

Grafting of Methyl Methacrylate (MMA) onto *Antheraea assama* Silk Fiber

A. DAS,¹ C. N. SAIKIA,¹ S. HUSSAIN²

¹ Regional Research Laboratory, Jorhat - 785006, India

² Dibrugarh University, Dibrugarh - 786004, India

Received 31 May 2000; accepted 20 September 2000

ABSTRACT: Graft copolymerization of methyl methacrylate (MMA) onto nonmulberry silk fiber *Antheraea assama* was investigated in aqueous medium using the KMnO_4 -oxalic acid redox system. Grafting (%) was determined as a function of the reaction time, temperature, and monomer and initiator concentrations. The rate of grafting increased progressively with increase of the reaction time up to 4 h and then decreased. The extent of grafting was maximum at 55°C. The extent was also dependent upon monomer and initiator concentrations up to 75.5×10^{-2} and $6 \times 10^{-3} M$, respectively. The grafted products were evaluated by infrared spectroscopy and their thermal decompositions were studied by TG and DTG techniques in static air at $20^\circ\text{C min}^{-1}$ and $30^\circ\text{C min}^{-1}$ in the range 30–800°C. The kinetic parameters for ungrafted and grafted fibers were evaluated using the Coats and Redfern method. The grafted products were found to be thermally more stable than were those of the ungrafted fibers. The surface characteristics of the ungrafted and grafted fibers were evaluated by scanning electron microscopy. The water-retention values (WRVs) of the grafted fibers were in decreasing order with increase in the grafting (%). © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 81: 2633–2641, 2001

Key words: graft copolymerization; nonmulberry silk fibroin; vinyl monomer; homopolymer; activation energy; water-retention value

INTRODUCTION

Investigations have been carried out by many workers for improving some of the inferior performance properties of silk such as photoyellowing, wrinkle recovery, abrasion resistance, and wash and wear by adopting various graft copolymerization and/or chemical-modification techniques.^{1,2} Epoxides,³ glutaraldehyde,⁴ glycol diglycidyl ether,⁵ and aliphatic and aromatic dibasic acid anhydrides^{6,7} have been used for chemical modification of silk and wool.⁸ Graft copolymerization as such has become an attractive means of chem-

ical modification of protein fibers, since such treatments, in general, improve some of the disadvantages associated with these fibers.^{9,10} Graft copolymerization of silk fibers with vinyl monomers using different initiators is considered to be a powerful method for producing a substantial change in the physical, mechanical, and morphological properties of the fibers.^{11,12} Much work has been carried out during the last two decades or so on the grafting of mulberry and tussah silk fibroins with vinyl monomers.^{13,14} Methyl methacrylate (MMA) is one of the most widely used vinyl monomers for the grafting of silk fibers.¹⁵

Comparatively little attention has been paid toward improving the performance properties of nonmulberry silk fibers, in general, and the Muga

Correspondence to: C. N. Saikia.

Journal of Applied Polymer Science, Vol. 81, 2633–2641 (2001)
© 2001 John Wiley & Sons, Inc.

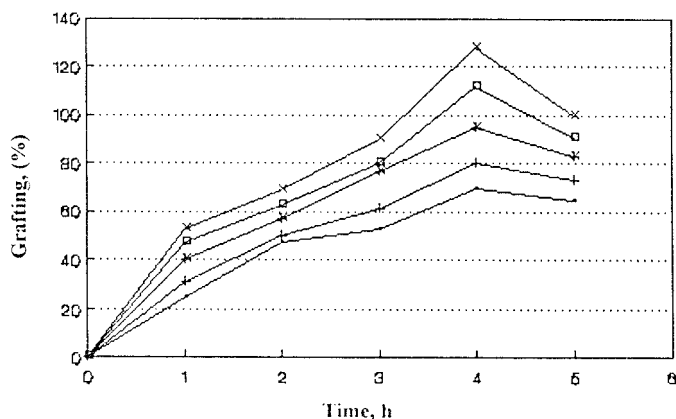


Figure 1 Effect of [MMA] on graft yield: $[\text{KMnO}_4] = 9 \times 10^{-3} \text{ M}$; $[\text{oxalic acid}] = 1 \times 10^{-2} \text{ M}$; $[\text{H}_2\text{SO}_4] = 15 \times 10^{-2} \text{ M}$; temperature = 55°C ; $M:L = 1:150$; (●) [MMA] = $50 \times 10^{-2} \text{ M}$; (+) [MMA] = $60 \times 10^{-2} \text{ M}$; (*) [MMA] = $70 \times 10^{-2} \text{ M}$; (x) [MMA] = $80 \times 10^{-2} \text{ M}$; (□) [MMA] = $90 \times 10^{-2} \text{ M}$.

(*Antheraea assama*) silk, in particular. This particular silk variety with a natural golden yellow hue of the fiber is one of the most important and commercially valuable silks but it also lacks some important performance properties as mentioned above. The golden yellow silk fibers are obtained from the silk worm, *A. assama* Westwood (Lepidoptera: Saturniidae), a multivoltine, sericogenic insect native to Northeastern India.¹⁶ In fact, little work has been reported on grafting of this particular variety of silk.

In this article, we present the results of the graft copolymerization of MMA onto *A. assama* silk fibers using a KMnO_4 -oxalic acid redox initiator. The effects of varying monomer and initiator concentrations on graft yields for varying

times and temperature of the reactions are reported. The grafted products obtained under optimum conditions of grafting were characterized using infrared (IR) spectra, scanning electron microscopy (SEM), thermogravimetric (TG), and differential thermogravimetric (DTG) techniques. The products were also further evaluated for their water-retention capacity.

EXPERIMENTAL

Materials

Muga silk fibroin, produced by following standard degumming and spinning techniques,¹⁷ was col-

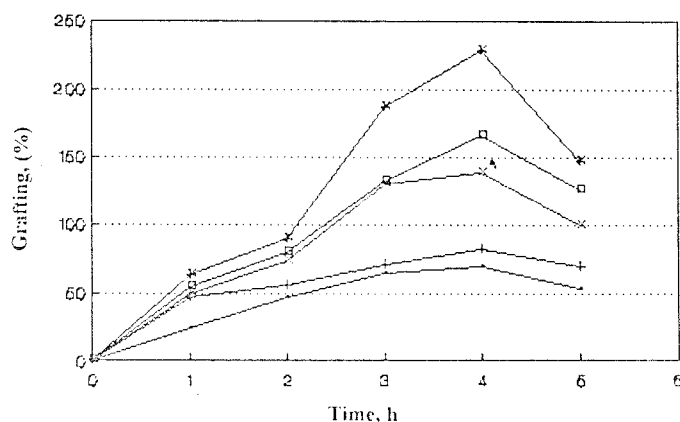


Figure 2 Effect of $[\text{KMnO}_4]$ on graft yield: $[\text{oxalic acid}] = 1 \times 10^{-2} \text{ M}$; $[\text{H}_2\text{SO}_4] = 15 \times 10^{-2} \text{ M}$; [MMA] = $50 \times 10^{-2} \text{ M}$; temperature = 55°C ; $M:L = 1:150$; (●) $[\text{KMnO}_4] = 9 \times 10^{-3} \text{ M}$; (+) $[\text{KMnO}_4] = 10 \times 10^{-3} \text{ M}$; (*) $[\text{KMnO}_4] = 11 \times 10^{-3} \text{ M}$; (□) $[\text{KMnO}_4] = 12 \times 10^{-3} \text{ M}$; (x) $[\text{KMnO}_4] = 13 \times 10^{-3} \text{ M}$.

Table I Graft Copolymerization of MMA onto *A. assama* Silk Fiber at Different Reaction Conditions

Time of Reaction (h)	Graft Yield (%)				Conversion of Monomer to Polymer (%)				Homopolymer Formation				Grafting Efficiency (%)			
	Temperature (°C)				Temperature (°C)				Temperature (°C)				Temperature (°C)			
	35	45	55	65	35	45	55	65	35	45	55	65	35	45	55	65
1	19	23	37	35	12.4	13.3	15.2	17.1	9.7	10.1	10.0	12.2	21.3	24.0	33.9	28.5
2	25	29	55	48	14.6	15.7	29.2	28.9	11.0	11.7	21.5	22.2	23.8	25.7	26.2	23.1
3	32	41	67	61	17.5	20.1	45.1	43.6	13.1	14.4	35.8	35.1	25.4	28.3	20.6	19.4
4	39	49	74	68	27.8	31.7	43.9	43.2	22.4	24.9	33.6	33.8	19.5	21.5	23.4	21.9
5	31	39	62	59	23.5	24.2	48.9	43.3	19.2	18.8	40.3	35.1	18.3	22.4	17.6	18.9

The results are averages of three readings. Silk fiber, 1 g; MMA, $50 \times 10^{-2}M$; $KMnO_4$, $9 \times 10^{-3}M$; oxalic acid $1 \times 10^{-2}M$; and H_2SO_4 , $15 \times 10^{-2}M$. Material-to-liquor ratio: 1 : 150.

lected from a private farm near Jorhat, India. As the silk fibroins were produced ready for weaving, no further purification was done. MMA (CDH, Mumbai, India) was first washed with a 5% NaOH solution and then dried with anhydrous sodium sulfate and distilled under nitrogen in reduced pressure before use.¹² $KMnO_4$ (AR, BDH, Mumbai, India), H_2SO_4 (AR, BDH), oxalic acid (AR, BDH), and acetone (AR, BDH) were used without further purification. Distilled water was used to prepare all solutions.

Methods

Grafting

All polymerization reactions were carried out in air.^{18,19} A three-necked 300-mL round-bottomed flask fitted with stirrer in a temperature-controlled water bath was used for the reactions. One gram of dry silk fiber of 10-mm length was swollen with water for 15 min. The swollen fiber was transferred to the reaction flask containing solu-

tions of $KMnO_4$, oxalic acid, and H_2SO_4 of different concentrations. The required amount of the monomer, MMA, was added to the reaction system. The reaction time was varied from 1 to 5 h and the temperature of the reaction from 35 to 65°C at a material-to-liquor ratio of 1:150. The reaction system was intermittently stirred. After the desired reaction time, the silk fibers were taken out and washed thoroughly with boiling distilled water several times, and the homopolymer adhering to the silk fiber was removed by extraction with acetone at 35°C for 24 h.^{12,20} The fibers were dried to a constant weight and kept in a desiccator over P_2O_5 .

The percent graft yield, total conversion, homopolymer formation, and grafting efficiency were calculated on an oven-dry weight of the fiber from the increased weight after grafting by using the following relations²¹:

$$\text{Graft yield (\%)} = (B - A) \times 100/A$$

$$\text{Graft conversion (\%)} = (B - A) \times 100/D$$

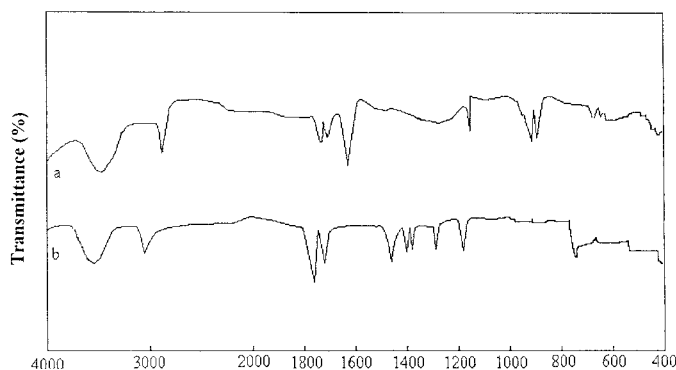


Figure 3 Infrared spectra of (a) ungrafted and MMA-grafted silk fibers at graft yield (%): (b) 49.

$$\begin{aligned} \text{Total conversion (Monomer to polymer) (\%)} \\ = (C - A) \times 100/D \end{aligned}$$

$$\text{Homopolymer formation (\%)} = E \times 100/D$$

$$\text{Grafting efficiency (\%)} = (B - A) \times 100/(C - A)$$

where A is the weight in grams of the original silk fiber; B , the weight in grams of the grafted silk fiber after washing; C , the weight in grams of the grafted silk; D , the weight in grams of the monomer; and E , the weight in grams of the homopolymer.

IR Studies

IR spectra of the ungrafted and grafted silk fibers were recorded on a Perkin-Elmer spectrometer (Model 580 B) using the KBr disk technique, in the range $4000\text{--}200\text{ cm}^{-1}$ with a resolution of 2 cm^{-1} using $5\times$ scans per sample.

SEM

The grafted fibers were mounted on specimen holders using electron conduction tape. The samples were coated with gold in an ion sputter coater (JFC 100, JEOL, Japan) in a low vacuum with a layer $150\text{--}2000\text{-\AA}$ thick. The observation was made in a JEOL, JSM-35 M-35CF, electron microscope at an accelerating potential of 15 kV. Micrographs were taken at this potential.

Thermal Behavior

TG and DTG were carried out using a Shimadzu (Model 30) thermal analyzer. The masses of the samples were in the range $4.05\text{--}5.92\text{ mg}$. α -Alumina was used as a reference material and the temperature ranged from $30\text{ to }800^\circ\text{C}$ at a heating rate of $20\text{ and }30^\circ\text{C min}^{-1}$ in a static air atmosphere.

Measurement of Water Sorbency

The water sorbency of the ungrafted and grafted silk fibers were determined by emerging the fiber in distilled water for 2 h. After that, the fibers were taken out and excess water was removed by putting inside two filter papers under gentle pressure. The fibers were weighed. This weight of the samples was recorded as WET and the samples were then dried in an oven at $65 \pm 2^\circ\text{C}$. The dry weight was recorded as DRY. The water sorbency was expressed as the water-retention value (WRV) in grams of water per gram of the o.d. sample and was calculated as follows²²:

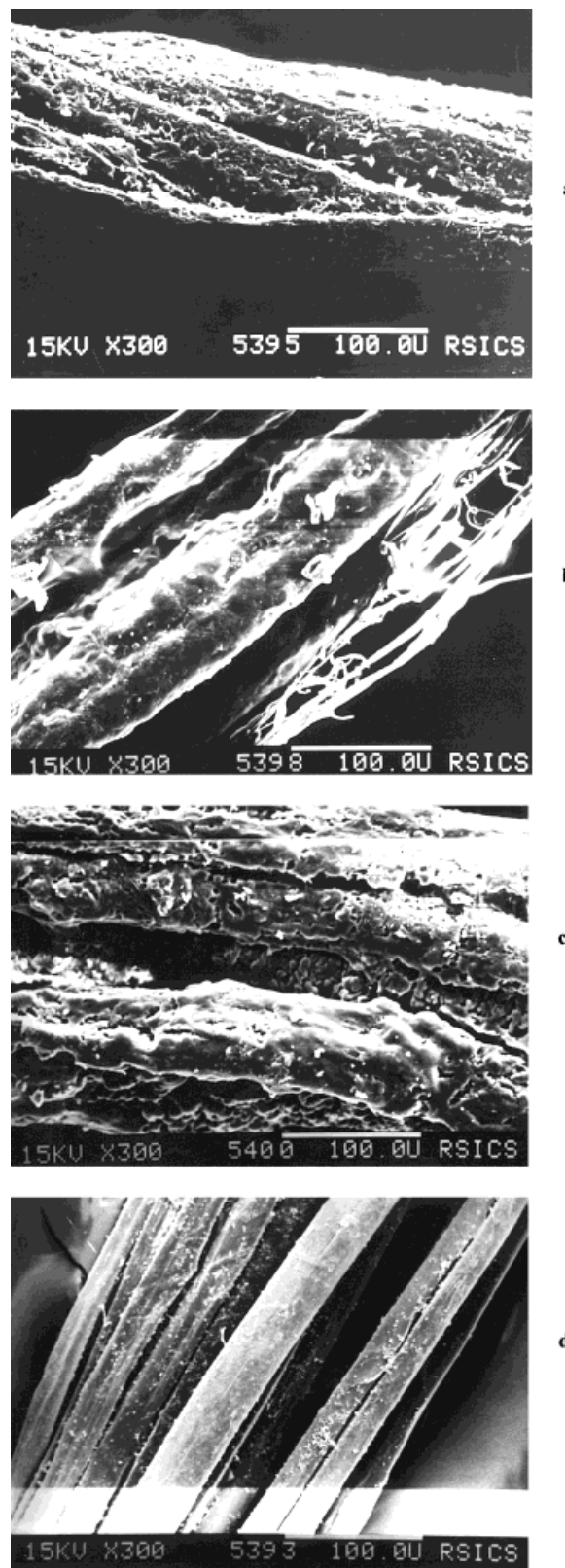


Figure 4 Scanning electron micrographs of MMA-grafted silk fibers. Graft yields (%): (a) 68; (b) 74; (c) 128; (d) 0.

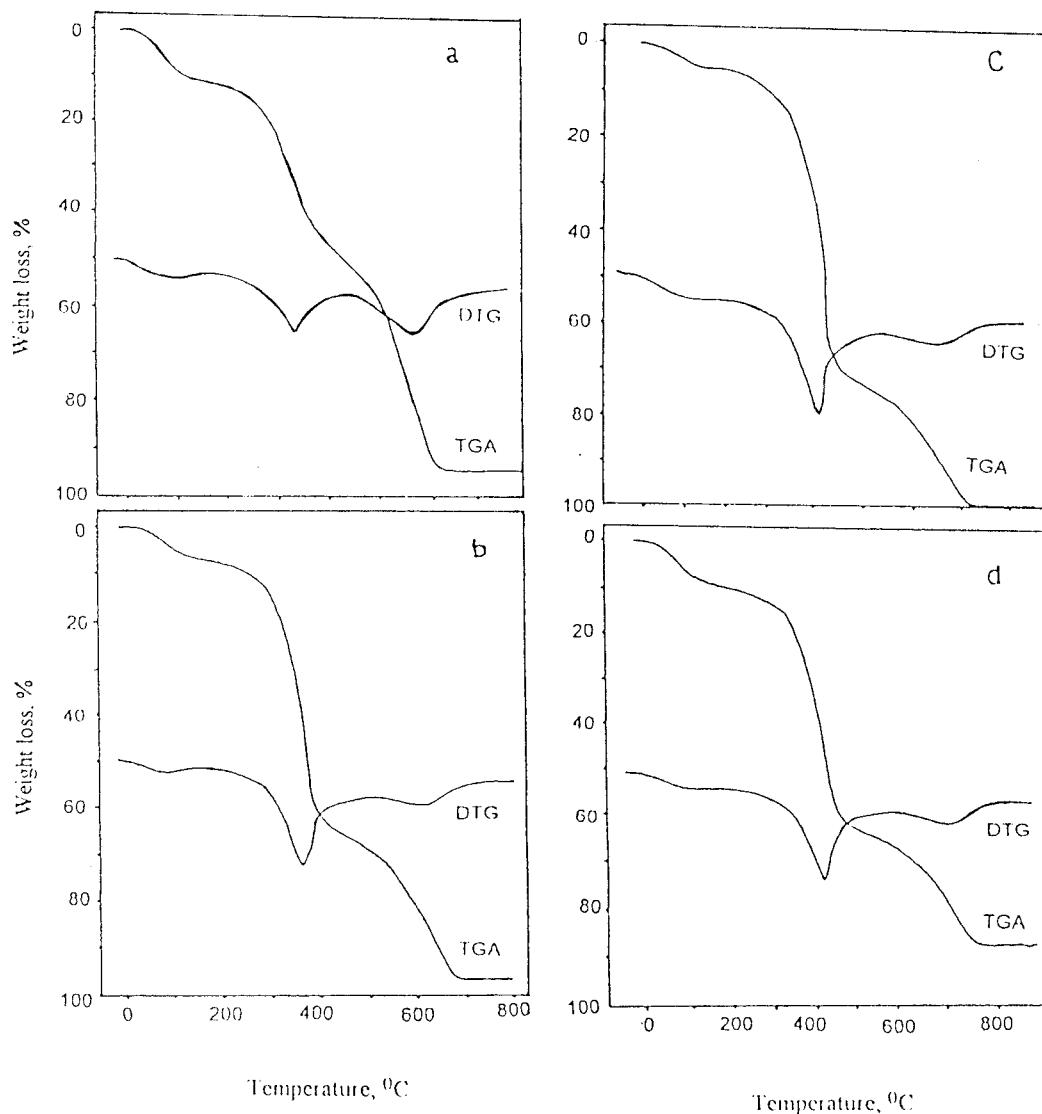


Figure 5 TG and DTG curves at heating rate of $20^{\circ}\text{C min}^{-1}$ of (a) ungrafted and grafted fibers at graft yields (%): (b) 49; (c) 59; (d) 74.

$$\text{WRV (g/g)} = (\text{WET} - \text{DRY})/\text{DRY}$$

RESULTS AND DISCUSSION

Effect of Monomer and Initiator Concentrations

The graft copolymerization of MMA onto silk was carried out by varying the monomer concentrations from 50×10^{-2} mol/L (M) to 90×10^{-2} mol/L (M), keeping all other conditions of the reactions constant. With increase in the monomer concentrations to 80×10^{-2} M , the rate of grafting increased significantly and then decreased (Fig. 1). The complex formation of silk with the monomer might be due to the diffusion of the

monomer to active sites in the silk backbone, thereby enhancing grafting. By varying the permanganate concentrations ($9\text{--}13 \times 10^{-3}$ M) (Fig. 2), the rate of grafting (%) was found to increase progressively with increase of the initiator concentration to 11×10^{-3} M and decreased thereafter. The extent of grafting was about 249% at 4 h with an initiator concentration of 11×10^{-3} M .

Effect of Temperature and Time

The graft copolymerization was carried out at four different temperatures ranging from 35 to 65°C . The relationship between the weight gain and reaction temperature is shown in Table I. The

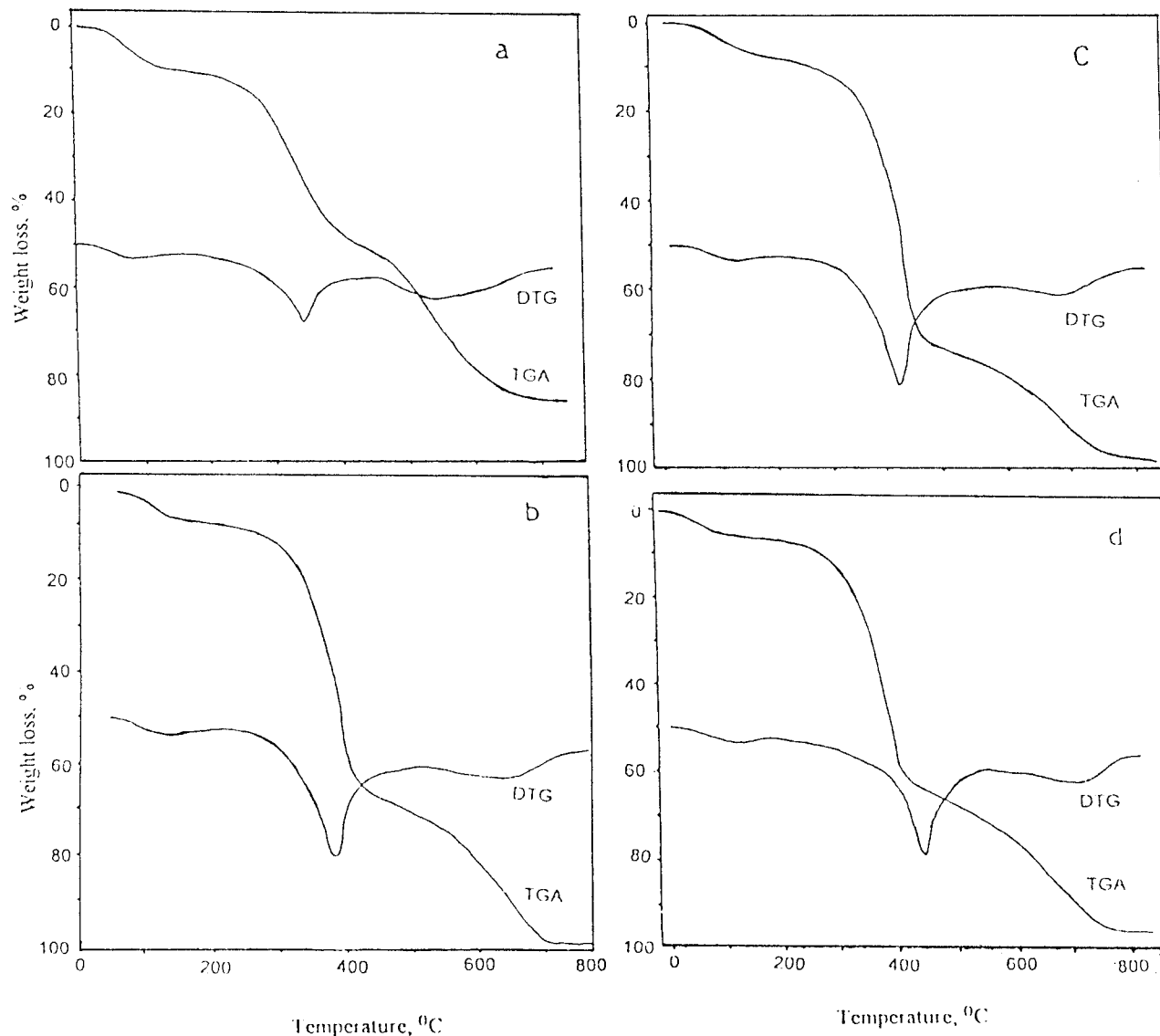


Figure 6 TG and DTG curves at heating rate $30^{\circ}\text{C min}^{-1}$ of (a) ungrafted and grafted fibers at graft yields (%): (b) 49; (c) 59; (d) 74.

weight gain increased steadily to 55°C , and beyond that, the rate gradually decreased. The increased in graft yield (%) in temperatures up to 55°C could be ascribed to a greater activation energy. As the temperature of the reaction increased, the swellability of the fiber was greatly enhanced and, as such, the diffusion of the monomer from the solution phase to the fiber phase took place easily.¹² Beyond 55°C , the weight gain (%) decreased considerably. The effect of the time of the reaction on the graft yield was studied for reactions carried out for 1–5-h duration. The graft yield (%) increased with increase in the time of reaction up to 4 h and, after that, it gradually decreased (Table I). It may be concluded that the

reaction temperature and time have pronounced effects on the grafting of MMA.

IR Studies

IR spectra [Fig. 3(a,b)] of the ungrafted and grafted silk fiber were recorded. The grafted products showed characteristic bands at 1760 cm^{-1} for the $>\text{C}=\text{O}$ group of the ester stretching vibration, 1380 cm^{-1} ($-\text{C}-\text{CH}_3$, stretching vibration), and 1290 cm^{-1} ($-\text{C}-\text{O}-$, stretching vibration).^{23–25} The band at 3030 cm^{-1} , indicating a $-\text{CH}_3$ vibration, was further confirmed by the presence of bands at 1460 and 1400 cm^{-1} for $-\text{CH}_3$ bending vibrations and the band at 1190

cm^{-1} for the $-\text{C}-\text{C}-\text{O}-$ stretching vibration, thereby confirming the formation of MMA grafted silk fiber. These bands were absent in the spectra of ungrafted silk fiber. The band for $-\text{NH}-$ stretching was shifted to 3590 cm^{-1} from 3570 cm^{-1} and for $-\text{NH}-$ hydrogen bonding for the amide group to 1720 cm^{-1} from 1630 cm^{-1} .

Morphological Studies

The surface characteristics of ungrafted and grafted silk fibers were studied by SEM. The SEM micrographs [Fig. 4(a–c)] show the surfaces of the MMA grafted silk fibers, while the micrograph in Figure 4(d) shows the surface of the ungrafted silk fiber, which was smooth and even. But in the case of the grafted one, there was some deposition on the surface of the fiber, resulting in unevenness of the surface, which indicated that MMA was chemically bonded and/or physically adhered to the surface of the silk fiber.²⁶ The roughness of the surface was increased with increase in the grafting (%).

Thermal Behavior

The thermal curves (TG and DTG) at heating rates of 20 and 30°Cmin^{-1} for ungrafted and grafted silk fibers are presented in Figures 5(a–d) and 6(a–d), respectively. Thermal decomposition of the fibers took place in three main degradation steps referred to as initiation, propagation, and carbonization.² All the TG curves showed an initial small mass loss step around 170°C , which was attributed to the removal of absorbed water. In the second stage, for a major weight loss at a heating rate of $20^\circ\text{C min}^{-1}$ for ungrafted and grafted products (B–B3), the decomposition started at 170°C for B, which increased for samples B1 (180°C), B2 (185°C), and B3 (195°C) depending on the increasing order of grafting. The decomposition peaks were within the temperature range $370\text{--}410^\circ\text{C}$ for samples B–B3. In the third stage, the rest of the decomposition took place in the temperature ranges $470\text{--}740$, $490\text{--}750$, $510\text{--}760$, and $560\text{--}770^\circ\text{C}$ for samples B, B1, B2, and B3, respectively. A similar trend was also observed at a heating rate $30^\circ\text{C min}^{-1}$. It is evident from Table II that, in both heating rates, the initial and maximum temperatures of decomposition increased with increase in the grafting (%) of the silk fiber.

Kinetic Studies

The retrieval of kinetic parameters from weight loss versus temperature data can be carried out

Table II Thermal Analysis Data: Active Decomposition Temperature and Weight Loss for Ungrafted and Grafted Silk Fibers at Heating Rates of 20 and $30^\circ\text{C min}^{-1}$

Samples	Weight Loss (%)						Active Decomposition Temperature					
	$20^\circ\text{C min}^{-1}$			$30^\circ\text{C min}^{-1}$			$20^\circ\text{C min}^{-1}$			$30^\circ\text{C min}^{-1}$		
	I	II	III	I	II	III	I	II	III	I	II	III
B	13.5 (30–170)	49.5 (170–470)	27.5 (470–740)	15 (30–180)	52.2 (180–500)	26.5 (500–760)	90 (endo)	370 (endo)	600 (endo)	95 (endo)	375 (endo)	610 (endo)
B1	11 (30–180)	40 (180–490)	39.2 (490–750)	12.8 (30–190)	38 (190–570)	39.5 (570–790)	100 (endo)	395 (endo)	650 (endo)	100 (endo)	415 (endo)	700 (endo)
B2	12.5 (30–185)	38.5 (185–510)	39.8 (510–760)	13.5 (30–195)	35.2 (195–575)	42 (575–790)	100 (endo)	400 (endo)	655 (endo)	100 (endo)	420 (endo)	700 (endo)
B3	12 (30–195)	53.2 (195–560)	12.2 (560–770)	12.8 (30–200)	32.9 (200–590)	42.5 (590–790)	100 (endo)	410 (endo)	660 (endo)	100 (endo)	425 (endo)	710 (endo)

B, ungrafted silk fiber; B1, 49% grafted; B2, 59% grafted; B3, 74% grafted. I, II, and III: Pre, second, and third stages. Temperature range (in $^\circ\text{C}$) in parentheses.

Table III Kinetic Parameters for Ungrafted and Grafted Silk Fibers at Heating Rates of 20 and 30°C min⁻¹

Samples	20°C min ⁻¹						30°C min ⁻¹					
	I			II			I			II		
	<i>E</i> (kJ mol ⁻¹)	<i>A</i> (S ⁻¹)	SED (%)	<i>E</i> (kJ mol ⁻¹)	<i>A</i> (S ⁻¹)	SED (%)	<i>E</i> (kJ mol ⁻¹)	<i>A</i> (S ⁻¹)	SED (%)	<i>E</i> (kJ mol ⁻¹)	<i>A</i> (S ⁻¹)	SED (%)
B	25.137	0.013	0.032	27.209	0.142	0.002	29.077	0.236	0.001	40.509	0.703	0.001
B1	34.949	0.314	0.001	37.339	0.395	0.001	33.490	0.349	0.007	47.171	1.317	0.001
B2	35.026	0.740	0.004	48.132	2.263	0.002	39.547	1.422	0.002	39.508	0.561	0.002
B3	49.433	13.868	0.013	54.101	7.555	0.003	55.728	24.156	0.003	43.608	0.910	0.001

using various methods.²⁷⁻³⁰ In the present work, the well-known Coats and Redfern method²⁸ was thought to be the most reliable for retrieving kinetic parameters from dynamic thermogravimetry. The general correlation equation used in the Coats and Redfern method is

$$\log_{10}[1 - (1 - \alpha)^{1-n}/T^2(1 - n)] = \log_{10}[AR/aE(1 - 2RT/E)] - E/2.3RT$$

where α is the fraction decomposed at temperature T ; n , the order of the reaction; A , the frequency factor (in S⁻¹); a , the heating rate (in K min⁻¹); R , the gas constant (in kJ mol⁻¹ K⁻¹); T , the temperature (in K); and E , the activation energy (in kJ mol⁻¹). A computer program in FORTRAN 77 was used for the linear least-square analysis with a Gauss-Jordan subroutine and applied to evaluate n , ΔE , A , and Standard Error Deviation (SED) simultaneously. The procedure basically involves a stepwise change of the order of the reaction n (over a range 0.6–1.6) to determine the SED in the least-square estimate of the parameters, ΔE and A . The data were found to fit well for a first-order reaction and are given in Table III.

The values of the activation energy and frequency factors for the grafted products are higher than are those of the ungrafted one. These values increase with increase in the molecular weight, that is, an increase in the grafting.

The Coats and Redfern method gave the values of E at 25.137 kJ mol⁻¹, 27.209 kJ mol⁻¹, 29.077 kJ mol⁻¹, and 40.509 kJ mol⁻¹ for the ungrafted one with the lowest molecular weight and 49.433 kJ mol⁻¹, 54.101 kJ mol⁻¹, 55.728 kJ mol⁻¹, and 43.608 kJ mol⁻¹ for the 74% grafted product B3 with the high molecular weight at heating rates 20 and 30°C min⁻¹, respectively. The values of

the frequency factor, A , was within the range 0.013–0.703 S⁻¹ in the above two heating rates for the ungrafted fiber and 0.910–24.156 S⁻¹ for the 74% grafted product (Table III).

WRV

The WRVs for ungrafted and grafted silk fiber are recorded in Table IV. The data for the WRV of ungrafted silk was 3.8 g/g. The values of the WRV were in decreasing order with increase in the grafting, thereby increasing the hydrophobic nature of the fibers.

CONCLUSIONS

Graft copolymerization of MMA onto *A. assama* silk fiber in an aqueous medium by a KMnO₄-oxalic acid redox reaction can be carried out in air with satisfactory results. From the SEM micrographs, it was evident that MMA was either chemically bonded or physically adhered to the silk mass. It was also found that the grafted silk fibers were thermally more stable than was the ungrafted one. The activation energies of the grafted products were found to increase propor-

Table IV WRV of Ungrafted and Grafted Silk Fibers

Samples	Graft Yield (%)	WRV (g/g)
Ungrafted	—	3.80
Grafted	55	1.82
	59	1.79
	62	1.61
	67	1.52
	74	1.37

tionately with increase of the grafting (%). It was also found that with increase in the grafting the hydrophobic nature of the fiber was also increased.

Two of the authors (A. D.; C. N. S.) are thankful to the Director, Regional Research Laboratory (CSIR), Jorhat, India, for kindly permitting publication of this article.

REFERENCES

- Mishra, M. *J Appl Polym Sci* 1982, 27, 2403.
- Mishra, M.; Nayak, P. L.; Sahu, G. *J Appl Polym Sci* 1982, 27, 1903.
- Tsukada, M; Nagura, M; Ishikawa, H; Shiozaki, H. *J Appl Polym Sci* 1991, 43, 643.
- Tsukada, M; Shiozaki, H. *J Ser Sci Jpn* 1986, 55, 257.
- Tsukada, M; Shiozaki, H; Gotoh, Y.; Freedi, G. *J Appl Polym Sci* 1993, 50, 1841.
- Tsukada, M; Shiozaki, H. *J Appl Polym Sci* 1989, 37, 2337.
- Tsukada, M; Shiozaki, H; Gotoh, Y.; Freedi, G.; Crighton, J. S. *J Appl Polym Sci* 1994, 51, 345.
- Tsukada, M; Shiozaki, H; Konda, A. *J Appl Polym Sci* 1990, 41, 1213.
- Samal, R. K.; Nanda, C. N.; Satrusallya, S. C.; Nayak, B. L.; Suryanarayan, G. V. *J Appl Polym Sci* 1983, 28, 1311.
- Tripathy, S. S.; Jena, S.; Singh, B. C. *J Appl Sci* 1983, 28, 1811.
- Samal, R. K.; Suryanarayan, G. V.; Dash, P. C.; Panda, G.; Das, D. P.; Nayak, N. C. *J Appl Polym Sci* 1981, 26, 2221.
- Panda, G.; Pati, N. C.; Nayak, P. L. *J Appl Polym Sci* 1981, 26, 775.
- Mahanty, N.; Pradhan, B.; Mahanta, M. C.; Das, H. K. *J Macromol Sci Chem A* 1983, 19, 1189.
- Mishra, B. N.; Mehta I. K.; Dogra, R. *J Appl Polym Sci* 1980, 25, 235.
- Tsukada, M.; Kasai, N.; Freddi, G. *J Appl Polym Sci* 1993, 50, 885.
- Hazarika, L. K.; Saikia, C. N.; Katakya, A.; Bordoloi, S.; Hazarika, J. *Biores Tech* 1998, 64, 67.
- Choudhury, S. N. *Silk and Sericulture*, 1st ed.; Directorate of Sericulture: Assam, India, 1992.
- Lepoutre, P.; Hui, S. H. *J Appl Polym Sci* 1975, 19, 1257.
- Kulkarni, A. Y.; Mehta, P. C. *J Appl Polym Sci* 1968, 12, 1257.
- Mansour, O. Y.; Nagieb, Z. A.; Basra, A. N. *J Appl Polym Sci* 1991, 43, 1147.
- Fernandez, M. J.; Casinos, I.; Guzman, G. M. *J Appl Polym Sci Part A Polym Chem* 1990, 28, 2275.
- Vitta, S. B. Ph.D. Thesis, North Carolina State University, 1984.
- Scheinmann, F. *An Introduction to Spectroscopic Methods for the Identification of Organic Compounds*; Pargonan: New York, 1970; p 125.
- Banwell, C. N. *Fundamentals of Molecular Spectroscopy*, 3rd ed.; Tata McGraw-Hill: New Delhi, 1972; p 107.
- Silverstein, R. M.; Bossless, G.; Clayton, M.; Trencce, C. *Spectrometric Identification of Organic Compounds*, 5th ed.; Wiley: New York, 1991; p 118.
- Tsukada, M. *J Appl Polym Sci* 1988, 35, 965.
- Chatterjee, P. K.; Conrad, S. M. *Text Res J* 1966, 36, 487.
- Coats, A. W.; Redfern, J. R. *Nature* 1964, 68, 201.
- Horowitz, H. H.; Metzger, G. *Anal Chem* 1963, 35, 1464.
- Broido, A. *J Polym Sci Part A-2* 1969, 7, 1761.