

## Reversible Amine Solubilization of Cured Siloxane Polymers

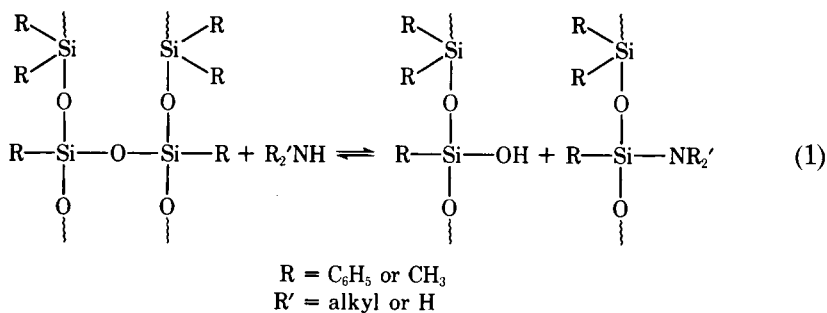
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### Synopsis

We report that aliphatic primary and secondary amines completely solubilize crosslinked silicone resins and rubber compositions at room temperature. The solubilization is attributed to nucleophilic cleavage of Si—O bonds by amines, which apparently occurs selectively at crosslinking sites. The selectivity may reflect the presence of three oxygen atoms at such sites, which are expected to enhance the electrophilicity of silicon. On evaporation of amine, crosslinks are apparently regenerated as evidenced by solubility characteristics as well as film properties of the reclaimed silicones. In addition to their theoretical interest, these results are potentially important from the standpoint of commercial applications as well, including the possible reclaiming of silicone-constituted furniture molds and the coating of heat-sensitive materials.

During the course of studies on the application of solubility parameter methods for swelling cured polymers,<sup>1-3</sup> we have found that aliphatic primary and secondary amines completely solubilize crosslinked siloxane polymers at room temperature. A major objective of this research was the development of solvent-based methods for facilitating the recovery of spores from plastic and rubbery materials utilized in spacecraft components. This goal was conveniently accomplished in high yields in the case of representative silicones by treatment with amines followed by plate counting methods (these results will be submitted elsewhere). Nevertheless, the unexpected finding of complete solubilization of cured silicones by amines prompted further studies on the nature of this interaction. The results are reported herein which indicate that amines react selectively at Si—O crosslinking sites by nucleophilic substitution, as illustrated in eq. (1). Furthermore, the reversibility of this reaction is evidenced by the reformation of crosslinked sites on evaporation of amine. In addition to their theoretical interest, these results are potentially important from a technological standpoint as well, including the possible applications of reclaiming silicone-constituted furniture molds and coating of heat-sensitive materials.

Initial studies were conducted with Dow Corning DC 840 silicone resin, which possesses a phenyl methyl polysiloxane backbone. The prepolymer also contains silanol (Si—OH) sites which are converted into Si—O—Si crosslinkages during curing. After curing at 240°C for 1 hr, 50-mg samples (as cubes approximately 3 mm on a side) were suspended in 2 ml amine solvent



in vials which were continuously shaken at room temperature. Most of the primary and secondary aliphatic monoamines examined, including the common  $\text{C}_2$  to  $\text{C}_5$  acyclic and cyclic amines, provided clear, homogeneous solutions within 2 hr. In contrast, pyridine, triethylamine, and *N*-methylaniline, as well as all other classes of solvents tested, including aromatic nitro compounds, esters, ketones, ethers, alcohols, and amides, either had no noticeable effect or caused swelling of the resin during the three-day test period.

Viscosity studies were conducted on *n*-butylamine solutions of prepolymer and cured DC 840 resin as well as Dow Corning silicone oil (dimethylsiloxane DC 200) for comparison. A plot of efflux time as a function of time after mixing is presented in Figure 1. In the case of the cured resin, the first reading was taken after solubilization, which occurred at 60 min after mixing. The figure demonstrates that the prepolymer and cured resin are degraded to a common viscosity, whereas the silicone oil is unaffected. These results are taken as evidence for selective cleavage of Si—O linkages at crosslinking sites

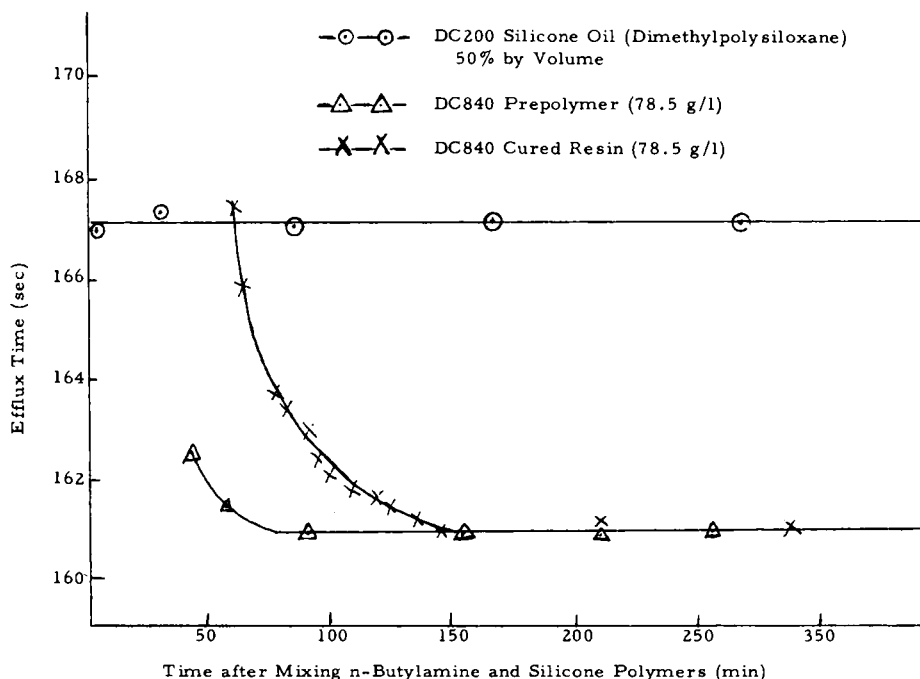


Fig. 1. Viscosity changes with time of silicone polymers in *n*-butylamine solution. Cannon viscometer 50-1711, at 45°C.

where three oxygens are attached to silicon. Such sites are not present in the silicone oil. This selectivity is in accord with the expected enhancement of silicon electrophilicity by oxygen substituents.<sup>4,5</sup>

Indirect support for formation of reactive Si—N bonds was obtained from NMR studies. When solutions of prepolymer and cured DC 840 resin in diethylamine (50% by weight) were added to anhydrous methanol and subsequently evaporated to dryness, NMR spectra of the residues in deuterated chloroform exhibited a proton resonance at  $\tau$  6.48, attributable to the Si—OCH<sub>3</sub> group. This signal was readily distinguishable from that of residual methanol at  $\tau$  6.56. The Si—OCH<sub>3</sub> resonance was not observed when the silicone oil was treated similarly, or after evaporation of a methanol solution of prepolymer DC 840 resin in the absence of amine. The Si—OCH<sub>3</sub> functionality is postulated to arise via Si—N(CH<sub>3</sub>)<sub>2</sub> groups produced by amine cleavage of Si—O bonds at crosslinking sites.

When 50% amine solutions of cured DC 840 resin were cast on glass or steel panels and allowed to air dry at room temperature for two days, films were obtained which appeared clear, glossy, colorless, and free of pin holes. The reclaimed coatings were found to exhibit Sward hardness<sup>6</sup> and reverse-impact resistance<sup>7,8</sup> equivalent to the original heat-cured samples. Chemical and solvent resistances were also found to be equivalent as determined by conventional treatment with sodium hydroxide, sulfuric acid, acetic acid, xylene, methanol, and methyl ethyl ketone. The extent of crosslinking was estimated to be approximately 75% that of the original sample by comparison of film weights before and after extraction with acetone in a Soxhlet extractor. This characteristic was improved (to 90% of original) by heating the reclaimed sample at 100°C for 2 hr.

Studies were also conducted on a room temperature-cured silicone rubber, Dow Corning Silastic J. As with the cured resin, the rubber was solubilized on treatment with primary and secondary aliphatic amines although ~30 times longer exposure to the amine solvents was required. A reclaimed sample, prepared by solubilization in *n*-butylamine followed by five days of storage and subsequent evaporation, was found to regain 60% of its original tensile strength and 80% of its original per cent elongation at breakpoint as determined with an Instron. No attempts were made to optimize the conditions of reclaiming, although it was noted that the tensile properties deteriorated with longer storage times. A possible deleterious factor is the presence of water, which is expected to hydrolyze the highly reactive silylamine functionality to Si—OH groups having relatively low reactivity in ambient curing.

In the equilibrium between silyl ether/amine and the corresponding silylamine/alcohol, eq. (2), the former pair is favored as shown by infrared analysis of equimolar mixtures of reactants.<sup>9</sup> Indeed, the silylation of alcohols by



treatment with silylamine derivatives represents a widely utilized procedure.<sup>10</sup> Based on these considerations, one may seriously question the validity of the forward reaction of eq. (1). However, in this case, the amine is present in large excess over the crosslinking sites. Furthermore, the normally favored Si—O over Si—N bonding (for bond energies, see ref. 11), due at least in part to the greater electronegativity of oxygen, is complicated by the pres-

ence of two additional oxygen substituents. The added electronegativity of these substituents would tend to diminish the advantage of the Si—O linkage in the simple case and possibly favor Si—N bonding. The forward reaction of eq (1) may also enjoy an entropic advantage due to increased degrees of freedom of the uncrosslinked polymer,<sup>12</sup> although this factor is complicated by additional considerations, including solvent effects and insolubility of the crosslinked polymer.

Our results are not consistent with a patent in which the preferred utilization of tertiary amines in solubilizing gelled silicones is claimed.<sup>13</sup> The indicated effectiveness of triethylamine (complete solubilization in one day) relative to diethylamine (partial solubilization in two days) is contrary to our findings, and we can offer no rationale for the discrepancies.

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