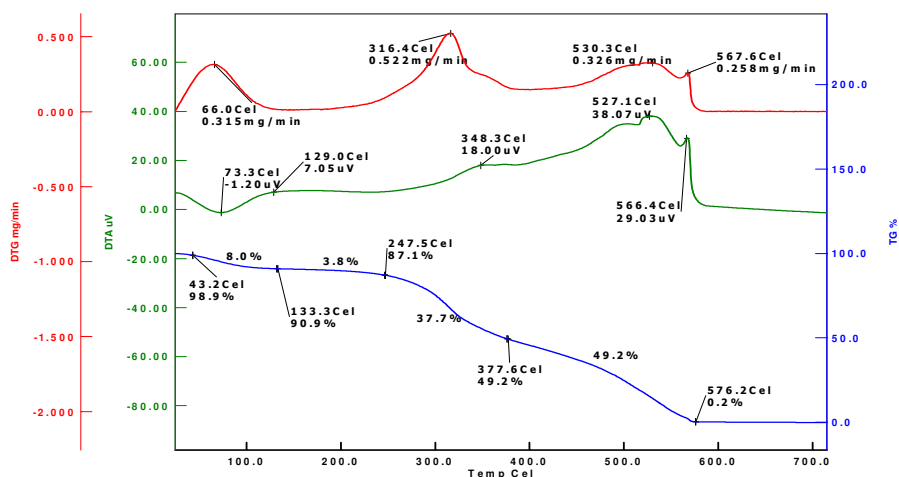


Figure-3a

Thermogravimetric analysis of ungrafted silk

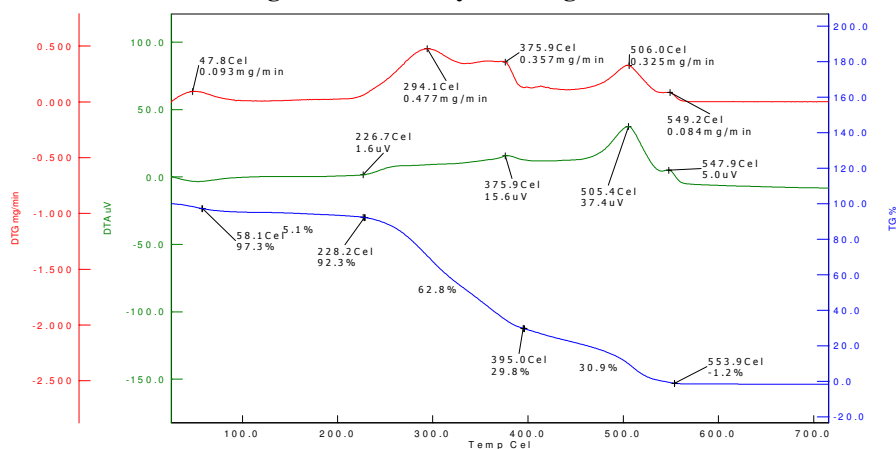


Figure-3b

Thermogravimetric analysis of silk-g-poly(MMA-co-BA)

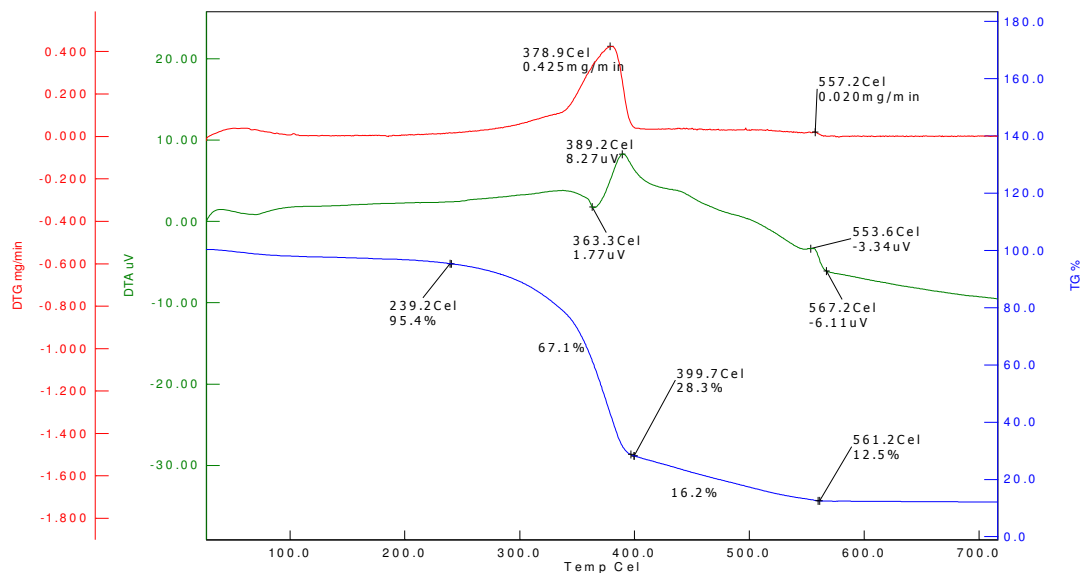


Figure-3c
 Thermogravimetric analysis of silk-g-poly(MMA-co-EA)

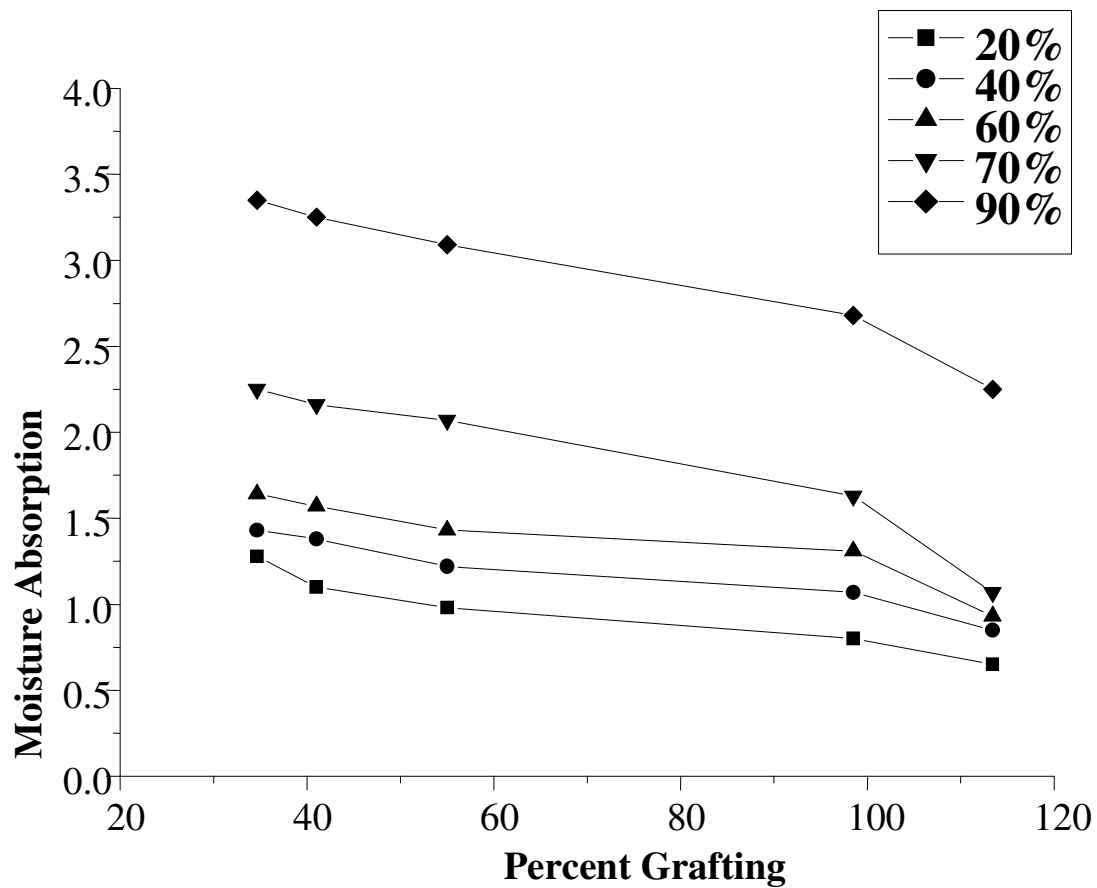


Figure-4a
 Moisture Absorbance of silk-g-poly(MMA-co-BA)

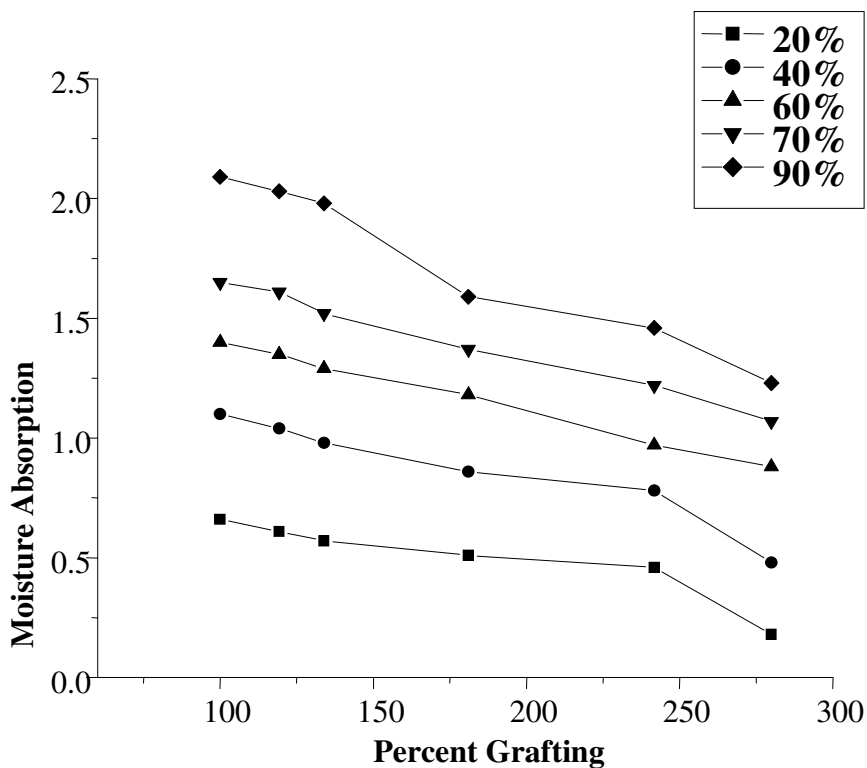


Figure-4b
Moisture Absorbance of silk-g-poly(MMA-co-EA)

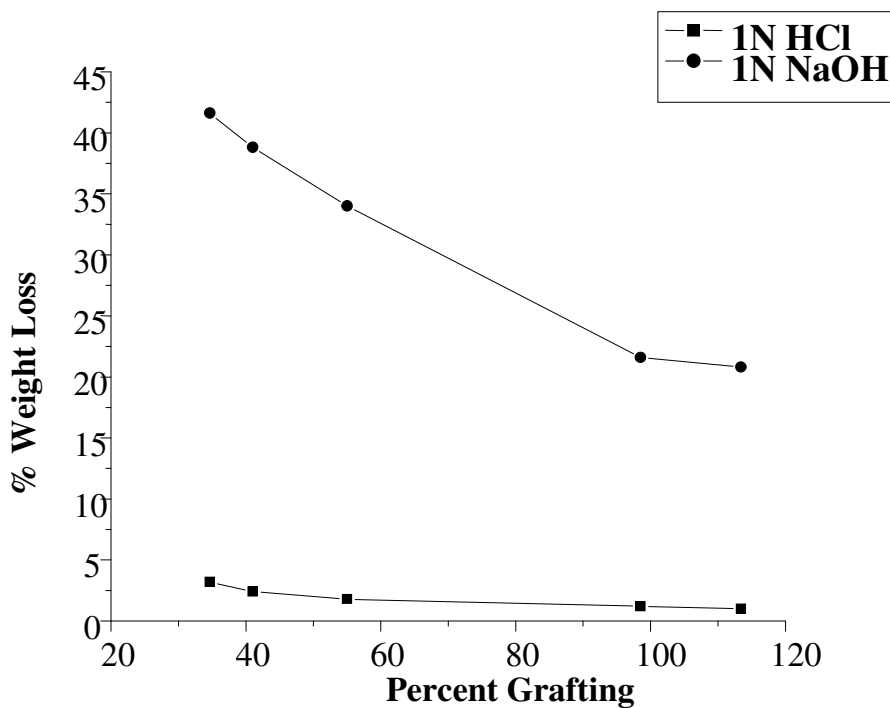


Figure-5a
Chemical Resistance of silk-g-poly(MMA-co-BA)

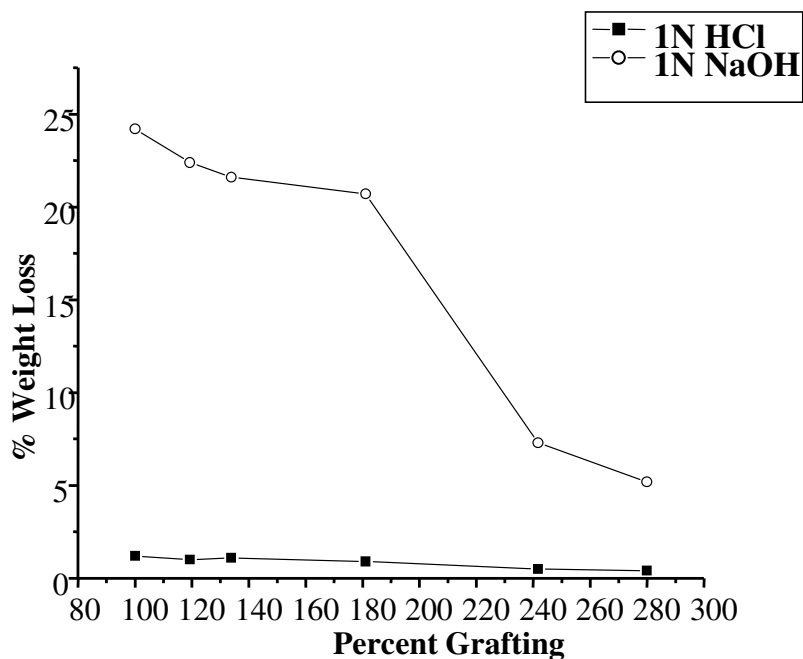


Figure-5b
Chemical Resistance of silk-g-poly(MMA-co-EA)

Conclusion

The graft copolymerization of the binary vinyl monomer mixture of two 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. Graft copolymers are characterized by physico-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 ungrafted silk fibre like chemical resistance and moisture absorption resistance.

References

1. Ghosh Pranab, Das Tapan and Das Moumita, Evaluation of Poly (acrylates) and their copolymer as viscosity modifiers, *Res. J. Chem. Sci.*, **1(3)**, 18 (2011)
2. Deepshikha and Basu T., The Role of Structure Directing Agents on Chemical Switching Properties of nanostructured conducting polyaniline (NSPANI), *Res.J.Chem.Sci.*, **1(6)**, 20-29 (2011)
3. Manimaran N., Rajendran S, Manivannan M and John Mary S, Corrosion inhibition of carbon steel by polyacrylamide, *Res.J.Chem.Sci.*, **2(3)**, 52-57 (2012).
4. Kaur I., Barsola R., Gupta A. and Misra B. N., Graft copolymerization of acrylonitrile and methacrylonitrile onto gelatin by mutual irradiation method, *J. Appl. Polym. Sci.*, **54**, 1131-1139 (1994)
5. Kubota G. and Ujita S., Reactivity of glycidyl-methacrylate-grafted cellulose prepared by means of photografting, *J. Appl. Polym. Sci.*, **56**, 25-31 (1995)
6. Chauhan G. S., Misra B. N., Kaur I., Singha A. S. and Kaith, B. S., Modification of Natural Polymers: Part I – Ceric ion initiated graft co-polymerization of methylmethacrylate onto *Cannabis* fibre, *Indian Journal of Fibre & Textile Research*, **24**, 269-275 (1999)
7. Chauhan G. S., Bhatt, S. S., Kaur I., Singha A. S. and Kaith B. S., A study in the evaluation of grafting parameters, swelling and thermal behaviour of Rayon and its methylmethacrylate graft co-polymer initiated by ceric ions, *J. Polym. Mater.*, **17**, 363-370 (2000)
8. Bajpai M., Bajpai S. K. and Gupta P., Development of cotton fabric with antibacterial properties: Part I: Preparation of poly(acrylamide-co-itaconic acid) grafted cotton fabric and its water uptake analysis, *J. Macromol. Part A: Pure & Appl. Chem.*, **45**, 179-185 (2008)

9. Chauhan G. S., Bhatt S. S., Kaur I., Singha A. S. and Kaith B. S., Evaluation of optimum grafting parameters and the effect of ceric ion initiated grafting of methyl methacrylate on to jute fibre on the kinetics of thermal degradation and swelling behaviour, *Polym. Degrad. Stab.*, **69**, 261-265 (2000)
10. Ferrero F., Periolatto M. and Songia M. B., Silk grafting with methacrylic and epoxy monomers: Thermal process in comparison with ultraviolet curing, *J. Appl. Polym. Sci.*, **110**, 1019-1027 (2008)
11. Li W., Qiao, X., Sun K. and Chen. X., Mechanical and viscoelastic properties of novel silk fibroin fibre/poly(ϵ -caprolactone) biocomposites, *J. Appl. Polym. Sci.*, **110**, 134-139 (2008)
12. Li W., Zou L., Zhou X., Zhang B., Wang X. and Chen D., Surface dyeability of cotton and nylon fabrics coated with a novel porous silk fibroin/silica nanohybrid, *J. Appl. Polym. Sci.*, **106**, 1670-1676 (2007)
13. Prachayawarakorn J. and Boonsawat K., Physical, chemical, and dyeing properties of Bombyx mori silks grafted by 2-hydroxyethyl methacrylate and methyl methacrylate. *J. Appl. Polym. Sci.* **106**, 1526-1534 (2007)
14. Panda G., Pati N. C. and Nayak P. L., Grafting vinyl monomers onto silk fibres. VIII. Graft copolymerization of methyl methacrylate onto silk using tetravalent manganese-oxalic acid redox system, *J. Appl. Polym. Sci.*, **25**, 1479-1489 (1980)
15. Gulrajani M. L., Gupta D., Periyasamy S. and Muthu S. G., Preparation and application of silver nanoparticles on silk for imparting antimicrobial properties, *J. Appl. Polym. Sci.*, **108**, 614-623 (2008)
16. Kaith B. S., Singha A. S. and Kumar S., Modification of mulberry silk through graft co-polymerization with methyl methacrylate and evaluation of swelling behaviour, moisture absorbance, wettability, chemical resistance and dyeing characteristics, *Int. J. Chem. Sci.*, **4**, 45-54 (2006)
17. Kalia S. Kumar S. and Kaith B. S., Effect of microwave radiations induced grafting on crystalline structure of flax cellulose, *Malaysian Polym., J.* **4**, 46-51 (2009)
18. Banyal S., Kaith B. S. and Sharma R. K., 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, *Adv. Appl. Sci. Res.*, **2**, 193-207 (2011)
19. Peng Q., Xu Q., Sun D. and Shao Z., Grafting of methyl methacrylate onto Antheraea pernyi silk fibre with the assistance of supercritical CO₂, *J. Appl. Polym. Sci.*, **100**, 1299-1305 (2006)
20. Das A. and Saikia C. N., Grafting vinyl monomers onto silk fibres: Graft copolymerization of methyl-methacrylate (MMA) onto – *Antheraea assama* silk fibre, *Ind. J. Chem. Tech.*, **9**, 41-45 (2002)
21. Das A., Saikia C. N. and Hussain S., Grafting of methyl methacrylate (MMA) onto *Antheraea assama* silk fibre, *J. Appl. Polym. Sci.* **81**, 2633-2641 (2001)
22. Munmaya, M. K., Graft copolymerization of methyl methacrylate (MMA) onto silk using potassium peroxydiphosphate-cysteine (PP-Cys) redox system, *J. Appl. Polym. Sci.*, **27**, 2403-2408 (2003)
23. Shashadhar S., Gangadhar S. and Padma N. L., Grafting Vinyl Monomers onto Silk Fibres: Graft Copolymerization of Vinyl Monomers onto Silk Using the Vanadyl Acetylacetonate Complex, *J Macromol Sci, Part A: Pure & Appl. Chem.*, **21**, 725-738 (1984)
24. Kaith B. S., Singha A. S. and Kumar S., Chemically induced graft co-polymerization of Mulberry Silk with Methyl methacrylate and evaluation of swelling behaviour, moisture absorbance and wettability characteristics”, Proceedings of International Conference on Emerging Technology [ICET-2003], Kalinga Institute of Industrial Technology, Bhubaneswar, Orissa, December 19-21, 132-133 (2003)
25. Chauhan G. S., Guleria L. and Sharma R., Synthesis, characterization and metal ion sorption studies of graft copolymers of cellulose with glycidyl methacrylate and some comonomers, *Cellulose.*, **12**, 97-110 (2005)
26. Banyal S., Kaith B. S. and Sharma R. K., 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, *Adv. Appl. Sci. Res.*, **2**, 193-207 (2011)