Composites Communications 4 (2017) 43–53

Contents lists available at ScienceDirect

Composites Communications

journal homepage: www.elsevier.com/locate/coco

Influence of biobased silica/carbon hybrid nanoparticles on thermal and mechanical properties of biodegradable polymer films

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ARTICLE INFO

Keywords:
Hybrid nanoparticles
Biopolymer composites
Thermal properties
Mechanical properties

ABSTRACT

In this study, biobased silica/carbon hybrid nanoparticles (SCNPs) were synthesized using pyrolysis process and reinforced in to polymer film using 3D printing technique. These polymer films were further tested for their thermal and mechanical properties to determine the influence of silica/carbon nanoparticles on the properties of the biopolymer. The SCNPs were synthesized from agricultural waste rice husk by high temperature pressure reaction. These nanoparticles were characterized using X-ray diffraction (XRD), Raman Spectroscopy, and Transmission electron microscope (TEM) analysis and revealed the formation of highly crystalline cristobalite silica/carbon hybrid nanomaterial. X-ray photon spectroscopy (XPS) analysis showed the presence of elemental Si, C, and O in the as-synthesized SCNPs. Brunauer–Emmett–Teller (BET) surface area measurements showed the surface area of 223.029 m^2/g, for as prepared nanoparticles. The 3D printed biocomposites thin films were characterized by XRD, Differential Scanning Calorimetry (DSC), Thermo Gravimetric Analysis (TGA), Raman spectroscopy, FE-SEM and Tensile analysis. The FE-SEM analysis of the composites showed the uniform dispersion of nanoparticles in the biopolymer. TGA and Tensile tests revealed significant enhancement in thermal stability, maximum strain and strain to failure properties due to the integration of 0.5 and 1.0 wt% of silica/carbon nanoparticles (SCNPs). Also, DSC analysis showed the moderate improvement of glass transition temperature and crystallization temperature as compared to the neat polymer. This increase may be due to the increased crosslinking of polymer by incorporation of thermally stable SCNPs nanoparticles.

1. Introduction

The innovation of biodegradable polymeric materials to resolve the environmental issues with soil pollution due to petroleum based non-biodegradable and non-recoverable polymeric materials such as polyethylene (PE) fragments is a major concern among researchers since few decades. Currently, the principal areas of the usage of biodegradable polymers are: food packaging, packaging foam filler, compostable bags, etc. with an annual growth rate of 15% in packaging sector itself [1,2]. This growth rate increased significantly because of its biodegradability, mechanical properties and availability.

Poly (butylene-adipate-co-terephthalate) (PBAT) biodegradable polymer can be used as sustainable alternatives to PE in packaging applications as well as agricultural mulch film for crop production with satisfying the required functional properties and agronomic performance. PBAT conventional flexible aliphatic-aromatic copolyester possesses a higher elongation at break, is widely used among most biodegradable polyesters for packaging applications [3]. This PBAT polymer has poor thermal and mechanical resistance that restricts their wider industrial packaging applications where strength is an important factor. These limitations can be overcome by improving the thermal and mechanical properties of PBAT through filler approach. Poly (lactic acid) (PLA), linear aliphatic biodegradable thermoplastic polyester, currently accounts for about **47%** of global biodegradable plastic demand, followed by starch-based plastics at **41%** though it has some inferior properties such as poor thermal stability, excessive brittleness, poor melt strength and processability issues [4]. These drawbacks can be reduced by adding nanoparticles or making a blend with another biodegradable polymer to enhance its applications, especially for food packaging [1,4].

Due to the high availability and also cost effectiveness of PLA, it is considered as an alternative to petroleum-based polyolefin, which are discarded into the environment at the end of their service life. This becoming a global warming precursor [1,4]. Poly (butylene-adipate-co-terephthalate) (PBAT) conventional flexible aliphatic-aromatic copolyester, is considered as a modifier of toughness of PLA [4]. To enhance the thermal stability and poor mechanical properties of biopolymers, nanocomposite approach through 3D printing is one of the best ways

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http://dx.doi.org/10.1016/j.coco.2017.04.005
Received 9 February 2017; Received in revised form 29 March 2017; Accepted 27 April 2017
Available online 11 May 2017

among other alternatives [5,6]. The synergistic effect of inorganic nanofiller as domain and polymeric matrix in nanobiocomposites leading to significant enhancement of various characteristics of the pristine polymers [7]. Nano silica a high-temperature material can be used to improve the thermal and mechanical properties of biodegradable PBAT polymer [1,2].

However, a vast quantity of rice husk (an excellent source of silica), is produced as a primary agricultural by-product which accounts for an average of 20% (w/w) agro-based waste [8]. It is occasionally considered as an energy source due to its high calorific value (approximately 13–16 Mj/kg), but mostly dumped as a waste. Even when it is used to fuel power plants, gaseous emissions from such usage lead to about 20–40% carbon dioxide (CO_2) emission into the environment. Since CO_2 plays the significant role in global warming, it is necessary to find an eco-friendly way to handle this gas or alternative uses of the rice husk should be explored. Rice husk contains the needed silicon and oxygen precursors for the formation of silica (SiO_2), a widely used material in electronics, ceramics, heat isolation, photoelectric materials, polymer industries and many other fields. This is due to its large surface area, and minuscule particle size (5–20 nm) [5].

Nano-silica (SiO_2) can be fabricated by different methods. Several authors have reported different synthetic methods for producing silica from waste rice husk. Among such techniques, the sol-gel method or chemical precipitation synthesis, high-temperature method, chemical method and microwave heating [8–12]. The Sol-gel method relies on low-temperature hydrolysis and condensation of the molecular precursors [9]. Also nano-silica was prepared through chemical precipitation by treating sodium silicate with inorganic acid while the thermal method involves a combination of pyrolysis and calcination process which is time-consuming. In this research, we synthesized biobased nano silica-carbon hybrid materials using self-pressurized high temperature reactor at 1000 °C for 2 h and explored its effects on poly (butylene-co-adipate) terephthalate (PBAT)(Ecoflex F blend C1200) biodegradable polymer which has high flexibility but poor thermal stability and mechanical strength. The typical applications of this polymer are packaging films, agricultural films, and compost bags. The nanocomposite approach of modifying this polymer has the potential to enlarge its scope of applications because nanoparticles possess minuscule particle size and high surface area which helps to create significant changes in interphase and intermolecular structure with the interaction of polymer matrix [5].

Therefore, the prime aim of this work is to use the agricultural waste as value added filler to improve the structural properties of biodegradable polymer (Ecoflex) through nanocomposites approach by making micron thick Ecoflex/SCNPs thin films using simple 3D printing process.

2. Materials and processing

2.1. Materials

The Ecoflex was commercial grades biopolymer available in the market and supplied by BASF Corporation, Villa Park, IL, USA. The precursor of nano silica and carbon particles, rice husk (RH), from the Three H's, LLC Crossett, Arkansas, was used for this study. The organic solvent Chloroform ($CHCl_3$, ≥ 99%) was used to dissolve the polymer pellets and disperse SCNPs.

2.2. Preparation of rice husk powder (RHP)

The as obtained RH was first washed with distilled water to remove dirt and foreign particles and then dried at 120 °C for 24 h. The dried RH was then ball milled at a ball to powder ratio of 8:1 for 3 h using stainless steel ball milling canister and 10 mm stainless steel balls.

2.3. Synthesis of SCNPs by pyrolysis process

The prepared RHP was taken (10 g) into the vertical reaction chamber of the Ni-based superalloy high-pressure/temperature reactor (GSL-1100X-RC). Then the vertical reactor heated using a temperature controlled furnace. The furnace first heated to 1000 °C at a rate of 10 °C/min ramp and then pyrolysis of RHP was carried out for 2 h under self-pressurized condition. After heat treatment, the as-obtained rice husk char (60% yields) was then mortared gently to make rice husk ash (RHA) at uniform size. The RHA contains 52% CO_2 and 48% SiO_2 confirmed by TGA analysis in presence of Oxygen.

2.4. Fabrication of Ecoflex/SCNPs biocomposites thin films by 3D printing

The biobased silica/carbon hybrid nanoparticles were dispersed at 0.5, 1.0 and 1.5 wt. % in chloroform using ultrasonic mixing for 30 min. The polymer solution was prepared by dissolving the polymer pellets in chloroform/SCNPs solution with continues magnetic stirring for 5–6 h until the clear solution is formed. This polymer solution was used to fabricate the thin films through 3D printing process. The Hyrel system 30 M model 3D printer was used for printing polymer films. The laser head with 201000 series Luer Tip Kit of 14 G SS was used at a feed rate of 3500 nL/sec. No external heat was applied to the printed hot bed. The films were dried at room temperature. AutoCAD software was used to model the structure of a set of five films with 200 mm (L) × 25 mm (W) × 100 μm (T) dimension and then slice the structure to create the machine readable G code file. After that Repetrel software was used to print the films using the G code file. About 20–25 mL solution was taken on to 30 mL metallic syringe and set it up into motorized laser head slot. The films were printed on a flat glass plate mounted on to motorized stage and removed after 5–10 min for drying at room temperature. A schematic flow diagram of 3D printing process showed in the below figure (Fig. 1).

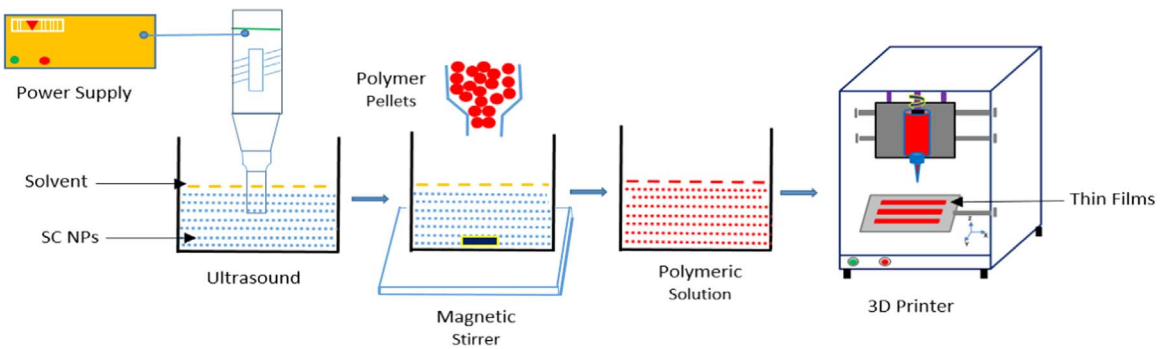

Fig. 1. Schematic diagram of 3D printing process of biocomposites thin films.