Strain-induced nonlinearity of filled rubbers

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Dynamic strain-induced nonlinearity in the modulus of filled rubbers shows a striking similarity to what is known about the glass transition of solid materials and the jamming transition of granular materials. This analogy stems from the reality that shear strain in dynamic mechanical measurements introduces fluctuations in a filler network by forcing the system to explore different configurations. Such fluctuations can be described by an "effective temperature" that has many attributes of a true temperature, and particularly is proportional to the strain amplitude. Thus, filled rubbers with respect to strain will display many unusual phenomena that are usually observed in glass-forming materials, but now demonstrated in filled rubbers, including asymmetric kinetics, crossover effects, and glasslike kinetic transitions. The nonlinearity in the modulus of filled rubbers simply reflects a dejamming transition of fillers in rubber matrices. The agglomeration of filler in an elastomeric matrix shares a common ground of physics with the jamming process and glass formation.

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I. INTRODUCTION

Filled rubbers, because of their promise as high-elasticity and relatively low-cost materials which can potentially have their physical characteristics matched to a given design specification, have been widely used for coatings, seals, dampers, cushions, transport belts, and automobile tires. The presence of fillers, e.g., carbon black or silica particles, in polymer matrices can significantly improve moldability, tenacity, durability, and abrasion properties. One of the fundamental issues is that filled rubbers have viscoelastic properties that depend strongly on strain amplitude. Payne [1] discovered 40 years ago that in unfilled amorphous polymers, cross linked or not, dynamic strains up to 40% ordinarily fell well within the range of linear viscoelasticity, but polymers loaded with solid particles had viscoelastic properties strongly dependent on strain amplitude, even for strains lower than 0.1%. The dynamic storage modulus G' of filled rubbers usually decreases with increasing strain amplitude, and the drop can be enormous at high strains.

Despite the technological significance of filled rubber materials, this nonlinearity in viscoelastic properties of highly filled rubbers is poorly understood. Various explanations for the reduction of dynamic storage modulus with increasing strain amplitude particular to filled polymers have been proposed, including filler network breakdown [1–4], filler deagglomeration [5,6], polymer-filler debonding from the filler surface [7,8], and strain softening of the polymer shell surrounding fillers [9]. Those past research activities often regarded the strain-induced softening phenomenon as a special area of physics specific to filled elastomers. However, this phenomenon is generally observed in many systems that differ widely in the strength and types of interparticle forces as well as the shape, average size, and nature of the matrix [1–11]. A complete understanding of the nonlinearity in filled rubbers still remains elusive.

Whereas the phenomenological theory of linear viscoelasticity of rubbers is essentially complete [12], the subject of the nonlinear viscoelasticity of filled rubbers has not reached the same stage of development. For nonlinear viscoelasticity, relations for interconversion of the functions of modulus and compliance are generally unknown. At present, nonlinear properties of rubbers such as stress-strain, creep compliance, and dynamic moduli are independently characterized and measured in rubber industries. The development of a model, even if only phenomenological, is desperately needed. This paper describes a study of the nonlinearity of carbon black filled rubbers in which we have unambiguously observed that the filled rubber displays glasslike kinetics and a glass transition under oscillatory shearing. We find that the strain-induced nonlinearity of filled rubbers shares a common physics with the glass transition of glass-forming materials and the jamming transition of vibrated granular materials. This result can be used to develop theoretical models.

II. MATERIALS AND EXPERIMENTS

Generic rubber compositions were prepared. The polymer used was a commercial polybutadiene with a molecular weight of about 150 kg/mol from Firestone Synthetic (commercial name Diene 40NF). The polymer had a vinyl-1,2 content of 12%, cis-1,4 content of 45%, T_g of about −90 °C, and Mooney viscosity of about 40 at 100 °C. Carbon black and other ingredients in the formulation were standard materials in the rubber industry and were commercially available. A master batch was formulated with 100 parts per hundred rubber (phr) polybutadiene, varied (50 to 70) phr N343 carbon black, 15 phr aromatic oil, 3 phr zinc oxide, 2 phr hydrocarbon resin tackifier, 0.95 phr antioxidant (Santoflex 13), 2 phr stearic acid, and 1 phr wax. Mixing was performed with a 300-g Brabender mixer using a mixing speed of 60 rpm. At time zero, the polymer was charged to the mixer, which was heated to an initial temperature of 110 °C. The remaining ingredients were added at $t=0.5$ min, and the batch was dropped at $t=5$ min when the temperature of the stock approached approximately 150 °C. This master stock was later mixed with curatives in the Brabender mixer at 60

rpm to form a final stock. The curatives used were 2.1 phr sulfur, 1.4 phr cyclohexyl-benzothiazole sulfenamide (accelerator), and 0.2 phr diphenylguanidine (accelerator). The master stock was added to the mixer held at 75 °C at time zero, the curatives were then charged at $t=0.5$ min, and the final batch was dropped at $t=1.3$ min when the temperature of the stock reached approximately 90 °C. The final stock was sheeted on a two-roll mill at 60 °C and cured in molds at 160 °C for 15 min. The T_g of the cured compound is about −89 °C. In preparation of samples of various filler concentrations, the master batch compounds that contained 50–70 phr carbon black were further diluted by adding some gum polybutadiene. Curatives and other ingredients were also correspondingly adjusted based on the selected formulation. The dilution process was carried out by using a two-roll mill at 60 °C. The prepared samples were finally cured in molds at 160 °C for 15 min.

Measurement of dynamic moduli (G' and G'') and strain effects was carried out using a Rheometrics ARES strain-controlled rheometer equipped with dual 200 and 2000 g cm force rebalance transducers and controlled using RSI ORCHESTRATOR V656 software. The following testing conditions were employed: oscillatory shear and 30 °C. The test specimen was a cylinder with a diameter of about 9.5 mm and with a length of about 5–15 mm, depending on the strain requirement. The specimen was superglued between a pair of parallel plates mounted in the instrument. Prior to testing, the specimen was dynamically strained in a sweep from 0.01% to 15%, and then dynamically sheared at the 15% strain amplitude for 3 h. The specimen was then allowed to recover while oscillating at 0.01% strain amplitude for at least 48 h. This procedure allowed the specimen to erase all of the previous load history, and was repeated at least twice to ensure that the dynamic mechanical spectra of the specimen were stable and reproducible. The strain during the oscillatory shearing varied according to $\gamma(t)=\gamma^0\sin(\omega t)$, where γ^0 is the strain amplitude. For simplicity, our use of γ in this paper corresponds to the amplitude value (we do not include the superscript 0). Reported strains represent values at the outer sample edge. Variation of strain across the sample radius does not significantly influence the findings herein compared to homogeneous deformation.

Measurement of the electrical conductivity (Γ) of rubbers and the effect of filler content was carried out on rubber compounds using a bridge-balanced Ohms-meter at 23 °C and 32% relative humidity. The test sample was a disk-shaped specimen and had a diameter of about 25 mm and a thickness of about 2 mm. The rubber sample was sandwiched between a pair of parallel metal plates that were mounted in the instrument. A normal load of about 2 kg force was used on the top plate to ensure a good contact between the rubber sample and the metal plates. Prior to the measurement, the setup was allowed to equilibrate for 20 min. Electric resistance measurements of rubbers were made directly between the two parallel metal plates.

III. RESULTS AND DISCUSSION

A. Glasslike kinetics

Under oscillatory shearing conditions, the modulus of the rubber decreases with time. However, immediately after the measurement at high amplitude, low-amplitude measurements give small values of modulus that gradually recover over a period of time and eventually regain their initial magnitude. This thixotropic behavior has been known for some time [1–4], but its detailed features have never been investigated thoroughly. As shown in Fig. 1, upon an abrupt change of the strain amplitude after reaching steady state, the mechanical properties of the rubber generally continue to evolve toward a new steady state at new amplitudes. However, the approach of the storage modulus G' to steady state will differ depending upon the direction of the change in the strain amplitude, when the rubber is allowed to equilibrate at a final dynamic strain. If the change $\Delta\gamma=\gamma_1-\gamma_0$ is positive, say from $\gamma_0=0.1\%$ to $\gamma_1=7\%$, the approach of the modulus to steady state is autoretarded. The rate of the evolution can usually be represented by an exponential (or stretched-exponential) expression such as $dG'(t)/\mathrm{dt}\sim -G'/\tau$, where τ is a characteristic relaxation time and G' is the instantaneous value of $G'(t)$. However, if the change in $\Delta\gamma$ is negative, say from $\gamma_0=14\%$ to $\gamma_1=7\%$, the approach of the modulus to the steady state is ill activated as the rate of the evolution can be fitted by an expression $dG'(t)/dt\sim k_a$ with $k_a\sim 1/t$. The asymmetric behavior cannot be interpreted by simple kinetic models such as those proposed in the literature [1–4], because a simple kinetic model such as $A\leftrightarrow B$ has the nature of symmetry.

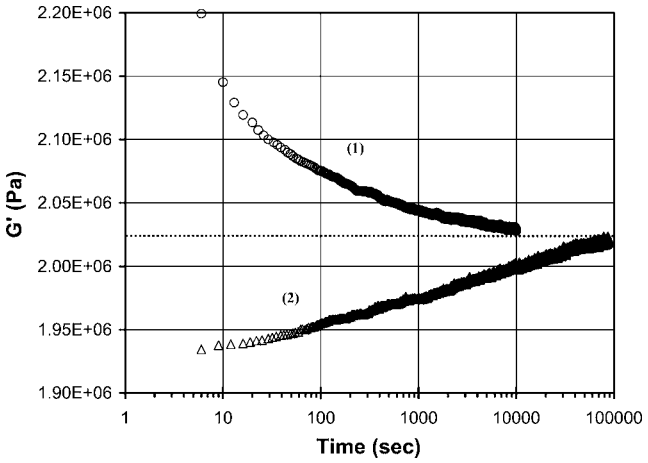

FIG. 1. Asymmetric approach to steady state of the filled rubber ($\phi=16.8\%$) at constant strain amplitude $\gamma_1=7\%$ on changing γ (1) from 0.1% to 7% and (2) from 14% to 7%. The test conditions: 0.5 Hz and 30 °C.

After the filled rubber specimen has been oscillatory sheared for a long time, it will reach a steady state. Although there is a defined average modulus, the results shown in Fig. 2 suggest that there are large fluctuations about the mean value. Further examination has shown that the fluctuations are real because they have their unique saw-shaped patterns that differ from the instrument's noise and they are about two orders of magnitude higher than the instrument's uncertainty. The shape of the distribution for the fluctuation amplitude can be obtained by plotting the logarithm of the probability of occurrence $D(\delta G'/\langle G'\rangle)$ versus $\Psi=(\delta G'/\langle G'\rangle)^2\mathrm{sgn}(\delta G')$, where $\delta G'=G'-\langle G'\rangle$. A Gaussian random process will have a triangular shape. As can be

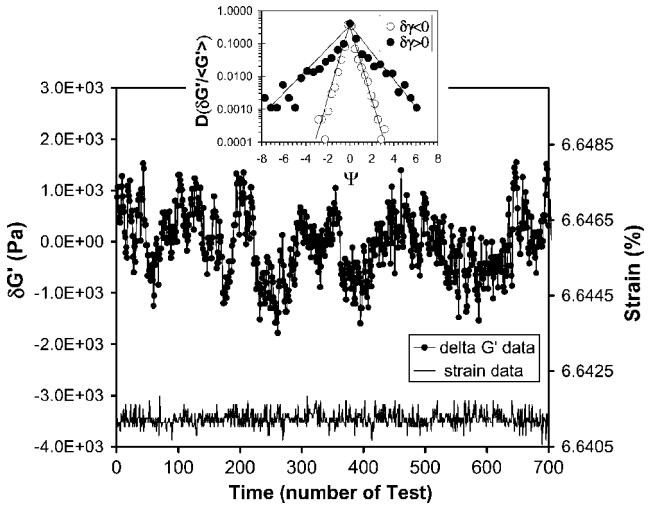

FIG. 2. Fluctuations in modulus of the filled rubber ($\phi = 16.8\%$) near the equilibrium state. The fluctuations have unique saw-shaped patterns that differ from the instrument's noise (e.g., the strain). Inset shows the distribution $D(\delta G'/\langle G'\rangle)$ vs the occurrence of fluctuation $\Psi = (\delta G'/\langle G'\rangle)^2 \mathrm{sgn}(\delta G')$. The test conditions: 0.5 Hz and 30 °C.

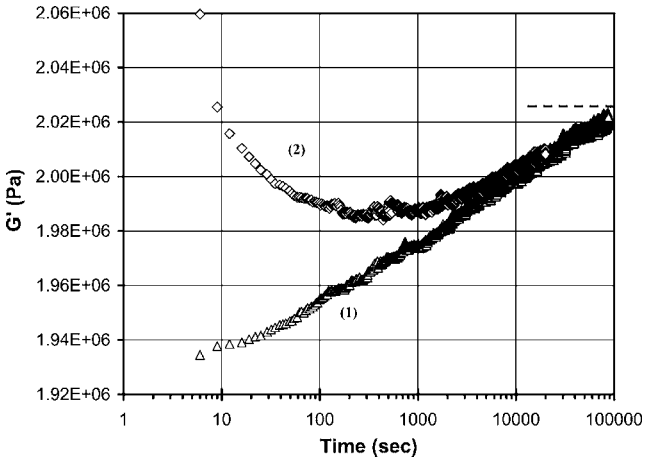

FIG. 3. Unusual crossover effects of the filled rubber ($\phi = 16.8\%$) at $\gamma_1 = 7\%$ on changing γ (1) from 14% to 7% and (2) from 14% to 1% for 15 min followed by a change from 1% to 7%. The test conditions: 0.5 Hz and 30 °C.

seen in Fig. 2 (see the inset), the modulus fluctuation data do show the Gaussian character. However, the distribution in the fluctuations is broader in the case when $\Delta\gamma > 0$ than that in the case when $\Delta\gamma < 0$. This behavior suggests that the heterogeneity in dynamical properties of the material, due to filler-filler interactions, differs and depends upon the direction from which the material is approaching the steady state.

Throughout the literature, there are two other systems that are known to show the same asymmetric behavior as their thermodynamic properties approach equilibrium. One is the structural relaxation process in glassy materials, most notably the relaxation and recovery of enthalpy and volume [13,14]. In this case, the specific volume of a glass after abruptly cooling to a temperature T is known to approach equilibrium faster than a glass heated to the same temperature [13]. The reason is that the cooled sample arrives at the temperature T with a larger free volume than the heated glass. This implies a more open structure characterized by a high mobility of molecules. Another situation with asymmetric relaxation behavior is the density fluctuation in a vibrated granular material [15–20]. In this case, the granular material is in its jamming state. Once a void large enough to contain a grain is created, it will be quickly filled by a new particle. The rate of density settling from above or below equilibrium [15] depends on the rate of void creation and the initial density of the material. Nevertheless, in both cases, the free volume plays a crucial rule in determining the rate of approaching equilibrium. Current wisdom suggests that these two cases share a common ground of physics [18–20]. Interestingly, filled rubbers under oscillatory shearing also show the same physical behavior. The modulus of the filled rubber after abruptly increasing to a strain γ is shown to approach the steady state faster than the rubber released from a higher strain to the same strain amplitude (see Fig. 1).

More complicated features are observed when the rubber is loaded with a dynamic strain amplitude, say $\gamma_0 = 1\%$, for a period of time t_1 insufficient to reach equilibrium, and then changed to another amplitude, say $\gamma_1 = 7\%$, and allowed to equilibrate. As shown in Fig. 3, the storage modulus initially decreases with time and crosses over the actual equilibrium, leading to a surprising minimum that depends upon the prior loading history applied to the sample. After that, the sample G' slowly approaches the equilibrium value. This phenomenon again was only observed in glass-forming materials in the glassy state [13,14], and the behavior was usually referred to as a crossover effect. Our experiments show that granular materials (e.g., fillers) may also display such a crossover effect if they are impregnated in a soft elastomeric matrix.

The existence of remarkable similarity between dynamic strain-induced nonlinearity in the modulus of filled rubbers and the physics of the glass transition of glass-forming materials and the jamming transition of vibrated granular materials has important implications with regard to our understanding of the strain-induced nonlinearity of filled rubbers. The similarity stems from the fact that filler particles in the rubber matrix agglomerate, given sufficiently high volume concentration of filler, and tend to form filler networks. The agglomeration and network formation of filler in elastomeric matrix are typically jamming processes that are analogous to glass formation. It is therefore understandable that the filled rubbers will show glasslike kinetics.

The physical origin of the fluctuation in modulus shown in Fig. 2 may be due to a competition between the breakup and the reformation of filler aggregates and networks in the rubber matrix. The net result of the competition determines the amplitude of the modulus. Depending upon the direction that the material is approaching the steady state, the sizes and the distributions of filler aggregates must be widely different in the rubber matrix. Consequently, the differences in sizes and concentrations of filler aggregates affect the local heterogeneities in the breakup and reformation rates. The existence of such heterogeneities can be seen in recent predictions of mode-coupling theories on colloidal glasses [21].

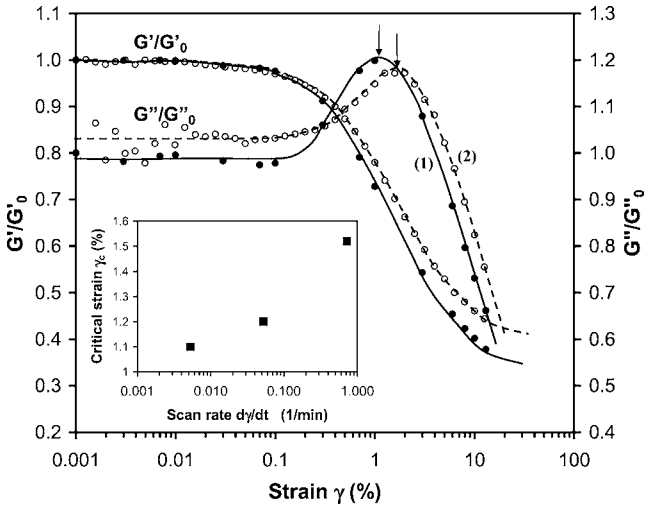

FIG. 4. Effects of strain history on the dynamic modulus of the filled rubber ($\phi=16.8\%$) with scan rate $d\gamma/dt$ (1) 0.0053 and (2) 0.72 min^{-1}. Inset shows the rate dependence of the transition. The subscript 0 denotes the zero-strain limiting values. The test conditions: 0.5 Hz and 30 °C.

B. Glasslike transitions

The observations shown in Figs. 1–3 suggest that filled rubbers with respect to strain amplitude behave like glass materials with respect to temperature changes. Given that filled rubbers under dynamic strains behave like glasses, is there a strain-induced "glass transition" in filled rubbery materials? The answer is definitely positive. Figure 4 shows the effects of strain history on the dynamic modulus of the rubber. The storage modulus G' initially is constant at low strains, then falls stepwise with increasing strain amplitude, while the loss modulus G'' passes through a maximum. These phenomena signify a transition, though it is generally referred to as the Payne effect [1–9]. However, we see evidence indicating that the transition is kinetically controlled. The higher the scan rate of strain sweep, the higher the strain amplitude where the transition is located. In comparison to thermal analysis, the rate of strain sweep in dynamic mechanical measurements for filled rubbers, $d\gamma/dt$, acts like the rate in a temperature scan for glasses, dT/dt.

Why should there be a similarity between the shear strain in filled rubbers and the temperature in glass-forming liquids? The reason is that shear strain in dynamic mechanical measurements often introduces fluctuations in fillers by forcing the system to explore different configurations [11,22–24]. Such filler fluctuations can be described by an "effective temperature" that has many attributes of a true temperature. Here, we present a simple discussion which allows us to predict the main relations. For a filled rubber system, the shear rate $\dot{\gamma}$ can be simply written as $\dot{\gamma}\sim\gamma\omega$, where ω is the test frequency and γ is the strain amplitude. Since the filler particles are trapped inside the polymer matrix, the average tangential velocity of a particle v can be approximated linearly as $v\sim\dot{\gamma}l$, where l is the dimension of the sheared specimen. This leads us to define a mean mobility of the particles χ via the relation $f\chi=v$, where $f=6\pi\alpha\eta$ is the friction force experienced by the particle in a media of viscosity η. Using statistical arguments for the fluctuations, the ensemble average of particle displacements $\langle r(t)-r(0)\rangle$ is related to χ via $\langle r(t)-r(0)\rangle=vt=f\chi t$, and the ensemble average of square displacements is related to the apparent diffusivity of particles D via $\langle[r(t)-r(0)]^2\rangle=2Dt$. According to the Einstein fluctuation-dissipation relation, it is the diffusivity and the mobility that enable the calculation of an effective temperature T_{eff}. We thus have $\langle[r(t)-r(0)]^2\rangle=2[T_{eff}\langle r(t)-r(0)\rangle]/f$. Supposing that the fluctuations follow a Gaussian random distribution, one finds that $\langle[r(t)-r(0)]^2\rangle=3\pi/8[\langle r(t)-r(0)\rangle]^2$. With the aid of those results, we are ready to obtain an expression for the effective temperature; that is, $T_{eff}=(3\pi/16)[\langle r(t)-r(0)\rangle]f=(3\pi/16)fvt\sim f\dot{\gamma}t$. Since the fluctuations will be maximized at $\omega t=1$, we find that $T_{eff}\sim\gamma$. The "effective temperature" is thus proportional to the shear strain amplitude [11].

Recent computer simulations [22,23] and experimental measurement using tracers [24] also support the existence of a well-defined effective temperature for sheared jamming materials. Hence, the dynamics of a jamming system whose effective temperature is lowered by reducing deformation (e.g., the strain) toward jamming will be quantitatively similar to those of a glass-forming material whose temperature is lowered towards the glass transition. The shear strain in filled rubbers acts physically like the temperature in glass-forming liquids. As for the filled rubbers, conventional dynamic stresses and strains (e.g., from 0.1% to 10%) typically place the filled rubbers right in the middle of the jamming transition. Thus, the larger the strain amplitude applied to the rubber, the larger the mechanical energy placed on the filler, the higher the mobility of filler particles, the higher the degree of dejamming, and the lower the storage modulus of the rubber. This explains why the viscoelastic properties of filled rubber are strongly nonlinear. In addition, the application of the concept of effective temperature allows the extension of ideas from molecular statistical mechanics to filled rubbers.

C. Isoenergetic character

The dynamic moduli (G' and G'') for filled rubbers as functions of strain amplitude and frequency are presented in Fig. 5. At low strains, again a strain-independent state is usually observed. As the strain is increased, the storage modulus G' falls with increasing strain amplitude, while the loss modulus G'' passes through a maximum (G''_{max}). Remarkably, despite the marked difference in frequencies, all experimental data can collapse onto a single master curve; this is accomplished by normalizing G' by G'_0 and G'' by G''_0, and by plotting the resultant data against the mechanical energy input $\sigma\gamma$ (in terms of units of Joule per volume) (see Fig. 6), where σ is the stress amplitude and $\sigma=G'\gamma$.

The extent of the vertical normalization is certainly influenced by the test frequency, but the phenomenon of all data collapsing onto a single master curve (i.e., the dejamming transition) is not. The reason is that the filler structure has a relaxation time that would much exceed the time scale of a conventional frequency sweep. A dynamic frequency sweep in conventional tests detects only the polymer dynamics, which appears to influence mainly the magnitudes of the G'

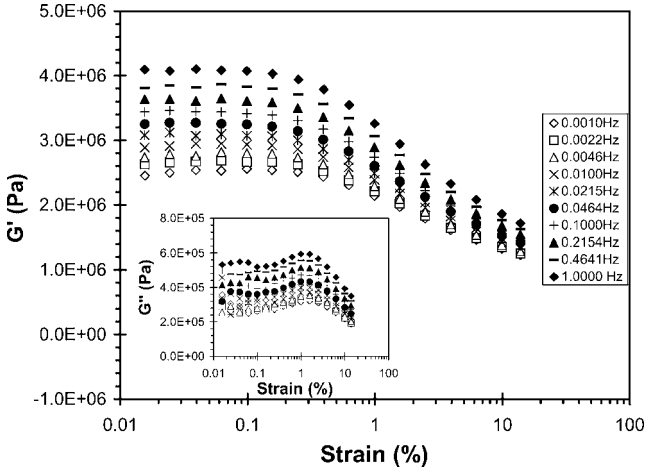

FIG. 5. Dynamic moduli (G' and G'') for the filled rubber ($\phi=16.8\%$) at 30 °C as functions of strain amplitude and frequency. The rate of strain sweep near transition $d\gamma/dt \approx 0.80$ min^{-1}.

and G'' at $\gamma=0$. To understand that, let us separate two filler particles in a rubber matrix to a distance of $x=500$ Å. This probably can be done in seconds by stretching a piece of rubber to about a few percent strain. However, if the particles are allowed to thermally diffuse over such a distance, this likely will require about a day for them to contact each other. A rough estimation of the thermal diffusion time for particles to travel such a distance can be made from Stokes equation $x^2/t=kT/(6\pi\eta a)$. For $\eta=10^5$ Pa and $a=30$ nm (typical values for carbon black in a diene-rubber matrix) the estimation gives $t\sim 10^5$ s. Hence, the jamming transition in filled rubber can be easily detected by a strain sweep, but not by a frequency sweep. Such a behavior of filled rubber is always observed as long as the polymer matrix is dynamically linear with the strain and as long as the test temperature (T) is fairly well above the T_g of the polymer. For cases when T is near T_g, the complication can be involved and will not be discussed here.

The effects of the filler loading on the dejamming transition in filled rubbers are presented in Fig. 7. The symbol ϕ represents the volume fraction of filler in the rubber matrix. Again, a linear behavior is observed below a strain of 1%. Upon further increasing the strain amplitude, the storage modulus G' falls off beyond a sort of critical-point strain (γ_c). At high strains, the drop in modulus is enormous and all compounds appear to approach the unfilled pure polymer gum whose modulus is low and linear through the strain-amplitude scale. Figure 8 shows that the magnitude of the critical strain γ_c at the transition decreases with increasing filler loading, while the magnitude of the critical stress σ_c increases with increasing filler loading. Remarkably, when the normalized storage modulus G'/G'_0 and loss modulus G''/G''_{max} are plotted against the variation of the mechanical energy $\sigma\gamma$, all experimental data appear to collapse approximately together (see Fig. 9). Of most importance is that the critical mechanical energy, defined as $\sigma_c\gamma_c$, at the transition is constant.

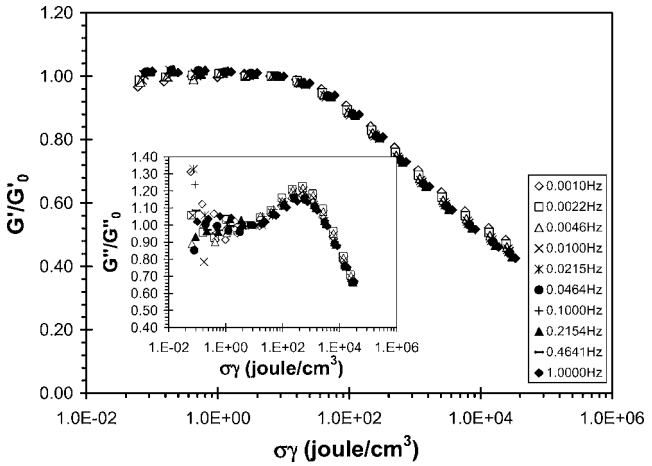

FIG. 6. Normalized dynamic moduli (G' and G'') for the filled rubber ($\phi=16.8\%$) at 30 °C plotted versus $\sigma\gamma$. The G' and G'' data are vertically rescaled by the zero-strain limited value of G' and G''.

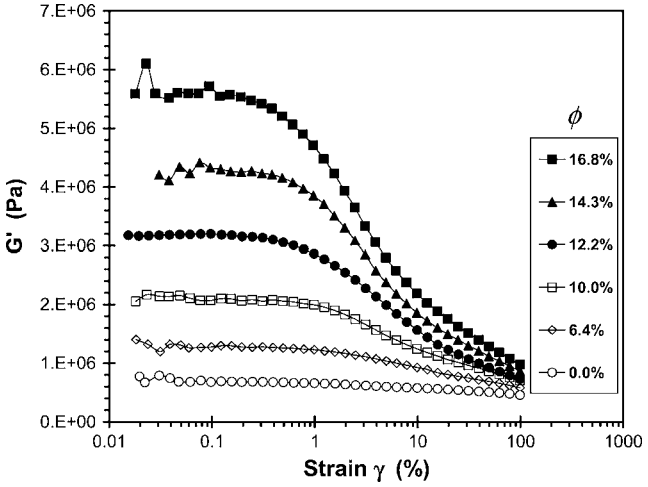

FIG. 7. Strain dependence of storage modulus for filled rubbers with indicated filler volume fractions. The test conditions: 0.5 Hz and 30 °C. The rate of strain sweep near the transition $d\gamma/dt \approx 1.5$ min^{-1}.

This isoenergetic behavior of the transition is not limited to the filled rubbers studied here. We have previously analyzed [10] other jammed systems, such as silica colloidal particles in oil, aqueous suspensions of boehmite alumina powders [25], and latex dispersions of polystyrene particles [26]. We found that all of them displayed the same isoenergetic behavior. This character of the jamming transition suggests that although jamming is kinetic, it may also be thermodynamic in nature. The physical significance of this isoenergetic behavior can be understood with the aid of the concept of the effective temperature T_{eff}. Based on the Einstein fluctuation-dissipation relation, we have found $T_{eff}=(3\pi/16)fvt\sim f\dot{\gamma}t$, where f is the friction force. From the force continuation principle, the force f must be proportional to the experimentally measurable shear stress σ. Thus, it would be more suitable to write $T_{eff}\sim\sigma\gamma$. Hence, a jammed material switches from elastic solid behavior to viscous fluid at a constant effective temperature T_{eff}. Throughout the literature thermoreversible gels are known to show the same behavior. For example, a solution of gelatin in water is a simple fluid at high temperatures. If we cool the solution, we

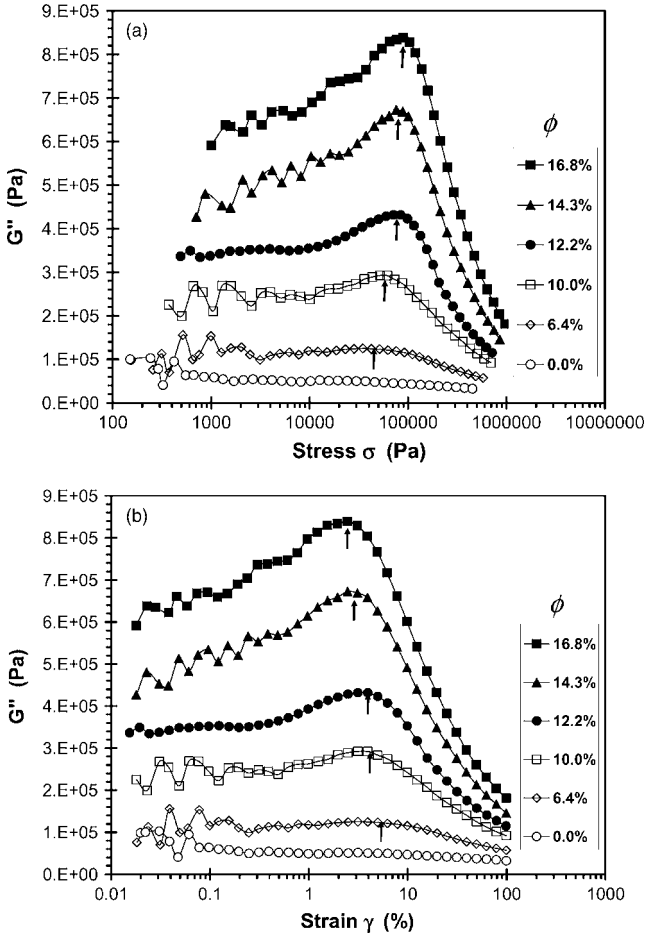

FIG. 8. (a) Stress dependence of loss modulus for filled rubbers with indicated filler volume fractions. (b) Strain dependence of loss modulus for filled rubbers with indicated filler volume fractions. Arrows mark the maximum locations. The test conditions: 0.5 Hz and 30 °C. The symbol legend is the same as that given in Fig. 7.

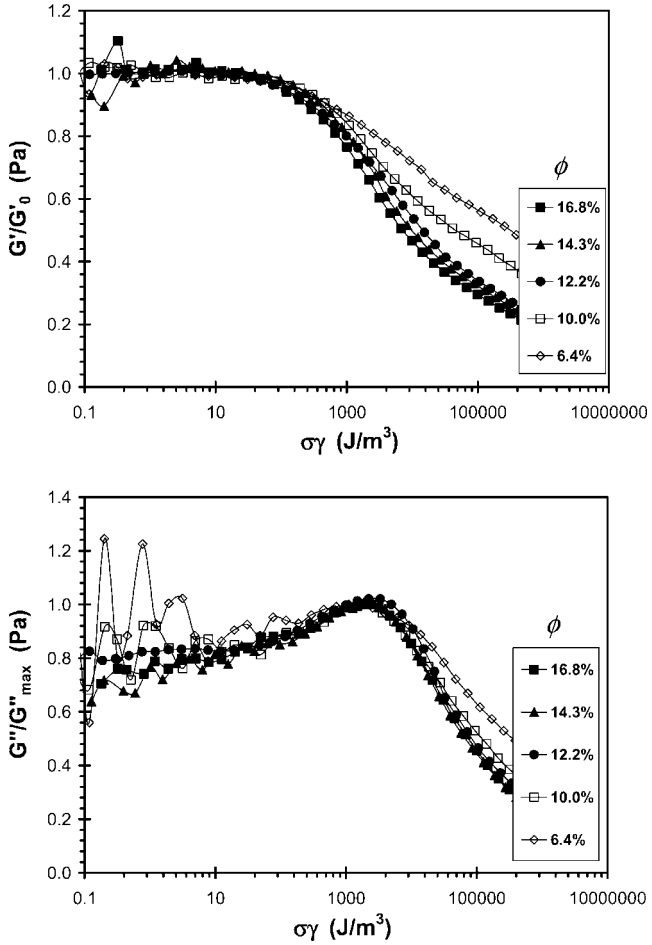

FIG. 9. Normalized dynamic moduli (G' and G'') for filled rubbers with indicated filler volume fractions plotted versus $\sigma\gamma$. The test conditions: 0.5 Hz and 30 °C. The G' data are vertically scaled by the zero-strain limited value of G'. The G'' data are vertically scaled by G''_{max}, the peak value of G''. The symbol legend is the same as that given in Figs. 7 and 8.

get a gel. If we raise the temperature again, we recover the solution. As is known, the crosslinks in many physical gels are produced by some physical associations between molecules, such as hydrogen bonding, ionic interactions, microcrystals, etc. Mostly the strength of those crosslinks depends on the nature of particular associations that break up at certain constant temperature T, but is not sensitive to the concentrations. This behavior has been described by de Gennes [27], who also stressed that there is a similarity between the thermoreversible gelation and the glass transition.

Although the $\sigma_c\gamma_c$ value in the filled rubber compounds is independent of frequency ω and filler concentration ϕ, it is sensitive to real temperature T. The effects of the temperature on the jamming transition in filled rubbers are illustrated in Fig. 10. As temperature decreases, the critical mechanical energy input required for this transition increases. The reason is that as temperature decreases the volume of the polymer is usually reduced, the mean distance between filler particles decreases, and interactions between particles intensify. In addition, polymer dynamics also has some contributions to the phenomenon. As temperature decreases, the polymer becomes less compliant and thus σ_c increases.

D. Percolating and jamming

What will happen to the conductivity (Γ) of rubber compounds loaded with various levels of carbon black if the system passes through the jamming transition? There are three basic properties of carbon black that are considered to affect the level of conductivity in rubber compounds. These are the primary particle size (or surface area), the primary aggregates, and the void space between those particles. Other factors in rubber compounds might play a role in determining conductivity but not to the extent of the above noted properties. Given that the primary particle size is constant and the degree of the primary aggregates is approximately the same after compounding, the void spaces between particles and aggregates therefore vary with varying filler loading and thereby control electrical flow through rubbers. Figure 11 presents the conductivity (Γ) of the filled rubbers as a function of carbon black loading. As the loading passes through a threshold $\phi_{c\Gamma}$, there is an abrupt increase in electrical flow with increasing carbon black loading. The transition is analogous to the general critical phenomena in terms of percolating.

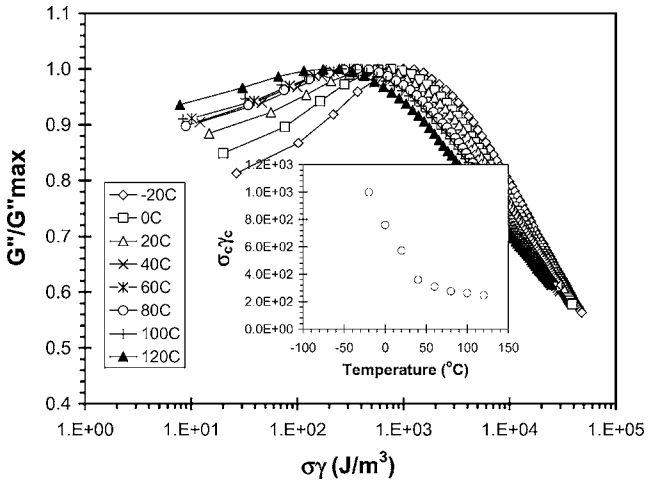

FIG. 10. Dynamic storage modulus (G'') for the filled rubber ($\phi=16.8\%$) as functions of strain amplitude and temperature. The G'' data are vertically scaled by G''_{max}, the peak value of G'. The inset shows a plot of critical $\sigma_c\gamma_c$ versus temperature. The rate of strain sweep near the transition $d\gamma/dt \approx 0.80\ \mathrm{min}^{-1}$.

Figure 12 shows the critical mechanical energy $\sigma_c\gamma_c$ as a function of carbon black concentration. Prior to a jamming threshold ϕ_{cm}, the magnitude of $\sigma_c\gamma_c$ increases linearly with increasing filler concentration. However, when the filler loading exceeds the threshold ϕ_{cm}, the behavior of $\sigma_c\gamma_c$ vs the filler concentration ϕ changes drastically and $\sigma_c\gamma_c$ becomes independent of ϕ as illustrated earlier. Surprisingly, we find that the threshold observed in dynamical mechanical measurements ϕ_{cm} is the same point as that observed in conductivity measurements $\phi_{c\Gamma}$. Hence, this study reveals that the jamming and percolating of fillers in rubber composite share the same physical origin.

E. Phase diagram

We now understand that different routes, through strain, volume fraction, and temperature changes, can effectively

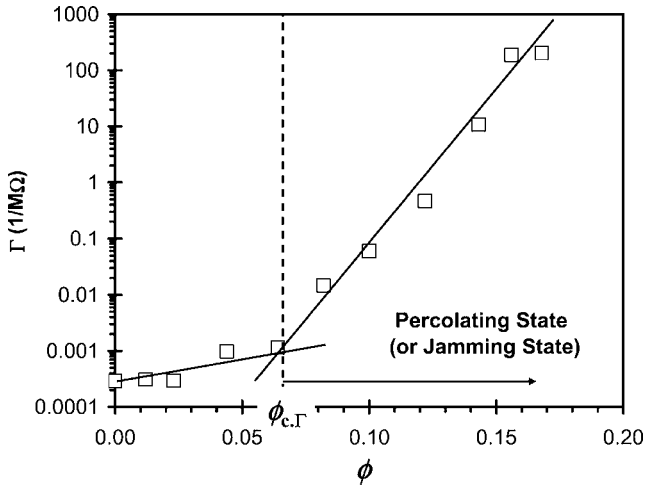

FIG. 11. Conductivity (Γ) of filled rubbers as a function of filler volume fractions. $\phi_{c\Gamma}$ marks the percolation threshold. Test conditions: 23 °C and 32% relative humidity.

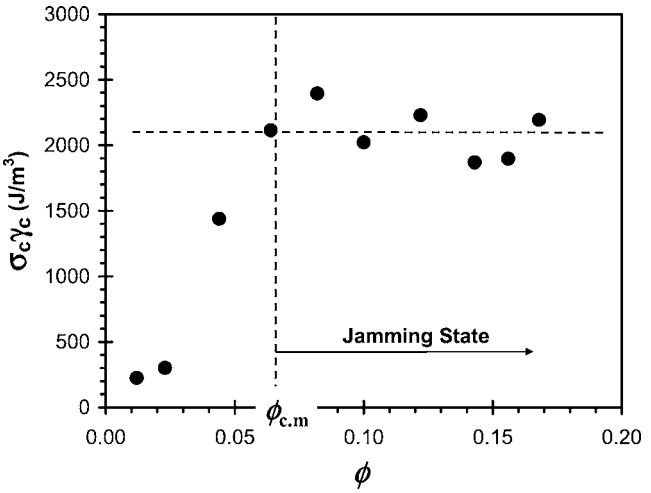

FIG. 12. Critical mechanical energy ($\sigma_c\gamma_c$) as a function of filler volume fractions. ϕ_{cm} marks the jamming threshold. The test conditions: 0.5 Hz and 30 °C. The rate of strain sweep $d\gamma/dt \approx 1.5\ \mathrm{min}^{-1}$.

lead filled rubbers to the same jammed state. A large unified physical picture in describing the dynamics in the frustrated systems would be a jamming phase diagram that is able to address the glass and jamming transitions. Based on our experimental observations, we propose a unified diagram as schematically shown in Fig. 13. The phase diagram for isoviscosity lies in the vertical $(1/\phi)$-T plane. The line that separates the jammed solids and unjammed liquids generally represents the glass transition. The classical empirical equation proposed by Doolittle [28] describes approximately the location of this transition. The transition line marks a critical viscosity of the system that in practice is impossible to track in the time scales accessible to experiment. The phase diagram for isoenegetic state lies in the horizontal $(1/\phi)$-$\sigma\gamma$ plane. The isoenergetic behavior comes from our experimental observation on various systems [10]. The effects of the temperature on the jamming transition are illustrated in the T-$\sigma\gamma$ plane. The magnitude of the energy is a function of the elasticity of the jammed fractal structure and the interaction strength between filler particles. Our experimental data show that $\sigma_c\gamma_c$ increases as temperature decreases. The transition

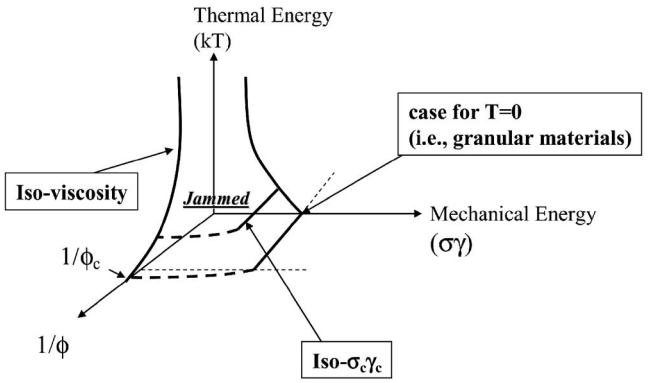

FIG. 13. A schematic drawing of the jamming phase diagram.

line marks a critical mechanical energy needed to dejam the system. The significance of this jamming phase diagram is that it has incorporated all variables that are derivable from Hamiltonians and may facilitate crucial comparisons between theories and experiments.

Some years ago Liu and Nagel [18–20,29] also proposed a phase diagram for jamming. In their phase diagram, however, very unusual axes were selected; i.e., the temperature T, density ϕ, and the shear stress σ. The quantities T and ϕ are traditional axes for phase diagrams, but σ is not. The physical origin of selecting σ in the phase diagram is not clear, though recent mode-coupling theories have attempted to include the shear stress [30]. In this study, we have found experimentally that using $\sigma\gamma$ instead of σ as the critical parameter can significantly simplify the phase diagram. It is also noteworthy that this mechanical energy $\sigma\gamma$, similar to the thermal energy kT, is theoretically derivable from Hamiltonians, which makes it is a natural choice as an axis in constructing phase diagrams.

F. Some thoughts on modeling

Interpretation of the nonlinearity in the modulus of filled rubbers as a consequence of the filler deagglomeration and filler network breakdown with increasing strain is not new. However, previous investigations [1–6] did not reach a large unified physical picture in describing the dynamics in frustrated systems like filled rubbers. Particularly, they often described the strain-induced nonlinearity using a two-stage $A \leftrightarrow B$ kinetic model [1–4], where A stands for the filler network, and B stands for the broken pieces. This model, because of oversimplicity, is unable to provide any insights into the observed asymmetric kinetics, crossover effects, and glasslike transitions of filled rubbers. At present, nonlinear properties of rubbers such as stress-strain, creep compliance, and dynamic moduli are independently characterized and measured in rubber industries.

There may be other factors in rubber compounds, such as polymer-filler debonding from the filler surface [7,8] and strain softening of the polymer shell surrounding the filler particles [9], that may play a role in determining the nonlinearity. However, these effects are not nearly as significant as the above noted properties and they are only observed in particular cases. Our investigation suggests that the strain-induced nonlinearity in the modulus of filled rubbers is due to a dejamming process. Filled rubbers show glasslike kinetics because the glass transition and jamming process share a common ground in physics. This knowledge can be used to develop theoretical models for describing the nonlinearity of filler-rubber composites.

Let us follow the development of the Kovacs multiparameter model [13,14] of the nonequilibrium glassy state and replace the temperature variable with the strain due to its direct connection to the effective temperature. The departure of stress (σ) from steady state (σ_s) can be defined as $\delta_\sigma = \sigma - \sigma_s$. At any strain amplitude, the relevant expression for $\delta_\sigma(t,\gamma)$ is then given by a convolution integral $\delta_\sigma = -(G_0 - G_s)\int_0^t R(t-t')(d\gamma/dt)dt'$; where $R(t)$ is a normalized retardation function. If we assume that the retardation function is a stretched exponential, i.e., $R(t) \sim \exp(-t/\tau)^\beta$ with $0 \leqslant \beta \leqslant 1$, we thus obtain a model for describing the modulus. Further introduction of a δ_σ dependence of τ, such as $\tau \sim \exp\{A/[\gamma(1-B/\gamma_f)]\}$ and $\gamma_f = \gamma + \delta_\sigma/(G_0 - G_s)$ similar to that used in the Tool-Narayanaswamy-Moynihan models [12] for glasses, will provide a phenomenological model for describing the nonlinearity in modulus. We found that this model qualitatively describes the asymmetric kinetics, crossover effects, and glasslike transitions. There are many details needing to be thought out. Nevertheless, we believe that this proposed approach will lead to a better model of the nonlinearity, because it captures the fundamentals of the process.

IV. CONCLUSIONS

In this article we present experimental evidence suggesting the existence of an analogy between dynamic strain-induced nonlinearity in the modulus of filled rubbers, the physics of the glass transition of glass-forming materials, and the jamming transition of vibrated granular materials. This analogy stems from the fact that shear strain in dynamic mechanical measurements introduces fluctuations in filler networks by forcing the system to explore different configurations. Such fluctuations can be described by an effective temperature T_{eff} that has many attributes of a true temperature. We show theoretically that the T_{eff} value is proportional to strain amplitude. Thus, filled rubbers with respect to strain must display many unusual phenomena, including asymmetric kinetics, crossover effects, and glasslike transitions. The nonlinearity in modulus of filled rubbers simply reflects a dejamming transition of the fillers in rubber matrices. The agglomeration of filler in an elastomeric matrix shares a common ground of physics with the jamming process and glass formation. In addition, we demonstrate experimentally that the jamming transition in filled rubbers also behaves as an isoenergetic thermodynamic transition. This evidence suggests that although jamming is kinetic, it may also be thermodynamic in nature. The coexistence of kinetic and thermodynamic descriptors of the jamming transition is analogous to observations about thermoreversible gels. Based on those experimental results, we propose a unified phase diagram for jamming transitions. The significance of this jamming phase diagram is that it has incorporated variables that are all derivable from Hamiltonians and may facilitate crucial comparisons between theories and experiments.

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