Rheological and thermal characteristics of three-phase eco-composites

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ARTICLE INFO

ABSTRACT

The purpose of this study is to evaluate the rheological and thermal properties of poly(L-lactic acid) (PLA) composites incorporated with microcrystalline cellulose (MCC) and lignin. The MCC/lignin/PLA composites were fabricated through direct melt compounding. In particular, the effect regarding the addition of MCC was analyzed from a rheological perspective. Additionally, the morphological properties of the composite were explored via SEM observation. From the thermal analysis, it revealed that well-dispersed MCC at the nanoscale level increased cold crystallization temperature and that the addition of lignin enhanced the thermal stability of composites.

1. Introduction

Recently, decreasing environmental footprint is one of the main issues in material science and engineering areas (Siro & Plackett, 2010). For composite materials, biodegradable composites, the so-called eco-composites have received remarkable attention to meet such a strong demand. In general, eco-composites are prepared by incorporating fillers provided by nature such as natural fibers with natural (or recycled) polymers (Abdul Khalil, Bhat, & Ireana Yusra, 2012). Indeed, one of the most fascinating natural fillers is cellulose when considering production cost, physical and chemical features, and production security. Basically, cellulose constitutes natural fibers such as cotton, flax, jute, hemp, and bamboo encompass cellulose together with hemicelluloses and lignin (Brahmakumar, Pavithran, & Pillai, 2005; Oksman, Skrifvars, & Selin, 2003). While cellulose has a relatively simple chemical structure, the morphology of cellulose is highly complicated as a result of the inherent interaction with other plant constituents such as hemicelluloses and lignin (Nogi, Iwamoto, Nakagaito, & Yano, 2009; Siro & Plackett, 2010).

Biopolymers can be produced using natural cellulose, monomer, and microorganism. Typical examples are poly(L-lactic acid) (PLA), poly(butylene adipate) (PBA), and polyhydroxyalkanoate (PHA) (Cho et al., 2007; Pracella, Chionna, Anguillesi, Kulinski, & Piorkowska, 2006; Vilaseca, Lopez, LLauro, Pelach, & Mutje, 2004; Yuanjian & Isaac, 2007). In particular, PLA is one of the most promising biodegradable polymers due to its fairly good physical properties. It is usually manufactured using the fermentation of biomass such as sugar, potatoes, and corns (Plackett, 2004; Sarki, Hassan, Aigbodion, & Oghenevweta, 2011). On the other hand, there is a need for overcoming the drawbacks of PLA such as low thermal stability and poor brittle characteristics by reinforcing the resin compared with other synthetic polymers (Jacob & Thomas, 2008; Karus & Kaup, 2002; Wu, 2009).

There are two kinds of cellulose fillers used as a reinforcement in a polymer matrix: one is microcrystalline cellulose (MCC) and the other is microfibrillated cellulose (MFC) (Chen et al., 2011; Iwatake, Nogi, & Yano, 2008; Souza Lima & Borsali, 2004). Compared to MFC with a web-like structure, MCC is particularly appropriate for the melt compounding method for the preparation of composites. MCC is produced by combining mechanical (e.g., pressure homogenizing) and chemical (e.g., acid hydrolyzing) processes of natural celluloses such as plant and wood (Capadona et al., 2009; Lu, Askeland, & Drzal, 2008; Lu, Wang, & Drzal, 2008; Mathew, Oksman, & Sain, 2005). Depending on the cellulose origin and the preparation conditions, the diameter and length of MCC change in the range from 2 nm to 20 nm and from 100 nm to several micrometers, respectively. In this respect, MCC possesses a relatively high specific surface area compared with other fillers such as natural fiber, glass fiber, talc, mica, and so on. Furthermore, the modulus and strength of MCC are estimated to be approximately 130 GPa and 7 GPa, respectively, since it does not have many defects and is free of chain folding (Lu, Askeland, et al., 2008; Lu, Wang, et al., 2008). As a result, MCC contains great potential to be used as a reinforcing filler in composites.

Since lignin has a complex and non-uniform structure with aliphatic and aromatic components, it has been regarded as a waste or low value by-products of cellulose for a very long period of time.

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Table 1
Compositions of prepared composites.

Sample	PLA (%)	Ligin (%)	MCC (%)
PLA	100	–	–
Lignin5	95	5	–
MCC10	90	–	10
Lignin10/MCC10	80	10	10
Lignin5/MCC20	75	5	20
Lignin10/MCC20	70	10	20

Currently, it is being utilized as a binding and dispersing material in various industries (Casetta & Bertini, 2007; Guigo, Vincent, Mija, Naegele, & Sbirrazzuoli, 2009; Morandim-Giannetti et al., 2012; Stewart, 2008; Wood, Coles, Maggs, Meredith, & Kirwan, 2011). For composite applications, lignin can serve as a nucleating agent (Casetta & Bertini, 2007), antioxidant (Morandim-Giannetti et al., 2012), compatibilizer (Graupner, 2008; Wood et al., 2011) or even base matrix (Guigo et al., 2009; Stewart, 2008). In particular, lignin has great potential to replace phenolic resin.

The purpose of this study is to identify the processability of green composites prepared by incorporating a biopolymer with MCC and lignin and to investigate the rheological and thermal properties of the prepared three-phase composites. From the perspective of productivity via mass production, since the melt compounding method instead of using the solvent based one is desirable, the composite constituents including PLA, MCC, and lignin were mixed using a twin screw extruder. Various compositions of composite ingredients were considered in an effort to find the likelihood of the direct dispersion of MCC through melt compounding. In addition, morphological observation was carried out to verify the dispersion state of MCC in the composite.

2. Experiments

2.1. Sample preparation

PLA resin was purchased from Greenchemical (PLA 3251D), and its glass transition temperature (T_g) and melting point (T_m) were 55 °C and 168 °C, respectively. The MCC obtained from Acros Organics had a length of 50 μm. Lignin was supplied in powder form with 93% purity from Econex Co. (Korea). All the materials were kept at 100 °C in a vacuum oven for 24 h prior to the sample production. Thereafter, the materials were compounded with a twin screw extruder (Hakke). The screw speed was 20 rpm, and temperatures of 180 °C, 190 °C, and 200 °C were applied to the feed zone, compression zone, and metering zone, respectively. The compositions of the composites produced are listed in Table 1.

2.2. Measurements

Dynamic rheological tests were conducted using a rheometer (AR2000EX, TA Instruments) with a parallel plate with a 40 mm diameter. After removing previous shear stress history, the tests were carried out. In the oscillatory shear mode, dynamic viscoelastic properties such as the storage modulus, loss modulus, tangent delta, and complex viscosity were obtained applying an angular frequency sweep of 0.1–500 rad s^{-1} at a constant oscillation stress of 0.2 Pa at 200 °C. The simple shear experiment was performed at a shear rate in the range of 0.01–500 s^{-1} at a shear stress of 1 Pa. The fracture surface of tensile specimens was observed morphologically by using scanning electron microscopy (JEOL, JSM-5410LV). Before the observation, all the specimens were coated with platinum using an ion sputter coater (JEOL, JFC-1100E). The thermal characteristics of specimens were investigated via differential scanning calorimetry (DSC, METTLER TOLEDO DSC822E) and thermogravimetric analysis (TGA, METTLER TOLEDO TG50). The samples for
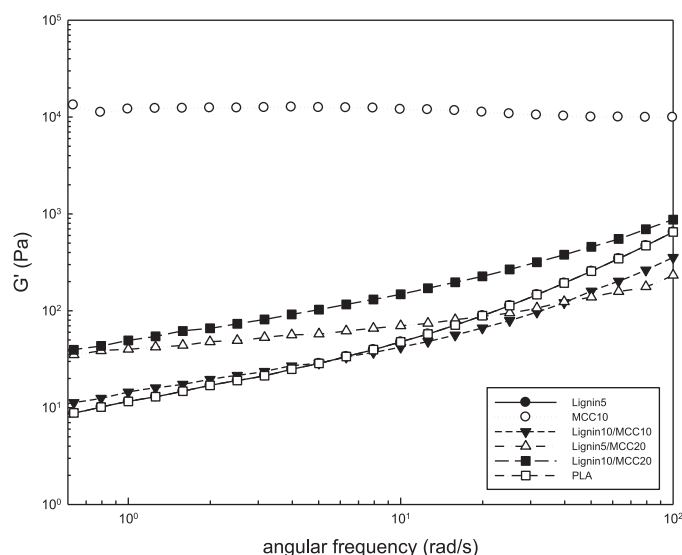

Fig. 1. Storage modulus of composites.

the DSC experiment were scanned between 0 °C and 200 °C at ±5 °C/min. The TGA specimens were heated up from 25 °C to 600 °C at a rate of 20 °C/min.

3. Results and discussion

Rheology is a powerful tool to look into the internal structure of complex material systems without putting in much effort and time. In particular, viscoelastic features such as storage and loss moduli can offer some valuable information, e.g., size, dispersion state, interdistance, interaction, surface properties of the particles in the case of the multiphase composite system. The storage modulus results of PLA/lignin/MCC composites are demonstrated in Fig. 1. Only the MCC10 sample revealed a drastically different behavior in regards to the storage modulus. That is, it has the very high storage modulus and more importantly, the low terminal slope, which is indicative of the so-called solid-like behavior, compared with the other samples. The solid-like behavior is generally described using the following three characteristics: (i) higher storage modulus than loss modulus, (ii) long relaxation time, and (iii) non-terminal behavior of the modulus slope (i.e., frequency independence at lower frequencies). In this sense, the MCC10 sample exhibited a typical solid-like behavior. This result implies that there is a strong particle–particle interaction (e.g., percolation network structure) and good particle dispersion in the composites. On the other hand, the lignin5/MCC20 specimen also exhibits quite different solid-like behavior from the samples showing liquid-like rheological behavior. It is presumed that the addition of lignin diminishes the storage modulus. Fig. 2 presents the loss modulus of the composites. In general, loss modulus is known to be less sensitive to the internal structure of material than storage modulus. Similar to the results shown in Fig. 1, the loss modulus of the MCC behaves differently. That is, compared with the other samples, the modulus value is very small, which also implies the solid-like behavior.

Tan delta can act as a meaningful indicator of obscured material properties. For instance, the geometry-independent value can offer information on the internal structure of multiphase composite systems. Fig. 3 illustrates the tan delta of the composites. The MCC10 exhibits a very distinct phase angle (∼10°) from the other samples (∼90°), which means that the contribution of the storage modulus is dominant. In addition, the delta value of the lignin5/MCC10 is a