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Molecular Model for the Mechanical Properties of Elastomers. 2. Synergic Effects in Bimodal Cross-Linked Networks

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ABSTRACT: We have extended a model developed previously to a detailed investigation of the elastic properties of cross-linked networks made of blends of very short and relatively long polydimethylsiloxane (PDMS) chains. Our study points to the importance of the polydispersity index of the short-chain component. High polydispersities lead to a strong decrease in tenacity for the pure low molecular weight component whereas these effects are much less pronounced in a blend with much longer chains. This leads, at particular blend compositions, to tenacity and toughness values that are much higher than those for the pure components. Our results are in qualitative agreement with experimental data reported by Mark et al.

1. Introduction

It is now well accepted that the molecular weight distribution has a strong influence on the mechanical properties of polymeric materials. A wealth of experimental and theoretical studies have demonstrated the effect of polydispersity on tensile strength[1-3] and rheological behavior.[4,5] Other investigations have focused more specifically on bimodal molecular weight distributions.[6,7] One of the motivations for those studies was the search for blend compositions leading to particularly attractive mechanical properties. The results, however, were disappointing in that the tenacity of blends of macromolecules differing in length was found to follow the simple weight-average summation of the component properties.[7]

All of the above studies were restricted to systems of *linear* macromolecules. Recently, Mark et al. have made an exhaustive investigation of the elastic properties of *cross-linked* networks made of blends of very short and relatively long poly(dimethylsiloxane) (PDMS) chains (for a review, see ref 8). These bimodal networks exhibit synergism in their elastic properties and show surprisingly high tenacity values that do not follow the expected "weight-average" rule. In view of the obvious interest in these materials, we have extended a model developed previously[9] to a detailed investigation of the molecular origin of those unusual properties.

2. Model and Parameter Values

The model has been described at length in ref 9 and will only briefly be summarized here. We start by generating on the computer a network made of chains of two different lengths. These chains are then cross-linked at their ends with probability p. In order to conform as close as possible to the experimental studies of ref 8, the short chains are given a molecular weight M_1 well below the molecular weight between entanglements M_e.[9] For the long chains, we take $M_2 \approx 4M_e$. A typical network before deformation is schematically depicted in Figure 1. The figure is for a blend with a weight fraction of short chains, $p_1 = 0.5$. The long chains are represented by the heavy dark lines and have each four entanglements (symbols ●) along their contour. The short chains, on the other hand, are represented by the light lines bounded between successive tetrafunctional crosslinks (symbols □). The number of statistical segments for the short chains is taken to be 2 whereas that between entanglements is set equal to 8.[10] This is a convenient feature that leads to a great simplification in the construction of the network. Indeed, since the end-to-end length of an undeformed chain varies as the square root of the number of statistical segments, the distance between nearest-neighbor entanglements is twice the end-to-end length of the short-chain segments bounded between successive cross-links; see Figure 1. Note also that, in order to ensure a uniform density throughout the sample, the volume occupied by a chain strand between entanglements is made equal to 4 times that between cross-links.

Figure 1 is for the case of fully reacted crosslinks; i.e., for a degree of advancement of the reaction $p = 1$. In practical situations, however, $p < 1$. This leads to the presence in the network of cross-links with only one or zero reacted ends. The latter are not elastically active and therefore need to be removed from the network. Additional attention also has to be paid to entanglement points that, because of an incompleteness of the reaction, are not trapped between cross-links. These also need to be removed since they do not contribute to the mechanical properties of the network *at elastic equilibrium*.

Upon completion of the construction of the network and removal of the non load-bearing junctions, the mechanical properties are tested using the procedure described at length in ref 9 and 11 and 12. In that procedure, the fiber is first stretched to a small strain value. Chains are then allowed to slip through entanglements and to break at maximum extension. After relaxation of the whole network toward mechanical equilibrium, the overall stress is recorded. The external strain is then incremented by a small constant amount, and the whole cycle of chain slippage and network relaxation processes is repeated. This leads to the generation of a complete stress–strain curve for a given value of the weight fraction of short chains, p_1, and degree of advancement of the reaction, p. Throughout the calculations, we assume the chains to be non-Gaussian and take an inverse Langevin function for their force–extension relation.

3. Results and Discussion

A series of stress–strain curves for the case of fully reacted tetrafunctional cross-links ($p = 1$) is shown in Figure 2. The figure is for the case of no slippage of chains through entanglements. The curves for the pure low ($p_1 = 1$, curve a) and pure high ($p_2 = 0$, curve d) molecular weight samples are qualitatively very similar and both exhibit an important strain hardening near the

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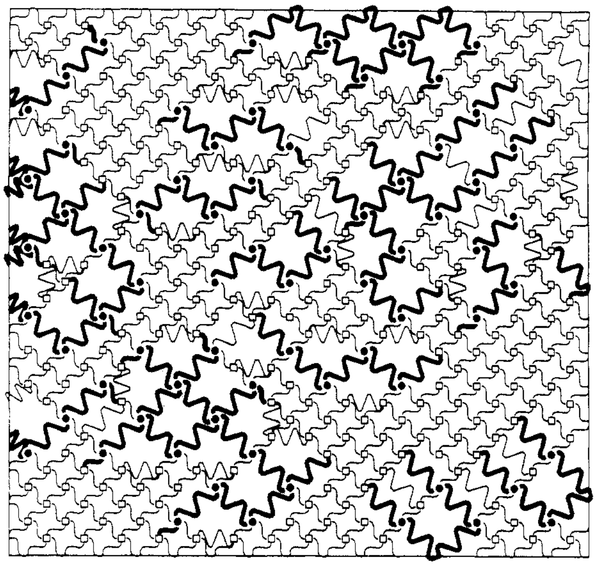

Figure 1. Typical bimodal network before deformation. The short chains (light lines) have a molecular weight M_1 well below the molecular weight between entanglements, M_e. For the long chains (heavy dark lines), we take $M_2 = 4M_e$. The figure is for a weight fraction of short chains $p_1 = 0.5$ and a degree of advancement of the reaction $p = 1$. Symbols are as follows, ●, entanglement; □, tetrafunctional crosslink.

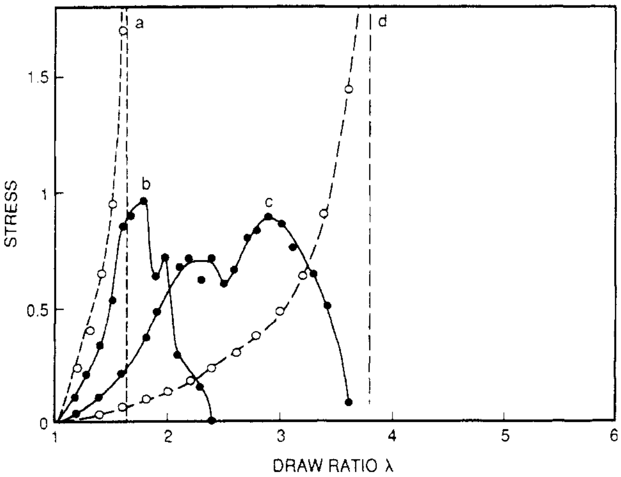

Figure 2. Stress–strain curves for fully reacted cross-links ($p = 1$). The stress is in arbitrary units. The curves are for different values of the weight fraction, p_1, of the low molecular weight component: curve a, $p_1 = 1$; curve b, $p_1 = 0.66$; curve c, $p_1 = 0.33$; curve d, $p_1 = 0$. The figure is for the case of no slippage of chains through entanglements.

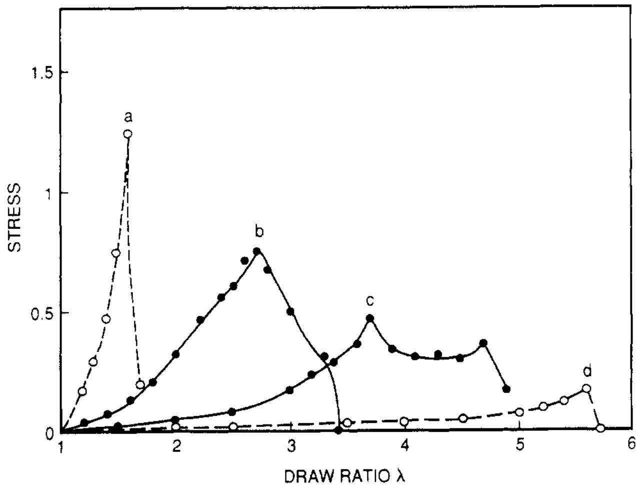

Figure 3. Stress–strain curves for incomplete reaction ($p = 0.95$). Notation is the same as for Figure 2: curve a, $p_1 = 1$; curve b, $p_1 = 0.43$; curve c, $p_1 = 0.18$; curve d, $p_1 = 0$. The figure is for the case of chain slippage with an entanglement friction force [9] $f_e = 0.01$.

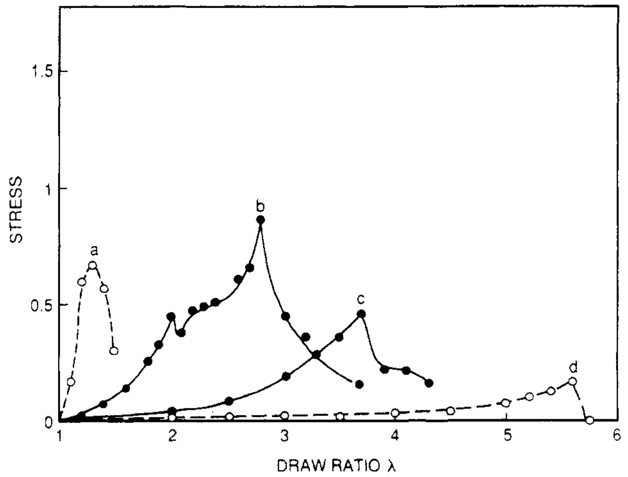

Figure 4. Same as Figure 3 but, for a short-chain component with a polydisperse molecular weight distribution (see text): curve a, $p_1 = 1$; curve b, $p_1 = 0.36$; curve c, $p_1 = 0.15$; curve d, $p_1 = 0$.

breaking point. Intermediate compositions (see curve c, for example) show the presence of two well-defined peaks. The peak at low strain corresponds to hardening and fracture processes involving the low molecular weight component and that at higher strain relates to similar effects for the high molecular weight component. The curves, however, exhibit much lower tenacities than those for the pure components, and no synergetic effect is found. The toughness, measured by the area under the stress–strain curve, seems to increase with the weight fraction of the high molecular weight component. Model results, in which chain slippage is taken into account, are qualitatively similar to those presented in Figure 2. Finally, the shape of the stress–strain curves near rupture deserves some discussion. The curves for the blends in Figure 2 (and also in Figures 3 and 4, later) exhibit a rapid, but not sudden, decrease in stress with increasing strain. This is at variance with experimental observation that shows abrupt and catastrophic failure near rupture. One possible reason for the absence of such "tails" on the actual stress–strain curves is the difference in structure between our perfect model representation and actual networks. The latter, indeed, are known to contain defects that dominate the failure mechanism near rupture of the sample.

The case of incomplete reaction ($p = 0.95$) is studied in Figure 3. Here, the pure high and low molecular samples exhibit a dramatically different behavior. Although the curve for the pure low molecular weight component (curve a) is qualitatively similar to that of Figure 2, that for the high molecular weight component (curve d) shows a substantial decrease in tenacity. The latter is due to the fact that, in entangled networks ($M \gg M_e$), the number of elastically active strands falls off sharply with a decrease in the degree of completeness of the reaction, p.[9] As in Figure 2, stress–strain curves at intermediate compositions (curve c) exhibit two peaks related to the limited extensibility of the low and of the high molecular weight components, respectively. Note also that curves b and c exhibit higher toughness than those for the pure components. The curves, however, fall short of reproducing the abnormally high stress values reported experimentally in ref 8.

All the results presented above were for blends made out of two *monodisperse* molecular weight components.

This is a situation that is difficult to realize experimentally, and polydispersity indexes as high as 2.23 have been reported for the pure components used in ref 8. For that reason, we now turn to a detailed study of the effect of polydispersity on the theoretical results of Figure 3. Polydispersity in the high molecular weight component should not be of great importance for the present study because mechanical properties at $M > M_e$ are mainly controlled by the number of statistical segments *between entanglements*, which is independent of molecular weight. This is not the case, however, for the low molecular weight component ($M \ll M_e$) for which properties are highly sensitive to the distribution of chain lengths *between cross-links*. Of particular importance is the length of the shortest chains that mainly control the elongation at break. We chose $M_n = 1.6$ and $M_w = 1.7$ (in statistical segment units) for the pure low molecular weight component.[13] That distribution leads to a distribution of polymer chains whose elongations at break vary from 10 to 60% strain.

The results are presented in Figure 4. The figure indicates a marked effect of polydispersity on the stress-strain behavior for the pure short chains component. Curve a, indeed, exhibits a much lower tenacity than that observed in Figure 3 for a monodisperse distribution. That decrease is due to the small extensibility of the very short chains in the distribution which break near 10% strain, leading to premature failure of the sample at $\lambda = 1.3$ (vs $\lambda = 1.6$ for the monodisperse distribution in Figure 3). Curves for the blends on the other hand, are found to be almost insensitive to the degree of polydispersity of the low molecular weight component, except for the presence of a small peak at $\lambda = 2$ for curve b. The latter is attributed to strain hardening and fracture processes involving the shortest chains in the low molecular weight component, referred to above. These early fracture processes however do not lead to premature failure of the sample, as in curve a, because of (i) the low weight fraction of those very short chains in the blend and (ii) the presence of the high molecular weight chains M_2 whose high extensibility can easily accommodate the extra load resulting from those early chain breaks. Similar conclusions on the role of the long chains M_2 have been arrived at in experimental studies by Andrady et al.[14] The above observations lead, at some particular blend compositions ($p_1 = 36\%$, curve b), to stress values which are higher than those for the pure components. These bimodal networks thus exhibit synergism in their elastic properties and show surprisingly high tenacity and toughness values similar to those reported in ref 8. Our results, in turn, indicate that one possible explanation for those unexpected properties in an elastomeric blend is the high polydispersity of the low molecular weight component.

References and Notes

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(10) That choice is thus at variance with the value $n = 22$ used in ref 9.
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(12) Termonia, Y.; Meakin, P.; Smith, P. *Macromolecules* **1985**, *18*, 2246; **1986**, *19*, 154.
(13) That distribution was obtained by mixing the original chains of two statistical segments with an equal number of still shorter chains, 1.2 segments long. For simplicity, the two sets of chains were given the same end-to-end vector length in the undeformed state. That simplification, which allows retainment of the convenient feature of starting from a regular network of equally spaced cross-links prior to deformation, should not affect the main conclusions of the study.
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