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Silk nanocrystals stabilized melt extruded poly (lactic acid) nanocomposite films: Effect of recycling on thermal degradation kinetics and optimization studies

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ABSTRACT

In this work highly crystalline β sheets of silk nanocrystals (SNCs) have been studied for their effect on the thermal stability of poly (lactic acid) (PLA) during multiple reprocessing. Stable onset degradation temperature was obtained for PLA-SNC nanocomposite ($T_{5\%}$ ~334 °C), and compared to neat poly (lactic acid) (NPLA), which drastically reduces from 336 °C (first cycle) to 322 °C (fifth cycle). The activation energies were estimated using isoconversional Kissinger-Akahira-Sunose and Flynn-Wall-Ozawa methods. Stable activation energy values (~130 kJ/mol) were obtained for SNC-PLA at three consecutive extrusion cycle. Whereas in the case of NPLA, it significantly reduces from ~150 kJ/mol (first cycle) to ~110 kJ/mol (second cycle). Nelder-Mead simplex method was used to optimize the kinetic parameters of nucleation and growth model (A2); which was observed to be the best fit of the experimental thermogravimetric analysis (TGA) data. Decomposition products were analyzed by Thermogravimetry coupled Fourier transform infrared spectroscopy.

1. Introduction

In recent times, development of ecofriendly and sustainable bio-polymeric materials has received significant attention with the aim of providing an alternative way to tackle the problem related to the conventional polymers. For an application which requires short life time, biodegradable polymers are ideal candidates to be utilized due to their renewability. Poly (lactic acid) (PLA) is a well-recognized biodegradable polymer with comparable properties to the conventional polymers [1] and it is produced from glucose rich plants by fermentation process [2,3]. It has been used in various areas such as in medical and food packaging applications [4,5]. However due to the cost of the material and an enhanced focus on reducing carbon foot print, recycling of PLA has become an interesting area of research. PLA can be recovered through reusing, mechanical recycling [6], chemical recycling [7,8], energy recovery and composting [9,10]. Among all recycling techniques, reprocessing (mechanical recycling) is observed to be attractive way due to its simplicity, low investment requirement and environmental friendly solvent-free processes. However, PLA is highly sensitive to processing conditions. High temperature and shearing force result in molecular weight reduction due to thermomechanical degradation, and it will be pronounced if there is any catalyst residue [11]. Thermal properties (thermal stability, crystallization and melting behavior) can be affected by the reduction in molecular weight and/or increment in molecular weight distribution which is highly expected when the material is processed multiple times. There are several approaches proposed in literature to overcome these limitations of PLA such as: (a) blending PLA with conventional polymers, (b) synthesize stereo-complex PLA, and (c) introduce inorganic and organic fillers in to the PLA matrix. In this particular work the third approach has been followed, targeting fully biodegradable PLA nanocomposite with stable thermal properties, while it is subjected to multiple reprocessing.

Introduction of the fillers into the polymer matrix has a tendency to improve the thermal stability and the slow crystallization behavior of PLA [4,12,13]. Based on the interaction and dispersion of fillers in the polymer matrix, important properties such as thermal stability, mechanical properties (tensile strength, modulus and elongation at break), oxygen and water barrier properties can be tailored [5,12,14–19]. However, in most scenarios processing of PLA/fillers through melt extrusion is a big challenge due to fillers induced matrix degradation. This phenomenon is more pronounced for the case of multiple reprocessing. In contrary to this, reprocessing may enhance the dispersion of fillers which may

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be the reason for better improvement in material properties. It is therefore important to study the impact of adding different fillers into PLA matrix, when it is subjected to multiple reprocessing.

Over the past few decades, a number of fillers from organic [20–23] and inorganic [24–27] origin have been investigated to reinforce the PLA matrix. Bio-fillers from plant and animal origin have been a subject of growing interest which exhibits different attractive characteristics. Their degradability, compatibility, availability, ease of processability and low cost makes them ideal for selection in the fabrication of green composites. From these domain of bio-fillers, cellulose, chitosan, chitin, gum starch, and sucrose palmitate [28,29] have been studied as nontoxic reinforcement for PLA matrix. Among all the bio-fillers, cellulose has been extensively studied as PLA matrix reinforcement in the form of fibers and nanocrystals [30–33]. In recently published research work, agglomeration of cellulose nanocrystals (CNC) due to the presence of strong intermolecular hydrogen bonding has been discussed as a challenging task in the fabrication of PLA-CNC nanocomposite using melt extrusion process [34]. Beside this, the sulfate functional groups attached to CNCs during the acid hydrolysis increases the degradation rate of PLA matrix when it is subjected to extrusion [34]. Similar phenomena can be observed for bio-fillers such as chitosan, chitin, gum starch, sucrose palmitate, due to their high surface functionality (presence of —OH functional groups). Therefore, significant research work needs to be done to determine suitable fillers which can maintain or enhance the thermal stability of PLA during thermal processing. In view of this, this work has been focused on silk nanocrystals in order to utilize their structural characteristic to stabilize the thermal properties of PLA during multiple reprocessing.

The structure of silk fibers (produced from different silkworm species) has enabled the development of different materials for wide range of applications. Fibroin is the main structural protein components of silk fiber and it is composed of a highly repetitive and well-ordered structure units called β-sheets [35]. These β sheets are present in highly crystalline form and are interlinked by hydrogen bonding that plays a major role in strengthening and stiffening the silk fibers [36,37]. Due to its remarkable properties, silk has been extensively used for textile applications. However, to the best of our knowledge, the effect of SNCs on the thermal stability of PLA while it is multiple times reprocessed is not available in literature. Therefore, in this particular research work, SNCs were extracted and used in the fabrication of PLA-SNC nanocomposite by using melt compounding and reprocessed multiple times to investigate the effect of SNCs on the properties of PLA during the exposure to repetitive thermal and shear process. Isoconversional methods (Kissinger-Akahira-Sunose (K-A-S) and Flynn-Wall-Ozawa (F-W-O)) and Kinetic Invariant Parameters (KIP) method were used to estimate the activation energy and the "true" kinetic parameters. The kinetics triplets were also studied by coupling the Coats and Redfern method with Nelder-Mead simplex optimization technique for selected models based on the master plot technique. The evolved gases during thermal degradation were also analyzed using the Thermogravimetry coupled Fourier transform infrared spectroscopy (TG-FTIR).

2. Materials and methods

2.1. Materials

Poly (lactic acid) (PLA) was obtained from NatureWorks (grade 2003D) with melt flow index of 7.3 g/10 min at 210 °C and is used as polymer matrix. Number average molecular weight (M_n), weight average molecular weight (M_w) and polydispersity index (PDI) were determined by gel permeation chromatography (GPC) as 135 KDa, 250 KDa and 1.82 respectively. Silk nanocrystals (SNCs) used for this investigation were prepared in the laboratory from Muga silk (*Antheraea assama*) cocoons as reported in literature [35,36]. The materials were dried in vacuum oven for 24 h at 60 °C.

2.2. Preparation of silk nanocrystals (SNC)

Muga silk (*Antheraea assama*) cocoons were provided by Regional Muga Silk Station, Assam, India. The cocoons were first cleaned to remove eggs and plant debris, then degummed twice using 0.5% (w/w) sodium carbonate (Na_2CO_3) at 98 °C for 30 min and then washed multiple times in de-ionized water to remove salts [35]. The degummed Muga fibroin were dried overnight at 60 °C in hot air oven to remove water. SNCs were produced via acid hydrolysis of the dried Muga fibroin in aqueous sulfuric acid (64 wt%) for 2 h at 45 °C [36]. The hydrolysate was washed multiple times with de-ionized water followed by three cycles of centrifugation (each at 10,000 rpm for 15 min) and dialysis under running tap water for 48 h to ensure removal of free acid and a final pH of 7. Sonication was used to homogenize the dispersion. Insufficiently hydrolyzed fractions were removed by filtration. The SNC suspension in deionized water was then freeze-dried after quench freezing with liquid nitrogen to obtain dried SNC powder for the current work.

2.3. Preparation and reprocessing nanocomposite

The nanocomposites were prepared by melt mixing of PLA with 1% SNC and reprocessed 4 times in Haake minilab co-rotating twin screw extruder. Each time, the samples were feed at a screw speed of 10 rpm and processed in the recycling mode for 1 min at 100 rpm with processing temperature of 200 °C. Neat PLA (NPLA) was also melt processed in the same condition to have it as reference material. After each reprocessing cycle the nanocomposite and NPLA were collected in the form of strips and designated as Ri-SNC-PLA and Ri-PLA respectively. (Where i denotes for number of reprocessing cycle).

2.4. Thermal degradation study

Thermal analysis of NPLA and SNC-PLA at each reprocessing stage were carried out on Perkin-Elmer TGA4000 equipment. Samples weighing ~8 mg were heated from 30 °C to 700 °C at heating rates of 5, 10, 15 and 20 °C/min. The flow rate of nitrogen (N_2) was maintained at 20 mL/min. Furthermore, the analysis of evolved gas was performed using Perkin-Elmer TGA-FTIR hyphenated system. An interface line having gas transfer tube and gas cell was used to couple TGA with FTIR spectrophotometry and heated up to 250 °C to avoid condensation of the evolved gases. The TGA experiments were repeated three times at heating rate of 10 °C/min for R0-NPLA and R0-SNC-PLA to confirm the repeatability of the generated data. Very small deviations were observed and it is reported in terms of average relative deviation as indicated in Eq. (1)

$$ARD\,(\%) = \frac{100}{N}\sum_{i=1}^{N}\left|\frac{x_i^{exp} - x_{av,i}}{x_{av,i}}\right| \quad (1)$$

In Eq. (1) x_i^{exp} and $x_{av,i}$ represents the temperature and normalized mass data collected from the TGA experiments with their average values having i number of data points. The result showed that the ARD (%) is 0.0089–0.018 (for mass) and 0.25–0.51 (temperature). Activation energy values estimated from linear fittings were reported with error bars, which is calculated from the uncertainties of the slopes.