Carbohydrate Polymers 92 (2013) 1006–1011

Contents lists available at SciVerse ScienceDirect

Carbohydrate Polymers

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

Rheological and thermal characteristics of three-phase eco-composites

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ARTICLE INFO

Article history:
Received 29 September 2012
Received in revised form 7 October 2012
Accepted 19 October 2012
Available online 29 October 2012

Keywords:
Microcrystalline cellulose
Lignin
Rheology

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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0144-8617/$ – see front matter © 2012 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.carbpol.2012.10.046

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 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.

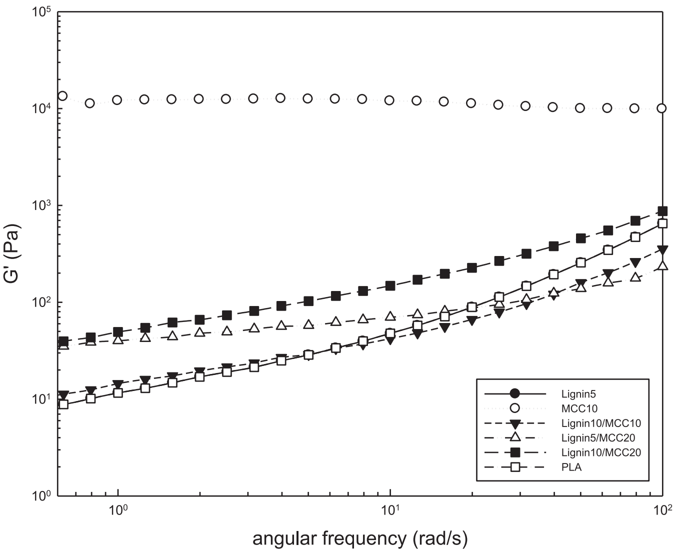

Fig. 1. Storage modulus of composites.

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

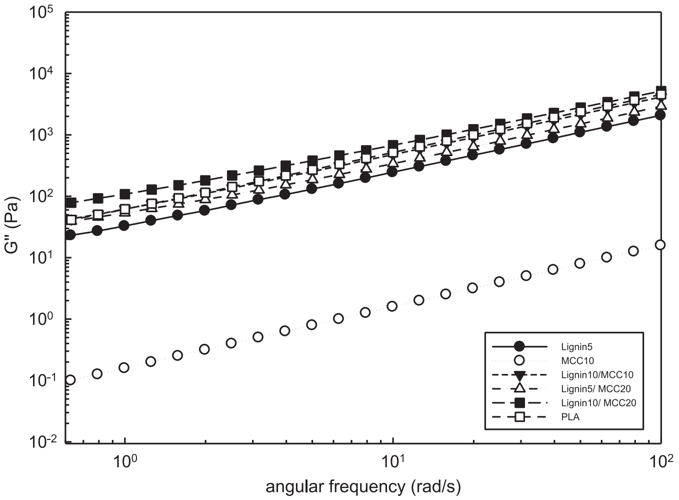

Fig. 2. Loss modulus of composites.

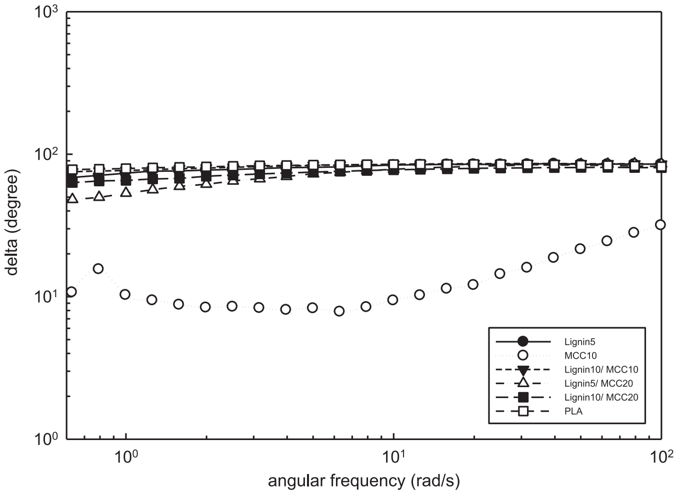

Fig. 3. Tangent delta of composites.

bit different from those of the liquid-like samples in the range of low frequencies.

The complex viscosities of the composites are demonstrated in Fig. 4. It is observed that the MCC10 sample possesses the higher complex viscosity, and also the viscosity decreases with increase in the angular frequency. Fig. 5 shows the shear viscosity of the composites. As expected, the strongest shear thinning behavior is detected in the MCC10 specimen. This result supports the storage

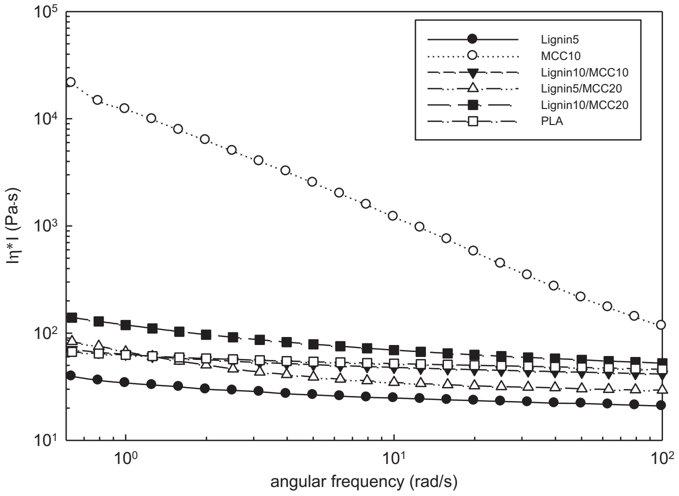

Fig. 4. Complex viscosity of composites.

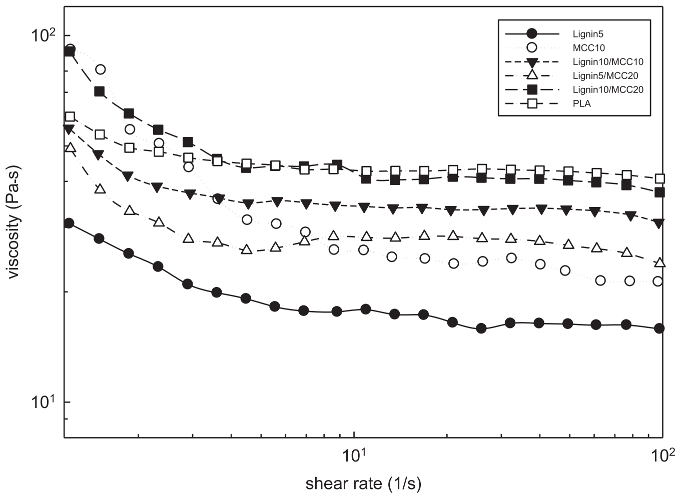

Fig. 5. Shear viscosity of composites.

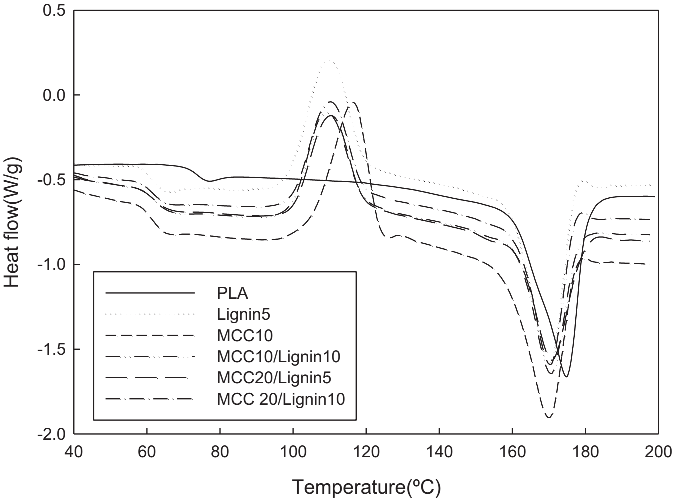

Fig. 6. DSC of composites.

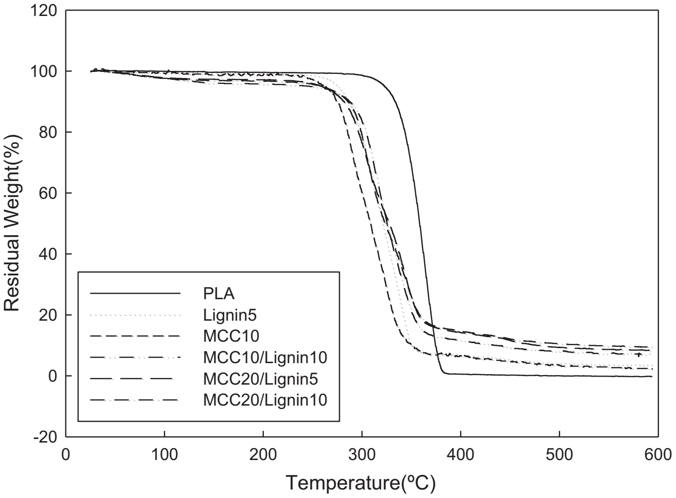

Fig. 7. TGA of composites.

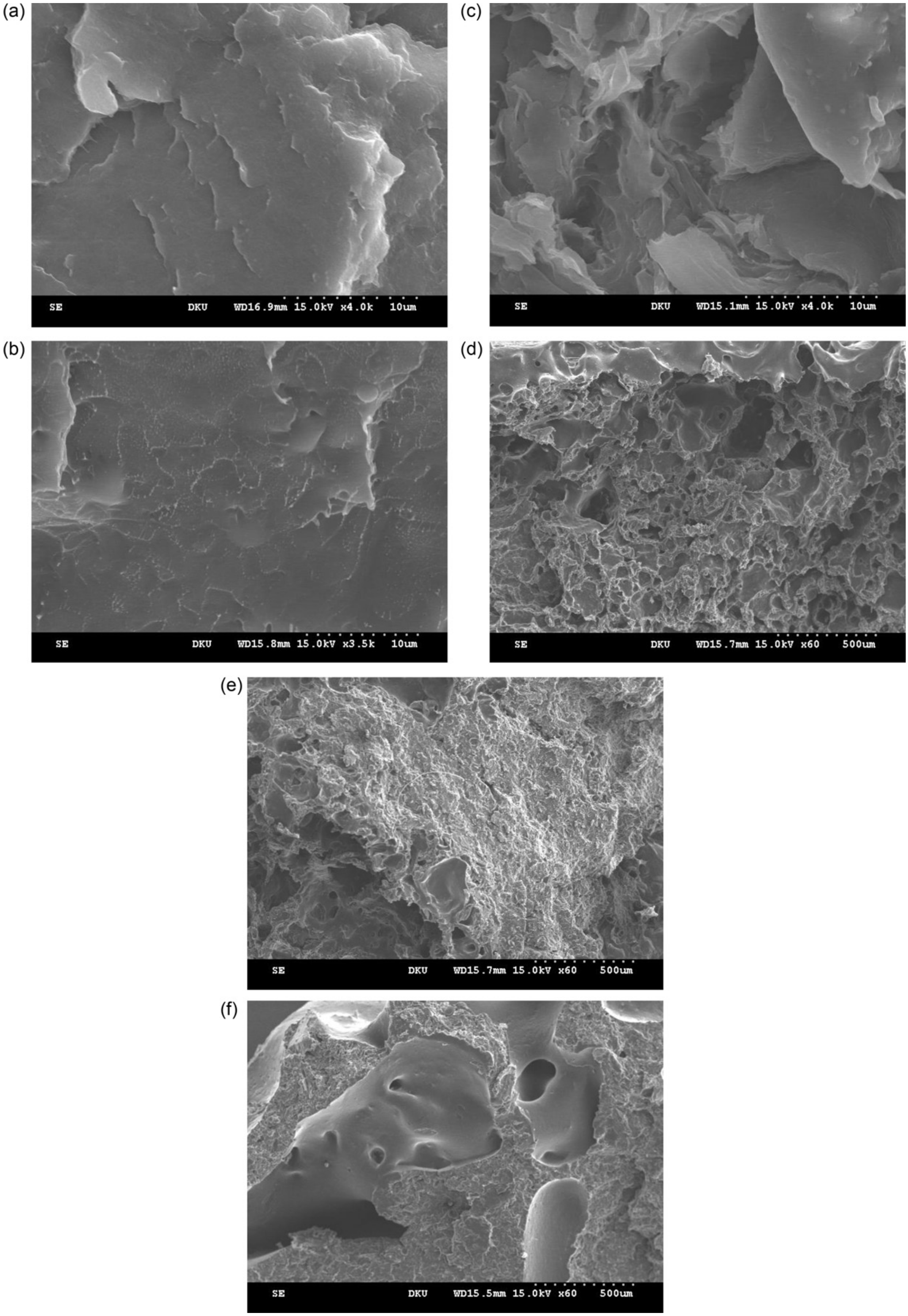

Fig. 8. Images of the fracture surface of composites: (a) PLA, (b) lignin5, (c) MCC10, (d) lignin10/MCC10, (e) lignin5/MCC20, and (f) lignin10/MCC20.

Table 2
Characteristic temperatures of prepared composites from DSC.

Sample	T_g (°C)	T_{cc} (°C)	T_m (°C)
PLA	55	115	168
Lignin5	59	110	168
MCC10	60	115	169
Lignin10/MCC10	59	109	170
Lignin5/MCC20	59	110	171
Lignin10/MCC20	59	110	170

modulus result shown in Fig. 1. Also, the MCC particles that have quite strong particle–particle interactions are aligned in the applied shear direction. In addition, in comparison between the pure PLA sample and the other composites, the addition of lignin to the composites results in the decrease of shear viscosity. It is interesting to compare the complex viscosity with the shear viscosity results. It is well-known that according to the Cox–Merz rule, the magnitude of complex viscosity equals that of shear viscosity at the corresponding values of frequency and shear rate, i.e., $\eta(\dot{\gamma}) = |\eta^*|_{\omega=\dot{\gamma}}$ (Doraiswamy et al., 1991). Indeed, the MCC10 is found not to follow such a rule.

Fig. 6 presents the DSC curves of the composites, and the resulting characteristic temperatures are listed in Table 2. The composite samples display relatively large peaks, compared with the pure PLA. As given in Table 2, the effect regarding the addition of lignin and MCC on the glass transition temperature (T_g) and melting temperature (T_m) is not very strong. However, the MCC10 shows the significantly increased cold crystallization temperature (T_{cc}). Such an increase is possibly because the nano-sized MCC acts as a nucleating agent (Lu, Askeland, et al., 2008; Lu, Wang, et al., 2008). Fig. 7 presents the TGA thermograms of the composites. For the MCC reinforced composites, there is an initial weight loss at around 100 °C, which can be attributed to the loss of existing moisture in the MCC. The maximum decomposition temperatures of the composites are lower than that of the neat PLA. More specifically, the lignin5 sample has a higher maximum decomposition temperature than the MCC10 one, which can be explained by the fact that cellulose degrades between 240 °C and 350 °C, but lignin between 280 °C and 500 °C (Morandim-Giannetti et al., 2012). The thermally stable phenylpropanoid unit of lignin offers such a relatively high degradation temperature. The second decomposition stages around 400 °C appear in the composites, which is induced by the decomposition of lignin and MCC (Sahoo, Misra, & Mohanty, 2011).

Fig. 8 presents SEM images of the fracture surface for the composites. More rough fracture surfaces are observed as the content of fillers increases. This may be why the fillers can cause a phase separation and serve as a reinforcing material in the composite. In particular, the SEM image of the MCC10 is different from those of the others. This indicates that the MCC is well-dispersed most probably at the nanoscale level and contains strong interactions not only between fillers and the matrix but also between the fillers themselves. This result coincides with the rheological results presented above. Overall, this study is expected to show a melt compounding based preparation possibility of MCC and lignin filled eco-composites and to provide meaningful insight into the physical properties of the composites.

4. Conclusions

The rheological and thermal properties of PLA/lignin/MCC composites prepared using a melt compounding method were investigated in this study. The 10% MCC reinforced composites demonstrated exceptionally different rheological behavior, i.e., solid-like behavior. From this, we assumed that MCC was well-dispersed at nanoscale, and that strong particle–particle interaction existed. Such well-dispersed nanofillers raised the cold crystallization temperature. Although the prepared composites started degrading earlier than neat PLA, the addition of lignin lowered the decrease in the decomposition temperature due to its thermal stability. In addition, the microstructures of the composites were identified from morphological analysis.

Acknowledgement

The present study was conducted by the research fund of Dankook University in 2012.

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