Morphological and Thermal Evaluation of Soy Protein Concentrate on Graft Copolymerization with Ethylmethacrylate

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ABSTRACT: Soy protein concentrate was grafted with ethylmethacrylate using ascorbic acid/potassium persulphate as a redox initiator. Different reaction parameters, such as reaction time, reaction temperature, solvent amount, initiator ratio, and pH, and monomer concentration were optimized to get maximum graft yield (134.12%). The graft copolymer formed was characterized by Fourier transform infrared spectrophotometer, X-ray diffraction, and scanning electron microscope techniques. Thermogravimetric analysis, differential thermal analysis, and differential thermogravimetric analysis studies showed that graft copolymer was thermally more stable than the backbone. Thermal decomposition studies indicated that the rate of weight loss per minute was found more in case of backbone when compared with that of graft copolymer. Further, graft copolymer was also found more resistant toward acid–base attack and was found to be more water repellent. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 120: 2183–2190, 2011

Key words: soy protein concentrate; graft copolymer; EMA; ascorbic acid; potassium persulphate; TGA; FTIR

INTRODUCTION

Continuous depletion of petroleum reservoirs draws the attention of researchers toward bioresources especially agro-based products such as cellulose,[1] starch,[2] and proteins[3] due to their renewability and ecofriendliness. Proteins are one of the suitable substitutes for synthetic polymers. Among proteins, plant proteins are abundant and are found in different plants such as wheat,[4] corn,[5] zein,[6] and soy.[7] These plant proteins have been investigated for various applications.[8–10]

Soy protein obtained from plant *Glycine max* (L.) Merrill is an industrial crop cultivated mainly for oil and proteins. This plant contains about 20% of oil and about 50% proteins. It contains 18 amino acids including polar ones such as cystein, arginine, lysine, aspartic acid, and histidine.[11] The commercially available varieties of soy proteins are soy flour, soy protein concentrate (SPC), and soy protein isolate (SPI). SPC contains about 65% proteins and 18% carbohydrate. SPC is obtained by the removal of soluble carbohydrates from defatted soy flour.[12]

Because of its abundance and relatively low cost, soy is attracting much attention but the major drawback is its poor water resistance. Functional properties of soy proteins can be improved by altering their molecular conformation with the help of physical, chemical, or enzymatic agents. Soy proteins have been modified using alkali,[13] urea,[14] and guanidine hydrochloride–sodium dodecylsulphate.[15] Cross-linking,[16] acylation,[17] blending with other polymers,[18] and enzymatic modifications[19] are the other methods to modify the soy proteins. Modification of natural polymers like proteins by graft copolymerization is an important method to alter the properties. Graft copolymerization onto various natural polymers such as casein,[20] corn,[21] silk,[22] and wool[23] has been reported by different workers. However, only a few investigations have been found about the graft copolymerization of different vinyl monomers onto SPI,[24,25] whereas, no investigation has been reported about the graft copolymerization onto SPC.

In this study, we investigated the graft copolymerization of ethylmethacrylate (EMA) onto SPC in aqueous medium using ascorbic acid (AAc) and potassium persulphate (KPS) as an initiator system. Graft copolymer formed was evaluated for its thermal behavior and physical properties.

EXPERIMENTAL

Materials

Soy flour was purchased from local market. EMA used was obtained from E-Merck Chemicals. AAc and KPS were procured from S. D. Fine Chemicals.

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Graft copolymerization

SPC was obtained from defatted soy flour after removal of sugar and minor constituents using aqueous alcohol process.[26] SPC (0.5 g) was immersed in known amount of distilled water for 24 h. A definite ratio of AAc–KPS was added to the reaction flask followed by drop by drop addition of EMA. The reaction was carried-out for specific time interval at a definite temperature. Optimum conditions of reaction temperature (45°C), reaction time (120 min), solvent amount (100 mL), initiator ratio (1 : 1 molar ratio), pH (8.0), and monomer concentration (2.39×10^{-3} mol L^{-1}) were worked-out to get maximum graft percentage (Pg). Homopolymer formed was removed by soxhlet extraction with acetone for 24 h. Graft copolymer obtained was dried at 40°C to constant weight. % Graft yield (Pg), % graft efficiency (Pe), and % homopolymer (Ph) obtained were calculated as[27]:

$$\text{Percentage graft copolymerization (Pg)} = \frac{(W_2 - W_1)}{W_1} \times 100$$

$$\text{Percentage graft efficiency (Pe)} = \frac{(W_2 - W_1)}{W_3} \times 100$$

$$\text{Percentage homopolymer (Ph)} = 100 - (\text{Pe})$$

where W_1 = initial wt. of sample; W_2 = wt. of sample (after removal of homopolymer); W_3 = wt. of monomer taken.

Characterization

FTIR

IR spectra were recorded with Perkin Elmer Fourier transform infrared (FTIR) spectrophotometer using KBr pellets.

X-ray diffraction

X-ray diffraction studies were performed on XPERT-PRO X-ray diffractometer at 40 kV and 35 mA. The samples were scanned from 5° to 50° at 2θ scale using Cu Kα X-ray radiations of 1.5418 Å.

Scanning electron microscope

Scanning electron microscopic studies of SPC and its graft copolymer were carried-out on electron microscope machine LEO 435 VP.

Thermogravimetric analysis/differential thermal analysis/differential thermogravimetric analysis

Thermogravimetric analysis (TGA), differential thermal analysis (DTA), and differential thermogravimetric analysis (DTG) studies were carried-out in the temperature range of 50–700°C at a heating rate of 10°C/min on TG/DTA 6300, SLL EXSTAR 6000.

Acid and base resistance

Acid resistance of the grafted vis-à-vis ungrafted sample was studied by adding a known weight of sample (0.1 g) in 25 mL 1*N* HCl, and the weight of each sample was noted at the interval of every 6 h until a constant weight was obtained. Similarly base resistance was studied with 1*N* NaOH. % weight loss was calculated as[28]:

$$\%\ \text{Wt. loss} = [(W_i - W_f)/W_i] \times 100$$

where, W_i = initial wt. of sample; W_f = final wt. of sample.

Moisture absorbance study

Moisture absorbance studies were carried out as per ASTM D5229 standard. Percentage moisture absorbance of samples was studied by placing a known weight (0.1 g) of oven dried samples in small bags to provide dust free environment having %RH = 80 for 24 h. Final weights (W_f) of the samples were taken, and % moisture absorbance was calculated as:

$$\%\ \text{Moisture absorbance} = [(W_f - W_i)/W_i] \times 100$$

where, W_i = initial wt. of sample; W_f = final wt. of sample.

RESULTS AND DISCUSSION

Mechanism

Reaction between AAc (I) and KPS generated SO_4^{-*} radicals [eq. (1)], which further in the presence of H_2O gave rise to OH* free radicals [eq. (2)]. OH* on abstraction of hydrogen free radical from AAc resulted in the generation of AAc free radical species [(III), eq. (3)], which in the presence of persulphate ion gave SO_4^{-*} [eq. (4)]. Thus, these primary free radical species on further reaction with monomer and backbone resulted in the generation of active sites on them [eqs. (5) and (6)]. Monomer free radicals propagated the chain reaction further resulting in growing active chains [eqs. (7)–(10)]. Moreover, reaction between active backbone and growing monomer chains gave graft copolymer [eq. (11)]. Termination of the growing chain reactions occurred either by reaction between the two live chains [eqs. (12) or (13)] or due to encounter between the active chains and AAc free radical [eq. (14)]

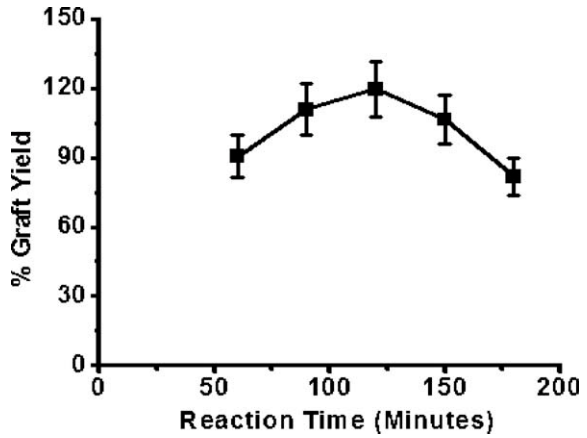


Figure 1 Effect of reaction time on grafting.

Initiation

$$\underset{\text{(I)}}{AH_2} + S_2O_8^{2-} \longrightarrow \underset{\text{(II)}}{AH^-} + SO_4^{-*} + HSO_4^- \quad (1)$$

$$SO_4^{-*} + H_2O \longrightarrow OH^* + HSO_4^- \quad (2)$$

$$\underset{\text{(II)}}{AH^-} + OH^* \longrightarrow \underset{\text{(III)}}{AH^*} + OH^- \quad (3)$$

$$\underset{\text{(III)}}{AH^*} + S_2O_8^{2-} \longrightarrow \underset{\text{(IV)}}{A} + SO_4^{-*} + HSO_4^- \quad (4)$$

Propagation $[X^* = AH^* \text{ or } SO_4^{-*}]$

$$SPC + X^* \longrightarrow SPC^* + X - H \quad (5)$$

$$M + X^* \longrightarrow X - M^* \quad (6)$$

$$SPC + X - M^* \longrightarrow SPC - M^* + X - H \quad (7)$$

$$SPC - M^* + nM \longrightarrow \underset{\text{Growing Graft Copolymer Chain}}{SPC - (M)_n - M^*} \quad (8)$$

$$SPC^* + nM \longrightarrow SPC - M_{n-1} - M^* \quad (9)$$

$$X - M^* + nM \longrightarrow \underset{\text{Growing Acing Homopolymer}}{X - M_{(n)} - M^*} \quad (10)$$

Termination

$$SPC - M_{(n)} - M^* + X - M_{(n)} - M^* \longrightarrow \underset{\text{Graft copolymer}}{SPC - M_{(2n+2)} - X} \quad (11)$$

$$SPC - M_{(n-1)} - M^* + SPC - M_{(n-1)} - M^* \longrightarrow SPC - M_{(n-1)} - M_2 - M_{(n-1)} - SPC \quad (12)$$

$$X - M_{(n)} - M^* +^* M - M_{(n)} - X \longrightarrow \underset{\text{Hompolymer}}{X - M_{(2n+2)} - X} \quad (13)$$

$$SPC - M_{(n)} - M^* + X^* \longrightarrow SPC - M_{(n+1)} - X \quad (14)$$

where SPC = Soy protein concentrate; M = Ethylmethacrylate; AH_2 = Ascorbic acid

Optimization of different reaction parameters

Effect of reaction time

Optimum condition for the reaction time was found by studying the reaction at different temperatures between 60 and 150 min keeping other variables constant. Results are shown in Figure 1. It was observed that Pg increased when reaction time varies from 60 to 120 min, whereas further increase in reaction time above 120 min decreased the graft yield. The increase in graft yield with reaction time could be due to increased interaction of the primary free radicals with the monomer and SPC resulting in the generation of more free radical sites and hence more graft copolymerization. However, after reaching an optimum level further increase in the time interval resulted in more homopolymerization thereby suppressing the graft copolymerization.[29]

Effect of reaction temperature

The grafting is carried out at different temperatures between 25 and 75°C keeping other variables constant. Pg increased with the increase in temperature upto 45°C, whereas further increase in reaction temperature resulted in decreased Pg (Fig. 2). It could be due to the fact that at low temperatures, reaction between SPC and initiators was slow, and as a result fewer free radical sites were formed. But as the temperature was increased, the reaction got accelerated giving rise to more free radical content thereby leading to more Pg. However, increase in temperature beyond 45°C resulted in predominance of homopolymerization over graft copolymerization, and hence, decreased graft yield was found.[30] At high-temperature thermal polymerization as well as increase in chain transfer reaction also resulted in lower graft yield.

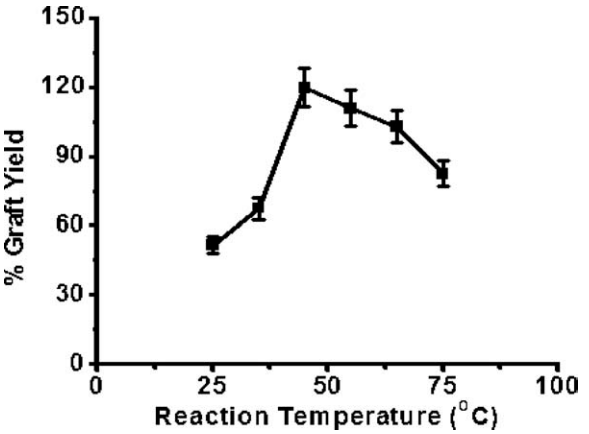


Figure 2 Effect of reaction temperature on grafting.

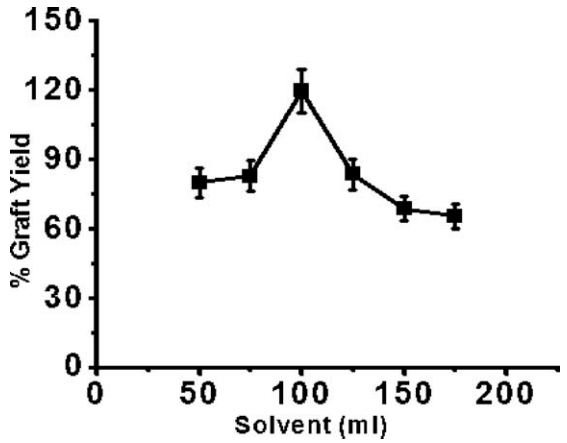


Figure 3 Effect of solvent on grafting.

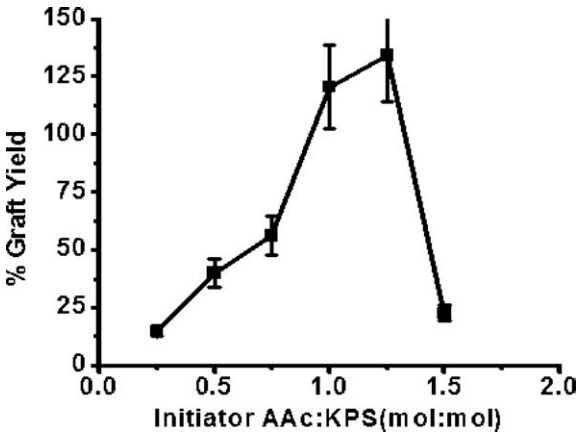


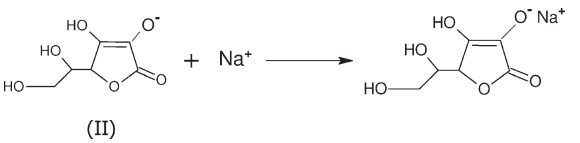
Figure 5 Effect of initiator ratio on grafting.

Effect of amount of solvent

Graft percentage was found to be affected by the amount of the solvent (Fig. 3). Graft percentage increased with the initial increase in the amount of the solvent from 50 to 100 mL. The maximum grafting was found to take place in case of 100 mL solvent. However, further increase in the amount of solvent resulted in decreased graft copolymerization. This was probably due to dilution of reaction medium, which lowered the concentration of primary free radicals per unit volume and ultimately decreased the graft percentage.[31]

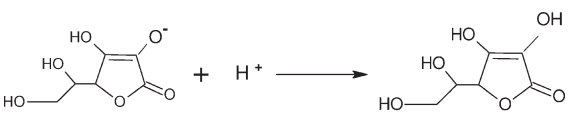
Effect of pH

In protein concentrate, majority of polar and nonpolar groups were unavailable for graft copolymerization due to internal secondary bonding forces such as van der Waals forces, H-bonds, and hydrophobic interactions. Dispersion and unfolding of proteins were enhanced with variation in pH.[32] Unfolding of protein molecules exposed the functional groups for free radical attack, and thus, enhanced graft copolymerization was observed with increase in pH from 2.0 to 8.0. Maximum grafting was found at pH 8.0 (Fig. 4). However, further increase in pH was found to result in decreased Pg, which could be due to screening effect of Na^+ ions [eq. (15)] thereby preventing the formation of AAc free radical species (III) and generation of SO_4^{-*} ions [eqs. 3 and 4].



(II) (15)

Although at lower pH, the excess of H^+ ions are playing an important role for preventing the conversion of AAc ionic species [II, eq. (3)] into a free radical, thereby further creating hindrance in the generation of SO_4^{-*} [eqs. (4) and (16)].



(II) (16)

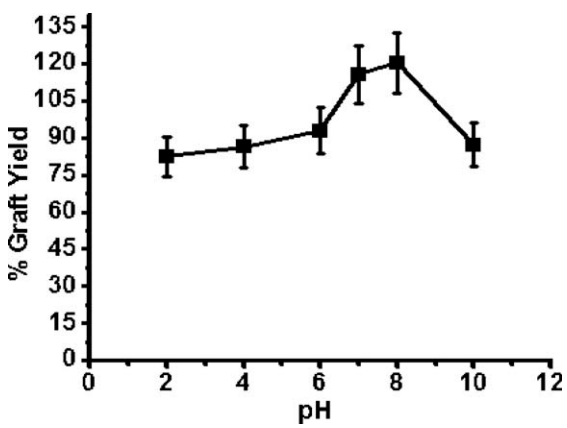


Figure 4 Effect of pH on grafting.

Effect of initiator ratio

It was observed that Pg increased with the increase in initiator ratio (KPS : AAc) from 1 : 0.25 to 1 : 1.25, whereas further increase in initiator ratio decreased the graft yield (Fig. 5). Thus, the optimum molar ratio for the maximum Pg was found to be 1 : 1.25 (KPS : AAc). Initial increase in molar ratio resulted in more generation of free radicals [eqs. (1)–(3)], which on further reaction gave rise to increased concentration of SO_4^{-*} free radicals. These primary free radicals resulted in more free radical site generation on backbone as well as on vinyl monomer and hence an increased graft yield. However, further increase

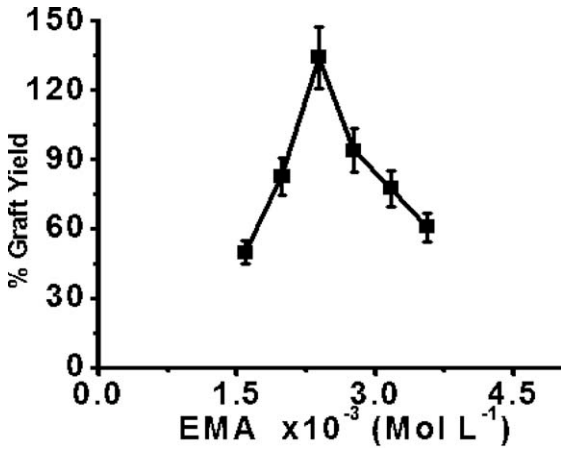


Figure 6 Effect of monomer concentration on grafting.

in molar ratio enhanced the termination reactions [eq. (14)], and hence, a decreased graft yield was found.[33] Moreover, increase in molar ratio resulted in increased concentration of HSO_4^- ions (eqs. (1) and (2)] and hence increased acidic conditions in the reaction medium which ultimately resulted in the deactivation of AAc ionic species (II) and decreased graft yield [eq. (16)].

Effect of monomer concentration

The effect of monomer concentration was studied by varying [EMA] from 1.59×10^{-3} mol L^{-1} to 3.56×10^{-3} mol L^{-1}. The results obtained are presented in Figure 6. With the initial increase in monomer concentration, there was an increase in the concentration of monomer free radicals in the vicinity of SPC chains, and maximum Pg (134.12%) was found at increased monomer concentration of 2.43×10^{-3}mol L^{-1}. However, further increase in monomer concentration resulted in more homopolymerization [eq. (13)], and hence, a decreased Pg beyond optimum monomer concentration was observed. Moreover, due to homopolymerization viscosity of the reaction medium was found to increased, which hindered the approach of monomer free radicals toward growing SPC chains.[34]

Characterization of graft copolymer

FTIR spectroscopy

The FTIR spectra of SPC and SPC-*g*-poly(EMA) are shown in Figure 7. SPC showed broad peak at 3284.4 cm^{-1} due to free —OH and —NH groups, peak at 1653.3 cm^{-1} due to C=O stretch of amide group (amide-I) and a peak at 1540.4 cm^{-1} due to N—H bending (amide-II). On the other hand, SPC-*g*-poly(EMA) showed peak at 1731.3 cm^{-1} due to C—O stretch and peaks at 1241.6 and 1147.9 cm^{-1} due to C—O stretching of poly(EMA). IR spectra of graft copolymer also showed decrease in the intensity of

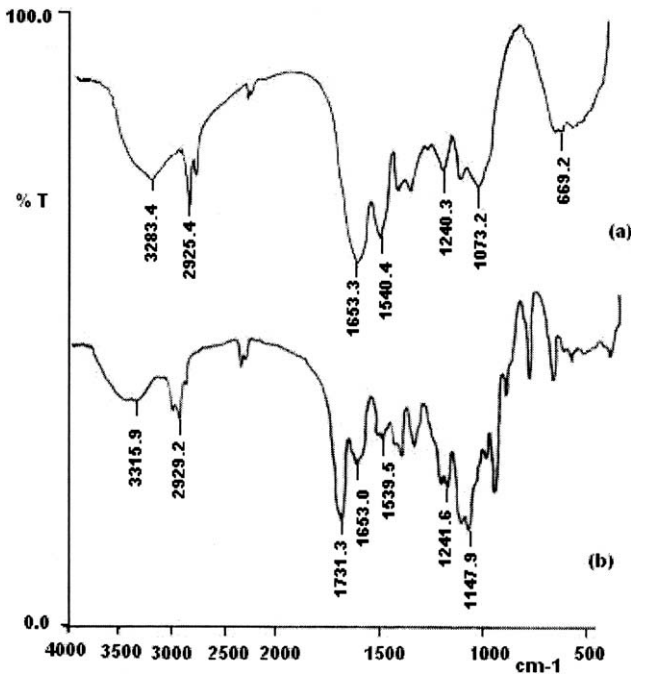


Figure 7 FTIR spectra of (a) soy protein concentrate and (b) SPC-*g*-poly(EMA).

amide-I and amide-II peaks, which exhibited the evidence for the grafting of poly(EMA) chains onto protein backbone.

XRD studies

XRD analysis of powdered samples of SPC and SPC-*g*-poly(EMA) with five different % graft yields is depicted in Figure 8. XRD pattern of soy protein showed the amorphous nature of soy protein. However, on grafting with EMA, crystallinity of the backbone sample was found to increase, which is evident from increase in coherent length along with increase in d-spacing values with increase in Pg. The experimental data of XRD was used to compute coherent lengths by using Scherrer equation:

$$L = 0.9\lambda/B \cos\theta$$

where λ is the wavelength of X-ray radiations for Cu Kα, equal to 1.5418 Å. θ is glancing angle in

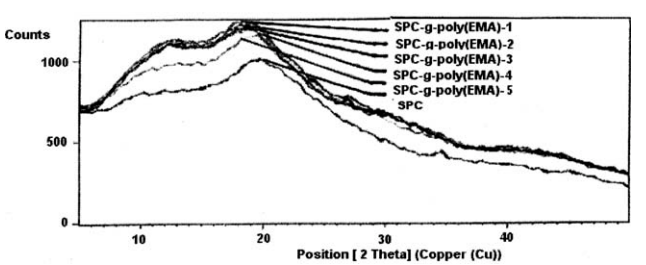


Figure 8 X-ray diffraction pattern of powdered samples of SPC and different SPC-*g*-poly(EMA).

TABLE I
X-ray Diffraction Studies of SPC and SPC-*g*-poly(EMA)

Sample code	% Graft yield	2θ	d-Spacing	Coherent length (*L*) (Å)
SPC-*g*-poly (EMA)-1	134.12	18.0334	4.86289	40.1516
SPC-*g*-poly (EMA)-2	110.82	18.5053	4.79473	33.5896
SPC-*g*-poly (EMA)-3	93.76	18.6512	4.75756	31.3053
SPC-*g*-poly (EMA)-4	68.96	19.0304	4.66360	21.5649
SPC-*g*-poly (EMA)-5	40.16	19.5384	4.54348	20.1666
SPC	–	19.6995	4.50669	14.154

radians, and *B* is the width of peak at half of the maximum intensity. Coherent length and d-spacing at different 2θ scale in case of SPC and SPC-*g*-poly(EMA) with different % graft yields are given in Table I.

Thus, with increase in Pg, anisotropy kept on increasing and SPC became more crystalline in nature on incorporation of poly(EMA) chains with graft copolymerization process. Maximum anisotropy was found with 134.12% graft yield where coherent length and d-spacing were found to be 40.1516 and 4.86289 Å, respectively.[35]

Scanning electron microscopy

A clear cut morphological differentiation has been observed in the scanning electron micrograph of SPC and SPC-*g*-poly(EMA) (Figs. 9 and 10). This exhibited the incorporation of poly(EMA) chains onto SPC through covalent bonding on graft copolymerization.

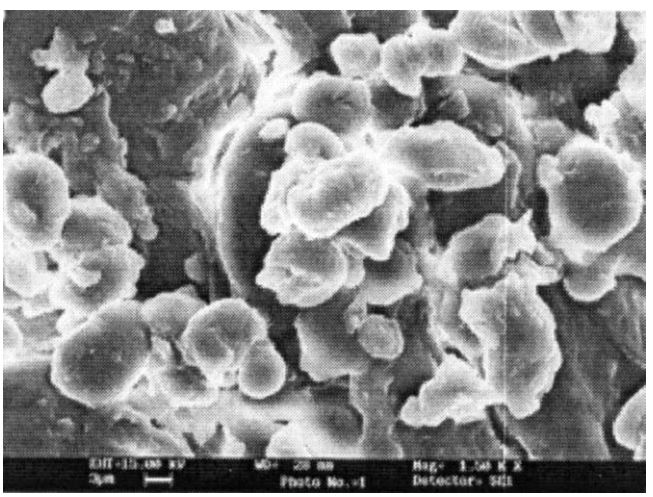


Figure 9 Scanning electron micrograph of soy protein concentrate (SPC).

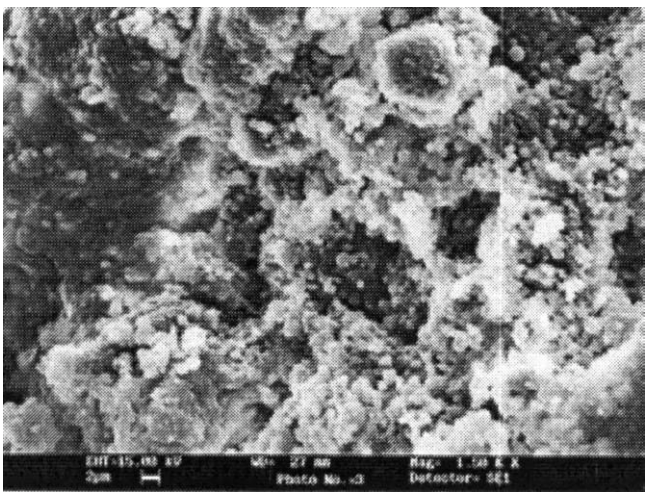


Figure 10 Scanning Electron Micrograph of SPC-*g*-Poly(EMA).

Thermal studies

Thermogravimetric analysis of grafted and ungrafted SPC was carried-out as a function of % wt. loss versus temperature. Soy protein has a three-dimensional structure involving sequence of amino acids. Proteins have electrostatic–hydrophobic interactions and hydrogen bonding along with the covalent bonding.

In case of SPC, three phase decomposition was found in temperature range of 46.4–218°C involving 8.8% wt. loss, 218–501.5°C with 62.7% wt. loss, and 501.4–561.7°C with 21.3% wt. loss (Fig. 11). First-stage decomposition corresponds to elimination of water and dissociation of quaternary structure of proteins. Second phase of decomposition involved two stages, one in the temperature range of 218–358.9°C (43.7% wt. loss) due to cleavage of peptide bonds of amino acid residues and second in the temperature range of 358.9–501.4°C (19.0% wt. loss) corresponding to dissociation of S—S, O—O, and O—N bonds.[36] Third

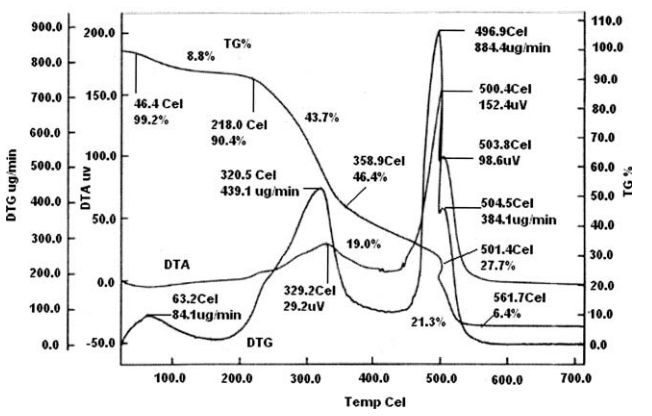


Figure 11 TGA/DTA/DTG of soy protein concentrate (SPC).

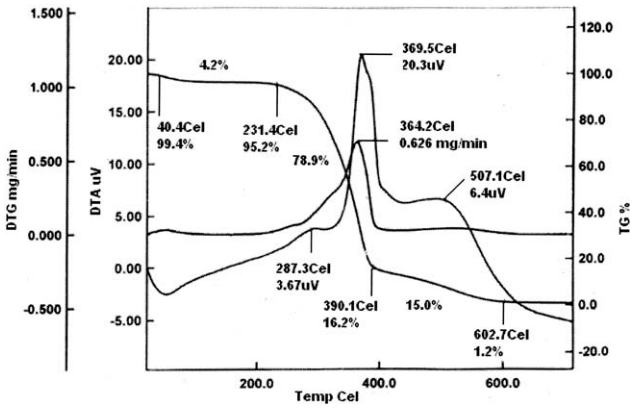


Figure 12 TGA/DTA/DTG of SPC-*g*-poly(EMA).

phase of decomposition involved complete decomposition of proteins, resulting in the liberation of various gases such as CO, CO_2, and NH_3.[37] In case of SPC-*g*-poly(EMA), a two-phase thermal decomposition in the temperature range of 231.4–390.1°C (78.9% wt. loss) and 390.1–602.7°C (15% wt. loss) was observed (Fig. 12). As the initial and final decomposition temperatures of SPC backbone have been found to be 218.0 and 561.7°C, respectively, which are lower than the initial (231.4°C) and final (602.7°C) decomposition temperatures of grafted SPC, therefore, in nutshell, it could be concluded that SPC-*g*-poly(EMA) was thermally more stable than ungrafted SPC. This increase in thermal stability was due to incorporation of poly(EMA) chains onto SPC backbone through covalent bonding.

In case of DTA studies, SPC showed three exothermic peaks at 329.2°C (29.2 μV), 500.4°C (52.4 μV), and 503.8°C (98.6 μV) corresponding to TGA decomposition stages of 218–358.9°C, 358.9–501°C, and 501–530.4°C, respectively. In case of SPC-*g*-poly(EMA), DTA showed exothermic peaks at 369.5°C (20.4 μV) and 507.1°C (6.47 μV) corresponding to thermal degradation that occurred in the temperature range of 231.4–390.1°C and 390.1–602.7°C in TGA.

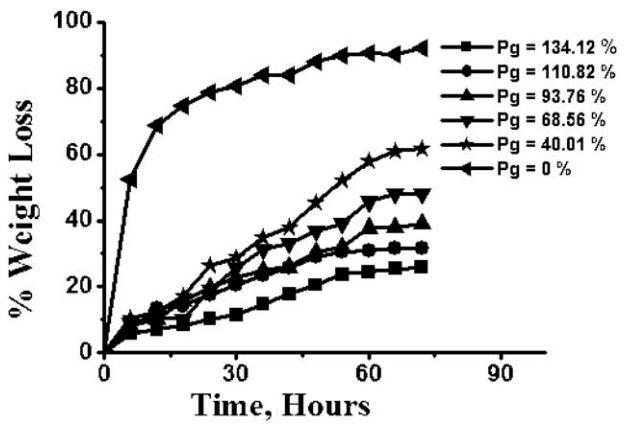


Figure 13 Effect of acid on the grafting.

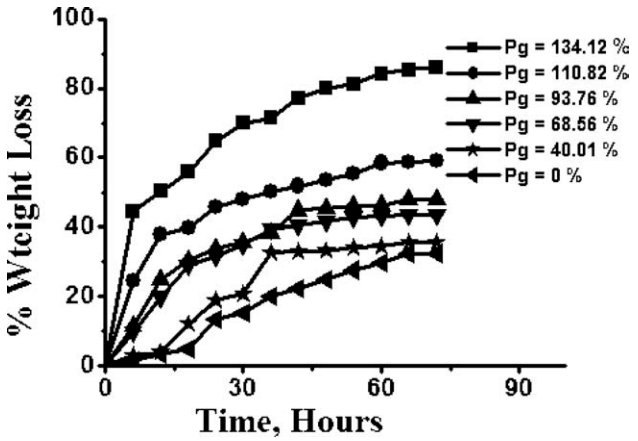


Figure 14 Effect of base on the grafting.

Thermal decomposition, in case of DTG analysis of SPC, showed exothermic peaks at 63.2°C (0.0841 mg/min), 320.5°C (0.439 mg/min), and 496.9°C (0.884 mg/min), whereas, in case of SPC-*g*-poly-(EMA), decomposition occurred at 364.7°C (0.626 mg/min). Thus, DTG results clearly showed that at higher temperature the rate of thermal decomposition was higher in case of SPC than that of grafted protein. Hence, incorporation of poly(EMA) chains onto SPC backbone resulted in the better thermal stability.

Acid and base resistance studies

Acid and base resistance of grafted protein concentrate was found to increase with increase in % grafting (Figs. 13 and 14). This could be due to fact that poly(EMA) chains being highly hydrophobic in nature possess less chemical affinity for both acid and base.[38] Thus, incorporation of poly(EMA) chains onto SPC backbone through graft copolymerization resulted in increased acid and base resistance.

Moisture resistance studies

It was observed that moisture absorbance of SPC decreased with increase in % grafting (Table II). This was due to incorporation of hydrophobic poly(EMA)

TABLE II
Effects of Grafting of Ethylmethacrylate onto Soy Protein Concentrate on Moisture Absorbance

Sample code	% Graft yield	% Moisture absorbance
SPC-*g*-poly(EMA)-1	134.12	28.765
SPC-*g*-poly(EMA)-2	110.82	32.537
SPC-*g*-poly(EMA)-3	93.76	34.754
SPC-*g*-poly(EMA)-4	68.96	39.886
SPC-*g*-poly(EMA)-5	40.16	45.112
SPC	–	62.225

chains onto sites vulnerable for moisture absorbance, thereby resulting in moisture retardancy with increase in Pg.[38]

CONCLUSIONS

Thermal stability of SPC was found to increase on grafting with EMA in presence of AAc–KPS initiator. Moreover, the sample was found to undergo physicochemical changes on graft copolymerization resulting in retardancy toward moisture and acid–base attack. Thus, increase in thermal stability, resistance toward acid–base, and moisture retardancy in the SPC on graft copolymerization with EMA is important from technology point of view. Since work on biodegradable composites is already under progress, therefore, the further studies will be focused on the use of grafted SPC as the reinforcing material for the development of green composites.

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