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Elastomeric Properties of Polysiloxane Networks. Bimodal Elastomers that are Spatially Inhomogeneous and Others that are Very Broadly Multimodal

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End-linking poly(dimethylsiloxane) was used to prepare bimodal elastomers networks so as to have inhomogeneous nanostructures, and also to prepare others having very broadly multimodal chain-length distributions. Macroscopic phase separation, probably high crosslink density clusters, was observed to occur in some of the bimodal networks. The mechanical properties in simple extension and in equilibrium swelling were measured. The bimodal elastomers that were not obviously inhomogeneous showed very good mechanical properties, but the macroscopically phase-separated networks, and the broadly multimodal network were weak. Analysis of the Mooney-Rivlin profiles suggests that the reinforcing mechanism could have a structural component in addition to that from the limited extensibilities of the short chains. The mechanical properties and the extents of swelling support the cluster conjecture, in accord with previous morphological studies on spatially-inhomogeneous polysiloxane elastomers.

Keywords: poly(dimethylsiloxane); end-linking; elastomers; model networks; bimodal distributions; multimodal distributions; mechanical properties; rubber elasticity theory

1 Introduction

End-linking functionally-terminated polymers have become the ubiquitous method for preparing “model” elastomers. For example, end-linked unimodal poly(dimethylsiloxane) (PDMS) elastomers, formed from a relatively narrow molecular weight distribution of telechelic chains, are often used to gauge the predictions of classical rubber-like elasticity theory for mechanical properties and degrees of equilibrium swelling (1). An interesting variant on the end-linked model elastomer theme has been the preparation of “bimodal” PDMS networks (having bimodal distributions of network chain lengths) (2–4). Traditionally, these elastomers are formed by end-linking a large *mole* fraction of very short chains (molecular weight less than 1,100 g/mol) with a small mole fraction of chains having much larger molecular weights. The resulting type of network is illustrated in Figure 1.

Bimodal elastomers show a synergism in the mechanical properties between the high extensibilities common to long chains and the large retractile forces common to short chains. As a result, bimodal elastomers are unusually tough, particularly in simple extension, which is of great practical importance. For this and other reasons, extensive investigations of the effects of the length and the amounts of the short chains have been conducted (5, 6). The best reinforcement occurs for very large molar percentages of short chains (greater than 90 mol%). Of interest here is the assumption that the shorter the short chains, the better the reinforcement. This was based on results such as a bimodal network with 95 mol% of short chains with molecular weight 660 g/mol providing better reinforcement than networks containing 95 mol% of 1,100 g/mol. The hallmark of the bimodal reinforcement is a sharply increasing modulus with increasing strain at large strains, and is generally thought to arise from the “limited-chain extensibility” of the short chains in the formulation. In this work, we have used the shortest possible chains, including monodisperse dimer and trimer having molecular weights less than 300 g/mol, which should emphasize the limited-chain extensibility effect.

It has generally been assumed that bimodal networks have no structural details that give rise to the bimodal reinforcement effect. That is, the representative bimodal structure

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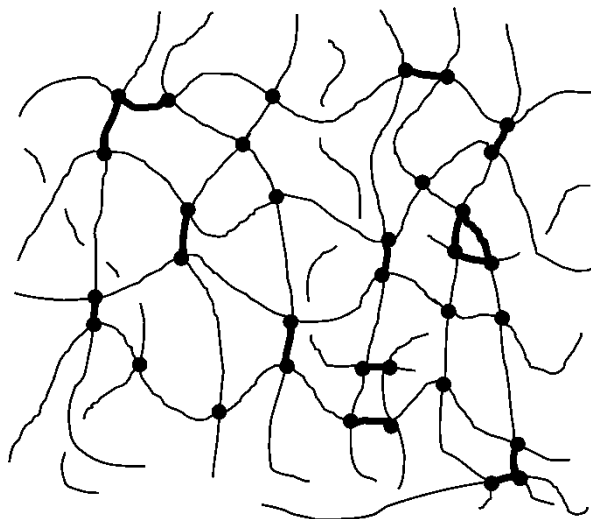


Fig. 1. Hypothetical sketch of a bimodal network, in which the short chains are arbitrarily drawn in heavier than the long chains.

was thought to be as simple as that shown in Figure 1. Relevant in this regard is the observation that early static scattering studies revealed little notable structural difference between comparable bimodal and unimodal networks (7, 8). Intentionally inhomogeneous bimodal networks, however, were prepared via pre-reacting the short chains with a substoichiometric amount of the crosslinking agent (which ostensibly generated short chain clusters) which were then mixed with the long chains and the remainder of the crosslinking agent (9, 10). The mechanical properties for these particular networks were very poor, and the soluble fraction was very high which indicated poorly formed networks. Although not specifically mentioned, it can be assumed that these networks appeared homogeneous. Recently, we have shown that a number of “model” end-linked networks (with low soluble fractions) can macroscopically phase separate into domains of high cross-link density (11–14). The necessary and sufficient conditions for forming macroscopically phase-separated networks are a large proportion of short chains and a large amount of the catalyst used to end-link the chains to the crosslinking agent (11). More important, introduction of long chains to form a bimodal network appeared to attenuate the growth of some macroscopically phase separated structures formed during end-linking using condensation reactions (12, 14). Furthermore, the monodisperse very short chains used in this work could be expected to be incompatible with the long chains, in part because the shorter the chains, the larger the effects of chain ends, which have to be different from the chain’s repeat units. These mixtures could still form seemingly “homogeneous” condensation end-linked bimodal networks, however. Thus, a reanalysis of the structural basis of the bimodal reinforcement effect is in order for macroscopically inhomogeneous and apparently “homogeneous” bimodal networks.

2 Experimental

2.1 Preparation of Tetramethyl Disiloxane 1,3 diol (hydroxyl dimer $M = 166$ g/mol)

The dimer was prepared following a protocol suggested by Drs. John Saam and Wallace Joselyn, both at the Michigan Molecular Institute in Midland, Michigan. Specifically, 3.0 g (0.02 mol) of 1,1,3,3-tetramethyl disiloxane (United Chemical Technologies) was added to a solution of 4 g (0.2 mol) deionized water in 16 g THF (11). Small aliquots of 5% palladium on water-wet activated charcoal (Aldrich) were added under a nitrogen purge until discernible evolution of hydrogen gas had ceased. The slurry was stirred for 1 h, and then the charcoal was filtered off. The volatile components were removed by rotary evaporation, which gave white, needlelike crystals. The crystals were recrystallized from toluene, giving a yield of 60%. m.p. 66–67°C (lit. 68°C) (15). $^1\text{H-NMR}$ (Brüker AC 250) was conducted using deuterated chloroform without TMS. In this case, the peaks were referenced to the chloroform resonance at 7.24 ppm. Found: δ 0.1 ppm (s, 3H, Si-CH₃) 4.78 ppm (conc. dependent) (broad s, 1H, Si-OH). The broad Si-OH peak clearly indicates hydrogen-bonding interactions (11).

2.2 Preparation of Hexamethyl Trisiloxane 1,5 diol (hydroxyl trimer $M = 240$ g/mol)

Isolation of this compound was based on a small modification of Harris’ protocol (15). Dichlorodimethyl silane (130 g, 1 mol) (Aldrich) was added dropwise with constant stirring at 0°C over a 2.5 h period to a biphasic mixture of distilled water (36 g, 2 mol), ammonium carbonate (134.5 g, 1.4 mol) (Fisher) and diethyl ether (1,160 ml). Stirring was continued after the addition of chlorosilane until visible evolution of CO₂ had ceased, and the pH was 7–8. The solid ammonium chloride was filtered off, and the volatile components removed by rotary evaporation. The condensed silicone oil was dried at 50°C in an attempt to remove the smaller, volatile cyclic impurities. The remaining material was vacuum distilled through a 12 in. vacuum jacketed-silvered fractionating column packed with glass beads, which afforded an exceptionally pure product. The yield was 10 g (13% based on the chlorosilane), b.p. 90°C/1 mm Hg (lit. 89–91°C, 3 mm Hg) (15), $n_D^{20} = 1.403$ (lit. 1.405) (15). $^1\text{H-NMR}$ (Brüker AC 250) was conducted using deuterated chloroform. The peaks were referenced to the chloroform resonance at 7.24 ppm. Found: δ 0.01 ppm (s, 3H, internal Si-CH₃), 0.02–2 ppm (conc. dependent) (s, 6H, terminal Si-CH₃) 0.5–2.3 ppm (conc. dependent) (broad s, 1H, Si-OH).

2.3 Commercially-Available PDMS Chains

A number of long chain hydroxyl-terminated and vinyl-terminated PDMS were obtained from Gelest and used as received. The cited polydispersity index M_w/M_n was ~ 2 ,

Table 1. Mechanical properties of various bimodal networks

M_n short g/mol ^a	M_n long g/mol ^b	mol% short	M_c g/mol ^c	v_{2c} ^d	α_r ^e	f/A_r^{*f} N/mm ²	$10^3 E_r^g$ J/mm ³	v_{2m}^h
166	22,100	50	11,500	0.97	1.96	0.67	0.38	0.359
166	22,100	65	7,850	0.97	2.07	0.69	0.44	0.357
240	22,100	90	3,400	0.96	2.34	0.80	0.60	0.353
240	22,100	90	3,400	0.96	2.17	0.45	0.21	0.5 ⁱ
240	22,100	95	1,700	0.93	2.41	0.51	0.45	0.348
300 ^j	57,000	97	2,000	0.95	2.03	0.48	0.25	0.28
186 ^k	22,000	99	404	—	1.11	0.34	0.02	—
Multi modal	Table 2	—	2,088	0.93	1.89	0.47	0.27	0.35

^aNumber-average molecular weight of the short chains ($M_w/M_n \sim 1$).^bNumber-average molecular weight of the long chains ($M_w/M_n \sim 2$).^cEstimated number-average molecular weight between crosslinks.^dVolume fraction of polymer successfully incorporated into the network (1 – sol fraction).^eElongation at rupture.^fRefractive force (stress) at rupture.^gEnergy of rupture, as represented by the area subtended by the force-elongation profile.^hVolume fraction of elastomer in swelling equilibrium with benzene at room temperature.ⁱSample swollen in linear PDMS oligomers.^jMacroscopically phase-separated condensation cured bimodal network, polydispersed sphere (binodal) texture.^kMacroscopically phase-separated hydrosilylation cured vinyl bimodal network, interpenetrating (spinodal) texture.

which was confirmed by GPC (11). The long chains used are described in Tables 1 and 2. A sample of nearly monodisperse trimeric hydroxyl end-capped PDMS was generously donated by Dr. Mark Buese of PCR Chemicals. Its M_n was 300 g/mol, $M_w/M_n \sim 1.1$, and it was reported to be essentially free of cyclics.

2.4 Preparation and Testing of the Networks

We utilized the traditional one-pot procedure for “room temperature” vulcanization, which generated the previously studied bimodal and unimodal networks (2–6,11–14). In the condensation approach, known molar amounts of hydroxyl-terminated short chains and long chains (Table 1) were mixed with the stoichiometric amount of the end linker tetraethoxysilane (TEOS) (Aldrich, 99+ purity) and 1 wt/wt% dibutyltin(IV) dilaurate catalyst (M&T Chemicals) and allowed to cure for 1 day. The bimodal networks prepared from the vinyl-terminated chains were prepared by mixing 99 mol% of 1,3-divinyl-1,1,3,3-tetramethyldisiloxane (Gelest) with 1 mol% of 22,000 g/mol vinyl-terminated PDMS (Gelest) and the stoichiometric amount of tetrakisdimethylsiloxy silane (Aldrich) with 1 ppm of a Pt/Siloxane “Karstedt” catalyst (Gelest) and allowed to cure for 1 day.

It was not possible to obtain a homogenous mixture of the crystalline hydroxyl-terminated dimer/long chains at room temperature, but was easily achieved at temperatures above the melting point of the dimer (60°C). A modified procedure for making bimodal elastomers from these short chains entailed placing the inhomogeneous mixture into a mold in an oven heated to 80°C. Open jars of TEOS (95+%, Gelest) and distilled water were also placed in the

oven to help accommodate any evaporation. This procedure gave a sufficiently long pot life so that the crystals melted and the sample appeared very homogeneous before and after gelation thus giving a clear “model” elastomer.

The equilibrium volume fraction of elastomer in benzene and the extractable soluble fraction were measured in the normal manner (11). A special series of experiments utilized samples swollen in linear, unreactive, nonvolatile PDMS oligomers (trimethylsilyl terminated PDMS $M_n \sim 700$ g/mol, United Chemical Technologies PS 039). Dried, extracted samples were placed in the low-viscosity oligomers for a period of at least one week, and the samples

Table 2. Multimodal network components

Molecular Weight g/mol	weight added w_i	Moles added N_i
300	1	3.33×10^{-3}
700	1	1.43×10^{-3}
1700	1	5.88×10^{-4}
2500	1	4.00×10^{-4}
4200	1	2.38×10^{-4}
18000	1	5.56×10^{-5}
26000	1	3.85×10^{-5}
36000	2	5.56×10^{-5}
43500	2	4.60×10^{-5}
49000	2	4.08×10^{-5}

$$M_n = \frac{\sum w_i}{\sum N_i} = 2088 \text{ g/mol.}$$

$$M_w = \frac{\sum w_i N_i}{\sum w_i} = 23876 \text{ g/mol.}$$

$$M_w/M_n \sim 10.$$

absorbed diluent oligomers until constant weight was noted (volume fraction of elastomer = 0.5).

3 Results and Discussion

3.1 Mechanical Properties of the Macroscopically Phase-Separated Network and Broadly Multimodal Network

Our previous morphological studies (11–14) demonstrated that phase separation in “model” PDMS networks can occur when short chains are end-linked in the presence of relatively large amounts of catalyst. The phases appeared to be high crosslink density clusters in a low crosslink density matrix. The low crosslink density phase emulates a long-chain component, and thus bimodal networks naturally lend to phase separation. Indeed, we found that the right crosslinking conditions (11–14) cause the phase separation to pervade the system making the entire network volume turbid. Interestingly, this phase separation phenomenon does not presuppose a specific crosslinking chemistry, and was shown to apply to both bimodal networks formed by hydrosilylation as well as condensation crosslinking approaches. The differences between the phase separation appeared to be in the final morphology, where the hydrosilylation network had a interpenetrating (spinodal) morphology and the condensation network had a spherical, nucleated (binodal) morphology.

The ultimate mechanical properties of a condensation network with binodal phase separated structure and a hydrosilylation network with spinodal structure are shown in Table 1 and Figure 2. Both networks were relatively weak, but for different reasons. The hydrosilylation-cured spinodal network failed after a very small strain, but with a relatively large ultimate stress, whereas the condensation-cured binodal one failed at much larger strains and relatively low ultimate stress. In both cases, the toughness was small. The strain

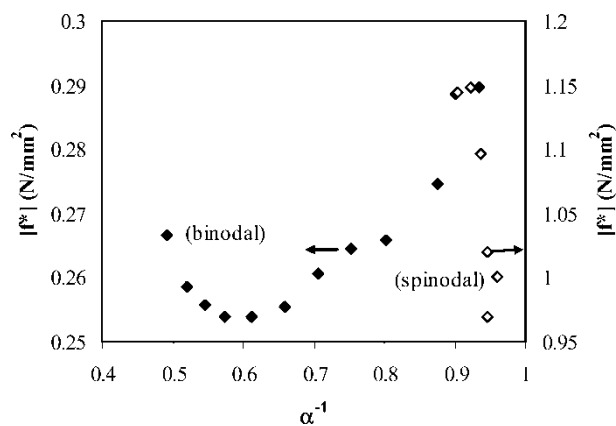


Fig. 2. Mooney-Rivlin plot of macroscopically phase-separated bimodal elastomers. The curves are labeled with the gross morphology. (◆, left axis) binodal 97 mol% 300 g/mol from hydroxyl-condensation end linking, (◇, right axis) spinodal 99 mol% 186 g/mol from vinyl-hydrosilylation end linking.

dependence of the modulus of these particular networks as expressed in the usual Mooney-Rivlin fashion (1) is shown in Figure 2. The hydrosilylation elastomer showed a continuous upturn in modulus that clearly indicates the limited-chain extensibility effect was operative at all states of strain due to the extremely short dimeric short chains. In fact, the Mooney-Rivlin curve would suggest that the short chains in this particular network were never elastic, but acted instead like rigid rods. Relevant here is the fact that a network formed from rigid rods has been observed to deform easily and reversibly (16). Such isotherms similarly showing constantly increasing Mooney-Rivlin moduli profiles have been observed for swollen bimodal networks, where the swelling dilation presumably pre-strains the short chains (17). Conversely, the condensation-cured binodal macroscopically phase-separated network showed a Mooney-Rivlin profile similar to bimodal networks studied earlier, in that it had an initial modulus decrease followed by a slight upturn at large strains. This upturn was too small to provide significant reinforcement. The combined results can't unambiguously determine whether large-scale structure contributes to bimodal reinforcement. The majority of the prior studies (2–6) of the bimodal reinforcement effect used condensation end-linked elastomers, and thus the remainder of this study dealt with that particular end-linking chemistry.

Erman and Mark speculated that a network containing a wide spectrum of chain lengths would always have some chains that sensibly have “limited” but elastic (and reinforcing) extensibility at any point in the deformation (18). In effect, the hope was that no matter what the property or deformation, a very broad distribution of chain lengths would guarantee that there would be a subset of chains ideal for a specific purpose. To that end, we prepared a very broadly multimodal network by end-linking hydroxyl terminated PDMS chains according to the formulation is listed in Table 2. This gave the number-average molecular weight M_n (first moment of the distribution) of 2,088 g/mol and the weight-average to number-average (polydispersity) ratio $M_w/M_n \sim 10$. The polydispersity ratio M_w/M_n can be easily changed by incorporating much larger molecular weight chains or by skewing the weight fractions of the individual components to give $M_w/M_n = 50$ or greater. The network did not have unusually good mechanical properties, as illustrated by the results listed in Table 1. The sample had a relatively good extensibility, but not large values of the stress. Thus, the toughness was also low, and the mechanical behavior was similar to that of a long chain unimodal network. It should be mentioned that this network was observed to be transparent.

3.2 Condensation Cross-Linked Short Chain Bimodal Networks Templated Toward Nanostructure

Linear low molecular weight hydroxyl-terminated PDMS oligomers are the water-soluble byproducts of environmental degradation (19). The water solubility conceivably comes

from hydrogen bonding interactions from the hydroxyl end-groups, and thus some degree of incompatibility is to be expected with high molecular weight PDMS, which is hydrophobic. For example, the linear hydroxyl-terminated dimer is crystalline, with a melting point of 60°C. A homogeneous mixture of the hydroxyl dimer with polymeric PDMS occurred only when heated to temperatures above the melting point, and formed a clear network when using a high temperature cross-linking procedure. The monodisperse hydroxyl trimer is a liquid and readily mixes in and “room temperature vulcanizes” with long-chain PDMS to form model elastomers that are transparent. It seems likely that the hydrogen-bonding interactions persisted (especially for networks formed from extremely short chains) and thus these bimodal elastomers intrinsically had an inhomogeneous short chain clustered network structure, which is herein termed “templated nanostructure.” The prevalence of hydrogen-bonded clusters could lead to the nucleation and growth type morphology observed in the macroscopically phase separated condensation cured networks (11–14), but is apparently arrested in these “homogeneous” bimodal elastomers. The ultimate mechanical properties of a number of these bimodal networks are listed in Table 1, and the toughness is seen to be much larger and representative of the bimodal reinforcement effect.

3.3 Stress-Strain Behavior

An analysis of the bimodal stress-strain isotherms (Figure 3) from the monodisperse dimeric and trimeric short chains,

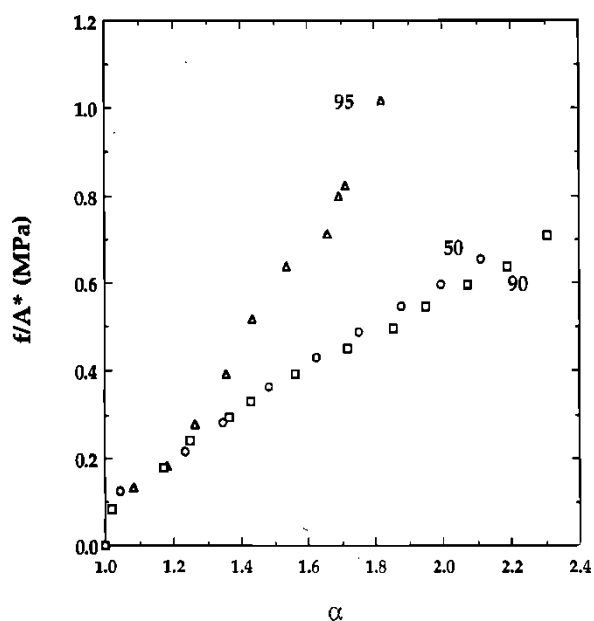


Fig. 3. Force-elongation results on model networks formed from monodisperse hydroxyl short chains. The curves are labeled with the mol% short chains. Networks have 95 mol% 166 g/mol chains (Δ), 50 mol% 166 g/mol chains (\circ), and 90 mol% 240 g/mol chains (\square).

however, shows differences from previously reported stress-strain isotherms from bimodal elastomers (20). A network containing 95 mol% of dimeric short chains is toughened primarily by having a large stress, and the stress increases rapidly but linearly as a function of strain. Conversely, a network containing 90 mol% of a trimeric short chain is toughened primarily by having a large elongation. Moreover, a network containing as few as 50 mol% of the dimer is also tough, with the stress-strain profile almost indistinguishable from that for the 90 mol% trimer network. After a short initial increase, the stress-strain relation is effectively linear for these high-extensibility networks. These results contrast with the results of the Andradý, Llorente and Mark bimodal elastomers (20). These elastomers showed stress-strain behavior at low/intermediate strains that is very similar to the lower curve in Figure 3. At high elongations, these earlier networks showed a sigmoidal upturn in the stress that was largely responsible for the observed reinforcement.

3.4 Mooney-Rivlin Behavior

The Mooney-Rivlin plots similar to the stress-strain profiles of the lower curves of Figure 3 are presented in Figure 4. The modulus is initially quite large, and decays rapidly with increasing strain. However, the most important feature is the absence of a large sweeping upturn in modulus. Instead,

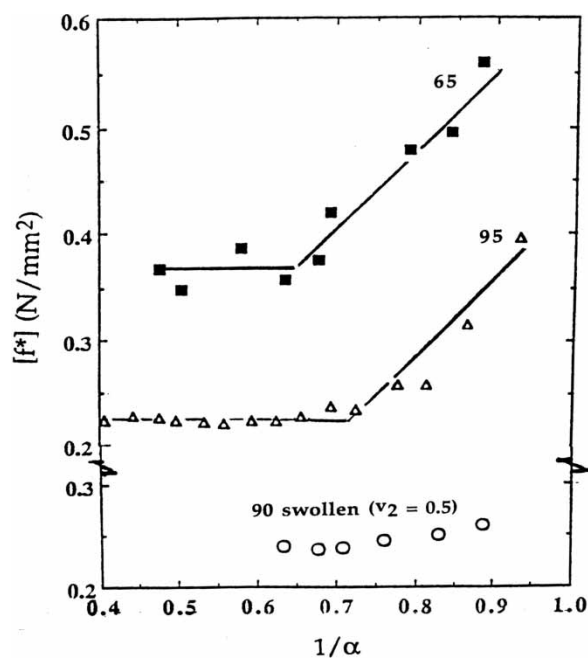


Fig. 4. Mooney-Rivlin plot of bimodal elastomers formed from monodisperse hydroxyl-terminated short chains. The curves are labeled with the mol% of short chains. Networks have 65 mol% 166 g/mol short chains (\blacksquare), or 95 mol% 166 g/mol short chains (\triangle). Also shown are results for a 90 mol% 240 g/mol network swollen in non-volatile PDMS diluent (\circ).

the modulus is invariant with strain, a behavior that persists for extremely large strains (140% extension and until rupture) for the 95 mol% trimer. The Mooney-Rivlin behavior of a bimodal network containing 90 mol% of the trimer swollen with a non-volatile diluent is included as the lowest curve in Figure 4. The diluent was a low-viscosity mixture of non reactive trimethylsilyl PDMS oligomers ($M_n \sim 700$ g/mol). The volume fraction of elastomer in the swollen system was 0.5, which is significantly larger than the equilibrium volume fraction, but comparable to that of some incompletely swollen bimodal elastomers that showed greatly increasing Mooney-Rivlin upturns (17). There was an overall reduction in modulus, which would occur since dilation decreases the number of elastic chains per unit cross-sectional area. However, there was no indication of a limited chain extensibility upturn at any state of strain.

3.5 Equilibrium Swelling

Values of the volume fraction of elastomer in several templated-nanostructure bimodal networks in swelling equilibrium with benzene are shown in Figure 5. The solid line reflects the classical prediction for the effect of molecular weight between crosslinks on the degree of swelling (1, 18). This theoretical prediction also used for comparisons in the case of the previously studied bimodal networks (20). The fit between theory and experiment is seen to be poor. The networks containing the largest mole fraction of short chains (smallest average molecular weight between crosslinks) swelled more than predicted. These swelling results agreed with those for the previously studied bimodal networks (20), which also had smaller volume fractions than the theoretical predictions. However, the networks with the lowest mole fraction of short chains had a much

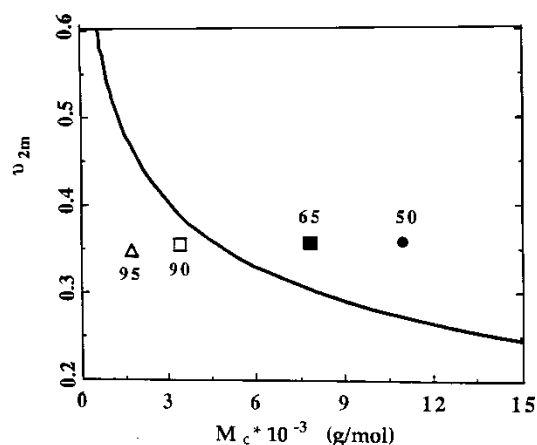


Fig. 5. Volume fraction of elastomer in swelling equilibrium for bimodal elastomers formed from monodisperse hydroxyl short chains. The curve is the classical rubberlike elasticity prediction used for comparisons in prior studies. Long chains are 22,100 g/mol. Networks have 50 (●) or 65 (■) mol% 166 g/mol short chains, 90 (□) or 95 (Δ) mol% 240 g/mol short chains.

larger volume fraction of rubber in swelling equilibrium than the prediction. To the best of our knowledge, these results are the first examples of significant under-swelling. The combined results suggest that the swelling of these bimodal elastomers is not well characterized by an average molecular weight between crosslinks.

4 Some Other Relevant Results

The original “weakest link” theorem postulated that short chains would be the locus of failure for elastomers (1), but was disproven by some prior bimodal elastomer studies. However, many older systems known to contain short chains were not particularly strong. For example, elastomeric networks that had 10–20 mol% of short chains were not reinforced (21, 22). Furthermore, a network that had a very broad distribution of mesh lengths (including short chains) would be the expected result of random crosslinking, where chains are tacked together at random points along their contour. Relevant here is a study in which Falcão and coworkers (23, 24) prepared PDMS networks by irradiating a high molecular weight PDMS gum (100,000 g/mol). They found that the mechanical properties agreed reasonably well with the classical prediction of equilibrium swelling of a unimodal network. Although the ultimate mechanical properties were not explicitly stated, it can be inferred that they were unexceptional. This would be consistent with the present observation that our broadly multimodal network, which emulates a randomly crosslinked elastomer, did not appear to be well reinforced. The assumed randomness of the multimodal elastomer would also likely randomize the nanostructures that would be present in the elastomer.

Sharaf has attempted to study some networks that may have been “inadvertently” bimodal (25–28). Such networks had obvious unusual nanostructures, such as polysulfidic sulfur vulcanized elastomers or multifunctional polymers end linked to telechelic PDMS. Classical rubber-like elasticity is based in mean-field theories (1, 18), and thus deviations from classical theory could sensibly have a structural basis. We tacitly assume that the classical theories would describe the system provided that the structures do not provide an unusually large deviation from a mean-field approach. In a similar vein, significant differences from prior bimodal results could also be related to structural differences. Many differing types of elastomeric networks exhibit a “non-Gaussian” upturn in modulus (18) so it is not surprising that our elastomers would show an upturn. It was surprising, however, that a swollen elastomer would not show the upturn but instead just a plateau. The simplest explanation for a plateau in the Mooney-Rivlin profile is due to high functionality cross-linking sites (18). A nanoscopic cluster of short chains would “inadvertently” emulate a high functionality crosslinking junction, as illustrated in Figure 6. Furthermore, significant cluster formation could be expected to attenuate the overall swelling, particularly for the oligomeric

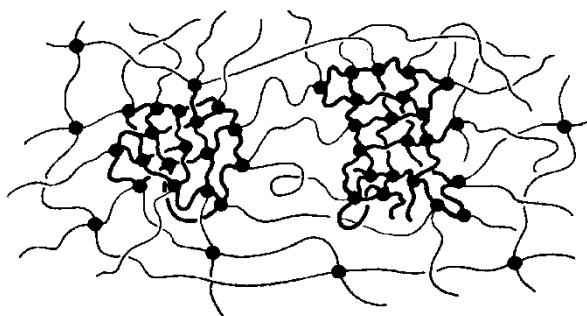


Fig. 6. Sketch of a bimodal network in which the short chains have a clustered, high functionality nanostructure.

PDMS swelling “solvents”, which might not be able to infiltrate a cluster due to its large excluded volume.

Clustering could delay the limited chain extensibility effect, likely due to the large topological restraints of highly cross-linked regions. The fact that some of our networks containing extremely large molar amounts of short chains did not show the upturn may be due in part to the degree of cluster formation. Clusters are still reinforcing, likely preventing catastrophic failure by blunting microcrack growth. McGill and coworkers noted that the tear strength of sulfur-vulcanized polyisoprene networks was higher when the curing conditions favored cross-link distribution inhomogeneity, which arguably emulates a bimodal network (29). Similarly, the tear strength in bimodal PDMS networks is unusually high (30). Beaucage et al. (31) have analyzed size effects of dense, silicate structures in organic-inorganic hybrids. They argue that nanometer-size silicate particles mainly affect the modulus, while micron-size particles affect failure properties. The one-pot procedures used to prepare the reinforced bimodal networks apparently fortuitously favors an optimal size for the reinforcing clusters due to nucleation and growth of the associating hydroxyl-terminated chains.

5 Conclusions

The mechanical properties of end-linked PDMS networks that were macroscopically turbid or templated toward nanostructure formation were studied. Macroscopically phase-separated bimodal PDMS networks were weak, but showed evidence of the “limited chain extensibility” upturns in the modulus like previously studied, reinforced bimodal networks. A multimodal network formed from a varied population of chain lengths, some of which were ostensibly at the limited extensibility thresholds was also weak. On the other hand, similar (although transparent) bimodal networks formed from extremely short chains were found to be well reinforced, although they were probably nanostructurally clustered due to hydrogen bonding interactions. The Mooney-Rivlin isotherms for these nanostructure templated bimodal elastomers

did not show a marked upturn in modulus, but instead a plateau which suggested high functionality clusters in the system. Equilibrium swelling results also support the notion of clustered short chains. In total, these results suggest that the remarkable mechanical properties seen in bimodal PDMS networks may have a structural component, as well as being due to limited chain extensibility. Furthermore, the size and/or mode of formation of the high crosslink density structure could play a role in the reinforcing mechanisms.

6 Acknowledgement

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