

Effect of platelet size in a soft nanocomposite: Physical gelation and yielding

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Abstract

We investigated the role of the platelet size in the viscoelasticity of a soft solid nanocomposite, which consisted of exfoliated clay in a liquid polymer matrix. The internal connectivity of the nanocomposite reduced significantly when made up of smaller platelets. This expresses itself in a lowering of the modulus and an increase in relaxation times. Sample preparation played a critical role in these experimental findings. Two liquid polybutadienes served as matrix fluids, a nonfunctionalized polybutadiene (PB), which is a noninteracting liquid, and a carboxyl terminated polybutadiene (sPB), which caused the clay to exfoliate. Unexfoliated clay particles were suspended in PB and treated to high-intensity chaotic flow in a planetary mixer for size reduction. The size-reduced clay particles were exfoliated through the addition of sPB followed by annealing at an elevated temperature. The exfoliated clay in the 50/50 PB/sPB blend formed a percolating network, a physical gel. The resulting soft solid was characterized before and after having been sheared above its yield strain. Yielding caused the already soft physical gel to soften even further by irreversibly reducing its internal connectivity. The samples comprised of large platelets softened but still remained a solid after yielding, while nanocomposites made up of smaller platelets underwent an irreversible solid to liquid transition during yielding. © 2018 The Society of Rheology. <https://doi.org/10.1122/1.5016535>

I. INTRODUCTION

Particle filled polymer composites take advantage of the reinforcement which non-Brownian fillers provide when dispersed in a soft polymer matrix. In addition to particle loading, particle/polymer interactions, and particle/particle interactions, geometrical parameters of the filler govern the composite's performance including its shape, size, and orientation. A standard grouping of particle effects is based on shape 1D (rods/fibers), 2D (platelets), or 3D (spheres) [1,2]. Best understood among asymmetric particles are the rheological effects of 1D fillers (fibers) in a composite. In a recent review, Pickering and coworkers [3] emphasized the need for oriented, high aspect ratio fibers to maximize the composite's final tensile modulus. However, eventually, this effect begins to saturate at higher degrees of orientation and/or increasing fiber length [4]. A liquid to solid transition was reported to occur in a liquid polymer matrix when 1D fillers connect into a sample spanning structure. Studies on carbon nanotubes of varying lengths in different polymer matrices have shown the percolation threshold to shift to lower loadings as the aspect ratio of the fiber increases [5,6]. For carbon nanotubes, shear induced orientation was found to reduce the network connectivity and even dissolve the network structure so that the composite reverts to a liquid, as determined by the composite's storage modulus (under shear) [7].

The rheological effects of 2D fillers on a composite are less explored. This may be due to difficulties associated with

achieving and characterizing single sheet platelets. To our knowledge, only four experimental studies explored the reinforcing effect the platelet size has on polymer composite's final properties [8–11]. Weon and coworkers used clay similar to the one in the present study. They extruded nylon 6/clay composites and altered the clay's platelet size and orientation by varying the extrusion conditions and found that both factored into the composite's mechanical properties. However, rheological effects were somewhat overshadowed by the high viscosity of the neat nylon matrix. It became clear that a softer polymer matrix is preferable for our study to amplify the effect of fillers.

This research builds on our earlier rheological study of a soft solid composite comprised of organically modified montmorillonite clay (oMMT) in a liquid polybutadiene matrix [12,13]. Interestingly, exfoliation was only achieved if the matrix polymer was end-terminated with carboxyl (or hydroxyl) groups (sPB), while nonfunctionalized polybutadiene (PB) had no noticeable rheological effect with the organoclay maintaining its initial spacing [13,14]. We will make use of the fact that a sPB/PB blend is also a very efficient matrix for exfoliating oMMT [15]. Exfoliation allows the clay sheets to form a sample-spanning structure. The nanocomposite becomes a physical gel, which yields when exposed to a sufficiently large strain [16–18]. Once yielded, the structure shows no recovery at all, meaning that the strain effect is permanent [12]. The exfoliation mechanism and yielding processes are still not fully understood. Due to the extensive rheological characterization of the composite, we selected it as a model system for studying the effect of the platelet size and orientation.

In this study, we reduce the average platelet size in a model nanocomposite and measure the resulting linear

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viscoelastic (LV) properties before and after yielding the structure. Samples were subjected to a sequence of two very different forms of flow treatment. The first was flow grinding of a clay/PB suspension to reduce the size of the clay particles, which was followed by exfoliation of the clay particles. A second flow treatment was performed in the rheometer which oriented the exfoliated clay sheets in the polymer matrix. Shear yielding shifted the LV properties by lowering the modulus and increasing relaxation times (in the case of soft solids). The combination of size reduction and yielding caused the sample to permanently soften and transition into a liquid. Size reduction or yielding alone was not enough to induce a transition into the liquid state.

II. EXPERIMENTAL

A. Material

Dicarboxy terminated “sticky” liquid polybutadiene (sPB) and nonfunctionalized liquid polybutadiene (PB) from Sigma-Aldrich served as matrix polymers for the nanocomposite with molecular weights of $M_n = 4200$ and $M_n = 2150$, respectively. oMMT particles (Fenghong Clay Corporation) had their sodium counterions substituted with octadecyltrimethylammonium. Antioxidant (Irganox B225 from BASF) of 0.2 wt. % was added to minimize degradation of the polymer at elevated temperatures. Tetrahydrofuran (THF) from Fisher Scientific served as the solvent.

B. Sample preparation

A key point of this work was to have particle size reduction occurring first followed by clay exfoliation. This avoids competition between the size reduction and physical gelation (exfoliation). Clay exfoliation was postponed by embedding the particles in PB which is known to prevent particle aggregation but has no effect otherwise [14]. In this way, clay particles were merely suspended in a liquid PB matrix. The clay/PB suspension is in the liquid state as needed for an effective particle size reduction in the planetary mixer, which relies on flow at extensive stress.

Specific steps are as follows: 84 wt. % PB and 16 wt. % clay were massed and homogenized in a planetary mixer at 3000 RPM for 1 min. The mixture turned opaque due to the clay being suspended in the liquid PB matrix. Samples were then subjected to chaotic flow treatment in the mixer by adding four cylindrical ceramic pebbles into the mixing cup. A rotational speed of 3000 RPM was used in 2 min cycles with a 1 min cooling period inbetween. For increased levels of size reduction, the amount of high shear treatment was increased to as much as 20 min. The exfoliation was then initiated by adding sPB into the system. This reduced the clay loading from 16 to 8 wt. % with respect to the total polymer (50/50 mixture of PB and sPB). Immediately after gently mixing the sPB into the clay/PB suspension (3000 RPM for 1 min without the mixing pebbles), samples were loaded into the rheometer, which was then set to the prescribed gap height of the cone-plate geometry. It is essential to place the sample between the rheometer fixtures before structure formation can occur. This avoids the sample's

structure being altered during sample loading [12]. We utilize the fact that exfoliation requires time. Next, annealing at 80 °C for 10 h caused the clay to exfoliate in the PB + sPB matrix and form a physical gel. At that time, the samples turned transparent, suggesting at least some degree of exfoliation. The above prescribed method presents a standardized way to generate stress-free physical gels (denoted as “virgin” samples), which are unaffected by the mixing and/or by the sample loading into the rheometer. This established a reproducible starting condition for LV characterization. An alternative method to create a well-defined structure would be by applying large shear after loading the exfoliated sample into the rheometer. We employ both methods while noting that the two sample states are vastly different in their rheology (random versus aligned clay particles). We also noted that the sample is poorly reproducible when exfoliating before loading into the rheometer but not shearing afterward.

C. Chaotic flow treatment in a planetary mixer

Samples were prepared in a planetary mixer (FlackTek SpeedMixer DAC 150), which allowed gentle mixing of clay/PB as well as mixing under large stress as needed for reducing the size of the clay particles. The planetary mixer is basically a fast spinning centrifuge with a tilted sample holder, which rotates around its tilted axis while spinning. The combination of gravitational forces at various positions along the mixing arm enables efficient stress application and mixing of the suspension.

Intense stressing and mixing were achieved by adding four cylindrical ceramic pebbles ($h = 10.0$ mm, $r = 4.80$ mm) into the mixing cup with the clay/PB suspension. The presence of the pebbles changed the sample's flow profile. The sample divides when flowing around a pebble and recombines again behind the pebble. During the division, the suspension gets subjected to large shear forces, which caused clay particles to reduce their size. In addition to the large shear forces, size reduction was attributed to both particle-particle and particle-pebble collisions. In the remainder of the text, clay subjected to this treatment will be referred to as “size reduced samples.”

D. Rheological measurements

Rheological measurements were performed on a stress-controlled Stresstech ATS with 25-mm cone and plate (or 25-mm parallel plate) fixtures. Freshly mixed samples were loaded and annealed in the rheometer for exfoliation. The structure was studied with small amplitude oscillatory shear (SAOS) frequency sweeps at 0.1% strain amplitude from 0 to 80 °C in increments of $\Delta T = 10$ K with frequencies ranging from 1 to 100 rad/s. For comparison, the annealed samples were yielded at a shear rate of 5 s^{-1} for 180 s ($\gamma = 900$) followed by a second SAOS characterization. After yielding, creep recovery experiments were performed by applying a stress of 1 Pa for 2.5 h and then releasing the stress and monitoring the strain behavior for an additional 2.5 h.

E. X-ray

Medium angle x-ray scattering (MAXS) was used to characterize the clay spacing and the extent of exfoliation of the

clay platelets (Ganesha 300 XL SAXS). The experiment was set at a wavelength of 0.154 nm, an exposure time of 180 s, and a sample to detector distance of 0.691 m with a 2 mm beam stop. MAXS was performed in various phases in the exfoliation process.

F. Size distribution measurements by microscopy

Clay particle size distributions were measured using a FEI Magellan Field emission scanning electron microscope (SEM). The oMMT particles had been separated from the polymer for improved contrast. For this purpose, clay/PB was dissolved in THF and clay particles were allowed to settle to the bottom of the vial. The supernatant, containing the polymer and THF, was removed, and the washing process was repeated until the majority of polymer had been removed. Although the supernatant appeared clear, some small clay particles may have been lost during washing. These exceedingly small particles are not the focus of this study as their rheological effect would be minimal compared to that of the larger platelets.

The sediment was diluted with THF to appropriate concentrations, spin coated on a silicon wafer, gold sputtered, and imaged using SEM. This allowed us to determine the size distribution of clay platelets. Such an analysis assumes that the clay particle's aspect ratios were large enough to cause them to lay flat, not standing, on the silicon wafer after having been spin coated. This provides the platelet lateral dimensions.

III. EXPERIMENTAL RESULTS

A. Rheological response of the polymer and the composite before size reduction

The neat PB, sPB, and their 50/50 blend (no clay) exhibit the typical LV features of a liquid polymer [Fig. 1(a)]. This is not surprising because both polymers are of low molecular

weight and were measured above their glass transition temperature. The sPB, PB, and its 50/50 blend have almost identical LV properties. This indicates that PB and sPB are miscible and that the overall rheological response is unaffected by the dilution of functional end-groups when mixing the sPB into PB in a 50/50 blend.

Addition of clay (no size reduction yet) drastically changes the LV properties. Eight weight percent clay was added to PB, sPB, and the 50/50 blend; their LV properties are compared in Fig. 1(b). As described in Sec. II B, the clay/polymer samples were mixed and quickly transferred into the rheometer before exfoliation could take place (only needed for sPB or PB/sPB matrices) and then annealed in the rheometer. The procedure resulted in the formation of a stress-free structure, which quickly transitioned into a solid state in the rheometer (physical gel due to clay exfoliation). The solid state is indicated by the appearance of a plateau in the storage modulus, G' , at low frequencies [Fig. 1(b)]. In terms of connectivity, differences between clay/sPB and the clay/blend are minimal [Fig. 1(b)]. This highlights the importance of having the carboxyl functionality to form the physical gel. The corresponding shift factors for the unfilled and filled samples are shown in Fig. S1 [19].

The rheological behavior is fundamentally different when using PB instead of sPB as the matrix material. Without the functional end-groups, the clay/PB mixture remains in a liquid state. It is a suspension of clay particles in a viscoelastic liquid as needed for size reduction flow in the planetary mixer. These findings were key in designing our size reduction procedure.

B. Particle size reduction

The clay/PB suspension was subjected to intense flow treatment as previously described. In this state, PB simply acts as a carrier for the clay particles (no gelation occurred) and as a stress transfer medium. The chaotic flow treatment breaks

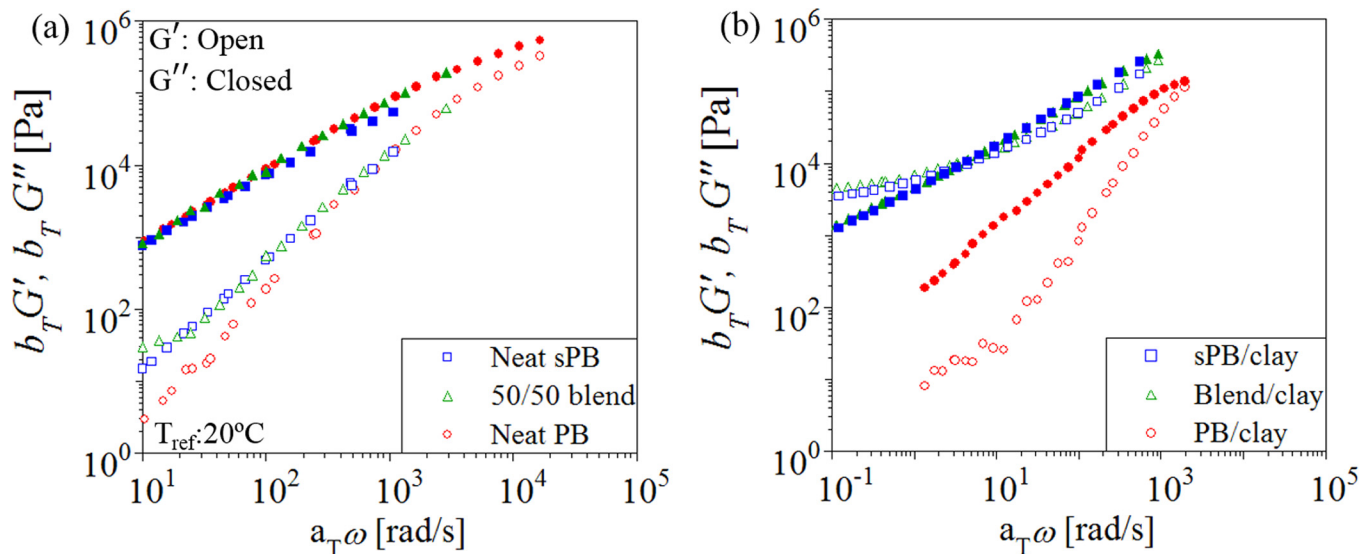


FIG. 1. SAOS master curves of (a) neat polymers (and blend) and (b) their composites after adding eight weight percent clay. The clay composites containing sPB were exfoliated in the rheometer to avoid any shearing during sample loading (“virgin samples”). Composites containing sPB with its functional end-group form a soft solid as indicated by the low frequency plateau in G' .

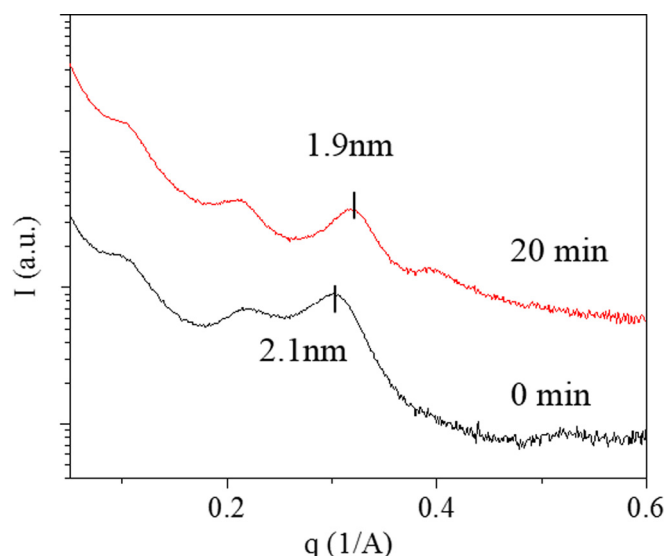


FIG. 2. Scattering profiles of samples measured before and after 20 min of flow treatment. This indicates that the flow treatment did not significantly exfoliate the clay particles.

agglomerates into individual clay particles and, under strong flow conditions, reduces the particles' lateral size. Furthermore, the flow treatment may also reduce the number of platelets per clay stack and even may cause partial exfoliation of clay. Figure 2 compares the x-ray scattering profiles of the clay/PB suspension before and after 20 min of flow treatment. In this case, the extent of exfoliation is minimal as indicated by a minimal reduction in peak intensity. Figure 3 compares the particle's lateral size distribution after 0 (left), 10 (middle), and 20 (right) minutes of flow treatment based on measuring the projected 2D surface area of the particles on a spin coated substrate. The imaged area of the original clay

particles (nonreduced; polymer removed) was found to be $0.75 \mu\text{m}^2$ as compared to 0.51 and $0.45 \mu\text{m}^2$ after 10 or 20 min of flow treatment, respectively. Size reduction can be seen clearly in both the images and the size distribution profiles. The most significant change in the platelet size distribution was in the large platelets, i.e., larger platelets being made much smaller. This is reflected in the histograms by disappearance in the tail end of the distributions. Large particles occupy more space, and thus, the probability of having a platelet cut by the grinding or collisions is increased. At these specific flow conditions, the effect of chaotic flow begins to saturate at increased treatment time. The 10 to 20 min size distribution profiles differ only slightly. This further indicates that flow treatment is most effective while large particles are present.

C. Effect of size reduction on rheology

SAOS master curves of the virgin stress-free nanocomposites with size reduced clay [Fig. 4(a), yellow triangles] are slightly lower than those of large nonreduced clay [Fig. 4(a), blue circles]. The difference between the two samples is noticeable but not very pronounced. Both still form soft solid physical gels where the size reduced had a slightly lower plateau modulus and increased relaxation times, thereby indicating a slight loss in connectivity. The master curve of the virgin size reduced composite could be shifted on top of the nonreduced sample through a second (free) shift. An acceptable superposition was observed with a slight deviation in $\tan\delta$ at high frequencies [Fig. S3(a)]. Size reduction caused an increase in the relaxation time (horizontal shift factor 1.05) and a modulus reduction (vertical shift factor 0.70). Such a "second shift" is not perfect, but it helps to quantify the effect of size reduction in the virgin samples.

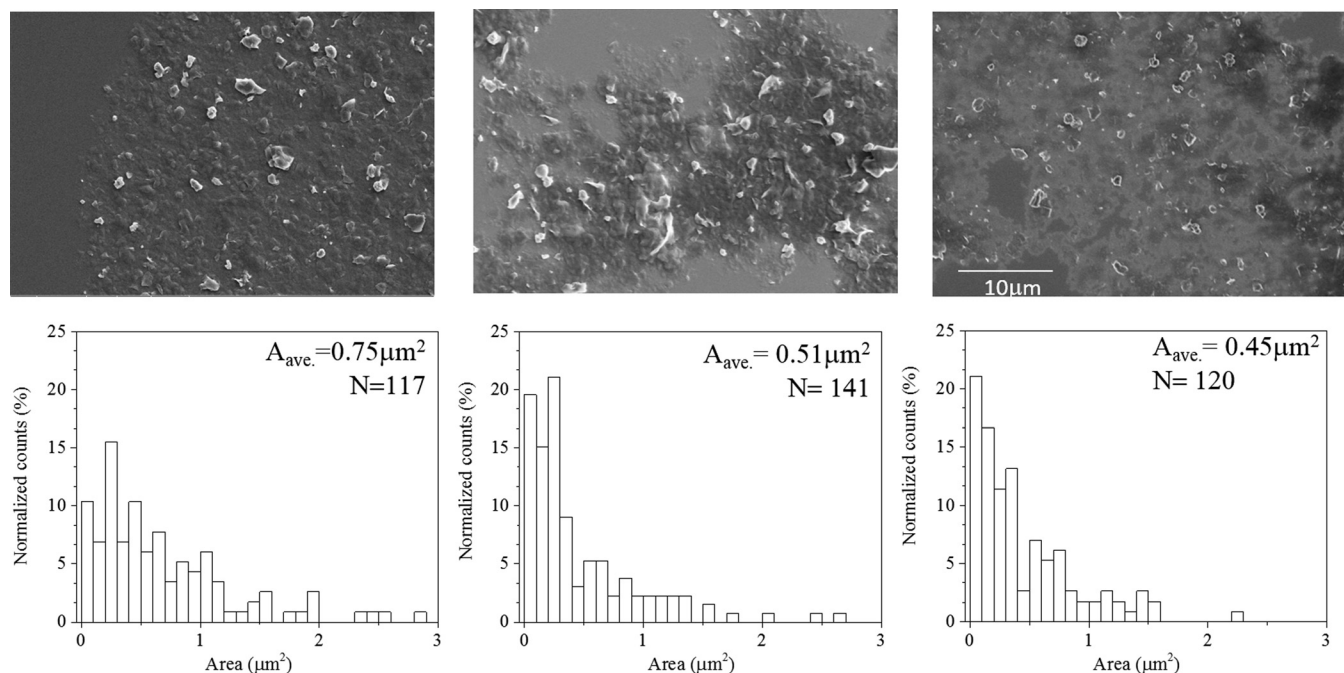


FIG. 3. SEM images of nonreduced clay after 0 min (left), 10 min (middle), and 20 min (right) of chaotic flow in the planetary mixer, along with 2D size distribution profiles.

The exfoliated virgin samples were then yielded by shear, which is known to irreversibly soften the structure through a reverse gelation type process [12]. Such yielding was invoked by exposing the sample to a shear rate of 5 s^{-1} for 180 s between cone and plate fixtures (Fig. S2). The same uniform shear treatment was chosen for all samples. Afterward, the samples were subjected to SAOS for LV characterization. Without size reduction, yielding reduced the SAOS modulus, but the sample clearly remained a solid [Fig. 4(b), green, triangles]. In the case of the reduced platelet size, a much larger loss in connectivity occurred: The yielded sample is no longer a solid, i.e., yielding after size reduction induced a solid to liquid transition [Fig. 4(b), red, squares]. To further highlight the effect of yielding, the virgin and yielded samples for the nonreduced [Fig. 4(c)] and size reduced clay [Fig. 4(d)] are plotted against each other. The moduli of the yielded nonreduced clay containing samples [Fig. S3(b)] were superimposed onto the corresponding virgin sample. Yielding caused a substantial shift in both characteristic times and characteristic moduli, particularly at low frequency. A much larger horizontal time shift of 2.0 and a modulus shift of 0.30 were needed for the

superposition, relative to the size reduced virgin sample (without yielding). This indicates that the yielding plays a key role in the softening process, especially for the size reduced composites. Obviously, the dynamic moduli of the liquid and solid samples do not superimpose due to their inherent differences in the low frequency regime.

D. Effect of varying platelet size + yielding

So far, we compared the LV properties of composites with the most severely size-reduced clay with those with nonreduced clay. Intermediate states of size reduction (varying the amount of flow treatment) show the gradually increasing effect of size reduction. SAOS measurements were carried out with a parallel plate geometry for ease of the experiment. The parallel plate geometry, as compared to the cone-and-plate geometry, no longer provides a uniform strain; however, the viscoelastic differences between the two are negligibly small in this context (Fig. SI 4). The storage modulus, loss modulus, normalized storage modulus, and normalized loss modulus from the SAOS characterization are shown in Figs. 5(a)–5(d) at varying degrees of size

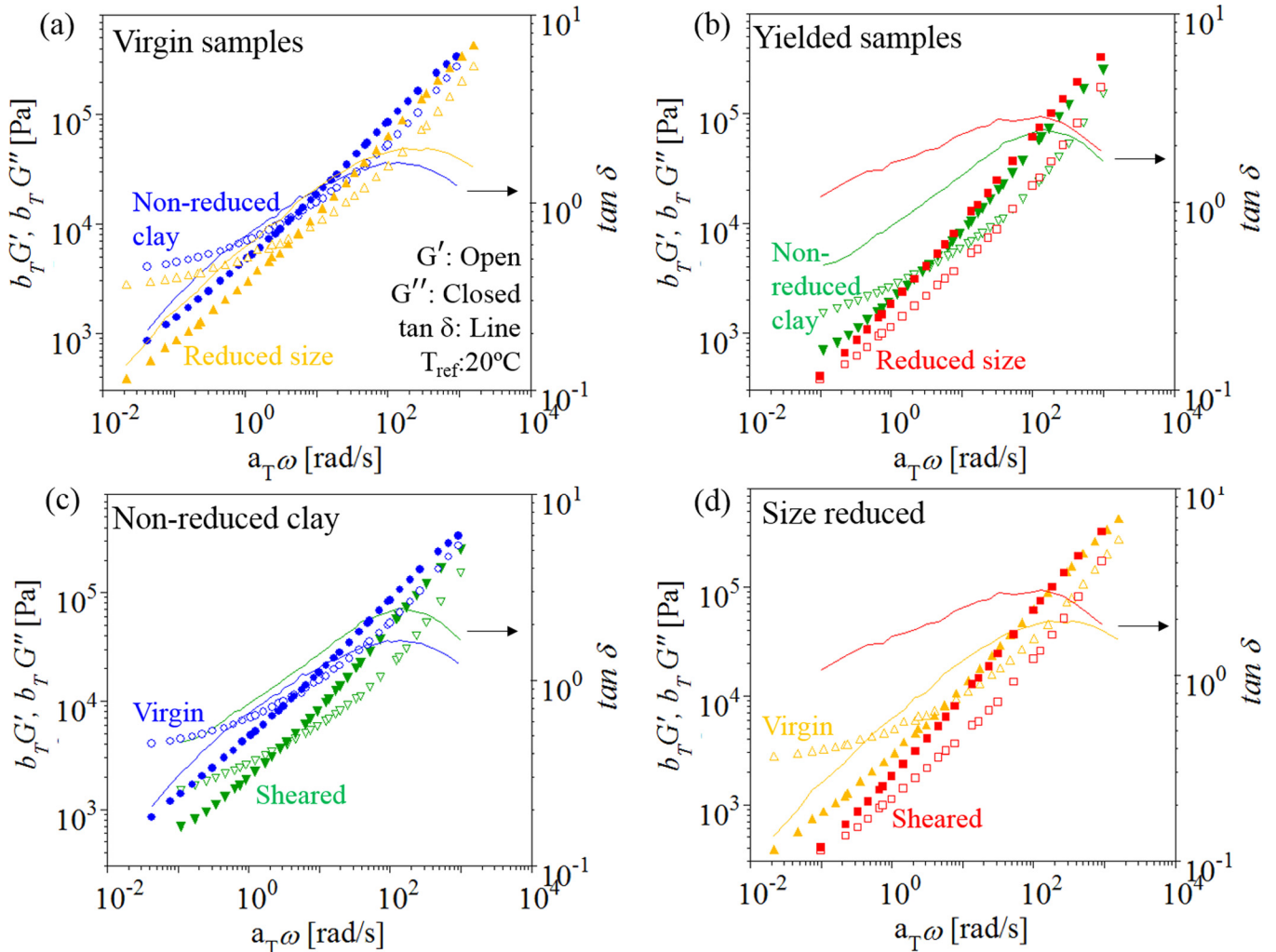


FIG. 4. SAOS master curves of the virgin (a) and the yielded (b) composite with nonreduced and size reduced samples. Virgin and yielded sample data are also plotted for nonreduced (c) and size reduced (d) composites. The combination of size reduction and yielding induced a solid to liquid transition. Either yielding or size reduction by themselves caused a softening in the solid.

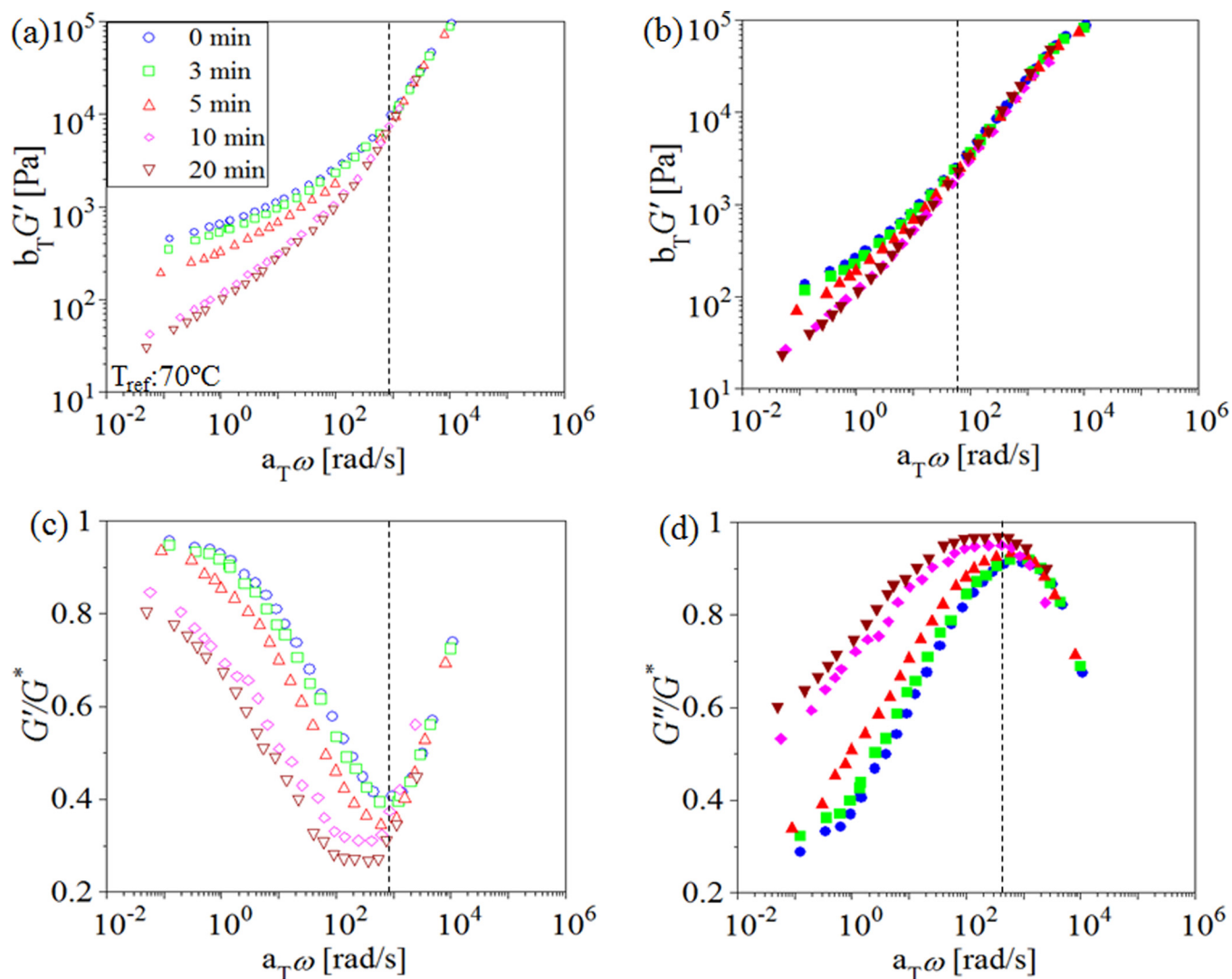


FIG. 5. SAOS master curves after various amounts of size reduction and yielding (5 s^{-1} for 180 s) (a) storage modulus, (b) loss modulus, (c) normalized storage modulus, and (d) normalized loss modulus. The dashed line in each figure marks the division between a strong dependence (left of the dashed line) and a weak platelet size dependence (right of the dashed line).

reduction, via increased treatment time of the clay/PB suspension, in the pebble-stacked planetary mixer. The datasets can be divided into two regimes, marked by the dashed lines in Fig. 5. In the low frequency regime, there is a heavy dependence on shear treatment (yielding + size reduction). However, at higher frequencies, all the samples converge and become almost independent of shear treatment. The divergence of these curves in the low frequency regime indicates a loss in connectivity due to stronger and stronger size reduction. However, at high frequencies, the dynamic moduli converge and become independent of the amount of flow treatment. Potential reasons for this will be explored in the discussion.

Further examination of the storage modulus in the low frequency regime suggests that the solid to liquid transition occurs when size reduction extends beyond 10 min of flow treatment. To further highlight this, a Winter plot was constructed [Fig. 6(a)]. The disappearance of the straight vertical line, indicating a frequency independent modulus value, highlights that the solid to liquid transition occurs when

treating the sample with more than 10 min of chaotic flow [20]. To further confirm this, samples were transferred into glass vials and left at room temperature. After two weeks, an image of the vials was taken [Fig. 6(b)]. Only the sample exposed to 10 min of flow treatment could flow down the vial after two weeks, indicating that it was either a liquid or had such a low modulus that it was not able withstand the force from gravity. This type of experiment represents a simplified creep test under elongation flow with the imposed stress being due to gravity. Creep and recovery experiments were performed on samples about this critical solid to liquid transition [Fig. 6(c)]. A shear stress of 1 Pa was applied to the shear aligned composites followed by releasing the stress while monitoring the sample's strain response. The sample with 3 min of treatment showed a full recovery back to its initial state, indicative of a solid, while 10 min of treatment never fully recovered, indicating that it was in fact a liquid. Correlating the SAOS rheology, images, and creep recovery provides further proof of the solid to liquid transition. Mild size reduction treatment resulted in a softening of the gel,

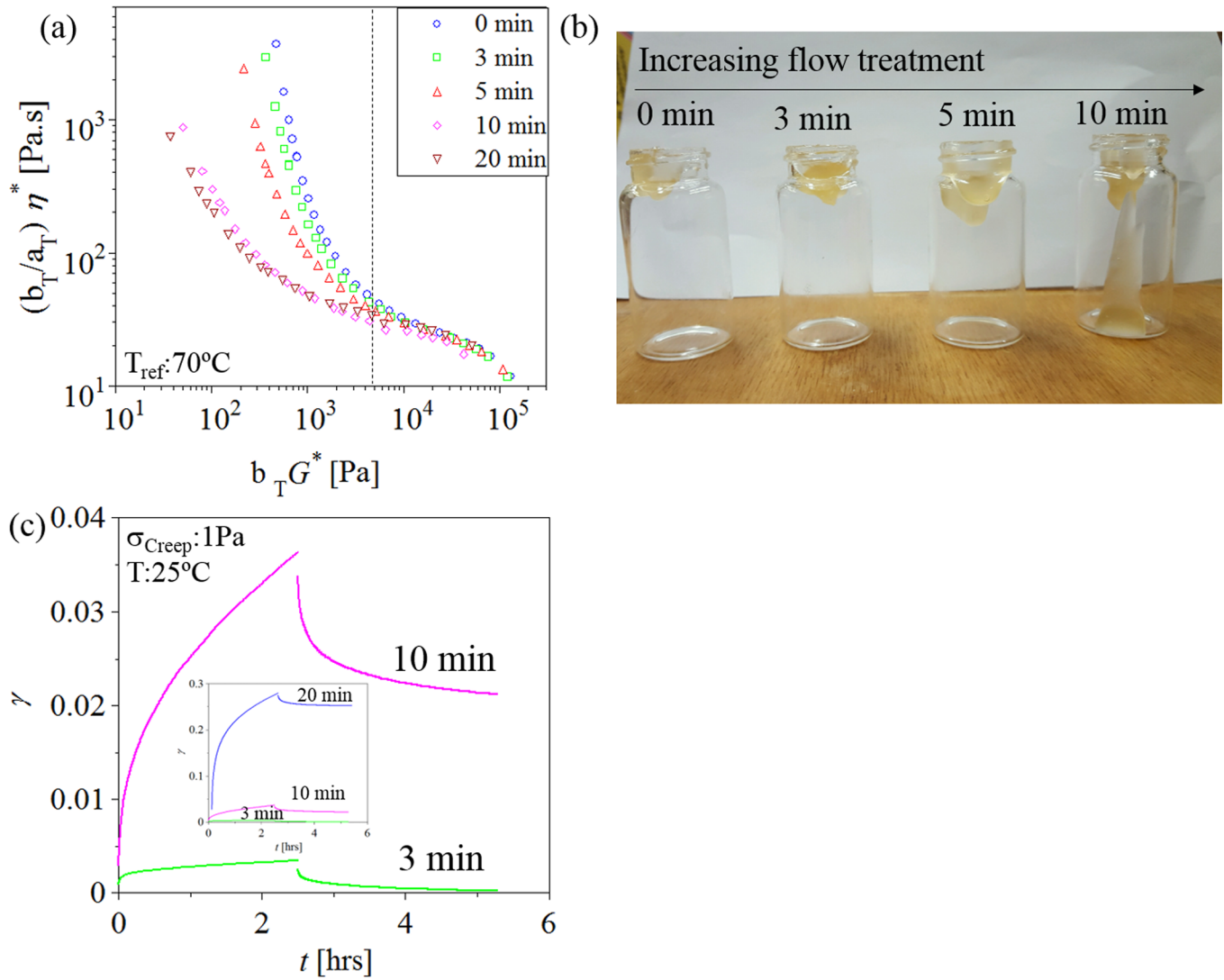


FIG. 6. Exfoliated clay in the sPB/PB matrix after size reduction and shear alignment; (a) Winter plot, (b) after transfer to a vial and resting for 2 weeks, and (c) exposure to creep at the outer diameter with $\sigma = 1$ Pa for 2 h followed by recovery for 2.5 h (zero stress). Samples with mild size reduction (flow treatment < 5 min) are solids, while samples with smaller clay platelets (extended flow treatment > 10 min) behave as liquids on the measured timescales.

but the samples remain solids. It should be noted that the sample subjected to 20 min of flow treatment also flowed, but an image is not included in Fig. 6(b).

E. X-ray

After rheological measurements, x-rays were used to characterize the microstructure of the composite. The transparent color of each sample along with the disappearance of a MAXS peak indicates that the clay is in fact exfoliated as seen in Fig. 7. This agrees with results from the study by Zhu *et al.*, who used a blend of functionalized and nonfunctionalized PB as the matrix polymer and effectively achieved clay exfoliation [16].

IV. DISCUSSION

The liquid polybutadiene/clay composite proved to be a model system for the study of rheological effects caused by the 2D filler size and orientation. Rheological effects due to size reduction are most pronounced when combined with

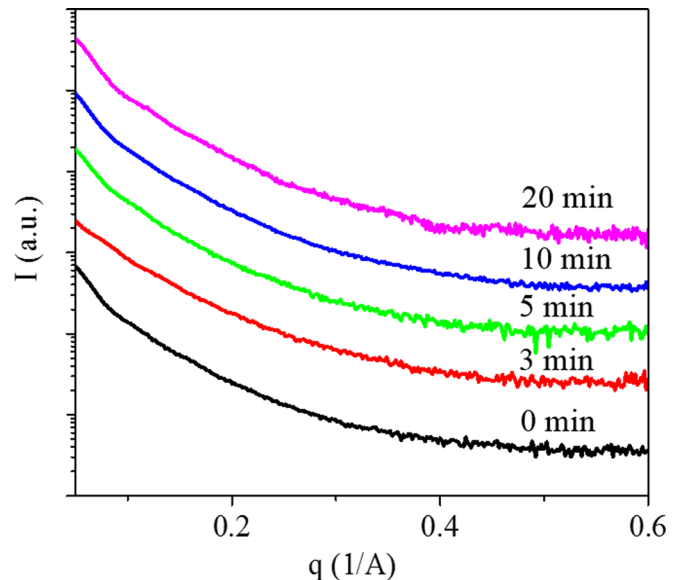


FIG. 7. Scattering profiles of samples with various amounts of size reduction and exfoliation in the rheometer.

orienting the clay platelets. The platelet size was reduced by intense flow treatment. The effect begins to saturate at 10 to 20 min of flow treatment where the difference became very small already (Figs. 3 and 5, respectively). This is to say that, under our specific operating conditions, the highest possible size reduction (a 40% surface area reduction in the clay platelet size) is reached. To further reduce the particle size, more intense forms of shear would have been needed in the planetary mixer or under alternative inherent surface charges.

The clay particles are highly irregular and asymmetric. Because of this, the chaotic flow affects the particle's size and shape on multiple length scales. This involves breaking up of clay agglomerates, reduction in particle lateral dimensions, and breaking apart of stacks into smaller particles including exfoliation. The breaking down of clay agglomerates is the first step in the process but has little effect on the desired final state of exfoliated sheets in a polymer matrix. Critical to this study is the reduction of the lateral dimensions of clay particles. However, some exfoliation of clay may already occur during the reduction in the platelet size in the flow treatment. Previous studies have seen this using electron microscopy and XRD on oMMT [21]. The fact that the SAXS peak mostly remains indicates that our flow treatment is not strong enough to exfoliate the clay in significant ways (Fig. 2).

Surprising are the narrowing of the peak in Fig. 2 and the shift in the average spacing from 2.1 to 1.9 nm after flow treatment. We attempt to explain this by the following phenomenon: The polydisperse spacing between clay sheets in a stack broadens the SAXS peak. The largest spacings belong to locations of weakest cohesive force in clay stacks. We assume that this is the location where stacks most likely break under stress. The remaining sheets in broken fragments are spaced more narrowly, but they are still assembled in stacks. Their average spacing is smaller and more uniform. This results in the shifted and narrowed peak of Fig. 2. The main exfoliation occurs at a later stage of sample preparation after having added sPB and immediately loaded the sample

into the rheometer. Exfoliation occurs over time and causes the modulus to grow substantially as measured in the rheometer. These are the so-called virgin samples.

Upon achieving exfoliated virgin samples of varying platelet sizes, the composite was shear yielded. As previously discussed, yielding caused the modulus to permanently soften [12]. We speculate that this softening is due to the alignment of clay sheets [22–24]. Softening due to orientation would agree with the findings observed in nanocomposites with 1D fillers. The shear sensitivity is largest for the most reduced platelet size, which also requires the smallest strain for effective shear yielding. Vice versa, the original larger platelets create a physical gel which requires a larger shear strain before it yields. Further experimental characterization would be needed to quantify (and confirm) the extent of alignment of clay within the polymer, but this is beyond the scope of this study.

Both size reduction and yielding cause the modulus to soften and, when used in combination, can induce a solid to liquid transition. The key question is to understand the roles the platelet size and orientation play in the connectivity of the physical gel. From a gelation point of view, size reduction increased the number of platelets needed to form a sample spanning (percolating) network. This in turn reduces the probability of forming all the physical bonds required. We speculate that this effect is amplified with yielding because orientated clay sheets require an even larger number of platelets to form a percolating network. The connectivity of the gel gets probed at low frequencies, which is clearly reduced with the decreasing platelet size (Figs. 5 and 6). As the amount of flow treatment was increased, a reduction (and eventually disappearance) in the amount of physical cross-linking was seen. Figure 8 shows how this clay/polybutadiene composite maps onto the traditional viscoelastic response of a soft solid above and below its gel point. The initial virgin sample is a soft solid with a well-defined plateau modulus corresponding to a discrete value (G_e , τ). Softening occurs and moves the sample closer and closer to

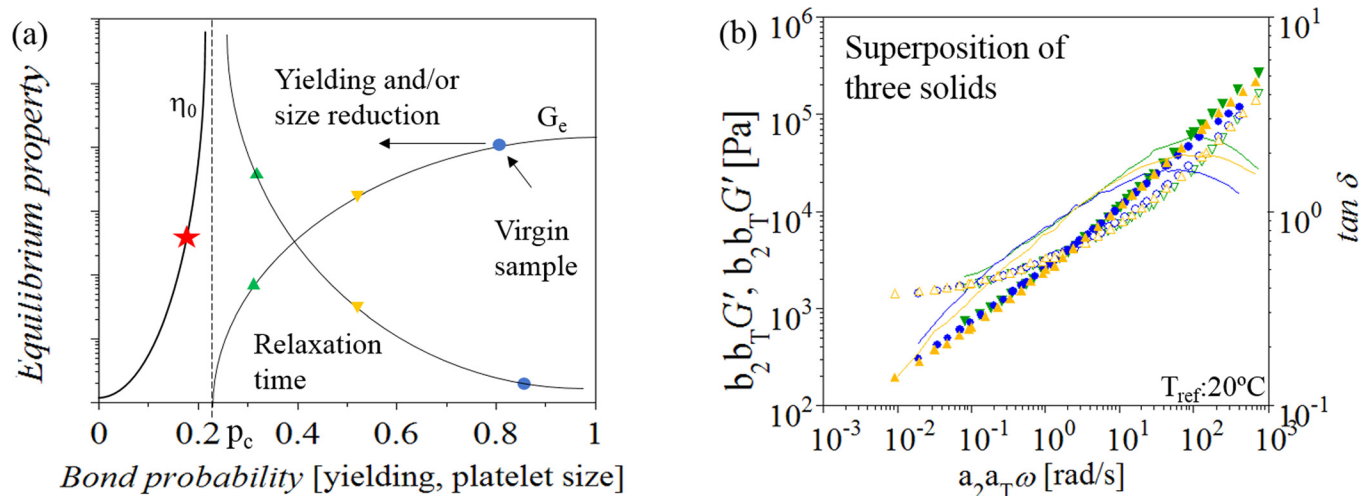


FIG. 8. Traditional LV response of soft solids, including physical gels, below and above their gel point, p_c [25]. In this study, the “virgin” sample is defined as a stress-free sample containing nonreduced clay (blue circles). Through size reduction (red squares) (without yielding) or yielding (green triangles), the sample is pushed closer to its gel point, thus increasing relaxation times. The superposition of the virgin sample, the yielded sample, and size reduced solids is shown in (b). The combination of yielding and size reduction (gray star) of the sample past its gel point allows it to flow.

its gel point p_c until the solid to liquid transition is induced and the liquid sample is governed by its viscosity, η . Above the gel point, this is seen by the fairly successful superposition of a size reduced and yielded sample onto the virgin, nonsize reduced sample [Fig. 8(b)]. Size reduction partially reverses gelation as indicated by a “move” back toward the gel point but not beyond the gel point as schematically shown in Fig. 8(a). The reverse gelation moves past the gel point when both size reduction and yielding are applied.

The above discussion is an attempt to gain understanding for the low frequency regime observed in Figs. 5 and 6. The convergence of the modulus in the high frequency regime still needs further explanation. The high frequency regime probes small length scales. We believe that as frequency is increased, the contribution of the single layered elastic clay platelets (exfoliated throughout the polymer matrix) begins to be amplified. The phenomena should be independent of interactions between the polymer and clay (along with clay-clay and polymer-polymer interactions). The dashed lines in Figs. 5 and 6 clearly show the transition from this high frequency regime and the connectivity regime below some critical frequency. This behavior is observed in all the LV material functions. The two regimes in Figs. 5 and 6 (above and below the dashed line) provide two different insights into the role of platelets.

V. CONCLUSIONS

This study was focused on the LV characterization of an exfoliated clay/polybutadiene composite comprised of different sized platelets. A key point was to fabricate virgin stress-free composites by having structure formation occurring in the rheometer so as to have the sheets randomly distributed throughout the polymer matrix. When the sheets were randomly dispersed, the LV properties were only reduced slightly with the decreasing particle size. However, when shear yielding the composites, major softening occurred, presumably due to the alignment of clay sheets. The softening process can be viewed as reserve gelation with a solid to liquid transition occurring when shear yielding was performed on the composite comprised of the smallest platelets. These effects were probed in the low frequency portion of the data. The high frequency regime was found to be independent of particle size, highlighting the importance of probing sample structures at different frequencies and thus varying sizes and length scales.

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