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(SANS) study reported separately[6a] and to be presented as the third installment of this series,[6b] quantitatively confirm the mean-field predictions of Leibler[1] concerning the structure and phase behavior of block copolymers. This study has demonstrated that the rheological analysis of block copolymers represents a powerful method of investigating polymer–polymer thermodynamics.

Acknowledgment. I am grateful to V. Reddy Raju for helpful discussions and for his assistance in using the mechanical spectrometer and to Mark A. Hartney for his collaboration in preparing the samples.

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Simultaneous Curing and Filling of Elastomers

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ABSTRACT: A method previously developed for the precipitation of reinforcing silica filler within an already cured elastomer is extended so as to permit simultaneous curing and filling. Specifically, tetraethyl orthosilicate is used to end-link hydroxyl-terminated chains of poly(dimethylsiloxane), with the excess present being hydrolyzed to finely divided SiO_2. Increase in the amount of filler thus formed decreases the elongation required for the desired upturns in modulus and increases the maximum extensibility, ultimate strength, and energy required for rupture of the network.

Introduction

Elastomers which cannot readily undergo strain-induced crystallization are very weak in the unfilled state.[1-3] Networks of poly(dimethylsiloxane) (PDMS) [$-Si(CH_3)_2-O-$] are in this category, primarily because of the very low melting point (−40 °C)[4] of this polymer. As a result, PDMS elastomers used in most applications are invariably filled with a "high-structure" particulate silica (SiO_2) in order to improve their mechanical properties.[5-8] The incorporation of such fillers in PDMS or any high-viscosity polymer, however, is a difficult, time-consuming, and energy-intensive process.[5-8] It can also cause premature gelation ("structuring" or "crepe hardening").[9] For these and other reasons,[10] it would be advantageous to be able either to precipitate reinforcing SiO_2 into an already cured network or to generate it during the curing process. The first goal was achieved in two earlier studies[10,11] in which tetraethyl orthosilicate (TEOS) [$Si(OC_2H_5)_4$] was hydrolyzed to precipitate the desired SiO_2 filler into a cross-linked PDMS network. The present investigation extends this work so as to permit the simultaneous curing and filling of an elastomer material.

Experimental Details

The polymers employed, two hydroxyl-terminated PDMS samples having number-average molecular weights corresponding to $10^{-3}M_n = 21.3$ and 8.00, respectively, were generously provided by Dow Corning Corp. Portions of them were mixed with TEOS in amounts characterized by the molar feed ratio $r = [OC_2H_5]/[OH]$, where the OC_2H_5 groups are on the TEOS and the OH groups appear as chain ends on the PDMS. Specific values of this ratio, which range upward from 1.0 (stoichiometric balance), are given in the third column of Table I. The catalysts employed, dibutyltin diacetate and stannous 2-ethyl hexanoate, were present to 0.8–1.0 and 1.7 wt %, respectively, of the PDMS. Both series of mixtures of these three components appeared to be perfectly homogeneous. They were poured into molds to a depth of 1.0–1.5 mm, and the reaction was allowed to proceed at room temperature for 3 days. The water required for the hydrolysis of the TEOS was generally simply absorbed from the humidity in the air,[12] but in a few test cases, additional liquid water was added to the reaction media.

The resulting networks were extracted in tetrahydrofuran and toluene in the usual manner;[13,14] the sol fractions thus obtained are small, as can be seen from the values given in column four of Table I. The densities ρ of these extracted materials were determined by pycnometry. Swelling measurements in benzene at room temperature were also carried out on portions of the extracted samples. Similarly, other unswollen portions were used in the elongation experiments carried out to obtain the stress–strain isotherms at 25 °C.[13,14] The nominal stress was given by $f^* \equiv f/A^*$, where f is the elastic force and A^* the undeformed cross-sectional area, and the reduced stress or modulus[1,13-15] by $[f^*] \equiv f^*/(\alpha - \alpha^{-2})$, where $\alpha = L/L_i$ is the elongation or relative length of the sample.

Results and Discussion

The simplest equation for the hydrolysis of TEOS is

$$Si(OC_2H_5)_4 + 2H_2O \rightarrow SiO_2 + 4C_2H_5OH \qquad (1)$$

but the reaction in the presence of the hydroxyl-terminated PDMS is probably much more complicated, with some chains bonded to incompletely hydrolyzed products. In any case, electron microscopy results[16] indicate the particles to be unagglomerated, with an average diameter of

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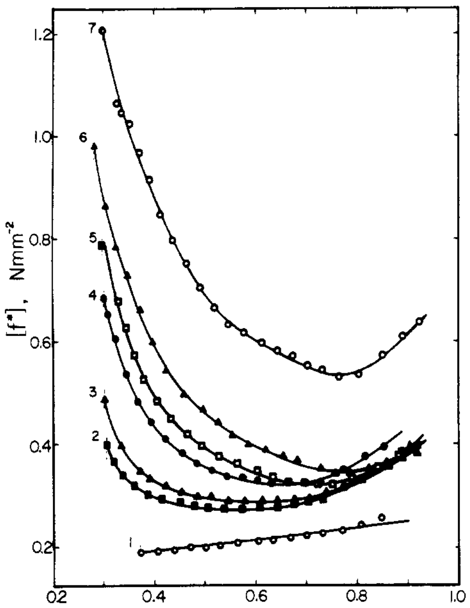

Figure 1. Reduced stress shown as a function of reciprocal elongation for the first series of SiO_2-filled PDMS networks at 25 °C. Each curve is identified by the designation given in column one of Table I, and the vertical dashed lines locate the rupture points. The results shown in the remaining figures also pertain to this series of networks.

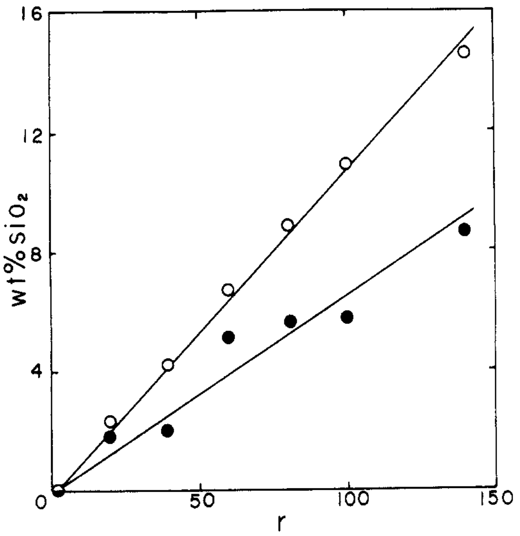

Figure 2. Weight percent silica precipitated within the PDMS networks shown as a function of the feed ratio $r = [OC_2H_5]/[OH]$, where the OC_2H_5 groups are on the tetraethyl orthosilicate and the OH groups are at the ends of the polymer. The open circles show the results obtained from the change in weight of the polymer and the filled circles from the density of the filled network.

200 Å. There was also ample evidence for very strong reinforcing effects from the precipitated silica. Specifically, the degree of swelling decreased as the feed ratio r increased; this is shown in column five of Table I by the increasing values of the volume fraction v_{2m} of polymer at swelling equilibrium. Also, the densities (given in column six) increased with increase in r, because of the high density of silica (~2.6 g cm^{-3})[17] relative to PDMS (~0.95 g cm^{-3}). Finally, the networks prepared with an excess of TEOS ($r \gg 1$) have values of the modulus which are much higher than those of the network prepared using $r = 1.0$ (curve 1). Typical results, for the first series of networks, are shown in Figure 1. Furthermore, the upturns in $[f^*]$ observed at high elongations clearly demonstrate the desired reinforcing effects.[1,10,11,18]

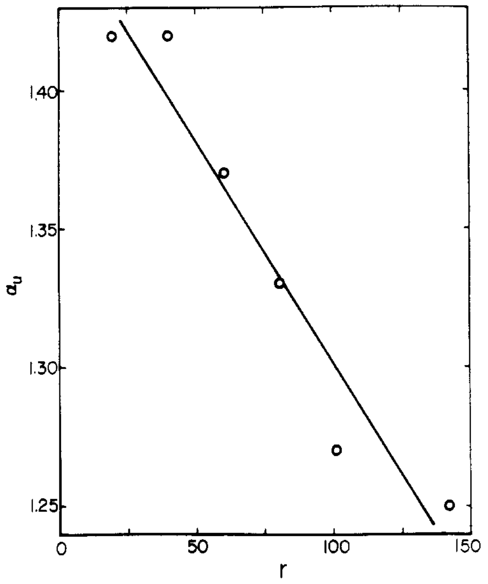

Figure 3. Effect of the feed ratio on the elongation at the initial upturn in modulus.

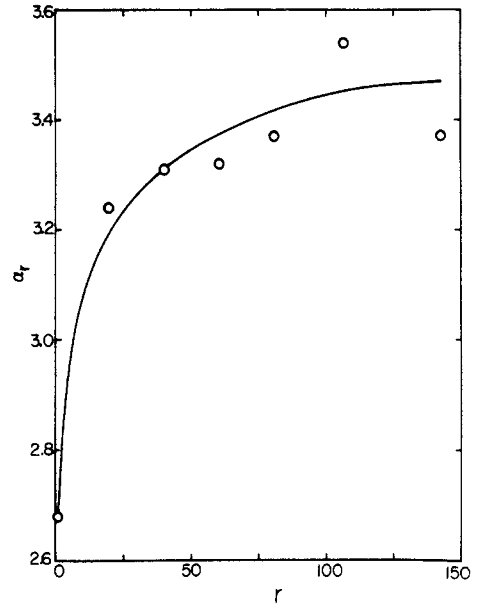

Figure 4. Dependence of the maximum extensibility on the feed ratio.

The amounts of SiO_2 precipitated were estimated in two ways. Values obtained from the increase Δw in weight of polymer are given in column seven of Table I, and those from the densities of filled network, polymer, and silica are given in the following column. The latter values are approximately 30% smaller than the former, which is consistent with the expectation, already mentioned, that the filler is not entirely pure SiO_2. Larger amounts of silica were precipitated in the case of the shorter chain network ($10^{-3}M_n = 8.00$), presumably because these networks contained larger amounts of TEOS. The amounts are represented relative to the stoichiometrically balanced amount, and this reference amount is larger for the end-linking of shorter chains. In both series of networks, the weight of filler does show the expected increase with increase in r, as in shown in Figure 2.

The values of the elongation α_u at which the modulus increases because of the reinforcing effects are given in column nine of Table I. They show the expected decrease

Table I
Preparation and Properties of the Silica-Filled Networks

network	$10^{-3}M_n$	r^a	sol fraction	$v_{2m}{}^b$	ρ, g cm^{-3}	wt % SiO$_2$ from Δw	wt % SiO$_2$ from ρ	$\alpha_u{}^c$	α_r	$(f/A^*)_r$,^{d} N mm^{-2}	10^3E_r,^{e} J mm^{-3}
1	21.3	1.0	0.043	0.293	0.955	0.00	0.00		2.68	0.481	0.489
2	21.3	19.5	0.034	0.319	0.966	2.28	1.80	1.42	3.24	1.25	1.18
3	21.3	39.9	0.033	0.326	0.967	4.56	1.96	1.42	3.31	1.58	1.49
4	21.3	60.4	0.032	0.328	0.987	6.75	5.12	1.37	3.32	2.21	1.93
5	21.3	80.8	0.031	0.334	0.990	8.83	5.59	1.33	3.37	2.59	2.03
6	21.3	101.3	0.030	0.338	0.993	10.83	5.74	1.27	3.54	3.39	2.93
7	21.3	142.2	0.029	0.373	1.010	14.56	8.61	1.25	3.37	3.99	3.73
8	8.00	1.0	0.046	0.324	0.954	0.00	0.00		1.59	0.310	0.120
9	8.00	5.2	0.047	0.363	0.962	1.29	1.16	1.68	1.87	0.507	0.240
10	8.00	10.0	0.047	0.384	0.983	5.02	4.44	1.47	2.05	0.730	0.417
11	8.00	20.4	0.050	0.409	1.002	8.31	7.50	1.24	2.49	2.11	1.21

[a] Feed ratio of OC$_2$H$_5$ TEOS groups to OH chain ends. [b] Volume fraction of polymer present at swelling equilibrium in benzene at room temperature. [c] Elongation at initial upturn in modulus. [d] Ultimate strength as represented by the nominal stress at rupture. [e] Energy required for rupture.

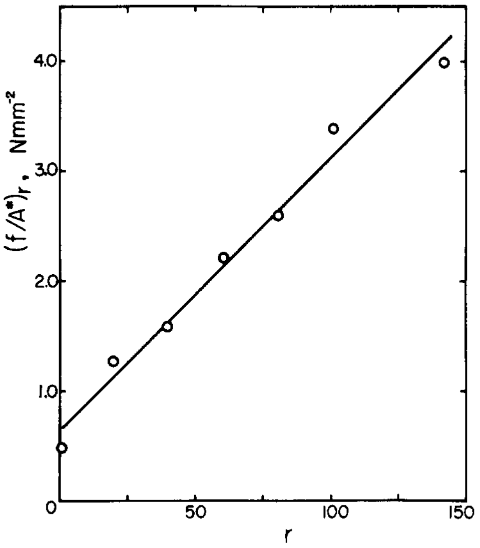

Figure 5. Effect of the feed ratio on the ultimate strength as characterized by the nominal stress at rupture.

with increase in the amount of silica generated, as is shown by the typical results presented in Figure 3. Values of the maximum extensibility or elongation α_r at rupture are given in the following column. Their increase with r, as shown in Figure 4, clearly demonstrates the reinforcement-induced improvement in this ultimate property. Much more striking increases are observed for the ultimate strength, as represented by the nominal stress at rupture. These results are shown in part in Figure 5 and are tabulated in their entirety in column 11 of Table I. Networks prepared in contact with excess water were not as strong as those described in Table I. The fact that these samples were cloudy indicates the presence of unusually large silica particles, which would be less effective as reinforcing agents.

Figure 6 shows the data of Figure 1 plotted in such a way that the area under each stress–strain curve corresponds to the energy E_r of rupture,[19] which is the standard measure of elastomer toughness. The values of 10^3E_r for the two series of networks range from 0.49 and 0.12 J mm^{-3} (r = 1.0) to 3.73 and 1.21 J mm^{-3} ($r \gg 1$), respectively. The specific values are given in the last column of Table I, and typical results are shown as a function of r in Figure 7. Thus, this reinforcement technique can easily bring about a tenfold increase in toughness. Furthermore it is achieved in a manner that avoids the complications of the elaborate milling techniques usually used to blend an already formed filler into a high molecular weight polymer.

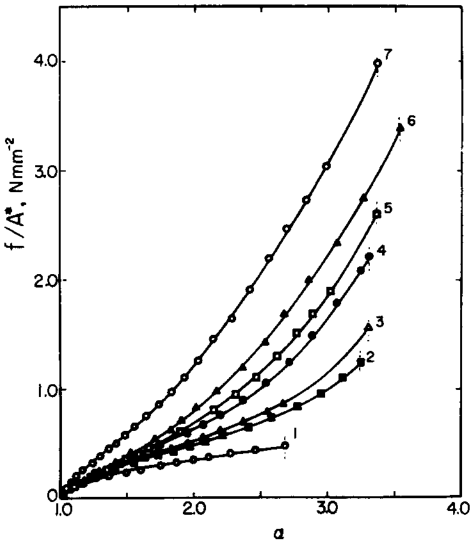

Figure 6. Nominal stress shown as a function of elongation for the same networks characterized in Figure 1. In this representation, the area under each curve corresponds to the energy required for network rupture.

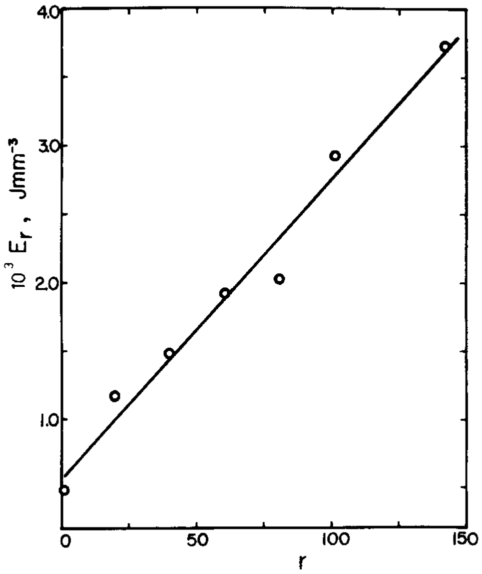

Figure 7. Effect of the feed ratio on the energy required for network rupture.

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Effect of Composition and Cross-Link Functionality on the Elastomeric Properties of Bimodal Networks

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ABSTRACT: Hydroxyl-terminated poly(dimethylsiloxane) chains were tetrafunctionally and trifunctionally end-linked to give bimodal elastomeric networks in which the short chains had a number-average molecular weight of 660 and the long chains 21.3×10^3. Elongation measurements were carried out at 25 °C to obtain the stress–strain isotherms for these materials up to their rupture points. Decrease in the mol % of short chains was found to cause an increase in the elongation at which the modulus shows a strong upturn because of limited chain extensibility and also an increase in maximum extensibility. The ultimate strength and energy for rupture increase with cross-link functionality and go through a maximum upon changes in composition, with approximately 95 mol % short chains giving the largest values for these two properties.

Introduction

Elastomeric networks of known structure may be prepared by reacting suitably terminated polymer chains with an end-linking agent of functionality three or greater.[1] If a mixture of very short and relatively long chains is treated in this way, the resulting (unfilled) elastomer has a bimodal distribution of network chain lengths. Networks of this type have been prepared from chains of poly(dimethylsiloxane) (PDMS) $[-Si(CH_3)_2O-]$ and were found to have unusually good ultimate properties.[1-3] The present investigation explores in detail the way in which the elastomeric properties of trifunctional and tetrafunctional bimodal networks of PDMS depend on the relative proportions of short and long chains.

Experimental Details

The two polymers employed were hydroxyl-terminated PDMS chains having number-average molecular weights M_n of 660 and 21.3×10^3, respectively. They were generously provided by Dow Corning Corp. of Midland, MI. After careful drying, these two components were mixed to give the compositions listed in columns three and four of Table I. One series of mixtures was tetrafunctionally end-linked by using $Si(OC_2H_5)_4$, and two other series were trifunctionally end-linked by using the corresponding vinyl and phenyl derivatives $ViSi(OC_2H_5)_3$ and $PhSi(OC_2H_5)_3$, respectively. The reactions were run in the usual manner,[1,4,5] with the end-linking agents present in amounts stoichiometrically equivalent to the number of polymer chain ends and the catalyst (stannous 2-ethyl hexanoate) present to the extent of 1.7 wt. % of the polymer mixture. The ingredients were thoroughly mixed to give perfectly clear solutions, which were then poured into glass molds. The reaction was allowed to proceed at room temperature for 2 days, with the molds covered during the first part of the process to prevent volatility losses of the end-linking agents.

The bimodal networks thus prepared were extensively extracted as described elsewhere.[4-6] Specifically, tetrahydrofuran and toluene were used as solvents (with stirring), at room temperature, for a period of several days. Values of the amount of soluble (un-cross-linked) polymer extracted, given in column five of Table I, are seen to be quite small. Strips having the approximate dimensions 1 mm × 3 mm × 30 mm were cut from each unswollen network sheet and then used in elongation experiments to obtain the stress–strain isotherms at 25 °C.[1,4-6] The elastomeric properties of primary interest are the nominal stress $f^* \equiv f/A^*$ (where f is the equilibrium elastic force and A^* the undeformed cross-sectional area) and the reduced stress or modulus[1,4,7] $[f^*] \equiv f^*/(\alpha - \alpha^{-2})$ (where $\alpha = L/L_i$ is the elongation or relative length of the strip). All stress–strain measurements were carried out to the rupture points of the samples and were generally repeated in part to test for reproducibility.

Results and Discussion

The first representation of the stress–strain data was based on the Mooney–Rivlin equation[7,8]

$$[f^*] = 2C_1 + 2C_2\alpha^{-1} \qquad (1)$$

where $2C_1$ and $2C_2$ are constants. These plots, of the

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