



# Viscous and elastic properties of polylactide melts filled with silica particles: Effect of particle size and concentration

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## ABSTRACT

Mixing of inorganic particle into polymer material is widely used to tailor polymer with desired physical properties and processibility, in which the size and concentration of the former play a critical role in polymer processing. In this study, rigid spherical silica particle with varying size (average diameter of 7 nm, 40 nm, and 9  $\mu\text{m}$ ) were used to reinforce polylactide (PLA) by melt compounding. The dependence of rheological properties of PLA/silica composites on the silica size and concentration were examined by dynamical mechanical and creep-recovery experiments. Our results demonstrate that mixing of silica particles into PLA matrix could increase the thermal stability of PLA. Oscillatory shear tests in the linear viscoelastic regime revealed a strong concentration-dependent behavior for the storage, loss moduli, and complex viscosity of the PLA/silica composites by the addition of nanosilica, while these properties were slightly affected by the addition of microsilica at low frequency range. A linear relationship between the silica concentration and the logarithmic form of zero shear viscosity ( $\log\eta_0$ ) of the composites is found when the concentration is below the rheological percolation threshold, whereas the growth rate is inversely influenced by the silica particle size. Creep-recovery experiments indicated that the elastic properties of PLA were more sensitive by the addition of silica than the viscous properties. Even for microsilica, a remarkable enhancement of the elastic properties was found at low silica concentration. A model based on the radius of gyration of polymer matrix  $R_g$  and the mean distance between particles  $D$  is proposed to describe the interactions between polymer matrix and particles. When  $D$  is larger than  $2R_g$ , the particles-polymer interactions are suggested to be responsible for the rheological properties. On the other side, when  $D$  is smaller than  $R_g$ , a silica network structure will be formed and the rheological properties of the composites are dominated by the interactions of particle-particle and particle-polymer.

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## 1. Introduction

Polylactide (PLA), as a biodegradable polymer which is nontoxic to the human body and the environment [1] and, therefore, highly biocompatible, has attracted attention not only in academia but also in industry [2,3]. PLA can be synthesized by ring opening polymerization of lactides which are typically derived from renewable biomass via fermentation [4], thus it is usually considered as “green plastic”. Although the universal application of PLA in

various biomedical, agriculture and industrial fields [5,6], disadvantageous features such as obvious brittleness, low melt strength, and poor heat resistance have limited the expansion and diversification of its application.

In recent decades, extensive modification approaches have been developed aiming to fabricate PLA materials with desirable performance [7–10]. A widely used strategy is the incorporation of inorganic fillers, such as silica, clay, into polymer matrices to improve the physical properties of PLA. As is well known, silica is usually used as reinforcement material in plastic owing to its low cost, rich resource, high strength and modulus [11]. In addition, silica particles with different shape and size could influence the polymers' properties, such as, transparency, thermal stability as well as rheological features in distinct ways [12]. In recent years, it has been recognized that small fractions of nanoscale particles can more significantly improve the performance of polymers above

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what is achieved by microscale particles [13,14]. Apart from the modification of physical properties induced by silica particle, the processibility of the polymer matrix in the molten state is notably influenced as well.

As is well known, rheology is a powerful tool to investigate mesoscopic and microscopic structure of polymer/filler system, and it can also be used to predict the processing behavior of various composites [15]. The short time response such as moduli and viscosity of polymer in molten state over the whole frequencies range could be investigated by oscillation shear measurement, while the creep-recovery test usually measures the long time response of materials [16]. For polymer nanocomposites, the storage modulus  $G'$  and loss modulus  $G''$  increase gradually with the loading of fillers at low frequency range, and the dependency of these two moduli on angular frequency is remarkable weakened at high nanofiller concentration [17]. When the nanofiller fraction exceeds a certain level, the interactions between the fillers are strong enough and lead to the formation of percolated filler network. In this case, the nanocomposites exhibit a solid-like behavior at low frequency range [11,18]. Cassagnau [19] studied the frequency dependence of polystyrene/silica nanocomposites and found that percolated silica network structures formed when silica loading reaches up to 5 wt.%. In the work of Wu et al. [20], it was found that the forecast percolation threshold  $\phi_c$  of the PLA/CNs (carbon nano-tubes) nanocomposite was about 4 wt.%, and the network structure was very sensitive to both the quiescent and the large amplitude oscillatory shear deformation. Wu et al. [21] pointed out that the viscoelastic properties are highly related to the fillers' dispersion state and the interactions between the fillers and the polymer matrix. In the paper of Osman et al. [22], a distinct increase of the moduli and viscosity was also observed at low angular frequency range with the loading of fillers, and this increase was attributed to hydrodynamic effects caused by the presence of solid particles in the melt stream. The influence of micro-particles on rheological properties of polymer has also been discussed in some literature [23,24], similar results were observed by oscillatory shear experiments.

In order to study the elasticity of polymers, creep-recovery experiment up to steady state at molten state was developed. Münstedt et al. [17] found that the elastic properties of poly (methyl methacrylate) melt in the linear range deformation were more significantly influenced by the addition of fillers than viscous ones, and this effect was strongest in the steady-state which needs a long time to reach. Unfortunately, the often used dynamic-mechanical experiments were not very suitable for this situation. Therefore, creep-recovery experiment was evolved as a very suitable tool to characterize the filled materials for its time window can extend to a very wide range [25].

It is well established that the mechanical properties of polymers, such as stiffness, strengthens and toughness, are significantly influenced by particles size, particle/matrix interface adhesion and particle loading [26]. Nofar et al. [27] reported the effects of various additives with different sizes on the crystallization kinetics of PLA, and Katsikis et al. [28] studied the thermal stability of PMMA/silica nano- and micro-composites by dynamic-mechanical experiments. However, there is little publication focus on effect of particle size on the viscous and elastic properties of PLA/silica system.

In this work, three types of different silica particles with a diameter from micro-to nano-were used to fill PLA, and the melt viscosity and elasticity of PLA/silica composites with various silica concentrations were fully studied by dynamic-mechanical experiments and creep-recovery experiments. The correlation between particles size and rheological behavior of PLA/silica composites will be fully analyzed.

## 2. Experimental section

### 2.1. Materials

PLA (trade name 4032D), containing 2% D-lactic acid and 98% L-lactic acid, was purchased from NatureWorks (USA). It is a grade designed for realization of films, density = 1.24 g/cm<sup>3</sup>, the weight average molar mass and number average molar mass are  $M_w = 2.1 \times 10^5$  g/mol and  $M_n = 1.2 \times 10^5$  g/mol, respectively, according to GPC test.

Three types of spherical silica with different size were used in this study. For convenience, we record these three particles as silica 300, silica OX50 and silica 63, respectively. They have different average primary particle size ( $d_{50}$ ) and specific surface area (BET). The details characterization and the morphology structures of silica particles are given in Table 1 and Fig. 1. All silica was used as received without any further treatments.

### 2.2. Preparation of PLA composites

An internal kneader (Haake polyDrive, Thermo Scientific, Germany) is used to prepare the PLA/silica composites with various silica concentrations (1.1, 2.8, 5.8 and 9.0 vol. %). The melt mixing was carried out at 180 °C for 10 min with a screw speed of 100 rpm. For comparison, the neat PLA was subjected to the same treatment as the composites. After granulation the pellets were compression molded to 2 mm thick disk shape plates with a diameter of 25 mm at 180 °C and 200 bars for rheological measurement. Prior to the blending, molding and the measurements, all the samples were dried in a vacuum oven at least 12 h at 60 °C.

### 2.3. Experimental method

#### 2.3.1. Scanning electron microscope (SEM)

SEM (LEO 435VP, Zeiss Leica, Germany) was used to investigate the morphology of silica particles and the fracture surface of PLA composites. Before SEM observation, the polymer composites were fractured in liquid nitrogen to get a good cross section.

#### 2.3.2. Rheological measurements

The rheological measurements were performed under a nitrogen atmosphere by stress controlled rheometer (TA-ARG2, TA, USA) using a plate–plate geometry (25 mm diameter, 2 mm gap). A new sample was used for each run, and a waiting time of 5 min was applied for each test. The reproducibility for all rheological experiments in shear was better than  $\pm 5\%$ .

In order to determine the linear viscoelastic reign, dynamic strain sweep was experienced first and a strain level  $\gamma = 1\%$  is chosen for the dynamic mechanical experiments. The oscillatory time sweeps at low frequencies were performed to ensure the long time rheological tests were carried out in linear range, angular frequency of 0.03 rad/s and strain of 1% were adopted. Oscillatory frequency sweeps ranging from 0.1 to 500 rad/s were performed at different temperature for neat PLA and PLA/silica composites. The storage modulus  $G'$ , the loss modulus  $G''$  and complex viscosity  $\eta^*$  were recorded as a function of angular frequency.

**Table 1**  
The characterizations of silica particles.

Silica	Supplier	$d_{50}$ (nm)	BET (m <sup>2</sup> /g)	Density (g/cm <sup>3</sup> )
AEROSIL® 300	Evonik Industries AG	7	300 ± 30	2.2
AEROSIL® OX50	Evonik Industries AG	40	50 ± 15	2.2
TIXOSIL 63	Rhodia Group	9000	55 ± 5	2.2

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