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Model Networks of End-Linked Polydimethylsiloxane Chains

15. Spatially Heterogeneous Networks Containing Domains of Very High Crosslink Density

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Summary

Extremely short hydroxyl-terminated polydimethylsiloxane (PDMS) chains (having a molecular weight M_n of approximately 220 g mol^{-1}) were end-linked with much longer PDMS chains ($M_n \approx 18{,}500$ g mol^{-1}) to form bimodal elastomeric networks. The end-linking was carried out in two stages, the first of which was prereaction of the short chains into domains of very high crosslink density. One interest was to determine whether these domains might act as deformable filler particles with exceptionally good bonding to the elastomeric matrix, thereby giving enhanced reinforcement. Unfortunately, stress-strain measurements on these very heterogeneous networks in elongation did not reveal any such effects. The moduli of these networks, however, were found to support the previous conclusion that the unusually good ultimate properties of bimodal networks in general are due to an intramolecular effect, specifically the very limited extensibility of the short network chains.

Introduction

Polydimethylsiloxane (PDMS) $[Si(CH_3)_2O-]$ is a good example of a polymer which forms elastomeric networks that are inherently weak. This shortcoming is due to the fact that the melting point of the polymer is very low (BRANDRUP, IMMERGUT, 1975), and thus a PDMS network generally can not reinforce itself by strain-induced crystallization. As a result, silicone elastomers are heavily filled for almost all applications, generally with a high-structure silica (POLMANTEER, LENTZ, 1975; WAGNER, 1976; WARRICK et al., 1979).

Fillers for elastomers generally consist of very hard particulates and, at least in some systems, their

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non-deformability can cause difficulties such as debonding at the filler-polymer interfaces. (Possibly relevant in this regard is the fact that the dispersed domains in high-performance multi-phase polymers generally have significant deformability). It is therefore of considerable interest to explore a variety of approaches for preparing networks possibly having attractive elastomeric properties through the use of unusual filler-type reinforcement.

This study, a first approach to elastomers containing unusual types of fillers, involves end-linking extremely short hydroxyl-terminated PDMS chains with much longer chains in order to from bimodal elastomeric PDMS networks. The end-linking is carried out in two steps, the first of which is pre-reaction of the short chains into domains of very high crosslink density (MARK, ANDRADY, 1981). One interesting question is whether or not these domains might act as deformable filler particles with exceptionally good bonding to the elastomeric matrix, thereby giving enhanced reinforcing effects. These networks are also very useful for elucidating the origin of the unusually good ultimate properties exhibited by elastomeric bimodal networks in general.

Experimental

The two polymers used were unfractioned samples of PDMS (from the Dow Corning Corporation, Midland, Michigan) having hydroxyl groups at both ends, and number-average molecular weights M_n of 220 and 18,500 g mol^{-1}, respectively. The short chains were thus of much lower molecular weight than those (1,100 g mol^{-1}) used in a previous, related study (MARK, ANDRADY, 1981). A dried and weighed amount of the short-chain sample was mixed with an amount of tetraethyl orthosilicate end-linking agent corresponding to one-half the amount needed for exact balance between ethoxy and hydroxyl groups. Stannous-2-ethyl hexanoate catalyst of about 4-5% by weight of the mixture was then added. The system was agitated by magnetic stirring and the reaction permitted to proceed at room temperature until the viscosity of the mixture increased to a significant extent, but short of gelatin (about 30-40 min.). The long-chain PDMS was then mixed into each pre-reacted system, in an amount which decreased the short-chain component to approximately 90, 85, 80, 75 and 60 mol % of the mixture, respectively. The average molecular weights calculated for the five mixtures are given in the second column of Table I. An additional amount of end-linking agent, just sufficient to react with all the as-yet unreacted hydroxyl chain ends, and catalyst (in an amount maintaining a total of approximately 0.5% catalyst content by weight in the mixture) were then incorporated (MARK, ANDRADY, 1981). This second part of the reaction was permitted to proceed for 24 hrs. The network sheets thus formed were then turned over (to facilitate removal of the ethanol byproduct) and allowed to react for an additional 24 hrs.

TABLE I

Properties of the Segregated Bimodal PDMS Networks

Mol % short chains	10^{-3} M_n, g mol^{-1}	v_{2C}	$2C_1$, N mm^{-2}
89.9	2.07	0.941	0.184 ± 0.011
84.9	2.98	0.951	0.181 ± 0.003
79.9	3.89	0.953	0.201 ± 0.028
75.0	4.79	--	0.181 ± 0.027
60.9	7.37	0.952	0.190 ± 0.038

The tetrafunctional networks thus prepared were extracted at room temperature in tetrahydrofuran (THF) for 3 days, and then deswollen in a series of THF-methanol mixtures of increasing methanol content. The total amount of material thus removed was used to calculate the volume fraction v_{2C} of polymer incorporated in the network structure. Values are given in the third column of the Table.

The stress-strain isotherms in elongation were obtained on unswollen extracted strips cut from the various network sheets. The strips had cross-sectional areas A^* of approximately 7-8 mm^2, and lengths L_i of the central test portions of approximately 10-15 mm. The apparatus consisted of a glass cell in which the sample was mounted between two clamps, one clamp fixed at the bottom of the cell and the other connected to a movable force transducer. The input from the transducer was displayed on a recorder and was calibrated using a set of standard balance weights. The cell was thermostatted at a constant temperature of 25°C. Stress-strain measurements were made using a sequence of increasing values of the elongation or relative length of the sample $\alpha = L/L_i$, with frequent inclusions of values out of sequence to test for reversibility. Values of the elastic force f were recorded only after they had become sensibly constant (no discernible change for at least 15 min.). The elongation was eventually increased to the rupture point of the sample, and a number of runs were carried out on different samples cut from the same sheet in order to determine the reproducibility of the measurements.

Results and Discussion

The data thus obtained were interpreted in terms of the "reduced stress" or modulus defined by (FLORY, 1953; MARK, FLORY, 1966; MARK, 1975; MARK, ANDRADY, 1981)

$$[f^*] \equiv f/[A^*(\alpha - \alpha^{-2})] \qquad (1)$$

The resulting values of $[f^*]$ were then plotted against reciprocal elongation, as suggested by the semi-empirical equation of Mooney and Rivlin (MOONEY, 1948; RIVLIN, 1948; MARK, 1970, 1975; TRELOAR, 1975).

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

in which $2C_1$ and $2C_2$ are constants independent of α. In the crude approximation that this simple linear relationship is obeyed for all $\alpha > 1$, the value of the modulus $[f^*]_\infty$ in the limit at large deformation $(\alpha^{-1} \rightarrow 0)$ would be $2C_1$. It should be pointed out, however, that the most realistic molecular theory of rubberlike elasticity indicates that plots of $[f^*]$ vs. α^{-1} for elongation should be sigmoidal rather than linear (FLORY, 1977; ERMAN, FLORY, 1978, 1982; FLORY, ERMAN, 1982). Equation (2) is thus an approximation which may be relatively poor, particularly in the case of the assumption that $[f^*]_\infty \simeq 2C_1$ for unswollen networks. Since the present study simply involves comparisons between segregated and unsegregated bimodal networks, however, the constant $2C_1$ should suffice here for representation of the elongation modulus.

The stress-strain isotherms obtained are shown in Figure 1. The values of the elastic constant $2C_1$

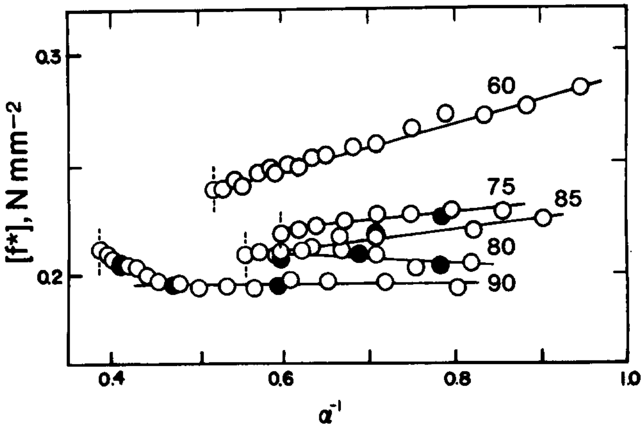

Figure 1. Stress-strain isotherms at 25°C for PDMS bimodal networks of high spatial heterogeneity. Each curve is labelled with the mol % of the much shorter chains (M_n = 200 vs. 18,500 g mol^{-1}). The open circles locate the results gotten using a series of increasing values of the elongation α, and the filled circles the results obtained out of sequence to test for reversibility. The vertical dotted lines show the values of the elongation α at which rupture occurred.

are given in the last column of the Table. Their comparison with previous results (LLORENTE, et al. 1981; PAN, 1982) on unsegregated bimodal PDMS networks of comparable amounts of 220 and 18,500 molecular-weight chains indicates that the segregation of the short chains within the network structure caused a decrease in modulus (of approximately 35%), rather than an increase. Thus, it was not possible to obtain a filler-particle response from the highly cross-linked domains. It may, however, be possible to achieve this highly desirable effect by other techniques.

The fact that the segregation of the short chains did not increase the ultimate strength can be used to elucidate the origin of the unusually good ultimate properties of bimodal networks in general. Specifically, had the improvement in properties been due to an intermolecular effect, it would presumably have been enhanced by the segregation. Thus, the present results confirm the previous conclusion (ZHANG, MARK, 1982) that the increase in modulus and improvements in ultimate properties are due to an intramolecular effect, specifically to a non-Gaussian response arising from limited chain extensibility. A network chain near its maximum extensibility can no longer increase its end-to-end separation by configurational changes, i.e., by simple rotations about its skeletal bonds. Deformations of bond angles (and possibly even bond lengths) would be required, and the energies for these processes are much greater than those for configurational changes. This would correspond to making the elastomer deform thermodynamically the way a metal deforms (MARK, 1981), and this change in deformation mechanism is apparently the origin of the very marked increase in the modulus at high elongations and the much-improved ultimate properties.

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