

POLY(METHYL METHACRYLATE)/SOY PROTEIN GREEN COMPOSITES AS GAS BARRIER MATERIALS*

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Abstract Poly(methyl methacrylate)/soy protein (PMMA/SP) composites were prepared by emulsion polymerization method using potassium persulphate (KPS) as the radical initiator. The interaction of soy protein with PMMA was evidenced by Fourier transformed infrared (FTIR) spectroscopy. The structure of PMMA/SP composites was investigated by X-ray diffraction (XRD) study and scanning electron microscopy (SEM). The thermal properties of soy protein and PMMA/SP composites were compared with soy protein and virgin PMMA sample. PMMA/SP composites were found to be flame retardant materials from the measurement of limiting oxygen index (LOI) of samples. The oxygen permeability of PMMA/SP composites was substantially decreased as compared to virgin PMMA.

Keywords: Soy protein; Emulsion polymerization; Biodegradability; Oxygen permeability.

INTRODUCTION

The environmental pollution from plastics consumption has become a serious issue, particularly when they are used as one-time use packaging materials. To overcome this problem, biopolymers produced from natural resources are regarded as an attractive alternative since they are abundant, renewable, inexpensive and environmentally friendly^[1]. Among biopolymers, soy protein could be a potential replacement for petroleum-based polymers due to its availability and biodegradability^[2–4].

Soy proteins are composed of a mixture of albumins and globulins, 90% of which are storage proteins with globular structure, consisting mainly in 7s (β -conglycinin) and 11s (glycinin) globulins^[5]. Globulins are protein fractions in which the subunits are associated *via* hydrophobic and hydrogen bonding^[6]. Soy bean products are available commercially as defatted soy flour, soy protein isolate and soy protein concentration. Soy protein is globular, reactive and often water soluble as compared to helical or planar, non reactive and water resistant synthetic polymers. Soy protein consists of various polar and reactive amino acids such as cystine, arginine, lysine and histidine which can be used for crosslinking it and improving the tensile and thermal properties^[7]. In all of the protein resources, soy protein has been regarded as a readily renewable biopolymer and potential source not only for the use as biodegradable plastics^[8], textile fibers^[9], biodegradable membranes^[10] and adhesives^[11, 12], but also for the fact that it can be acetylated^[13], transglutaminase-treated^[14] and blended with organic and inorganic nanoparticles. Effects of molding temperature and pressure on properties of soy protein polymers have been studied by Mo *et al*^[15]. Characterization of flax yarn and glutaraldehyde/poly(vinyl alcohol) modified soy protein concentrate composites was done by Chabba and Netravali^[16]. As a result of the cross-

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linking, the strength/toughness of the soy protein decreased. Lodha and Netravali^[17] used stearic acid to modify soy protein isolate fabricated unidirectional flax yarn as well as flax fabric reinforced green composites using glutaraldehyde cross-linked soy protein concentrate as well as PVA blended resins. Both composites showed good tensile and flexural properties. Wu and Zhang^[18] studied the effect of the molecular weight on the properties of thermoplastics prepared from soy protein isolate. Morphology and properties of soy protein and polylactide blends were studied by Zhang *et al.*^[19]. Soy protein films have better oxygen permeability and lower water vapour permeability due to their more polar nature and more linear structure and lower free volume^[20]. Soy protein has been of great interest to researchers for its thermoplastic properties and its potential as a biodegradable plastic. However, because of its poor response against moisture and high rigidity, its biodegradability has not been exploited effectively^[21]. Soy protein is also blended with plasticizers to overcome brittleness. Nanocomposite films of soy protein and clay showed reduced water vapour permeability, improved elastic modulus and tensile strength^[22]. A Significant improvement of the mechanical strength and thermal stability of soy protein isolate/montmorillonite bionanocomposites was reported by Xiang *et al.*^[23].

Although, many works in the past have reported the biodegradability, hydrogel properties of the polymer soy protein composite, the studies of the properties like oxygen permeability and flame retardancy are sparse. So in the present work PMMA/SP composites were synthesized by *in situ* emulsion polymerization method^[24] and their oxygen permeability and flame retardancy were studied with variation of soy protein content.

EXPERIMENTAL

Materials

The monomer methyl methacrylate (MMA) was purchased from Merck, Germany, which was used after further purification. Potassium persulphate (KPS) was also purchased from Merck, Germany which was used as received. Soy protein was supplied by the HiMedia Laboratories Pvt. Ltd, Mumbai, India, which was used without further purification. The solution of KPS and Soy were prepared with double distilled water. The ammonium ferrous sulphate was of analytical grade and purchased from Merck India.

Synthesis of PMMA/Soy Protein Composites

Various weight percents of soy protein (1 wt%, 2 wt%, 3 wt%, 4 wt% and 5 wt%) were dispersed with calculated amount of methyl methacrylate in double distilled water and stirred for 30 min. After stirring for 30 min, the suspension was sonicated for 15 min with the help of ultrasound cleaners of 120 W/80 kHz. The sonicated mixture was allowed to stirring for 10 min. Then 0.1 mol/L KPS stock solution was added raising the temperature to 60°C, and the stirring was continued for 3 h. The 0.1 mol/L ammonium ferrous sulfate solution was added to arrest the polymerization process. Then the precipitate was filtered followed by repeated washing with double distilled water to get the PMMA/soy protein composite. The synthesized PMMA/soy protein composites were dried at 50°C for 24 h. The synthesized composites were coded as PMMA/SP1, PMMA/SP2, PMMA/SP3, PMMA/SP4 and PMMA/SP5 for 1%, 2%, 3%, 4%, and 5% soy protein concentrations respectively.

Characterization

In order to confirm the chemical interaction of soy protein with polymer matrix, FTIR spectroscopy was performed. The IR spectra of PMMA and PMMA/SP composites in the form of KBr pellets were recorded in the model Paragon-500 FTIR of Perkinmer spectrometer. The synthesized PMMA/SP composites were grinded to powder form with pestle of uniform pressure. The powder materials were placed in a sample holder for X-ray diffractometry. X-ray diffraction patterns were recorded in a reflection mode and in angular 2θ value of range up to 40° at ambient temperature by a Rigaku X-ray machine model no P-DD966 diffractometer, operated at $\text{CuK}\alpha$ wavelength 0.154 nm, 40 kV and 15 mA. The diffractometer was equipped with a 1° divergence slit, a 16 mm beam bask, a 0.2 mm receiving slit and a scatter slit of 1°. The morphology and dispersion of soy protein in PMMA were investigated by using scanning electron microscopy (SEM) utilizing a JEOLJSM-5800 model.

Measurements of Thermal Properties

PMMA/SP composites powders were dried in oven at 105°C for 3 h. Thermal properties of the powdered composites were measured with a TGA-DTA thermal analyzer (model DTG-60, SHIMADZU Corporation, Japan). The sample of 7 mg to 8 mg was heated from room temperature to 600°C at a heating rate of 10 K/min in a nitrogen atmosphere.

Measurements of Oxygen Permeability

Oxygen permeability of the composites was measured with ASTM F 316-86 by using an oxygen permeation analyzer (PMI instrument, model GP-201-A, NY, USA). For testing, the synthesized powdered composites were converted to films of 0.5 mm thickness with the help of a Polymer Press at a pressure of 10 tons and a temperature of 170°C. The results were recorded as average of the values obtained from five samples.

Measurements of Limiting Oxygen Index (LOI)

The LOI value corresponds to the minimum concentration of oxygen in the mixture of nitrogen and oxygen, necessary to burn the sample during 2 min over a weight of 0.5 mg. The flame retardancy^[25] of the composites was assessed by limiting oxygen index (LOI) test according to ASTM D-618, using LOI apparatus from Testmaster, India with a digital read out of oxygen and nitrogen concentration to $\pm 0.1\%$.

Measurements of Biodegradability Properties

The activated sludge water was collected from tank areas receiving toilet and domestic waste water. The sludge water contains many microorganisms (bacteria, fungi, yeast, *etc.*) responsible for the biodegradation of waste materials. The sludge was collected in a polypropylene container, which was filled completely and then fully closed. Then the waste water was brought to the lab immediately. The activated sludge water (10 mL) and a polymer sample (0.1 g) were incubated together in a sterilized vessel at room temperature ($(28 \pm 2)^\circ\text{C}$). The composite samples were removed at time intervals for biodegradation study *via* weight loss. A vessel containing composite samples without sludge water was treated as control.

RESULTS AND DISCUSSION

Structural Properties of PMMA/SP Composites

The FTIR spectrum of PMMA had a strong absorption band 1735 cm^{-1} corresponds to carbonyl group which was also present in PMMA/SP composite at 5 wt% of soy protein (Fig. 1). The main absorption peaks of soy protein are related to >C=O stretching at 1693 cm^{-1} where as the peak at 1566 cm^{-1} was related to N—H bending of the peptide linkage of soy protein. The broad band observed in the $3500\text{--}3000\text{ cm}^{-1}$ range is attributable to free and bound O—H and N—H groups, which are able to form hydrogen bonding with carbonyl group of the peptide linkage in the protein^[1]. The absorption peaks at 2953 cm^{-1} of PMMA and PMMA/SP composite were due to >CH_2 stretching. In the FTIR of PMMA/SP composite the peak at 1735 and 3676 cm^{-1} is evidenced for formation of composite.

The structural properties of soy protein, PMMA and PMMA/SP composites were studied by XRD (Fig. 2). The XRD pattern of the soy protein shows a broad peak at 2θ values around 20° , and the XRD of virgin PMMA resulted in a peak at 14° . When beam of X-ray passed through the PMMA sample, some of the regularly arranged atoms reflected the X-ray beam constructively and produce enhanced intense pattern. The soy protein peak at 2θ value of 20° was not appeared in PMMA/SP composites. This might be due to the fact that the structure of soy protein was destroyed after making composites with PMMA. However, the peak at 2θ value of 13.7° in case of composites may be due to structural peak of PMMA which also appeared in case of virgin PMMA. Hence it was noted that the soy protein was completely dispersed and chemically interacted with the PMMA matrix. The dispersion of soy protein in the PMMA matrix was evidenced by SEM.

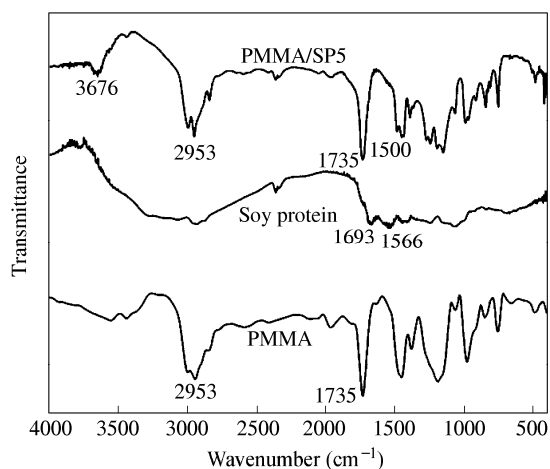


Fig. 1 FTIR spectra of soy protein, PMMA and PMMA/SP5 composite

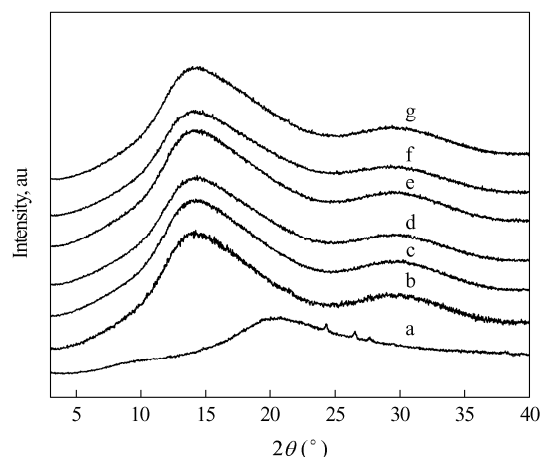


Fig. 2 X-ray diffraction patterns of (a) soy protein, (b) PMMA, (c) PMMA/SP1, (d) PMMA/SP2, (e) PMMA/SP3, (f) PMMA/SP4 and (g) PMMA/SP5

The surface morphology of PMMA/SP composites was compared with that of PMMA and soy protein by SEM. The SEM image of virgin PMMA (Fig. 3a) was studied with that of the soy protein and their composites. It was found that the PMMA microparticles are distributed with average diameter of 1 μm . In Fig. 3(b) the soy protein granules look to be almost uniform in size with average diameter of less than 1 μm . The PMMA/SP composite with 5 wt% of soy protein opens the polymer matrix and shows an appreciable deposition of soy protein on the backbone of the PMMA surface (Fig. 3c). It was also observed that soy proteins were uniformly dispersed with PMMA matrix during the formation of composites.

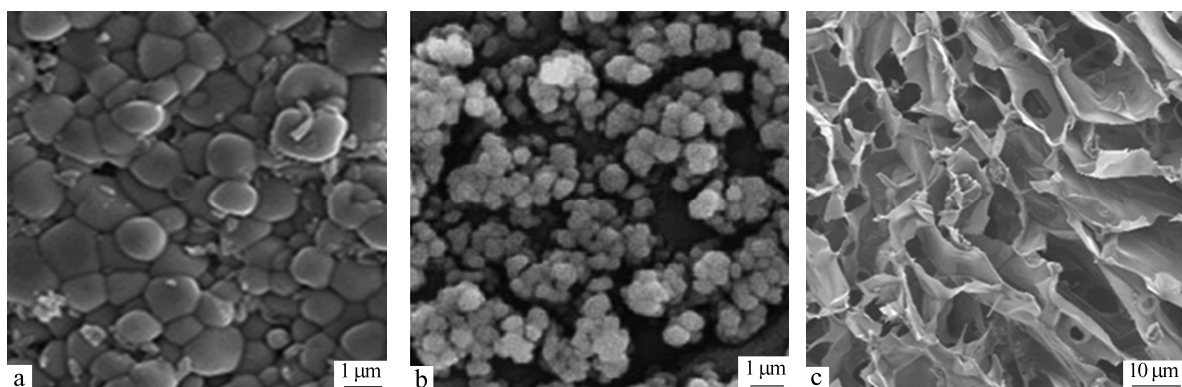


Fig. 3 SEM images of (a) PMMA, (b) soy protein and (c) PMMA/SP5 composites

Thermal Properties of PMMA/SP Composites

The thermal properties of soy protein, PMMA and PMMA/SP composites materials have been evaluated by thermogravimetric analysis (TGA) upto the temperature of 600°C as shown in Fig. 4. The thermal decomposition of soy protein occurred in a three-step reaction with maximum decomposition at 150°C. The first step is due to water loss, second step is due to the protein decomposition at 320°C and third step is due to oxidation of partially decomposed protein above 510°C. It was also observed that, the weight loss of PMMA started from 276°C, where as in the case of composites, the weight loss started from 293°C. From TGA analysis, it was seen that PMMA decomposed completely where as a residue was observed in case of PMMA/SP composites.

The PMMA/SP composites residue after weight loss at 600°C was about 5% for 1% soy protein content, 12% for 2% soy protein content, 16% for 3% soy protein content, 20% for 4% soy protein content and 24% for 5% soy protein content. It was observed that the residue left after decomposition was directly proportional to the protein concentration. The degradations of soy protein, PMMA, and PMMA/SP composites start at 150°C, 276°C and 293°C respectively. The addition of soy protein to PMMA increases the thermal stability of composites due to the dispersion of soy protein within the polymer matrix. The thermal stability of PMMA/SP composites is better than that of the virgin PMMA matrix due to insertion of soy protein fiber in to PMMA matrix. In other words the dispersion of soy protein within the PMMA matrix is the main mechanism for enhancement of thermal stability of the composites.

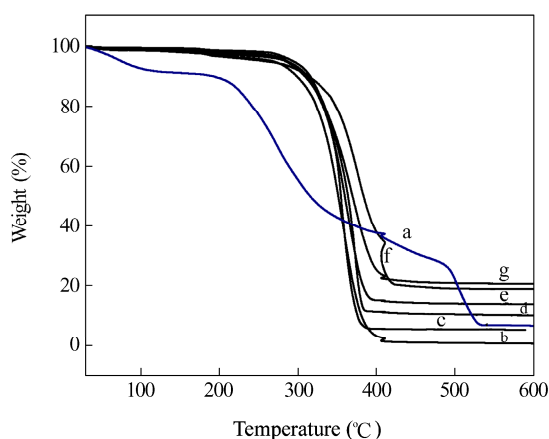


Fig. 4 TGA curves of (a) soy protein, (b) PMMA, (c) PMMA/SP1, (d) PMMA/SP2, (e) PMMA/SP3, (f) PMMA/SP4 and (g) PMMA/SP5

Oxygen Permeation Properties of PMMA/SP Composites

Polymer based composites which have shown to provide barrier to oxygen are being studied for packaging applications. The oxygen permeability of virgin PMMA and PMMA/SP composites was studied (Figs. 5 and 6). PMMA/SP composites are the class of reinforce biodegradable plastics suitable for manufacturing packaging films. The dispersion of soy protein in PMMA matrix may provide huddles to oxygen entrance whereas; virgin PMMA may have voids for oxygen permeation. Oxygen permeability of PMMA/SP composites was conducted to measure the effect of soy protein concentrations on the PMMA matrix. The oxygen flow rate through all the composites was observed to be less in comparison to the virgin PMMA at constant pressure of 3447.378 Pa (Fig. 5). It was found that the flow rate decreased with increase in percentage of soy protein loading. The remarkable reduction in oxygen permeability may be due to microstructure dispersion of soy protein within the PMMA matrix. The oxygen flow rates through all the composites were also observed to be less in comparison to the virgin PMMA at different pressures up to 13789.514 Pa (Fig. 6). There was an increase in PMMA barrierability due to the dispersion of soy protein flakes in the PMMA matrix, and the PMMA/SP composites can be applicable as packaging materials.

Limiting Oxygen Index Properties of Composites

Limiting oxygen index (LOI) is a popular research measurement to evaluate flame retardant properties of materials. The errors associated with LOI measurements were $\pm 0.2\%$, and the results were reported with the average of five determinations. The LOI values of PMMA/SP composites were measured and compared by varying soy protein concentrations as shown in Fig. 7. It was observed that the LOI of the composites gradually increased with increase in soy protein loading. Further, the results established that the LOI was increased by about 100% with addition of 5% of soy protein as compared to that of the virgin PMMA. That might be due to the fact that the composites exhibit particular physical barrier properties, which reduce the heat release rate

(HRR) under forced flaming conditions. The improvement of extinction behavior of composites may be due to the uniform dispersion of the soy protein within the polymer matrix.

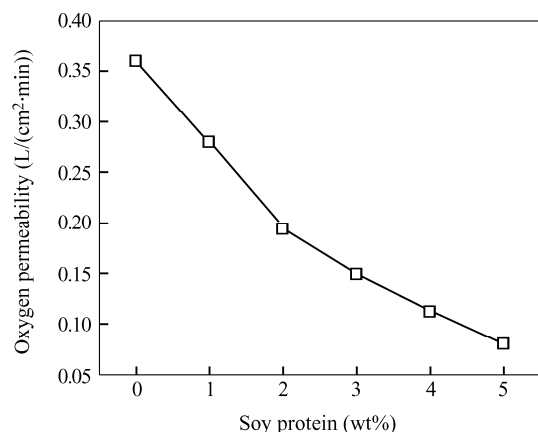


Fig. 5 Oxygen permeability of PMMA/SP composites as a function of soy protein content at a constant pressure of 3447.378 Pa

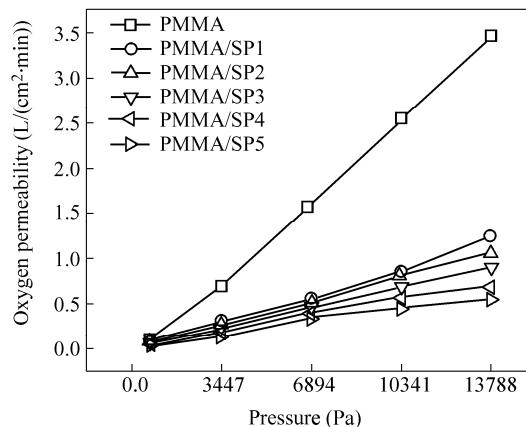


Fig. 6 Oxygen permeability of PMMA/SP composites as a function of soy protein content at difference pressure up to 13789.514 Pa

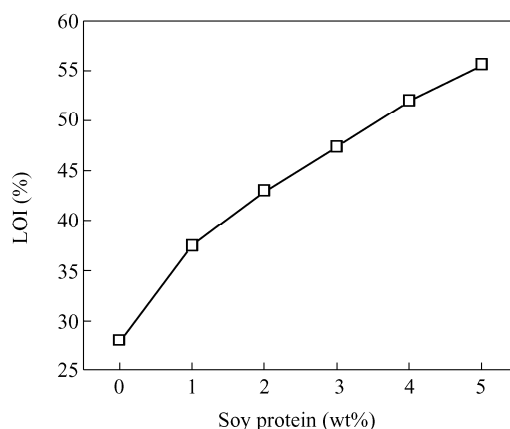


Fig. 7 Limiting oxygen index of composites as a function of soy protein content

Biodegradation Properties of PMMA/ASP Composites

The biodegradation of PMMA/SP composites was compared with that of the virgin PMMA in a study for one month with intervals of one week. The degradation was studied in order to calculate the percentage weight loss in activated sludge water (Fig. 8). It was found that the percentage weight loss of composites was increased with increase in percentage of soy protein. Biodegradation of composites as well as virgin PMMA was further increased with increase in duration time in the active sludge water. The similar works have been reported earlier^[26–28]. The chemical interactions of soy protein with PMMA matrix may be the cause for improvement of biodegradation properties. Further the enhancement of biodegradable properties of the PMMA/SP composites may be due to the well dispersion of soy protein within PMMA matrix in the composites. It was interesting to note that the biodegradation of composites with 5% soy protein after 30 days was about thirty times more than that of the virgin sample after 7 days.

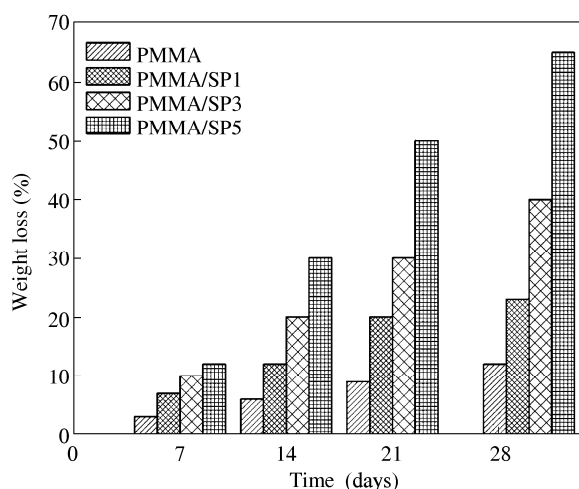


Fig. 8 Biodegradation of PMMA, PMMA/SP1, PMMA/SP3 and PMMA/SP5

CONCLUSIONS

Biodegradable PMMA/SP composites were synthesized at different concentrations of soy protein by emulsifier-free emulsion polymerization. The dispersion of soy protein in PMMA matrix resulted in the substantial improvement in oxygen barrier and flame retardancy properties of the composites. The thermal stability of composites was quite higher than that of the virgin PMMA. The biodegradability of PMMA/SP composites increases with increasing soy concentration.

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