



Thermal degradation kinetics of sucrose palmitate reinforced poly(lactic acid) biocomposites



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ABSTRACT

The current work is focused on investigating the influence of novel bio-filler, “sucrose palmitate (SP)” on the thermal degradation behavior of poly(lactic acid) (PLA) biocomposites in order to render its suitability for food packaging application. Thermal degradation behavior of the PLA biocomposites was investigated by thermo-gravimetric analysis (TGA) using dynamic heating regime. The differential TG analysis revealed that there is no change in the T_{max} value (357 °C) for PLA and its composites up to 5 wt% of bio-filler loading. This reveals that the sucrose palmitate acts as a protective barrier by decelerating the thermal degradation rate of PLA. In the case of 10 wt% of the filler incorporated in the PLA matrix, T_{max} rapidly shifted to lower temperature (324 °C). This downturn in T_{max} at higher loading of the filler is due to the increase in acidic sites and enhancement in the rate of degradation is observed. Differential scanning calorimetry (DSC) analysis revealed unimodal melting peak indicating the α -crystalline form of PLA. Based on the thermal degradation profile of sucrose palmitate, possible mechanism for degradation of PLA composites is proposed. The activation energies (E_a) of thermal degradation of PLA and PLA composites were evaluated by Flynn–Wall–Ozawa and Kissinger methods.

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1. Introduction

Environmental and sustainability issues concerning petroleum-based feed stocks have begun a growing emphasis on the opportunity of novel category of eco-friendly materials. The domination of biodegradable plastics for packaging sector is expanding as a result of the depletion of resources of petroleum-based plastics and the increasing environmental problems associated with the plastic wastes. In this perspective, the possible replacement of bulk plastics with biodegradable and renewable polymers has been explored during the past decade. In the current scenario, poly lactide is considered to be the most potential representative of biodegradable and biobased polymers to replace the conventional non-biodegradable polymers like poly(ethylene terephthalate) (PET) [1]. PLA possesses comparative mechanical, thermal and barrier properties with respect to existing oil-based polymers [2]. Recent efforts to improve food quality and shelf life while reducing plastic waste have stimulated the exploration of new biopolymer composite-based packaging materials.

The choice of filler materials to be used for preparation of PLA based biocomposites is usually limited by the requirement of the packaging application. In particular, for food packaging applications, only nontoxic substances can be considered as filler materials due to their legitimate food contact [3,4]. In addition, the biodegradability of the PLA composites after incorporation of the filler material is also expected to be a pre-requisite factor. The utilization of renewable sources for both polymer matrices and reinforcement material is the vital solution for sustainable development of ecologically attractive structural composite technology [5,6]. Hence, efforts toward the exploration of non-toxic reinforcement material for synthesizing PLA based composites have been devoted by scientific community in very recent years [5–7]. In general, thermal degradation plays extremely crucial roles during processing of PLA composites [8,9]. Therefore, despite exploration of novel fillers, understanding the influence of the reinforcements on the thermal degradation behavior of the PLA composites become essentially important in order to render these materials suitability for food packaging applications. Investigating the thermal degradation behavior of bio-filler based PLA composites is important in determining how molten PLA should be processed without causing serious thermal decomposition.

Thermogravimetric analysis (TGA) is one of the effective thermal analysis techniques to study the solid-state thermal degradation kinetics [10,11]. Overall kinetics can be easily obtained by measuring the change in mass of a composite material with time

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based isothermal and non-isothermal decomposition profile of TGA analysis [12,13]. Many solid-state kinetic models have been developed to describe the thermal degradation behavior of biopolymer based composites. Models with different approaches (model-fitting and model-free isoconversional) have been proposed to determine kinetic triplets, i.e., activation energy (E_a), pre-exponential factor (A), and reaction order (n) [14]. The model-fitting approach involves fitting various models to conversion versus temperature curves and simultaneously determining the activation energy and pre-exponential factor. In general, model-fitting methods make use of only one TGA curve recorded at a certain heating rate to evaluate the kinetic parameters. Although model-fitting methods allow direct determination of kinetic triplet, these methods are associated with different reaction models that satisfactorily fit the kinetic data at the expense of drastic variations in the Arrhenius parameters. Hence, several researchers suggested that model-fitting methods produce unreliable kinetic parameters [14–17]. On the other hand, the model-free approach has gained popularity among the scientific communities due to its potential to estimate E_a values as a function of conversion without previous assumption of a kinetic model ($f(\alpha)$) [18]. In solid-state kinetic studies, the “apparent” E_a is defined as the excess energy obtained from the vibration of an atom or molecule at certain temperature. This energy can also be related to the rupture of chemical bonds [19]. Since the E_a derived from TGA data is the sum of activation energies of chemical reactions and physical processes, the same is denoted as apparent activation energy throughout this study. To avoid the problems peculiar to model-fitting methods, isoconversional methods for estimating the activation energy are used.

In the current research work, we aimed to use a food additive as eco-friendly filler for fabrication of PLA composites. The US food and drug administration (FDA) has approved “sucrose fatty acid ester” as direct food additive. To the best of our knowledge, no research work is devoted to the fabrication of sucrose palmitate based PLA (hereafter it is referred as SP based PLA) composites. In the present study, based on the thermal degradation profile of PLA-SP composites, hypothetical mechanism for the degradation of the same is proposed. The two well-known representatives of model-free approaches, i.e., Flynn–Wall–Ozawa [20] and Kissinger methods [21] are used to investigate the thermal degradation behavior of PLA and PLA-SP composites.

2. Experimental

2.1. Materials and methods

Sucrose palmitate procured from SISTERNA (Netherlands) is used as the filler material. Poly(lactic acid) (PLA) obtained from Nature Works (grade 2003D) is used as the biopolymer matrix. Chloroform obtained from Merck is used as the solvent for synthesizing PLA-SP composites.

2.2. Synthesis of PLA-SP composites

A series of PLA-SP composites with various concentration of SP were fabricated by solution casting method as follows: 0.953 g of PLA was weighed and mixed in 50 mL of chloroform. PLA suspension in chloroform was stirred for 2 h in order to dissolve the PLA completely. Sucrose palmitate (1, 3, 5, 10 wt% with respect to PLA matrix) was dispersed in chloroform by stirring for 1 h separately. Then, the chloroform solution containing dispersed SP was transferred into PLA-chloroform mixture and stirred for 2 h. PLA-SP composite solution was casted on Teflon petriplates and dried under ambient conditions for 24 h. The dried composite films were peeled off carefully from the petriplates. The resulting films were

finally oven dried under vacuum for 12 h at 40 °C for complete removal of solvent and then stored in a desiccator to carryout thermogravimetric analysis. Here, all the compositions are designated as SP, PLA, PLA-SP1, PLA-SP3, PLA-SP5 and PLA-SP10 for sucrose palmitate, poly lactic acid, poly lactic acid/sucrose palmitate 1 (wt%), poly lactic acid/sucrose palmitate 3 (wt%), poly lactic acid/sucrose palmitate 5 (wt%) and poly lactic acid/sucrose palmitate 10 (wt%), respectively.

2.3. Characterization

Thermogravimetric analysis was performed on a Mettler Toledo thermo gravimetric analyzer (TGA/SDTA 851[®] model). Samples (10.5 ± 0.3 mg) were placed in 900 μl alumina crucibles. Pure PLA and PLA-SP biocomposites were heated from 25 to 700 °C in a 60 ml/min flow of N₂ at heating rates of 10, 20, and 30 °C/min.

Differential scanning calorimetric analysis was carried out to study the thermal properties and crystallization behavior of PLA and PLA-SP bionanocomposites using Mettler Toledo-1 series. Samples (10 ± 0.5 mg) were hermetically sealed in aluminum pans and heated from 25 to 180 °C at a heating rate of 5 °C/min in an inert atmosphere (N₂ flow, 50 mL/min). All the samples were first heated from 25 to 180 °C and held at this temperature for 5 min to eliminate the effect of the thermal and processing history. Glass transition temperature (T_g), cold crystallization temperature (T_c), and melting temperature (T_m) of neat PLA and bionanocomposites films were determined from the DSC thermograph during second heating cycle. The T_g was obtained from the midpoint of heat changes from the DSC curves.

3. Results and discussion

Fig. 1 illustrates the typical temperature-dependent weight loss and the derivative of the weight loss curves for SP, PLA and PLA-SP composites in nitrogen atmosphere at a heating rate of 20 °C/min. In Fig. 1(a), three stages of decomposition can be observed (~100, 180, and 240 °C) for SP. The surface adsorbed moisture is removed around 100 °C which is the first weight loss region. The second region of weight loss from 180 to 240 °C reflects the sucrose hydrolysis during which splitting of glycosidic linkage between glucose and fructose moieties takes place [22,23]. The third region of weight loss of SP begins from 240 °C. This corresponds to the deterioration of ester groups present in the palmitate molecular chains [24,25]. The thermal decomposition profile of PLA exhibits two stages of degradation, in which the first stage is due to removal of absorbed moisture (up to 110 °C) and the main degradation region is observed in the temperature range of 300–375 °C. The degradation of PLA in this temperature range can be principally attributed to hydrolysis by trace amounts of water, intra-molecular transesterification leading to cyclic oligomers, cis-elimination leading to acrylic acid, and fragmentation leading to acetaldehyde and CO₂ [26–34].

The onset of thermal degradation temperature ($T_{10\%}$) corresponding to 10% weight loss for pure SP, pure PLA and PLA-SP composites is determined from the TGA curves (see Fig. 1(a)). Temperatures of at 10% weight loss ($T_{10\%}$), 50% weight loss ($T_{50\%}$) and maximum rate of degradation (T_{max}) is presented in Table 1. All of the TGA curves for PLA and PLA-SP composites exhibit a unique stage of main degradation region [26–34]. When 10% weight loss is taken as a point of comparison, the onset degradation temperature ($T_{10\%}$) for PLA is 301 °C and declines to 288 °C as the SP loading increases to 1 wt%. With respect to further increase in the SP loading (3, 5, 10 wt% SP content), the onset degradation temperature of the composites decreases to 278, 261, and 249 °C, respectively. The possible reason for this fact can be derived from the thermal

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