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A Novel Method for Preparing Bimodal Elastomeric Networks

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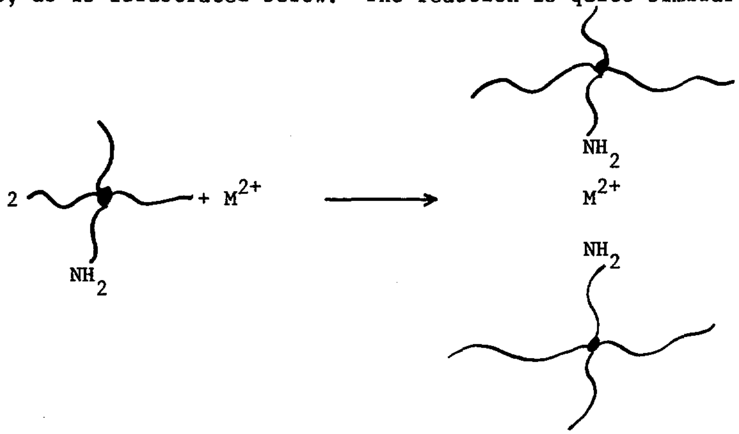
Summary

Hydroxyl-terminated chains of poly(dimethylsiloxane) (PDMS) were end linked with a trifunctional silane containing 3-aminopropyl groups. $CuCl_2$ or $CoCl_2$ added to the networks forms complexes with the amino groups on the cross links, thus introducing additional chains that are very short. The resulting PDMS networks are in this sense bimodal, and were found to have increased values of the ultimate strength.

Introduction

Bimodal elastomeric networks are of considerable interest because they have unusually good ultimate properties (1-3). They are usually prepared by tetrafunctionally end linking a mixture of relatively long and very short chains having reactive groups at both ends. An alternative, novel way of introducing very short chains in a long-chain network is to join chain fragments present on the end-linking agent. This approach is illustrated in the present investigation by end linking chains of poly(dimethylsiloxane) (PDMS) [$-Si(CH_3)_2O-$] with the molecule 3-aminopropyltriethoxysilane [$H_2N(CH_2)_3Si(OEt)_3$]. The amino groups are then reacted with a Cu^{2+} or Co^{2+} salt to form coordination complexes with two or more $H_2N-CH_2-CH_2-CH_2-$ groups attached to the trifunctional cross-links, as is illustrated below. The reaction is quite similar to that



(1)

used to form model networks by using metal atoms M^{2+} to chelate acetylacetonate groups placed along a polymer backbone (4-7). The reaction shown increases the cross-link functionality ϕ to four but, more important, introduces elastically effective chains having 8-10 skeletal bonds, which is approximately the desired length for the short chains in a bimodal network (2,3). In addition, they are probably short enough to remain miscible with the longer PDMS chains. [It should be noted that omitting the CH_2 groups would be expected to be detrimental, since coordinating NH_2 groups directly attached to the Si atom at a cross-link would merely convert, for example, two trifunctional cross-links into one hexafunctional cross-link. Since the network modulus is proportional to $\mu(1 - 2/\phi)$, where μ is the number of cross-links, the modulus and ultimate strength would be expected to decrease (8,9)].

Coordination networks prepared so as to have the desired bimodal distributions of network chain lengths are studied in elongation with regard to their ultimate properties, in particular their ultimate strength.

Experimental Details

The two PDMS networks were prepared from hydroxyl-terminated PDMS chains obtained from the Petrarch Corporation; they had a number-average molecular weight corresponding to $10^{-3}M_n$ = 18.0 and 6.0 g mol^{-1}, respectively. The chains were trifunctionally end linked with 3-aminopropyltriethoxysilane in the usual manner (10,11), and the resulting networks extracted with tetrahydrofuran for a total of six days to remove soluble material. Strips cut from the two network sheets were then dried, and one from each sheet was set aside as a reference material.

The network strips were swelled with tetrahydrofuran containing either $CuCl_2$ or $CoCl_2$. The swollen strips were then put into methanol for one day in order to remove tetrahydrofuran and unreacted metal halide, dried in air for 24 hrs., and then under vacuum to constant weight. The increase in dry weight gave the amount of halide reacted with the networks. The wt %'s are given in the third column of Table I.

Portions of each of the networks were used in elongation experiments to obtain the stress-strain isotherms at 25°C (10,11). The elastomer properties of primary interest were 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 (10-13) $[f^*] \equiv f^*/(\alpha - \alpha^{-2})$ (where $\alpha = L/L_i$ is the elongation or relative length of the strips). 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 stress-strain isotherms obtained on the bimodal coordination networks were first represented as plots of the reduced stress against reciprocal elongation, as suggested by Mooney-Rivlin equation (14)

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

Table I

Structure, Composition, and Ultimate Properties of the Networks

Structure and Composition			Ultimate Properties		
$10^{-3} M_n$[a], g mol^{-1}	Salt Formula	Salt Wt %	α_r[b]	f_r^*,[c] N mm^{-2}	$10^3 E_r$[d], J mm^{-3}
18.0	--	0.0	3.4	0.25	0.28
	$CuCl_2$	11.1	3.2	0.28	0.45
		16.6	2.3	0.44	0.25
		22.9	1.9	0.52	0.29
	$CoCl_2$	5.6	2.6	0.26	0.28
		7.4	3.2	0.33	0.47
		13.0	3.1	0.35	0.46
6.0	--	0.0	1.4	0.30	0.080
	$CuCl_2$	7.1	1.5	0.40	0.12
		8.4	1.5	0.42	0.12

[a] Molecular weight of the long network chains.

[b] Elongation at rupture.

[c] Ultimate strength, as represented by the nominal stress at rupture.

[d] Energy required for rupture.

where $2C_1$ and $2C_2$ are constants independent of elongation.

Some typical stress-strain isotherms obtained as described are presented in Figure 1. As was hoped, significant increases in modulus were obtained, presumably because of both the increase in the number of elastically effective chains and the network bimodality. Figure 2 shows typical stress-strain data plotted in such a way that the area under each curve corresponds to the energy E_r of rupture (15), which is the standard measure of elastomer toughness. Values of it and the maximum extensibility and ultimate strength are given in the last three columns of the Table.

Both the Cu^{2+} and Co^{2+} salts seems to provide sufficiently strong coordination to give the desired bimodal character to the PDMS networks, with significant increases in ultimate strength.

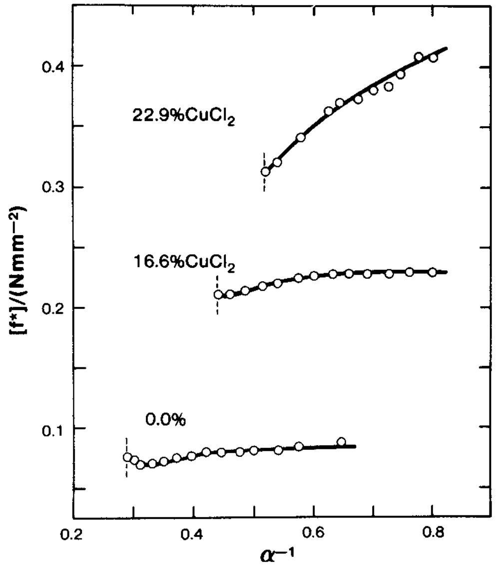


Figure 1. The reduced stress at 25°C as a function of reciprocal elongation for the networks in which the long chains have a molecular weight M_n of 18.0 x 10^3 g mol^{-1}. The wt % of $CuCl_2$ is given for each curve, and the vertical dashed lines locate the rupture points.

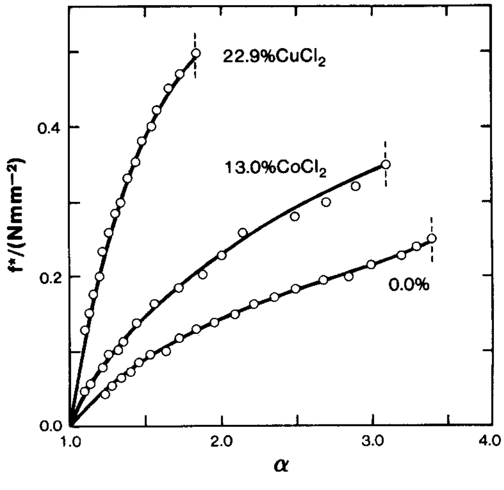


Figure 2. The nominal stress shown as a function of elongation for some typical networks having M_n = 18.0 x 10^3 g mol^{-1}.

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