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Communications to the Editor

Percolation Transition and Elastic Properties of Block Copolymers[†]

Recent advances in percolation theory have provided a new conceptual framework for a better understanding of composite materials and their properties, which are known for their complexity and intractability.[1] The central question in the original formulation of percolation theory, in which sites (or bonds) of a lattice can be occupied randomly with a certain probability p, concerns the conditions under which there would be a macroscopic association of occupied sites (or bonds) that pervades the whole lattice. In addition to this size information, modern percolation theory also addresses the question whether there is any singular behavior in relevant physical quantities when the average size of connected cluster of one component diverges, since the occupied and empty sites (or bonds) may possess contrasting physical properties. For example, they may represent, respectively, conductor and insulator, absorbing and transparent materials, or rubbery and brittle components. Although recent theoretical and experimental work on composite properties in conductivity,[1-5] dielectric constant,[6,7] Hall effect and magnetoresistance,[8] optical transmissivity and reflectivity,[9] and magnetism[10] has established several interesting correlations with the underlying percolation transition, analogous studies on mechanical properties have not been reported. We show here that elastic properties also undergo a rapid change near the percolation threshold. Our strategy is to first formulate an effective medium theory[11] for the elastic moduli and interpret out results by using concepts from percolation theory.[1] By analogy to the conductivity problem and applying scaling arguments,[12] we have identified the relevant critical exponents and their values. We then apply our results to block copolymers of styrene and butadiene[13] between the two glass transitions. The computed shear modulus with *no* adjustable parameter agrees very well with the torsion pendulum data. The same theory has also successfully accounted for the tensile properties of wet perfluorinated ionomers.[14] We conclude with a brief comparison of the present theory and interpretation with the previous attempts.

We consider in the following an ideal composite system in which spherical particulates of one material are randomly dispersed in the matrix of another. For simplicity each component is assumed to be macroscopically homogeneous and isotropic and thus can be characterized by the values of any two of the elastic modulii, say the bulk modulus K and the shear modulus G. The problem is to evaluate the effective moduli K_{eff} and G_{eff} in terms of the component values K_1, G_1 and K_2, G_2. For the case of glass particles, e.g., polystyrene below its glass transition temperature T_g (~100 °C), embedded in a rubber, say polybutadiene above T_g (~0 °C), a rubber-to-glass transition is expected. Qualitatively, this arises as follows. At low polystyrene contents, the hard styrene segments form separated domains that cannot react cooperatively, and the composite is controlled by the continuous, rubbery, polybutadiene phase. In the opposite extreme the glassy phase forms an extended network that pervades the entire system and collectively dominates the elastic properties. Somewhere between these limits a critical level of styrene loading exists at which the solid domains start interacting coherently—this is the percolation threshold. Around this composition the shear modulus would change rapidly.

This phenomenon can be established more rigorously by using the effective medium theory.[11] In this approach we imagine replacing the composite system by a homogeneous effective medium that has the same macroscopic properties (the bulk modulus K_{eff} and the shear modulus G_{eff}) as the composite system. The changes in the stresses and strains in the medium are calculated when a small portion of the effective medium is replaced by one of the components that make up the composite material. To ensure self-consistency we require the average change in these quantities to be zero when the particles are dispersed randomly.[15] These procedures are basically similar to those employed in the studies of transport,[16,17] optical,[18] and acoustic[19] properties. When states of pure shear and compression are considered, the following pair of equations emerge:

$$\frac{c(1 - K_1/K_{\text{eff}})}{3K_1 + 4G_{\text{eff}}} + \frac{(1 - c)(1 - K_2/K_{\text{eff}})}{3K_2 + 4G_{\text{eff}}} = 0 \qquad (1a)$$

$$\frac{c(1 - G_1/G_{\text{eff}})}{\alpha G_1 + G_{\text{eff}}} + \frac{(1 - c)(1 - G_2/G_{\text{eff}})}{\alpha G_2 + G_{\text{eff}}} = 0 \qquad (1b)$$

where $\alpha = (8 - 10\nu_{\text{eff}})/(7 - 5\nu_{\text{eff}})$, c is the volume fraction of component 1, and ν_{eff} is the effective Poisson ratio for the composite. Eliminating K_{eff}, we obtain

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$$\frac{3cK_1}{3K_1 + 4G_{\mathrm{eff}}} + \frac{3(1-c)K_2}{3K_2 + 4G_{\mathrm{eff}}} + 5\left[\frac{cG_2}{G_{\mathrm{eff}} - G_2} + \frac{(1-c)G_1}{G_{\mathrm{eff}} - G_1}\right] + 2 = 0 \quad (2)$$

which leads to a quadrinomial for G_{eff}. The corresponding equation for K_{eff} can be derived similarly. To identify the percolation transition we consider the limiting case of solid particles in a fluid. Setting $G_2 = 0$ in eq 2 and recalling that $G \geq 0$, we find[20]

$$\begin{aligned} G_{\mathrm{eff}} &= 0 & c \leq 0.4 \\ &= 5G_1(c - 0.4)/3 & 0 \leq c - 0.4 \ll 1 \end{aligned} \quad (3)$$

giving an apparent threshold of 0.4 and an exponent $t = 1$. This is analogous to the behavior of conductivity near the percolation threshold. The analogy is exact for a lattice-spring model.[21] Standard scaling arguments[12,21] then allow us to show asymptotically[22]

$$\begin{aligned} G_{\mathrm{eff}} &\propto G_2(c_0 - c)^{-s} & \Delta < c_0 - c \ll 1 \\ &\propto G_1(c - c_0)^t & \Delta < c - c_0 \ll 1 \end{aligned} \quad (4)$$

where $G_1 \gg G_2 > 0$, c_0 is the percolation threshold, and s and t are critical exponents.[1] Physically, s is for rigid (or superconductive) particles in an incompressible (or normal conducting) medium and t is for solid (or conductive) particles in a fluid (or insulative) phase. The rapid transition from one type of behavior to the other occurs smoothly[22] in a small interval 2Δ near c_0. Physically, the sigmoidal behavior of $\ln G_{\mathrm{eff}}$ implied by eq 4[22] is due to the increasing average size of connected clusters.

The analogy between the elasticity of a gel and the conductivity of a random network was first drawn by de Gennes.[21] Mean field theories that take into account the size distribution of connected clusters of the dispersed particles predict $t = 3$[23,24] and a logarithmic divergence that can be viewed as equivalent to $s = 0$.[24] These results are expected to be exact for high dimensionalities ($d > 6$). In three dimensions, numerical and renormalization group calculations[25,26] give $s \cong 0.7$ and $t \cong 1.5$, which agree quite well with experimental data.[2,6] For an ideal, continuous, random mixture, $c_0 \cong 0.15$ in three dimensions.[1,27] However, c_0 can be affected by extrinsic factors such as the state of dispersion, wetting characteristics, and particle size, shape, distribution, and orientation. Therefore, c_0 is best determined empirically.

To test the theory we have compared our effective medium result (eq 2) to the data of Angelo, Ikeda, and Wallach on block copolymers of styrene and butadiene.[28] These polymers were prepared in tetrahydrofuran solution by anionic polymerization initiated by sodium-α-methylstyrene.[13] Selected samples were characterized in dilute solution by osmometry, ultracentrifugation, and light scattering and were found to be genuine block copolymers with narrow molecular weight distributions and little compositional heterogeneities.[13] The volume compositions were determined from densities and proton NMR. The two-phase nature of these polymers was confirmed by electron microscopy and by the two glass transitions characteristic of the individual segment types. The invariance of the butadiene T_g with copolymer composition and the equality of the mechanical response of two copolymers with identical compositions but inverted monomer sequences, i.e., B/S/B vs. S/B/S, indicated the phase separations were pure and random.

Typical temperature dependences of the shear modulus G for the homopolymers and two of the block copolymers are shown in Figure 1. They were obtained on a compound torsion pendulum[29] in which the upper clamp assembly acts as the inertia member and is suspended by a thin torsion wire. The samples were clamped rigidly at the bottom, and free oscillations were used exclusively. The temperature was mediated by dry nitrogen that could be cooled or heated as desired. The test specimens were prepared by pressing thin (10–20 mils) films in a Carver press at temperatures ranging from 25 °C for homopolybutadiene to 150 °C for homopolystyrene. The complex shear modulii were computed by using the appropriate form factor,[30] and corrections were made for the slight tensile stress on the samples[31] and also for the modulus component due to the torsion wire. In Figure 1 the drops at 0 and 100 °C arise from the glass transitions of the polybutadiene and polystyrene segments, respectively. Between these two transitions the system corresponds to a random mixture of glassy (polystyrene) and rubbery

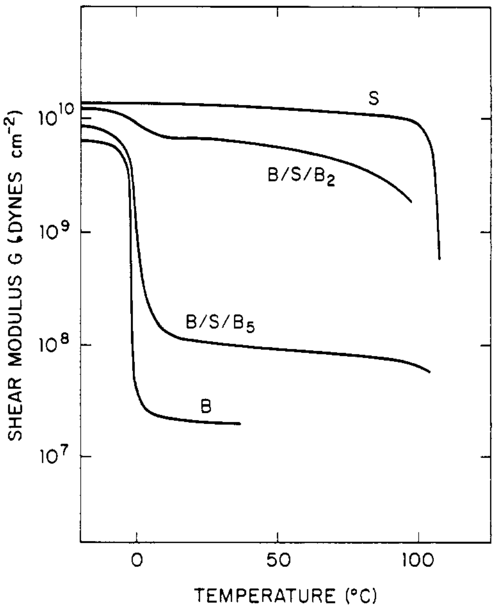

Figure 1. Temperature dependence of shear modulus for polystyrene (S), polybutadiene (B), and two block polymers of 67 vol % (B/S/B$_2$) and 27 vol % (B/S/B$_5$) styrene, respectively.

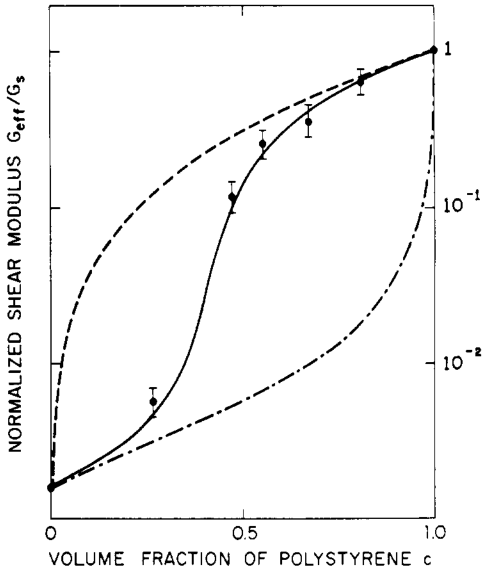

Figure 2. Normalized shear modulus of block copolymers of styrene and butadiene (filled circles). The solid line is the prediction of eq 2 using known elastic moduli of homopolymers. For comparison, the predictions of two other popular theories[38,39] are also shown.

(polybutadiene) phases. The experimental volume dependence of the average normalized shear modulus is shown in Figure 2 by the filled circles. The uncertainties (vertical bars) arise from a slight temperature variation in G between 20 and 80 °C. The data were limited to this range to avoid the finite glass transition regions. The uncertainties can be reduced somewhat with prolonged sample annealing. The solid line represents the prediction of eq 2 using measured moduli for homopolymers at 50 °C,[13,32,33] which are $K_S = 3.37 \times 10^{10}$ dyn cm^{-2}, $G_S = 1.28 \times 10^{10}$ dyn cm^{-2}, $K_B = 1.58 \times 10^{10}$ dyn cm^{-2}, and $G_B = 2.2 \times 10^7$ dyn cm^{-2}. The associated Poisson ratios are $\mu_S = 0.335$ and $\mu_B = 0.499$. The predicted and observed sigmoidal behavior underscores the percolation transition and signifies the switching of the roles (filler vs. host) for the two components. Although the general agreement between theory and experiment is good, we do not have enough compositions below 50 vol % of polystyrene to pinpoint the threshold and determine the critical exponents. Further work is contemplated.

The equations resulting from the effective medium approach were first derived by Hill[34] and independently by Budiansky,[34] using less transparent methods. However, the singular behavior near the threshold under extreme conditions had led them to limit the validity of their work to dilute regimes and also caused criticisms of the theory by later authors.[35-37] Using percolation concepts, we have shown here that these singular results are more general than previously believed. Recently, Berryman[19] has also argued in favor of the effective medium theory based on both theoretical and experimental observations.

Other popular theories include Kerner's treatment[38] and Smith's modification of van der Poel's approximation.[39] In these formulations the filler particles are always coated by the matrix medium at all compositions so that percolation channels only exist, albeit trivially, at the homopolymer limits. For comparison some of the results from these *biased* percolation approaches are shown in Figure 2. The dashed curve is the prediction of Smith's theory for polybutadiene in polystyrene. It really corresponds to a polystyrene-coated polybutadiene instead of a random mixture of the two. The steep initial rise is associated with the continuous glass framework existing even at the limit of infinitesimal styrene content. Kerner's result for this case is qualitatively the same and will not be repeated. The dash–dot curve is for polybutadiene-coated polystyrene evaluated according to Kerner's prescription. Notice that the rubber phase dominates even at high styrene content since the styrene domains are disjointed. Smith's prediction behaves similarly. Although Smith's theory does not apply here, it is reasonably successful whenever its basic assumptions are met, such as in fiber glass reinforced polymers.[40] Under those conditions our theory can also be applied if the percolation threshold is adjusted empirically.

To conclude, we have correlated the elastic-to-glass transition in block copolymers of styrene and butadiene to the percolation transition. This is a mechanical analogue of the well-known insulator-to-conductor transition. The elastic properties of block terpolymers and the mechanical aspects of polychromatic percolation[1,41] are currently under investigation.

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