Evaluation of Physio-chemical and Thermal properties of Soy Protein Concentrate and Different Binary Mixtures Based Graft Copolymers

Jaspreet Kaur, Balbir Singh Kaith, Rajeev Jindal*

Abstract— Present investigation deals with the modification of biopolymer to improve physio-chemical and thermal properties. In air synthesis of graft copolymers of soy protein concentrate (SPC) with vinyl monomer mixtures of ethylmethacrylate (EMA) with methylmethacrylate (MMA), methylacrylate (MA) and ethylacrylate (EA) was carried-out using ascorbic acid/ potassium persulphate (AAc/ KPS) redox initiator system. Graft copolymers formed were characterized using techniques like FTIR, SEM and XRD. Initial optimization of different reaction parameters was carried out for graft copolymerization of principal monomer EMA onto soy protein concentrate to get maximum graft yield (134.12%). The maximum graft yields with binary monomer mixtures; EMA+MMA, EMA+EA and EMA+MA were 120.54%, 142.38% and 293.58%, respectively. The graft copolymers were studied for thermal stability and were found to show high thermal stability. Modified protein was found to show improved chemical resistance toward acid and base. Moreover, grafted protein also showed enhanced moisture retardance.

Index Terms— Soy protein concentrate, graft copolymerization, binary monomer mixture, moisture resistance, thermal stability.

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1 INTRODUCTION

Increased consumption rate of petroleum based polymers resulted in the problem of waste management and environmental hazards. Polymers from natural resources have offered scientists a possible solution to the problem associated with traditional non-biodegradable polymers. Biopolymers from natural resources such as starch, cellulose and proteins have been regarded as an alternative material due to their renewability, abundance and biodegradable nature [1], [2], [3]. Various vegetable proteins like corn, silk, wheat and soy have been investigated for various applications [4], [5], [6]. Due to abundance and relatively low cost soy is attracting much attention. Soy protein obtained from plant Glycine max contains about 20% of oil and 50% of proteins [7]. Among the commercial available varieties of soy i.e. soy flour, soy protein concentrate and soy protein isolate, soy protein concentrate (SPC) contains about 65% proteins and 18% carbohydrates. SPC can be obtained from defatted soy flour by removal of soluble carbohydrates [8]. Soy proteins have been used by scientists for developing adhesives, plastics, composites and elastomers [9],[10], [11] but the problem of low mechanical strength and high moisture absorbance required the modification of soy protein. Soy proteins have been modified using alkali, urea, guanidine hydrochloride and sodium dodecylsulphate [12],

[13], [14]. Cross linking [15], acylation [16], blending with other polymers [17] and enzymatic modifications [18] are the other methods to modify the soy proteins.

Graft copolymerization is one of the techniques employed for the incorporation of desired properties into the backbone [19], [20], [21]. Graft copolymerization of different vinyl monomers onto natural polymers like starch [22], [23], chitosan [24], [25], casein [26], silk [27] and wool [28] has been reported. However, only a very few authors have studied soy protein isolate graft copolymers [29], [30], whereas no report was found about the graft copolymerization onto soy protein concentrate. Graft copolymerization of binary monomer mixtures is of special importance as it results in the incorporation of properties of both monomers [31], [32], [33]. Grafting of binary monomer mixture inducts the tailor-made properties for specific applications.

In the present investigation the graft copolymerization of binary vinyl monomer mixtures was carried-out onto SPC in aqueous medium using ascorbic acid (AAc) and potassium persulphate (KPS) as an initiator system. Graft copolymers formed were evaluated for their thermal behaviour. The behaviour of graft copolymers towards acid, base and moisture were studied to find out the effect of modification of soy protein concentrate on its physio-chemical properties.

2 EXPERIMENTAL

2.1 Materials

Ethylmethacrylate (EMA), methylmethacrylate (MMA),

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Jaspreet Kaur Bhatia is assistant Professor at Lyallpur Kahalsa College, Jalandhar, Punjab, India PH: 0181-2465104 E. Mail:
jaspreetbhatia81@gmail.com
Balbir is Kaith is Professor at Department of Chemistry, National Institute of Technology, Jalandhar, Punja, India, PH: 9780684883 E. Mail:
bskaith@yahoo.co.in
Rajeev Jindal is Associate Professor at Department of Chemistry, National Institute of Technology, Jalandhar, Punja, India, PH: 09779914264
E.Mail: r_jindal@nitj.ac.in

ethylacrylate (EA) and methylacrylate (MA) used were obtained from e-Merck chemicals. Ascorbic acid (AAc) and potassium persulphate (KPS) were procured from S.D. Fine chemicals ltd.

2.2 Synthesis of graft copolymers

Soy protein concentrate (SPC) was obtained from defatted soy flour after removal of sugar and other minor constituents using aqueous alcohol process [34]. SPC (0.5 g) was immersed in known amount of distilled water in reaction flask. A definite ratio of AAc - KPS was added to the reaction flask followed by drop by drop addition of monomer. The reaction was carried-out for specific time interval at a definite temperature. Homopolymer formed was removed on soxhlet extraction with acetone for 24 hours. Graft copolymer obtained was dried at 40 oC to constant weight. % graft yield (Pg), was calculated as [35] :

Percentage graft yield (Pg)= [$(W_2 - W_1)/W_1$] x 100

where W_1 = initial wt. of sample and W_2 = wt. of sample (after removal of homopolymer).

2.3 Characterization

IR spectra were recorded with Perkin Elmer Fourier transform infrared (FTIR) spectrophotometer using KBr pellets. X-Ray diffraction studies were performed on XPERT-PRO X-Ray diffractrometer at 40 kV and 35 mA. The samples were scanned from 50 to 500 at 2θ scale using Cu Kα X-Ray radiations of 1.5418 A^0. Scanning Electron Microscopic studies of SPC and its graft copolymers were carried-out on electron microscope machine LEO 435 VP. TGA, DTA and DTG studies were carried-out in the temperature range of 50° –700 ℃ at a heating rate of 10 ℃/minute on TG/DTA 6300, SII EXSTAR 6000.

2.4 Acid and base resistant studies

Acid resistance of the grafted vis-à-vis ungrafted sample was studied by putting a known weight of sample (0.1 g) in 25 ml 1N HCl and the weight of each sample was noted at the interval of every 6 hours till a constant weight was obtained. Similarly, base resistance was studied with 1N NaOH. % weight loss was calculated as [36] :

% Wt. loss = [$(W_i - W_f)/W_i$] x 100

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

2.5 Moisture resistant studies

Moisture absorbance studies were carried out as per ASTM D5229 standard. Percentage moisture absorbance was found by placing a known weight (W_i) of dry grafted and ungrafted samples in the appropriate environment having %RH= 80 for 24 hours. Final weights (W_f) of the samples were taken and % moisture absorbance was calculated as:

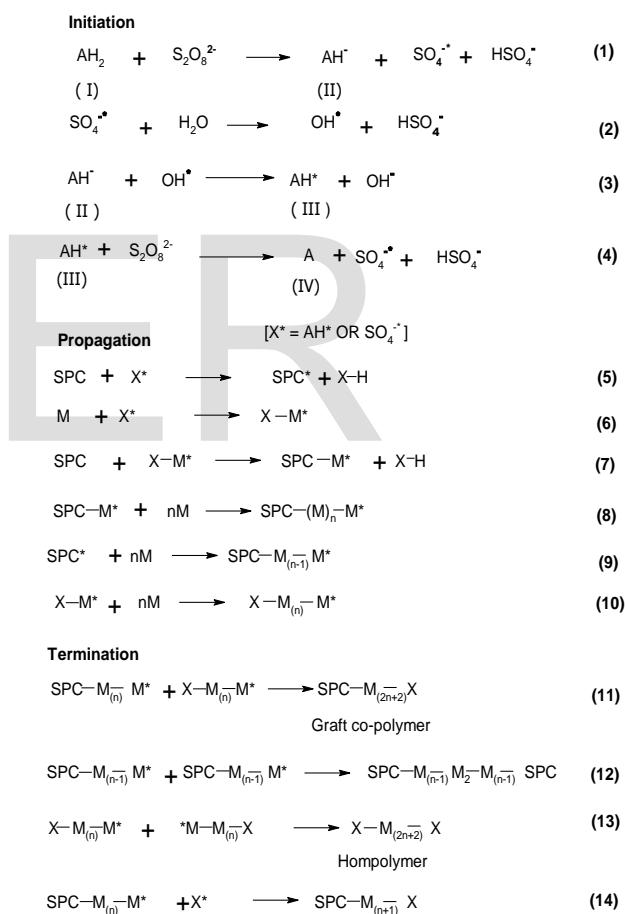% Moisture absorbance = [$(W_f - W_i)/W_i$] x 100

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

3 RESULTS AND DISCUSSION

3.1 Mechanism

Potassium persulphate in the presence of ascorbic acid gener-

ated SO4-* free radical ions [Eq. 1] which in the aqueous medium gave rise to OH* free radicals [Eq. 2]. Ascorbic acid released an electron to OH* and get converted to ascorbic acid free radical [III, Eq. 3]. Persulphate ions further generated SO4-* in the presence of ascorbic acid free radicals [Eq. 4]. Thus, ascorbic acid free radicals and SO4-* free radical ions act as the primary free radicals to initiate the graft copolymerization by generating the active sites on the monomer and the backbone [Eqs. 5-7]. Further propagation resulted in the growing active c hains [Eq. 8] and graft copolymers are formed by reactions between active backbone and growing monomer chains [Eqs 9-11]. The reaction between two live chains resulted in the termination of growing chains [Eq. 11 or 12]. Ascorbic acid free radicals also play important role in termination by interacting with the active chains [Eqs. 13 and14].

Initiation

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

$$SO_4^{\cdot\cdot} \ + \ H_2O \longrightarrow OH^{\cdot} \ + \ HSO_4^{\cdot} \qquad (2)$$

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

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

$$[X^* = AH^* \ OR \ SO_4^{\cdot\cdot}]$$

Propagation

$$SPC \ + \ X^* \longrightarrow SPC^* \ + \ X\text{–}H \qquad (5)$$

$$M \ + \ X^* \longrightarrow X\text{–}M^* \qquad (6)$$

$$SPC \ + \ X\text{–}M^* \longrightarrow SPC\text{–}M^* \ + \ X\text{–}H \qquad (7)$$

$$SPC\text{–}M^* \ + \ nM \longrightarrow SPC\text{–}(M)_n\text{–}M^* \qquad (8)$$

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

$$X\text{–}M^* \ + \ nM \longrightarrow X\text{–}M_{(n)}\text{–}M^* \qquad (10)$$

Termination

$$SPC\text{–}M_{(n)}^- M^* \ + \ X\text{–}M_{(n)}^- M^* \longrightarrow SPC\text{–}M_{(2n+2)}X \qquad (11)$$
$$\text{Graft co-polymer}$$

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

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

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

Where SPC = Soy protein concentrate; M = Monomer ; AH_2 = Ascorbic acid

3.2 Effect of binary mixture concentration on percentage grafting

In case of graft copolymerization of EMA onto soy protein concentrate maximum graft percentage was found to be 134.12% and optimum conditions for maximum graft percentage were: reaction time (minutes), 120; reaction temperature

(^{O}C), 40; solvent (ml), 100; AAc : KPS (molar ratio), 1:1.25; EMA concentration (mol L^{-1}), 2.43x 10^{-3} and pH, 8.0 [37]. Grafting of different binary mixtures, EMA+MMA, EMA+EA and EMA+MA, using EMA as a principal monomer under pre-optimized reaction conditions showed graft percentage of 120.54%, 142.38% and 293.58%, respectively (Figs. 1-3).
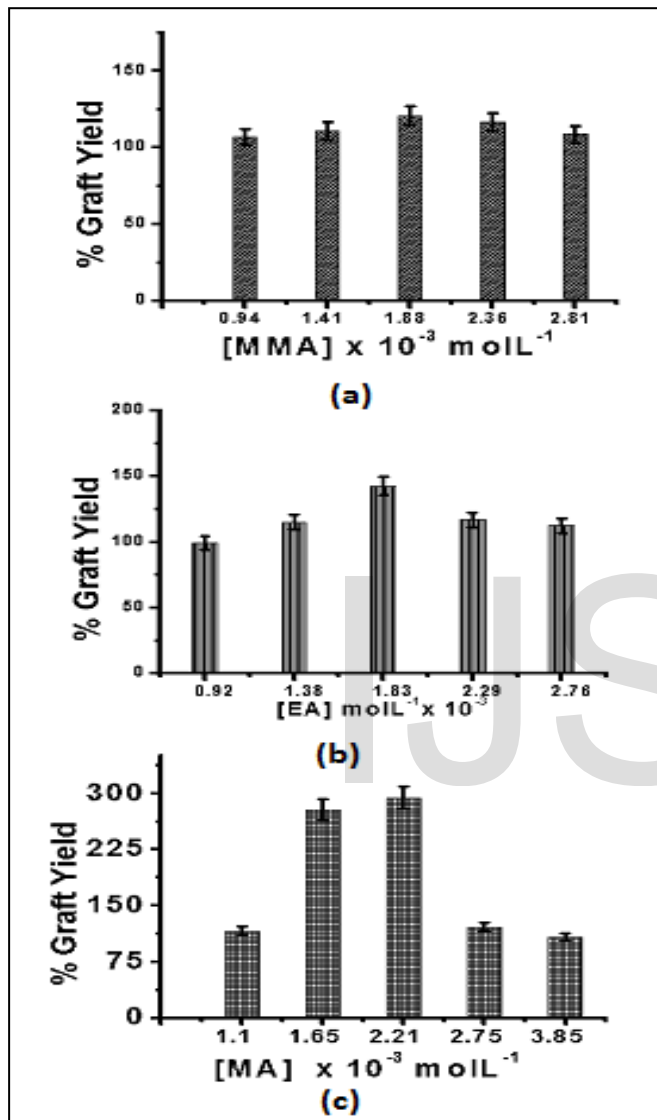

Fig. 1 Effect of concentration of (a) MMA (b) EA (c) MA in binary mixture on Pg; [EMA] = 2.39 x 10-3 Mol L^{-1}

It is evident that in case of binary mixtures consisting of EMA with MA and EA higher percentage grafting has been found as compared to EMA alone (134.12%). The higher percentage of grafting in case of these binary monomer mixtures can be explained by the fact that addition of electron acceptor monomers increased the reactivity of EMA towards graft copolymerization. The reactivity ratio values of these monomer mixtures were calculated with the help of Price-Alfrey's Q-e approach [38]. The reactivity ratio values in case of binary monomer mixture EMA+MA were found to be r_1 = 1.47, r_2 = 0.65. Low r_2 value shows that MA reacts with EMA in preference to their monomeric units thus producing more of growing co-

polymer chains and as a result higher percentage of grafting is observed. Further, it is supported by the higher r_1 value resulting in higher copolymer formation and suppression of homopolymerization. In case of EMA+EA binary mixture though r_1 value (0.91) is lower than r_2 value (1.06) which exhibits the higher reactivity among the similar monomeric units giving rise to homopolymerization yet a higher graft yield was found. This can be explained on the basis that percentage graft yield also depends on rate of free radical transfer towards the backbone and monomeric moieties thereby resulting in more generation of free radical sites and hence higher graft yield [39]. Moreover, it also depends upon rate of propagation and termination and gave rise to higher graft yield. The low graft yield with EMA+MMA binary mixture was again due to tendency of MMA and EMA units to react with their own monomer radicals and resulted in more homopolymerization in place of copolymerization. Thus, gave rise to low graft yield. This is further supported by monomer reactivity ratios (r_1=0.798, r_2 =1.058) [40].

3.3 FTIR analysis

FT-IR spectrum of SPC showed a 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) (Fig. 2a). SPC-g-poly(EMA-co-MMA) showed peak at 1731.9 cm^{-1} due to ester carbonyl group of MMA along with peaks at 1242 cm^{-1} and 1148.2 cm^{-1} due to C-O stretchings (Fig. 2b). SPC-g-poly(EMA-co-EA) exhibited peaks at 1736.1 cm^{-1} due to C=O group of EA and at 1243.1cm^{-1} and at 1151.5cm^{-1} due to C-O stretch (Fig. 2c). In case of SPC-g-poly(EMA-co-MA) peaks due to C=O stretch of MA was observed at 1737.9 cm^{-1} and due to C-O stretch were obtained at 1240.6 cm^{-1} and 1147.8cm^{-1} (Fig. 2d). The presence of additional peaks in the IR spectra of graft gave evidence of grafting on protein backbone.
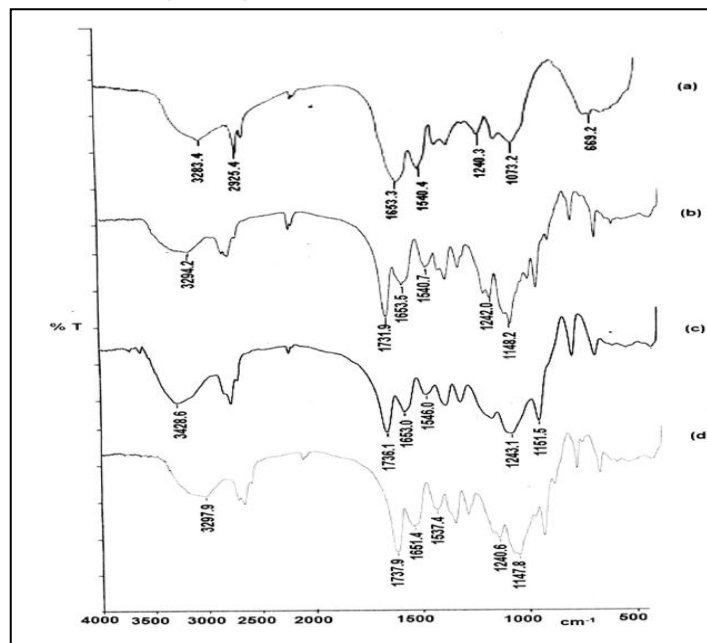

Fig. 2 FTIR spectra of (a) SPC (b) SPC-g-poly(EMA-co-MMA) (c) SPC-g-poly(EMA-co-MA) (d) SPC-g-poly(EMA-co-MA)

3.4   XRD Studies

XRD pattern of soy protein showed the amorphous nature of soy protein. However, on grafting with vinyl monomers, crystallinity of the backbone sample was found to increase which is evident from increase in coherent length along with increase in d-spacing values and increase in Pg. The experimental data of XRD was computed for coherent lengths by using Scherrer equation [41]:

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

where λ is the wavelength of X-Ray radiations for Cu-Kα, equal to 1.5418 A^O. θ is glancing angle in radians and B is the width of peak at half of the maximum intensity. Coherent lengths and d-spacings at different 2θ scale in case of SPC and grafted protein concentrate with different % graft yields are given in Table 1. Thus, with increase in Pg, anisotropy kept on increasing and SPC became more crystalline in nature on incorporation of monomer chains with graft copolymerization process.

TABLE 1

. X-RAY DIFFRACTION STUDIES OF SPC AND GRAFTED SPC WITH BINARY MONOMER MIXTURES

Sample	Pg	2θ(°)	d-Spacing	Coherent length (L)
Backbone	--	19.70	4.5067	14.15
SPC-g-poly(EMA-co-MMA)	120.54	17.30	5.1270	40.69
	116.36	17.48	5.0745	36.65
	110.60	18.13	4.8925	26.91
	108.46	18.13	4.8925	24.46
	106.74	18.68	4.7507	23.75
SPC-g-poly(EMA-co-EA)	142.38	17.30	5.1255	33.26
	116.44	18.57	4.7772	26.86
	114.78	18.66	4.7533	26.67
	112.04	18.76	4.7294	23.02
	99.06	19.08	4.6525	22.98
SPC-g-poly(EMA-co-MA)	293.58	18.80	4.7212	50.64
	278.10	18.83	4.6228	40.45
	120.68	18.99	4.6285	31.21
	115.36	19.68	4.5810	20.17
	107.54	19.77	4.5103	17.38

3.5 Scanning Electron Microscopy (SEM)

A clear cut morphological differentiation has been observed in the scanning electron micrograph of SPC, SPC-g-poly(EMA-co-MMA), SPC-g-poly(EMA-co-EA) and SPC-g-poly(EMA-co-MA) (Figs. 3a-d). The heterogeneity of soy protein concentrate was found to increase on graft copolymerization. This exhibited the incorporation of monomer chains onto SPC backbone
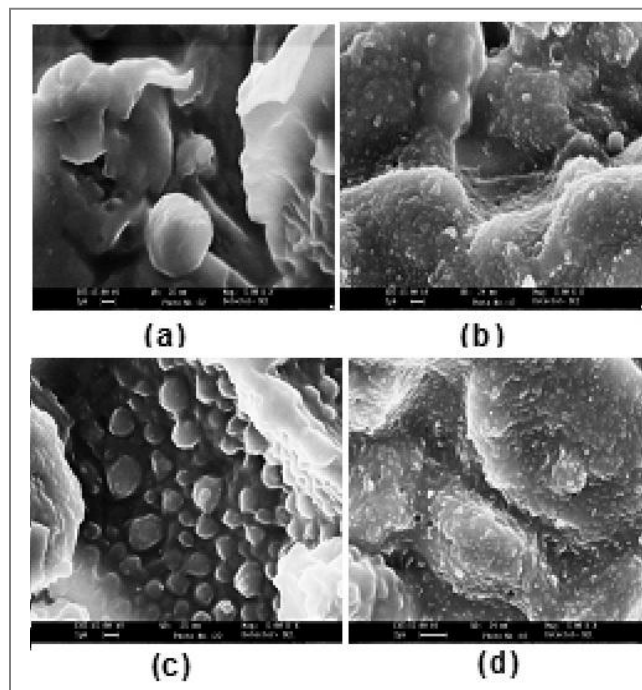
through covalent bonding.

Fig. 3 Scanning Electron Micrograph of (a) SPC (b) SPC-g-poly(EMA-co-MMA) (c) SPC-g-poly(EMA-co-EA) (d) SPC-g-poly(EMA-co-MA)

3.6 Thermal Studies

Thermogravimetric analysis of grafted and ungrafted soy protein concentrate was carried-out as a function of % wt. loss vs temperature. Soy protein has a three dimensional structure involving sequence of amino acids. Covalent bonds present in soy proteins are either peptide bonds between amino acid residues or disulphide bonds. Proteins also have electrostatic-hydrophobic interactions and hydrogen bonding.

In case of SPC two phase decomposition was found in temperature range of 218^0 - 501.4^{0}C with 62.7% wt. loss and 501.4^0-561.7^{0}C with 21.3% wt. loss (Table 2). Initial decomposition corresponds to elimination of water and dissociation of quaternary structure of proteins. First phase of decomposition involved two stages, one in the temperature range of 218^0-358.9^{0}C (43.7% wt. loss) due to cleavage of peptide bonds of amino acid residues and second in the temperature range of 358.9^0-501.4^{0}C (19.0% wt. loss) corresponding to dissociation of S-S, O-O and O-N bonds. Second phase decomposition involved complete decomposition of proteins, resulting in the liberation of various gases like CO, CO$_2$, and NH$_3$ [42]. In case of grafted proteins with binary monomer mixtures, EMA+MMA, EMA+EA and EMA+MA, two phase thermal decomposition was found. SPC-g-poly(EMA-co-MMA) showed thermal decomposition in the temperature range of 262.8^0 - 388.8^{0}C (76.7% wt. loss) and 388.8^0- 595.2^{0}C (12.2% wt. loss). Thermal decomposition stages observed in case of SPC-g-poly(EMA-co-EA) are in the temperature range of 241.5^0-358.7^{0}C (79.1% wt. loss) and 358.7^0- 597.6^{0}C (14.7% wt. loss). In case of SPC-g-poly(EMA-co-MA) thermal decomposition was observed at 241.9^0- 398.8^{0}C (72.9% wt. loss) and 398.9^0-589.1^{O}C (19.3% wt. loss).

TABLE 2
THERMAL STUDIES OF SPC AND GRAFTED SPC WITH BINARY MONOMER MIXTURES

Sample	TGA				DTA	DTG
	IDT (^{0}C)	1st stage Decomposi-tion, ^{0}C (% wt. loss)	2nd stage Decomposi-tion, ^{0}C (% wt. loss)	FDT (^{0}C)	Exothermic peaks at differ-ent decom-position Tem-perature (µV)	Decomposition Temperature, $^\circ$C (Rate of wt. loss in mg/min)
SPC	218.0	218.0-501.0 (62.7%)	501-561.7 (21.3%)	561.7	329.2(29.2µV), 500.4 (152.4µV) 503.8 (98.6 µV)	63.2(0.0841), 320.5(0.439) 496.9 (0.884)
SPC-g-poly(EMA-co-MMA)	262.8	262.8-388.8 (76.7%)	388.8-595.2 (12.2%)	595.2	371.50C (18.28µV)	366.4 (0.718)
SPC-g-poly(EMA-co-EA)	241.5	241.5-358.7 (79.1%)	358.7- 597.6 (14.7%)	597.6	397.7 (64.6µV)	391.0 (2.258)
SPC-g-poly(EMA-co-MA)	241.9	241.9- 398.8 (40.4%)	398.9-589.1 (48.3%)	589.1	389.8(92.3µV)	389.3 (2.659)

The initial decomposition temperatures as well as final de-composition temperature of grafted proteins were found to be higher than that of SPC. Thus, the grafted soy protein was found thermally more stable than ungrafted SPC. This in-crease in thermal stability was due to incorporation of polyvi-nyl chains onto SPC backbone through covalent bonding.

In case of DTA studies, SPC showed three exothermic peaks at 329.2^{0}C (29.2µV), 500.4^{0}C (152.4µV) and 503.8^{0}C (98.6 µV) cor-responding to TGA decomposition stages of 218^0-358.9^{0}C, 358.9^0-501.4^{0}C and 501.4^0-561.7^{0}C. Whereas, SPC-g-poly(EMA-co-MMA), SPC-g-poly(EMA-co-EA) and SPC-g-poly(EMA-co-MA) showed their respective exothermic decompositions at 371.5^{0}C (18.28µV), 397.7^{0}C (64.6µV) and 389.8^{0}C (92.3µV), re-spectively.

Thermal decomposition in case of DTG analysis of SPC, showed exothermic peaks at 63.2^{0}C, 320.5^{0}C and 496.9^{0}C with 0.0841mg/min, 0.439 mg/min and 0.884 mg/min weight loss, respectively. Whereas, in case of SPC-g-poly(EMA-co-MMA), SPC-g-poly(EMA-co-EA) and SPC-g-poly(EMA-co-MA) exo-thermic peaks were found at 366.4^{0}C, 391.0^{0}C and 389.3^{0}C with 0.718mg/min, 2.258mg/min and 2.659mg/min weight loss, respectively (Table 2).

3.7 Acid and Base Resistant Studies

Acid and base resistance of grafted protein concentrate was found to higher as compared to ungrafted SPC. Moreover, acid and base resistance was found to increase as % grafting increased (Figs. 4-5). This could be due to fact that poly(EMA), poly(MMA), poly(MA) and poly(EA) chains being highly hy-drophobic in nature, possess less chemical affinity for both acid and base. Thus, incorporation of hydrophobic monomer chains onto SPC backbone through graft copolymerization resulted in increased acid and base resistance. [43].
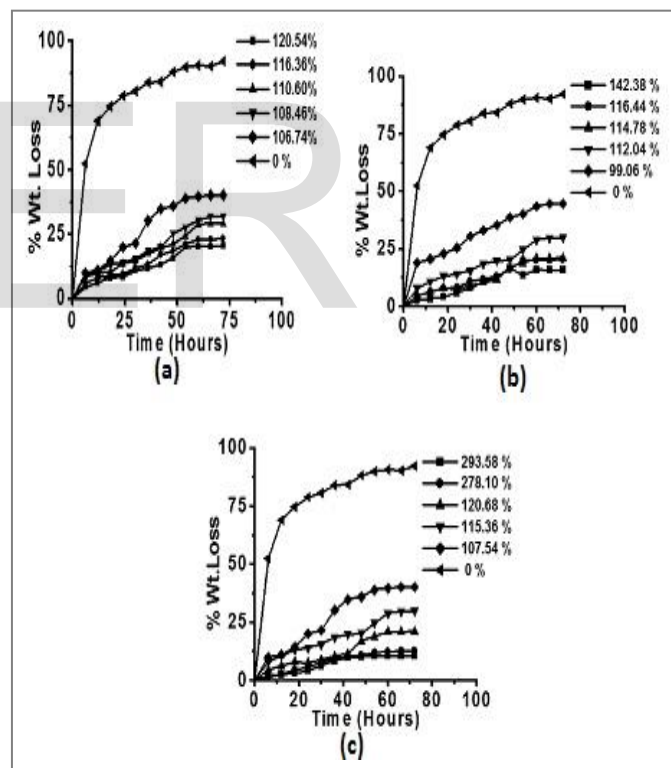

Fig. 4 Acid Resistance Studies of (a) SPC (b) SPC-g-poly(EMA-co-MMA) (c) SPC-g-poly(EMA-co-MA) (d) SPC-g-poly(EMA-co-MA
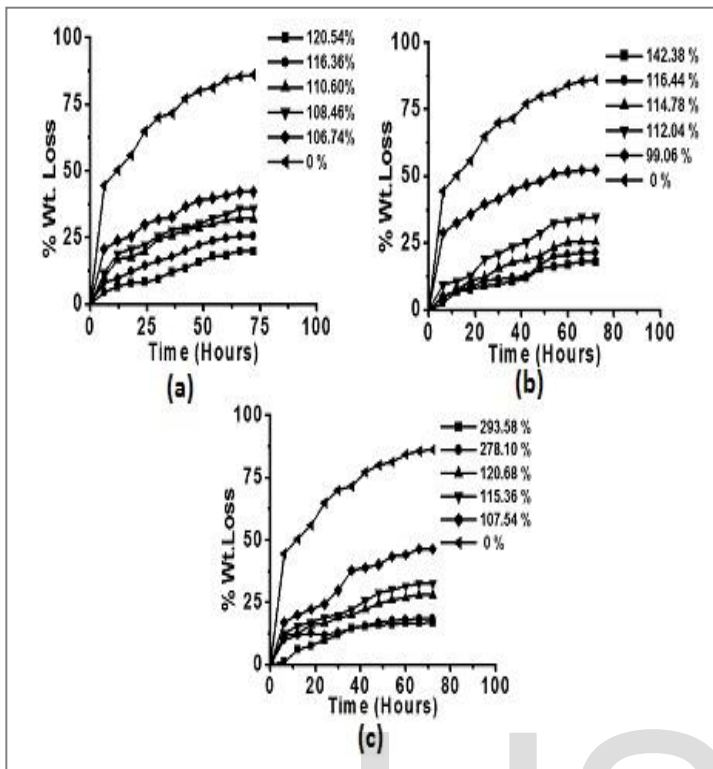
Fig. 5 Base resistance studies of (a) SPC (b) SPC-g-poly(EMA-co-MMA) (c)
SPC-g-poly(EMA-co-MA) (d) SPC-g-poly(EMA-co-MA

TABLE 3
**MOISTURE RESISTANCE STUDIES OF SPC AND GRAFTED SPC WITH
BINARY MONOMER MIXTURES**

Sample	Pg	% Weight Gain
Backbone	--	62.225
SPC-g-poly(EMA-co-MMA)	120.54	30.345
	116.36	32.647
	110.60	34.778
	108.46	37.846
	106.74	39.042
SPC-g-poly(EMA-co-EA)	142.38	23.778
	116.44	31.806
	114.78	32.963
	112.04	36.775
	99.06	42.156
SPC-g-poly(EMA-co-MA)	293.58	20.014
	278.10	21.965
	120.68	24.845
	115.36	33.856
	107.54	36.887

mer has been found to be thermally more stable in comparison
to backbone. These thermally and chemically stable products
with high moisture retardance are important components for
various industrial applications.

3.8 Moisture Resistant Studies

It was found that grafting of binary monomer mixtures on soy
protein concentrate backbone had made impact on the moisture absorbance behaviour of protein. SPC showed 62.2% wt.
gain whereas SPC-g-poly(EMA-co-MA) showed 20% wt. gain
in 24 hours. (Table 3). This was due to incorporation of hydrophobic poly(EMA), poly(MMA), poly(MA) and poly(EA)
chains onto sites vulnerable for moisture absorbance, thereby
resulting in moisture retardancy. Moisture absorbance of soy
protein concentrate decreased with increase in % grafting as
with the increase in Pg more and more active sites, responsible
for moisture absorbance, get incorporated with hydrophobic
monomers [43].

4 CONCLUSION

The grafting of each monomer mixture of EMA+MMA,
EMA+EA and EMA+MA onto soy protein concentrate in the
presence of ascorbic acid/potassium persulphate as a redox
initiator system has been found to influence the physico-chemical, thermal as well as morphological properties of protein backbone. The incorporation of poly(EMA+MMA),
poly(EMA+EA) and poly(EMA+MA) chains onto soy protein
concentrate resulted in higher resistance towards the attack of
acid and base. Moreover, lesser moisture absorbance has been
observed in case of grafted protein. Further, the graft copoly-

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