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Studies of poly(lactic acid) based calcium carbonate nanocomposites

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The effect of nano-calcium carbonate on chain linked poly(lactic acid) was investigated. In order to improve inorganic nanofillers/polymer compatibility $CaCO_3$ nanoparticle surface was treated by stearic acid. The nanocomposites were prepared by means of solution blending and further studied by using dynamic mechanical analysis, fourier transform infrared spectroscopy, scanning electron microscopy and thermogravimetric analysis. Morphological analysis performed on nanocomposites fractured surfaces has revealed that the $CaCO_3$ modification induces homogeneous and fine dispersion of nanoparticles into polymer as well as strong interfacial adhesion between the two phases. An increase in the Tg and storage modulus of the resulting nanocomposites was observed with the increase of calcium carbonate ratio. Thermogravimetric results showed a lower degradation temperature with the increase of calciium carbonate ration in the polymer matrix.

1. Introduction

Now a day's biodegradable materials are of prime interest for both environmental reasons and for biomedical applications. Poly(L-lactide) (PLA), a typical linear aliphatic thermoplastic polyester, has been viewed as the most popular commercial biodegradable material because it is biodegradable, compostable, and nontoxic to the human body and to the environment; moreover, it can be produced from renewable plant resources (mainly starch and sugar) [1,2]. This polymer possesses reasonably good mechanical and optical properties, thermal plasticity, and processability, so it has tremendous market potential for packaging materials, fibers, agricultural films, and biomaterials [3,4]. In order to have redeemable mechanical properties the molecular weight should be higher. A high molecular weight PLA can be synthesized by a number of methods including, ring opening polymerization, azeotropic condensation polymerization, solid state polymerization and chain linked polymerization. In this work chain linked polymerization has been studied since this method for the synthesis of PLA requires lesser time and energy [5–7].

Over the last few years, a new class of mineral reinforced thermoplastics known as nanocomposites has attracted increasing interest for researchers in the field of polymer and materials science from both academia and industry [8,9]. Fillers as dispersed phases in nanocomposites are nanometer sized, preferably with at least one of its dimensions on the order of a few nanometers (1–100 nm). Because of the small particle size and extremely high surface area, the incorporation of nanoparticles into a polymer creates a great amount of interphase and changes the intermolecular interaction of the matrix, thus obtained materials is characterized by a lower density and a better processability. As a result, dramatic improvements in the physical and mechanical properties, including stiffness and toughness, thermal stability, gas barrier properties, and electrical and thermal conductivity, can be achieved by the incorporation of a few weight percentages of particulate fillers into polymer matrices.

On the basis of these advantages of nanocomposites, many excellent studies have been reported on the preparation and properties of PLA nanocomposites. PLA/layered silicate nanocomposites have been extensively studied, including some reviews [10,11]. PLA nanocomposites incorporating hydroxyapatite, carbon nanotubes, Fumed silica and titanium dioxide have also been reported [12–14] the crystallinity, thermal stability and mechanical, gas barrier, degradation, and flame-retardant properties of PLA have been greatly improved. SiO_2 has also been widely used as a nanofiller the preparation of polymer/SiO_2 nanocomposites. A few studies on PLA/CC (nano calcium carbonate) nanocomposites have been reported [15]. In the present work the effect of calcium carbonate on the chain linked poly(lactic acid) have been studied. Since $CaCO_3$ is among the cheapest commercially available inorganic material and is extensively used as a particulate filler in the manufacture of paint, paper, rubber, plastics, and so forth [16]. Recently, nanosized $CaCO_3$ has received a lot of attention because of its wide range of potential applications and its low cost. Various methods, including high gravity reactive precipitation, have been developed to prepare nanosized $CaCO_3$ particles with a narrow size distribution [17]. The introduction of nano $CaCO_3$ in PLA matrix improves the modulus of elasticity and the resulting nanocomposite shows no brittle fracture [18]. $CaCO_3$ can be mod-

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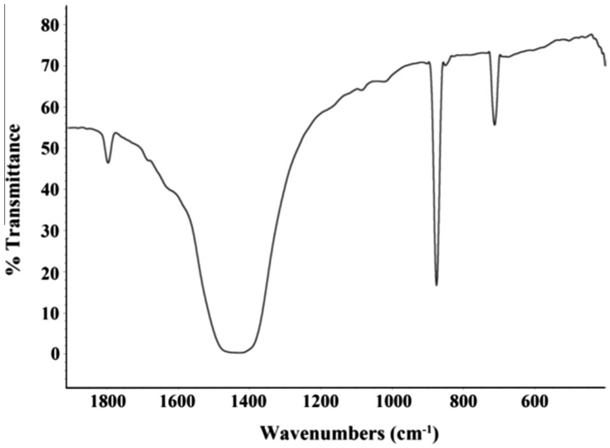

Fig. 1. FTIR spectrum of calcium carbonate.

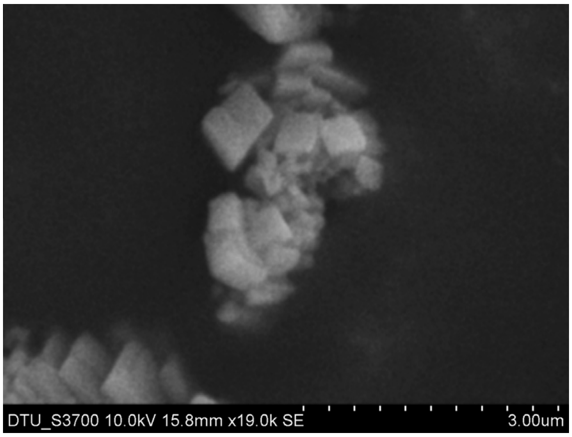

Fig. 2. SEM image of modified calcium carbonate.

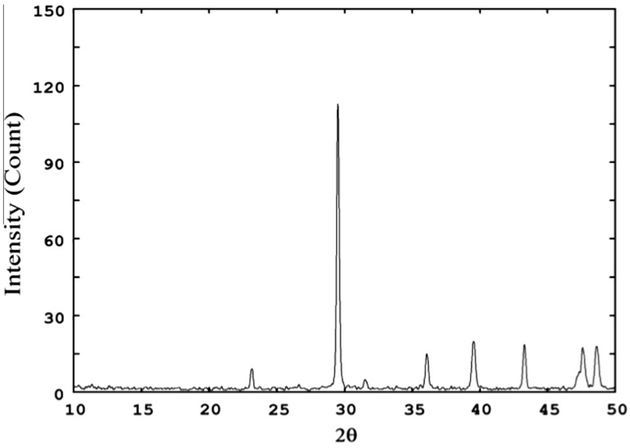

Fig. 3. X-ray pattern of calcium carbonate.

ified with different surfactants such as fatty acids, phosphonate, and titanate to facilitate dispersion in the polymer matrix, hence influences the wetting and adhesion properties of the two phases with enhanced compatibility and better mechanical properties. In this study, $CaCO_3$ nanoparticles were pretreated with stearic acid, which provided them with high compatibility between the nanofillers and CLPLA.

2. Experimental

2.1. Material

Lactic acid (90% aqueous solution) was purchased from Merck, ethylene glycol, polyethylene glycol (6000), Na_2CO_3, $CaCl_2$ and stearic acid from Thomas Baker and tin octoate from Sigma Aldrich. Chloroform (Thomas Baker) was distilled over calcium chloride before used. Methylene diphenyldiisocyanate (MDI) from BASF. Nano calcium carbonate was synthesized by the in situ deposition method.

2.2. Method

Chain linked poly(lactic acid) (CL–PLA) was synthesized as discussed in our previous work [5,6], briefly hydroxyl terminated poly(lactic acid) was synthesized using ethylene glycol. It was further chain linked by MDI as a chain coupler in the melt using tin octoate as a catalyst.

Nano-$CaCO_3$ was synthesized with in situ deposition described elsewhere. Briefly the complex of $CaCl_2$ was prepared with PEG in a 4:1 molar ratio in distilled water. Another solution of Na_2CO_3 was prepared in distilled water. The first complex was kept for 12 h, and then the second complex was slowly added to it; the mixture was kept for 24 h. The precipitate was filtered, washed with water, and dried *in vacuo* [19]. In order to make hydrophobic surface the dried calcium carbonate was further treated with stearic acid. The solution mixing technique was employed for the preparation of CLPLA/CC nanocomposites. Nanocalcium carbonate in the ratio of 1.5, 3.0, 5.0 and 7.0% (w/w) was used for the preparation of nanocomposites. Chloroform was added to the predired calcium carbonate. Then this mixture was added to the solution on predried CL–PLA solution and mixed, the solvent was first evaporated at room temperature, followed by in vacuum at room temperature for two days.

2.3. Measurements

Dynamic mechanical studied were performed on Parkin Elmer DMA 8000 using compression molded samples with dimension $30 \times 5 \times 4$ mm, analyzed at frequency of 1 Hz from −20 to 65 °C at ramp of 2 °C/min in single cantilever mode. Liquid nitrogen was used to lower down the temperature.

The FTIR spectra of the nanocomposites were recorded using a Nicolet 380 FTIR spectrophotometer in transmittance mode as a function of wavenumber using KBr. A scan from 4000 cm^{-1} to 400 cm^{-1} with a resolution of 4 cm^{-1} was recorded. To reduce the noise 64 scans was recorded.

Morphological study of nanocomposites was investigated with Hitachi S-37000 scanning electron microscope at 5 kV. The specimens were frozen under liquid nitrogen, and then fractured, before running the samples; a fine gold coating was given by using the Biorad fine gold coat ion sputtering-coating instrument under the vacuum of about 10–3 torr.

Thermal degradation of nanocomposites was analyzed on Mettler Toledo thermal Analyzer in the dynamic mode and weight loss of samples was subjected to controlled temperature program. The sample were taken in the crucible situated in the electric furnace and heated from room temperature to 500 °C at the controlled heating rate of 10 °C/min in the nitrogen atmosphere. The approximate 6–10 mg of each sample was used for analysis.

3. Result and discussion

3.1. Nano-calcium carbonate

Fig. 1 shows the FTIR of calcium carbonate in transmittance mode. The different crystal form of $CaCO_3$ shows different