Relation between Glass Transition Temperatures in Polymer Nanocomposites and Polymer Thin Films

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Motivated by recent experiments, we examine within a percolation model whether there is a quantitative equivalence in the glass transition temperatures of polymer thin films and polymer nanocomposites. Our results indicate that, while the qualitative behaviors of these systems are similar, a quantitative equivalence cannot be established in general. However, we propose a phenomenological scaling collapse of our results which suggests a simple framework by which the results of the thin films may be used to quantitatively predict the properties of polymer nanocomposites.

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A fundamental understanding of the influence of confinement and interfacial interaction effects on the properties of polymeric materials proves to be of importance for many applications. For example, the changes in the elastic moduli and glass transition temperatures (T_g, relative to that of bulk materials) observed in polymer thin films have significant implications upon the reliability of imaged patterns in nanolithography applications [1,2]. Not surprisingly, a number of recent theoretical and experimental efforts have focused on developing a fundamental and quantitative understanding of such effects [2–5].

In this Letter, we consider the correspondence between the behaviors of polymer thin films and particle-filled polymer systems [referred to as polymer nanocomposites (PNCs)]. Of these systems, thin polymer films are more easily fabricated, and sophisticated experimental tools allow for the properties of the film to be discerned at specific locations relative to the confining surface [4,6–8]. In contrast, PNCs are typically harder to design and characterize, and much less fundamental understanding exists regarding the origins of their properties [8–13]. Since the properties in both of these systems are known to be strongly influenced by the presence of polymer-surface interactions and confinement effects, one line of research enquiry has pursued the idea of trying to establish a quantitative equivalence between their properties [8,13]. In this Letter, we specifically focus on the correspondence, if any, on the glass transition temperatures (T_g) between these two systems. The motivation for this work arises from the numerous applications which require knowledge of the T_g to enable successful fruition. Moreover, recent experiments have come to different conclusions while examining the issue of equivalence in T_g between thin films and PNCs. Explicitly, a set of experimental investigations have suggested that the T_g of polystyrene (PS)-silica PNCs at an average interparticle distance h_p are quantitatively comparable to freestanding PS thin films at a thickness h_f when $h_f \simeq h_p$ [13]. In contrast, in other experiments, only a qualitative correspondence was observed between the properties of PNCs and thin films [8].

In this work, we seek to answer the fundamental questions, "Is there a quantitative equivalence in the glass transition phenomena and temperatures between PNCs and polymer thin films?" and "More generally, is it even possible to relate the properties of PNCs to the properties of thin films by universally valid relationships?" We propose to address these issues from a phenomenological, universality perspective by relying on recent ideas developed in the context of T_g in colloidal and polymeric materials. Specifically, the onset of the glass transition in these materials has been shown to be characterized by the percolation of slow, immobile domains through the system. The existence of such percolated slow domains has been observed in experiments and simulations of colloidal systems [14–16] and simulation studies of bulk and thin films of polymers [17,18] and have also formed the basis for a number of theoretical models of the glass transition [5,19]. In fact, Long and Lequeux [5] recently used such a percolation idea to successfully explain the thickness dependence and the long-range nature of T_g changes in polymer thin films. While the origin of the "dynamical heterogeneities" remains to be unequivocally established [20–22], the universality of their existence across different systems leads us to suggest that by examining the onset of percolation of immobile domains we can discern whether a correspondence between polymer thin film and PNC T_g's exists.

We adopt a simple model for dynamical heterogeneities by postulating that the slow, immobile domains nucleate randomly in the material. While more sophisticated "facilitation-based" ideas have been suggested for the occurrence of dynamical heterogeneities [23], our preliminary explorations on such models indicate only *qualitative* influence on the results presented in this Letter, and hence we present results only for the simplest version of the model. We implement our model in a lattice framework, with the different lattice sites representing the different

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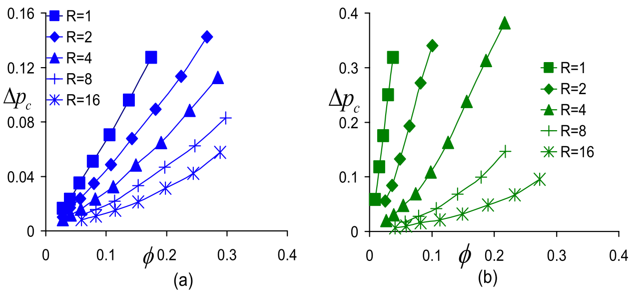
polymer domains, which are designated as arrested or mobile with a probability that depends on the observation temperature [5]. The lattice spacing is representative of the size scale of the units of dynamical heterogeneities. The temperature at which the arrested domains percolate through the sample is characterized as the "glass transition" temperature in this model. While the temperature dependence of the probability of being in an arrested state is necessary to extract a quantitative value for the T_g, we eschew this step and instead assume that this functional form remains the same for the polymer sites in a thin film, PNC, and a bulk polymer and hence compare directly the changes in the percolation thresholds (p_c) of PNCs and thin films relative to the bulk polymer. In this representation, an increase in the p_c can be viewed as a lowering of the T_g and vice versa.

Polymer thin films are modeled in the above framework by considering the influence of bounding surfaces upon the percolation of the slow domains, and the number of sites spanning the film is denoted as h_f. The particles in the PNCs are modeled as randomly placed lattice impurities of finite size R subject to the constraint that the impurities cannot be nearest neighbors. We studied situations for which the particles can be either wetted or dewetted by the polymer, by modeling the particle as a collection of either occupied (wet) or void (dewet) sites. For the wetting case, our model embodies the physics where arrested polymer sites in contact with the particle necessarily span across the particle. For dewetting polymers, our model mimics the physics where arrested polymer domains are prevented from spanning across the particle. To normalize for the presence of particles, the occupation probability is defined based only on the polymer sites (i.e., excludes the impurity sites). To study the influence of particle-polymer interactions, we also allow for the nanoparticles to have (overlappable) "skins" of influence on the polymer, characterized by two parameters: (i) the strength of the interaction, quantified by an altered probability of occupation δ, which embodies the ease of forming a slow domain relative to the bulk polymer, and (ii) the range of lattice sites over which such a perturbed polymer region exists (Δ). A similar skin of influence is also incorporated into the model for thin films for appropriate comparisons.

Preliminary results suggest that the qualitative features of the wetting and dewetting cases are very similar, and hence we discuss only the dewetting case. The results presented correspond to the case of 2D square lattices, with impurity fractions probed up to site fractions $\phi = 0.3$. Calculations in 3D are expected to differ in the quantitative details and exponents but retain the qualitative aspects of universality presented later in this Letter. The percolation threshold of the system is evaluated according to the following steps: (i) A lattice configuration is generated and occupied with a probability p according to the rules described above; (ii) cluster analysis is performed using the Hoshen-Kopelman algorithm to determine whether a percolating cluster of occupied (arrested) domains exist [24]; (iii) this process is repeated a large number of times to determine the probability of the system to percolate $P(p)$; (iv) the common intersection point of $P(p)$ for different lattice sizes L is taken as p_c. The algorithm was validated by evaluating the well-known case of site percolation on a impurity-free square lattice ($p_c = 0.593$).

Figure 1(a) displays our results for the increases in p_c (equivalently, the decrease in T_g) of PNCs of different sized particles as a function of the site fractions of the particles. It is observed that either an increase in the concentration of the particles or a decrease in the size of the particles leads to an increase in the magnitude of the change in the percolation thresholds. While the effects of ϕ (at a fixed R) can be understood as due to a corresponding increase in the number of percolation obstacles, the effect of R can be rationalized by noting that, at a specified particle loading, the larger particles typically result in larger intersurface distances and smaller particle surface areas, and hence both the confinement and surface effects become less pronounced. These considerations are substantiated in Fig. 1(b), which illustrates the effects arising from the presence of a skin layer around the particles. Here it is observed that, while the presence of a skin layer always enhances the magnitudes of changes in the percolation thresholds (relative to the particle-only influence), such effects are more significant for the case of smaller sized particles. We also point out that these results are consistent with experimental observations [25] in PNCs which have shown that, in cases where nanoparticles influence the T_g of polymers, larger particles (or agglomerates) of the same chemical makeup may have no resolvable influence upon the T_g of the same polymers.

The above results, especially the particle size dependencies, demonstrate the importance of confinement effects and hence support the notion that a quantitative equivalence between the T_g of thin films and PNCs may be



(a) (b)

FIG. 1 (color online). Changes in percolation thresholds (Δp_c) of PNCs with particles of different size R as a function of the particle site fraction ϕ (lines are a guide to the eye). (a) PNCs with no skin layer of influence ($\Delta = 0$; $\delta = 0$); (b) PNCs with a skin of influence with $\Delta = 3$; $\delta = 0.4$.

sought. In Fig. 2, we examine this equivalence by comparing the results for Δp_c of PNCs as a function of the average nearest neighbor intersurface distance h_p with the corresponding results for an identical film of thickness h_f. It is observed that not even the results for the PNCs of different particle sizes (both with and without the skin layer) collapse onto a single universal function when plotted in this representation. Moreover, it is also seen that, while both the PNC and thin film models exhibit the same qualitative behavior, the quantitative influence of confinement effects is much more pronounced for thin films as compared to PNCs. Finally, we see that incorporating polymer-particle interactions effects through the skin layers renders the quantitative differences between PNCs and thin films even stronger at larger film thicknesses [26].

What is the physical origin of the differences between PNC and thin film T_g? We believe that the differences arise due to the fact that the morphology of the intersurface spaces in PNCs are much more complex than embodied in a thin film model. Indeed, confinement effects arising in thin films from the bounding surfaces would necessarily impact upon the percolation paths and, hence, the onset of percolation and the glass transition [5]. In contrast, addition of particles may or may not affect the T_g in PNCs, especially if percolation paths avoiding the particles may exist. This suggests that, except for very high concentrations of particles or for very large particles (conditions for which the geometry of the intersurface gaps resembles thin films), even quantitatively similar T_g values for the two systems may not be expected.

Can the p_c (T_g) of thin films and PNCs be quantitatively related? The answer to this question is nontrivial, since the T_g of PNCs are expected to be dependent on h_p, R, Δ, and δ, whereas the T_g of films depend upon h_f, Δ, and δ. However, since the particle influences vanish in dilute concentrations, we expect that as $h_p/R \to \infty$, $\Delta p_c \to 0$. On the other hand, if we were able to reach a limit wherein $h_p/R \ll 1$ (which would require very high volume fractions), based on the reasoning proposed in the above paragraph, we expect that the T_g changes in thin films and nanocomposites may become quantitatively comparable. Moreover, we might think about Δ and δ as parameters which would renormalize h and R in the preceding picture. Based on these considerations, and the expectations of universalities in percolation phenomena [24], we were able to *empirically* scale our PNC data over the entire regime of particle sizes, skin layers, and surface interaction strengths into a remarkable collapse of the form (cf. Figure 3): $(\Delta p_c)_{\mathrm{PNC}} = 0.063R'(h'_p)^{-1.63}$. R' and h'_p represent the shifts of R and h, respectively, to account for the presence of skin layers. Explicitly, $h'_p = h_p - \Delta\delta$ and $R' = R + g(\Delta, \delta)$ (an analytical functional form of g could not be determined [27]). Within the same approach, we found that all of the thin film results could also be satisfactorily collapsed (Fig. 3) into a function of the form $(\Delta p_c)_{\mathrm{Film}} = 1.117(h'_f)^{-0.66}$, with $h'_f = h_f - \Delta\delta$. Together, these universal scaling results suggest that

$$\frac{\Delta p_c(h', \mathrm{PNC})}{\Delta p_c(h', \mathrm{film})} \simeq 0.054\left(\frac{h'}{R'}\right)^{\gamma}, \qquad (1)$$

with $\gamma \approx -1.0$.

The above universal scaling result is one of the main results of this Letter. It suggests that, despite the lack of quantitative equivalence between PNCs and thin films, the p_c (and T_g) results of the thin films may be used to *predict* the corresponding values for the PNCs. Explicitly, Eq. (1)

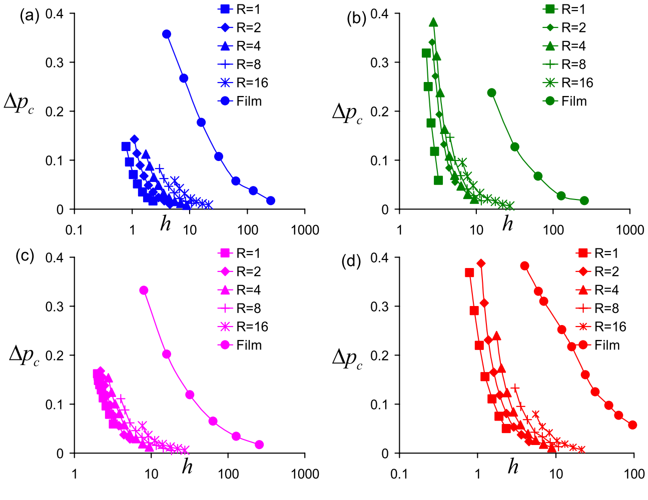


FIG. 2 (color online). A comparison of the changes in percolation thresholds (Δp_c) of PNCs with particles of different size R with those of films as a function of the average intersurface distance h (lines are a guide to the eye): (a) no skin layer of influence ($\Delta = 0$; $\delta = 0$); (b) a skin of influence with $\Delta = 3$; $\delta = 0.4$; (c) $\Delta = 3$; $\delta = 0.1$; (d) $\Delta = 1$; $\delta = 0.4$.

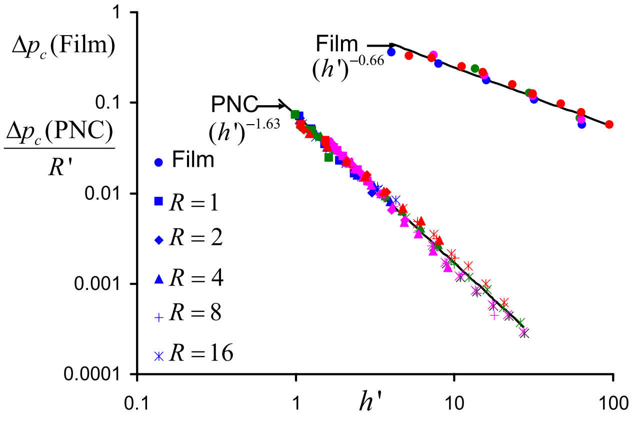


FIG. 3 (color online). Scaling collapse of Δp_c values displayed in Fig. 2. The different symbols above represent the results for the different radii. Blue: $\Delta = 0$, $\delta = 0$; green: $\Delta = 3$, $\delta = 0.4$; pink: $\Delta = 3$, $\delta = 0.1$; red: $\Delta = 1$, $\delta = 0.4$. The meanings of h' and R' are discussed in the text. $R' = R + g(\Delta, \delta)$, where we empirically determined $g(0, 0) = 0$, $g(3, 0.4) = 3.5$; $g(3, 0.1) = 4$; $g(1, 0.4) = 0$.

suggests that the ratio of Δp_c for thin films and PNCs, when compared at the same shifted value of film thickness and intersurface distance, scales as a power law of the ratio of the shifted thickness to the shifted radius. Importantly, the shift factors are predicted to be only a function of the polymer-surface pair considered and, hence, are independent of the particle radii and/or concentrations. This relationship hence suggests a means for prediction of PNC properties, containing particles of any size and concentration, by using the corresponding results for thin films in conjunction with two shift parameters that depend only on the polymer-surface pair. While the values of the exponent γ and the shift factors would necessarily depend on the fact that our simulations were effected in 2D, from considerations of universality, the phenomenological form of Eq. (1) is expected to hold for 3D systems and apply to experimental observations.

The above result also confirms our speculation that the changes in p_c (and T_g) for the PNCs and thin films may become comparable only when $h/R \ll 1$, a regime attainable only for high volume fractions of particles. This insight may also provide a possible rationalization of the discrepancies in experimental observations noted in the introduction. The experiments of Schadler and Kumar, which noted the quantitative equivalence between PNCs and films, considered PNCs of high loadings (up to 40%) [13]. In contrast, the experiments of Torkelson and coworkers (whose results were qualitatively similar to our Fig. 2) [8] considered PNCs at much lower loadings and noted only qualitative agreement between the T_g values of thin films and PNCs.

In summary, we have examined the changes in T_g for PNCs and their equivalence with thin films in terms of a percolation model. While the qualitative behaviors of these systems were similar, clear quantitative differences were discerned, thereby dismissing the possibility of a general quantitative equivalence. However, upon collapsing our results using a novel scaling picture, a phenomenological model was suggested that can use the thin film results to *predict* quantitatively the properties of PNCs. This unique correspondence provides a simple approach to relate the T_g of PNCs and thin films and may open up the possibility to explore relationships involving other comparable properties such as aging characteristics, permeabilities [8,28], etc. However, future work is needed to verify this scaling in other dimensions, for other particle shapes and interactions, and from microscopically based T_g theories [29]. More importantly, systematic experimental studies are also needed to validate this idea.

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[27] See EPAPS Document No. E-PRLTAO-101-037832 for a description of the manner in which the scaling collapse of Fig. 3 and Eq. (1) was accomplished. For more information on EPAPS, see http://www.aip.org/pubservs/epaps.html.
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