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Gentian Violet Dye Uptake by Graft Copolymers of Vinyl Binary Monomers onto Silk Fibre

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Abstract

Binary vinyl monomers were grafted onto mulberry silk fibre in aqueous medium by using ceric ammonium nitrate (CAN) as redox initiator. Grafting of binary monomer mixtures of methyl methacrylate (MMA) with butyl acrylate (BA), ethyl acrylate (EA) acrylamide (AAm) and vinyl acetate (VAc) were reported earlier. FTIR, TGA and SEM techniques were used to characterize the graft copolymers. Swelling studies of grafted and ungrafted fibres was done with DMF, water, methanol and n-butanol. Graft copolymers were investigated for dye uptake (gentian violet) photo-calorimetrically at 420 nm.

Keywords:Silk fibre, graft copolymer, gentian violet dye.

Introduction

Some natural occurring as well as synthetic polymers have commercial application[1-3]. 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[4-8]. The natural polymers are open to degradation by acids and bases, which limit their applications. The graft copolymerization technique improve the characteristics of polymeric backbones. Grafting of vinyl monomers improve their chemical resistance, thermal resistance and dye uptake behaviour[9-17]. Silk is one of the most omnipresent natural biopolymers. It finds applications in textile and in surgical applications. Literature survey reveals that various initiators like $KMnO_4$–oxalic acid redox initiator[18,19], benzoyl peroxide[20], CAN[21] and potassium peroxydiphosphate-cysteine redox initiator[22] were reported for grafting of methyl methacrylate (MMA) onto silk fibres. Grafting of binary vinyl monomer mixture (MMA-co-BA)[23], (MMA-co-EA)[23], (MMA-co-AAm)[24] and (MMA-co-VAc)[24].

In our earlier work we have reported modification of mulberry silk fibre by grafting of binary vinyl monomer mixtures (MMA-co-BA)[23], (MMA-co-EA)[23], (MMA-co-AAm)[24] and (MMA-co-VAc)[24] by initiation with ceric ammonium nitrate. In the present study we have studied the swelling properties of graft copolymers in DMF, water, methanol and *n*-butanol. The graft copolymers were also preliminarily investigated for Gentian violet dye uptake to explore their potential applications in separation technologies, textile industry and biomedical applications.

Material and Methods

Materials: Mulberry silk (origin Assam, India) was purchased from market. MMA (Merck) was purified by washing with 5% NaOH and subsequent drying over anhydrous Na_2SO_4 followed by distillation. Butyl acrylate (BA), ethyl acrylate (EA) acrylamide (AAm) and vinyl acetate (VAc) (Merck, US) 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 binary monomer mixtures of MMA with BA, EA, AAm and VAc onto silk were reported in our earlier publications [23,24]. A standard procedure of grafting was adopted and homopolymers were removed from graft copolymer by soxhlet using acetone. The graft copolymers were dried at 50ºC till constant weight was obtained.

Swelling and Dyeing behavior: Swelling studies of grafted and ungrafted silk fibres was done with water, methanol, Dimethyl formamide (DMF) and *n*-butanol as per our earlier reported method. Distilled water is used for preparation of 0.1% gentian violet solution for dyeing experiments. Few drops of 10% common salt solution and of acetic acid were added. The fibre was immersed in resultant solution in 1:50 ratio. The adsorption of dye was studied at room temperature (35 ºC). The optical density of solutions were determined by using photo-colorimeter (model 313E, Environment & Scientific Instruments Co. India) at different time intervals of 1, 2, 3, 4 and 5hrs, respectively. The concentration of each solution after dye uptake by the fibre and percent 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, $I_i$and 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 grafting of vinyl monomers. Grafting with suitable monomers can improve various physical and chemical properties of backbone polymers.

Swelling of Graft Copolymers: The swelling behavior of the graft copolymers was studied to define their end-uses. Swelling of polymeric samples were 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*-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 maximum swelling of graft copolymers was observed in DMF (figures 1-4). 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. Further, the incorporation of hydrophobic polymers like poly(MMA) or poly(EA) or poly(BA) or poly(VAc) 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 silk-g-poly(MMA-co-BA) and silk-g-poly(MMA-co-EA) as the function of P_g followed the order: DMF > n-BuOH > H_2O > MeOH (figure 1a and 1b). Where as in case of silk-g-poly(MMA-co-AAm) swelling behaviour is in order of DMF > H_2O > MeOH > n-BuOH (figure-3) and in silk-g-poly(MMA-co-VAc) swelling behaviour in different solvent is in order of DMF > H_2O > n-BuOH > MeOH (figure-4).

Dying Studies of Mulberry Silk and Its Graft Copolymers: The dying 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 1. The dyeing property of silk fibre is declined in grafted hydrophobic binary monomer mixtures, but it increases with increase in P_g in case of silk-g-poly(MMA-co-AAm) and it 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 improved swelling in non aqueous solvent, at the same time because of hydrophobic monomers the dying ability of silk fibre get reduced. Thus dye uptake behavior depends upon interactions between the dye and the grafted fibre.

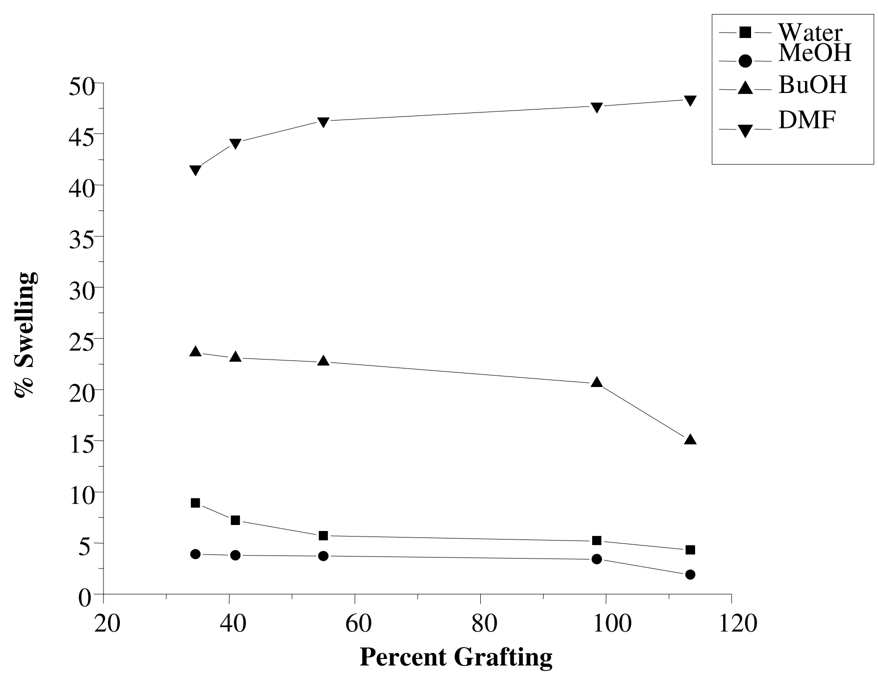

Figure-1
Swelling study of silk-g-poly(MMA-co-BA)

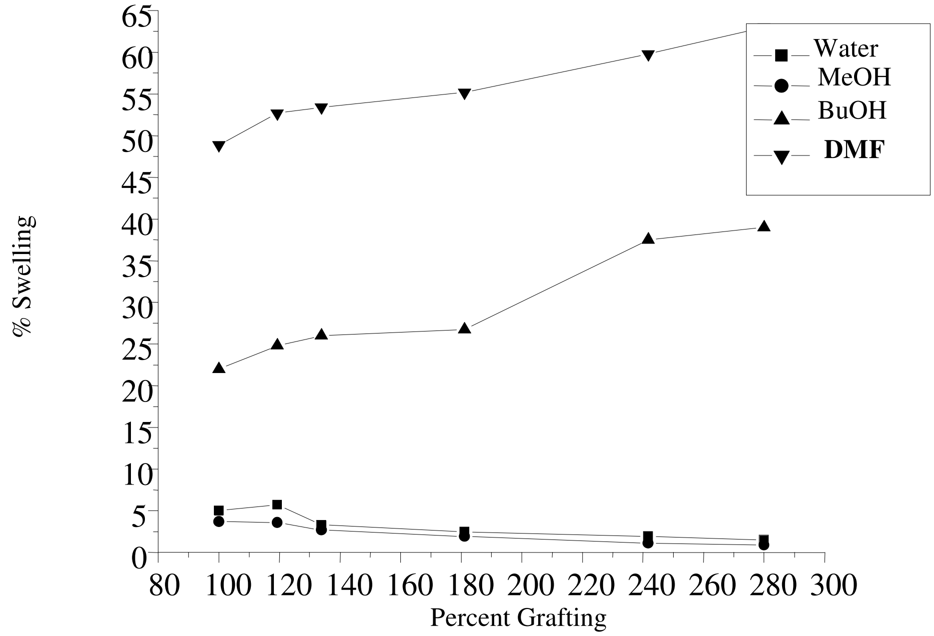

Figure-2
Swelling study of silk-g-poly(MMA-co-EA)

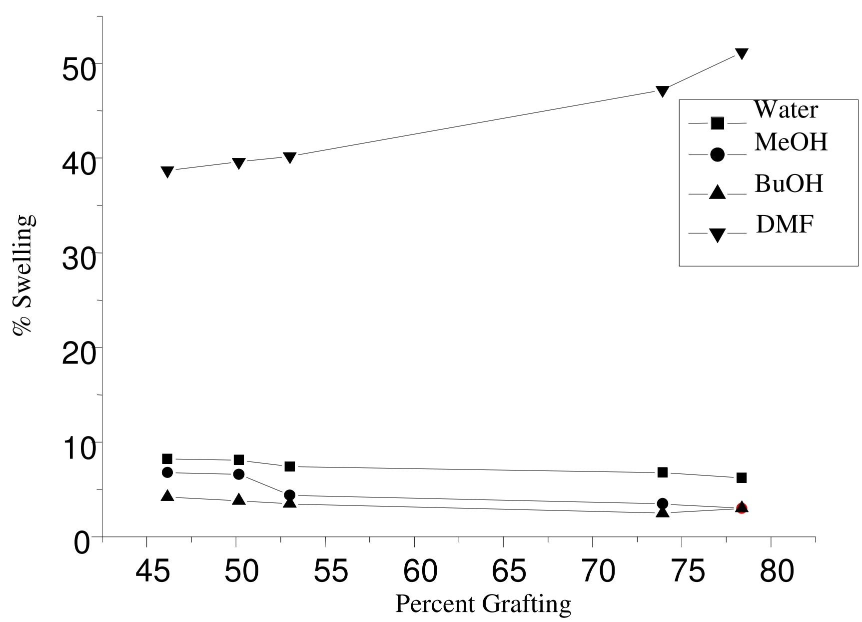

Figure-3
Swelling study of silk-g-poly(MMA-co-AAm)

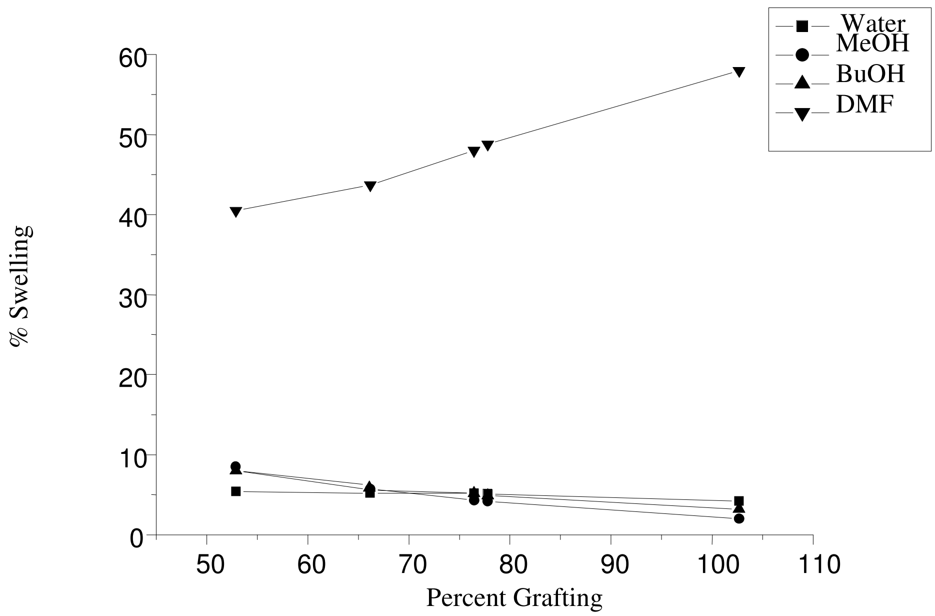

Figure-4
Swelling study of silk-g-poly(MMA-co-VAc)

Table-1
Gentian Violet Dye uptake by the silk and its Graft Copolymers Un-grafted Silk

Sr. No	P_g	I_i [Conc. of test solution (× 10^{-4} mol/L)]					Transmittance (%)				
		Ungrafted silk									
		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*-BA)

Sr. No	P_g	I_i [Conc. of test solution (× 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	34.67	0.19 [5.04]	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
2	41.33	0.17 [4.76]	0.16 [4.48]	0.16 [4.48]	0.16 [4.48]	0.16 [4.48]	80.95	76.19	76.19	76.19	76.19
3	55.03	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
4	98.53	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
5	113.43	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

Silk-*g*-poly (MMA-*co*-EA)

Sr. No	P_g	I_i [Conc. of test solution (× 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	100.00	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
2	119.03	0. 20 [5.60]	0.18 [5.32]	0.18 [5.32]	0.18 [5.32]	0.18 [5.32]	95.24	85.71	85.71	85.71	85.71
3	133.87	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	181.10	0.19 [5.32]	0.18 [5.32]	0.18 [5.32]	0.18 [5.32]	0.18 [5.32]	90.48	85.71	85.71	85.71	85.71
5	231.00	0. 20 [5.60]	0. 18 [5.32]	0. 18 [5.32]	0. 18 [5.32]	0. 18 [5.32]	95.24	85.71	85.71	85.71	85.71
6	241.77	0. 20 [5.60]	0. 18 [5.32]	0. 18 [5.32]	0. 18 [5.32]	0. 18 [5.32]	95.24	85.71	85.71	85.71	85.71
7.	279.96	0. 20 [5.60]	0. 18 [5.32]	0. 18 [5.32]	0. 18 [5.32]	0. 18 [5.32]	95.24	85.71	85.71	85.71	85.71

Silk-*g*-poly (MMA-*co*-AAm)

Sr. No	P_g	I_i [Conc. of test solution (× 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	46.17	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	50.17	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
3	53.03	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	73.93	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
5	78.37	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

Silk-*g*-poly (MMA-*co*-VAc)

Sr. No	P_g	I_i [Conc. of test solution (× 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	52.90	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
2	66.17	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	76.47	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
4	77.80	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
5	102.67	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

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

Conclusion

The graft copolymerization of the binary mixture of four 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 dying ability as the hydrophobic monomers (BA, EA and VAc) exhibited less efficiency than the other monomer i.e. AAm. The dye uptake behavior was also explained by the interaction occurring between the dye and the grafted fibre. Thus, the present study was a successful attempt to understand the role of type of monomers to improve the properties of the native silk fibre those are useful in widening its use-spectrum in textile as well as biomedical applications.

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