Grafting vinyl monomers onto silk fibres: Graft copolymerization of methylmethacrylate (MMA) onto - Antheraea assama silk fibre

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Received 17 January 2001; revised 14 May 2001; accepted 6 June 2001

Graft copolymerization of methylmethacrylate (MMA) onto non-mulberry silk fibre Antheraea assama was carried out in aqueous medium using KMnO₄-oxalic acid redox initiator. The rate of grafting (%) was evaluated as a function of initiator (oxalic acid) and H₂SO₄ acid concentrations, reaction temperature and time. The rate of grafting increased progressively with the increase of oxalic acid and H₂SO₄ concentrations up to 1.25×10⁻² and 16×10⁻² mol/L respectively. The extent of grafting (%) depends upon reaction time and temperature also. The grafted products were characterized with the help of infra-red (IR) spectroscopy, while the thermal decompositions of the ungrafted and grafted silk fibres were studied using TGA, DTG and DTA techniques at two heating rates 20°C and 30°C min⁻¹ in static air in the temperature range 30-800°C. The grafted products were found to be thermally more stable than the ungrafted ones. The water retention values (WRV) of the grafted fibres were in decreasing order with the increase in grafting (%).

Modification in the properties of natural protein fibres through graft copolymerization has become an attractive means of chemical modification, since such treatments, in general, improve some of the disadvantages associated with these fibres. In fact, grafting of vinyl monomers onto natural macromolecules like silk, wool and cellulose have received considerable attention during last two decades or so. Some vital changes in properties like photoyellowing, wash and wear, wrinkle recovery, water repellancy, improved dyeability, soil resistance and thermal stability etc. can be brought about by grafting with various vinyl monomers. Further more, qualitative and quantitative analysis of MMA grafted silk fibres exhibited improved performance properties.

In most of these studies, mulberry and tussah silk fibroins have been used. Comparatively, little attention has been paid towards improving the performance properties of non-mulberry silk fibres obtained from silk worms like Endi (Philosomia ricini) and Muga (Antheraea assama). The silk worm, Antheraea assama Westwood (Lepidoptera : Saturniidae), a multivoltine, sericogenic insect and the silk fibre, popularly known as Muga silk with natural golden yellow hue of the fibre, is one of the most important and commercially valuable silks available in North Eastern India. This silk also lacks some important performance properties as mentioned above. To improve upon some of these properties, work has been carried out on graft copolymerization of the fibre by using methylmethacrylate (MMA) and acrylamide (AAm) with different initiator systems.

In this paper, the results of the graft copolymerization of MMA onto Antheraea assama silk fibre using KMnO₄-oxalic acid redox system as initiator have been reported. The effects of varying initiator (oxalic acid) and H₂SO₄ acid concentrations on weight gain for varying temperature and time of reaction have been studied. The grafted products were characterized with the help of infra-red (IR) spectra, thermogravimetric analysis (TGA), differential thermogravimetry (DTG) and differential thermal analysis (DTA) techniques. The products were also evaluated for their water retention capacity.

Experimental Procedure

Raw materials

Muga silk fibrion produced by following standard degumming and spinning techniques, was collected from a private farm near Jorhat, India. As the silk fibrions were processed ready for weaving, no further purification was required. Methylmethacrylate (CDH) was washed with 5% NaOH solution, dried with anhydrous sodium sulphate and distilled under nitrogen in reduced pressure before use. KMnO₄ (AR, BDH), H₂SO₄ (AR, BDH), Oxalic acid (AR, Loba) and acetone (AR, CDH) were used without further purification. Distilled water was used to prepare all solutions.

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Grafting

All the polymerization reactions were carried out in air.16,17

A three necked 300 mL round bottomed flask fitted with stirrer in a temperature controlled water bath was used for the reactions. 1 g dry silk fibre of 10 mm length, was swollen with water for 15 min. The swollen fibre was transferred to the reaction flask containing solutions of KMnO₄, oxalic Acid and H₂SO₄ of different concentrations. The required amount of monomer, MMA, was added to the reaction system at the required temperature. The reaction time was varied from 10-110 min and temperature of reaction from 25-55°C at material to liquor ratio 1:150. The reaction system was intermittently stirred. After the desired reaction time, the silk fibres were taken out and washed thoroughly with boiling distilled water for several times, and the MMA monomer and its oligomers adhering to the silk fibre were removed by extracting with acetone at 35°C for 24 h18,19. The fibres were dried to constant weight and kept in desiccator over P₂O₅.

The per cent graft yield, total conversion, homopolymer formation and grafting efficiency were calculated on oven dry (o.d) weight of fibre from the increase in weight after grafting by using the following relations.20

Graft yield (%)=\( \frac{(W₂-W₁)}{W₁} \times 100 \)

Graft conversion (%)=\( \frac{(W₂-W₁)}{100/W₄} \)

Total conversion (Monomer to polymer)(%)=\( \frac{(W₂-W₁)}{100/W₄} \)

Homopolymer formation (%)=\( W₅ \times 100/W₄ \)

Grafting efficiency (%)=\( \frac{(W₂-W₁)}{100(W₄+W₁)} \)

where, \( W₁ \) is the weight in grams of original silk fibre; \( W₂ \) the weight in grams of the grafted silk fibre after washing; \( W₄ \) the weight in grams of the grafting monomer; \( W₅ \) the weight in grams of the homopolymer.

Measurement of water sorbency

The water sorbencies of the ungrafted and grafted silk fibres were determined by immersing the fibre in distilled water for 2 h. The fibres were taken out and excess water was removed by putting the fibres between two filter papers under gentle pressure. The fibres were weighed. This weight of the sample was recorded as WET and the sample was then dried in an oven at 65 ± 2°C. The dry weight was recorded as DRY. The water sorbency was expressed as the water retention value (WRV) in gram of water per gram of the o.d sample and was calculated as follows.21

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WRV (g/g) = \frac{(WET-DRY)}{DRY}
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Infrared (IR) studies

IR spectra of ungrafted and grafted silk fibres were recorded on a Perkin-Elmer spectrometer (Model 580B) using KBr disk technique, in the range 4000-200 cm⁻¹ with a resolution of 2 cm⁻¹ using a 5× scans per sample.

Thermal behaviour

The thermogravimetric (TGA), differential thermogravimetric (DTG) and differential thermal analysis (DTA) were carried out using a Shimadzu (Model 30) thermal analyzer. The masses of the samples were in the range 3.95-5.78 mg. α-Alumina was used as a reference material and the temperature ranged from 30 – 800°C at a heating rate of 20° and 30°C min⁻¹ in a static air atmosphere.

Results and Discussion

Effect of oxalic and sulphuric acid concentrations

The graft co-polymerization of MMA onto silk fibre was carried out by varying the initiator (oxalic acid) concentrations from 0.5x10⁻² to 1.5x10⁻² mol/L (M), keeping all other conditions of the reactions constant. So also, the concentrations of H₂SO₄ were varied from 10x10⁻² M to 18x10⁻² M. With the increase in oxalic acid concentrations up to 1.25x10⁻² M, the rate of grafting increased significantly and decreased thereafter (Fig. 1). The extent of grafting (%) in-
increased with increase in H$_2$SO$_4$ acid concentrations up to $16 \times 10^{-2}$ M and then decreased (Fig. 2). The acid enhanced the oxidizing power of permanganate ion up to $20 \times 10^{-2}$ M and reduced thereafter.

**Effect of temperature and time**

The graft co-polymerization was carried out at four different temperatures ranging from 25-55°C. The graft yields (%) were found to increase with increase in temperature (Fig. 3). As the temperature of the reaction increased, the swellability of the fibre was greatly enhanced and as such, the diffusion of the monomer from the solution phase to the fibre phase took place easily, resulting in gradual increase in the complexation of monomer with the silk matrix. The effect of varied reaction time (10-110 min) on graft yield (%) was studied and the results are recorded in Table 1 and Fig. 4. The graft yields (%) increased with the increase in time of reaction. So also, the conversion of monomer to polymer (%) increased with increase in time and temperature of reactions. Similarly, the homopolymer formation (%) also increased, whereas the graft efficiency (%) increased with temperature up to 70 min of reaction time, and thereafter, decreased as evident from Table 1.

The chemical composition of muga silk fibroin consisted predominantly of amino acid residues of glycine, alanine and serine ($80.5 \text{ mol}\%$) with small side chains. These three amino acids form the fibrous component of most of the known silks. The other amino acids present in muga silk fibroin are aspartic acid, threonine, glutamic, valine, cystine, methionine, leucine, tyrosine, phenylalanine, lysine,

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<th>Time of reaction (min)</th>
<th>Graft yield (%)</th>
<th>Conversion of monomer to polymer (%)</th>
<th>Homopolymer formation (%)</th>
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<td>10.2 10.6 24.3 36.4</td>
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*Silk fibre 1 g, MMA $45 \times 10^{-2}$ M; KMnO$_4$ $4 \times 10^{-3}$ M; Oxallic acid $0.5 \times 10^{-2}$ M and H$_2$SO$_4$ $8 \times 10^{-2}$ M; (M = molar), Material to liquor ratio 1:150. The results are averages of three readings.*
proline, tryptophan, histidine and arginine etc. The polypeptide chains in the silk are arranged in β-antiparallel conformation and due to presence of functional groups like -OH, -NH₂, -COOH etc. in the constituent amino acids, the initiating radical may attack the polypeptide backbone as well as the side chain functional groups, thereby, facilitating formation of macroradicals during grafting. In the system, the mechanism of formation of free radicals (C₂O₄) by interaction of Mn(IV) with oxalic acid and then formation of silk macroradicals by graft copolymerization has been explained.

Comparative IR spectra of ungrafted and grafted silk fibres were shown in Figs 5 (a,b). The IR spectra of grafted polymethyl methacrylate silk fibre (b) showed a characteristic band at 1740 cm⁻¹ for carbonyl group of ester stretching vibrations. The band at 3030 cm⁻¹ indicating a -CH₃ vibration was further confirmed by the presence of a band at 1460 cm⁻¹ and 1400 cm⁻¹ for methyl bending vibrations.

Moreover, the band at 1190 cm⁻¹ for -C-C-O-stretching confirmed the formation of MMA grafted silk fibre. The above bands were absent in the spectra of ungrafted silk fibre (a). The band for NH-stretching had shifted to 3570 cm⁻¹ from 3590 cm⁻¹ and NH-hydrogen bonding for amide group also shifted to 1720 cm⁻¹ from 1630 cm⁻¹.

The thermal curves (TGA and DTG) for ungrafted and grafted silk fibre are shown in Figs 6 (a,b,c,d) and Figs 7 (a,b,c,d) at heating rates 20°C min⁻¹ and 30°C min⁻¹ respectively. Thermal decomposition of ungrafted and grafted silk fibres took place in three distinct stages referred as initiation, propagation and carbonization. In the first stage, up to 160°C for A, 170°C for A₁, 175°C for A₂ and 180°C for A₃ at 20°C min⁻¹, only slight loss in weight was observed, which could be attributed to the removal of absorbed water. In the second stage, a major weight loss took place at heating rate 20°C min⁻¹ for ungrafted and grafted products (A-A₃). The decomposition of protein took place in the temperature range 170-450°C for A, which increased for samples A₁ (175-475°C), A₂ (190-480°C) and A₃ (200-490°C) depending on the increasing order of grafting (%). In the third stage, the decomposition of rest of the polymers started at 450°C for A, 475°C, 480°C and 490°C for A₁, A₂ and A₃ respectively. In this stage, the complete decomposi-
tion of the MMA grafted polypeptide backbone along with side chains took place. The weight loss (%) of the grafted fibre was found to be less than that of the ungrafted fibre. It is evident from Table 2, that in both the heating rates, the initial, maximum and final temperatures of active decomposition increased with increase in grafting (%) of the silk fibre.

The DTA curves at heating rate 20°C min⁻¹ showed an endothermic peak at 150°C for ungrafted silk fibre and the same appeared at 155°C, 160°C and 165°C for 44%, 57% and 66% grafted fibres respectively. Similarly, the second endothermic peak appeared for the ungrafted silk at 340°C which shifted to 390°C, 410°C and 420°C for the above grafted products. Exothermic peaks also appeared for grafted products at 350°C (44% grafted), 360°C (57% grafted) and 365°C (66% grafted) due to change in crystallinity 27.

The water retention value (WRV) of the ungrafted and grafted fibres are given in Table 3. The WRV was in decreasing order with the increase in grafting, thereby increase in the hydrophobic nature of the fibre.

Conclusion

Graft co-polymerization of methylmethacrylate onto non-mulberry silk fibre (Antheraea assama) by KMnO₄ - oxalic acid redox system could be carried out in presence of air. The grafted silk fibres were
found thermally more stable than that of the ungrafted one. It was observed that with the increase in grafting, the water retention value decreased.

**Acknowledgement**

The authors wish to thank the Director, Regional Research Laboratory (CSIR), Jorhat - 785 006 for his kind permission to publish this paper.

**References**