



# Percolation networks and transient rheology of polylactide composites containing graphite nanosheets with various thicknesses



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## ABSTRACT

The polylactide (PLA) composites with various layered graphite particles were prepared by the approach of solution mixing for the viscoelasticity study. Four kinds of particles with various layered structures, including natural graphite flakes, and graphite nanosheets with the thickness of ~25 nm and ~5 nm, as well as graphene were used as the filler, aiming at establishing the relationship between viscoelasticity of composites and filler structure and networks. The results reveal that transient rheological response of PLA composites shows evident sheet thickness dependence, and the stress overshoot behavior is closely related to the percolation network density during startup and reverse flow. But the strain-scaling characteristic of overshoots is independent of thickness of nanosheets and their networks. The linear dynamic rheology (molten state) and creep measurements (solid state) as well as thermal analyses were then performed to further explore the difference in dispersion and distribution among those layered graphite fillers.

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## 1. Introduction

Apart from being derived from renewable resources, polylactide (PLA) is biodegradable, biocompatible, recyclable, and compostable. Its production also consumes carbon dioxide. These sustainability and eco-friendly characteristics make PLA an attractive biopolymer and an alternative to petrochemical-derived products [1]. Despite a number of promising properties, PLA fails to show similar satisfactory outcomes in its impact strength, heat distortion temperature and gas barrier properties in different fields [2–4], which limit its further application. Increasing realization of how those properties can be improved to achieve the compatibility with end-use requirements, has therefore fueled technological and commercial interest in recent years. Among the most commonly-used modification approaches, hybridization with nanoscaled particles has been revealed to be a simple but very effective strategy to

design or to control hierarchical structures and final properties of PLA [5]. Many kinds of nanoparticles such as silica [6,7], layered silicate [8–13], and carbon nanotubes [14–17], as well as cellulose nanocrystal [18], have been used as the filler successively to improve final properties of PLA, or even to produce new bio-based nanocomposites with unexpected properties [19].

Graphite nanoplatelets (GNPs), also called graphite nanosheets or nanoflakes, are a new carbonous material composed of stacked 2D graphene sheets with outstanding electrical, thermal, and mechanical properties [20]. In comparison with other classic 2D nanoparticles, such as clay, GNPs have lower mass density, and are highly electrically and thermally conductive due to the sp<sup>2</sup> hybridized carbons in the monolayer graphene within GNPs [21]. Therefore, GNPs, including the graphene, have been considered as the next generation filler to improve the properties of polymers [22]. Large numbers of GNPs-based polymer nanocomposites have so far been prepared successfully [23–25], also including the PLA/GNP composites [26–45]. The structure and properties of PLA/GNP composites have hence been extensively studied and the focus points are: 1) crystallization behavior and kinetics [26–31]; 2) interface tailoring and morphology control [32–34]; 3) thermal

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and electric conductivity behaviors [34–38]; 4) mechanical properties, especially the reinforcing and toughening effect of GNPs or graphene [38–42]; 5) thermal degradation and biodegradation as well as other biological evaluations [41–43].

From processing and application points of view, the rheological behaviors of a polymer composite system are very important to because the flow/deformation histories determine the final mesoscopic structure and supermolecular morphology of composite materials [46]. On the other hand, rheology can be used as a powerful tool to investigate hierarchical structures of a polymer/GNP composite system [21,24,25], such as the percolated network or the flocculated structure of GNPs or their tactoids, and the confinement effect of GNPs on the motion of polymer chains. The rheological behavior of PLA/GNP composites has been studied preliminarily [42,44,45]. Similar with the nanocomposites containing layered silicates [47] or carbon nanotubes [48], PLA/GNP composites also show typical non-terminal modulus responses at the low-frequency region during small amplitude oscillatory shear, which is attributed to the formation of a GNP network. The percolation thresholds can then be determined according to the transition from liquid to pseudo-solid-like responses at terminal region [44,45]. Those reported studies mainly focused on the linear rheology, which is limited in a quite narrow strain/stress region and, can merely give steady-state data during shear flow. It is well known that the percolation of nanofiller in the polymer matrix is time-dependent during shear flow [48]. The transient responses may hence reveal much more useful information on the mesoscopic structure of the PLA composites with graphite nanoplatelets or graphene because the transient rheological behavior are closely related to the evolution of transient percolation network. However, there is no relative report can be found in the literatures. In this work, therefore, the transient rheology of the PLA composite filled with graphite nanoplatelets were studied in detail. Three kinds of graphite nanoplatelets, including much-layered one (thicker nanosheets), few-layered one (thinner nanosheets), and graphene (thinnest nanosheets), were used as the filler to further explore the relations between short-term structure of filler particles and their long-term percolation structure. The natural graphite flakes (thickest one) were also incorporated with PLA for the better comparison with other three kinds of composites. Besides, the linear viscoelastic behavior, such as creep and creep-recovery, and the thermal stability of those composites were also studied, aiming at providing a full understanding on property-graphite structure relations of the PLA composites.

## 2. Experimental

### 2.1. Material preparation

Poly lactide (PLA, 2002D) was purchased from NatureWorks Co. Ltd., USA, which has a *D* content of 4.25 wt% and a residual monomer content of 0.3 wt%, with the density of 1.24 g cm<sup>-3</sup>. Its number average molecular weight is about 80,000 g mol<sup>-1</sup>. The graphite nanoplatelets used in this work are also the commercial products. The thicker one (XF021, Purity > 99.5%, ≤25 nm, hereafter referred to as TGN) was purchased from Nanjing XFNano Material Tech Co. Ltd., P. R. China, and the thinner one, namely few-layered graphite nanoplatelets, (SGNP-F2, Purity > 99.5%, ≤5 nm, hereafter referred to as FGN) from Nanjing SCF Nano Tech Co. Ltd., P. R. China. The former is black particle and the latter black floccule. Both have a special surface area of 50 m<sup>2</sup> g<sup>-1</sup>. The detailed structure parameters of these two nanoplatelets are listed in Table 1. Apart from those two nanoplatelets mentioned above, the graphene nanosheets prepared in the laboratory were also used in this work. Firstly, the graphite oxide powder was synthesized from natural graphite

flakes by the modified Hummers method [49], and then, dispersed into CH<sub>2</sub>Cl<sub>2</sub> and sonicated with an ultrasonic cell smash (Scientz II-D, Ningbo Scientz Biotechnology Co., Ltd, P. R. China.) to obtain the graphene suspension for the following composite preparation. The TEM images of as-prepared graphene nanosheets are shown in Fig. S1 of the Supporting Information. Their structure parameters are also listed in Table 1. The natural graphite flakes (30–70 μm, Purity > 99.95%, abbreviated as NG) used here were provided by Shandong Jinrilai Material Co. Ltd., P. R. China. The PLA composites containing various graphitic fillers were prepared by a solution mixing method reported by Qiu et al. [27,28]. The filler loading for all composite samples is 3 wt%. The neat PLA also experienced same solution process to keep identical thermal and stress histories with those of the composites.

### 2.2. Morphology and structure characterizations

The microstructure of the graphite nanosheets was detected by a D8 ADVANCE X-ray diffractometer (XRD, BRUKER AXS, Germany) with Cu target and a rotating anode generator operated at 40 kV and 40 mA. The scanning rate was 2° min<sup>-1</sup> from 2° to 40°. The dispersion state of graphite nanosheets in the PLA matrix was investigated using a Tecnai 12 transmission electron microscope (TEM, Philips, Netherlands) with 120 kV accelerating voltage. The microtomed sample sections with 100 nm thickness were used for the TEM observation. The distribution of graphite particles in matrix was evaluated by an optical microscope (OM, Leika DMLP, Germany). The sheet samples used for the OM observation were prepared by compression molding at 180 °C and 10 MPa.

### 2.3. Mechanical property characterizations

The tensile properties of the PLA composites were determined by an Instron Mechanical Tester (ASTM D638) at a crosshead speed of 50 mm/min at 25 °C using the dog-bone shaped specimens. Dynamic mechanical analysis (DMA) were performed on a DMA 242 C analyzer (NETZSCH Instruments, Germany) with bending mode over a temperature range from 20 °C to 100 °C at various frequencies (1 Hz, 5 Hz and 10 Hz). The heating rate was 3 °C/min. Three rectangular specimens (30 mm × 5 mm × 1 mm) were tested for each composite. Creep tests were conducted on a DMA Q800 analyzer (TA Instruments, USA) with tensile mode at various temperature and stress levels. The applied stress 1.0 MPa was determined by the tensile tests, which is within the linear viscoelastic region of all samples. The duration of measurements was determined as 10 min and 30 min for the creep and creep-recovery tests, respectively. The creep/recoverable strain and compliance were recorded as a function of the time. Three rectangular specimens (30 mm × 5 mm × 1 mm) were tested for each composite sample.

### 2.4. Melt rheology measurements

The melt rheological tests were performed on a rotational rheometer (HAAKE RS600, Thermo Electron Co., USA) equipped with a parallel plate geometry (20 mm diameter plates). The samples with the thickness of 1.0 mm were melted at 180 °C for 3 min in the parallel plate fixture to eliminate residual thermal histories and then experienced various shear flows. During steady shear flow, the stress and viscosity responses to the shear rates were recorded. In the transient rheological measurements, the flow reversal and startup of shear were applied. Firstly, the sample experienced shear flow at the predetermined rates, during which the transient shear stress was monitored until the stress response tended to be steady. The flow was stopped then, and the sample was kept quiescently for a time period (hereafter referred to as the

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