

Peroxide Treatment of Soy Protein Fibers Followed by Grafting of Poly(methyl acrylate) and Copolymers

Pushpa Bhardwaj¹, Susheel Kalia^{2,3,*}, Amit Kumar¹ and Hemant Mittal⁴

¹Department of Chemistry, Shoolini University, Bajhol – 173 229, Dist. Solan (H.P.) India

²Department of Civil, Chemical, Environmental and Materials Engineering, University of Bologna, via Terracini 28, 40131, Bologna, Italy

³Department of Chemistry, Bahra University, Wahnaghat – 173 234, Dist. Solan (H.P.) India

⁴Department of Applied Chemistry, University of Johannesburg, Doorfontein - 20280 Johannesburg, South Africa

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ABSTRACT: The objective of the present study is to elucidate the effect of peroxide treatment and graft copolymerization on water absorption behavior of soy protein fibers in order to make them suitable as a reinforcing material. Grafting of poly(methyl acrylate) and copolymers was successfully carried out on peroxide-treated soy protein fibers. Different reaction parameters were optimized in order to get maximum percentage grafting. The grafted fibers were evaluated for water absorption behavior in deionized water. Maximum grafting has been found at 0.219 mol/l of methyl acrylate, 0.0096:0.145 mol/l of FAS:H₂O₂, 323 K, and 90 minutes. Graft copolymerization results in remarkable changes in morphology of soy protein fibers. The FT-IR spectrum confirms the graft copolymerization of methyl acrylate and binary monomer mixture onto soy protein fibers. Grafted soy protein fibers showed minimum water absorption as compared to original and peroxide-treated soy protein fibers because active sites were blocked due to grafting of poly(methyl acrylate) and other copolymers.

KEYWORDS: Grafting, peroxide treatment, soy protein fibers, water absorption

1 INTRODUCTION

Various researchers have improved the surface properties of natural fibers through different chemical and green methods. Chemical treatments include mercerization, acetylation, benzylation, peroxide treatments, polymer grafting, etc., and environmentally friendly methods such as plasma treatment; treatments using fungi, enzymes and bacteria were also used for the surface modification of natural fibers [1]. Mishra *et al.* [2] have reported that mercerization leads to an increase in the amount of amorphous cellulose due to hydrogen bonding. Acetylation is also beneficial as it reduces the moisture absorption, and increases dimensional stability and environmental degradation capacity of natural fibers. Improvement in the processability and mechanical properties of natural fibers after treatment with peroxides were studied [3]. Graft copolymerization is an important

method for surface chemical modification of natural fibers. Various researchers have used graft copolymerization for the surface modification of natural fibers [4–6]. Kaith and Kalia [7,8] have also modified the properties of natural fibers through graft copolymerization and found them suitable for composite materials.

There is scant information in the literature about peroxide treatment of alkali-treated soy protein fibers followed by grafting of poly(methyl acrylate) and copolymers. So attempts have been made for grafting of copolymers onto peroxide-treated soy protein fibers in order to make them suitable for reinforcing materials. Grafted soy protein fibers can be potentially used as reinforcement for the fabrication of composite materials.

2 EXPERIMENTAL

2.1 Materials

Methyl acrylate, ethyl acrylate, and acrylic acid (S d fine), sodium hydroxide (CDH), benzoyl peroxide (CDH), and ferrous ammonium sulfate (CDH), hydrogen peroxide (CDH) were used as received. Soy

*Corresponding author: susheel.kalia@unibo.it,
susheel.kalia@gmail.com

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protein concentrate were provided by Spinning King (India) Limited.

2.2 Methods

2.2.1 Alkali Treatment

Soy protein fibers (SPF) were soaked in 5% NaOH solution for 20 minutes at 70°C. Fibers were then rinsed with distilled water thoroughly until the removal of unreacted sodium hydroxide. Soy protein fibers were then dried in a hot air oven at 70°C.

2.2.2 Benzoyl Peroxide Treatment

After alkali treatment, soy protein fibers were subjected to benzoyl peroxide treatment. Alkali soy protein fibers were soaked in 5% benzoyl peroxide solution. Fibers were then kept in the solution for 20 minutes at 75°C. Finally, soy protein fibers were washed with distilled water and dried at 70°C in a hot air oven.

2.2.3 Graft Copolymerization of Methyl Acrylate onto Peroxide-Treated Soy Protein Fibers

Peroxide-treated soy protein fibers (500 mg) were immersed in 100 ml of distilled water for 24 hours prior to their grafting in order to activate the reactive sites. Amide groups of soy protein fibers are the reactive sites involved in graft copolymerization. A definite ratio of ferrous ammonium sulphate-hydrogen peroxide (FAS:H₂O₂) as initiator and a known amount of methyl acrylate as monomer were added to the reaction mixture with constant stirring. The reaction mixture was kept at definite temperature for definite time interval. Homopolymer was separated from graft copolymer by washing with distilled water and stirring with acetone for 24 hours. The grafted fibers were then dried in a hot air oven at 323 K till a constant weight was obtained. Optimization of different reaction parameters such as reaction time, reaction temperature, and concentration of monomer and initiator was performed. Percentage grafting (% grafting) was calculated as follows [5]:

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

Where W_1 and W_2 are the weight of original and grafted soy protein fibers, respectively.

2.2.4 Grafting of Copolymers onto Peroxide-Treated Soy Protein Fibers

Peroxide-treated soy protein fibers (500 mg) were immersed in 100 ml of distilled water for 24 hours in

order to activate the active sites on the fibers surface for grafting of copolymers. An optimized concentration of methyl acrylate was added to the reaction flask and monomers such as acrylic acid and ethyl acrylate of varied concentration were added. Optimized amount of FAS:H₂O₂ were also added to reaction mixture and reaction was carried out at optimized temperature for optimized reaction time. Synthesized graft copolymers were washed with distilled water and soxhlet extracted with acetone for 24 hours in order to remove unreacted homopolymer and copolymers. The grafted samples were dried in a hot air oven at 50°C. The percentage grafting (P_g) was calculated using the same formula as given above.

2.2.5 Water Absorption Behavior

Water absorption behavior of original and grafted fibers was carried out in deionized water. A known amount of fibers were dipped in deionized water for a particular period of time. The excess of water was removed with the help of filter papers. The final weight of samples was noted and percentage of water absorption was calculated using the following formula [9].

$$Ps = \frac{W_f - W_i}{W_i} \times 100$$

Where W_i and W_f are the initial and final weight of fibers, respectively.

2.2.6 Characterization of Synthesized Graft Copolymers

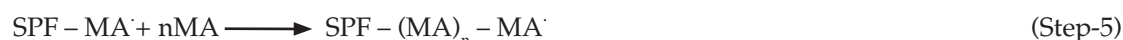
X-Ray diffraction studies were performed on a Bruker X-ray diffractometer (D8 Advance) [10]. The FTIR spectroscopy was performed in the range 500-4000 cm⁻¹ in a Shimadzu M850 FTIR spectrophotometer. The scanning electron microscopic analysis of soy protein fibers and its graft copolymers was carried out on an electron microscopy machine (SEM QUANTA 250 FEI D9393).

3 RESULTS AND DISCUSSION

3.1 Graft Copolymerization of Methyl Acrylate onto Peroxide-Treated Soy Protein Fibers

Various reaction parameters such as reaction time, reaction temperature, monomer concentration, and initiator concentration were optimized to obtain the maximum grafting yield. The graft copolymerization of methyl acrylate onto soy protein fibers was carried out as per mechanism proposed by Kaith and coworkers (Scheme 1) [4].



Initiation:**Propagation:**

(Growing graft copolymer)



(Growing Homopolymer)

Termination:

Graft copolymer



(Homopolymer)

**Scheme 1** Probable mechanism for graft copolymerization onto soy protein fibers [4].**3.1.1 Effect of Reaction Time on Percentage Grafting**

The effect of increased reaction time onto percentage grafting is shown in Figure 1a. Percentage grafting was found to increase with the increase of reaction time up to 90 minutes and then decreased to some extent with a further increase in reaction time. Maximum grafting yield (57%) was observed at 90 minutes. The increase in percentage grafting is due to the extension of initiation and propagation of graft copolymerization with reaction time. Whereas decrease in percentage grafting after 90 minutes may occur because initially synthesized graft copolymer prevented the further diffusion of monomer into the fiber surface. So no more reactive sites are available

for further attachment of monomer on the surface of soy protein fibers [11].

3.1.2 Effect of Reaction Temperature on Percentage Grafting

The percentage of grafting increased with an increase of temperature up to 323 K and then decreased beyond this temperature (Figure 1b). Increased reaction temperature results in the production of a large number of active primary radicals, which also increases the number of grafting sites for more diffusion of monomer into the fiber matrix. The decrease in percentage of grafting at higher temperature might be due to the formation of homopolymer over grafting and premature termination of growing grafted

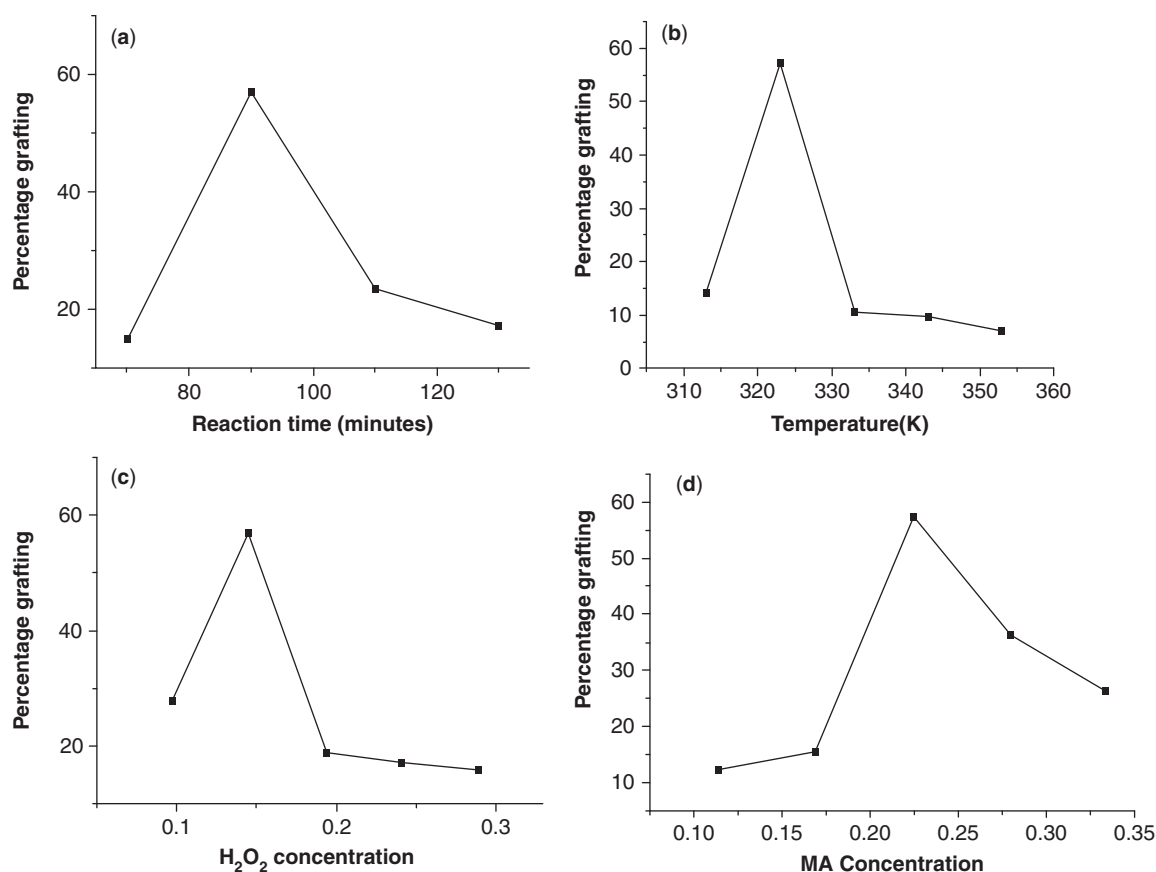


Figure 1 Variation of percentage grafting of poly(methyl acrylate) onto soy protein fibers: (a) reaction time; (b) temperature; (c) H₂O₂ concentration; (d) methyl acrylate concentration.

chains by excess Fe³⁺ ions produced in oxidation on Fe²⁺ ions [12].

3.1.3 Effect of H₂O₂ Concentration on Percentage Grafting

It has been observed that the percentage of grafting increases up to 0.145 mol/l of H₂O₂ and then was found to decrease beyond this concentration of H₂O₂ (Figure 1c). The increase in percentage grafting occurs by reaction of Fe²⁺ ions with H₂O₂. This reaction results in the production of more hydroxyl radicals, which attack fibers to produce macroradicals. The decrease in percentage grafting beyond optimized concentration of H₂O₂ may be due to an increase in numbers of fiber radicals, which cause termination prior to monomer addition. Another factor responsible for the decrease in percentage grafting at higher initiator concentration may be the increased homopolymer formation, which competes with the grafting reaction for available monomer [13,14]. Ferrous ammonium sulfate was used as a co-catalyst with H₂O₂ to accelerate the production of hydroxyl radicals because H₂O₂ alone does not decompose

to produce radicals. The Fe²⁺ sped up decomposition of H₂O₂ to produce radicals, thus increasing the amount of free radicals needed for the reaction, and hence increasing percentage grafting. Another reasonable factor for the decrease in percentage grafting at higher initiator concentration is the presence of large numbers of free radicals, which interact with each other and cause termination prior to monomer addition [15,16].

3.1.4 Effect of Methyl Acrylate Concentration on Percentage Grafting

The percentage of grafting increases with the increase in concentration of methyl acrylate (Figure 1d). It has been observed that the percentage of grafting increases up to 0.219 mol/l monomer concentration. Percentage grafting was decreased beyond 0.219 mol/l of MA due to gel effect. As a result, the chain mobility gets reduced and the ability of active ends of two long chains to come together and terminate is decreased. But the small monomer molecules can still diffuse to the active chain ends and cause an increase in the polymerization rates. Thus higher

molecular masses result due to the decrease in termination rate, and hence increased percentage grafting was observed. Grafting was found to decrease with a further increase in monomer concentration, because a substantial amount of polymer had been grafted onto fibers and no more reactive sites were available for further diffusion of monomer molecule. Another factor responsible for the decrease in percentage grafting beyond optimized concentration may be increased homopolymer formation, which competes with grafting reaction for available monomer [13,14].

3.2 Grafting of Binary Monomer Mixtures onto Soy Protein Fibers

Soy protein fibers were graft copolymerized with binary vinyl monomer mixtures such as methyl acrylate + acrylic acid and methyl acrylate + ethyl acrylate. The graft copolymerization was carried out using optimized concentration of methyl acrylate and initiator at 323 K for 90 minutes. Percentage grafting increases initially with an increase in the monomer (AAc) concentration but slowly decreases with a further increase in concentrations of acrylic acid (Figure 2a). Similar behavior was observed in the case of ethyl acrylate and methyl acrylate. Percentage grafting increases with an increase in concentration of ethyl acrylate but decreases with further increased concentration (Fig. 2b). The increase in percentage grafting with an increase in monomer concentration was observed because more monomer molecules diffuse to the active chain ends

which reduces the termination and results in higher molecular weights. The decrease in percentage grafting beyond optimized concentration of acrylic acid and ethyl acrylate occurred due to the increase in homopolymer and copolymer formation, which competes with the grafting reaction for available monomer [14].

3.3 Water Absorption Behavior

Water absorption behavior of soy protein fibers is shown in Table 1. Original soy protein fibers showed maximum water absorption due to greater affinity for water of the reactive groups present in fibers in comparison to peroxide-treated and grafted soy protein fibers. In the case of peroxide-treated and grafted soy protein fibers, reactive sites on the surface of fibers were blocked by reaction with peroxide radicals and grafting of copolymers and no longer available to react with water molecules.

Table 1 Water absorption behavior of original fibers, peroxide-treated fibers and SPF-g-poly(MA).

Sr. No.	Fibers	Water absorption (%)			
		2 hr	4 hr	6 hr	8 hr
1.	Original SPF	28	50	68	92
2.	Peroxide treated SPF	14	38	62	80
3.	SPF-g-poly(MA)	10	30	62	66

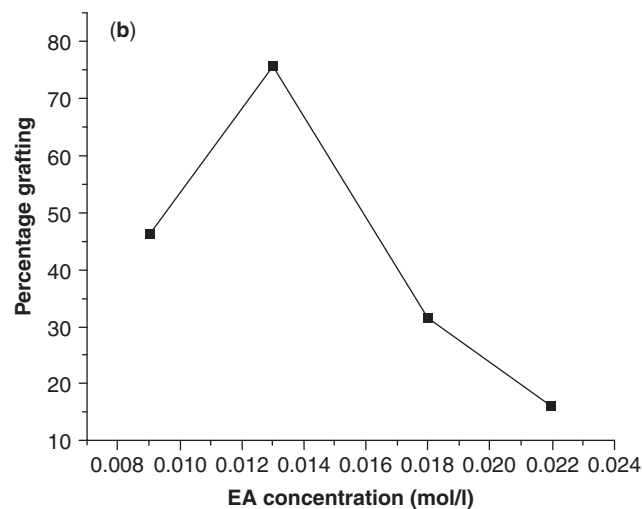
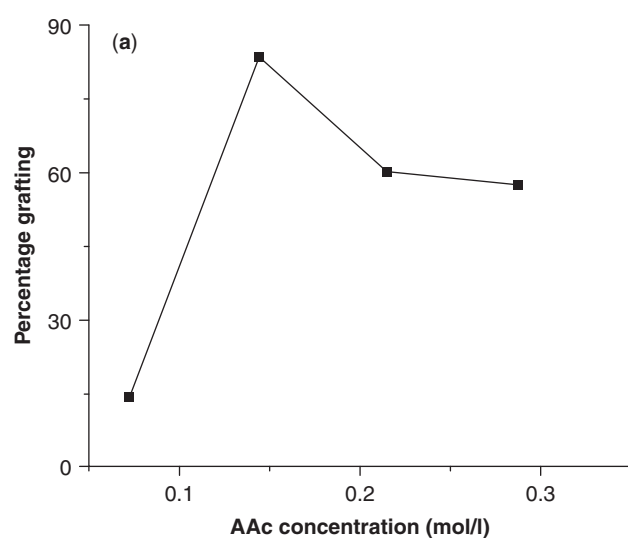


Figure 2 Variation of percentage grafting with (a) MA + AAc concentration and (b) MA + EA concentration [Temperature = 323 K, Reaction time = 90 minutes, MA concentration = 0.219×10^{-2} mol L⁻¹, FAS:H₂O₂ concentration = 0.0096:0.0145 mol L⁻¹].

3.4 FT-IR of Original and Modified Soy Protein Fibers

Figure 3a shows the FT-IR spectrum of original soy protein fibers. IR spectrum of original soy protein fibers showing a broad peak at 3343.12 cm^{-1} due to free $-\text{OH}$ and $-\text{NH}$ groups, a peak at 2914.94 cm^{-1} due to C-H stretching, a peak at 1660.77 cm^{-1} due to C=O stretching of amide group (amide-I) and a peak at 1539.63 cm^{-1} due to N-H bending (amide-II) have been observed. The peak at 1443.90 cm^{-1} was due to C-H structure. The peaks at 1140.84 cm^{-1} was due to C-O structure. The peak at 1017.71 cm^{-1} was due to C-O stretching. The peak at 846.73 cm^{-1} was due to C-H stretching vibration in the molecule. Whereas, SPF-g-poly(MA) showed an additional peak at 1739.61 cm^{-1} due to C=O stretching which confirmed the grafting of poly(MA) onto soy protein fibers (Fig. 3b). Similarly, SPF-g-poly(MA+AAc) and SPF-g-poly(MA+EA) showed additional peaks at 1737.81 cm^{-1} (Fig. 3c) and 1736.14 cm^{-1} (Fig. 3d), respectively, due to C=O

stretching along with peaks of SPF, because of the presence of carbonyl group in both molecules, i.e., acrylic acid and ethyl acrylate. This confirmed the grafting of binary monomer mixtures onto soy protein fibers.

3.5 X-ray diffractogram (XRD) Study of Original and Modified Soy Protein Fibers

It is evident from Table 2 that original soy protein fibers, peroxide-treated soy protein fibers, SPF-g-poly(MA), SPF-g-poly(MA+AAc) and SPF-g-poly(MA+EA) showed 86.5, 84.6, 80.8, 77.4 and 84.8 percent crystallinity, respectively (Figure 4). A very small decrease in percentage crystallinity was observed in the case of SPF-g-poly(MA), SPF-g-poly(MA+AAc) and SPF-g-poly(MA+EA) because of the incorporation of poly(MA), poly(MA+AAc) and poly(MA+EA) into soy protein fibers which impaired the crystallinity of fibers.

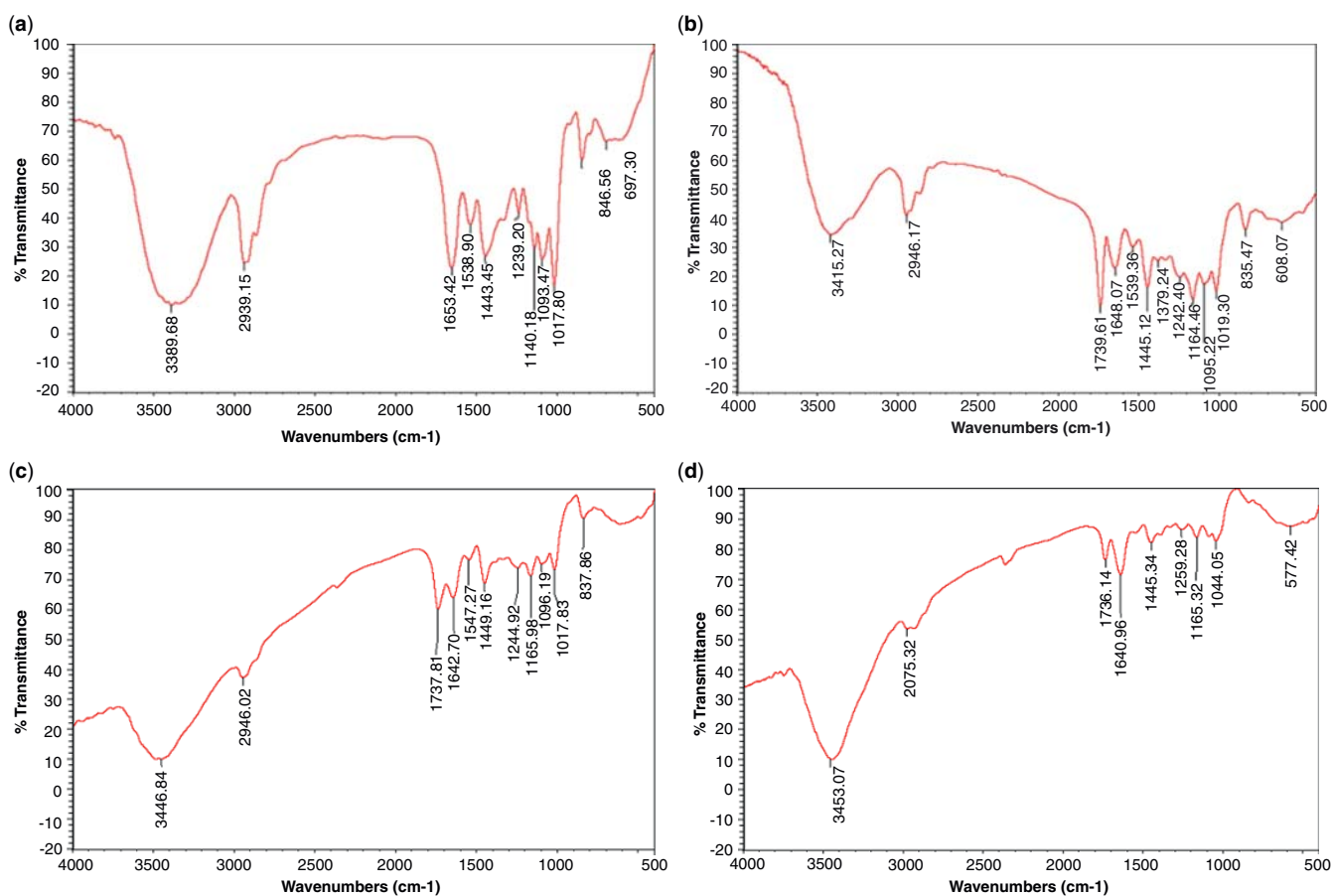
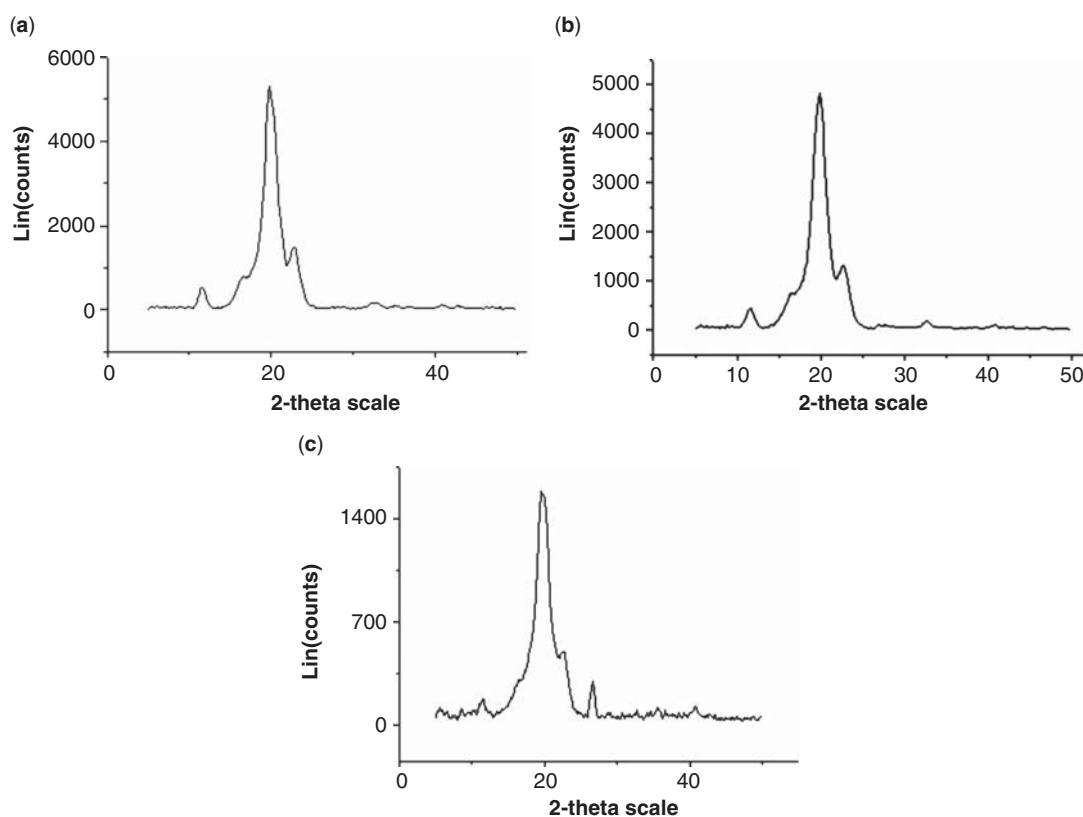


Figure 3 Fourier transform infrared spectroscopy (FTIR) spectra of (a) soy protein fibers, (b) SPF-g-poly(MA), (c) SPF-g-poly(MA+AAc), and (d) SPF-g-poly(MA+EA).

Table 2 Percentage crystallinity of original and chemically treated soy protein fibers.

Sr. No.	Sample	$I_C=22$	$I_A=18$	Cr (%)
1.	Original SPF	5133.84	860.42	86.5
2.	Peroxide treated SPF	4729.71	858.64	84.6
4.	SPF-g-poly(MA)	2002.59	474.32	80.8
5.	SPF-g-poly(MA+AAc)	1021.03	297.70	77.4
6.	SPF-g-poly(MA+EA)	1339.60	240.01	84.8

**Figure 4** X-ray diffractogram (XRD) of (a) soy protein fibers, (b) peroxide-treated SPF, and (c) SPF-g-poly(MA).

3.6 Morphology of Original and Modified Soy Protein Fibers

Figure 5 shows the scanning electron micrographs of raw soy protein fibers (Fig. 5a), peroxide-treated soy protein fibers (Fig. 5b), SPF-g-poly(MA) (Fig. 5c), SPF-g-poly(MA+AAc) (Fig. 5d) and SPF-g-poly(MA+EA) (Fig. 5e), respectively. These micrographs clearly show the differences in their surface morphology. It has been observed from the figure that the surface morphology of original soy protein fibers differs in smoothness and roughness compared to peroxide-treated and grafted soy protein fibers. The surface of original soy protein fibers is smooth because it is free from any deposition

of polymer chain. The surface of peroxide-treated soy protein fibers has become rough due to the removal of oil, waxes and other impurities. The surface of soy protein fibers becomes rough upon graft copolymerization because a considerable amount of polymer has been grafted on the surface of fibers.

CONCLUSION

The grafting of poly(methyl acrylate) and copolymers was successfully carried out onto peroxide-treated soy protein fibers. The XRD studies indicated a negligible decrease in crystallinity after graft copolymerization,

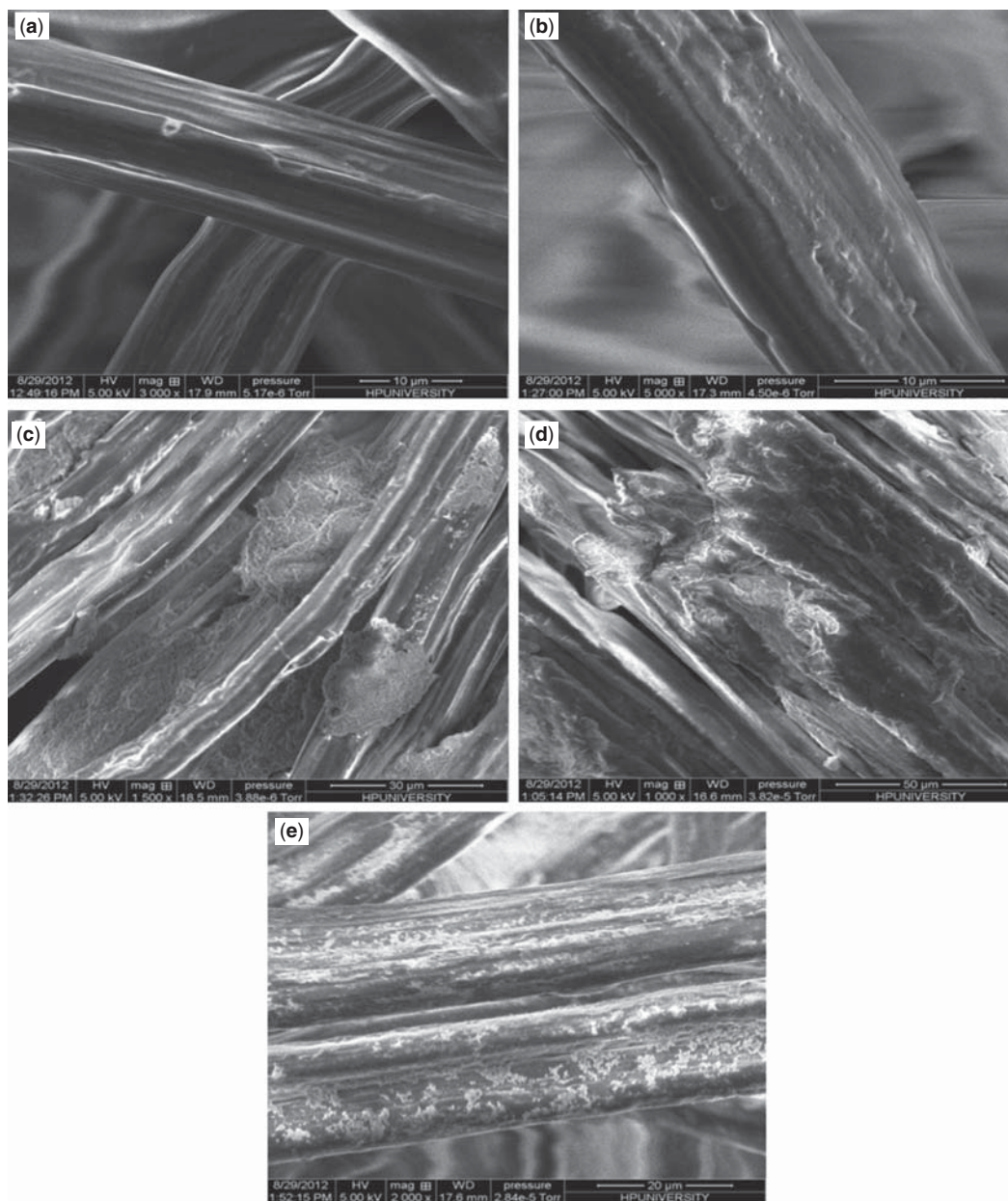


Figure 5 Scanning electron microscopy (SEM) of (a) Soy protein fibers, (b) peroxide-treated SPF, (c) SPF-g-poly(MA), (d) SPF-g-poly(MA+AAc), and (e) SPF-g-poly(MA+EA).

which may be due to a small disturbance in fiber structure during grafting of polymer molecules. Grafted soy protein fibers showed minimum water absorption as compared to original and peroxide-treated soy protein fibers because active sites were blocked due to grafting of poly(methyl acrylate) and other copolymers.

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