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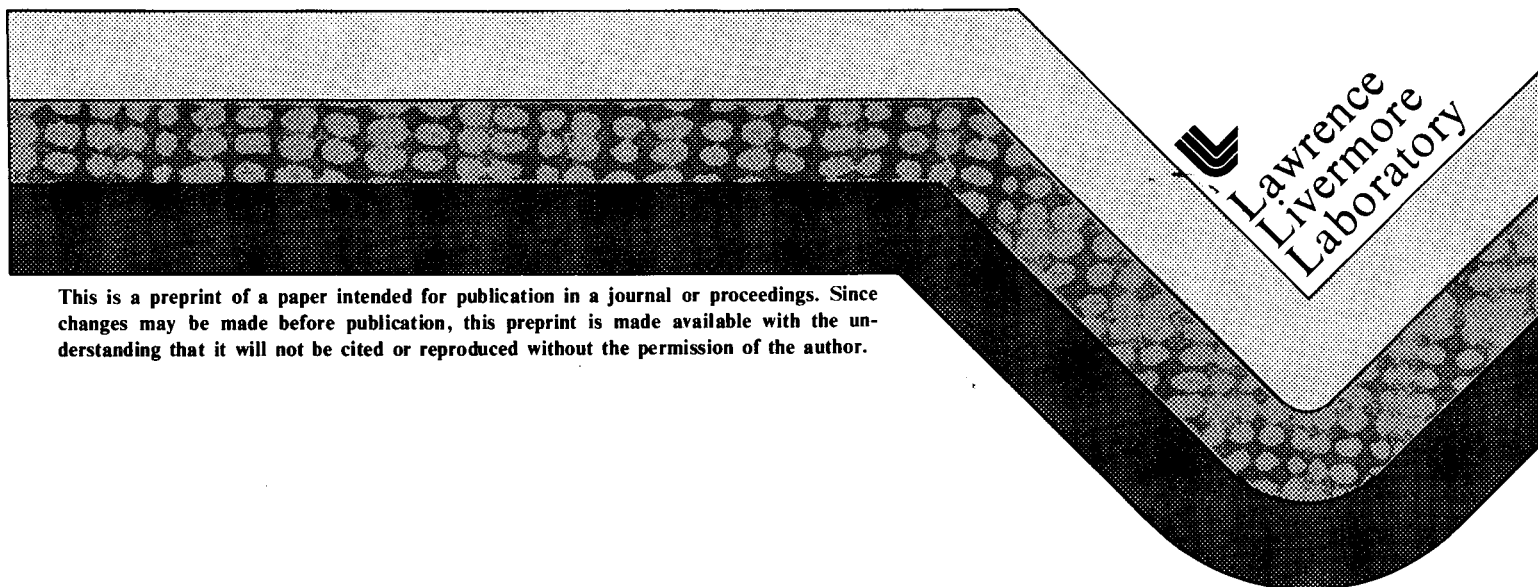
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STRUCTURE-PROPERTY RELATIONSHIPS OF LINEAR
METHYL-PHENYL-VINYL SILOXANE TERPOLYMERS

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STRUCTURE-PROPERTY RELATIONSHIPS OF LINEAR METHYL-
PHENYL-VINYL SILOXANE TERPOLYMERS*

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ABSTRACT

LLNL has an active interest in the synthesis and characterization of siloxane polymers with properties tailored to meet specific design requirements. We have synthesized a series of 15 random terpolymers of dimethyl-diphenyl-methylvinyl siloxane. In seven terpolymers the concentration of the methylvinyl repeat unit was varied from 0 to 5 weight percent maintaining phenyl content constant at 12 percent. The other eight terpolymers contained 0 to 18 weight percent phenyl repeat unit maintaining vinyl at one percent. As nearly as possible comparable molecular weights (5×10^5) were maintained. The gum stocks were reinforced with ~25 percent fumed silica. Silicones of different vinyl content were cured with a vinyl specific peroxide and characterized by swelling and mechanical properties. The moduli increased directly with vinyl concentration, but the elongation to break decreased until at about two percent vinyl the rubber becomes extremely friable. Increasing the phenyl content in the silicone decreased the degree of crystallinity and increases the polymer class transition in accord with theoretical predictions. The major effect of incorporation of phenyl groups is the elimination of the polymer's ability to crystallize at about three percent phenyl. This extends the rubbery plateau to the glass transition (-117°C) instead of the melting point (-44°C).

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INTRODUCTION

Cellular silicone cushions have been employed in various designs at the Lawrence Livermore National Laboratory (LLNL) as support materials, space fillers, and shims for many years. As a result of the disappearance of suitable commercial silicone elastomers and flexible foams from the market-place due to limited demand for the products, LLNL initiated a synthetic silicone program. This report will deal with the preparation of one type of polysiloxane elastomer-the random terpolymer which results from a synthetic sequence in which cyclotetrasiloxanes, initiator and endblocker are reacted at an elevated temperature and polymerized in situ. Although this method of preparation of silicone elastomers is well known in various forms in the literature,¹ we at LLNL had had no prior experience in the area of silicone synthesis.

Parallel to the preparative effort at LLNL was an investigation into the structure-property relations of these materials. Our elastomers are composed of the standard dimethylsiloxane units (DMS), diphenylsiloxane units (DPS) to reduce elastomer crystallinity and extend the service life of the foam, and methylvinylsiloxane (MVS) units to facilitate crosslinking. In the W97 commercial material the levels for DPS and MVS had been nominally set as 12 weight percent (as $\text{Si}(\text{C}_6\text{H}_5)_2\text{O}$) and 0.2 weight percent (as $\text{SiCH}_3(\text{CH}=\text{CH}_2)\text{O}$) respectively. Treating these numbers as targets as we learned preparative silicone chemistry, we decided to investigate the effect that a smooth variation in phenyl and vinyl contents and \bar{M}_w would have on the properties of the silicone rubbers and foams based on our random terpolymers. In this report we describe the effect upon these properties accompanying changes in silicone structure.

EXPERIMENTAL

The cyclotetrasiloxanes (octamethyl, octaphenyl, and symmetrical tetramethyl-tetravinyl) were purchased from Silar Laboratories, Inc. The endcapping fluid DC200, a trimethylsilyl-terminated, 10-centistoke

polydimethylsiloxane, was purchased from Dow Corning Corporation. A representative reaction will be detailed here. The reaction utilizes a low molecular weight potassium silanolate (K-catalyst) as initiator. Another initiator, tetramethylammonium silanolate (N-catalyst) has been used with equal success. Care must be taken before and during the reaction to exclude all moisture and carbon dioxide. The reactions are carried out under inert gas in previously flamed reaction vessels.

In a typical preparation 352 g $\text{Si}_4(\text{CH}_3)_8\text{O}_4$, 48g $\text{Si}_4(\text{C}_6\text{H}_5)_8\text{O}_4$, 0.8 g $\text{Si}_4(\text{CH}_3)_4(\text{C}_2\text{H}_3)_4\text{O}_4$, and 1.23g DC200 are charged into a 500 ml reaction kettle. After sufficient flushing with inert gas, the slurry is heated as rapidly as possible to 160°C at which point the phenyl tetramer goes into solution. K-catalyst (1.44g) is added to the crystal clear, colorless solution and stirring is continued for 30 minutes. Polymerization time is proportional to phenyl content. The stirrer and peripheral glassware are removed and the kettle capped and placed in an oven at 160°C for five hours. The kettle is then removed from the oven and allowed to cool completely before exposure to the atmosphere. Finally, fumed silica (1% of the gum mass) is milled into the gum to deactivate the initiator.

Gums were analyzed for \bar{M}_w , \bar{M}_n , MWD, phenyl and vinyl contents, volatiles content, T_g and densities. Full thermal analyses were run on each of the gums of varying DPS contents. The molecular weights between crosslinks (M_c) were determined by solvent swelling on gums cured with the vinyl-specific catalyst 2,5-dimethyl- 2,5-bis(t-butylperoxy)hexane. Stress-strain behavior was also determined on cured ring specimens using an Instron universal test machine operating at a constant crosshead speed of 10 cm/min.

RESULTS AND DISCUSSIONS

We find that we may synthesize with a high degree of reproducibility silicone elastomers of whatever phenyl and vinyl contents are deemed appropriate. Gum molecular weights were controlled at $\sim 5 \times 10^5$ by the

inclusion of the endblocker DC200. One may use either a potassium- or a tetramethylammonium silanolate initiator. The deactivation of the transient N-catalyst by heat² is convenient but our results indicate a greater control of polymerization parameters is possible here through use of the K-catalyst. As the relative percent of DPS increases, one must increase the reaction temperature above 160°C and increase polymerization time (from a minimum of 15 minutes for a gum without phenyl). Holding DPS content constant at 12 weight percent, we prepared gums with 0, 0.2, 0.5, 1.0, 2.0, and 5.0 weight percent MVS. With a constant MVS content of 1.0 weight percent, gums of 0, 3, 6, 9, 12, 15, and 18 weight percent DPS content were prepared.

The Flory-Rehner equation³ was used to calculate the molecular weight between crosslinks (M_x) of the silicone polymers cured with the vinyl-specific peroxide. The equation is:

$$M_x = - \left\{ V_1 \rho_2 (C^{1/3} - 2C/f) / [\ln(1-C) + C + \chi_1 C^2] \right\} \quad (1)$$

where ρ_2 is the polymer density, V_1 is the molar volume of solvent, C is the volume fraction of polymer at equilibrium, f is the functionality of the crosslink ($f = 4$), and χ is the polymer-solvent interaction parameter ($\chi_1 = 0.47$ for silicone in chlorobenzene).⁴ For the filled gums c was evaluated from

$$V_2 = (1 - \phi_f) W_d / \rho_2 \quad (2)$$

$$C = V_2 / V_E \quad (3)$$

where ϕ_f is the weight fraction of filler, W_d is the weight of dried reinforced polymer after swelling, V_2 is the volume of polymer in the crosslinked network, and V_E is the total swollen volume at equilibrium.

The molecular weight between crosslinks as a function of the weight percent of vinyl groups in the polymer chain is shown in figure 1 for filled (lower curve) and unfilled (upper curve) silicones. As is well known, this equation is only accurate at low crosslink densities and above about one percent MVS the experimental values obtained from it do not agree with estimates based on the molecular weight of chains between vinyl groups for a random copolymer. One reason for this is that multiple vinyl groups may be attacked by peroxide radicals at higher vinyl concentrations resulting in a large number of ineffective cyclic polymer chains.

Of further interest is that the calculation based on filled and unfilled systems indicates clearly that crosslinks to the filler are formed. That filled and unfilled systems behave similarly as a function of vinyl concentration is expected since the crosslinks formed to the filler are not dependent on the presence of double bonds. It should also be mentioned that the simplistic estimate of the effect of filler on the swelling behavior used here does not account in a quantifiable way for the reduced number of chain configurations near, physical adhesion to, or chemical reactions with fumed silica fillers.

The stress-strain curves of reinforced silicone polymers (0.2 to 2% MVS) are shown in figure 2. The concentration of vinyl is directly proportional to the modulus and inversely proportional to the stress and strain at break. These results complement the swelling measurements: neither modulus nor stress at break varies linearly with MVS content. This is further evidence that the effective crosslink density for these rubbers is reduced by the mechanism of multiple vinyl attack proposed above.

The effect of reinforcing filler on the mechanical properties is two-fold: 1) the modulus increases because of modulus-filler interactions (higher modulus of filler); and 2) the stress and strain at break is increased approximately two orders of magnitude. The increase in strength is the result of disruption of crack propagation by the filler. Evidence

for this comes from stress whitening of the filled rubber and the microscopic observation that, although void formation occurs, the voids do not propagate.

It is surprising that the characteristic Gaussian behavior of unfilled rubbers is not observed. This effect may have been washed out by the reinforcing filler or by the effect of adsorption and desorption of silicone on the filler under stress.

DPS comonomer units were introduced into the silicones to improve the low temperature elasticity of the rubber. Increasing the phenyl concentration increased the glass transition temperature (T_g) but decreased the degree of crystallinity. The Gordon-Taylor-Wood equation⁵

$$T_g = (T_{ga} + (KT_{gb} - T_{ga})W_b) / (1 - (1 - K)W_b) \quad (4)$$

or the simpler Fox equation

$$T_g = (W_a/T_{ga}) + (W_b/T_{gb}) \quad (5)$$

can be used to explain the increase in T_g resulting from increased high- T_g comonomer concentration. Here W_i and T_{gi} are the weight fraction of monomer i in the copolymer and the T_g of a homopolymer of monomer i respectively, and K is a constant. Using the Fox equation to fit the data we estimate T_g for pure poly (DPS) to be about -10°C (Fig. 3). Clearly, the increase in T_g is not responsible for the improved low temperature elasticity.

The major effect of incorporation of phenyl side groups is the elimination of the polymer's ability to crystallize. Only 3 weight percent DPS comonomer is required to remove the melting endotherm at -44°C from DSC traces of unfilled silicones. Isothermal crystallization of 1% vinyl siloxane at -85°C is complete in 17 minutes. No crystallization was observed in the 3% DPS/1% MVS terpolymer even after one hour (Fig. 4). The

enhanced low temperature elasticity of phenyl-containing siloxanes must be the result of the loss of crystallinity at the expense of a small increase in glass transition temperature.

REFERENCES

1. (a) J.F. Hyde and O.K. Johannson (Dow Corning Corp.), U.S. Patent No. 2,453,092, (11/2/48), (b) K.J. Saunders, "Organic Polymer Chemistry," Chapman and Hall, London, 1973, Chapter 15.
2. A.R. Gilbert and S.W. Kantor, J. Poly. Science, XL, 35 (1959).
3. P.J. Flory, "Principles of Polymer Chemistry," Cornell University Press, Ithaca, NY, Chapter 13 (1953).
4. P.J. Flory, Trans. Faraday Soc., 49, 7 (1970).
5. N. Johnston, J. Macromol. Sci., Rev. Macromol. Chem., C14, 215 (1976).

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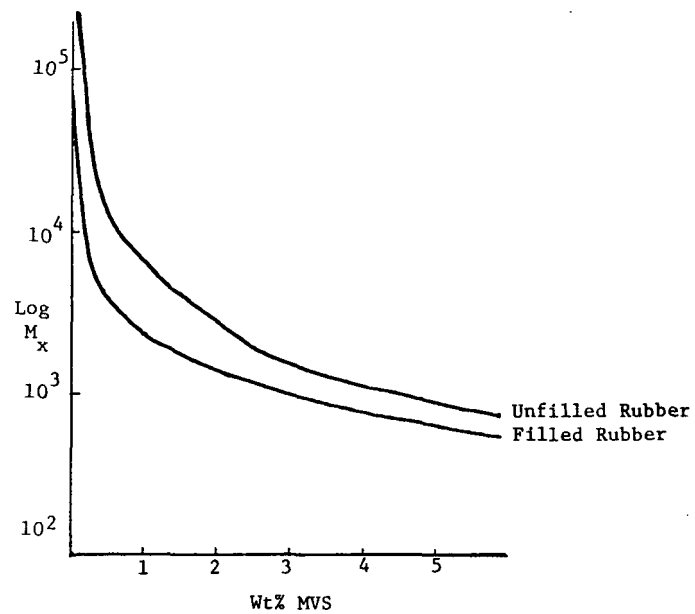


Fig. 1. The molecular weight between crosslinks (M_x) is a nonlinear function of siloxane vinyl content.

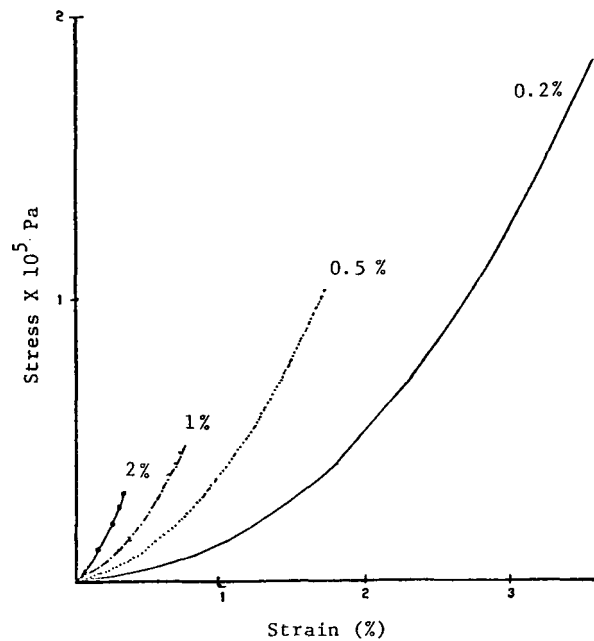


Fig. 2. Strain-to-break decreases as vinyl content of the polysiloxanes increases.

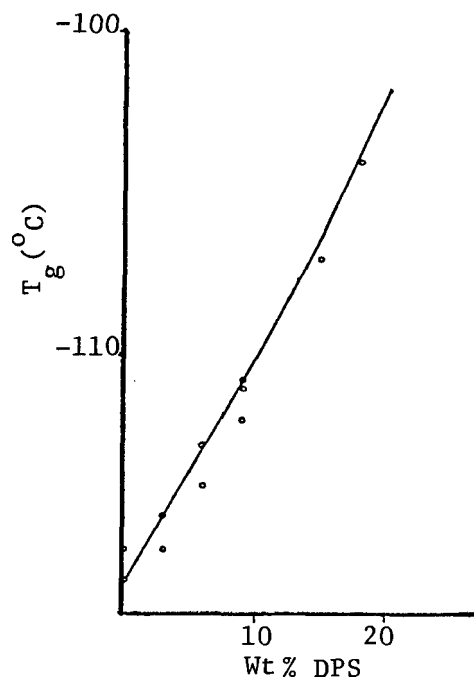


Fig. 3. As the phenyl content of the gum increases, T_g is seen to increase correspondingly.

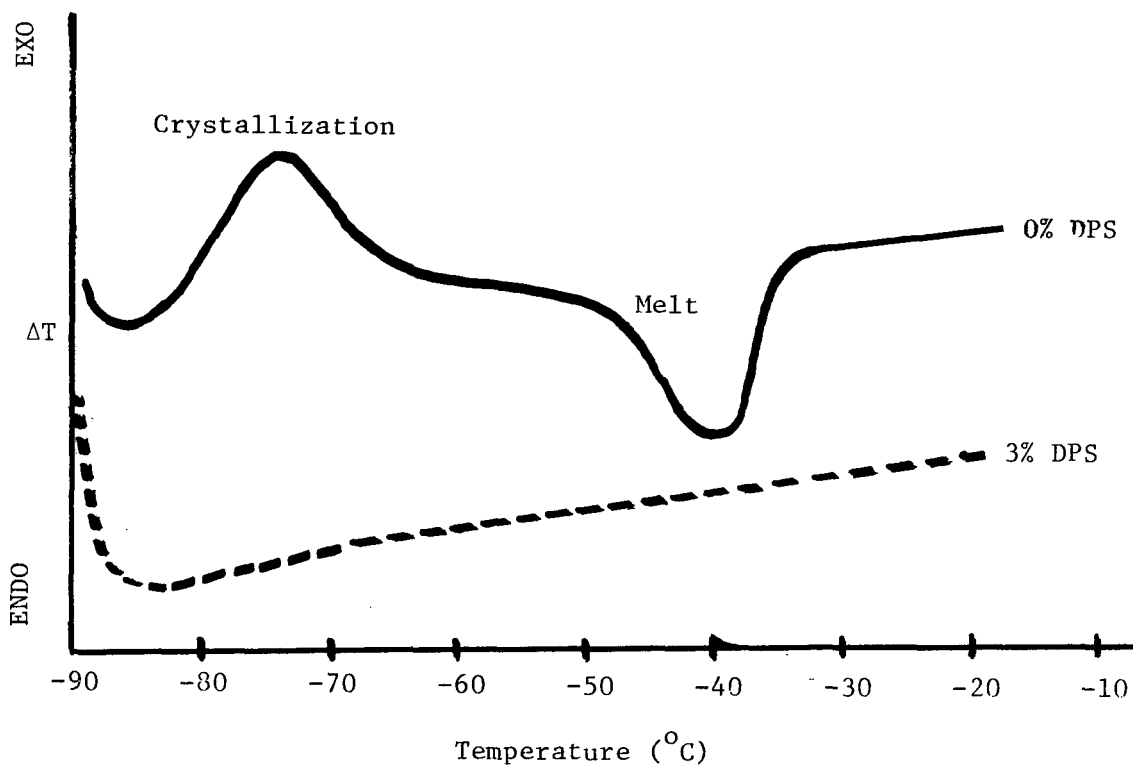


Fig. 4. Crystallization of siloxane gums disappears with as little as three percent DPS content.

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