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# Structure and linear viscoelasticity of polymer nanocomposites with agglomerated particles

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#### ABSTRACT

The connection between the structures and the linear viscoelasticity was revealed in this work for polymer nanocomposites containing agglomerated particles. A new image analysis method using the greyscale histogram of TEM images was suggested to determine the local volume fraction of nano-particles inside an agglomerate, which represents the degree of agglomeration. It is found that the local volume fraction of nanoparticles is strongly related to the particle-polymer interaction. Such result was justified by a new rheological analysis based on the recently suggested modulus decomposition in the linear viscoelastic properties of polymer nanocomposites, from which the combined shift factor due to the hydrodynamic effect was used to quantify the local volume fraction of nanoparticles. Moreover, a two phase model was suggested to describe the linear viscoelasticity of such polymer nanocomposites. The success of this model in different polymer nanocomposites implies the rationality to regard the isolated agglomerate as a composite droplet in the polymer matrix.

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#### 1. Introduction

Polymer nanocomposites have attracted great attentions from academy and industry due to the significant roles of nanoparticles (NPs) in enhancing or altering the mechanical, electrical, magnetic, and optical properties. Great efforts have been paid to understand the contribution of particles to the mechanical properties either from experimental aspects or from theoretical aspects [1]. It is well known that the state of particles dispersion is essentially important in the nanocomposites, which is determined by the competition between particle-particle interaction and particle-polymer interaction [2-5]. Attractive interaction between particles is very common in polymer nanocomposites, which may result in agglomeration of particles, and the smaller the particle size, the more evident the agglomeration. Actually, agglomeration has been observed in various systems, including nanosilica in styrenebutadiene rubber [6,7], polystyrene [8,9], polypropylene [10], poly(methyl methacrylate) [11], poly(ethylene oxide) [12,13], polyolefin elastomer [14–16], and carbon black in polyethylene [17,18], polypropylene [19,20], polystyrene [21], poly(methyl methacrylate) [22,23]. The agglomeration of NPs is not limited for the spherical shape, and it is also observed for fibrous particles [24–26]. In practice, the dispersion of NPs is also affected by sample preparation methods, such as solvent evaporation, rapid precipitation and melt mixing. The structure of agglomerated NPs can be observed in real space

by transmission electron microscopy (TEM) or atomic force microscopy (AFM), or in reciprocal space by (ultra) small angle X-ray scattering (SAXS). Fractal clusters of particles can be readily recognized from the observation in real space, from which the shape and the size of agglomerates can be determined. To understand how NPs agglomerate, it is necessary to know the number of particles in an agglomerate, which is rather difficult using the observation either in real space or in reciprocal space. Only a few studies [5,8] had tried this problem, where the minimum number of particles in the agglomerates could be estimated.

Because the state of dispersion (or agglomeration) determines the contribution of particle to the mechanical properties, rheology becomes a frequently used method to study the dispersion of particles in polymers. Some aspects on the linear viscoelasticity of polymer nanocomposites has been reviewed recently [27]. Indeed, several common characteristics have been found, e.g., the transition from viscoelastic liquid ( $G' \sim \omega^2$  and  $G'' \sim \omega^1$ ) to viscoelastic solid ( $G' \sim \omega^0$  and  $G'' \sim \omega^0$ ) as NP's content increases, more evident

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increment in the storage modulus than that in the loss modulus, and more significant increment of dynamic moduli at low frequency than at high frequency. Many theoretical works have been devoted to understand the linear viscoelasticity of polymer nanocomposites. The work pioneered by Einstein [28,29], followed by Batchelor and co-workers [30–32] and others [33–35] have solved the problem in Newtonian matrix with well dispersed particles. The agglomerates of particles, however, are not considered because only pair correlation function is adopted. It is also difficult to include the viscoelasticity of polymer matrix [36]. For agglomerated system, several phenomenological methods (such as Maxwelltype models) have been adopted [37,38], however, neither the low frequency modulus nor the high frequency modulus can be accurately described.

In fact, considering the respective contribution from hydrodynamics at high frequency and structural units at low frequency, it is tended to model them separately, which is the approach called "two-phase" model. The hydrodynamic contribution is calculated from the viscoelasticity of matrix by multiplying an amplification factor, which depends on the volume fraction of particles only. Such hydrodynamic factor is usually determined from the theoretical works of Batchelor [30-32], or from experiments by using the loss modulus [40] or the complex modulus [41]. However, as pointed out in our recent work [14], the hydrodynamic contributions in the storage modulus and the loss modulus are quite different in viscoelastic matrix. These approaches to determine the hydrodynamic effect cannot describe the dynamic moduli in a quantitative manner simultaneously. Phenomenological models to account for the structural contribution have also been suggested by Leonov et al. [42,43], Isayev et al. [44,45], and Grmela et al. [46-48], for either spherical particles or layered particles. But the quantitative comparisons are not satisfactory, and the deviations from experimental data still remain in the recently modified versions of Leonov model [49,50]. An empirical expression with three fitting parameters has been suggested by Song and co-workers [51,52] recently, where the elastic and viscous contributions were represented by two empirical different scaling functions, and the frequency dependency is tuned by a relaxation exponent. Such model can fit the experimental data in a satisfactory manner especially above percolation concentration, however, these adjusting factors are suggested to depend on the filler content only, which is unable to predict the change of linear viscoelasticity of polymer nanocomposites after subjecting to shear flow [53].

In this work, we will suggest two methods to quantify the local concentration of NPs in an agglomerate. One is the image analysis based on the greyscale histogram of TEM images, the other is the rheological analysis based on the modulus decomposition. Furthermore, we will suggest a new approach to model the linear viscoelasticity of polymer nanocomposites. The starting point is to regard the agglomerates together with the surrounding polymer as the elementary structural unit, which implies that the nanocomposites resemble an emulsion with droplets filled by high content of particles. The model predictions are compared with the experimental data of different nanocomposites.

#### 2. Experimental

#### 2.1. Materials

Three polymers are used in this work. Poly(ethylene-co- $\alpha$ -butene) (PEB, Tafmer A-70090) with the melt flow index (MFI) of 70 g/10 min (190 °C, 2.16 kg) and density of 0.893 g/cm<sup>3</sup> was obtained from Mitsui Chemicals, Japan. Linear low density polyethylene (LLDPE, Dowlex 2047AC) with density 0.917 g/cm<sup>3</sup> and MFI 2.3 g/10 min (190 °C, 2.16 kg) is obtained from the Dow

Chemical Company. Poly(methyl methacrylate) (PMMA, IF850) with weight average molecular weight 159 kg/mol and polydispersity of 1.85 was supplied by LG Chemical Ltd. The zero shear viscosity of polymers is estimated by fitting the complex viscosityfrequency curve using the Cross model [54]. The zero shear viscosity of PEB is 2833 Pa s at 180 °C and 13762 Pa s at 120 °C. The zero shear viscosities of LLDPE at 160 °C and PMMA at 180 °C are 6874 Pa s and 85108 Pa s, respectively.

Hydrophobic fumed silica nanoparticles (R202, named as SiO<sub>2</sub>-A) was purchased from Degussa, which is prepared by a flame hydrolysis process. The primary particles have nearly spherical shape, and are fused together to form aggregates with a branched structure. The average primary particle size is about 14 nm with the specific area of  $100 \pm 20$  m<sup>2</sup>/g. Those aggregates tend to build up large agglomerates. It has been partially treated by poly-dimethylsiloxane according to the supplier. The other silica (Ludox SM-30, SiO<sub>2</sub>-B) is a colloidal one, and purchased from Sigma Aldrich. The average particle size is about 8 nm with the specific area of 320-400 m<sup>2</sup>/g. Its dispersion in polymer matrix depends on the interactions Carbon Black (CB, Vulcan XC200), a conductive grade by Cabot Corporation, is also used in this work.

#### 2.2. Sample preparation

PEB and silica nanoparticles (SiO<sub>2</sub>-A) were dried at 50 °C in a vacuum oven for at least 48 h before processing. PEB/SiO<sub>2</sub>-A nanocomposites were prepared by melt mixing in a torque rheometer (XSS-300, Shanghai Kechuang Rubber & Plastic Equipment Co, China) at a rotational speed of 120 rpm for 30 min at the mixing temperature 180 °C. To reduce the thermal degradation, a stabilizer, 0.05 wt% Irganox 1010 (Ciba Specialty Chemical), was added to the materials before blending in an internal mixer. The samples for rheological measurements were prepared by compression moulding into a disc-like form with diameter 25 mm and about 1 mm thick at 120 °C under 10 MPa. Four PEB/SiO<sub>2</sub>-A nanocomposites with volume fraction 0.8%, 1.7%, 2.5% and 3.3% were prepared by this method.

PMMA was dissolved in dimethyl formamide (DMF) and stirred for 12 h. Nanoparticles (SiO<sub>2</sub>-B) were dispersed in DMF. The nanoparticle solution was sonicated 12 h before being mixed with the PMMA solution. Then the nanoparticle solution was mixed with the PMMA solution, and the mixed solution was dried under vacuum at 150 °C for 1 h, which allows the solvent to evaporate rapidly. The cast samples were then moulded into 1 mm thick and 25 mm diameter by a hot compression at 180 °C under the pressure of 10 MPa for 10 min. Two PMMA/SiO<sub>2</sub>-B nanocomposites with volume fraction 1.4% and 4.7% were prepared by this method.

LLDPE and carbon black were vacuum-dried at 85 °C for 8 h before mixing. To prepare LLDPE/CB composites, LLDPE is mixed in a HAAKE Rheocord 90 Mixer first. When the torque of mixer reached an equilibrium value, certain amount of CB is added and mixed for 15 min under 30 rpm and 160 °C. The samples were then compressed into 1 mm thick sheet by a hot compression at 160 °C under the pressure of 10 MPa for 10 min. Three LLDPE/CB nano-composites with volume fraction 2.5%, 3.9% and 4.8% were prepared by this method.

#### 2.3. Methods

Rheological measurements were performed on a straincontrolled rotational rheometer (ARES-G2, TA Instruments, USA). Parallel-plates with 25 mm in diameter were used. The gap was set as 1 mm. Dynamic frequency sweeps were conducted from 100 rad/ s to 0.01 rad/s under 1% strain amplitude. Such small amplitude of strain guarantees the linear viscoelastic behaviour of samples. For Download English Version:

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