

Protein Filled Polymer Composites for Biodegradable Packaging

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Abstract: The present study describes the preparation of biodegradable polymer composites filled with protein hydrolysate (HP), a proteinaceous biomaterial isolated from chrome-tanned solid leather waste by enzymatic hydrolysis. Metallocene linear low density polyethylene (mLLDPE) was the synthetic polymer used to prepare mLLDPE/HP (20-40%) composites by melt mixing. This paper also reports about the effect of ultraviolet (UV) radiation on polymer morphology, on physico-chemical structure, and on biodegradation of protein filled polymeric material. Morphological studies performed on fractured surfaces of composites showed uniform and fine HP particles dispersion which implies complete blending of mLLDPE and HP and exhibits the effect of UV on polymer morphology as well as its biodegradation. This modified polymeric material shows a reasonably good biodegradability in case of UV-untreated sample contrary to UV-treated one.

Key-Words: polymer composites, mLLDPE, leather waste, protein hydrolysate, UV treatment, morphology, biodegradation, packaging

1 Introduction

Biodegradable packaging is also called compostable packaging as it is made from entirely natural materials such as corn, wheat and sugar cane etc. Packagings made from organic materials such as carbohydrate (starch, cellulose, lactose, sucrose) protein (whey, casein, collagen or protein hydrolyzed) are also recycled naturally and no additional energy is required to break the materials down. However, the commonly used synthetic polymers like polyethylene, polypropylene etc. are normally non-biodegradable under environmentally triggered conditions hence create a problem of waste disposal. Thus, uses of green polymeric materials especially renewable polymeric materials are most encouraging from ecological, economical, environmental protection, and as well as resource recycling point of view. Biodegradable material derived from renewable sources has many functional properties whereas the disadvantage of this material is that its degradation occurs very slowly. However, renewable polymeric materials are recyclable, can be produced indefinitely, with strong environmental benefits and derived from a living tree, plant, animal or ecosystem which has the ability to regenerate itself [1].

A remarkable use of plastics is recorded in packagings as carry bags for delivery of food stuff,

clothes, gift and other perishable commodities. The uses of plastic shopping bags are now a day a common practice in several countries. These bags are sometimes called single-use bags, referring to carrying items from a store to a home. However, reuse for storage or trash (bin bags) is common. According to the UK's Environment Agency, 76% of carrier bags are reused [2]. An estimated 90% of individuals reuse plastic bags, and 56% of individuals reuse all plastic shopping bags [3]. These plastic bags are often made from polyethylene (PE). This synthetic carbon based polymer is mostly hydrophobic and biologically inert which creates a considerable impact on the environment, including deleterious effect on the wild life and aesthetic qualities of cities and forest. Consequently, for the past two decades, there has been a growing public and scientific interest regarding the use and development of biodegradable polymers as an ecologically useful alternative to plastics which must still retain the desired physical and chemical properties of conventional synthetic plastics, thus offering solution for the existing severe problem of plastic waste.

It is reported that leather industry generates a large quantity of waste leather [4, 5] which could be the source of protein; a renewable biomaterial. This biopolymer/renewable biomaterial can be useful for

valuable applications like packaging (e.g. garbage/carry bag). In this context, it can be mentioned that one of the fruitful achievements of our research was preparation of protein-based polymeric material through polymer modification. A novel polymeric material was prepared using metallocene linear low density polyethylene (mLLDPE) and hydrolyzed protein (HP), isolated from chrome-tanned solid leather waste by enzymatic hydrolysis [6]. The modified polymer (mLLDPE + 20% HP) showed reasonable strength properties to carry load and demonstrated an acceptable range of biodegradability as well [7, 8] under controlled biodegradation conditions. Further, here in this paper we mainly aimed to report about an effect of UV on biodegradation of protein filled polymer composites which could be used as packaging material.

2 Problem Formulation

The increasing use of plastics and their non-biodegradability have raised environmental awareness and hence there is a need for the development of environmentally friendly degradable materials. Since the most utilized plastic is polyethylene (PE; ca. 140 million tons/year), any reduction in the accumulation of PE waste alone would have a major impact on the overall reduction of the plastic waste in the environment [9]. Safe disposal of plastic waste via biodegradation should focus on the most consumed polymers, i.e. PE, polypropylene and polystyrene. Unfortunately, these polymers are also the most durable plastics and not degrade naturally (environmental trigger). In view of these obstacles and in order to obtain safe waste disposal one of the ways could be the modification of the synthetic polymer with biopolymers (e.g. mLLDPE modified with protein hydrolysate (HP)).

3 Problem Solution

3.1 Experimental

3.1.1 Preparation of biodegradable polymer

The modified biodegradable polymer is a composite of commercially available synthetic polymer and biopolymer. Metallocene linear low density polyethylene (mLLDPE, Engage 8100), was obtained from DuPont Dow Elastomers company. Its density is 0.87 g/cm^3 , melt flow index 1.0 dg/min and DSC melting peak 60°C at a rate of 10°C/min . The second component, protein hydrolysate (HP), a

biopolymer was isolated from chrome-tanned solid leather waste of tanning industry by enzymatic hydrolysis [6]. The density of HP is 1.072 g/cm^3 .

MLLDPE/HP composites (20–40 wt.%) were prepared by melt mixing in a Brabender Plastimeter. Mixing of these two polymers was carried out at 70°C and 30 rpm for 12 min. The polymer blends were moulded into thin films (1 mm thick) by manual hot pressing at 100°C and then cooled down to the ambient temperature under 10 MPa. The protein filled polymer films with 20% HP were then used for biodegradation study (in presence of fungi: *A.oryzae*) using UV-treated and UV-untreated samples.

3.1.2 UV-treatment of protein filled polymer

The modified protein filled polymer (20 HP) was selected to observe the effect of UV treatment on biodegradation as we had noticed in our previous work that this polymer of 20 HP had showed acceptable range of mechanical strength property as well as biodegradability [7]. The samples (25 mm diameter, 1 mm thick) were placed under ultra-violet radiation, 25 cm away from the source (UV lamp) for 140 hours. Laminar flow box BDK (SRN) was used for UV-treatment of polymer samples.

3.1.3 Fourier transform infrared spectroscopy

The Fourier transform infrared spectroscopy analysis was done to identify the changes occurred in physico-chemical structure of protein filled polymer (20 HP) after UV treatment. ATR-FTIR spectroscopic analysis was conducted using the samples (25 mm diameter, 1 mm thick) using a NICOLET 320 FTIR spectrophotometer with the “Omnic” software package over a range of $4000\text{--}600 \text{ cm}^{-1}$ at room temperature. A uniform scan resolution of 2 cm^{-1} was maintained in all cases.

3.1.4 Scanning electron microscopy (SEM)

The SEM analysis was carried out to observe the morphological changes in polymer films. It was conducted on VEGA II LMU (TESCAN) operating in the high-vacuum/secondary electron imaging mode at an accelerating voltage of 5–20 kV. The samples were sputter coated with a thin layer of palladium/gold alloy to improve the surface conductivity and tilted 30° for better observation. The images were taken at magnifications of 100x–2kx.

3.1.5 Biodegradation of protein filled polymer

The biodegradation study of protein-filled polymer was conducted in presence of fungus *Aspergillus oryzae* (CCMF-172), cultured in an aqueous phase

of 5% malt extract medium at pH 5.6 (initial) and temperature 30°C as these are the suitable cultural conditions for protease enzyme synthesis by the above mentioned fungus. The polymer samples (25 mm diameter, 1 mm thick) of 20-40 HP were used for biodegradation study.

The rheological behaviour of the polymer films was used as a tool for measuring the biodegradability of samples. The protein filled samples were measured before and after biodegradation for 21 days (3 weeks) by using a rotational rheometer (ARES, Rheometrics Scientific, USA). The relative changes in the complex viscosity $\Delta\eta^*(t)$ of protein filled blend polymers were measured at a temperature of 80°C, a frequency of 0.1 Hz and a strain of 1%, and expressed by using the following equation:

$$\Delta\eta^*(t) = \frac{\eta^*(t)}{\eta_0^*} 100(\%)$$

where t is the time of degradation, and represents the complex viscosity for degradation times of zero and t respectively. The biodegradability of the test samples was calculated on the basis of the relative change in the complex viscosity, by using the following equation:

$$D(t) = 100 - \Delta\eta^*(t) (\%)$$

where, $D(t)$ represents the biodegradability of the sample and the complex viscosity for a particular biodegradation time t .

The above mentioned modified protein filled polymeric material (mLLDPE/HP composite) has considerable range of mechanical property and biodegradability [7, 8]. For further improvement of material properties the following experiments were done and results are explained below.

3.2 Results and Discussion

3.2.1 Effect of UV on morphology

Morphological studies performed on fractured surfaces of composites showed uniform and fine particles dispersion which implies complete blending of mLLDPE and HP (Fig. 1). It can be seen, that noticeable morphological changes occurred after UV-treatment of protein filled polymer. The initial colour of the protein filled (20 HP) polymeric material changed from whitish to pale yellow. These observed changes maybe happened due to an internal modification or

structural changes of chemical bonds during UV radiation. The FTIR spectra of UV-untreated and treated samples are the evidence, as shown in Fig.2. Moreover, the scanning electron micrographs prove that the modified protein filled polymer is a composite and confirm that UV treatment has some effect on the protein filled polymer as well (Fig.1). UV-untreated sample of 20 HP exhibits some uneven surface view compared to UV-treated sample. The observed smooth surface in UV-treated sample may be due to an increase of internal cross-linking between mLLDPE and HP.

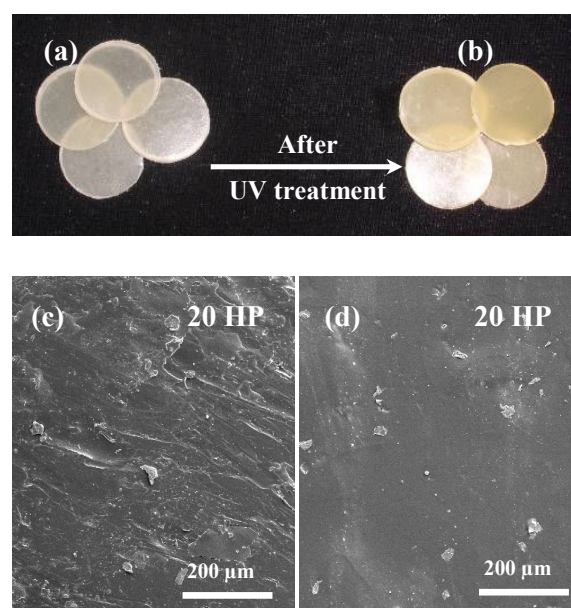


Fig.1: Morphology of 20HP filled polymer samples: (a) UV-untreated and (b) UV-treated [optical], (c) UV-untreated and (d) UV-treated [SEM]

3.2.2 Effect of UV on physico-chemical structure

Fig.2 shows FTIR-ATR spectra of 20 HP filled mLLDPE before (a) and after UV treatment (b) at wavenumbers between 4000 and 500 cm^{-1} . Absorption peaks at positions of 2906/10 and 2844/8 (strong C-H aliphatic stretching), 1462/54 (CH_2 scissoring), and 715 cm^{-1} (C-H bending/long-chain methyl rocking) correspond to mLLDPE [7]. After UV treatment (Fig.2b) the shapes and heights of pronounced peaks of mLLDPE remained almost constant in all cases. In contrast, the other peaks of the composites which belong to HP filler [7] at the region 3255 (broad-complex band of N-H of Amide A stretching / O-H of H_2O stretching), 1641/9 ($\text{C}=\text{O}$ stretching of Amide I band), 1544 (complex of C-N stretching / N-H bending of Amide II band), 1073/7 and 1026/38 cm^{-1} (C-O stretching / side-chain vibrations) almost disappeared after 140 h UV treatment. On the other hand, a new functional group at 1365 cm^{-1} (C-H methyl rocking / O-H

bending) appeared which is typical for pure mLLDPE. Hence, similarly to morphology, UV treatment showed a great effect on physico-chemical structure of HP filled modified polymer of mLLDPE. These changes were connected with the high reduction of HP absorption peaks which means weaker polarisation of its bonds. Moreover, UV treatment caused a shift in most of the peaks positions towards higher wavenumbers which signifies strengthening (shortening) of the polymer composite bonds by the Hooke's Law. Contrary to other peaks, a peak at a position of 1462 cm^{-1} after UV treatment shifted to a lower wavenumber which can be caused by the fact that this is a complex peak of mLLDPE (CH_2 scissoring) and also of HP (C-N stretching and N-H bending of Amide II band).

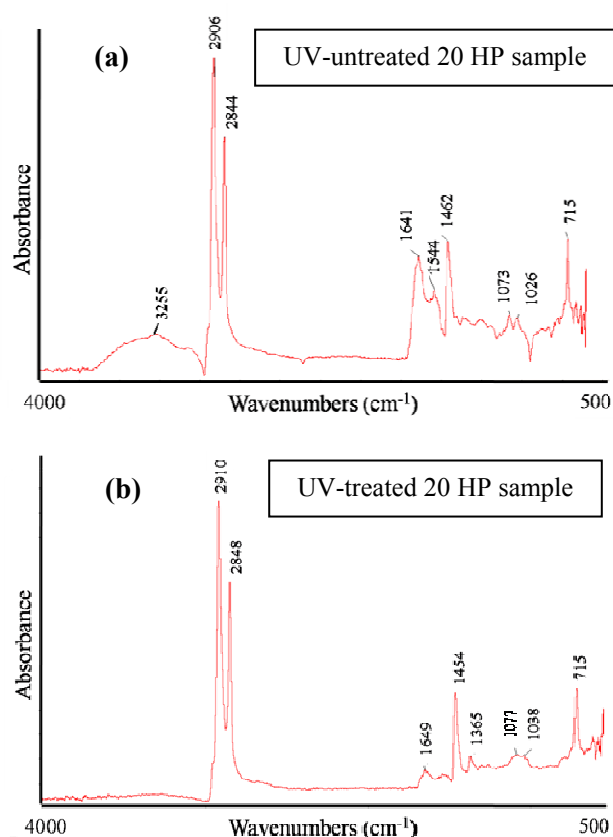


Fig.2: FTIR spectral views of 20 HP filled polymer: (a) UV-untreated and (b) UV-treated

3.2.3 Effect of UV on biodegradability

The protein filled polymer has shown a significant biodegradable property in respect to concentration of filler component as shown in Fig.3. Maximum degradation rate was observed in presence of 40 % of HP within a week. The biodegradability curve of the HP filled polymer follows the “Power-law” model. Further, it can be mentioned that around 45 % degradation occurred in the test sample where 40 % of HP was as filler (Fig.3). It provides evidence

that some fraction of mLLDPE has also degraded due to the metabolic activity of microorganisms where HP enhanced the biodegradability. It has already been reported in our earlier publication that biodegradation starts from the surface of polymer film and then gradually penetrate and degradation occurs following the percolation theory [8]. Thus to observe the rate of degradation, the tested samples were assayed every week interval (Fig.4). It can be seen from Fig.4 that the rate of degradation is

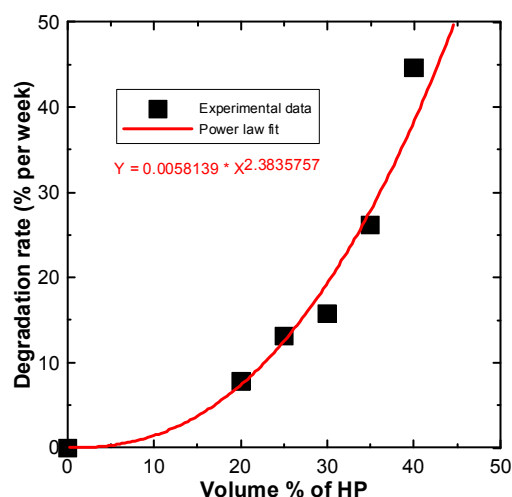


Fig.3: Biodegradability of HP filled polymer

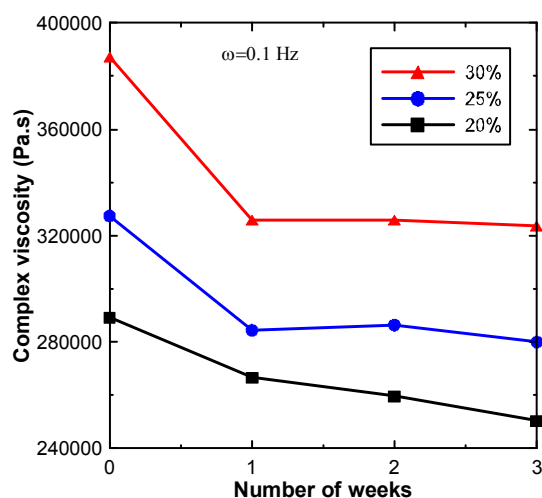


Fig.4: Biodegradation of HP filled polymer with time

very high within 1st week and then degradation occurs at steady state up to 3 weeks in case of at least 25 HP. But, here it is required to mention that when considering the biodegradability of UV-untreated sample, it shows effective quantity of biodegradation under controlled aqueous environment whereas UV-treated sample creates a delay in degradation process by microorganisms (that may be bacteria or fungus) and also the percentage of degradation is very low.

Images of biodegraded UV-untreated and treated samples are shown in Fig.5. Here, it is clearly visible that within 3 weeks a good amount of degradation occurs in UV-untreated sample whereas there is no sign of degradation or very small degradation in UV-treated sample. This may occur due to the increase of crosslinking of mLLDPE during UV-irradiation (as shown in Fig.1 and 2).

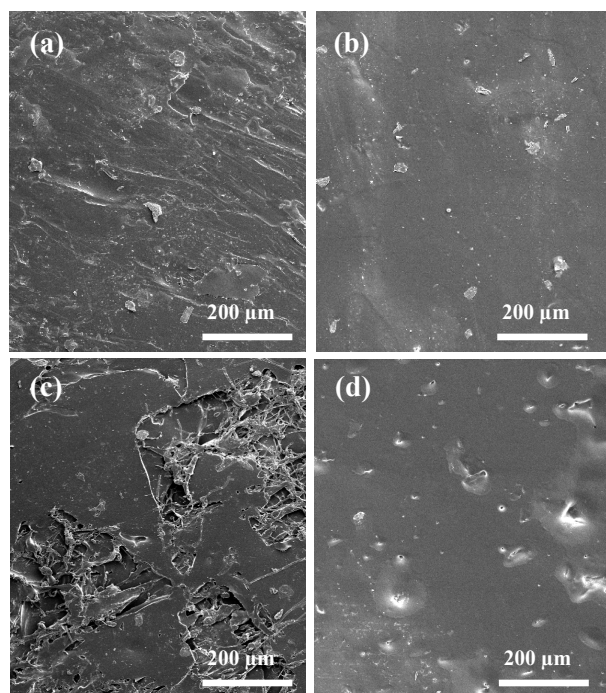


Fig.5: SEM images of 20 HP filled polymer samples in presence of *Aspergillus oryzae* (a, b) before and (c, d) after biodegradation: (a, c) UV-untreated and (b, d) UV-treated

4 Conclusion

Protein filled polymeric material can be considered as a functional green material. The reutilization of protein hydrolysate derived from the leather industry for the production of biodegradable thermoplastic films appears feasible and promising. This modified protein filled polymeric material shows a reasonably good biodegradability in the case of UV-untreated samples. Though, after UV treatment the mechanical strength property of protein filled polymeric material may be strengthened, but that shows low percentage of biodegradability. Thus, UV-untreated 20 HP filled mLLDPE is recommended to use for packaging.

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