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Morphological, thermal and mechanical properties of ramie crystallites—reinforced plasticized starch biocomposites

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Abstract

A series of environmentally friendly glycerol plasticized starch (PS) biocomposites were successfully prepared, using ramie cellulose nanocrystalites (RN) of 0–40 wt% as fillers. The ramie cellulose nanocrystalites, having lengths of 538.5 ± 125.3 nm and diameters of 85.4 ± 25.3 nm on average, were prepared from ramie fibers by acid hydrolysis. The morphology, thermal behavior and mechanical properties of the resulting composites were investigated by scanning electron microscopy, differential scanning thermal analysis, dynamic mechanical thermal analysis, and measurements of mechanical properties and water absorption. The results indicate that the synergistic interactions between fillers and between filler and PS matrix play a key role in reinforcing the composites. The PS/RN composites, conditioned at 50% relative humidity, increases, respectively, in both tensile strength and Young's modulus from 2.8 MPa for PS film to 6.9 MPa and from 56 MPa for PS film to 480 MPa with increasing RN content from 0 to 40 wt%. Further, incorporating RN fillers into PS matrix also leads to a decrease in water sensitivity for the PS based biocomposites.

Keywords: Starch; Cellulose nanocrystalites; Biocomposite; Ramie

1. Introduction

Advanced technology in the field of petrochemical-based polymers has brought many benefits to mankind. However, it is becoming more evident that the ecosystem is considerably disturbed and damaged as a result of the non-degradable plastic materials for disposable items. So there is an urgent need to develop renewable source-based environmental benign materials, which are novel materials of the 21st century and would be of great importance to the materials world, not only as a solution to growing environmental threat but also as a solution to the uncertainty of petroleum supply (Fishman, Coffin, Onwulata & Konstance, 2004; Lu, Tighzert, Berzin & Rondot, 2005; Lu, Weng, & Zhang, 2004; Mohanty, Misra, & Drzal, 2002; Ray & Okamoto, 2003). Among the many kinds of candidates of biodegradable polymers, starch is one of the most promising materials for biodegradable plastics because it is a versatile biopolymer with immense potential and low price for use in the non-food industries (Choi, Kim, & Park, 1999; Mohanty, Misra, & Hinrichsen, 2000). Incorporating plastifying agent, such as water and /or poly-alcohols, starch can be made thermoplastic called thermoplastic starch (TPS) or plasticized starch (PS) through destructurization by the introduction of mechanical and heat energy (Carvalho, Job, Alves, Curvelo, & Gandini, 2003; Gaudin, Lourdin, Forssell, & Colonna, 2000). During the past two decades, PS has received considerable attention and offered an interesting alternative for synthetic polymers where long-term durability is not needed and rapid degradation is an advantage (Van Soest, De Wit, & Vliegenthart, 1996). However, compared to the common thermoplastics, biodegradable products based on starch, unfortunately, still reveal many disadvantages, mainly attributed to the highly hydrophilic character of starch polymers (Santayanon & Wootthikanokkhan, 2003). To cope with these problems while persevering the biodegradability of the materials, one of the effective strategies is to associate PS with various fillers derived from renewable resources to obtain the biocomposites. Various types of fillers have been tested such as potato pulp based microfibrils (Dufresne, Dupeyre, & Vignon, 2000; Dufresne & Vignon, 1998), bleached leafwood fibres (Averous & Boquillon, 2004; Funke, Bergthaller, &

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Lindhauer, 1998), bleached eucalyptus pulp fibres (Curvelo, De Carvalho, & Agnelli, 2001), wood pulp (De Carvalho, Curvelo, & Agnelli, 2002), flax and jute fibers (Soykeabkaew, Supaphol, & Rujiravanit, 2004; Wollerdorfer & Bader, 1998) and tunicin whiskers (Anglès & Dufresne, 2000; Anglès & Dufresne, 2001; Mathew, & Dufresne, 2002). The researches mentioned above indicated that a high compatibility occurs between starch matrix and fillers and the high improvements of the performances (e.g. mechanical properties and water resistance) due to the occurrence of intermolecular interactions formed between the different components.

It is known that native celluloses, when subjected to strong acid hydrolysis, readily break down into 'micro- or nano-crystalline cellulose' (whisker) with almost no weight loss (Battista, 1975; Ebeling et al., 1999). Due to its high aspect ratio and a high Young's modulus (Ishikawa, Okano, & Sugiyama, 1997), the use of cellulose crystallites for preparation of high performance composite materials has been, therefore, explored extensively (Dufresne, Cavaillé, & Vignon, 1997; Eichhorn et al., 2001; Noishiki, Nishiyama, Wada, Kuga, & Magoshi, 2002; Anglès et al., 2000, 2001). When the cellulose crystallites were homogeneously dispersed into polymer matrices, they gave a remarkable reinforcing effect, even at concentrations of a few percent (Favier, Chanzy, & Cavaille, 1996).

Ramie, or China grass (*Boehmeria nivea* (L.) Gaud.) is a perennial herbaceous plant of the Urticaceous family. This crop is mainly planted in China and other Asian countries including Philippines and India. Ramie fibers have been used as a textile fiber for centuries due to their excellent fiber chacteristics (Angelini, Lazzeri, Levita, Fontanelli, & Bozzi, 2000). Ramie fibers are very fine and silk-like, naturally white in color, and have a high luster. Other advantages of it are good resistance to bacteria, mildew, and insect attack. The fibers are stable in alkaline media and not harmed by mild acids. Further, it also exhibits even greater strength when wet (Mohanty, Misra, & Drzal, 2005). Due to the excellent fiber properties mentioned above, ramie fibers have, therefore, a high potential as a reinforcing fiber for polymer composites. In this work, we want to prepare cellulose nanocrystallites from ramie fiber by acid hydrolysis, and then use the resulting nanocrystallites to reinforce the plasticized starch for preparation of high performance biocomposites. The resulting materials were prepared by casting the aqueous dispersion of cellulose nanocrystalites and glycerol plasticized starch in various blend ratios. The morphology, structure and performance improvement of the biocomposites were investigated by scanning electronic microscopy, dynamic mechanical thermal analysis, differential scanning calorimetry, and measurements of the mechanical properties and water absorption.

2. Materials and methods

2.1. Materials

Purified ramie fiber was supplied by Textile Factory, Xianning. The starch used in this work is commercial industrial-grade wheat starch, which is composed of 25% amylose and 75% amylopectin. The glycerol (99.5% purity) was purchased from Aldrich and used as received.

2.2. Preparation of ramie cellulose nanocrystallites

The suspensions were prepared by acid catalyzed hydrolysis of ramie fiber similar to the method as described by Dong, Kimura, Revol, and Gray (1996). Briefly, the ramie fiber (20 g) was mixed with sulfuric acid (175 mL, 64%) and stirred vigorously at 45 °C for 4 h, and then a dispersion of ramie cellulose nanocrystalites (RN) was obtained. After sonication of 15 min, the suspension was neutralized with 0.5 N NaOH and then washed by dialysis. The final aqueous suspension of RN does not sediment or flocculate because of the electrostatic repulsion between the surface sulfate groups grafted during the sulfuric acid treatment (Chazeau, Paillet, & Cavaillé, 1999).

2.3. Preparation of plasticized starch (PS)/RN biocomposites

Starch and glycerol were first mixed and dispersed in distilled water. The mixture contained 7 wt% wheat starch, 3 wt% glycerol and 90 wt% water, respectively. The gelatinization of starch was performed in a sealed reactor equipped with a stirrer operating at 100 °C for 20 min. The resulting starch pastes were cooled down to 70 °C in order to prevent evaporation of water. Subsequently, the RN dispersion was added and stirred for 20 min. After mixing, the mixture was degassed under vacuum and cast in a polystyrene mold, followed by drying in an oven at 40 °C and 50% relatively humidity. By changing the content of RN of 0, 5, 10, 15, 20, 25, 30, 40 wt%, a series of PS/RN biocomposites were prepared and coded as PS, SR-5, SR-10, SR-15, SR-20, SR-25, SR-30 and SR-40, respectively, in which the RN content was expressed on water free PS matrix.

Before various characterizations, the resulting composite films, with a thickness of about 0.3 mm, were kept in a conditioning cabinet of 50% relative humidity (RH) at 25 °C, respectively, to ensure the equilibration of the water content in the films.

2.4. Characterizations

Atomic force microscopy (AFM) imaging of RN was performed on a Digital 3100 IIIa microscope. A droplet of a dilute RN suspension was coated onto a flake of mica, and the water was evaporated at room temperature.

The DSC analysis of the biocomposites was determined using a modulated differential scanning calorimeter (TA2920, USA) with refrigerator cooler. Each sample conditioned at 50% RH was subjected to the heating/cooling cycle between −50 °C and 100 °C to obtain reproducible glass temperature (T_g) values. For a polymer, T_g was taken at the half-variation of the heat capacity in the second run occurring at the glass–rubber transition. Scanning rate in the second run was 5 °C/min.