



SYNTHESIS AND CHARACTERIZATION OF Poly (HYDROXY ETHYLMETHACRYLATE)/SOY PROTEIN COMPOSITE AND STUDY ITS GAS BARRIER PROPERTY

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ABSTRACT

Poly (HydroxyethylMethacrylate)/Soy protein biodegradable composites were synthesized by *in situ* emulsifier free emulsion technique. Various weight percents of soy protein (1wt%, 2wt%, 3wt% and 4wt%) were dispersed with calculated amount of HEMA in double distilled water and it was sonicated for 15 mins with the help of ultra sound cleaners of 120W/80 KHz. It was allowed to stir for 10 mins. Then 0.1M potassium persulfate (0.1M KPS) initiator was added to this mixture raising the temperature to 60°C and stirring was continued for 3 hrs. 0.1M ammonium ferrous sulfate solution was added to arrest the polymerization process. The synthesized composites were characterized by FTIR spectroscopy in order to know the interaction of PHEMA with soy protein. The structure and morphology of the prepared composites were studied by XRD and SEM. The results showed that there was a significant continuous reduction of gas permeability with increase in clay wt% as well as with rise in ultrasonic amplitude. The reduction of Oxygen permeability of the polymer based biodegradable composites may be enabled the materials for packaging applications and better commercialization.

KEYWORDS: Emulsifier free emulsion; Sonication; Soy protein; Gas barrier; Biodegradation.

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] Soy protein, the major component of the soya bean, has the advantages of being economically competitive and present good water resistance as well as storage stability.

Soybean or soya bean, or soy pea, a leguminous plant (*glycine max. g. soja*, or *soja max*) of the family *leguminosae*, sub-family *papilionaceae* (*pulse* family named, renamed as *fabaceae*), is native to tropical warm temperate regions of Asia, where it has been cultivated as principal crop for at least 5,000 years. There are over 25,000 varieties in cultivation, producing beans of many sizes (ranging from as small as a pea to as large as a cherry), shapes, and colors as in various combinations of red, yellow, green, brown and black^[2] as a crop, soybeans are high in yield and easy to harvest; succeed on nearly all types of soil and among biopolymer, soy protein could be a potential replacement for petroleum-

based polymers due to its availability and biodegradability.^[3-5] The effect of molding temperature and pressure on properties of soy protein polymers were studied by some investigators.^[6] Also some investigators have modified soy flour with polyester amide to fabricate composites using hemp fibers.^[7] 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.^[8]

Soy protein offers several advantages over synthetic polymers. Firstly the soy protein purification process is benign and environment friendly; secondly, these proteins can form ductile and viscous polymers that can be used as resins and thirdly, the cost of raw materials is low. Because of the worldwide environmental pollution problem with petroleum polymers, soy protein polymers have been considered as alternatives for biodegradable plastics. In the 1930s, Henry Ford pioneered the use of soy protein for plastics and fibers.^[9]

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.^[10] Among hydrophilic monomers, 2-hydroxyethyl methacrylate (HEMA) is used for commercial applications. Poly-HEMA (PHEMA) is a favorable biomaterial because of its excellent biocompatibility and physicochemical properties similar to those of living tissues.^[11] The polymerization of hydrophilic polymer such as PHEMA also improves the biodegrading properties.^[12,13] We have synthesized (SCBF-g-PHEMA)/MMT composite using microwave irradiation technique in our laboratory as superabsorbent.^[14]

Although, many works in the past have reported the biodegradability, hydrogel properties of the polymer soy protein composite, the study of the properties like oxygen permeability and flame retardancy are sparse. So in the present work PHEMA/SP composite was synthesized by *in situ* emulsion polymerization method^[15] and their oxygen permeability and flame retardancy were studied with variation of soy protein content.

MATERIALS AND METHODS

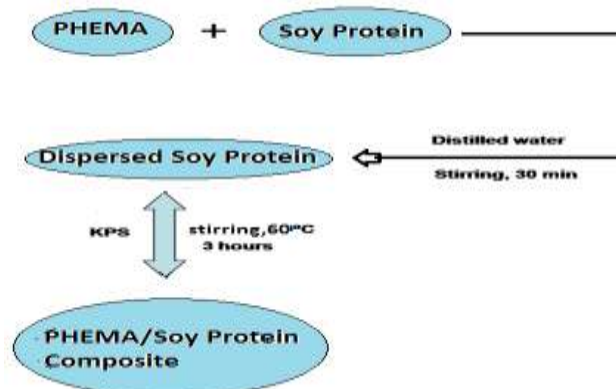
Materials

The monomer hydroxyethyl methacrylate (HEMA) was purchased from Merck, Germany, which was used after further purification. Potassium persulphate (KPS) was also purchased from Merck, Germany which was used as such. 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 analytical grade chemical and purchased from Merck India.

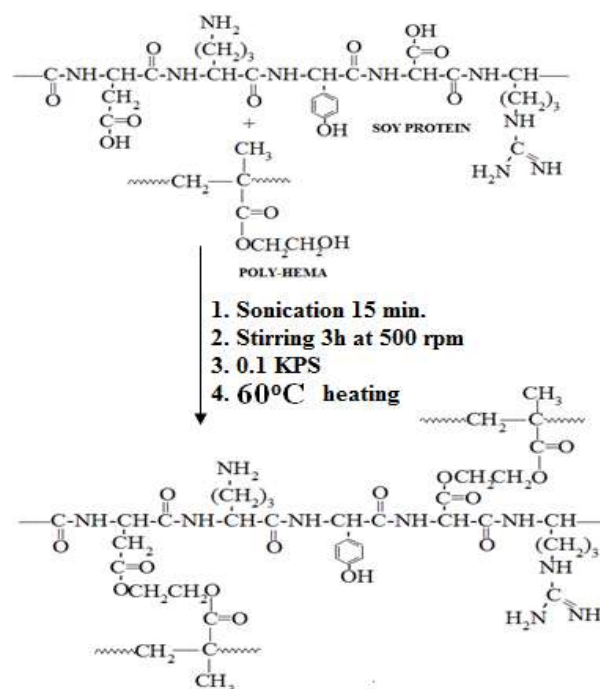
Experimental

Synthesis of PHEMA/Soy protein Composites

Various weight percents of soy protein (1 wt%, 2 wt%, 3 wt% and 4 wt%) were dispersed with calculated amount of hydroxyethyl methacrylate in double distilled water and stirred for 30 minutes. After stirring for 30 minutes, the suspension was sonicated for 15 minutes with the help of ultrasound cleaners of 120 W/80 KHz. The sonicated mixture was allowed to stirring for 10 minutes. Then 0.1M KPS stock solution was added raising the temperature to 60 °C and the stirring was continued for 3 hours. The 0.1M 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 PHEMA/Soy protein composite. The synthesized PHEMA/Soy protein composites were dried at 50°C for 24 hours. The Synthesized composites were coded as PHEMA/SP1, PHEMA/SP2, PHEMA/SP3 and PHEMA/SP4 for 1%, 2%, 3% and 4%, soy protein concentrations respectively. The schematic representation of synthesis of PHEMA/soy protein composites is illustrated in Scheme 1. The experimental parameters for synthesis of PHEMA/Soy protein composites are summarized in table 1 and also formation of composite is shown in scheme 2.



Scheme 1: Synthesis route of PHEMA/Soy protein composites.



Scheme 2; Formation of PHEMA/Soy Protein Composite.

Characterization

In order to confirm the chemical interaction of soy protein with polymer matrix, FTIR spectroscopy was performed. The IR spectra of PHEMA and PHEMA/SP composites in the form of KBr pellets were recorded in the model Paragon-500 FTIR of Perkinmer spectrometer. The synthesized PHEMA/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 CuKα wavelength 1.54 Å. The radiation from anode operated at 40KV and 15mA. The diffractometer was equipped with 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 PHEMA were investigated by using Scanning Electron Microscopy (SEM) utilizing JEOLJSM-5800 model.

Measurement of Thermal Property

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

Measurement of Oxygen Permeability

Oxygen permeability of the composites was measured with ASTM F 316-86 by using 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 four same samples.

Measurement 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 minute over a weight of 0.5mg. The flame retardancy^[11] of the composites were 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 $\pm 0.1\%$.

Measurement of Biodegradability Property

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 (10ml) and a polymer sample (0.1g) 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. Vessel containing composite samples without sludge water was treated as control.

RESULTS AND DISCUSSION

Table 1: Experimental parameters for synthesis of PHEMA and PHEMA/Soy Protein composites.

Sample	[HEMA] Mol.dm ⁻³	[KPS] Mol.dm ⁻³	Soy protein wt %	%age Conversion
PHEMA	1.40	1×10^{-2}	0	30.6
PHEMA	1.40	1×10^{-2}	0	59.0
PHEMA/SP1	1.40	1×10^{-2}	1	60.2
PHEMA/SP2	1.40	1×10^{-2}	2	55.3
PHEMA/SP3	1.40	1×10^{-2}	3	60.6
PHEMA/SP4	1.40	1×10^{-2}	4	55.3

IR Spectra for Structural Properties of PHEMA/SP Composites

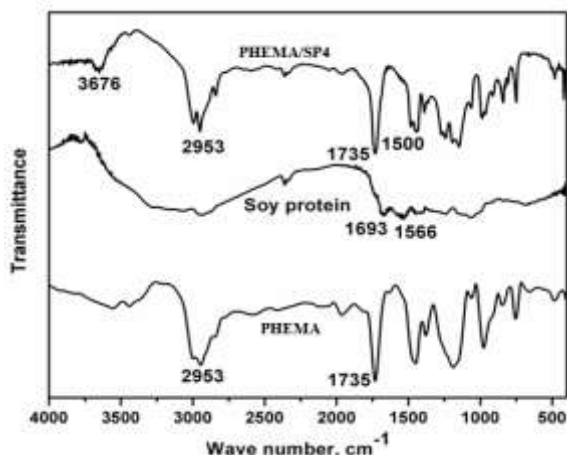


Figure 1: FTIR spectra of soy protein, PHEMA, PHEMA/SP4 composite.

The FTIR spectrum of PHEMA had a strong absorption band 1735 cm⁻¹ corresponds to carbonyl group which

was also present in PHEMA/SP composite at 4 wt% of soy protein (Figure 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 3500-3000 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. The absorption peaks at 2953 cm⁻¹ of PHEMA and PHEMA/SP composite were due to >CH₂ stretching. In the FTIR of PHEMA/SP composite the peak at 1735 cm⁻¹ and 3676 cm⁻¹ is evidenced for formation of composite.

X-ray diffraction

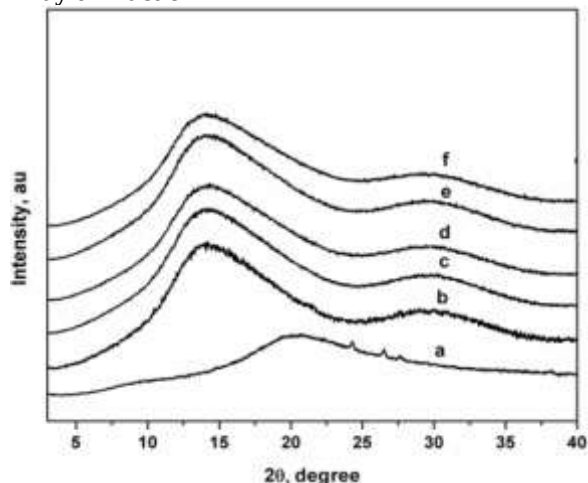


Figure 2: X-ray diffraction patterns of (a) Soy Protein (b) PHEMA (c) PHEMA/SP1 (d) PHEMA/SP2 (e) PHEMA/SP3 (f) PHEMA/SP4.

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

Scanning Electron Microscopy

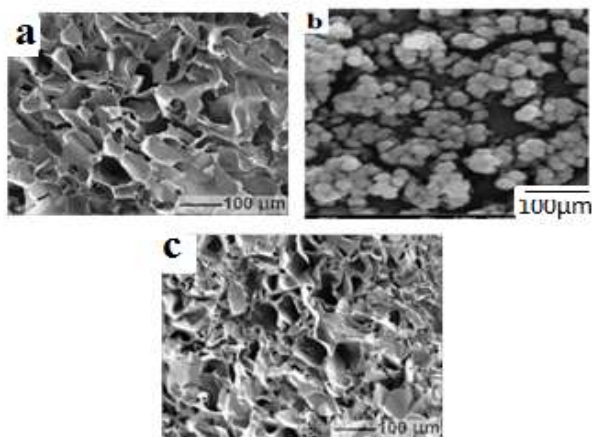


Figure 3: SEM images of (a) PHEMA (b) Soy Protein (c) PHEMA/SP4 composites.

The surface morphology of PHEMA/SP composites was compared with PHEMA and soy protein by SEM as shown in Figure 3. The SEM image of virgin PHEMA (Figure 3a) was studied with that of the soy protein and their composites. It was found that the PHEMA microparticles are distributed with average diameter of $1\ \mu\text{m}$. In Figure 3b the soy protein granules are looks to be debonded and almost uniform in size with average diameter of less than $1\ \mu\text{m}$. The PHEMA/SP composite with 4 wt % of soy protein opens the polymer matrix and shows an appreciable deposition of soy protein on the backbone of the PHEMA surface (Figure 3c). It was also observed that soy proteins were uniformly dispersed with PHEMA matrix during the formation of composites.

TGA-DTA-Thermal Properties of PHEMA/SP Composites

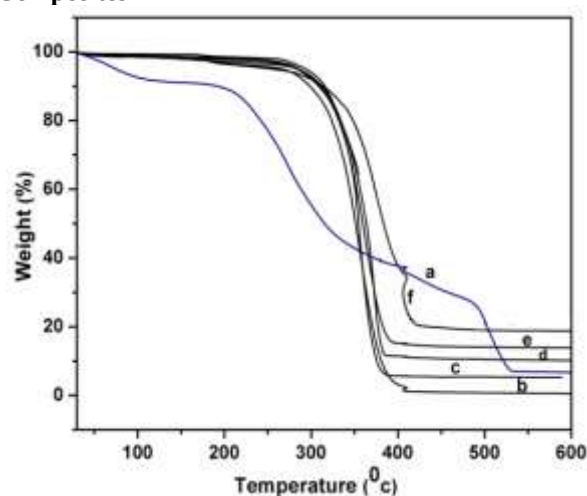


Figure 4 TGA of (a) Soy Protein (b) PHEMA (c) PHEMA/SP1 (d) PHEMA/SP2 (e) PHEMA/SP3 (f) PHEMA/SP4.

The thermal properties of soy protein, PHEMA and PHEMA/SP composites materials have been evaluated by thermogravimetric analysis (TGA) upto the temperature of 600°C as shown in Figure 4. The thermal decomposition of soy protein occurred in a three step reactions with maximum decomposition at 150°C , the first step is due to water loss, second step is due to the decomposition protein 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 PHEMA starts from 276°C , where as in case of the composite, the weight loss starts from 293°C . From TGA analysis, it was seen that soy protein decomposed completely where as a residue was observed in case of PHEMA/SP composites. The PHEMA/SP composites residue after weight loss at 600°C was about 4% for 1% soy protein content, 12% for 2% soy protein content, 16% for 3% soy protein content, 20% for 4% soy protein content. It was observed that the residue left after decomposition was directly proportional to the protein concentration. Further, it was noted that the weight loss in soy protein is greater than that of the composite and virgin PHEMA. The degradations of soy protein, PHEMA and

PHEMA/SP composite start from 150⁰C, 276⁰C and 293⁰C respectively. The addition of soy protein to PHEMA increases the thermal stability of composites due to the dispersion of soy protein within the polymer matrix. The thermal stability of PHEMA/SP composites is more than that of the virgin PHEMA matrix due to insertion of soy protein fiber in to PHEMA matrix. In other words the dispersion of soy protein within the PHEMA macromolecules is the main mechanism for enhancement of thermal stability of the composites.

Oxygen Permeation Properties of PHEMA/SP Composite

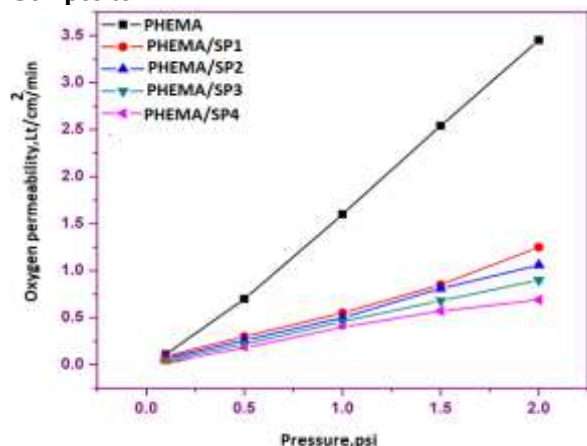


Figure 5: Oxygen permeability as a function of soy protein content at difference pressure up to 2 psi.

Polymer based composites which have shown to provide barrier to oxygen are being studied for packaging applications. The oxygen permeability of virgin PHEMA and PHEMA/SP composites can be studied from Figure 5 and Figure 6. PHEMA/SP composites are the class of reinforce biodegradable plastics suitable for manufacturing packaging film. The dispersion of soy protein in PHEMA matrix may provide huddles to oxygen entrance whereas; virgin PHEMA may have voids for oxygen permeation. Oxygen permeability of PHEMA/SP composites was conducted to measure the effect of soy protein concentrations on the PHEMA matrix. The oxygen flow rate through all the composites was observed to be less in comparison to the virgin PHEMA at constant pressure of 0.5 psi (Figure 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 PHEMA matrix. The oxygen flow rates through all the composites were also observed to be less in comparison to the virgin PHEMA at different pressures up to 2 psi (Figure 6). There was an increase in PHEMA barrier through soy protein flakes being dispersed with PHEMA matrix and blocking voids that provide barrier to oxygen permeation, for which the composites can be applicable as packaging materials.

Limiting Oxygen Index Properties of Composites

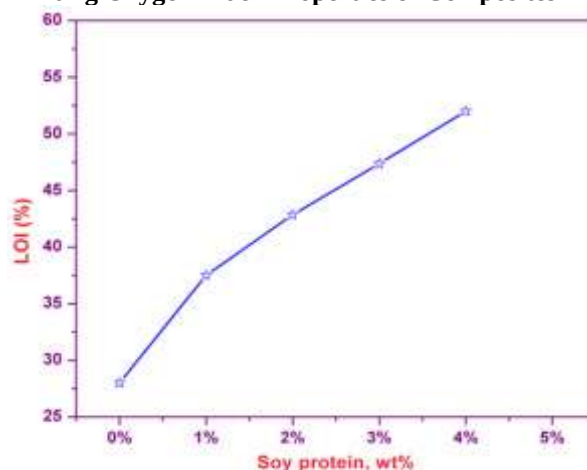


Figure 6: Limiting Oxygen Index of composites as a function of soy protein content.

Limiting oxygen index (LOI) is a popular research measurement to evaluate flame retardant properties of materials. The errors associated with LOI measurements are $\pm 0.2\%$ and the results were reported with the average of four determinations. The LOI values of PHEMA/SP composites were measured and compared by varying soy protein concentrations as shown in Figure 6. It was observed that, the LOI of the composites were gradually increased with increase in soy protein loading. Further, the result established that, the LOI was increased near about 65% with addition of 4% of soy protein as compared to that of the virgin PHEMA. That might be due to the fact that composites exhibit as particular physical barrier properties, which reduces the heat release rate (HRR) under forced flaming conditions. The improvement of extinction behavior of composite may be due to the uniform dispersion of the soy protein within the polymer matrix.

Biodegradation Properties of PHEMA/SP Composites

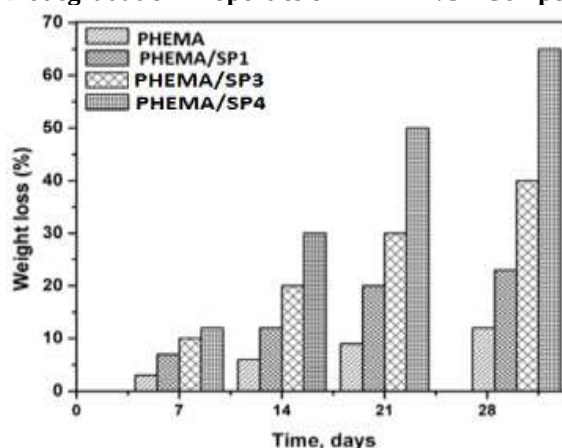


Figure 7: Biodegradation of PHEMA, PHEMA/SP1, PHEMA/SP3, PHEMA/SP4 composites.

The biodegradation of PHEMA/SP composites were compared with virgin PHEMA in a study for one month with intervals of one week. The degradation was studied

in order to calculate percentage weight loss in activated sludge water (Figure 7). It was found that, the percentage weight loss in composites was increased with increase in percentage of soy protein. Biodegradation of composites as well as virgin PHEMA were further increased with increase in time duration in the active sludge water. The similar works have been reported earlier.^[12-14] The chemical interactions of soy protein with PHEMA matrix may be cause for improvement of biodegradation properties. Further the enhancement of biodegradable properties of the PHEMA/SP composites may be due to the well dispersion of soy protein with PHEMA matrix in the form of composites.

CONCLUSION

PHEMA/Soy protein (PHEMA/SP) composites have been prepared by emulsifier-free emulsion green technique. The interactions of soy protein with PHEMA were evidenced by FTIR and XRD techniques. The dispersion of soy protein in PHEMA matrix resulted in the substantial improvement in oxygen barrier and flame retardancy properties of the composites. The thermal stability of PHEMA/SP composites was quite higher than that of the virgin PHEMA. It was concluded that the synthesized soy protein based materials may be suitable for thermal resistance and gas barrier packaging materials.

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