Investigating Linear and Nonlinear Viscoelastic Behavior Using Model Silica-Particle-Filled Polybutadiene

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ABSTRACT: We explore filler reinforcement (i.e., increase of elastic modulus G' due to incorporation of fillers) and Payne effect (i.e., decrease of G' at large strain amplitudes) in terms of the matrix molecular weight, filler loading, and time scales used to probe the viscoelasticity of filled melts. Use of monodisperse non-cross-linked 1,4-polybutadiene (PBD) along with a silica filler allows illustration of different mechanisms of filler reinforcement in the elastic and liquid regimes. The greater filler reinforcement for matrices of higher molecular weight indicates the filler association through chain adsorption and bridging. The role of matrix-mediated filler−filler interactions is explicitly illustrated in terms of the increased elastic modulus in the terminal region due to replacement a fraction of the matrix chains with longer chains of the same kind. The Payne effect is seen to be time-dependent and comprised of an instantly recoverable and a slowly recovering component. Measuring G' at both high and low strain amplitudes through stepwise ramping allows us to reveal that (a) these multiphase materials exhibit lower G' at large γ if the corresponding shear stress exceeds a certain level required to break down the filler networking and (b) the filler−filler dissociation is partially immediately repairable upon switching to a small γ. Large step-strain experiments reveal a two-step stress relaxation process, where the initial rapid drop of the relaxation modulus $G(t)$ is due to disintegration of the filler networking under sufficient shear stress. The disintegration in both large-amplitude oscillatory shear and large step-strain shear is not expected to be uniform across the sample thickness as commonly assumed.

I. Introduction

Rubbery and semicrystalline polymers are often too soft as end-use materials. A popular way to enhance mechanical properties of polymers is to incorporate rigid fillers. Upon incorporation of rigid fillers, the filler reinforcement is typically reflected in the increased elastic modulus and viscosity beyond those of the polymer matrix. The most successful and well-known example is carbon black filled natural and synthetic rubbers as the key raw materials for tire applications. The mechanisms for the filler reinforcement and for the drop of the storage modulus G' with increasing oscillatory strain amplitude (a strain softening phenomenon commonly known as the Payne effect[1]) have been a long-standing topic.[2−4] The standard explanations of the observed filler reinforcement and strain softening are based on the picture of filler−filler association during the sample preparation and disintegration of the filler networking at sufficiently high strain amplitudes.

It should be made clear from the onset that filler reinforcement and strain softening effects also take place for small molecule liquids[5,6] through van der Waals force and other short-range interactions perhaps including confinement.[7] For polymeric matrices, filler−filler association may arise from chain bridging,[8−10] interlocking of adsorbed chains of neighboring fillers (so that the chain dynamics are like those of star and branched polymers where the adsorption sites are analogous to the branching points), and possibility chain confinement.[11] The state of filler dispersion is expected to play a crucial role in determining the filler effects on linear and nonlinear responses of the filled materials. The surface chemistry of fillers and filler compatibility with the dispersing medium dictates the spatial distribution of the fillers and the level of filler agglomeration. For polymer composites, polymer−filler interactions and sample preparation procedure are responsible for the final state of dispersion. It is tempting to say that in these filled polymeric systems the final state may not be an equilibrium state but a frustrated state somewhat like glasses. It is difficult to avoid agglomeration and to control the state of dispersion in reality.

Departing from this basic theme of filler aggregation and lack of uniform filler dispersion in practice, a recent study[12,13] examined filler effects near the glass transition temperature of the polymer matrix and concluded that presence of an interfacial layer around each filler with an elevated glass transition temperature is the origin of the filler reinforcement, and shear-induced "melting of the glassy shell" is mainly responsible for the Payne effect. This study was clearly motivated by the intensive experimental studies on the glass transition behavior of polymer thin films or polymers in confinement.[14−21] The present study on filled 1,4-polybutadiene at temperature more than 100 deg from the glass transition temperature will show that this "glassy shell" effect is not a universal mechanism, which appeared to be implied in refs 12 and 13.

The present work is further prompted by another recent study claiming that "the primary underlying mechanism for reinforcement and nonlinear behavior appears to be the filler−matrix interactions, but not filler agglomeration or percolation".[22,23] These authors saw the Payne effect at filler loadings below the percolation threshold and concluded therefore that fill structuring could not be important although the filler

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Table 1. Molecular Characteristics of PBD Samples

sample	T_g (°C)	1,2-PBD	1,4-PBD	M_n (kg/mol)	M_w (kg/mol)	M_w/M_n	source
1.5K	−89.0	25	75	1.5	3.2	2.13	Aldrich
3.9K	−101.9	9.9	90.1	3.5	3.8	1.10	Goodyear
5.8K	−102.0	9.0	91.0	5.5	5.8	1.06	Goodyear
8.9K	−102.5	8.6	91.4	8.5	8.9	1.04	Goodyear
12K	−100.9	8.6	91.4	11.3	11.6	1.03	Goodyear
16K		<10	>90	14	16	1.15	Polymer Source
44K	−100.0	8.3	91.7	43.45	43.8	1.01	Goodyear
100K	−100.1	8.2	91.8	98	99	1.01	Goodyear
200K	−100.5	8.1	91.9	207	208	1.01	Goodyear
400K	−99.5	7.7	92.3	410	412	1.01	Goodyear
1.2M		<10	>90	1051	1240	1.18	Polymer Source

reinforcement was clearly in the nonlinear regime. Indeed, nonlinear filler reinforcement does not necessarily have to involve filler agglomeration. On the other hand, transparency of nanoparticle filled liquids or being below percolation threshold does not imply absence of particle agglomeration. For example, xylene suspensions of nanoclay particles were clearly transparent, yet possess significant storage modulus that could only come from networking of the nanoclay particles rather than any change of the liquid (xylene) dynamics by matrix−filler interactions.[6]

At this juncture, it is important to clarify the role of filler−matrix interactions in influencing the filler−filler association. Filler−matrix interactions determine the surface coverage of fillers or the level of wetting by the matrix material and prescribe the strength of molecular adsorption. Therefore, they dictate the state of dispersion for a given preparation procedure and control how and whether filler agglomeration takes place. The compatibility between the filler and matrix can be modified for a given matrix by varying the filler surface chemistry. Adsorption of matrix molecules onto the filler surfaces may produce a monolayer of “shell” outside each filler. The shell thickness is determined by the state of molecular adsorption, and may therefore actually vary with the filler surface chemistry, but is not expected to be much thicker than the molecular dimensions of the matrix material. At temperatures *close to* glass transition temperature of the matrix for glass-forming materials, the “shell” surrounding each filler surface might emerge with thickness comparable to matrix molecular size, as suggested in ref 12 where the material undergoes glass transition in a different temperature range from the bulk. This effect is expected to be negligible far above the glass transition temperature.

When the filler−filler spacing is on the order of the matrix molecular size, which may happen at sufficiently high filler loadings and for fillers of dimensions comparable to the molecular size, filler association may take place through direct short-range interactions such as van der Vaals forces, through overlapping of adsorbed layers on neighboring fillers, chain bridging (if the matrix is polymeric), and even physical confinement (which is expected to be less significant when adsorption is weak or absent in the presence of high stress). Fillers tend to flocculate due to the depletion effect, which is the primary source of filler aggregation. The shells surrounding each fillers due to either chain adsorption or vitrification may participate, upon overlapping, in the formation of filler−filler association.[24] In other words, the slowed-down dynamics in spaces between neighboring fillers amounts to secondary filler aggregation or networking. Since the filler−matrix interactions dictate the nature of the shell formation, they play a direct role in the filler agglomeration process. Similarly, the Payne effect may occur through the stress-induced desorption or debonding of the matrix material from the filler surfaces such that the shells diminish with increasing strain amplitude, leading to partial dissociation among the fillers.

Finally, it is evident that poor compatibility, e.g., untreated silica particles (hydrophilic) in (hydrophobic) polymers such as polybutadiene or SBR (styrene−butadiene rubber), makes the dispersion difficult. But once the fillers are forced to blend with the matrix, a great deal of filler agglomeration occurs, often leading to the great filler reinforcement effect and Payne effect.[25] See Figure 5 in ref 25. The correlation between filler agglomeration and Payne effect is less straightforward.

In the present work we have systematically investigated linear and nonlinear viscoelastic behavior of model filled PBD melts as a function of matrix polymer molecular weight, filler loading, dynamic shear frequency, and temperature, while keeping the nature of filler−matrix interactions constant. Using a series of monodisperse linear polybutadiene (PBD) melts as the matrix polymer and silica particles as fillers, the viscoelasticity of filled PBD and unfilled PBD is explicitly compared.

II. Experimental Section

Linear polybutadiene (PBD) samples of molecular weight ranging from 1.5K to 410K are used in this study as matrix, whose molecular characteristics are listed in Table 1. All monodisperse PBD samples were synthesized and characterized by Goodyear Research Center, except for PBD1.5K from Aldrich, PBD16K, and PBD1.2M from Polymer Source Inc., and used as received. All the PBD samples have a glass transition temperature T_g at ca. −100 °C as determined by DSC and entanglement molecular weight M_e equal to 2.2K according to $M_e = \rho RT/G_N^0$, where G_N^0 is the elastic plateau modulus, except for PBD1.5K which has a slightly higher T_g due to its higher vinyl content. These samples are essentially the same as those studied before in our lab,[26,27] and more information such as zero shear melt viscosity η_0 can be found[27] in the literature. η_0 can be used to estimate the dominant relaxation time τ_d of these samples according to $\eta_0 \sim G_N^0 \tau_d$. Silicon oxide powder was obtained from Nanostructured & Amorphous Materials Inc. and contains primary particles of size around 15 ± 5 nm with an average surface area of 160 ± 20 m^2/g. Octadecyltrichlorosilane (OTS) was purchased from Aldrich to modify the silica surface[28] so that the filler can be readily dispersed in PBD matrix through solution mixing.

PBD/silica composites were prepared at silica loading from 5 to 100 phr (parts of filler per hundred parts of polymer by weight). This representation (phr) can be readily converted to volume fraction ϕ according to $\phi = \text{phr}/(\text{phr} + 100\rho_{\text{SiO}}/\rho_{\text{PBD}})$. Given $\rho_{\text{SiO}} = 2.2$ g/cm^3 for silica and $\rho_{\text{PBD}} = 0.9$ g/cm for PBD, the volume fraction ϕ ranges from 2 to 29% in the present study. The following procedure is based on a filler loading of 20 phr. 0.20 g of silica powder was first dispersed in 100 mL of anhydrous toluene and was exposed under ultrasound for

30 min in a beaker covered with aluminum foil to prevent solvent evaporation. Then 0.10 g of OTS was added, followed by 2 h of ultrasonication until the suspension became transparent. 1.0 g of PBD was then added into the solution followed by 3 h of ultrasonication. The relatively mild ultrasonication did not result in molecular degradation as verified by recovering the pure matrix. After that, the aluminum foil cover was removed to permit the evaporation of toluene under the hood overnight in the presence of ultrasound. The mixture was then put into vacuum oven at room temperature and dried for at least 48 h. PBD/silica composites were uniform on macroscopic scales by visual inspection. Since it is not transparent, significant filler agglomeration is present.

OTS reacts with hydroxyl groups on silica surface, resulting in an OTS monolayer with alkyl group extending outward, which changes the silica surface from hydrophilic to hydrophobic like. The chemical reaction and the properties of OTS monolayer on silica surface have been described in detail in the literature.[28,29] To determine the surface coverage by OTS on the filler surfaces, thermogravimetric analysis (TGA) was carried out for the OTS-treated silica that had been vacuum-dried. A mass loss of 7% was found. Thus, the maximum bound OTS would be about 7% of the silica weight. This translates to coverage of 200 Å^2 per OTS molecule (which is rather sparse), knowing that the average surface per unit weight of the fillers is 160 m^2/g. Since the OTS absorption is a small percentage of the silica weight, no correction was made in the calculation of the filler loadings.

A strain-controlled dynamic mechanical spectrometer (ARES) was applied in oscillatory shear mode to measure the linear and nonlinear viscoelastic response of the PBD/silica composites. The ARES is equipped with a 200−2000 g cm dual range force rebalance transducer, and oscillatory shear measurements were carried out at frequencies from 0.1 to 100 rad/s and temperatures from −80 to 80 °C at an interval of 20 °C. Three cone-and-plate flow cells are employed depending on the torque response of the samples: (1) diameter $D = 8$ mm and cone angle equal to 12°; (2) $D = 15$ mm and 5°; (3) $D = 25$ mm and 2°. Specifically, the 8 mm cone−plate was used for matrices and corresponding filled samples of molecular weight equal to or higher than 44K. Except those specified, all the rheological measurements were carried out at 40 °C, and all oscillatory shear measurements involved a strain amplitude of 0.5%.

III. Results and Discussion

A. Linear Viscoelasticity: Dependence on Frequency, Matrix Molecular Weight, and Filler Loading.

1. Frequency Dependence. Filler reinforcement, defined here as the increase in the storage modulus G' of filled polymers over G'_m of the matrix, e.g., in terms of the ratio G'/G'_m, is often measured at some fixed frequencies chosen arbitrarily or according to application requirements. For cross-linked materials whose G' does not vary much with frequency, it may suffice to select a few values of frequency. For non-cross-linked polymers, the reinforcement is expected to vary with the oscillation frequency. We begin our experimental investigation of the filler reinforcement mechanism by examining the oscillatory shear behavior as a function of frequency for both filled melts and pure melts. Figure 1 shows the master curves of storage and loss moduli G' and G'' for the pure PBD matrix of $M_w = 100$K and the corresponding filled sample as a function of the oscillation frequency using a shear-strain amplitude of 0.5% at a reference temperature equal to 40 °C, where time−temperature superposition procedure was applied. There are clearly two regions. In the plateau region where the matrices can be regarded as a rubbery solid, the degree of filler reinforcement, as measured by the ratio of G' and G'_m, is independent of ω. In this dynamic region, the fillers simply boast the medium's modulus as indicated in Figure 1. The parallelism between G' and G'_m remains even toward the transitional region beyond the plateau. However, G'' does not do so for frequencies higher than that corresponding to the minima of G'' and G''_m, suggesting that the chain dynamics in the transitional region become slightly modified by the presence of fillers. On the other hand, at low frequencies, i.e., in the terminal region, additional relaxation modes arise to prevent G' and G'' from dropping with ω as ω^2 and ω, respectively, as the pure melts do.

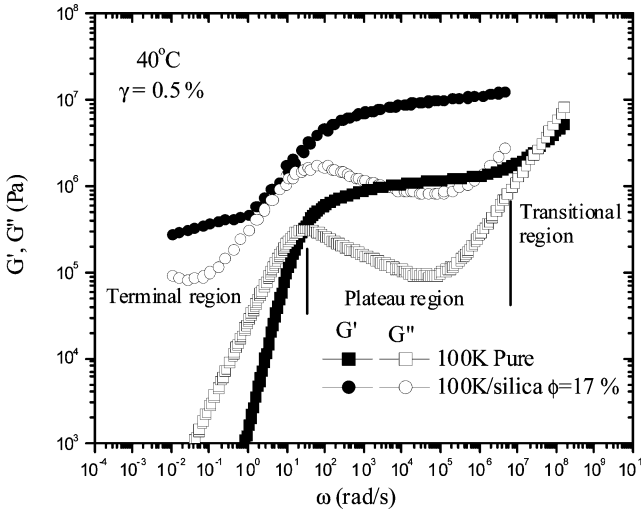

Figure 1. Master curve of storage and loss moduli G' and G'' for the pure PBD100K (taken from ref 26) and PBD100K/silica at volume fraction $\phi = 17\%$ at a reference temperature of 40 °C, after time−temperature superposition between −80 and 80 °C.

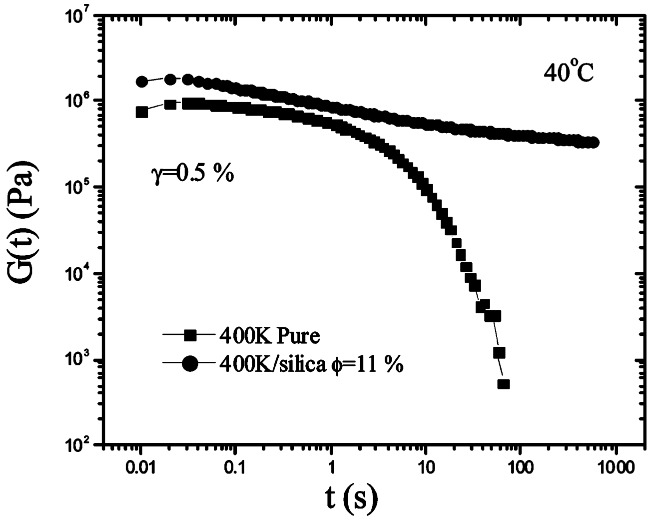

Figure 2. Relaxation modulus from stress relaxation experiment after a step strain of 0.5% for both the pure PBD400K and PBD400K/silica at $\phi = 11\%$ at 40 °C.

In confirmation with the oscillatory shear measurements, step-strain experiments also reveal presence of long relaxation times in the filled PBD relative to the pure PBD. Figure 2 compares the relaxation modulus of the pure PBD of $M_w = 400$K and the corresponding filled sample at a filler loading of $\phi = 11\%$.

2. Matrix Molecular Weight Dependence. It is important to determine whether the increase of linear viscoelasticity (i.e., filler reinforcement), as represented

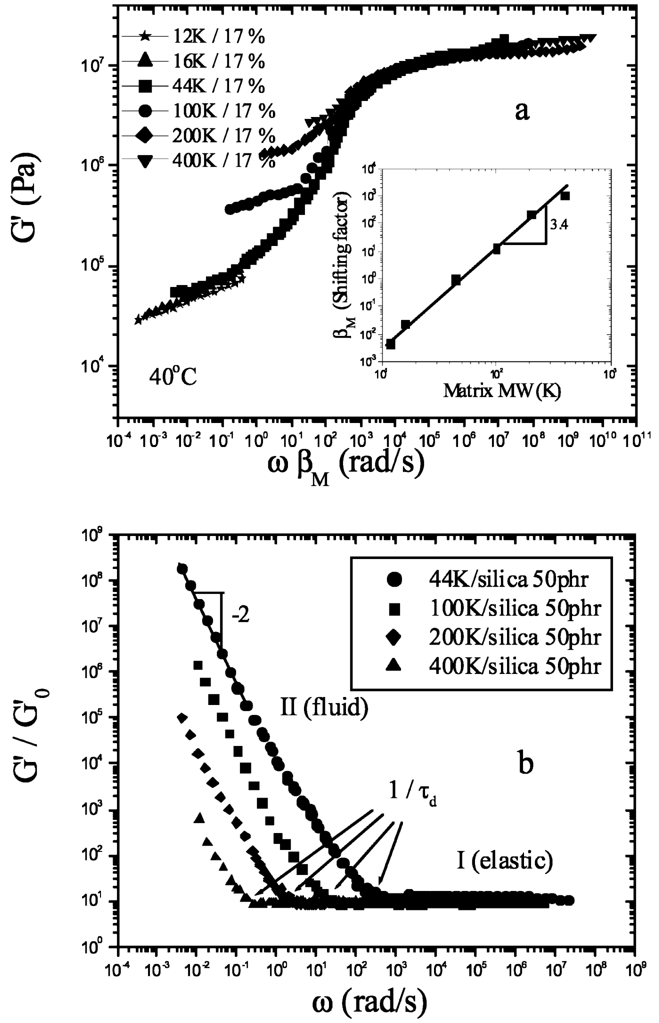

Figure 3. (a) Shifted master curves of storage modulus G' at $\phi = 17\%$ for matrices of molecular weight M = 12K, 16K, 44K, 100K, 200K, and 400K, where the reference (nonshifted) curve is that of the filled PBD44K. The inset shows the amount of horizontal shift as a function of the matrix molecular weight, which is necessary to construct the overlap in the plateau region for these samples. (b) The relative reinforcement ratio at 50 phr as a function of the oscillation frequency based on PBD44K, -100K, -200K, and -400K.

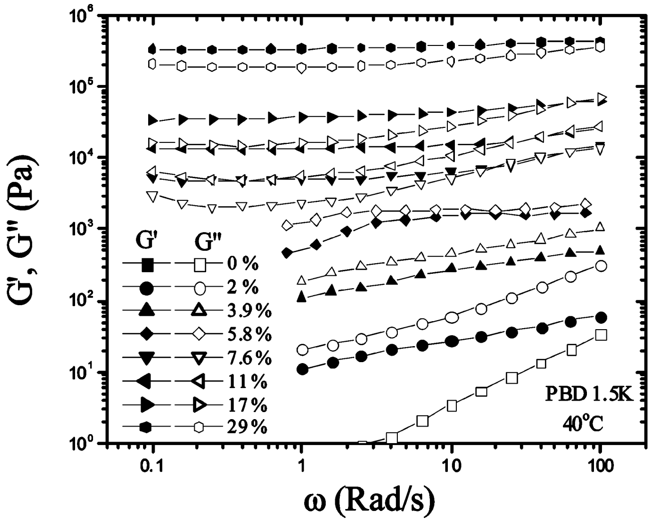

Figure 4. Oscillatory shear measurements of G' and G'' for the PBD1.5K melt and its mixtures with fillers at 40 °C. The cone-and-plate flow cell of 25 mm and 2° was employed for these measurements.

by G' and G'' due to the fillers, depends on the matrix chain molecular weight. Figure 3a shows the master curves for G' against the oscillation frequency for six molecular weights, where the reference matrix has M_w = 44 000 and the others were shifted to match either the plateau or terminal region characteristics. The shift is done here because the filler reinforcement effect is always measured relative to the linear viscoselasticity of the pure non-cross-linked matrix. After the shifting, we can compare the effect for the different matrix molecular weights on equal footing. First of all, as expected, the shift follows a 3.4 power law obeyed by the terminal chain dynamics with respect to the molecular weight. More importantly, the value of G' at the same equivalent frequency is higher for the matrix with a higher molecular weight (down to 44K) at this loading of $\phi = 17\%$. This observation is clearly a confirmation that the "shell" thickness depends on the molecular weight of the polymeric matrix. At the same filler loading, the thicker shells allow more filler—filler association to take place, leading to increasing elastic modulus with the matrix molecular weight in the terminal region, as shown in Figure 3a. It is our opinion that chain bridging is necessary to effectively produce filler association although overlapping of two neighboring "shells" made of adsorbed chains might also enhance G'. Obviously, the condition for shell overlapping is also the condition under which chain bridging would take place. For a fixed filler loading and the same state of dispersion, there is less filler networking with decreasing matrix chain length. There was actually little molecular weight dependence for the last three molecular weights of 44K, 16K, and 12K. Apparently increasing from 12K to 44K did not cause more filler association to increase at $\phi = 17\%$ (see Figure 7).

By and large, the relative filler reinforcement should only be evaluated with respect to the internal chain dynamics. Figure 3b shows that the ratio of G' of the filled samples at 50 phr to G' of the pure matrices PBD44K, -100K, -200K, and -400K as a function of the oscillation frequency. The relative reinforcement evaluated in terms of G'/G'_0 clearly has distinct frequency dependence: in the elastic regime I this ratio hardly changes with frequency and is the same independent of the matrix molecular weight. Apparently the "shell" effect seen in the terminal (fluid) regime is absent when the matrix behaves like an elastic solid at high frequencies. In the fluid regime II, G'/G'_0 rises rapidly with lowering frequency because G'_0 drops sharply in the terminal region. Clearly, if one was to examine this relative reinforcement at a single value of oscillation frequency for all four molecular weights, one would conclude that the relative reinforcement was higher for a lower molecular weight matrix as asserted in ref 22.

3. Filler Loading Dependence. Unlike other properties such as conductivity that can directly probe the connectivity of the filler—filler network and may reveal a percolation transition, rheological characterization by G' and G'' reveals a smooth scaling relationship between the enhanced G' and the filler loading, as seen in Figure 6. Specifically, Figure 4 shows G' and G'' for different filler concentrations based on a PBD matrix of M_w = 1500 in the terminal region. Similarly, Figure 5a illustrates G' as a function of oscillation frequency of four samples based on PBD of M_w = 100K, where both terminal and plateau dynamics show up. Evaluating the

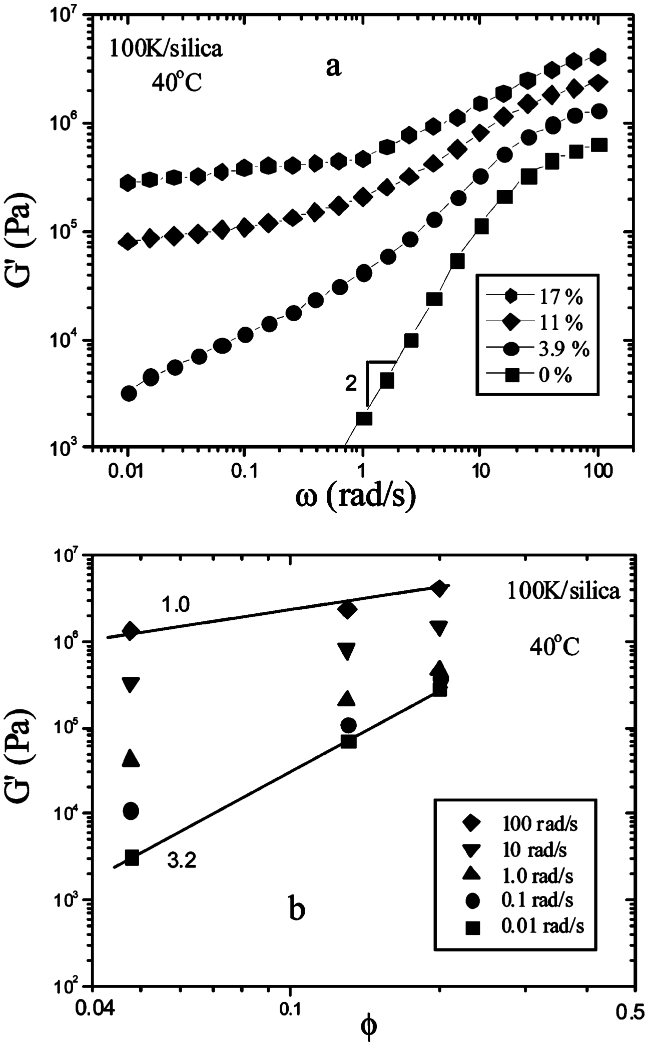

Figure 5. (a) Storage modulus G' of PBD100K reinforced by 3.9, 11, and 17% volume fractions of silica respectively in reference to the pure PBD100K. (b) Storage modulus of PBD 100K/silica as a function of filler loading at different frequencies.

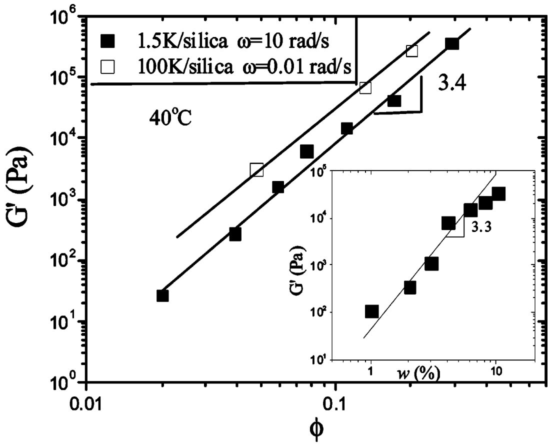

Figure 6. Storage modulus of PBD1.5K/silica at 10 rad/s (terminal) and PBD100K/silica at 0.01 rad/s (terminal) as a function of filler volume fraction, where the inset is replotted from Figure 2 in ref 6.

reinforcement effect in the terminal region, we plot G' at a fixed frequency as a function of the filler volume fraction ϕ in Figure 6. The observed scaling is strikingly similar to a previous result of nanosuspensions[6] as shown in the inset of Figure 6. In contrast, the ϕ dependence of G' is only linear in the plateau region as can be seen in Figure 5b.

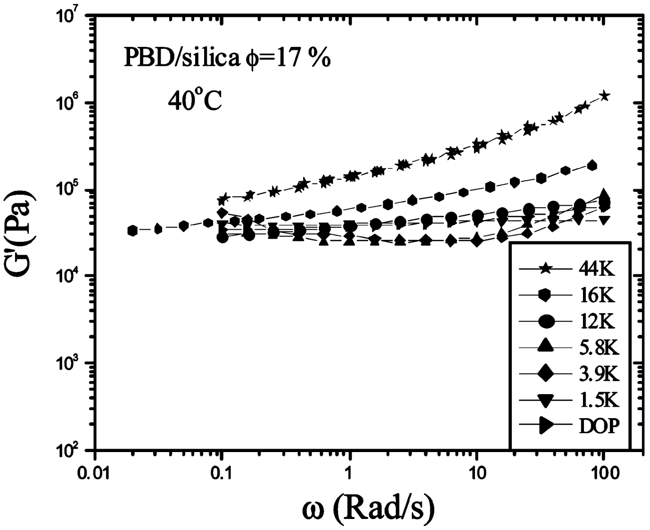

Figure 7. Storage modulus G' of filled systems as a function of the frequency at $\phi = 17\%$ ranging from six PBD to a small molecule liquid of DOP.

It appears that the scaling behavior of $G' \sim \phi$ in the elastic plateau region and $G' \sim f^{3.4}$ in the terminal region may be understood in terms of a recent theoretical model.[30] In the case of rigid fillers forming a fractal structure in an elastic medium, it was predicted[30] that at low filler volume fraction ϕ the enhanced elastic modulus E increases linearly with ϕ, and beyond a critical ϕ_c for percolation of the filler aggregates E would scale with ϕ as $E \sim f^{4}$ for a particular type of filler structuring. The filler reinforcement in the plateau region perhaps can be regarded as if it takes place in the limit of isolated fillers and unconnected filler clusters. In the terminal region, the enhanced G' arises from the large scale networking of the fillers. This filler reinforcement can be regarded to be the same as evaluating the elastic modulus of a percolating structure.

B. Shell Effect vs Chain Bridging. When the matrix chain length is sufficiently short, there is hardly any dependence as shown in Figure 7 for G' at $\phi = 17\%$ involving seven different media including a small molecule liquid of dioctyl phthalate (DOP). At sufficiently low frequencies all G' merges onto the same level as that represented by that based on DOP, indicating that the filler networking dynamics are due to "direct" filler–filler contact through a thin layer (perhaps on the order of a few angstroms) of liquid between the fillers. This comparison emphasizes the nonpolymeric nature of filler networking. Moreover, the time scale governing the filler–filler contacts are many orders of magnitude longer than the matrix relaxation time. These large-scale long-lived clusters of fillers are mainly due to the depletion forces and essentially independent of the matrix molecular weight in terms of their dynamics, in contrast to the time-dependent and molecular weight dependent effects seen in Figure 3a that are due to the chain-mediated interactions between the fillers.

Nevertheless, chain bridging can be shown to play an important role in enhancing the linear viscoelasticity of filled polymers. Besides the close contacts between fillers that produce the filler reinforcement effect, there

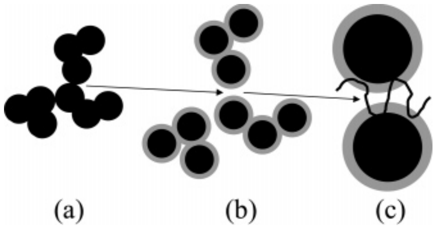

Figure 8. (a) A single cluster of nine primary particles made possible by the presence of long chains to bridge between the two larger gaps shown in (b) and (c) where the presence of "shells" (denoted by the gray shades) due to chain adsorption is unable to cause the three filler clusters of three particles each to associate into one.

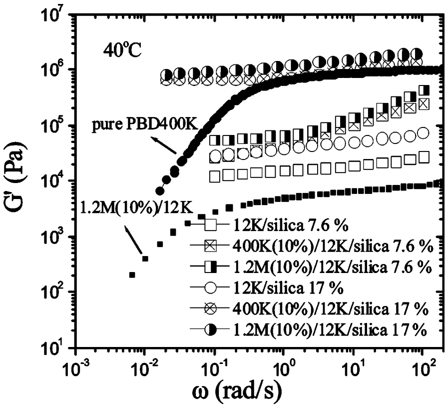

Figure 9. Storage modulus G' of PBD12K/silica composites at $\phi = 7.6$ and 17% as well as composites at the same filler loadings made of the matrices containing 10% PBD400K or 10% PBD1.2M and 90% PBD12K. Solid large circles represent G' of pure PBD400K. Solid small squares are G' of 10% solution of 1.2M in the PBD12K solvent, obtained by P. Tapadia.

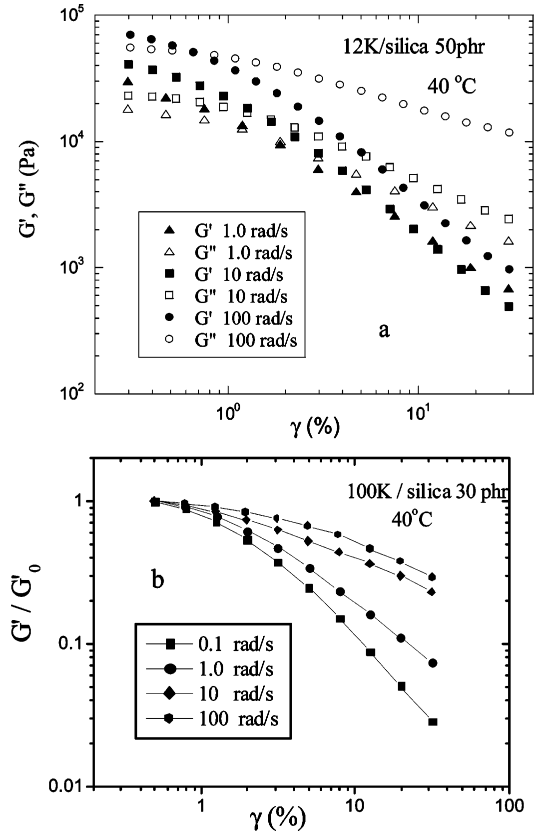

Figure 10. (a) Decrease of G' and G'' for PBD12K/silica composite at 50 phr as a function of the applied strain amplitude in oscillatory shear at three frequencies of 1, 10, and 100 rad/s, where the equal time interval for the strain sweep was adjusted so that the total time is 150 s for all the three sweeps. (b) Decrease of the normalized G'/G'_0 of PBD100K/silica at 30 phr at different oscillation frequencies as a function of γ, where the time interval for the strain sweep is 10 s.

are numerous small spaces among the fillers that only sufficiently long chains could reach to bridge as shown pictorially in Figure 8. A small amount of longer chains in a matrix of short chains could produce the effect depicted by Figure 8. More chain bridges are present at a higher filler loading. For example, at a small loading level of 3.9% the chain bridging is hardly effective because of the insufficient number of small spaces between the fillers. Figure 9 shows G' for two higher filler loadings at 7.6% and 17% involving a matrix of $M_w = 11\,600$. Upon adding 10% of long chains of molecular weights $M_w = 1.2 \times 10^6$ and 410 000 (PBD1.2M and PBD400K, respectively) to replace 10% of $M_w = 11\,600$ (PBD12K) while still keeping the same filler loadings, we show that these long chains make a considerable boost over the level of reinforcement without the long chains, where the effect is much greater for the filler loading of $\phi = 17\%$. The enhanced G' due to the incorporation of the long chains supports the chain bridging picture of Figure 8. A similar effect of chain bridging is found, based on the matrix of $M_w = 1500$, but the results are omitted here.

Figure 9 clearly shows the role of long chains in significantly boosting the storage modulus G' through chain bridging as illustrated in Figure 8. More strikingly, we notice that the 10% PBD400K long chains were able to provide a constant G' at the low frequencies where the pure PBD400K shows terminal behavior. This is clear evidence that these long chains have found themselves in between fillers of spacing on the order of the chain size where chain adsorption, confinement, and bridging would occur. In other words, the comparison between the filled circles (for the pure PBD400K) and the crossed-open circles indicate that additional structural buildup occurred due to the insertion of the 10% long chains in between tight spaces among the fillers. Had spacing between fillers been all much larger than the long chain dimension, we would not have observed any significant enhancement of G' as shown in Figure 9. We are inclined to think that chain bridging played a dominant role here because 10% long chains are not sufficient to uniformly increase the "shell" thickness through adsorption so as to allow overlapping of the shells.

In passing, it is perhaps useful to indicate that the effect of adding 10% long chains to the pure PBD12K is actually smaller in magnitude than the reinforcement effect of 7.6% filler. This can be seen by comparing the open squares with the small solid squares in Figure 9.

C. Nonlinear Viscoelasticity: Structural Breakdown in Oscillatory and Step Shear. 1. Oscillatory Shear. Filler reinforcement effects on linear viscoelasticity of melts and cross-linked rubbers are well-known. Also widely observed is one specific feature in nonlinear viscoelasticity of filled systems known as the Payne effect.[1] To save space, we omit all but two set of data collected using the standard procedure to perform strain sweep at a fixed frequency. Figure 10a shows the Payne phenomenon at several different frequencies. It is interesting to note the critical strain where the sample's G' begins to drop below G''. This critical amplitude appears to move to smaller values at the higher fre-

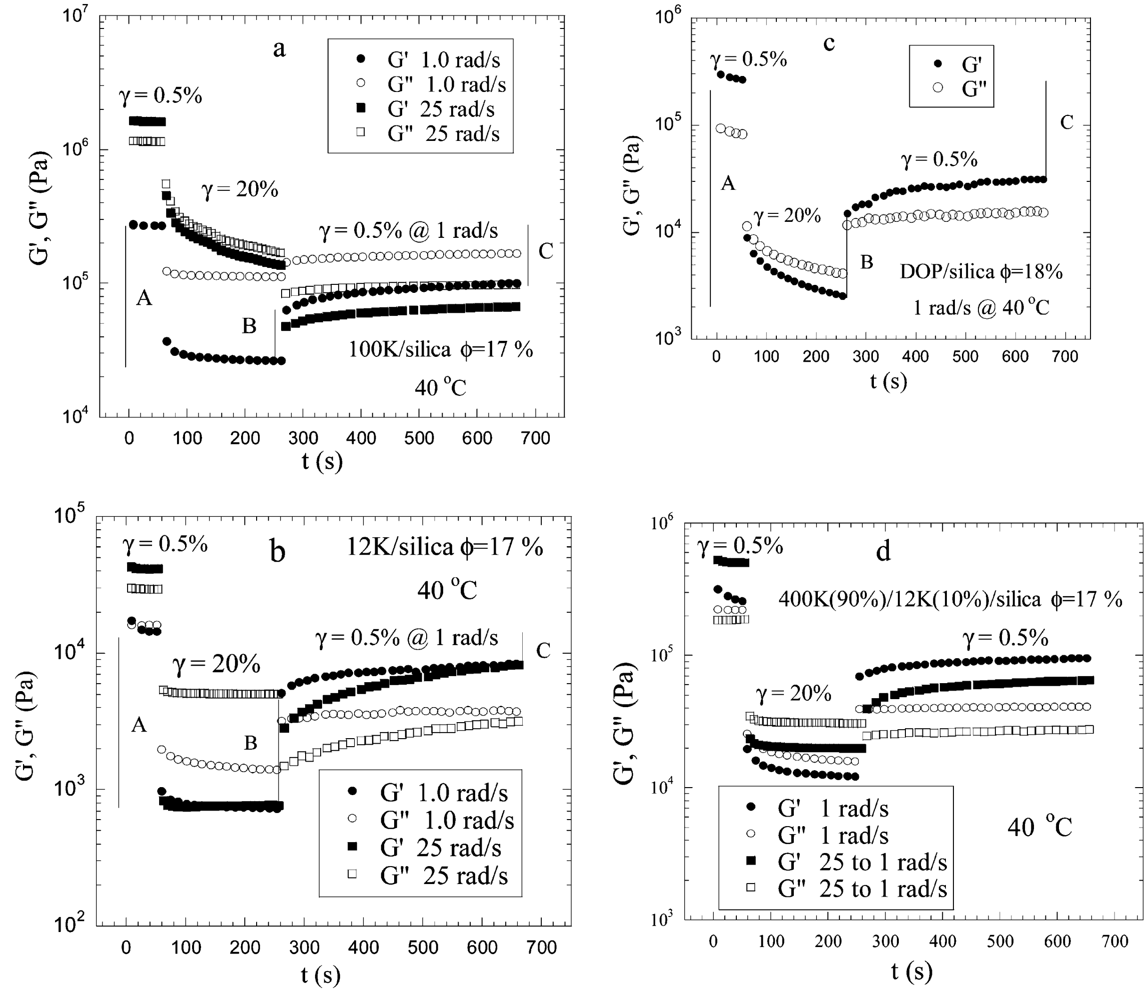

Figure 11. (a) G' and G'' of PBD100K/silica at $\phi = 17\%$ in response to a first strain of 0.5% at 1 rad/s (where G' and G'' overlapped) and 25 rad/s for 60 s, followed by 20% strain for 200 s at the two frequencies respectively before switching back to 0.5% at 1 rad/s at $t = 260$ s. Note that pure PBD100K would show strain-independent values of G' equal to ca. 2000 Pa and 300 kPa at frequencies 1 and 25 rad/s, respectively, according to Figure 1. (b) G' and G'' of PBD12K/silica at $\phi = 17\%$ in response to a first strain of 0.5% at 1 rad/s for 60 s, followed by 20% strain for 200 s at the two frequencies respectively before switching back to 0.5% at 1 rad/s at $t = 260$ s. (c) G' and G'' of DOP/silica at $\phi = 17\%$ in response to a first strain of 0.5% for 60 s, followed by 20% strain for 200 s at before switching back to 0.5% at $t = 260$ s, all at 1 rad/s. (d) G' and G'' of PBD400K(10%)/12K(90%)/silica at $\phi = 17\%$ in response to a first strain of 0.5% at 1 and 25 rad/s for 55 s, followed by 20% strain for 190 s at 25 rad/s and 205 s at 1 rad/s, respectively, before switching back to 0.5% at 1 rad/s at $t = 245$ and 260 s, respectively.

quencies (i.e., overall stresses). Figure 10b shows the Payne effect is weaker at higher frequencies in terms of the percentage drop. This is not surprising and is consistent with the information presented in Figure 5a,b: the reinforcement effect defined as G'/G'_0 is larger at a lower frequency.

In the remainder of section III.C.1, we present the response of the samples to stepwise oscillatory shear in the sequence of low, high, and low amplitudes. Figure 11a,b shows the respective responses of 100K/silica and 12K/silica composites to both small- and large-amplitude oscillatory strains. A comparison between them is again rather revealing: First of all, the decreases of G' and G'' at $\gamma = 20\%$ are smaller and less instantaneous in 100K/silica composites. It is suggestive that the filler networking among the much longer chain matrix of PBD100K was more resistant against failure. Second, the G' growth is faster for 12K/silica than for 100K/silica upon return to 0.5% strain. The different cone angles of the 8 and 12 mm cone−plate cells used in the measurements could also contribute. Actually the most serious effect is that the drop of G' is most likely related to a nonuniform breakdown of filler structuring. In other words, different layers across the sample thickness may undergo a different level of shear strain than the averaged 20%. We will work toward providing direct evidence of this assertion in the near future.

The most important revelation of Figure 11a,b is that a significant portion of the decreases in G' and G'' (e.g., represented by the vertical bar A for the sequence involving $\omega = 1$ rad/s), represented by the vertical bar B, is "instantly" recovered upon switching to a small amplitude. A second portion, represented by the vertical bar C, is essentially irrecoverable on the experimental time scales and must be due to large-scale disruption of the filler networking and perhaps filler spatial rearrangement under oscillatory shear.[31−33] Since neither the matrix chain of PBD100K nor PBD12K displays any inherent nonlinear viscoelastic responses (i.e., decreasing of G' with γ) at the applied frequency of $\omega = 1$ rad/s, which is well in the terminal regions of these PBD melts according to Figure 1 ($\omega_c = 20$ rad/s where $G' = G''|_{\omega=\omega_c}$), the drop indicated by A is due to stress-induced filler−filler dissociation.

To further explore the universality of this Payne effect, we proceeded to examine a suspension with 18%

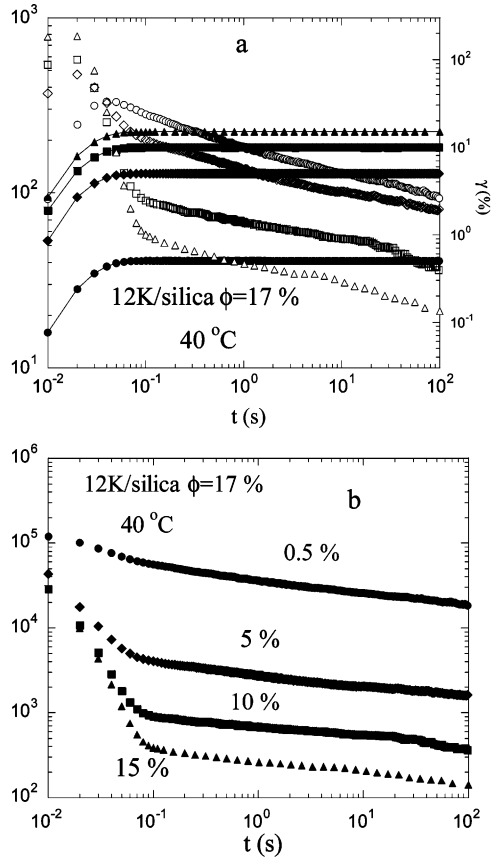

Figure 12. (a) Step-strain shear experiments for PBD12K/silica at $\phi = 17\%$: nearly instant shear of amplitudes 0.5, 5, 10, and 15% (in triangles, squares, diamonds, and circles, respectively, on the right-hand side vertical scale) were respectively and discretely applied, and the generated shear stress $\sigma(t)$ in corresponding symbols was monitored as a function of time on the left-hand side vertical scale. The actual strain $\gamma(t)$ took nearly 0.1 s to reach the preset value. (b) Relaxation modulus $G(t)$ calculated from $G(t) = \sigma(t)/\gamma(t)$ for the four applied strains of 0.5, 5, 10, and 15%.

volume fraction of the same silica particles dispersed in dioctyl phthalate (DOP). Phenomenologically speaking, Figure 11c looks rather similar to Figure 10a,b. In other words, the sample was clearly solidlike with $G' > G''$ at 0.5% and turned more liquidlike with $G' < G''$ at 20% before an instant recovery to solidlike behavior at 0.5%. For the polymeric matrices, since the filler networking is established with both direct filler–filler contacts and through insertion of chains between adjacent fillers, the breakdown of filler networking due to chain-mediated filler–filler association would have to involve chain desorption under high stresses and the instant partial recovery of G' due to chain readsorption. This point of view has suggested in the literature.[23,34] The fact that similar behavior is observed in a suspension based on DOP as shown in Figure 10c indicates that the phenomenon is more general in nature. We have carried out a similar measurement for a 400K-(10%)/12K(90%)/silica composite whose linear viscoelastic behavior has been described in Figure 9. It is important to note that even at the strain amplitude of 20% its G' is as high as G' of the 12K/silica composite at the same loading. The presence of the long (400K) chains have significantly reduced the filler dissociation and made the sample more resistant to the stress-induced destruction of filler networking.

2. Step Strain. Large-amplitude oscillatory shear measurements are a standard method widely used to explore the nonlinear viscoelastic behavior of filled polymers and suspensions. It is actually quite insightful to carry out step-strain shear experiment to further elucidate the response of the filled PBD melts. Figure 12a shows how the shear stress changed upon application of the four step strains involving four separate sample loadings in a cone/plate shear cell on ARES. In the regime of linear response, i.e., for $\gamma = 0.5\%$, the shear stress grows to its maximum at the same time as the actual strain reaches the preset value before the relaxation process took place. For the other three amplitudes, sufficiently high shear stresses were generated, apparently exceeding the value required to cause massive breakup of the filler–filler associations. Specifically, this stress level is between 300 and 500 Pa for this PBD12K/silicia composite, a range which is comparable to that ($\sigma \sim |G^*|\gamma$) at 20% of oscillatory shear shown in Figure 11b. We see in Figure 12a that the shear stress was dropping even though the applied strain was still growing toward the preset value. In essence, the samples became weaker in terms of its stiffness as the filler structuring collapsed upon the large step strains. This yieldlike behavior may not and is not expected to take place uniformly across the sample thickness. As a result of the structural breakdown, the relaxation modulus $G(t)$ in Figure 12b shows a large and rapid decline over a rather short time scale. This two-step relaxation feature occurred, with the first drop due to the *forced* structural disintegration and the second being the usual relaxation as seen in the linear response regime. It is important to mention that the same rheological behavior concerning the Payne effect as studied in section III.C is observed using grooved cone and plate. In other words, the origins of the observed Payne like effects are not due to interfacial wall slip.

IV. Conclusions

Using monodisperse linear melts of polybutadiene as the matrix, we are able to describe more explicitly the nature of filler association and its contribution to the linear viscoelastic properties of filled PBD melts by revealing presence of two regimes (elastic plateau and terminal) of interest in Figures 1 and 5, by demonstrating the presence of extraordinarily long relaxation times in Figure 2, by showing enhanced reinforcement for high molecular weight matrices in Figure 3a, and by illustrating how extra chain bridging (Figure 8) due to incorporation of long chains enhances dynamic modulus in the terminal region as shown in Figure 9. In the present systems, the filler–filler association to form clusters and connected structures are clearly the dominant factor for the observed filler reinforcement, i.e., the enhancement of dynamic moduli beyond those of the pure PBD matrices.

Oscillatory and step-shear experiments were carried out to elucidate how filler dissociation takes place under sufficiently high shear stresses, leading to nonlinear viscoelastic behavior. Specifically, the PBD/silica composites were shown to exhibit reduced elastic modulus and turn more liquidlike at sufficiently high shear stresses, independent of the specific modes of shear. In other words, there is evidence that filler networking broke down during shear. The ramp-up and ramp-down oscillatory shear experiments described in Figure 10a–d reveal instant drop at large amplitudes and rapid recovery of G' and G'' upon switching to low amplitude. Step-strain shear further illustrated how filled PBD melts respond to a sudden stress buildup by disintegration of the filler network as shown in Figure 11a,b. The two-step stress relaxation behavior of filled polymers appears to be a rather universal feature whenever the imposed shear stress would exceed a certain level sufficiently high to cause breakup of filler networking.

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