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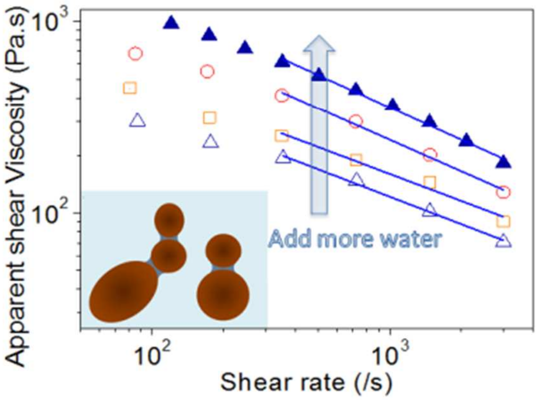
Graphical Abstract



We provided a reversible, simple, inexpensive and environmentally-friendly way to control the rheology of polymer composites.

Revised Manuscript

Increasing the apparent shear viscosity of polymer composites by uptake of a small amount of water

Dapeng Wang[a,c]*, Xiang Wang[c], Yuan Yuan[a], Weihua, Li[b], Huiwen Tian[b]*, Shugao Zhao[a*]

a. Key Laboratory of Rubber-Plastics of Ministry of Education/Shandong Provincial Key Laboratory of Rubber-plastics, Qingdao University of Science & Technology, Qingdao 266042, PR China

b. Key laboratory of Corrosion Science, Shandong, Institute of Oceanology, Chinese Academy of Sciences, Qingdao 266071, PR China

c. Department of Chemical and Biological Engineering, University of Colorado Boulder, Boulder, Colorado 80309, United States

*Corresponding author: Dr. Huiwen Tian

E-mail address: tianhuiwen1983@gmail.com (H.T)

*Corresponding author: Dr. Dapeng Wang

E-mail address: dapeng.wang@colorado.edu (W.D)

*Corresponding author: Prof. Dr. Shugao Zhao

E-mail address: zhaosgqd@hotmail.com (S.Z)

Abstract: The mixing of polymers and particles provides a new avenue for engineering composite materials that display advantageous magnetic, electrical, dialectical and mechanical properties. The mixing quality and the derived properties are highly determined and controlled by the rheological behavior of the composite materials during mixing. Here, we studied shear rheology of a protocol system, the polyamide/ferrite composites. The key findings of this study were that the apparent shear viscosity of polymer composites can be manipulated by uptake of a trace amount of water (less than 0.3 wt%). Compared to the traditional way to tune the viscosity by adding either lubricants or thickeners, our findings presented here provided a reversible, simple, inexpensive and environmentally friendly way to control the rheology of polymer composites.

Keywords: polymer composites; shear rheology; capillary forces; ferrites; polyamide;

1. Introduction

Polymer-based materials have attracted remarkable scientific and technological interest due to their wide applications[1]. Various functional fillers, e.g., carbon black[2], graphene[3] and single-wall nanotube[4] are commonly doped into polymer matrix to manipulate mechanical, electric and dielectric properties. In particular, polymer/magnetic particle mixtures, as a new class of polymer composites, have stimulated great interest recently due to their promising applications in biomedicine[5] and micromachine[6], et al. Mixing of magnetic particles into polymer matrix, not only introduces the magnetic properties, but also, for example, could induce a shape-memory effect by inductive heating of magnetic particles[7]. Compared to conventional metal-based magnets, the polymer/magnetic particle composites have several notable advantages, including the low-cost, easy-processing and environmentally-friendly, etc. However, in the case of polymer/magnetic particle composites, abundant magnetic particles should be filled into polymer matrix to obtain sufficiently magnetic properties. A high fraction of magnetic particles in composite could significantly impact the rheological behavior of polymer melts during the processing. Therefore, the fine control of the rheological behavior is very important to optimize the quality of polymer-based materials[8].

Physically, the mechanical and rheological behavior of the polymer composites is mainly determined by (i) the intrinsic properties of polymers[9] , (ii) the fraction of particles[10], (iii) the interfacial interaction between polymers and filler particles[11, 12] and (iv) the interaction among particles[13, 14]. In this study we highlight the effect of the interparticle interaction. It is well known that the interparticle interactions are strongly promoted by presence of pendular water bridges between particles, resulting in an attractive force, i.e., the capillary force formed due to both the surface tension and pressure differences at a curved surface[15, 16]. Theoretical calculations showed that the strength of capillary forces can much exceed that of ubiquitous interactions, e.g., the van der Waals forces[17, 18]. Accordingly, a significant increase of cohesiveness in wet granular materials was found.[19, 20] . This phenomenon could also reappear in the liquid state[21, 22]. For example, Koos et al. recently showed that particle suspensions can achieve a distinct increase of both yield stress and viscosity by mixing a trace amount of immiscible liquids[23-27]. Despite the attractive phenomena in wet granular materials and in particle suspensions, little is known, however, about the influence of secondary liquids on the rheology of polymer composites which usually carried out at a temperature well above ambient conditions.

Here, we present an initial study to investigate the rheology of polymer composites by uptake of secondary immiscible liquids. To mimic the extrusion which is commonly used in polymer processing, the steady shear flow behavior was explored by using a capillary rheometer. We demonstrated that addition of less than 0.3 wt% water resulted in a significant increase of the apparent shear viscosity for a typical polymer composite, consisting of polyamide (PA) and ferrite particles. The increase depends on the particle surface properties, viscosity of polymer matrix, the amount of added water and the shear rate, respectively.

2. Experimental

2.1 Sample preparation

The materials information can be found in supporting information. The polymers, polyamide 6 (PA6)/polyamide 6,10 (PA6,10) and ferrites were first dried at 80°C in a vacuum oven for 24 hours. Before extrusion processing, quantitative amounts of polymers, ferrites and coupling agents (1 wt% of silane, if need be) were preliminarily mixed under vigorous stirring. Then, mixtures were granulated by a Brabender two-screw extruder (ZKS-25, Krupp Werner & Pfleiderer GmbH, Stuttgart, Germany).

The rotation speed of screws was kept at a constant of 80 rpm. The neat PA6 was also granulated at the same condition.

The polymer composites for the rheological study were first dried in a vacuum oven for 48 h at 80°C. To add water, polymer composites were placed in a humid environment (relative humidity ≈ 60-70%; temperature ≈18-22°C for three months). The water absorption can be characterized by measuring the weight loss as a function of time in a vacuum oven at temperature of 80°C.

2.2. Materials Characterization

The steady shear rheological behaviors of the materials were measured by Rosand Precision rheometer (Bohilin Instrument, Malvern, UK) in the double-bore mode at 270°C. The length/diameter ratio of the capillary in one bore was 16/1 while the orifice die in the other bore was a zero length capillary. The apparent shear stress (τ) in capillary can be calculated by $\tau = \Delta P \cdot D / 2L$, where ΔP was the total pressure drop during extrusion, D and L were the diameter and length of the capillary (mm), respectively. ΔP was calculated according to the Bagley correction. The apparent shear rate ($\dot{\gamma}$) was defined as: $\dot{\gamma} = 4Q/\pi D^3$, where Q was the volumetric flow rate. Then the apparent shear viscosity (η_a) could be obtained by $\eta_a = \tau / \dot{\gamma}$. The final results were obtained as an average of independent experiments performed on different days.

The morphologies were observed by a scanning electron microscope (JEOL JSM-6700F). Specimens were fractured by tensile testing at a drawing speed of 10cm/s. The tensile-fractured surfaces were coated with a thin layer of gold by JFC-1600 Auto Fine Coater and then were examined by SEM.

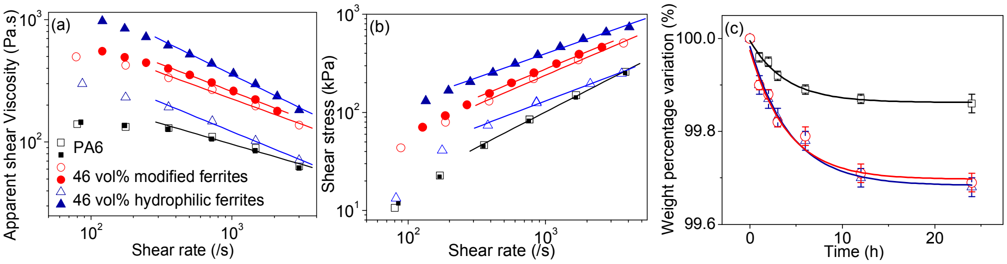


Figure 1 (a) The apparent shear viscosity vs. shear rate and (b) shear stress vs. shear rate for PA6 and PA6/ferrite composites. The hollow symbols represent the samples without uptake of water while the solid symbols indicate that PA6 and PA6/ferrite composites contain 0.15wt% and 0.3wt% added water, respectively; the solid lines represent fits by the power law in the range of 300-3000 s^{-1}; (c) The weight loss of the samples as a function of drying time. The symbols are the same as these in (a).

3. Results and discussion

Samples for rheological studies were prepared by extruding PA/ferrite mixtures. The volume fraction of ferrites in polymer composites is 46%. Two types of ferrites with different surface properties were used in this work: one was naturally hydrophilic and the other one experienced silane surface modification which made it more hydrophobic. It should be noted that because the silane used has an amino group at the end of its aliphatic chain, the surface of silane-modified ferrite particles is still hydrophilic. Our control experiment showed that a water droplet can wet on a stack of silane-modified ferrite particles. Figure1a shows typical curves of the apparent shear viscosity vs. the shear rate for PA6 and PA6/ferrite composites without uptake of water (hollow symbols). All the PA/ferrite composites exhibit shear thinning as the increase of the shear rate (Figure 1a), as expected due to chain alignment and disentanglement[28]. The rheological behavior of all samples studied obeys the power law $\eta_a = K\dot{\gamma}^{n-1}$ (Figure 1a) and $\tau = K\dot{\gamma}^{n}$ (Figure 1b) in the shear rate range from 300 to 3000 s^{-1}, where K and n are the consistency index and the power law index. The viscosity increases as the incorporation of the ferrites, in particular in the low shear rate range ($\dot{\gamma} < 300$ s^{-1}). Independent measurements for $\dot{\gamma}$ in the range of 3-80 s^{-1} are performed and averaged to obtain zero shear viscosity by extrapolating the viscosity to zero shear rate, yielding values of 162 ± 5 Pa·s for neat PA6, 390 ± 21 Pa·s and 582 ± 70 Pa·s for PA6 mixing with hydrophilic and silane-modified ferrites, respectively. We note that the zero shear viscosity of the polymer/silane-modified ferrite composites is almost two times higher than that of polymer/hydrophilic ferrite composites. We attributed this deviation to an increased wettability between PA6 matrix and silane-modified ferrites, as discussed below.

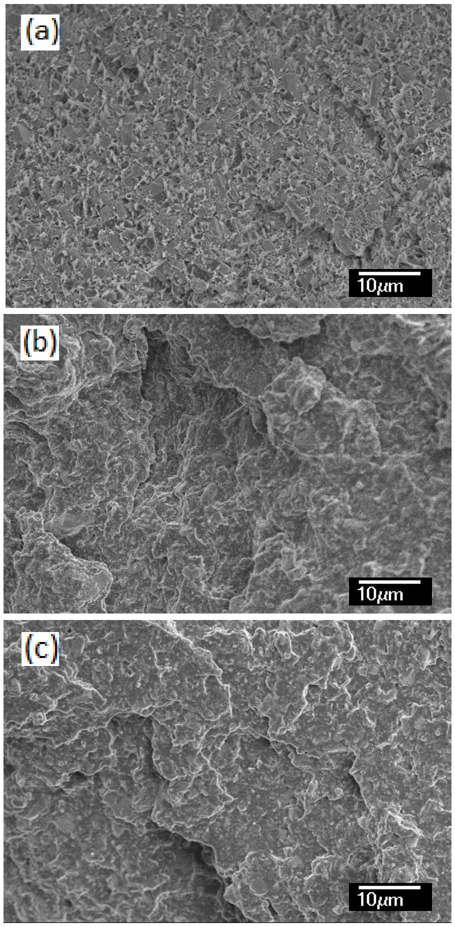


Figure 2 SEM images for the tensile fractured surface of PA6/hydrophilic ferrite composites (a) in the absence and (b) in the presence of 0.3wt% water, (c): tensile fractured surface of PA6/silane-modified ferrite composites in the absence of water. In (a), ferrite particles is clearly observed in SEM picture, indicating that the fracture occurs at the interface of ferrite particles and PA6 matrix. No particles are observed,

demonstrating that the broken occurs within the PA6 bulk during tensile testing. The scale bars are 10 μm.

To qualitatively compare the wettability of two types of ferrites to PA6 matrix, polymer composite specimens were fractured by tensile testing at a constant drawing speed of 10cm/s and the surface morphologies were inspected by SEM. As shown in Figure 2a, well-defined PA6-ferrite interfaces are observed for the samples containing hydrophilic ferrites, indicating that the fracture occurs at the interface of hydrophilic ferrites and PA6 during tensile testing. On the other hand, for the polymer composites consisting of silane-modified ferrites, few ferrites are observed on the fractured surface (Figure 2c), which indicated that the tensile fracture occurs within the polymer bulk rather than at the PA6-ferrite interface. Overall, our SEM observations evidently indicated an increase of wettability between silane-modified ferrites and PA6.

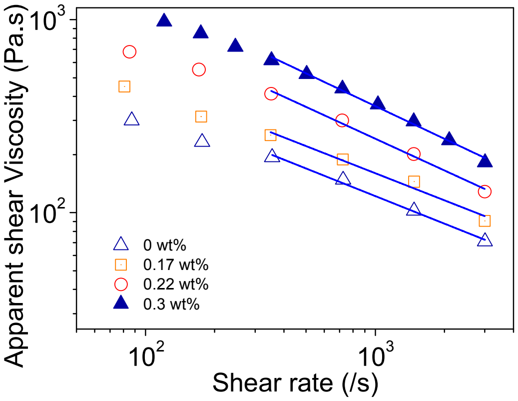


Figure 3 Effect of the amount of added water on the plots of apparent shear viscosity against the shear rate for PA6/hydrophilic ferrite composites.

In the following, the extruded samples were placed in a humid environment to add water. The detailed procedure can be found in the experimental section. Afterward, the amount of water was varied by controlling the drying time in a vacuum oven at 80°C (Figure 1c). From figure 1c, we note that addition of ferrite particle into PA6 bulk can increase the water absorption capacity because water molecules like to wet a curved hydrophilic surface due to the Laplace pressure. Moreover, the fact that the water absorption capacity of two types of polymer composites indicates that two types of ferrite particles have a similar wettability to water. Figure1a and 3 illustrated the effect of added water on logarithmic plots of the viscosity vs. the shear rate for PA6 and PA6/ferrite composites. The apparent shear viscosity vs. shear rate for both dry and humid PA6 is almost identical in the observed shear rate range. However, the PA6/hydrophilic ferrite composites were very sensitive to added water. For example, uptake of merely 0.3 wt% water resulted in a viscosity increase by a factor of 3.7 over dried samples at a shear rate of 170s^{-1}. Most notably, the rheological behavior of PA6/ferrite composites can be manipulated by controlling the amount of added water: decreasing the amount of added water can reduce the apparent shear viscosity in the studied shear rate range. Moreover, we noted that the variation of the apparent viscosity strongly depended on the particle surface properties. To better visualize the difference, we plotted the apparent viscosity difference, i.e., the ratio of the apparent viscosity for composites in the presence ($\eta_{a,p}$)/absence ($\eta_{a,a}$) of water as a function of the shear rate, as shown in Figure 4a. One observed that $\eta_{a,p}/\eta_{a,a}$ of PA6/hydrophilic ferrite composites was much higher than that of PA6/silane-modified ferrite composites. Furthermore, $\eta_{a,p}/\eta_{a,a}$ decreased as increasing the shear rate, with the fact that the slope for PA6/hydrophilic ferrite composites was much sharper than that for PA6/silane modified ferrite composites.

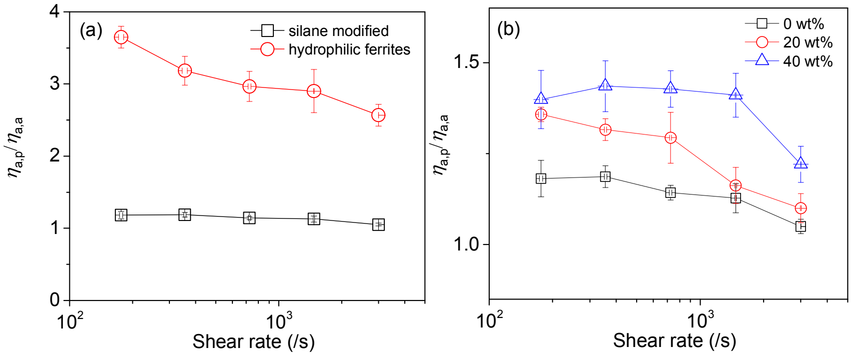


Figure 4 The ratio of apparent viscosity in the presence ($\eta_{a,p}$) and in the absence ($\eta_{a,a}$) of 0.3 wt% water as a function of the shear rate for (a) PA6 composites containing different types of ferrites and (b) PA6-PA610 mixture/silane-modified

ferrite composites; The fraction of PA610 in polymer matrix is 0, 20 and 40 wt%, respectively.

There are several possible sources for the unexpected increase after the humid aging. First, as PA6 is also capable of absorbing water, the presence of water must influence the rheological behavior of pure polymers[29]. Previous studies showed that water can penetrated into the hydrogen bonding networks of PA matrix, acting as the lubricant and the viscosity was accordingly decreased[30]. However, our control experiments indicated that a trace amount of water (0.1-0.2wt%), either directly or owing to placing in a humid environment, cannot visually influence the rheological behavior of both PA6 and PA6,10 at 270°C. Moreover, the aging of polymers in a humid environment may contribute to the viscosity increase. To rule out this effect, a humid aged sample is re-measured after placing the sample in a vacuum oven at temperature of 80°C for 48 hours. The viscosity of the evaporated sample was then compared with an original dried sample. These two samples exhibited same viscosity values in the studied shear rate range within experimental errors, indicating that the rheological behavior of polymer composites is completely reversible by adding and removing water. Further, absorbed water on ferrite surfaces may interact with the PA6 matrix by the hydrogen bonding, as suggested by Han, Larché and their coworkers[31, 32]. However, Figure1c demonstrates that the surface modification does not alter the water absorption capacity of the polyamide-ferrite composite. In this case, a nearly same amount of added water gives rise to a notable difference in the rheological behavior makes hydrogen bonding an unlikely mechanism for the viscosity increase.

Interestingly, we noted that, for PA6/hydrophilic ferrite composites in the presence of 0.3 wt% water, the fracture during tensile testing occurred within the polymer bulks, as shown in Figure 2b. As mentioned in the introduction, the rheological and mechanical properties are determined by, i) the intrinsic properties of polymers (ii) the fraction of particles, (iii) the interfacial interaction between polymers and filler particles and (iv) the interaction among particles We have ruled out the first two candidates because the polymer properties and the fraction of particles did not change during the humid aging. For (iii), hydrophilic ferrite particles have hydroxyl groups on surface. For silane-modified ferrite particles, only a small fraction of hydroxyl groups is functionalized by silane. Therefore, it is unlikely attributed this scenario to the increased interaction between polymers and particles, because the absorption of water does not change either the chemical affinity of hydrophilic ferrite particles or the surface chemistry of silane-modified ferrite particles. Accordingly, the observation in figure 2b inferred a drastically increase of particle-particle interaction. The forces between particles could be expressed as $F = F_c + F_B + F_E + F_{vdW}$ including the capillary force (F_c) and the ubiquitous interactions, consisting of chemical bonding force (F_B), electrostatic force (F_E) and the van der Waals force (F_{vdW}). Because water absorbs on the ferrite surface physically, the contribution of the chemical bonding forces was then neglected. As ferrite particles disperse in the PA6 matrix, the electrostatic forces are expected to be excluded. The van der Waals forces can be calculated by $F_{vdW} = A_H R / 12h^2$ where R is the particle radius, A_H is Haymaker's coefficient, and h is particle separation. A typical value of the van der Waals force between two 1μm-sized objects is approximate 1nN [24]. This value is of two orders of magnitude lower than what we predicted for capillary forces, as discussed below.

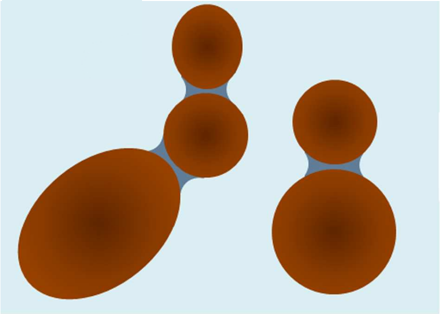


Figure 5 The schematic illustration shows the way that pendular water bridges connect particles. The blue objects and brown particles represent water and ferrite particles.

The secondary liquid used here, water, is able to preferentially absorb on particle surface. Then liquid menisci, between the two particles have a negative radius of curvature, exhibiting a pressure difference between liquids, i.e., the pressure inside the secondary liquid is lower than that in the primary liquid (Figure 5)[33]. The pendular bridges formed between two particle surfaces cause an attractive force, the capillary force. The strength of capillary forces links to the wettability of ferrite particles to the primary/secondary liquids. This can be described by the Young's equation: $cos\theta = (\gamma_{SA}-\gamma_{SB})/\gamma_{AB}$. Here, γ_{SA}, γ_{SB}, γ_{AB} are the interfacial tension of solid-primary liquid, solid-secondary liquid, and liquid-liquid interfaces, respectively. Pendular bridges are formed between particles only if $\gamma_{SA}-\gamma_{SB}>0$, i.e., secondary liquids preferentially wet particle surface[34, 35]. Qualitatively, the capillary force due to a pendular bridge between two particles in contact can be estimated as $F_c = 2\pi R\gamma_{AB}\cos\theta$[36]. Typical values for the capillary force are about 200 nN in which the particle radius R is 1μm, the interfacial tension γ_{AB} is 30 $mN\cdot m^{-1}$ and assuming the wetting angle θ =0°. This is in qualitative agreement with precise calculation of capillary forces for water between two 1 μm particles[18, 37]. For comparison, the value of the van der Waals force is much smaller (1nN, as described above). Then a distinct viscosity increase is attributed to the capillary forces.

It is known that for polymer composites during the shear flow, polymer chains, either chemisorbed or physisorbed on particle surface, can raise the viscosity by dynamically bringing particles together[38, 39]. It is striking to observe that water can play an analogous role in polymeric fluid flow even at 270°C. The pressure applied on the piston of the rheometer is 1MPa, where the boiling point of water is 157°C, well below the processing temperature used here. Klein and co-worker have previously demonstrated that water is able to be absorbed in a confined nanogap at temperature where the bulk is amorphous[40]. In this physical picture, a hydrophilic surface, compared to a more hydrophobic one, provides an additional surface force to promote the absorption. However, absorbed water on the surface still retains fluidity because the ordering effect cannot overcome the entropy of hydrogen bonding[40]. This is consistent with our observations in Figure 4a where polymer composites containing hydrophilic ferrites exhibit a more pronounced increase in apparent viscosity in the shear rate range studied.

The effect of the capillary force should depend on the dynamic contact between particles in a shear field. One can imagine that, when a pendular bridge is broken, a disjoined particle is freely diffusing until the contact with another single particles or particle clusters via the pendular bridge. In this picture, the effect of the capillary forces should depend on the diffusion of particles in polymer melts which is a function of ratio of particle size/mesh size of polymer melts. The size of ferrite particles is on a micro scale (figure S1) while the mesh size of a typical polymer melt is on the order of several nanometer[41]. For the case of particle size much larger than the mesh size, the motion of large particles is diffusive with diffusion coefficient determined by the bulk viscosity of polymer melts at a long time scale[42]. Then we hypothesized that acceleration of particle diffusion by decreasing the polymer bulk viscosity could promote the effect of the capillary forces in a shear field. To test this hypothesis, we tune the polymer melt viscosity by adding a control amount of PA610 into PA6 matrix. It is known that the incorporation of PA610 into PA6 matrix could reduce the viscosity[8]. The plots of $\eta_{a,p}/\eta_{a,p}$ versus the shear rate for PA/ silane-modified ferrite composites containing different PA610 concentrations are shown in Figure 4b. In general, the magnitude of $\eta_{a,p}/\eta_{a,p}$ is increased as increasing the concentration of PA610. For polymer composites which contain 0 and 20 wt% PA610 in polymer matrix, $\eta_{a,p}/\eta_{a,p}$ decreases gradually as the shear rate increases. Comparatively, for polymer composites containing 40 wt% PA610 in polymer matrix, $\eta_{a,p}/\eta_{a,p}$ keeps a constant at low shear till shear rate approaches $1500s^{-1}$, then a sharp decrease is observed at $3000s^{-1}$. The plateau of $\eta_{a,p}/\eta_{a,p}$ indicates that Brownian motion is sufficiently rapid to restore the equilibrium transient particle network from the distortion till the shear rate is higher than $1500s^{-1}$. Taken together, our experimental observations confirm the hypothesis that the increased particle diffusion promotes the effect of capillary forces. Likewise, we realized that our hypothesis can simply explain why the increase of particle size can weaken the effect of capillary forces for particle suspensions in a shear field[43].

It is tempting to compare our results with previous findings. In the past, particle suspensions attracted most of the attention. For example, Koos et al. pioneeringly demonstrated that a drastic phase transition of particle suspensions from a fluid-like to a gel-like state by adding a small amount of secondary immiscible liquids[23-27, 43]. The viscosities of particle suspensions with 0.5wt% secondary immiscible liquids exhibit two orders of magnitude increase in the shear rate of 10^{-2}-$10^{2}s^{-1}$. In contrast, for the PA/ferrite composite, only maximum 3.7 times difference is observed at a shear rate of ~$170s^{-1}$ by uptake of 0.3 wt% water. There are several possible reasons for the decreased effect of secondary liquids on the rheological behavior of PA/ferrite composites. (1), water is able to penetrate into the bulk PA. Therefore, the amount of water which used to form the pendular water bridge is lower than expected. This may result in the decreased number of particle contact induced by the pendular water bridge. Interesting, a very recent study[44] showed that for cocoa suspensions using water as the continuous phase and linoleic acid as the secondary phase, the increase in the yield stress due to the addition of oleic acid was in general within one order of magnitude, a scale comparable with viscosity increase for PA/hydrophilic composites. Since it is known that the solubility of oleic acid in water is moderate, these results consistently demonstrated that the penetration of secondary liquids into the continuous phase may play a negative role in the effect of capillary forces. (2), an irregular shape of ferrite particles (Supporting information, Figure S1) could reduce the strength of capillary force.

Although we have focus on a specific polymer composite, consisting of PA and ferrites, we expect that the manipulation of viscosity by uptake of water can occur for other polymer composites. Rather than adding lubricants or thickeners, the addition of a small amount of water could be regarded as a reversible, simple, inexpensive and environmentally-friendly way to manipulate the polymer rheology. The tuning of viscosity in such an easy way has promising applications on e.g., traditional rubber/plastic processing, the painting and the fiber fabrication, et al. Moreover, we note that uptake of secondary liquids can either decreased or increased the apparent shear viscosity by carefully design of particle surface properties[45]. In the further research, a design principle is expected to be proposed to give a systematic knowledge of how to control the polymer rheology by addition of a small amount of secondary liquids.

4. Conclusions

We have reported a new method to manipulate the polymer rheology. The PA/ferrite composites were used as a protocol system. We have demonstrated that the apparent shear viscosity can be increased by a factor of maximum 3.7, by uptake of merely 0.3wt% secondary liquids, water. This increase is attributed to the effect of the capillary force between particles. Rather than a traditional way to tune the viscosity by adding lubricants or thickeners, we provided here a reversible, simple, inexpensive and environmentally-friendly way to tailor the rheological properties of polymer composites.

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