Amorphous Solidification in Polymer-Platelet Nanocomposites

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Computer simulations are used to understand the molecular basis of the rheology changes in polymer melts when loaded with platelet filler particles, specifically when the polymer and nanofiller interact attractively. With decreasing temperature, there is increasing aggregation between chains and filler and an increase in the polymer matrix structural relaxation time. These lifetimes are predicted to diverge at an extrapolated temperature, which we identify with the emergence of an amorphous solid state. Our findings suggest that filled polymers are phenomenologically similar to solutions of associating polymers and to supercooled liquids near their glass transition.

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The promise of significant enhancement in the mechanical, electrical, optical, and thermal properties of a polymer on the addition of small quantities of filler has made the study of filled polymer systems very popular [1–5]. Here we shall focus on the important question of the mechanism of mechanical reinforcement afforded by the presence of nanofiller particles in polymer matrices. In particular, we point to pioneering work by Ren *et al.* [6] who find that the linear viscoelasticity of intercalated polymer-filler composites changes from liquidlike to solidlike when the clay content is increased beyond 6.7 wt %. Two separate lines of thinking have evolved to understand the molecular basis of these reults. Ren *et al.* [6] propose that the *percolation* of silicate sheets occurs at the onset of the solidlike behavior [6]. While this argument considers only the geometrical properties of the filler particles, these workers also stress the importance of favorable polymer-clay interactions, since solidlike behavior does not result when energetically neutral filler particles are utilized [7–9]. Schmidt *et al.* [10,11] also emphasize the role of favorable polymer-filler interactions, but suggest the formation of a dynamic polymer-filler network. The crucial role of polymer-filler interactions on transport properties is also demonstrated by other workers [12,13] who show that polymer diffusivity decreases with increasing filler content.

While the unusual mechanical properties of filled polymers are attributed to "favorable" polymer-nanofiller interactions, it is unclear if geometrical percolation of the silicate sheets or the creation of a dynamic polymer-filler network is the underlying cause of the mechanical reinforcement. We utilize computer simulations and show that the polymer chains progressively associate with the immobile nanofiller particles on cooling, leading to an abrupt increase in the structural relaxation time of the polymer matrix. A detailed analysis of chain dynamics shows that the evolution of solidlike behavior is phenomenologically similar to the vitrification of supercooled liquids and the reversible gelation of polymers with associating groups. We stress that, while it is well known that favorable clay-clay interactions can lead to the gelation of aqueous clay suspensions [14,15], the "gelation" in our filled polymers arises from favorable polymer-filler interactions, even when the filler is immobile [16].

We conduct simulations of polymer-filler systems on 20^3 cubic lattices with a coordination number of $z = 6$. Periodic boundary conditions are used in all three directions. The system comprises end-functionalized polymer chains (denoted here by p), solid filler particles (denoted by f), and vacant lattice sites or holes (denoted by v). Each polymer chain is represented by a fully flexible string of beads connected by rigid bonds of fixed length. To mimic weak polymer adsorption, the two end beads of each polymer chain are *stickers,* representing functionalized moieties that interact with the filler particles. We consider chains of length $N = 50$, with a polymer volume fraction of $\phi_p = 0.7$. The filler particles are modeled as impenetrable squares of side 5 (i.e., 25 beads) which are placed randomly in the system. For the results reported here, we consider five filler particles ($\phi_f = 0.016$). In a series of five separate simulations we generate different random orientations of the filler and average results over these different simulations. The filler particles in each simulation are immobile. Double occupancy of lattice sites are prohibited, and the only attractive interaction is between a tail bead on the polymer chain and a nearest neighbor filler site, $\epsilon_{pf} = \epsilon/k_B T$, which is favorable (i.e., $\epsilon_{pf} < 0$). For equilibration, a mix of ~ 2–4×10^{10} Monte Carlo moves, i.e., reptation (30%), bond flip (50%), and chain regrowth (20%) were employed. We monitored the

normalized end-to-end vector autocorrelation function, a_t, to examine the equilibration of the systems: $a_t \equiv \langle \vec{r}(t) \cdot \vec{r}(0) \rangle / |\vec{r}(0)|^2$. $\vec{r}(0)$ and $\vec{r}(t)$ denote the end-to-end vector of polymer chains at some reference time ($t = 0$) and at a later time t. This autocorrelation function decays from unity at $t = 0$, to zero at long times. Subsequent to equilibration we employ only local flip moves to study system dynamics. Kovacs and others [17,18] have shown that Monte Carlo simulations with local flip elementary moves allow for the simulation of the dynamics of these systems. However, it must be noted that momentum is not conserved during each Monte Carlo move. Since hydrodynamic interactions are ignored, the dynamics of the chains will follow the Rouse model.

The single variable, whose role we have considered extensively, is the quantity ϵ_{pf}. Figure 1 is a plot of the mean square displacement of the centers of mass of the chains as a function of time, in Monte Carlo cycles, for four different values of the tail group-filler attraction. For the two weakly attractive cases, the dynamics of these systems go from Rouselike motion at intermediate times (slope $<$ 1) to diffusive (slope $=$ 1) at long times. The slope of the curve in the diffusive regime is equal to 6 times the diffusion constant of the chains in the filled system. It is clear, even in this range of ϵ_{pf}, that the increase in attraction between the chain ends and the filler reduces the diffusivity of the chains in a manner that is in qualitative agreement with the experimental results, particularly of Manias *et al.* [12,13]. The run times in Fig. 1 are not long enough to obtain quantitative estimates of the diffusion coefficient, which are therefore not reported. Note that current run times are 1–3 months on a personal computer, and that running long enough to be in the diffusive regime is currently not feasible. As the interaction energy ϵ_{pf} becomes more favorable the mean square displacement acquires a plateau at inter-mediate times, analogous to the behavior of supercooled liquids at temperatures below the onset of caging [19,20], or of associating polymers below the "clustering transition" [21].

To understand if this plateau in the mean square displacement, which we interpret as the onset of chain localization, is analogous to the behavior of supercooled liquids near their glass transition, we have examined the static structure factor, $S(q)$ [20,22]. Since we deal with a cubic lattice the only allowable values of q are $(2/L\pi)(i, j, k)$ where i, j, and k are integers in the range $(-L/2, L/2)$. For all values of $\epsilon_{pf} < -2$ we find a secondary peak in $S(q)$ at $q = 0.544$ in units of inverse lattice spacings, which suggests that a structure is evolving in the system on "cooling" (i.e., increasing the strength of the polymer-filler interaction). We shall focus below on the nature of the structure that forms in these situations. Figure 2 then plots the self-intermediate scattering function, $S_{q,inc}(t)$, as a function of time in Monte Carlo cycles at the peak position, $q = 0.544$. For the two weakest polymer-filler interaction strengths we see that the self-intermediate scattering function decays from 1 to 0 through a single-step relaxation. However, for the two most negative ϵ_{pf} values, it is clear that the incoherent scattering function displays a two-step decay, which has been documented as being a signature of the dynamics of supercooled liquids approaching their glass transition [20,22].

A good measure of the approach of a system to vitrification is the polymer matrix structural relaxation time, which should diverge as this transition is approached. We estimate this time from the self-intermediate scattering function as it decays to $1/e$ [23]. In Fig. 3 we plot τ against $-1/\epsilon_{pf}$. While the data are limited, it is apparent
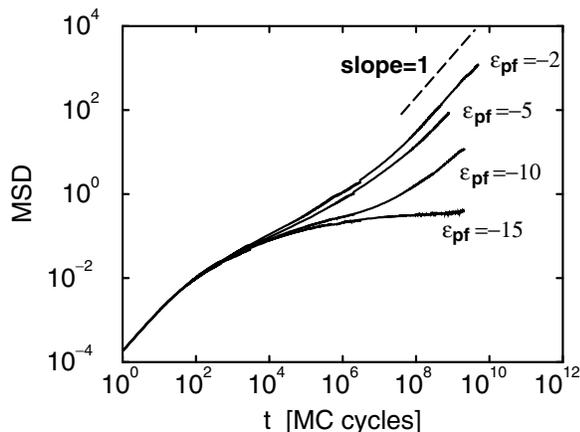

FIG. 1.   Behavior of mean square center of mass displacement of chains as a function of time in Monte Carlo cycles. The different curves correspond to different values of the sticker-filler interaction parameter, ϵ_{pf}, as indicated in the figure.
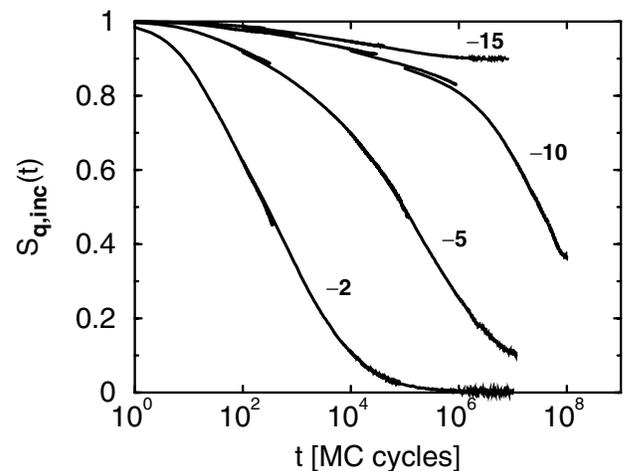

FIG. 2.   Plots of the self-intermediate scattering function as a function of time (in units of Monte Carlo cycles) at various ϵ_{pf} as indicated. The scattering function was evaluated at a $q = 0.544$, which corresponds to the secondary peak in the static structure factor.
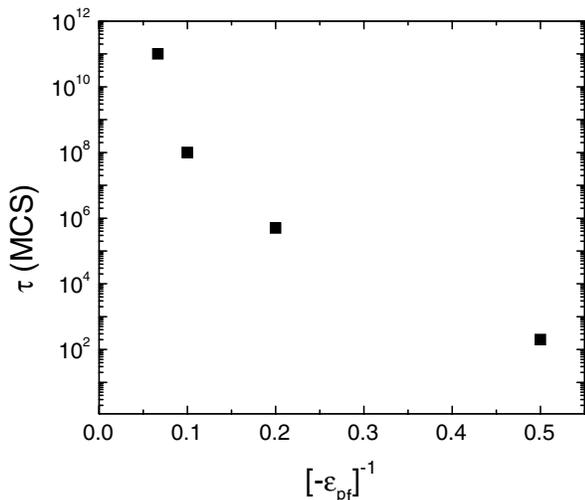
FIG. 3. Plot of the chain relaxation time, τ, as a function of $-1/\epsilon_{pf}$. The τ data were obtained from Fig. 2 by finding the time at which the self-intermediate scattering function decayed to a value of $1/e$. The time at the lowest temperature, $\epsilon_{pf} = -15$ is only a lower bound based on the equilibration data for this system. The error bars are smaller than the points for the two least favorable values of ϵ_{pf}. We do not have sufficient data to determine the error bars for the two most favorable values of ϵ_{pf}.

that τ appears to diverge at some finite value of ϵ_{pf}. We have fit this data to the Vogel-Fulcher functional form used to describe the dynamics of supercooled liquids with $-1/\epsilon_{pf}$ replacing temperature. However, we do not report these fits due to the limited number of data points. We expect the shear viscosity to diverge at the point where structural relaxation time, τ, diverges, and for the system to become a solid. In this sense, then, the polymer-filler system behaves in a manner that is analogous to solutions of associating polymers with stickers that directly cluster to each other. As temperature is lowered in the latter case, the chains progressively cluster, and the lifetimes of the clusters increases to the point that, at an extrapolated temperature, the whole system "freezes" into an amorphous solid [21]. By analogy, we suggest that the chain ends of the polymers progressively "stick" to the filler particles with decreasing temperature, so that chain clustering occurs *indirectly* through the mediation of the filler particles to which they are attached.

To provide a further basis for understanding these facts we consider two trains of thought. First, in Fig. 4 we examine the fraction of chains with no stickers attached to filler, chains with one sticker attached, and chains with both stickers attached. This last category is further broken up into "loops" (both chains ends associated with the same filler) and "tie" molecules (one chain associated with two different filler particles). For the weakest value of polymer-filler interaction, it is clear that most chains are either free or have one end attached to a filler. However, by the time one reaches the most favorable ϵ_{pf}, the
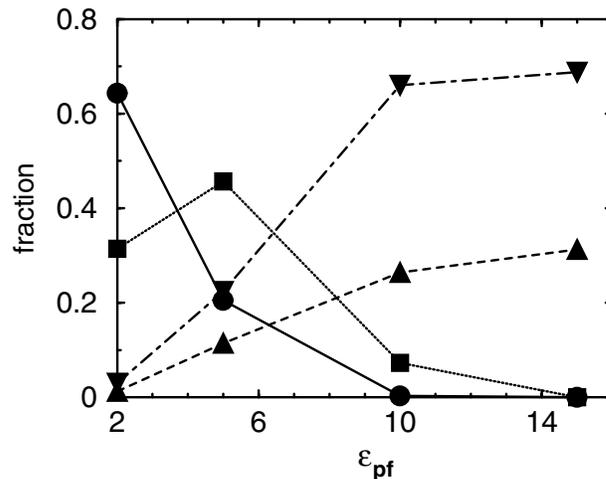

FIG. 4. Plot of the fraction of free chains (circles), chains attached at one end (squares), loops (inverted triangles) and bridges (triangles) as a function of ϵ_{pf}. The error bars are comparable to the size of the points.

trend completely reverses. There are practically no free ends available, and all the chains are either loops or tie molecules. The presence of these tie chains is critical since it is these that provide the connectivity between the fillers and sustain solidlike character. These data provide clear evidence that the chains progressively cluster with decreasing temperature through interactions with the filler particles.

A second train of thought comes from recent work by Krishnamoorti [24] and by Bonn *et al.* [25] who studied the aging and rejuvenation behavior of polymer-nanofiller composites and gels of filler solutions, respectively. Both of these works independently suggest that these filler systems behave in a manner similar to conventional glasses. These ideas are further substantiated by the experimental work of Eisenberg [26,27], who had examined the dynamical mechanical behavior of a variety of polymers mixed with silica nanofiller. For all silica contents above a critical value (typically 5 wt% silica) these workers found that, even though the unfilled polymer possessed a single glass transition, the filled system displayed two "glass transitions." While these past workers have identified the second transition as being associated with a bound polymer layer on the filler surface, we suggest that this transition is due to the formation of a macroscopic "gel" comprised of a percolated (i.e., macroscopic clusters) polymer-filler matrix with a long structural lifetime.

As a final point, we note the importance of percolation concepts in describing the emergence of solidlike behavior in filled polymer systems. By analogy to our previous work on solutions of associating polymers [21], if one made a plot of temperature vs filler content, then the "gel line" (i.e., the extrapolated temperature at which the relaxation time diverges) is expected to be more or less

horizontal (see Fig. 1 in Ref. [21]). In contrast, the percolation line rises effectively vertically in the same plot. These two lines will therefore intersect at some low temperature. For all temperatures below the intersection of these two lines, the gel line and the percolation line coincide. In these situations, all clusters that form are practically infinitely lived, and thus solidlike behavior will emerge precisely when these clusters percolate. We therefore argue that, while percolation is a necessary condition for the appearance of solidlike behavior, it is not always a sufficient condition. A sufficient condition is looking for the lifetimes of these percolating clusters and locating the extrapolated temperature at which they become infinitely long lived. At this point the percolating structure becomes effective at sustaining stress.

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[1] R. A. Vaia, K. D. Jandt, E. J. Kramer, and E. P. Giannelis, Macromolecules **28**, 8080 (1995).

[2] R. Krishnamoorti and R. A. Vaia, *ACS Symposium Series* (American Chemical Society, Washington, DC, 2002), Vol. 804.

[3] J. Huh, V. H. Ginzburg, and A. C. Balazs, Macromolecules **33**, 8085 (2000).

[4] M. Vacatello, Macromolecules **34**, 1946 (2001).

[5] J. E. Mark, Mol. Cryst. Liq. Cryst. **374**, 29 (2002).

[6] J. Ren, A. S. Silva, and R. Krishnamoorti, Macromolecules **33**, 3739 (2000).

[7] R. Krishnamoorti and E. P. Giannelis, Macromolecules **30**, 4097 (1997).

[8] R. Krishnamoorti, R. A. Vaia, and E. P. Giannelis, Chem. Mater. **8**, 1728 (1996).

[9] N. S. Enikolopyan, M. L. Fridman, I. U. Stalnova, and V. L. Popev, Adv. Polym. Sci. **96**, 1 (1990).

[10] G. Schmidt, A. I. Nakatani, P. D. Butler, A. Karim, and C. C. Han, Macromolecules **33**, 7219 (2000).

[11] G. Schmidt, A. I. Nakatani, P. D. Butler, and C. C. Han, Macromolecules **35**, 4725 (2002).

[12] E. Manias, H. Chen, R. Krishnamoorti, J. Genzer, E. J. Kramer, and E. P. Giannelis, Macromolecules **33**, 7955 (2000).

[13] Y. Zhang *et al.*, Macromolecules **34**, 7056 (2001).

[14] D. Bonn, H. Kellay, H. Tanaka, G. Wegdam, and J. Meunier, Langmuir **15**, 7534 (1999).

[15] M. Dijkstra, J. P. Hansen, and P. A. Madden, Phys. Rev. Lett. **75**, 2236 (1995).

[16] D. Gersappe, Phys. Rev. Lett. **89**, 058301 (2002).

[17] C. Crabb and J. Kovacs, Macromolecules **18**, 1430 (1985).

[18] K. F. Mansfield and D. Theodorou, Macromolecules **22**, 3143 (1989).

[19] S. Sastry, Nature (London) **409**, 164 (2001).

[20] C. Bennemann, C. Donati, J. Baschnagel, and S. C. Glotzer, Nature (London) **399**, 246 (1999).

[21] S. K. Kumar and J. F. Douglas, Phys. Rev. Lett. **87**, 188301 (2001).

[22] P. G. Debenedetti and F. H. Stillinger, Nature (London) **410**, 259 (2001).

[23] D. N. Perera and P. Harrowell, Phys. Rev. Lett. **81**, 120 (1998).

[24] R. Krishnamoorti (personal communication).

[25] D. Bonn, S. Tanase, B. Abou, H. Tanaka, and J. Meunier, Phys. Rev. Lett. **89**, 015701 (2002).

[26] G. Tsagaropoulos and A. Eisenberg, Macromolecules **28**, 396 (1995).

[27] G. Tsagaropoulos and A. Eisenberg, Macromolecules **28**, 6067 (1995).