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Elastomers with Multimodal Distributions of Network Chain Lengths

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Summary: The goal of primary interest in these investigations was the development of a novel method for preparing elastomeric networks having unusually good ultimate properties. The technique involves end linking mixtures of very short and relatively long functionally-terminated chains to give bimodal networks. Such (unfilled) "bimodal" elastomers show very large increases in reduced stress or modulus at high elongations because of the very limited extensibility of the short chains present in the networks. This non-Gaussian behavior also appears in compression or biaxial extension, shear, tearing, and cyclic fatigue tests. Non-Gaussian theories taking into account this limited extensibility give a good account of the experimental results. Bimodal distributions also facilitate strain-induced crystallization, and thus the reinforcement it provides. Suggestions are made for seeking additional advantages from multimodal distributions that are trimodal or higher.

Keywords: elastomers; end linking; networks; poly(dimethylsiloxane); toughness

Introduction

The main purpose of this review is to illustrate how manipulating the distribution of network chain lengths in an elastomer can give large improvements in its mechanical properties. The preparation of such networks of controlled structures obviously requires special crosslinking reactions. In fact, a variety of "model" networks can now be prepared using new synthetic techniques that closely control the placements of crosslinks in a network structure.[1-3] Specifically, end linking functionally-terminated chains, instead of haphazardly joining chain segments at random, controls the structure of the resulting network. The functionality of a crosslink is the same as the number of functional groups on the end-linking agent. More important in the present context, the molecular weight M_C between crosslinks and its distribution are the same as those of the starting chains prior to their being end linked.

Bimodal Networks

One of the most important networks of controlled structure are those having unusual distributions of chain-lengths.[4,5] The most novel such elastomer consists of a combination of

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unusually short network chains (molecular weights of a few hundred) and the much longer chains typically associated with elastomeric behavior (molecular weights of ten or twenty thousand). Such a network is sketched in Figure 1.

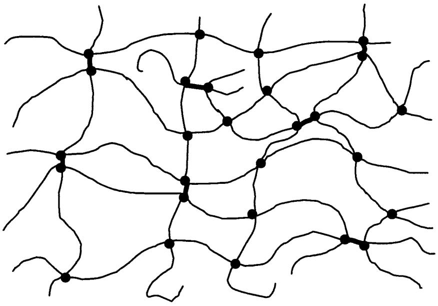

Figure 1. A network having a bimodal distribution of network chain lengths. The short chains are arbitrarily shown by heavier lines than the long chains, and the dots represent the crosslinks, typically resulting from the end linking of functionally-terminated chains.

The "bimodal" elastomers prepared by these end-linking techniques have very good ultimate properties, and for this reason there is currently much interest in preparing and characterizing such materials.[4,6,7] There is, of course, a long history of theoretical work in the area of rubberlike elasticity but almost all of it is based on monodisperse network chain-length distributions. Interest is now developing, however, in developing theoretical interpretations for the novel mechanical properties of bimodal elastomers.[8-16]

Materials and Synthetic Techniques. Most bimodal networks synthesized to date have been prepared from poly(dimethylsiloxane) (PDMS) [$-Si(CH_3)_2O-$].[4] One reason for this choice is the fact that the polymer is readily available with either hydroxyl or vinyl end groups, and the reactions these groups participate in are relatively free of complicating side reactions. These ideas can obviously be extended to higher modalities (trimodal, etc., eventually approaching an extremely broad, effectively-unimodal distribution).[17-19]

The distribution of network chain lengths in a bimodal elastomer can be extremely unusual, and much different from the usual unimodal distribution obtained in less-controlled methods of crosslinking. Figure 2 shows a schematic distribution, for the important example in which there is simultaneously a large number percent of short chains and a large weight percent of long chains. The major difference is the *large* amounts of both very short chains and very long chains in the bimodal network, which contrasts sharply with the *small* amounts of such chains in a typical unimodal distribution. The case shown here, where the short chains predominate numerically, is of particular interest with regard to improvements in mechanical properties.[1]

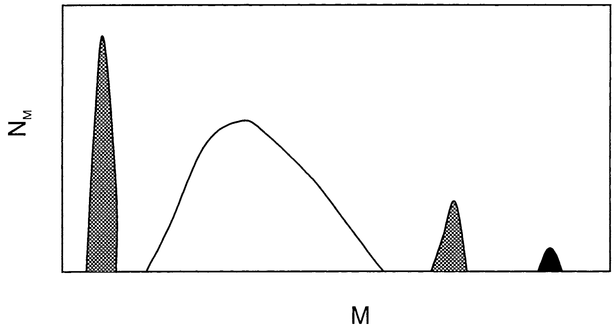

Figure 2. Network chain-length distributions, in which N_M is the number of chains in an infinitesimal interval around the specified value of the molecular weight M. For reference purposes, a unimodal distribution is shown between the two dotted parts of the bimodal distribution. A possible additional component for forming a trimodal network is shown by the solid peak.

Elongation Results. The great majority of studies of mechanical properties of elastomers of any type have been carried out in elongation, because of the simplicity of this type of deformation.[1,5] Results are typically expressed in terms of the nominal stress $f^* \equiv f/A^*$. Also frequently employed is the modulus or reduced stress defined by $[f^*] \equiv f^*/(\alpha - \alpha^{-2})$, where α is the elongation or relative length of the sample.

In the case of the bimodal materials, many of the stress-strain isotherms in elongation on were obtained on PDMS elastomers in the vicinity of 25 ^{o}C, a temperature sufficiently high to suppress strain-induced crystallization. The results thus determined were of considerable interest since they indicated that the bimodal nature of the distribution greatly *improved* the ultimate properties of the elastomer.[4] This is illustrated schematically in Figure 3, in which

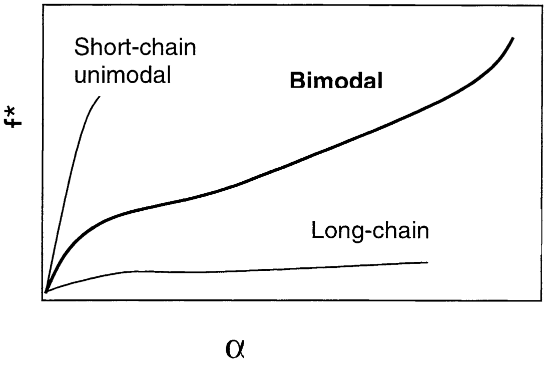

Figure 3. Typical dependence of nominal stress against elongation for two unimodal networks having either all short chains or all long chains, and a bimodal network having some of both.

data are plotted in such a way that the area under a stress-strain isotherm up to the point of failure corresponds to the energy required to rupture the network. If the network consists entirely of the short-chain component, then it is brittle (which means that the maximum extensibility is small). Similarly, if the network consists of only the long-chain component, its ultimate strength is very low. As a result, neither type of unimodal material has a large area under its stress-strain curve and, thus, neither is a tough elastomer. As can readily be seen from the figure, the bimodal networks are much improved elastomers in that they can have a high ultimate strength without the usual diminished maximum extensibility. This corresponds to high values of the energy required for rupture, which makes them unusually tough elastomers, even in the unfilled state. Apparently the short chains act primarily to increase the ultimate strength through their limited deformability, while the long chains somehow thwart the spread of rupture nuclei that would otherwise lead to catastrophic failure. If true, this could be analogous to what executives like to call a "delegation of responsibilities".

It should be pointed out that there are three requirements for obtaining these improvements. The first is that the ratio M_S/M_L of molecular weights of the short and long chains be very small (i. e., that their molecular weights be very different). The second is that the short chains be as short as possible; for example, a network having network chain molecular weights of 200 and 20,000 g/mol would be expected to show much greater improvements from the biomodality than one having molecular weights of 2,000 and 200,000. Finally, there should be a large *number* concentration of the short chains, typically around 95 mol %.

Quantitative characterization of this limited chain extensibility requires, of course, a non-Gaussian distribution function[20] for the end-to-end separation r of the short network chains. Ideal for this case is the Fixman-Alben distribution,[21] which was used[22] to calculate stress-strain isotherms in elongation for bimodal PDMS networks. Good agreement was found between theory and experiment. Other non-Gaussian distribution functions have also been successfully used for this purpose.[1,23,24] The experimental isotherms can also be interpreted using the van der Waals theory of rubberlike elasticity.[1,25,26]

Another approach, Monte Carlo simulations, utilizes the wealth of information that rotational isomeric state theory provides on the spatial configurations of chain molecules. In brief, Monte Carlo calculations based on the rotational isomeric state approximation are used to simulate spatial configurations and thus distribution functions for the end-to-end separations of the chains.[27,28] These distribution functions are then used in place of the Gaussian function in the standard three-chain model[20] in the affine limit to give the desired non-Gaussian theory of rubberlike elasticity. Stress-strain isotherms calculated in this way are strikingly similar to the experimental isotherms obtained for the bimodal networks.[1,27,28] The overall theoretical interpretations are thus quite satisfactory and would encourage other applications of these distributions, for example to segmental orientation in networks containing very short chains. Such segmental orientation is of critical importance, for example, with regard to strain-induced crystallization.

PDMS networks were found to be unsuitable for characterizing the effects of bimodality on strain-induced crystallization, because of their very low crystallization temperatures. The polymer chosen instead for these end-linked bimodal networks was poly(ethylene oxide), which has a relatively high melting point (~ 65 °C) and thus readily undergoes strain-induced crystallization.[29] The aspect of relevance here is the use of these networks to elucidate the dependence of strain-induced crystallization on network chain length distribution. Decrease in temperature was found to increase the extent to which the values of the ultimate strength of the bimodal networks exceed those of the unimodal ones.[29] A schematic representative of this is shown in Figure 4. These results suggests that bimodality facilitates strain-induced crystallization,[1] possibly through increased orientation of the more easily crystallizable long chains, into crystallization nuclei. Similar conclusions have been reached in studies of elongated bimodal networks of poly(tetrahydrofuran).[30]

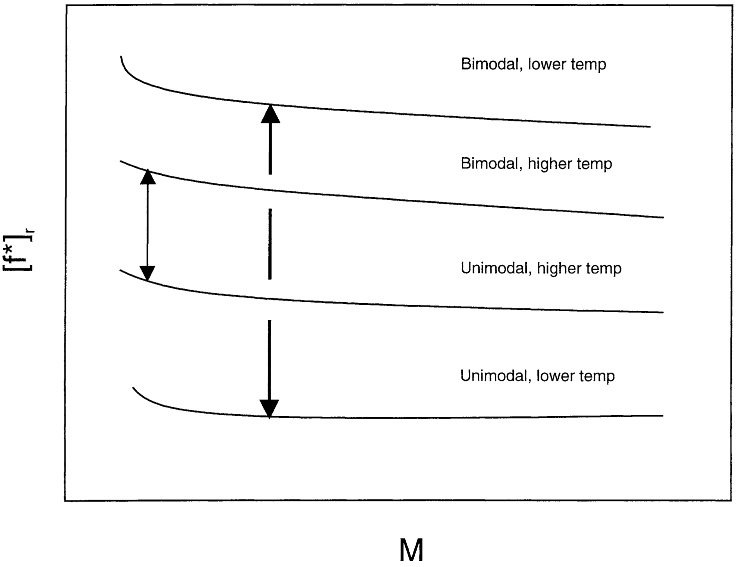

Figure 4. Ultimate strength, as represented by the modulus at rupture, shown as a function of the molecular weight between cross links for a unimodal and bimodal elastomer compared at two temperatures.

In practical terms, the above results demonstrate that short chains of limited extensibility may be bonded into a long-chain network to improve its toughness. It is also possible to achieve the converse effect. Thus, bonding a small number of relatively long elastomeric chains into a short-chain PDMS thermoset greatly improves both its energy of rupture and impact resistance.[31-33] Approximately 95 mol % short chains gives the maximum effect for the molecular weights involved. Lower concentrations give smaller improvements than can otherwise be achieved, and higher concentrations will convert the composite from a relatively hard material into one that is more rubberlike.

Results in Other Mechanical Deformations. Equi-biaxial extension results have been obtained by inflating sheets of unimodal and bimodal networks of PDMS.[34,35] Upturns in the modulus were found to occur at high biaxial extensions, as expected. Also of interest, however, are pronounced maxima preceding the upturns. Such dependences represent a challenging feature to be explained by molecular theories addressed to bimodal elastomeric networks in general.

In shear measurements on some unimodal and bimodal networks of PDMS,[36] the bimodal PDMS networks showed large upturns in the pure-shear modulus at high strains which were similar to those reported for elongation and biaxial extension. Tear tests have been carried out on bimodal PDMS elastomers,[37-39] using the standard "trouser-leg" method. Tear energies were found to be considerably increased by the use of a bimodal distribution, with documentation of the effects of compositional changes and changes in the ratio of molecular weights of the short and long chains. The increase in tear energy did not seem to depend on tear rate,[37] an important observation that seems to suggest that viscoelastic effects are not of great importance in explaining the observed improvements. A subsequent series of shear tests[38] established the dependence of the tearing properties on the composition of the bimodal networks and the lengths of the chains used to prepare them. The observed increases in strength with decease in the molecular weight of the short chains must eventually become *decreases* when the chains become too short to have any elastic effectiveness at all.

Some Rheovibron viscoelasticity results have been reported for bimodal PDMS.[40] Also, measurements have been made on permanent set for PDMS networks in compressive cyclic deformations.[41] There appeared to be less permanent set or “creep” in the case of the bimodal elastomers. This is consistent in a general way with some early results for polyurethane elastomers.[42] Specifically, cyclic elongation measurements on unimodal and bimodal networks indicated that the bimodal ones survived many more cycles before the occurrence of fatigue failure. The number of cycles to failure was found to be approximately an order of magnitude higher for the bimodal networks, at the same modulus at 10 % deformation![1]

Results on Non-Mechanical Properties. Birefringence measurements have been shown to be very sensitive to bimodality, and have therefore also been used to characterize non-Gaussian effects resulting from it in PDMS bimodal elastomers.[1,43] The freezing points of solvents absorbed into bimodal networks are also of interest since solvent molecules constrained to small volumes form only relatively small crystallites upon crystallization, and therefore exhibit lower crystallization temperatures.[44-46] Some differential scanning calorimetry measurements on solvent molecules constrained in the pores of PDMS elastomers gave evidence for several crystallization temperatures, which could be indicative of an unusual distribution of pore sizes.. Calorimetric measurements on bimodal poly(ethylene oxide) networks indicated that the short chains seemed to decrease the amount of crystallinity in the unstretched state.[47] This is an intriguing result since, as mentioned above, they *increase* the extent of crystallization in the stretched state. A similar study on a different polymer, poly(tetrahydrofuran), did not show any decrease, however.[48]

Dynamic light scattering experiments,[49] neutron scattering experiments[50] and calculations,[51] degradation experiments,[52] and the computer simulations mentioned above have also been used to obtain insight into the dynamics and structure of bimodal elastomers.

Trimodal Networks

Experimental Results. Although there have been attempts to evaluate the mechanical properties of trimodal elastomers, this has not been done in any organized manner. The basic problem is the large number of variables involved, specifically three molecular weights and two independent composition variables (mol fractions); this makes it practically impossible to do an exhaustive series of relevant experiments. For this reason, the only mechanical property experiments that have been carried out have involved arbitrarily chosen molecular weights and compositions.[17,18,53] Perhaps, not surprisingly, only modest improvements have been obtained over the bimodal materials.

Results from Theory and Simulations. Some recent computational studies,[8] however, indicate that it is possible to do simulations to identify those molecular weights and compositions which should maximize further improvements in mechanical properties. Such simulations are being extended to search for optimum properties of trimodal networks, specifically (i) the elastic modulus, (ii) maximum extensibility, (iii) tensile strength, and (iv) segmental orientability. Results to date[54] suggest that a trimodal network prepared by incorporating small numbers of very long chains into a bimodal network of long and short chains could have significantly improved ultimate properties.

Acknowledgement

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