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The influence of micro-/nano-CaCO₃ on thermal stability and melt rheology behavior of poly(lactic acid)

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Abstract

Poly(lactic acid) (PLA) has been an interesting biopolymer that could offer a potential alternative to petrochemical plastics. Modification of PLA by fillers has been widely carried out to obtain desired properties for various applications. This research aims to investigate the effect of micro-/nano-particle size of calcium carbonate (CaCO₃) on thermal stability and melt rheology behavior of PLA extrusion sheet. PLA pellets were compounded with CaCO₃ particles by a twin-screw extruder, and fabricated by a cast flat sheet process to produce CaCO₃-PLA extrusion sheets. Fatty acid treated on CaCO₃ surface showed profound impact on thermal stability of CaCO₃-PLA extrusion sheets as identified by thermal gravimetric analysis (TGA). The onset temperature of degradation (T_{onset}) and the peak degradation temperature (T_d) of CaCO₃-PLA biocomposites were lower than neat PLA. In the rheological study, it was found that addition of fatty acid treated CaCO₃ reduced the viscosity of CaCO₃-PLA biocomposites due to thermal degradation of PLA. Adding micro-CaCO₃ could maintain viscosity of extruded PLA to be close to neat PLA, while adding nano-CaCO₃ with the surface treatment, caused easier flow of high loading PLA.

Keywords: PLA; CaCO₃; Thermal Stability; Rheology

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1. Introduction

A linear aliphatic biodegradable thermoplastic polyester as poly(lactic acid) (PLA), produced from renewable resources [1], is an interesting biopolymer that could offer a potential alternative to petrochemical plastics in many applications [2]. Adding fillers into plastics are usually implemented to reduce cost and control some properties of products [3-6] such as physical, rheological, thermal and mechanical properties.

In consideration of various fillers, calcium carbonate ($CaCO_3$) is the most popular filling material due to its high amount of loading in plastics and low cost [6]. The reinforcing effect of nano- and micro-sized $CaCO_3$ particles has been studied in polymer systems such as polypropylene (PP) [7], polyketone [8] and acrylonitrile butadiene styrene (ABS) [9]. The mechanical properties of composites were significantly improved by the addition of fine $CaCO_3$ particles [7-9]. Large scale plastic deformation was found to be initiated by interfacial debonding and the subsequent relaxation of triaxial tensile stress [10].

Like many aliphatic polyesters, PLA degrades during thermal processing or under hydrolytic conditions, giving a rapid reduction of molecular weight that affects rheological behaviors of the polymer. However, there are many grades of PLA having various properties especially thermal stability and melt properties. The PLA grade extrusion/thermoforming is now the popular grade that is used for extrusion process and sometimes the blown film extrusion process. Thus, this research aims to investigate the effect of micro-/nano-particle size $CaCO_3$ and particle loading on thermal stability and melt rheology behavior of PLA biocomposites, fabricated by extrusion sheet process.

2. Methodology

2.1. Materials

In this research, PLA Extrusion/Thermoforming grade (Natureworks®2002D), with L/D isomer ratio of 96:4, glass transition temperature (T_g) of 58^oC and melting temperature (T_m) of 153^oC, weight-average molecular weight (M_w) of 212,300 Da and polydispersity (M_w/M_n) of 3.06 was used.

There were three types of $CaCO_3$ used in the research: $CaCO_3$ micro-particle (1QC, Quality Mineral Co., Ltd., Thailand), and two grades of $CaCO_3$ nano-particle by precipitation method (CNANO P-23, BRS Intertrade Co., Ltd., Thailand and NPCC 101, Behn Meyer Chemical Co., Ltd., Thailand). The average single particle size of micro-/nano-$CaCO_3$ providing from manufacturer are show in table 1 and their code names in this research were Micro-$CaCO_3$-1740, Nano-$CaCO_3$-1041, and Nano-$CaCO_3$-280, respectively.

2.2. Particle characterization

The morphology and average agglomerated particle size of $CaCO_3$ was observed by Scanning Electron Microscopy (SEM) and size analysis technique. The characteristic of the $CaCO_3$ particles was characterized by Fourier Transform Infrared (FT-IR, Bruker Vector-22) using KBr disk technique. Moreover, the amount of substance treated on the $CaCO_3$ surface was observed by Thermo Gravimetric Analysis (TGA, Mettler Toledo TGA model 1).

2.3. Preparation of PLA extrusion sheet

Prior to processing, PLA and $CaCO_3$ were dried overnight at $60\ ^oC$ in order to remove remaining water. The raw materials were compounded in a co-rotating twin screw extruder (EN MACH SHJ-25 twin screw extrude) and fabricated throughout a T-slit die, then drawn by cold nip rolls at speed of 15 Hz to cast flat sheets of 50 mm width and 0.4 mm thick. The extruder temperature profile was ranged from 150 ^oC in the feeding zone down to 170^oC in the die and the screw speed was 130 rpm. The amount of $CaCO_3$ in PLA biocomposites were varied in the range of 0 to 20 wt%. Neat PLA was also melt processed under the same condition and referred as extruded PLA.

2.4. Thermal stability study

Thermal Gravimetric Analysis (TGA) of neat PLA, extruded PLA and $CaCO_3$-PLA biocomposites was performed in nitrogen atmosphere condition by Mettler Toledo TGA model 1. Samples were heated from $50^{\circ}C$ to $500^{\circ}C$ with a heating rate of 10 $^{\circ}C$/min. The onset temperature of degradation (T_{onset}), peak degradation temperature (T_d), and the end temperature of degradation (T_{end}) were calculated from the TGA curve and reported.

2.5. Melt rheology study

The melt behavior of neat PLA, extruded PLA, and $CaCO_3$-PLA biocomposites at low shear rate was investigated by rotational rheometer (Plate & Plate Rheometer, Rheometric Scientific, TA Instruments) with steady shear rate sweep range of $0.01 – 150.0$ s^{-1}. The temperature of the test was fixed at $170^{\circ}C$ as same as die temperature in the processing. Moreover, the melt behavior of biocomposites at high shear rate as occurred in the extrusion sheet process was observed by capillary rheometer (Bohlin Instrument Company, model RH2200). The majority of the experiments were carried out using the barrel having diameter and length of 15 mm and 250 mm, respectively and a capillary die having the L/D ratio of 16/1 mm/mm in right barrel and a zero die as a reference in left barrel. The obtained data were corrected according to the Bagley correction. The temperature of testing condition was $170^{\circ}C$, equivalent to die temperature in the extrusion sheet process.

3. Results and discussion

3.1. Particle characterization

Particle shape and particle size of micro-/nano-$CaCO_3$ were characterized by SEM and sized analysis technique. SEM micrographs of various types of $CaCO_3$ used in this research and the average agglomeration size are shown in Fig. 1 and Table 1, respectively. In Fig. 1, the lower magnificence at 10,000X was used for micro-$CaCO_3$ ((a)-(b)) and the higher magnificence at 90,000X was used for nano-$CaCO_3$ ((c)-(f)) because of different particle sizes. The approximate single particle size observing by SEM was close to the average single particle size of micro-/nano-$CaCO_3$ reported by the manufacturers.

The average agglomerate size of micro-$CaCO_3$ and nano-$CaCO_3$ in Table 1 were investigated by size analysis technique using laser scattering and dynamic light scattering, respectively. Their abbreviated names were denoted as Micro-$CaCO_3$-1740, Nano-$CaCO_3$-1041, and Nano-$CaCO_3$-280, respectively.

FT-IR is the general technique used for identifying the functional group of inorganic and organic matter. The FT-IR spectra of $CaCO_3$ are presented in Fig. 2. As seen in the figure, the FT-IR absorption peaks of all $CaCO_3$ were qualitatively similar. All types of $CaCO_3$ displayed the absorption peak at about 875 cm^{-1} and 710 cm^{-1}. The absorption peak at wave number of 875 cm^{-1} indicated the $[CO_3]^{2-}$ out-of-plane deformation mode of the aragonite form while the absorption peak at wave number of 710 cm^{-1} showed the calcite form [11]. This implied that samples were the mixture of calcite and aragonite.

In addition, there were interesting absorption peaks appeared at about wave number of 1,780 cm^{-1}, 2,950-2,850 cm^{-1} and 3,600-3,200 cm^{-1}. These peaks indicated C=O stretching in carboxylic acid, alkyl C-H stretching and O-H stretching, respectively. The peaks of these functional groups verified that all types of $CaCO_3$ were treated by fatty acid on the surface for preventing the re-agglomeration of particles during storage and handling. This result confirms the information of surface treatment of $CaCO_3$ as reported from the manufacturers.

TGA was used to determine the amount of fatty acid treated on $CaCO_3$ surface. Fig. 3 shows TGA curves of all $CaCO_3$ used in the research. It was found that the content of fatty acid treated on the surface of two types of nano-sized $CaCO_3$ was nearly at the same amount (at about 4.2 wt%). The onset temperature of degradation showed that fatty acid treated on the Nano-$CaCO_3$-1041 degraded at the temperature lower than the fatty acid treated on the Nano-$CaCO_3$-280. The amount of fatty acid treated on the Micro-$CaCO_3$-1760 (about 0.7 wt%) was less than those of nano-sized $CaCO_3$. The higher onset temperature of degradation showed that Micro-$CaCO_3$-1760 was more stable than both nano-sized $CaCO_3$ particles.
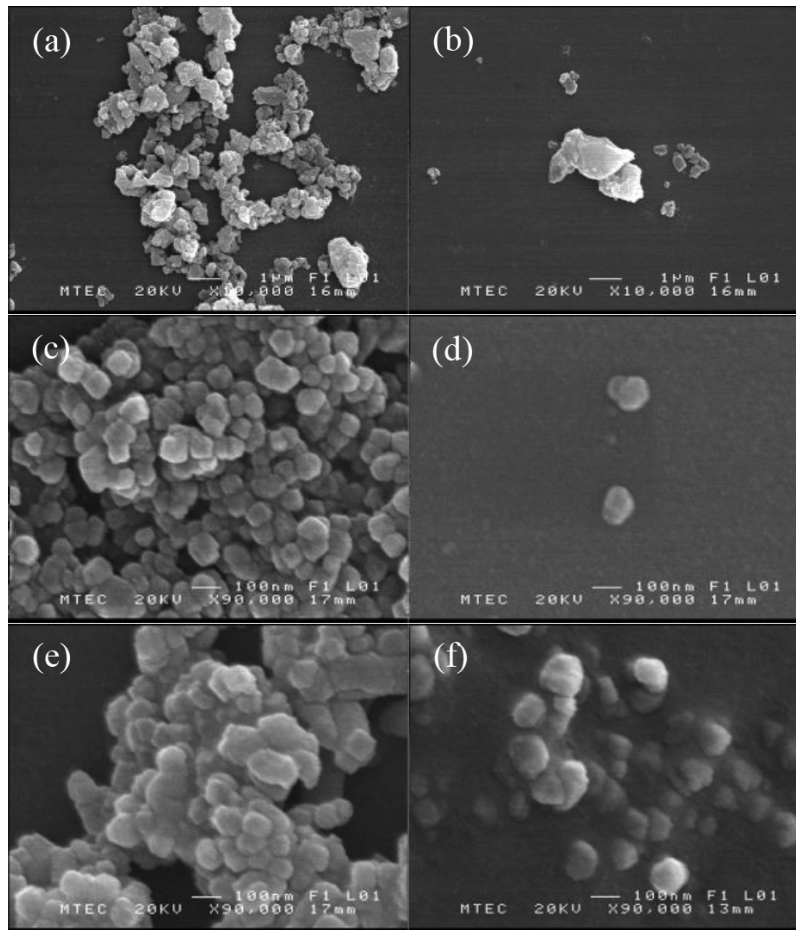
Fig. 1. SEM micrographs of agglomerate particle and single particle:
(a)-(b) Micro-CaCO₃-1740; (c)-(d) Nano-CaCO₃-1041; (e)-(f) Nano-CaCO₃-280.

Table 1. Single particle and agglomeration size of CaCO$_3$.

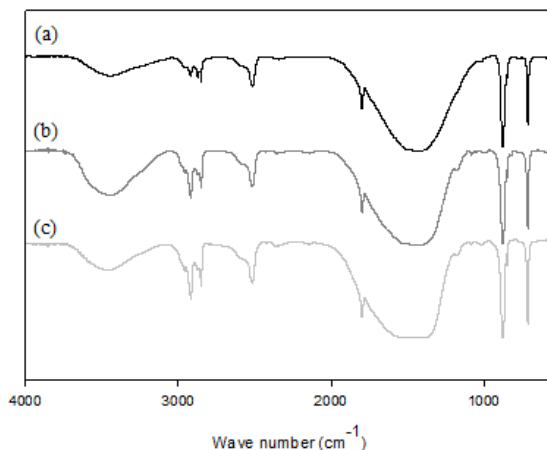| Type of CaCO$_3$	Single particle size (nm)	Agglomeration size (nm)
Micro-CaCO$_3$-1740	1,600	$1,746.7 \pm 5.8$
Nano-CaCO$_3$-1041	40-60	$1,066 \pm 37.4$
Nano-CaCO$_3$-280	40	278.4 ± 1.7

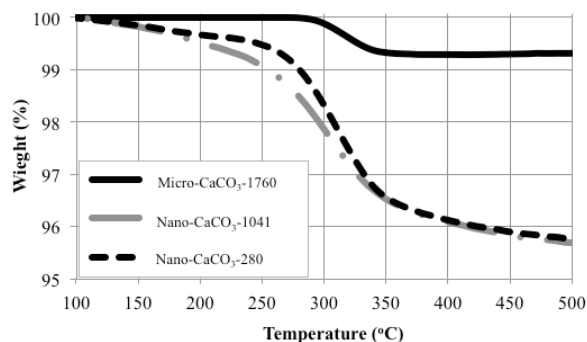Fig. 2. FT-IR spectra $CaCO_3$: (a) Mircro-$CaCO_3$-1760; (b) Nano-$CaCO_3$-1041; (c) Nano-$CaCO_3$-280.

Fig. 3. TGA Curves of $CaCO_3$ used in this research; Mircro-$CaCO_3$-1740, Nano-$CaCO_3$-1041 and Nano-$CaCO_3$-280 particles.

3.2. Thermal stability study

TGA was used to investigate the thermal stability of $CaCO_3$-PLA biocomposites. The test was performed in inert nitrogen atmosphere condition. The TGA curves of the filled and unfilled biocomposites are shown in Fig. 4 and the onset temperature of degradation (T_{onset}), peak degradation temperature (T_d), and the end temperature of degradation (T_{end}) are reported in Table 2. Adding $CaCO_3$ with fatty acid sizing agent had negative effect on thermal stability of PLA polyester because the ester linkage of PLA is susceptible to the chemical reaction with fatty acid at high temperature of melt processing.

Typically, the $CaCO_3$ particles are treated by fatty acid to prevent re-agglomeration during storage and handling. Unfortunately, the chemical reaction between fatty acid and ester linkage of PLA caused chain scission and induced thermal degradation of PLA, evidencing by T_d of $CaCO_3$-PLA biocomposites decreased from 392^oC (neat PLA) to be around 295-356^oC after melt processing.

It was found that T_d of PLA with Nano-$CaCO_3$-1041 and Nano-$CaCO_3$-280 were much lower than that of Micro-$CaCO_3$-1740. This was due to the higher amount of fatty acid coating on the particle surface as shown in the TGA investigation. Nano-sized particles have larger surface area, so they need higher amount of fatty acid to cover their surface.
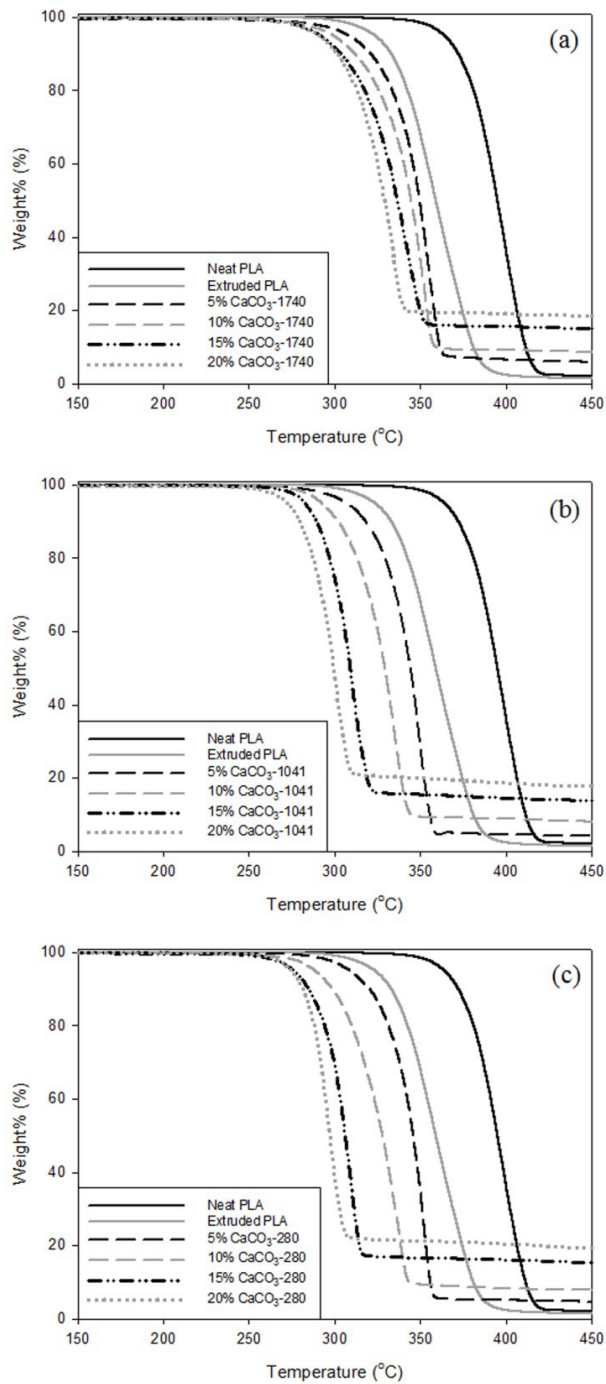
Fig. 4. TGA curves of the CaCO₃-PLA biocomposites with various loading of CaCO₃:
(a) Micro-CaCO₃-1740; (b) Nano-CaCO₃-1041; (c) Nano-CaCO₃-280.

Table 2. Thermal stability analysis of the unfilled and filled PLA biocomposites with various loading of CaCO$_3$.

Materials	T$_{onset}$(^{o}C)	T$_d$(^{o}C)	T$_{end}$(^{o}C)
Neat PLA	376.24	392.54	412.98
Extruded PLA	346.33	365.47	375.11
5% Micro-CaCO$_3$-1740	335.61	356.70	362.89
10% Micro-CaCO$_3$-1740	330.43	348.81	353.48
15% Micro-CaCO$_3$-1740	312.58	339.47	346.93
20% Micro-CaCO$_3$-1740	308.91	331.55	340.24
5% Nano-CaCO$_3$-1041	329.08	347.06	351.60
10% Nano-CaCO$_3$-1041	313.78	333.86	337.65
15% Nano-CaCO$_3$-1041	284.98	309.75	314.94
20% Nano-CaCO$_3$-1041	277.29	296.20	306.20
5% Nano-CaCO$_3$-280	330.05	347.77	351.47
10% Nano-CaCO$_3$-280	311.93	333.60	337.68
15% Nano-CaCO$_3$-280	280.52	306.35	311.28
20% Nano-CaCO$_3$-280	278.14	295.24	304.42

3.3. Melt rheology study

The rotational rheometer (plate & plate rheometer) was used to investigate viscosity of material at low shear rate. As seen in the Fig. 5, shear viscosity of PLA biocomposites were relatively constant at low shear rate. Generally, viscosity of extruded PLA is lower than neat PLA because of the reduction of PLA molecular weight by thermal degradation during melt processing. Adding CaCO$_3$ particles reduced the viscosity of PLA because of lubricating effect and fatty acid treated on CaCO$_3$, causing the decrease in PLA viscosity due to thermal degradation of PLA by transesterification with the presence of fatty acid. However, the opposite effect occurred when PLA was incorporated with high content of nano-sized CaCO$_3$. Viscosity of PLA nanocomposites was increased with the addition of Nano-CaCO$_3$-1041 loading more than 5 wt%, or the addition of Nano-CaCO$_3$-280 more than 15 wt%. This was due to agglomeration of small particles at high loading of nano-particle fillers in nanocomposite obstructed the flow.

Conventionally, polymers are fabricated at high shear rate melt processing. Capillary rheometer is typically used to investigate the melt properties in high shear rate range. For a given type and loading of CaCO$_3$ particles, shear stress of the melt increased with respect to increasing shear rate from 100 s^{-1} to 2500 s^{-1} in non-linear behavior.

Viscosity of the micro-CaCO$_3$-PLA biocomposites was higher than those of extruded PLA because rigid fillers can disturb PLA melts during shear flow as observed in other typical filled composites. Although adding nano-CaCO$_3$ into PLA increased shear viscosities marginally, incorporating nano-CaCO$_3$ with lower agglomeration into PLA, surprisingly reduced shear viscosity at low shear rate. Rigid fillers of CaCO$_3$ did not deform under stretching and hence exerted more resistance to flow deformation under extensional strain in a capillary rheometer

It was found that the micro-CaCO$_3$ obstructed movement of the polymer chains more than the nano- CaCO$_3$ did, even though PLA adding Nano-CaCO$_3$-1041 and Nano-CaCO$_3$-280 had higher number of particles than PLA adding Micro-CaCO$_3$-1740 at the same loading weight percent of CaCO$_3$. Thus, the nano-CaCO$_3$ presented profound lubricating effect. This was due to particle-particle interaction at nano-scale. It is expected that the lubricating effect of nano-particles on viscosity becomes more prominent with increasing of CaCO$_3$.
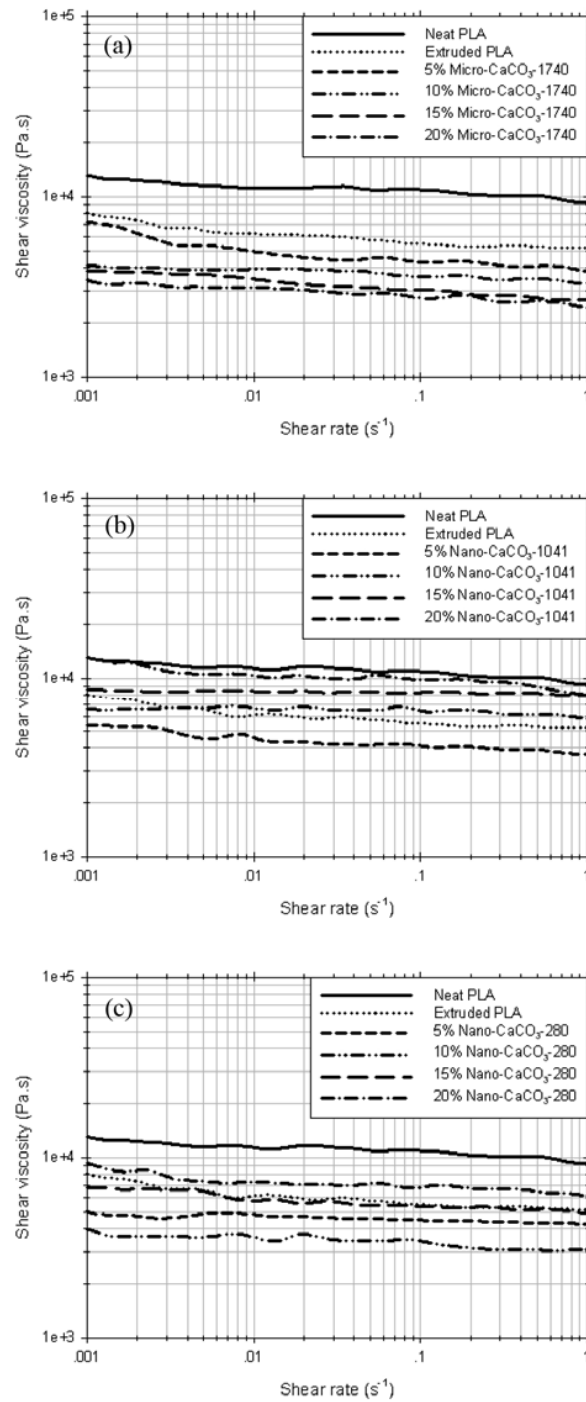
Fig. 5. Viscosity of PLA biocomposites at low shear rate: (a) Micro-CaCO$_3$-1740-PLA; (b) Nano-CaCO$_3$-1041-PLA; (c) Nano-CaCO$_3$-280-PLA.
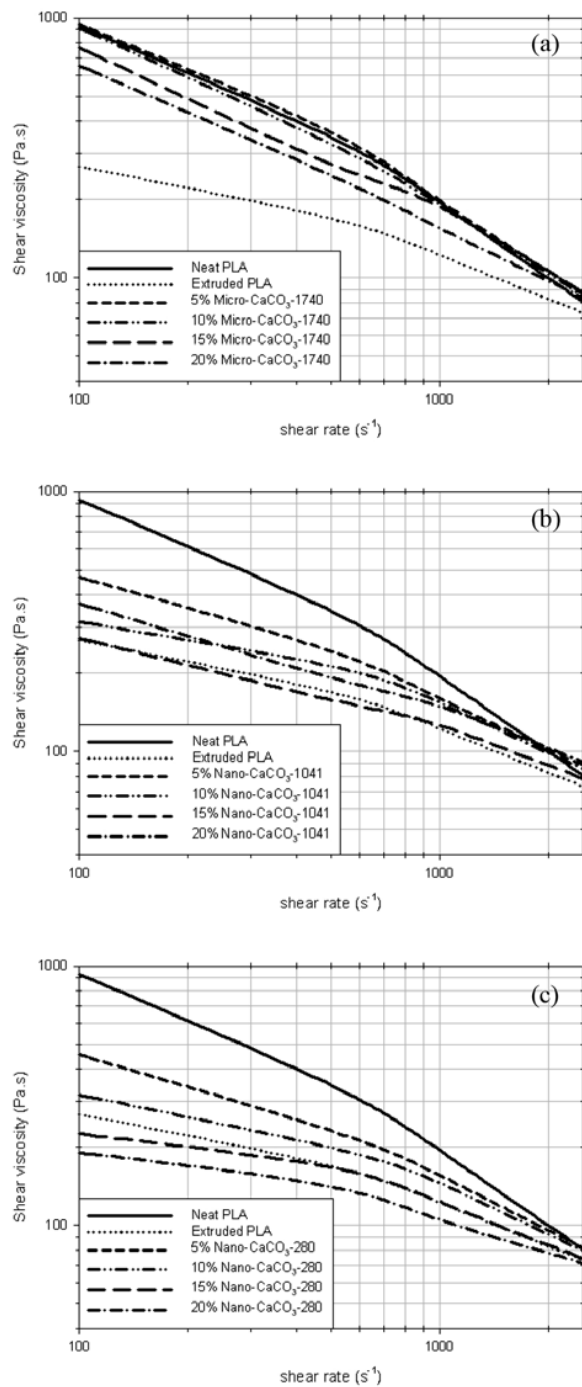
Fig. 6. Viscosity of PLA biocomposites at high shear rate: (a) Micro-CaCO$_3$-1740-PLA; (b) Nano-CaCO$_3$-1041-PLA; (c) Nano-CaCO$_3$-280-PLA.

Moreover, there was high content of fatty acid at the high loading of both $CaCO_3$. M_w of PLA tended to decrease with the increasing of fatty acid content and this reduction of molecular weight could be revealed via the reduction of both $CaCO_3$-PLA biocomposite viscosities. This effect also enhanced the decreasing of viscosity of both $CaCO_3$-PLA biocomposites at high content of fillers.

When nano-$CaCO_3$ re-agglomerated at higher loading, the distance between agglomerate particles was longer and caused the less lubricating effect and hindered the movement of polymer chains. Thus, viscosity of PLA with 20 wt% Nano-$CaCO_3$-1041 was nearly the same value as that of PLA with 10 wt% Nano-$CaCO_3$-1041.

In addition, the melt behavior of biocomposites at high shear rate (100-2500 s⁻¹) as occurred in the extrusion sheet process was observed by capillary rheometer. The relation between shear viscosity and shear rate of $CaCO_3$-PLA biocomposite are shown in Fig. 6.

In order to compare rheological behavior of the unfilled and filled PLA melts under steady shear, the data was fitted to the well-known power law model [12-15] as showed in equation (1). This model is used extensively to describe the flow properties of non-Newtonian liquids in theoretical analysis as well as in practical engineering applications.

$$\eta = k\dot{\gamma}^{n-1}$$
(1)

where η is shear viscosity, k is a constant, $\dot{\gamma}$ is shear rate and *n* is the power law index.

When shear viscosity and true shear rate of the melt are plotted in log scale, the slope of the graph relates to the power law index (*n*), which $n < 1$ indicates pseudoplastic behavior (or shear thinning), which shear viscosity decrease with the increasing of shear rate.

The relation between shear viscosity and shear rate of neat PLA, extruded PLA and $CaCO_3$-PLA biocoposite in Fig. 6 were not linear in the full range of shear rates. The slopes of graph were separated into 2 steps; the low shear rate of 100-500 s⁻¹ and the high shear rate of 500-2500 s⁻¹.

Extruded PLA had the power law index higher than neat PLA at both low and high shear rate ranges. When power law index is closed to 1, it means that polymer melt viscosity is less sensitive to shear rate. In consideration of neat PLA and extruded PLA, it is clearly seen that viscosity of extruded PLA is extremely lower than neat PLA. This is due to the thermal degradation causing polymer chains to be shorter and less entanglement during shear flow.

At low particle loading, micro-$CaCO_3$ increased shear sensitivity of PLA biocomposites more than nano-$CaCO_3$ since the agglomerate could be broken from shear stress. In contrast, the high loading of nano-$CaCO_3$ with less agglomeration (Nano-$CaCO_3$-280) reduced shear sensitivity of extruded PLA because of the lubricating effect and the reduction of PLA molecular weight by fatty acid coating on high surface area of nano-$CaCO_3$ particle as discussed earlier.

4. Conclusion

In this study, PLA were compound with micro-/nano- $CaCO_3$ in a co-rotating twin-screw extruder and fabricated by cast sheet process. The agglomerate particles size of micro-/nano-$CaCO_3$ was observed by SEM and size analysis technique. FT-IR absorption peaks revealed that all types of $CaCO_3$ were treated by fatty acid. The amount of fatty acid treated on micro-$CaCO_3$ surface was less than that treated on nano-$CaCO_3$. Thermal stability of fatty acid surface treated $CaCO_3$-PLA biocomposites was lower than that of neat PLA due to PLA thermal degradation. True viscosity of the unfilled and filled PLA melts decreased with increasing shear rate in a non-linear behavior. Adding micro-$CaCO_3$ could maintain viscosity of extruded PLA to be close to neat PLA, while adding nano-$CaCO_3$ with the surface treatment, caused easier flow of high loading PLA.

Acknowledgement

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