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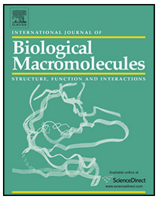

Hydrolytic degradation behaviour of sucrose palmitate reinforced poly(lactic acid) nanocomposites

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ABSTRACT

This work discusses the influence of novel biofiller, "sucrose palmitate" (SP) on the hydrolytic degradation behavior of poly(lactic acid) (PLA) nanocomposites. The influence of temperature and pH of the solution on the hydrolytic degradation behavior of PLA and PLA-SP nanocomposites was investigated. The variation in the crystallinity of PLA and PLA composites subjected to the hydrolytic degradation process is verified by XRD and DSC analysis. The morphological changes that occurred during the degradation process are observed by scanning electron microscopy (SEM). Thermo-gravimetric analysis confirms the loss of thermal stability of the neat PLA as well as composites after hydrolytic degradation process. Transparency measurements support the enhancement in opacity of both the PLA and PLA-SP nanocomposites with progress in hydrolytic degradation period.

1. Introduction

In recent years, biopolymers derived from renewable resources have received considerable attention for food packaging applications. Because biopolymers expressed superiority in terms of degradation and also demonstrated to be environmentally benign plastics as compared to petrochemical polymers [1,2]. Poly(lactic acid) (PLA) is one among the potential representative of biopolymers, which is being studied extensively for its appropriateness for commercialization in packaging sectors [3,4]. However, the drawbacks associated with PLA include its slow crystallization rate, poor ductility as well as barrier properties. These need to be addressed adequately for prospective utilization of the same as food packaging material [5–7]. In this regard, inherent research activities are aimed at development of PLA based nanocomposite systems, so as to improvise the crystallization and barrier effects of the bio-based polymer [1,8–15].

Apart from upgrading the above discussed characteristics, the compatibility of the food with the storage system is an imperative feature to be considered from a practical standpoint in designing a nanocomposite based food packaging material. The nanofillers to be reinforced in the PLA matrix should therefore be cautiously selected in view of avoiding the transmission of toxic substances into the food material in due course of storage. Several studies have explored the influence of non-toxic bio fillers such as cellulose nanocrystals [16], chitosan [17], starch [18] and soy protein [19] on the crystallization and barrier effects of PLA. As a part of such contribution, our research group has chosen a non-toxic food additive, sucrose palmitate (SP) as eco-friendly reinforcement for fabrication of PLA bionanocomposite system through solution casting approach [20,21]. It has been quite interesting that PLA-SP bionanocomposites demonstrated ~69% reduction in the oxygen permeation (OP) as compared to neat PLA [20]. The positive impact exhibited by PLA-SP bionanocomposites in terms of oxygen permeation substantiated the fact that SP served as a promising biofiller for designing a nanocomposite system for packaging application.

After the disposal of packaging material, it is highly desirable that the same should be degraded at a rapid pace owing to environmental concerns [22]. Several studies related to biodegradation aspects of PLA based composites have been investigated [23–25]. A study on the biodegradation of flax fiber reinforced poly(lactic acid) composites was reported by Kumar and co-workers [26]. In their research work, the prepared composites were subjected to biodegradation under farmland soil environment. The study

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indicated that only 10% loss in sample weight after 90 days was experienced [26]. The two important sequential steps that are associated with the biodegradation process include (i) hydrolysis reaction through which molecular weight of the polymer decreases and (ii) subsequent assimilation of the same by microbes [27]. Therefore, it is clear that water is likely to be the PLA's most interactive molecule, after completion of its life cycle. This in turn, indicates that understanding the hydrolytic degradation behaviour of any biopolymer is the most encouraging way to understand the biodegradation process. A series of literature reported that PLA has exhibited excellent hydrolytic degradation behaviour [28–33]. However, any filler incorporated in the PLA matrix is expected to certainly have implications in the hydrolytic degradation behaviour of the resultant nanocomposite material. In this regard, the present work aims to study the effect of reinforcement, i.e., sucrose palmitate (SP) on the hydrolytic degradation behaviour of PLA. Sucrose palmitate is an U.S Food and Drug Administration (FDA) approved food additive. To the best of our knowledge, studies related to hydrolytic degradation of SP reinforced PLA composites have not been investigated before. The hydrolytic degradation experiments for PLA and PLA-SP nanocomposites are carried out under different pH (acidic, neutral and basic) and temperature (35 and 55 °C) conditions. Thereafter, the variation in the crystallinity of PLA and PLA-SP nanocomposites is investigated using differential scanning calorimetry (DSC) and X-ray diffraction analysis. The influence of hydrolytic degradation on the thermal stability of the PLA and PLA-SP nanocomposite sample is also examined using thermo gravimetric analysis (TGA). Further, the morphological changes induced by the hydrolytic degradation process for PLA and PLA-SP nanocomposite are monitored by SEM. The transparency of the PLA and PLA-SP nanocomposite samples before and after hydrolytic degradation is analyzed using UV–vis spectrophotometer.

2. Experimental

2.1. Materials

Sucrose palmitate manufactured by Sisterna (Netherlands) was used as a filler material. Poly(lactic acid) (PLA) (grade 2003D) obtained from Nature Works® (USA) was used as a polymer matrix. Chloroform obtained from Merck (India) Ltd., was used as the solvent for fabrication of poly(lactic acid)-sucrose palmitate (PLA-SP) nanocomposites films.

2.2. Preparation of PLA and PLA-SP nanocomposite films

The steps followed for the fabrication of PLA and PLA-SP nanocomposite films through solution-casting approach are as follows: ~0.95 g of PLA was mixed in 50 mL of chloroform and subsequently the mixture was stirred for 2 h in order to completely dissolve the PLA. Likewise above, 5 wt% of sucrose palmitate with respect to PLA was dispersed in chloroform with continuous stirring for 1 h. Subsequently, this solution containing dispersed SP was transferred into PLA-chloroform mixture under vigorous stirring. PLA-SP solution was casted on teflon petriplate and further dried under ambient condition for 24 h. The dried composite film was peeled off carefully from the petriplates. The resulting film was finally dried under vacuum for 12 h at 40 °C and stored in airtight bags at room temperature for further characterization. Samples are designated as PLA and PLA-SP-5 for PLA/sucrose palmitate 0 (wt%) and PLA/sucrose palmitate 5 (wt%), respectively. The thickness of the fabricated films was measured using film thickness meter (Indi 1652). Twenty measurements were taken on each film and the average thickness of the films is found to be 60 ± 5 μm.

2.3. Hydrolytic degradation

PLA and PLA-SP-5 nanocomposite samples were subjected to hydrolytic degradation process at two different temperatures (35 ± 1 °C and 55 ± 1 °C) with three different pH solutions, i.e. acidic (pH ≈ 2), neutral (pH ≈ 7) and basic (pH ≈ 12). The pH of the solution was adjusted using HCl or NaOH. After placing the sample in the above solutions, the same was taken off from the container at a regular interval of time, washed with water and finally dried at 35 °C for a time period of 6 h. Thereafter, the weight change between before and after degradation was calculated in order to determine the residual weight fraction (Φ). The following relationship was used for the calculation of the residual weight fraction (Φ) as a function of degradation time (t).

$$\phi = \frac{W_t}{W_0} \times 100\% \tag{1}$$

where, W_0 and W_t correspond to the dry weight (g) of the sample prior to the degradation process and the dry weight (g) of the sample after certain time (t) of degradation process, respectively. Samples subjected to hydrolytic degradation were designated as PLA-pH-T-t and PLA-SP-5-pH-T-t, where, pH refers to the acidic (A), neutral (N) and basic (B) conditions under which the degradation process was performed. The symbols, "T" and "t" refer to the temperature condition and time adopted for the hydrolytic degradation process, respectively.

2.4. Characterization

2.4.1. X-ray diffraction (XRD) analysis

The influence of hydrolytic degradation on the crystalline behaviour of PLA and PLA-SP-5 nanocomposite before and after degradation was studied using X-ray diffractometer (Bruker A8 advance). The XRD analysis was done under an air atmosphere at room temperature using Cu-Kα (λ = 0.15406 nm) radiation and the instrument was operated at 40 kV and 40 mA. The diffraction data were obtained in the 2θ range of 1–50° with a scanning rate of $0.05^\circ\,s^{-1}$ and 0.5 s step size. The following relationship was used for the calculation of percentage crystallinity (% X_c)

$$X_c = \frac{\sum A_{crystalline}}{\sum A_{crystalline} + \sum A_{amorphous}} \tag{2}$$

where, $A_{crystalline}$ and$A_{amorphous}$ refer to the area under crystalline and amorphous fractions, respectively.

2.4.2. Differential scanning calorimetry (DSC) analysis

The variation in the thermal and crystallization behaviour of PLA and PLA-SP-5 nanocomposite before and after hydrolytic degradation was investigated using a differential scanning calorimetry (Mettler Toledo-1 series). All the samples were heated from the temperature ranging from 30 to 180 °C at a heating rate of 5 °C/min, under N_2 flow of 50 mL/min. First, all the samples were heated from 30 to 180 °C and held isothermally at 180 °C in order to erase the thermal history. DSC thermographs resulted during the second heating cycle were used for interpretation of glass transition temperature (T_g), cold crystallization temperature (T_{cc}), the enthalpy change at T_{cc} (ΔH_{cc}), melting temperature (T_m) and the enthalpy of fusion at T_m (ΔH_m).

2.4.3. Thermogravimetric analysis (TGA)

The thermal degradation profile of PLA and PLA-SP-5 nanocomposite before and after hydrolytic degradation was obtained using thermo gravimetric analyzer. The analysis was performed on a Mettler Toledo thermo gravimetric analyzer (TGA/SDTA 851® model). All the samples were heated from 40 to 600 °C, at a heating rate of 20 °C/min, with N_2 flow of 60 mL/min.