



Microwave radiation induced surface modification of silk fibers with methylmethacrylate and acrylonitrile monomers through graft-copolymerization

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ABSTRACT

The surface modification of the silk fiber was carried out with the aim to increase the weight loss and to improve its physical properties. The graft-copolymerization with ascorbic acid and hydrogen peroxide as the initiator system was investigated using methylmethacrylate (MMA) and acrylonitrile (AN) monomers under the influence of microwave radiations. The percent graft yield had a significant effect on various reaction parameters which include reaction time, temperature, monomer and initiator concentrations. The maximum graft yield was found to be 100.4% and 8.9% with MMA and AN monomers, respectively. The grafted fibers were characterized by various techniques such as infrared spectroscopy (FT-IR), scanning electron microscopy (SEM) and Thermogravimetric analysis (TGA).

Keywords: Silk fiber; Graft-copolymerization; Scanning electron microscopy

INTRODUCTION

Bombyxmori silkworm produces cocoons which are made of protein materials called silk fibroin and silk sericin. Silk fibroin is known to be strongest fiber because of its chemical structure that constitutes repetitive glycine-alanine-glycine-alanine-glycine-serine units which self assemble to form antiparallel β - sheet structure [1-2]. Due to some superior properties of the silk fiber compared to other fibers such as mechanical and aesthetic properties which include softness, luster and strength; silk fiber is known as the “Queen of fibers”. However, silk has certain drawbacks like photo yellowing, wrinkle recovery, less resistance to the attack of chemicals, wash and wear etc. which needs to be improved [3]. Modification of properties of natural protein fibers and plant fibers through graft copolymerization of vinyl monomers has become an attractive technique, have been reported by various workers and the fibers were reported to have high thermal stability and resistance to chemicals which were otherwise highly reactive to the attack of chemicals [4-7]. Graft-copolymerization involves the attachment of polymer chains to the backbone polymer and this process is the most commonly used methods to increase the compatibility between synthetic polymers and natural fibers [8]. The fibers modified under the microwave radiation (mwr) were found to have same or better properties similar to that of other conventional techniques. The microwave radiation induced graft-copolymerization technique reduces the level of the physico-chemical stresses, is cost effective and saves time and the obtained graft-copolymers can be used as reinforcement in the preparations of composites [9-10]. Composites reinforced with natural fibers have attained great interest in recent years because of their advantage over synthetic polymers which includes their biodegradability, low density and good mechanical properties and found various applications at industrial levels [11-12].

In the present paper, graft-copolymerization of silk fiber has been carried out with methylmethacrylate and acrylonitrile monomers under the influence of microwave radiations. The effect of reaction parameters such as reaction time, temperature, initiator and monomer concentration were optimized to have a better graft yield.

EXPERIMENTAL SECTION

Materials and Methods

Bombyx mori silk fibers were obtained from Silk Center, Kangra (Local region), Himachal Pradesh. Methyl methacrylate (MMA) and Acrylonitrile (AN) and sodium carbonate were received from CDH India. Acetone and Dimethyl Formamide supplied by Rankem laboratories of reagent grade were used for the extraction of homopolymer formed during the graft- copolymerization process.

B. mori silk fibers were separated from the silk sericin protein by washing with an aqueous solution of sodium carbonate. After washing with sodium carbonate the fibers were rinsed with distilled water to remove sericin protein and dried in hot air oven at 60°C.

The fibers were immersed in water before the graft-copolymerization process to activate the reaction sites on the fiber surface. After that the known amount of ascorbic acid was mixed with hydrogen peroxide and the mixture was poured into the reaction vessel containing the fibers. The monomers MMA and AN were added into different reaction vessels containing fibers along with the initiators. The reaction vessel was placed in a microwave at 70 watt power which was having a microwave (IFB 20PGI) frequency of 2450 MHz. The reaction parameters were determined to get the maximum graft yield.

After the graft-copolymerization process fibers SF-g-poly(MMA) fibers were washed with acetone and SF-g-poly(AN) fibers were washed with dimethyl formamide to remove the homopolymers from the fiber surface and were dried in hot air oven at 50°C.

The percentage grafting was calculated as follows:

$$\text{Grafting(\%)} = \frac{W_2 - W_1}{W_1} \times 100$$

Where W_2 is the final weight and W_1 is the initial weight of fibers before and after the graft-copolymerization.

Characterization

FT-IR spectra of the fibers were recorded with KBr pellet method on a Perkin Elmer spectrophotometer. The surface morphology of the fibers was observed by using FEI-Quanta 450SEG Scanning Electron Microscope (SEM). Thermogravimetric analysis studies were carried out under N_2 atmosphere on EXSTAR TG/DTA 6300 analyzer. The fibers were also evaluated for their chemical resistance studies.

RESULTS AND DISCUSSION

It was postulated that ascorbic acid interacts with hydrogen peroxide to produce OH^* , which leads to chain propagation reaction and thus creates active sites on the fiber backbone where grafting can take place. The mechanism for the grafting of monomer in the presence of ascorbic acid/hydrogen peroxide and spectroscopic analysis of the fibers has already been explained in our previous communication [13-14].

Effect of reaction parameters

It was observed that the graft yield increases with increase in time and then starts decreasing. The maximum graft yield of 100.4% was observed with MMA ($3.76 \times 10^{-1} \text{ mol L}^{-1}$), ascorbic acid ($1.41 \times 10^{-2} \text{ mol L}^{-1}$) and hydrogen peroxide ($0.80 \times 10^{-1} \text{ mol L}^{-1}$) as initiator in 15 minutes as shown in Table 1. Similarly, with AN ($3.03 \times 10^{-1} \text{ mol L}^{-1}$), ascorbic acid ($1.41 \times 10^{-2} \text{ mol L}^{-1}$) and hydrogen peroxide ($1.58 \times 10^{-1} \text{ mol L}^{-1}$), the graft yield obtained was 8.9% in 10 minutes under the influence of mwr as shown in Table 2. It was investigated that increase in time increases the movement of free radicals to the fiber backbone, results in high graft yield. But the further increase in time was followed by the decrease in percent graft yield and was also accompanied by the burning of the sample. The further increase in monomers and initiator concentration above optimized concentrations decreases the graft yield because of the predomination of homo-polymerization over graft co-polymerization. Although, the increased viscosity of the reaction medium also created obstacles in the movement of the free radicals to the active sites of the fiber backbone, thus results in decreased graft yield.

Table 1. Optimization of various reaction parameters for grafting of MMA onto silk fibroin fibers under the influence of microwave radiations

Sr. No.	Time (min.)	H ₂ O ₂ (mol/L×10 ⁻¹)	Ascorbic acid (mol/L×10 ⁻²)	Monomer (mol/L×10 ⁻¹)	P _g
1	5	0.80	0.71	0.47	5.12
2	10	0.80	0.71	0.47	11.38
3	15	0.80	0.71	0.47	11.76
4	20	0.80	0.71	0.47	10.86
5	25	0.80	0.71	0.47	7.78
6	15	0.80	1.41	0.47	12.3
7	15	0.80	2.12	0.47	8.28
8	15	0.80	2.83	0.47	6.7
9	15	0.80	3.54	0.47	4.3
10	15	0.52	1.41	0.47	6.24
11	15	0.80	1.41	0.47	12.3
12	15	1.05	1.41	0.47	8.24
13	15	1.32	1.41	0.47	7.5
14	15	1.58	1.41	0.47	6.06
15	15	0.80	1.41	0.94	14.14
16	15	0.80	1.41	1.41	15.84
17	15	0.80	1.41	1.88	33.86
18	15	0.80	1.41	2.35	66.36
19	15	0.80	1.41	2.82	81.36
20	15	0.80	1.41	3.29	98.84
21	15	0.80	1.41	3.76	100.4
22	15	0.80	1.41	4.23	89.44
23	15	0.80	1.41	4.70	74.34

Table 2. Optimization of various reaction parameters for grafting of AN onto silk fibroin fibers under the influence of microwave radiations

Sr. No.	Time (min.)	H ₂ O ₂ (mol/L×10 ⁻¹)	Ascorbic acid (mol/L×10 ⁻²)	Monomer (mol/L×10 ⁻¹)	P _g
1.	5	1.58	1.41	3.03	5.9
2.	10	1.58	1.41	3.03	8.9
3.	15	1.58	1.41	3.03	5.98
4.	20	1.58	1.41	3.03	5.52
5.	25	1.58	1.41	3.03	4.78
6.	10	1.58	0.71	3.03	7.54
7.	10	1.58	2.12	3.03	3.68
8.	10	1.58	2.83	3.03	3.48
9.	10	1.58	3.54	3.03	2.51
10.	10	0.80	1.41	3.03	2.62
11.	10	1.58	1.41	3.03	8.9
12.	10	2.38	1.41	3.03	5.52
13.	10	3.17	1.41	3.03	2.02
14.	10	3.96	1.41	3.03	1.28
15.	10	1.58	1.41	1.5	0.24
16.	10	1.58	1.41	2.2	1.82
17.	10	1.58	1.41	3.03	8.9
18.	10	1.58	1.41	3.79	3.72
19.	10	1.58	1.41	4.55	0.22

FT-IR spectroscopy

The FT-IR spectra of raw silk fiber and degummed silk fibers have already been explained in our previous communication [13]. The SF-g-poly(MMA) spectra shows an additional peak at 1739.09 cm⁻¹ which is due to the >C=O group which suggests that MMA has been grafted onto silk fiber through covalent bonding as shown in Figure 1(a). However, on the graft - copolymerization of silk fiber with AN monomer an addition, peak was observed at 2244.17 cm⁻¹ and that was assigned to the CN stretching of the acrylonitrile monomer confirming the graft-copolymerization of AN monomer on the fiber backbone as shown in Figure 1 (b).

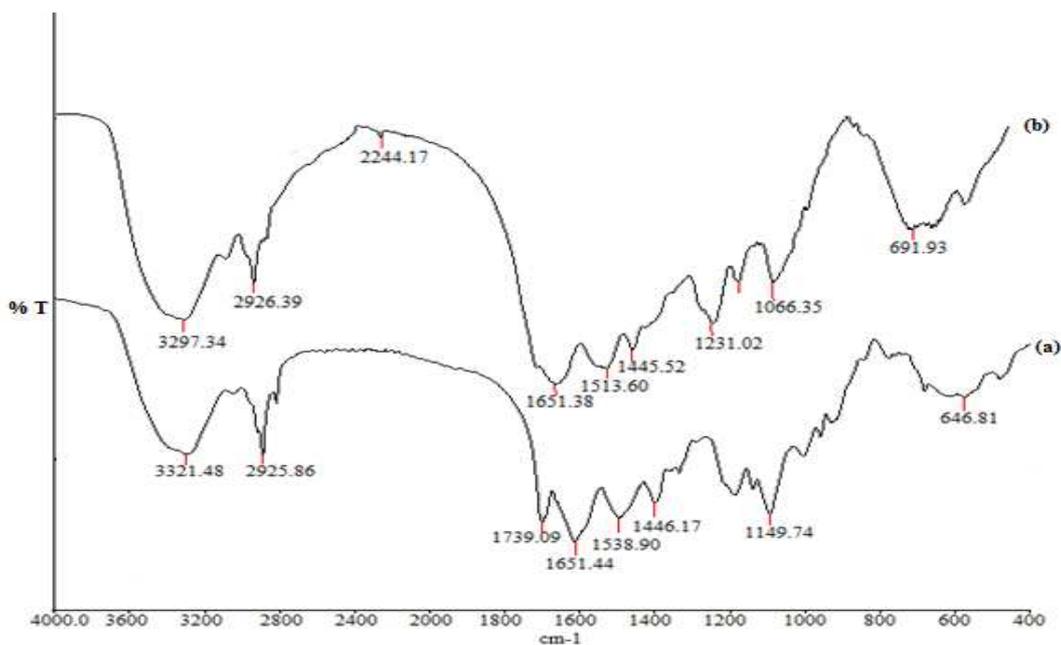


Fig 1 FT-IR Spectra of (a) SF-g-poly(MMA) and (b) SF-g-poly(AN) under the influence of microwave radiation

Thermal analysis

The weight loss in the initial temperature range from 60 to 100°C can be attributed to the moisture loss from the fiber surface. The thermal stability of the samples was measured as percent weight loss in their initial and final temperature decomposition temperature range. The initial and final decomposition temperatures for SF-g-poly(MMA) were found to be 225°C and 500°C as shown in Figure 2(a). For SF-g-poly (AN) the initial and final decomposition was found to be 211°C and 631°C as shown in Figure 2 (b). The increase in the decomposition temperature of the grafted fibers compared to raw and degummed silk fiber confirms their thermal stability at higher temperature ranges.

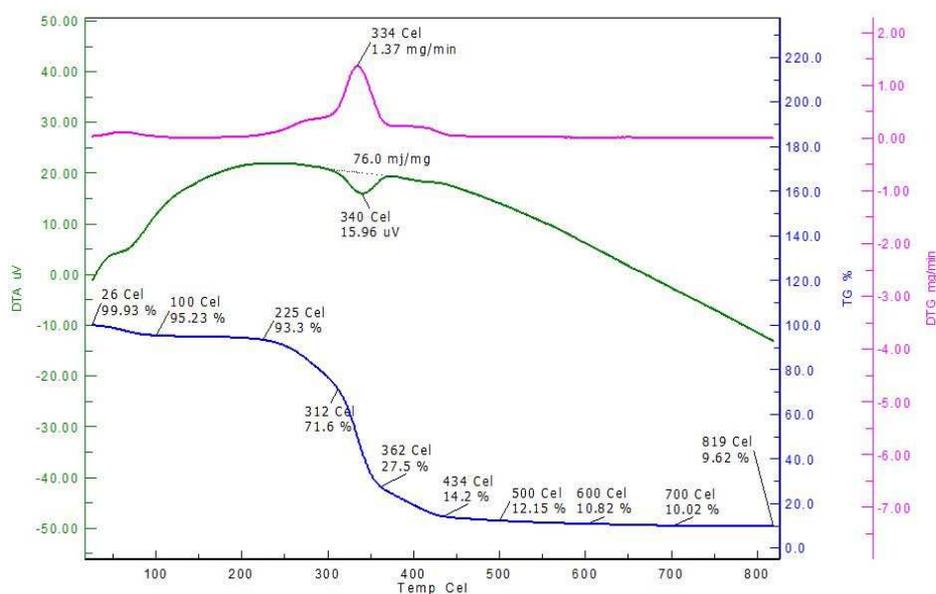


Fig 2(a) Thermograph of SF-g-poly(MMA) under the influence of microwave radiation

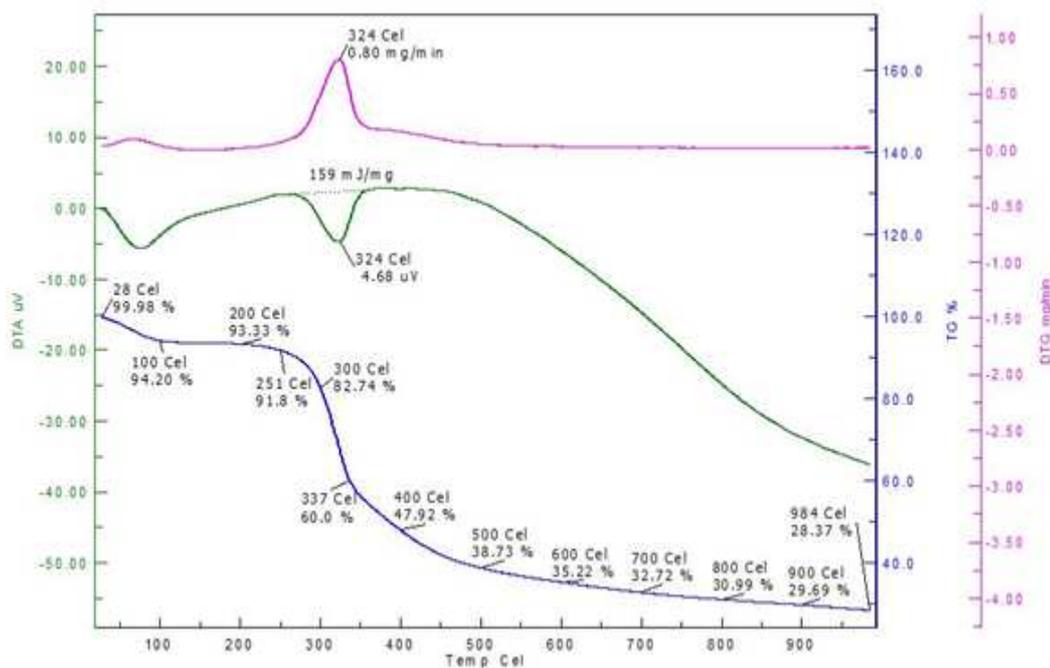


Fig 2(b) Thermograph of SF-g-poly(AN) under the influence of microwave radiation

Scanning electron microscopy

The scanning electron micrographs of raw fiber shows the presence of glue like sericin protein on the fiber surface and the fiber surface after the sericin removal was found to be smooth [13]. From the scanning electron micrographs Figure 3(a) and 3(b), it was found that there has been sufficient deposition of poly(MMA) and poly(AN) onto the silk fiber surface. The fiber surface was found to be rough after the graft-copolymerization process.

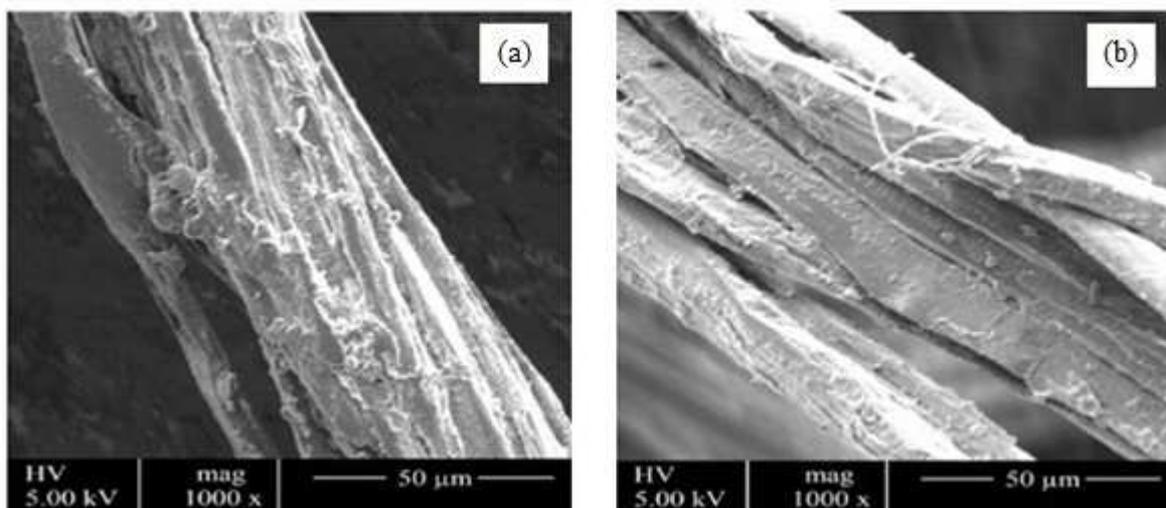


Fig 3 Scanning electron micrographs of (a) SF-g-poly(MMA) and (b) SF-g-poly(AN) under the influence of microwave radiations

Chemical resistance

The SF-g-poly(MMA) and SF-g-poly(AN) fibers were found to be resistant against the attack of the acid and bases as shown in Table 3. The enhancement in chemical resistance increases with rise in percent graft yield. This could be due to the reason that the active sites of the fibers were blocked after the graft-copolymerization processes which were otherwise highly active to the attack of chemicals.

Table 3. Chemical resistance of silk fibroin fiber, SF-g-poly(MMA) and SF-g-poly(AN) using HCl and NaOH of different strength under the influence of microwave radiations

Sr. No.	Sample	Pg (%)	% Wt. loss			
			0.5 N HCl	1 N HCl	0.5 N NaOH	1 N NaOH
1.	Silk Fibroin Fiber	-	9.30	13.92	26.30	34.24
2.	SF-g-poly(MMA)	100.4	4.26	5.14	15.60	19.91
3.	SF-g-poly(AN)	8.90	6.37	7.85	21.43	27.60

CONCLUSION

The surface modification of *Bombyxmori* silk fibers has been carried out through graft-copolymerization with MMA and AN monomers under the influence of microwave radiations. From the SEM analysis it was observed that the fiber surface became rough after the graft-copolymerization process and there was an increase in the percent graft yield. FT-IR spectra confirmed the grafting of PMMA and PAN chains onto the fiber backbone. The thermal stability of the fibers increased and were found to be resistant against the attack of chemicals. The surface modified fibers can be used as reinforcement for the synthesis of composites.

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