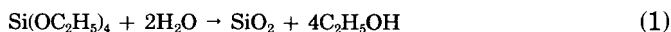


Precipitation of Reinforcing Filler Into Polydimethylsiloxane Prior to Its End Linking Into Elastomeric Networks

INTRODUCTION

Particulate fillers having high surface area are much used for the reinforcement of elastomers, a classic example being the addition of carbon black to natural rubber.¹ Another equally important example is the addition of silica (SiO_2) to polydimethylsiloxane (PDMS) [$-\text{Si}(\text{CH}_3)_2\text{O}-$],^{2,3} which would otherwise yield elastomers much too weak for most applications.^{4,5}

Such fillers are generally blended into the (uncrosslinked) polymers, which are invariably of sufficiently high molecular weight (and viscosity) to greatly complicate the mixing process. For this and other reasons,⁶ methods were recently developed for either precipitating silica into already-formed networks, or precipitating it simultaneously with the curing process.⁶⁻⁹ The reaction is the simple, catalyzed hydrolysis of tetraethylorthosilicate (TEOS)



In this *in situ* technique, however, removal of the byproduct $\text{C}_2\text{H}_5\text{OH}$ and unreacted TEOS causes a significant decrease in volume, which could be disadvantageous in some applications.

The present investigation was undertaken to determine a practical way to avoid this difficulty. The specific goal was the precipitation of the silica into samples of PDMS to give stable polymer-filler suspensions which remained capable of being end linked, subsequently, with no substantial changes in volume.

EXPERIMENTAL

Although both hydroxyl-terminated and vinyl-terminated PDMS have been end-linked into highly elastomeric networks, only the latter could be used in this study since the former reacts with TEOS.¹⁰ The two vinyl-terminated polymers chosen had number-average molecular weights of 5.5×10^3 and $13.0 \times 10^3 \text{ g mol}^{-1}$, and were provided by the McGhan NuSil Corp. The catalysts⁹ tested were sodium hydroxide, acetic acid, zinc acetate, ethylamine, triethylamine, and EDTA (ethylene diamine tetraacetic acid trisodium salt monohydrate). The TEOS to be hydrolyzed to filler was obtained from the Fisher Co., and all reactions were run at room temperature.

Preliminary studies conducted in aqueous solutions were unsuccessful, and those carried out using the water vapor present in the air were only partially successful. The best results were obtained as follows. Weighed amounts of the PDMS and TEOS, a small amount of the catalyst stannous-2-ethyl hexanoate, and a magnetic stirring bar were placed into a small beaker which was then placed (uncovered) into a larger covered jar containing a 2-5 wt % aqueous solution of ethylamine. In the case of the second polymer, a protective atmosphere of nitrogen was also employed. The stirred PDMS-TEOS mixtures were thus continuously exposed to water-ethylamine vapor. Sufficient filler was precipitated by this technique for the mixture to become cloudy after only 15 min. The reaction was allowed to proceed for 2 days at room temperature.

The polymer-filler suspensions prepared in this way were dried under vacuum for several days; they showed no signs of particle agglomeration or settling. The resulting viscous liquids were weighed and then end-linked¹¹ with $\text{Si}[\text{OSi}(\text{CH}_3)_2\text{H}]_4$, using chloroplatinic acid as catalyst

(5 ppm Pt). A sample of each of the unfilled polymers was included for purposes of comparison. These reactions were also run at room temperature, for a period of 2–3 days.

Portions of each of the networks were used in elongation experiments to obtain the stress-strain isotherms at 25°C.^{12,13} The elastomeric 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 modulus¹²⁻¹⁴ $[f^*] \equiv f^*/(\alpha - \alpha^{-2})$ (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 amounts of filler precipitated into the two polymers were obtained directly from the measured increases in weight. For the two samples of the lower molecular weight polymer the amounts were 3.3 and 10.2 wt %, and for the other 29.7 and 62.0 wt %. These values were actually somewhat larger than expected from complete hydrolysis of the TEOS, indicating that some OC_2H_5 groups may remain in the filler or water molecules may be absorbed onto the filler surfaces.

The stress-strain isotherms obtained are presented in Figure 1. The data are shown in the usual way,¹⁵ as the dependence of the reduced stress on reciprocal elongation. As is frequently the case for filled elastomers,¹⁻³ some of the isotherms did not exhibit complete reversibility. In any case, the presence and efficacy of the filler are demonstrated by the marked increases in modulus. In the case of the higher molecular weight polymer, the increases are larger, with marked upturns at the higher elongations. This is due to the larger amounts of filler these samples contain, and possibly also to more reactive particle surfaces (since these precipitations were carried out under nitrogen).

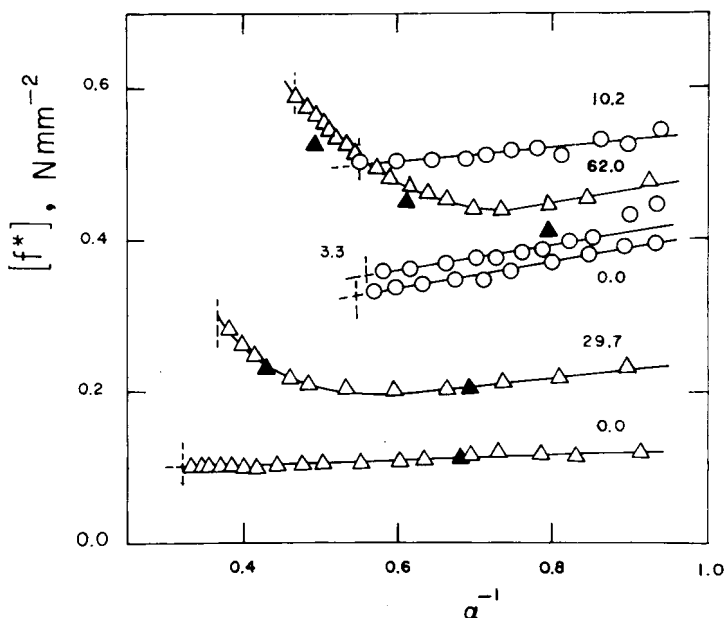


Fig. 1. The reduced stress shown as a function of reciprocal elongation for the two series of filled PDMS networks at 25°C. The circles locate results obtained using polymer having a molecular weight of $5.5 \times 10^3 \text{ g mol}^{-1}$, and the triangles a molecular weight of 13.0×10^3 . Filled symbols are for results obtained out of sequence to test for reversibility, and each curve is labelled with the wt % of filler present in the network. The vertical dashed lines locate the rupture points.

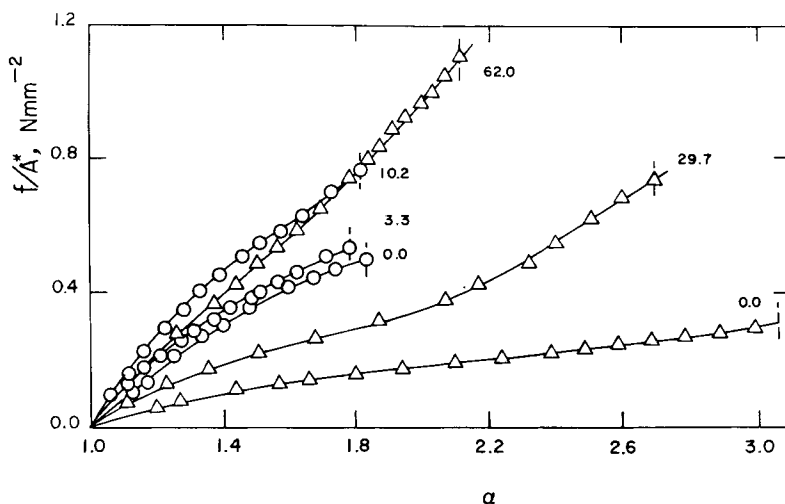


Fig. 2. The nominal stress shown as a function of elongation for the same networks characterized in Figure 1. In this representation, the area under each curve corresponds to the energy required for network rupture.

Figure 2 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,¹⁵ which is the standard measure of elastomer toughness. It is seen that this simple technique can easily increase the toughness of an elastomer by a factor of 2 and could therefore be of considerable practical importance.

CONCLUSIONS

Previous methods developed to precipitate reinforcing silica either into already-formed elastomeric networks or during the curing process are extended to permit precipitation into a polymer prior to its crosslinking. This modification avoids significant changes in volume during or after curing which could be disadvantageous in some applications.

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