



Mechanical properties, biocompatibility, and biodegradation of cross-linked cellulose acetate-reinforced polyester composites



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ABSTRACT

Composites of treated (cross-linked) cellulose acetate (t-CA) and acrylic acid-grafted poly(hydroxyalkanoate) (PHA-g-AA/t-CA) exhibited noticeably superior mechanical properties compared with PHA/CA composites due to greater compatibility between the two components. The dispersion covering of t-CA in the PHA-g-AA matrix was highly homogeneous as a result of condensation reactions. Human lung fibroblasts (FBs) were seeded on these two series of composites to characterize the biocompatibility properties. In a time-dependent course, the FB proliferation results demonstrated higher performance from the PHA/CA series of composites than from the PHA-g-AA/t-CA composites. The water resistance of PHA-g-AA/t-CA was higher than that of PHA/CA, although the weight loss of both composites buried in *Acetobacter pasteurianus* (*A. pasteurianus*) indicated that they were both biodegradable, especially at higher levels of cellulose acetate substitution. The PHA/CA and PHA-g-AA/t-CA composites were more biodegradable than pure PHA, implying a strong connection between cellulose acetate content and biodegradability.

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1. Introduction

Because of waste disposal problems there is increasing interest in the development of biodegradable polymers that can replace traditional plastics. Currently this, polymer research has focused mainly on biodegradable aliphatic plastics and the frequently used biosynthetic aliphatic polymers, including polylactic acid (PLA), polycaprolactone (PCL), and poly(hydroxyalkanoates) (PHA) (Chen et al., 2013; Jazkewitsch, Mondrzyk, Staffel, & Ritter, 2011; Ruth et al., 2007). Hundreds, or even thousands, of years are required to degrade traditional plastic, such as polyphenylene propylene (PP) and polyethylene (PE; Ito & Nagai, 2008; Shih, Huang, & Chen, 2010). In comparison, PHA, developed in recent years, is a biodegradable aliphatic (polyester) plastic that requires only a few months' time to degrade completely into a natural product. Because the majority of the PHA monomer is a copolymer constituted by 3-hydroxy fatty acid with carbon atoms in a chain length of 3–14 and is manufactured from natural renewable resources, it could be completely biodegraded, and possesses excellent plasticity, easy processing and forming characteristics, and biocompatibility (Chanprateep, Buasri, Muangwong, & Utiswannakul, 2010; Ha & Cho, 2002).

Biodegradable plastic prices remain much higher than that of petrochemical material-based plastic products. To lower the cost while considering environmental protection, natural biodegradable polymers, such as natural fiber, are blended into the material (Azwa, Yousif, Manalo, & Karunasena, 2013; Faruk, Bledzki, Fink, & Sain, 2012; Jawaid & Abdul Khalil, 2011). Natural fiber material has many advantages, including low density, low cost, and renewability; however, most importantly, such natural fiber material is biodegradable and nontoxic (Behera, Avancha, Basak, Sen, & Adhikari, 2012; Tian, Tang, Zhuang, Chen, & Jing, 2012). Among such natural fibers, adding wood fiber (lignocellulosic) filler into the thermoplastic has drawn the most attention because plastic can coat a natural fiber during the fiber and plastic mixing process. This significantly reduces the water absorption of the pure wood material and improves the durability of the end product (Frollini, Bartoluccia, Sisti, & Celli, 2013).

Cellulose acetate (CA) is an important and commonly used derivative of natural cellulose fibers (Cheng, Dowd, Selling, & Biswas, 2010; Fan et al., 2013). However, due to the weak binding force between natural fiber and a polyester-based polymer, particularly poor mechanical properties arise when too much natural fiber is added. Many studies have attempted to find a suitable compatibilizing agent or cross-linking agent to improve the interfacial compatibility between the natural fiber and plastic. To increase the adherence between the natural fibers and polyester during processing and mixing, Ibrahima, Dufresne, El-Zawawya, and Aglevorc (2010) used maleic anhydride (MA)-grafted polyester

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plastic as the interface compatibility agent between the polyester plastic and natural fiber, which greatly improved the mechanical strength of the composite material. Fernandes, Correlo, Mano, and Reis (2013) added a coupling agent to the polymer plastic to enhance the reinforcing effect between the polymer plastic and natural fiber. The results showed great improvement in terms of mechanical strength.

In this study, we investigated the mechanical properties, biocompatibility, and biodegradability of CA composites, with PHA and acrylic acid-grafted PHA. The composites were characterized using Fourier-transform infrared spectroscopy (FTIR) and ^{13}C nuclear magnetic resonance (NMR) to identify the bulk structural changes induced by the acrylic acid moiety. Additionally, the effects of CA content on biocompatibility and the cell proliferation rate of human dermal fibroblasts (FBs) on these membranes were evaluated for appropriate properties for wound dressing. Water absorption and the weight loss of blends exposed to *Acetobacter pasteurianus* were also measured as indicators of water resistance and biodegradability.

2. Materials and methods

2.1. Materials

Commercial-grade PHA (EM 5400F) was obtained from Shenzhen Ecomann Biotechnology Co., Ltd. (Shenzhen, China). Acrylic acid (AA), benzoyl peroxide (BPO), and dimethyl sulfoxide (DMSO) were purchased from Sigma-Aldrich Chemical Inc. (St. Louis, MO, USA). 3-(4,5-Dimethylthiazol-2-yl)-2,5-diphenyltetrazoliumbromide (MTT) was obtained from Promega (Madison, WI, USA). Fetal bovine serum (FBS) and Dulbecco's modified Eagle's medium (DMEM) were purchased from Gibco-BRL (Gaithersburg, MD, USA). Tetraethoxysilane (TEOS) was obtained from Merck KGaA (Frankfurt, Germany). Cellulose acetate (degree of deacetylation: 55%) was supplied by Showa Chemical Co. Ltd. (Tokyo, Japan). All buffers and other reagents were of the highest purity commercially available.

2.2. PHA-g-AA copolymer

The grafting reaction of AA onto PHA is illustrated in Scheme 1A. AA was grafted onto molten PHA in a dichloromethane solution under a nitrogen atmosphere at $30 \pm 1^\circ\text{C}$, and the polymerization reaction was initiated with BPO. The reaction system was stirred at 60 rpm for 6 h. The grafted product (4 g) was then dissolved in 200 mL of refluxing dichloromethane at $30 \pm 1^\circ\text{C}$, and the hot solution was filtered through several layers of cheesecloth. The cheesecloth was washed with acetone to remove the tetrahydrofuran-insoluble unreacted AA, and the product was then dried on the cheesecloth in a vacuum oven at 80°C for 24 h. The dichloromethane-soluble products in the filtrate were extracted five times using 600 mL of cold acetone for each extraction. The grafting percentage was 6.06 wt% by titration (Wu, 2005). BPO and AA loadings were maintained at 0.3 wt% and 10 wt%, respectively.

2.3. Processing of t-CA

Scheme 1B shows the dissolution of CA in acetone to increase its dispersion in the polymer matrix and to avoid aggregation. The mass ratio of CA to acetone was 1–20. The solution was stirred at room temperature at 50 rpm for 1 h. A mixture of cross-linking agents was prepared by dissolving a stoichiometric amount of TEOS, H_2O , and lactic acid catalyst in tetrahydrofuran, stirring the solution at room temperature for 1 h, and then allowing the solution to stand for 2 days. The molar ratios used were as follows: lactic acid/TEOS = 0.01 and $\text{H}_2\text{O}/\text{TEOS} = 2.2$. The CA and cross-linking

agents were mixed at room temperature for 1 h at a rotor speed of 50 rpm. Samples were prepared with mass ratios of CA to cross-linking agents of 1–5. The final product was dried under vacuum at $105\text{--}110^\circ\text{C}$ for 24 h.

2.4. Composite preparation

Prior to composite fabrication, the CA or t-CA samples were washed with acetone and dried in an oven at 105°C for 24 h. Composites were prepared in a Brabender (Dayton, OH, USA) "Plastograph" W50EHT 200-Nm mixer with a rotor blade. The blends were mixed at $140\text{--}150^\circ\text{C}$ for 20 min at a rotor speed of 50 rpm. The CA or t-CA contents in the hybrids (PHA/CA or PHA-g-AA/t-CA) were set at 0, 5, 10, 15, and 20 wt%. After mixing, the composites were pressed into thin plates using a hot press and placed in a dryer for cooling. These thin plates were cut into standard sample dimensions for further characterization.

2.5. Characterization

Solid-state ^{13}C NMR spectra were acquired with an AMX-400 NMR spectrometer (Bruker, Billerica, MA, USA) at 100 MHz under cross-polarization, while spinning at the magic angle. Power decoupling conditions were set with a 90° pulse and a 4-s cycle time. Infrared spectra were obtained using an FTS-7PC FTIR spectrophotometer (Bio-Rad, Hercules, CA, USA). The glass-transition temperature (T_g), melting temperature (T_m), and heat of fusion (ΔH_f) were determined with a differential scanning calorimeter (DSC; model 2010; TA Instruments, New Castle, DE, USA). Sample quantities ranged from 4 to 6 mg. Melting curves were recorded between -60°C and 160°C at a heating rate of $10^\circ\text{C min}^{-1}$. Values of T_g , T_m , and ΔH_f were extracted from the temperatures and areas of the melting peaks in the DSC heating thermograms. A capillary viscometer (Schott AG, Mainz, Germany) was used to measure the intrinsic viscosity of PHA or PHA-g-AA/t-CA dissolved in the dichloromethane solvent at various concentrations (0.5, 1.0, 1.5, and 0.2 g dL^{-1}). The solutions were cleared through a $0.45\text{-}\mu\text{m}$ filter (Lida, Kenosha, WI, USA), and the capillary viscometer was filled with 10 mL of sample and equilibrated in a water bath (B801; Schott AG) at $30.0 \pm 0.1^\circ\text{C}$. Each sample was passed through the capillary tube prior to flow-time measurements. The flow time was used to calculate the relative and reduced viscosities, which were plotted as a function of concentration; the intercept represented the intrinsic viscosity.

2.6. Mechanical testing

A mechanical tester (model LR5K; Lloyd Instruments, Bognor Regis, West Sussex, UK) was used to measure the tensile strength at break, in accordance with ASTM Standard D638. Test samples were prepared in a hydraulic press at 150°C and conditioned at $50 \pm 5\%$ relative humidity for 24 h before making measurements. Testing was done at a crosshead speed of 20 mm min^{-1} . The mean value was determined from five specimens of each sample.

2.7. Composite morphology

A thin film ($150\text{ mm} \times 150\text{ mm} \times 1\text{ mm}$) of each composite was prepared with a hydraulic press and treated with hot water at 60°C for 24 h. Specimens were cut according to ASTM Standard D638. After rupture, a thin section of the fracture plane was removed. The thin sections were then coated with gold, and the fracture surface morphologies were observed using scanning electron microscopy (SEM; model S-1400; Hitachi, Tokyo, Japan).

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