Crosslinking of Vinylsilicone Resins Initiated by Dicumyl Peroxide*

H. A. HARTUNG and S. E. BERGER

Silicones Division, Union Carbide Corporation, Tonawanda, New York

INTRODUCTION

Resins with many useful characteristics are obtained by the peroxide initiated crosslinking of silicone polymers having pendant vinyl groups.[1] The properties of such resins depend to a large extent upon the type and concentration of peroxide utilized as well as the temperature and time of cure. This is a report of a detailed study of the effects of variations in curing conditions on a single resin composition with a single initiator, dicumyl peroxide.
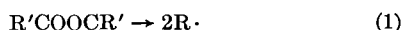
It is shown that maximum crosslinking is obtained with relatively low curing temperatures and long curing times. This is explained in terms of well-known principles of vinyl polymerizations.

CHEMISTRY OF VINYLSILICONE RESINS

The polymerization of vinylsilicones has been studied using prototype monomers such as $CH_2=CHSi[OSi(CH_3)_3]_3$.[2] Vinyl groups attached to silicon are comparatively unreactive below 100°C. and polymerization is best carried out in the temperature range of 110 to 150°C. Many peroxide catalysts are ineffective at such temperatures because they decompose too rapidly. Dicumyl peroxide, which has a half-life of 1.0 hr. at 135°C. and di-*tert*-butyl peroxide, which has a half-life of 3.5 hr. at 135°C.,[3] have been used successfully. The present investigation was limited to dicumyl peroxide because it is commonly used in many applications.
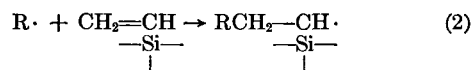
By analogy with the known chemistry of vinyl polymerizations,[4] the reactions listed below are presumed responsible for the bulk of the crosslinks formed in vinylsilicone resins:
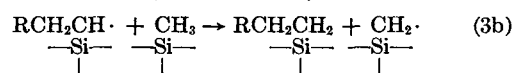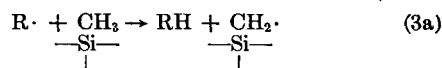
Catalyst decomposition:

$$R'COOCR' \rightarrow 2R\cdot \quad (1)$$

Initiation:

$$R\cdot + CH_2{=}CH \rightarrow RCH_2{-}CH\cdot \quad (2)$$

Chain transfer:

$$R\cdot + CH_3 \rightarrow RH + CH_2\cdot \quad (3a)$$

$$RCH_2CH\cdot + CH_3 \rightarrow RCH_2CH_2 + CH_2\cdot \quad (3b)$$

Propagation:

$$RCH_2{-}CH\cdot + CH_2{=}CH \rightarrow RCH_2CHCH_2CH\cdot \quad (4a)$$

$$CH_2\cdot + CH_2{=}CH \rightarrow CH_2CH_2CH\cdot \quad (4b)$$

Termination:

$$2\ RCH_2CH\cdot \rightarrow RCH_2CHCHCH_2R \quad (5a)$$

$$R\cdot + RCH_2CH\cdot \rightarrow RCH_2CHR \quad (5b)$$

$$RCH_2CH\cdot + CH_2\cdot \rightarrow RCH_2CHCH_2 \quad$$

$$2\ \dot{C}H_2 \rightarrow CH_2CH_2 \quad (5d)$$
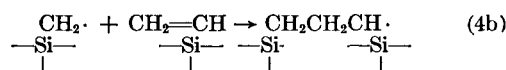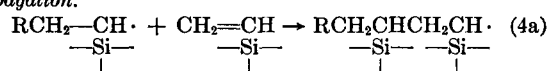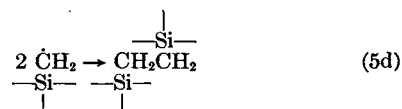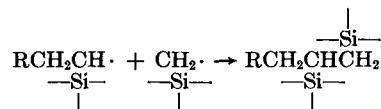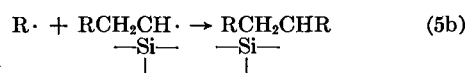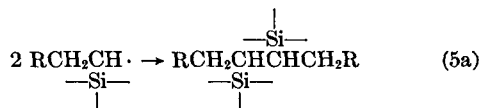
Chain transfer is shown only to methyl groups. Transfer to other polymeric units also is possible but the net effect is exactly analogous to the reactions illustrated.

Detailed consideration of the reactions listed leads to the conclusion that under optimum conditions one crosslink can be obtained for each vinyl group present. The termination reactions serve to reduce the ratio of crosslinks to vinyl groups below the theoretical optimum of unity. Termination by disproportion and chain transfer to initiator were not considered. The net effect is

to lower the ratio of crosslinks formed to vinyl groups originally present. Thus the concentration of crosslinks in a cured vinylsilicone resin is always somewhat less than the concentration of vinyl groups utilized. The maximum concentration of crosslinks with any given composition is attained when the propagation reactions are favored and the termination reactions are minimized. Since the termination reactions involve two radicals, these reactions are minimized when the radical concentration at any given time is kept low.

DISCUSSION

The experimental results are summarized in the figures. The effects of dicumyl peroxide concentrations ranging from 0.5 to 2.0 wt.-% on various physical properties are shown in Figures 1 through

5. In these tests the same cure schedule was always used: 4 hr., at 135°C. plus 2 hr., at 200°C. The effects of various cure temperatures are illustrated in Figures 6 through 8. In these tests the dicumyl peroxide concentration was kept constant at 1.5 wt.-%. The cure schedule was 4 hr., at temperature plus 2 hr., of postcure at 200°C. In addition, Figure 8 shows data for cures at 115 and 120°C. for 60 and 18 hr., respectively followed by the usual 2-hr. postcure at 200°C. The extended cure times at the lower temperature served to decompose over 90% of the dicumyl peroxide prior to the postcure while cures of only 4 hr. left much of the peroxide unreacted. The postcure at 200°C. was used to stabilize the test samples by decomposing any residual peroxide and driving out volatile fragments.
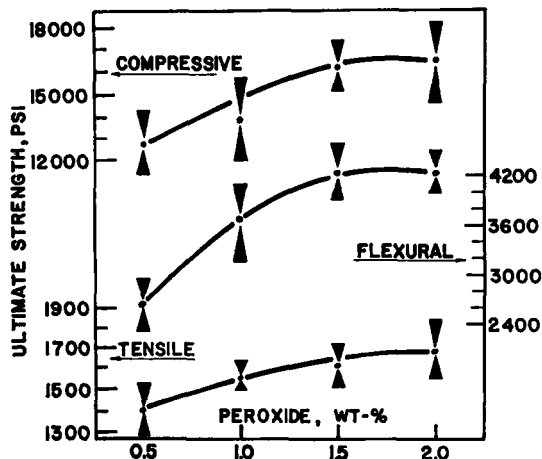
Fig. 1. Effect of initiator content on ultimate strength at room temperature. Cure was 4 hr. at 135° plus 2 hr. at 200°C. Breadth of points shows estimated 95% confidence limits.

Fig. 2. Effect of initiator content on ultimate strain. Data are from same tests as flexural and tensile strengths of Figure 1.

Fig. 3. Effect of initiator content on modulus. Data are from same tests as Figure 1.

Fig. 4. Effect of temperature on flexural strength. Numbers on curves give dicumyl peroxide content in wt.-%. Cure: 4 hr. at 135° plus 2 hr. at 200°C.

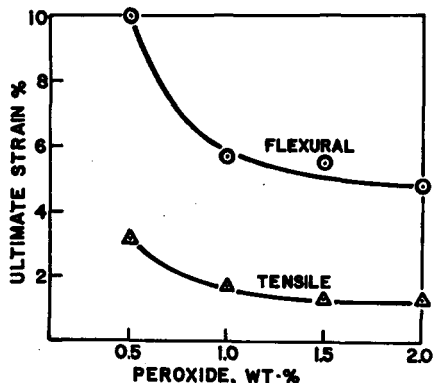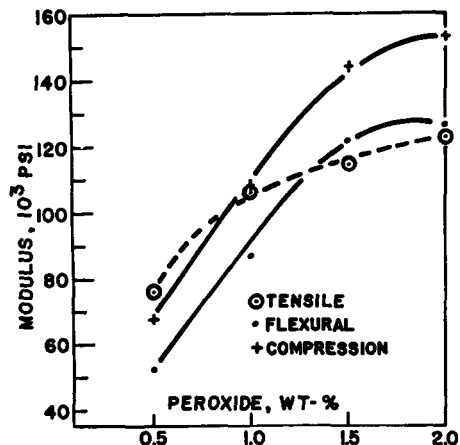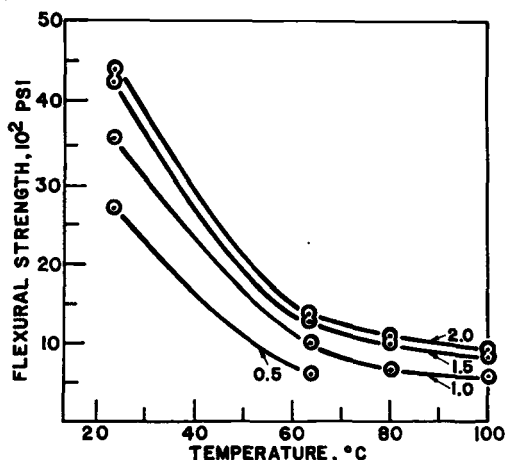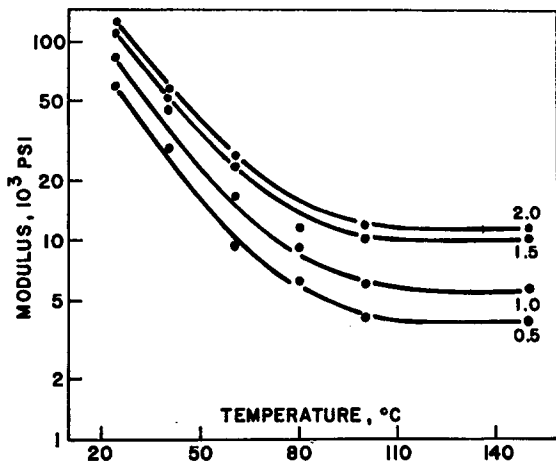Fig. 5. Modulus–temperature curves. Numbers give peroxide content in wt.-%. Cure: 4 hr. at 135° plus 2 hr. at 200°C.
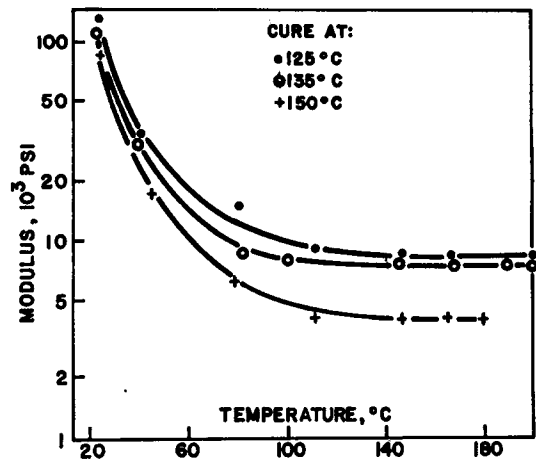

Fig. 7. Modulus–temperature curves for resins cured at various temperatures. Dicumyl peroxide content was 1.5 wt.-%. Cure: 4 hr. at temperature indicated. Postcure: 2 hr. at 200°C.
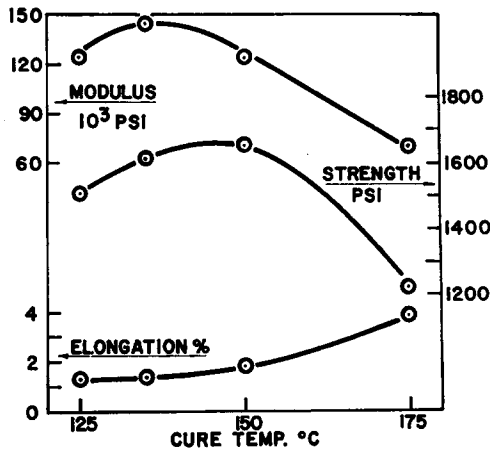

Fig. 6. Effect of cure temperature on tensile properties at room temperature. Dicumyl peroxide content was 1.5 wt.-%. Cure: 4 hr. at temperature. Postcure: 2 hr. at 200°C.
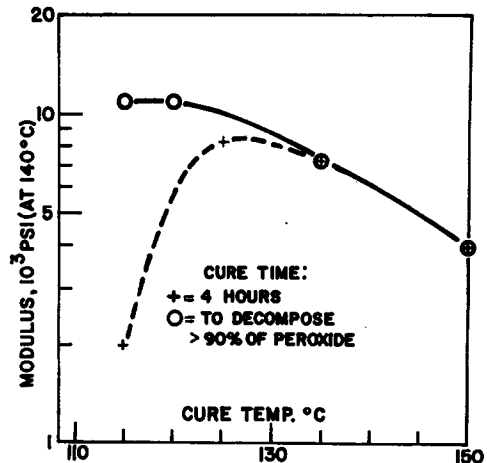

Fig. 8. Effect of curing temperature and time on hot modulus. Dicumyl peroxide content was 1.5 wt.-%. All specimens were postcured 2 hr. at 200°C.

Relatively large random errors were obtained in the tests of ultimate strength and the values plotted in the figures were averaged from five or more individual tests. Statistical calculations were made on the data used for Figure 1 and 95% confidence limits were calculated from the standard deviations. These are shown by the spans of the points in the figure. They were comparatively larger in the tensile and compressive tests than in flexure. Testing in flexure appeared the best method of ultimate strength measurement for inherent precision. In addition, flexural strength exhibited the greatest relative change over the range of peroxide concentrations studied.

Measurements of modulus and ultimate strain

exhibited small random variation. Probably, the largest source of error in room temperature tests of modulus was variations in ambient temperature. The test results shown in Figures 1, 2, 3, and 6 were obtained prior to testing at higher temperatures and no attempt was made to control or record the room temperature. The subsequent studies of the effect of temperature on various physical properties, as illustrated in Figures 4, 5, and 7, showed that small temperature changes in the 20 to 30°C. range had large effects on physical property measurements. Thus the differences in moduli measured in tension, flexure, and compression, which are shown in Figure 3, could have been due to a variation of only 4°C. in the room temperature

when the different series of tests were run. Because of this factor, absolute comparisons between the three types of modulus measurements are valid only when there is very careful temperature control.

Spurious effects due to uncontrolled changes in room temperature were avoided in each individual test series by running all the tests at the same time. Consequently each curve for room temperature tests represents data obtained at essentially a constant temperature even though the temperature might have been slightly different in each test series.

The large effect of temperature on properties in the range of 25 to 100°C. was indicative of a second order or glass transition. Above this transition region the properties were essentially unchanged by increase in temperature and the resin actually had the mechanical characteristics of a highly crosslinked elastomer. In this temperature region the modulus was proportional to the "true" crosslinking density because the physical forces between the polymer chains were effectively "melted" out and the principle mechanical constrains on the samples were the covalent chemical bonds. Hence for both theoretical and practical reasons the best test for crosslinking density is modulus measured above the transition region (i.e., above 100°C. in the present case). The practical advantage of tests in the high temperature range is in the fact that variations in temperature are not critical.

The results showed conclusively that 1.5 wt.-% dicumyl peroxide was optimum for maximum crosslinking at 135°C. A peroxide concentration or 2.0 wt.-% showed little or no advantage while a concentration of 1.0 wt.-% definitely gave less crosslinking than 1.5 wt.-%. This was consistent with the theory that the bulk of the crosslinking takes place through reaction of the vinyl groups. Apparently 1.5% dicumyl peroxide was sufficient to react all of the vinyl units present. It was interesting to note that this corresponded to a molar ratio of about 20 vinyl groups reacted per radical available from the initiator. This indicated a low degree of polymerization for the vinylsilicone. It was in accord with previous studies in which vinylsilicones polymerized slowly and yielded only low molecular weights.[2]

The variations of physical properties with cure temperatures, which are shown in Figures 6, 7, and 8, were probably all related to the effect of temperature on the rate of decomposition of dicumyl peroxide. At relatively high temperatures the catalyst decomposed more rapidly, thereby giving a higher free radical concentration and favoring the termination reactions. Thus, above about 135°C. the higher the cure temperature, the lower was the amount of crosslinking obtained. At 135°C. and higher, essentially all of the dicumyl peroxide was utilized in a 4-hr. cure period, but below that temperature the effect of cure time became an important variable. At 125°C. only 50% of the peroxide decomposed in four hours. Thus low degrees of crosslinking were obtained with 4-hr. cures at temperatures below 125°C. because only part of the peroxide was utilized at the cure temperature. With cure times which were sufficient to utilize most of the peroxide at the lower temperatures, high degrees of crosslinking were obtained. This was because slow decomposition of the peroxide initiator gave a low free radical concentration in the system and reduced the rates of the termination reactions.

The effect of cure temperature on tensile strength at room temperature as shown in Figure 6 was difficult to interpret. Tensile strength in resins depends upon a number of factors including the type of fracture and the presence of strains or flaws. In the present case the greater flexibility of the material cured at 150°C. may have made the test specimen less susceptible to brittle fracture, thereby counterbalancing the reduced crosslinking. This result showed that there is an inherent lack of reliability in ultimate strength as a measure of degree of cure.

EXPERIMENTAL

1. The Vinylsilicone

The vinylsilicone used throughout this investigation was prepared by the alkaline coequilibration of methylvinylsilicone cyclic tetramer, diphenylsilicone cyclic tetramer, dimethylsilicone cyclic tetramer and decamethyltetrasiloxane by the method of Hyde.[5] Based on starting materials utilized, the copolymer composition was as follows:

Unit	Wt.-%
$CH_3(C_2H_3)SiO$	20.2
$(C_6H_5)_2SiO$	62.2
$(CH_3)_3SiO_{1/2}$	3.2
$(CH_3)_2SiO$	14.5

After neutralization of the potassium used as equilibration catalyst, filtration, and devolatilization, a clear fluid with a viscosity of 48 poise at 25°C. was obtained. It had a density of 1.18 g./cc.

2. Sample Preparation and Testing Procedure

Crystalline dicumyl peroxide in the proper amounts was dissolved in the fluid copolymer and the catalyzed material poured into suitable molds and cured in forced draft ovens at controlled temperatures. The castings were removed from the molds for postcure in a forced draft oven. In all cases a milling cutter was used to machine the specimens to proper dimensions.

For tensile and hardness tests the molds were made from glass plates about 6 x 6 in. covered with Mylar film as a release agent, separated with a $1/8$-in. Teflon spacer on three sides and pressed together with "C" clamps. The filled molds were allowed to stand several hours at room temperature to facilitate release of air bubbles before being placed in the oven to cure. The tensile tests were in accordance with the methods outlined in ASTM D638–58, "Tentative Method of Test for Tensile Properties of Plastics," using Type 1 specimens.

For flexural test specimen an aluminum mold 4 x 1 x $3/4$ in. deep was used. The cured materials were machined to a cross section of about 0.900 x 0.250 in. The flexural tests were conducted in accordance with ASTM D790–58T, "Tentative Method for Test of Flexural Properties of Plastics," except that a span to depth ratio of 8 to 1 was used rather than the recommended 16 to 1. The lower span to depth ratio was necessary, particularly at high temperatures because of the low force values encountered in the test.

An aluminum mold 0.6 x 0.6 x 5 in. long was used to prepare bars for compressive tests. The test specimens were machined to about 0.4 x 0.4 x 0.8 in. The test was performed according to ASTM D695–54, "Standard Method of Test for Compressive Properties of Rigid Plastics."

3. Testing Equipment

The tests were conducted on a Baldwin-Tate-Emery Testing Machine, Model PTE 115, equipped with a Stress-Strain Recorder. Strain was measured by gages attached directly to the specimen. Grips were attached through extension rods into an oven built into the machine for elevated temperature tests. Samples tested at elevated temperatures were conditioned at the test temperature for 15 min.

CONCLUSIONS

The optimum concentration of dicumyl peroxide for curing a vinylsilicone resin was 1.5 wt.-%.

This corresponded to approximately 20 vinyl groups reacted per radical available from the peroxide. Maximum crosslinking was obtained when the cure was carried out at temperatures of 120°C. or lower for times sufficient to decompose the bulk of the peroxide. Curing at higher temperatures caused reduction in the amount of crosslinking. This was due to higher free radical concentrations stemming from more rapid peroxide decomposition. Detailed consideration of the reactions involved in crosslinking via vinyl groups showed that there is a theoretical maximum of one crosslink possible per vinyl group and that termination reactions tend to reduce the amount of crosslinking actually obtained. Conventional tensile tests at room temperature had a large degree of random variability. This was at least partially due to the fact that the resin tested had a second-order transition region extending from below 25 to 100°C. Modulus measurements above the second-order transition region exhibited a high degree of inherent precision and were the best physical test of degree of crosslinking.

References

1. Weyenberg, D., U. S. Pat. 2,714,099 (July 26, 1955). Hurd, D., U. S. Pat. 2,645,628 (July 14, 1953).
2. Thompson, B. R., J. Polymer Sci., 19, 373 (1956). R. M. Pike, and D. L. Bailey, ibid., 22, 55 (1956). R. Y. Mixer, and D. L. Bailey, ibid., 18, 513 (1956).
3. Doehnert, O., and O. Maglie, Paper presented at the 13th Annual Meeting, Reinforced Plastics Division, The Society of the Plastics Industry, Inc., Chicago, Illinois, 1958.
4. Flory, P. J., Principles of Polymer Sciences, Cornell Univ. Press, Ithaca, New York, 1953, p. 110 ff.
5. Hyde, J. F., U. S. Pat. 2,490,357 (December 6, 1949).

Synopsis

The effects of cure time, temperature, and initiator concentration on the mechanical properties of a vinylsilicone resin cured with dicumyl peroxide were investigated. The resin had a second-order transition extending from below 25 to about 100°C. The transition region broadened as the degree of crosslinking increased. Measurements of physical properties at room temperature were very sensitive to small temperature changes. Ultimate strength measurements were particularly unreliable indicators of degree of crosslinking because of large random variations and because they depended upon other structural factors besides crosslink density. The best test of degree of crosslinking was modulus measurements above the transition temperature of the resin. Such measurements have a sound theoretical basis and the practical advantage of being insensitive to small temperature changes. Modulus measurements have the additional advantages of being a nondestructive test with a high degree of inherent precision compared to other physi-

cal tests. A concentration of about 1.5 wt.-% dicumyl peroxide was optimum for crosslinking the vinylsilicone resin studied. Maximum crosslinking was obtained when the peroxide was utilized slowly at low temperatures for long cure periods. When a 4-hr. cure was used the optimum temperature range was 125 to 135°C.

Résumé

Les effets de la durée de traitement, de la température et de la concentration en initiateur sur les propriétés mécaniques d'une résine de vinylsilicone polymérisée par le peroxyde de dicumyle furent étudiés. La résine montre une région de transition de second ordre s'étendant de 25° jusqu'à 100°C. Cette région devient plus large lorsque le degré de pontage augmente. Les mesures des propriétés physiques à température ordinaire sont très sensibles à des petites variations de température. Les mesures des forces de rupture sont particulièrement peu caractéristiques du degré de pontage à cause de grandes variations dues au hasard et aussi parce qu'elle dépendent d'autres facteurs de structure que la densité de pontage. Le degré de pontage est mieux évalué par la mesure du module au dessus de la température de transition de la résine. De telles mesures ont une base théorique rationnelle et l'avantage d'être insensibles aux petits changements de température. Elles ont aussi l'avantage d'être un test non-destructif tout en ayant un haut degré de précision comparée à d'autres tests physiques. Une concentration d'environ 1.5% en poids de peroxyde de dicumyle est optimale pour le pontage des résines de vinylsilicone étudiées. Le pontage maximum a été obtenu lorsque le peroxyde fut consommé lentement, à basse température, pour le longues périodes de traitement. Lorsqu'un traitement de quatre heures est appliqué la région optimale de température est 125 à 135°C.

Zusammenfassung

Der Einfluss von Behandlungsdauer, Temperatur und Starterkonzentration auf die mechanischen Eigenschaften eines mit Dicumylperoxyd vernetzten Vinylsilikonharzes wurden untersucht. Das Harz hatte eine Umwandlung zweiter Ordnung, due sich von unterhalb 25° bis ungefähr 100°C erstreckte. Der Umwandlungsbereich verbreiterte sich bei steigendem Vernetzungsgrad. Messung der physikalischen Eigenschaften bei Zimmertemperatur waren gegen kleine Temperaturschwankungen sehr empfindlich. Die Messung der Reissfestigkeit war zur Festlegung des Vernetzungsgrades wegen grosser statistischer Abweichungen und wegen ihrer Abhängigkeit nicht nur vom Vernetzungsgrad, sondern auch von anderen strukturellen Faktoren besonders schlecht geeignet. Am besten wurde der Vernetzungsgrad durch Modulmessung oberhalb der Umwandlungstemperatur des Harzes bestimmt. Solche Messungen haben eine wohlbegründete theoretische Basis und den praktischen Vorteil der Unempfindlichkeit gegen kleine Temperaturschwankungen. Modulmessungen haben den zusätzlichen Vorteil, dass sie das Harz nicht zerstören und dass sie im Vergleich zu anderen physikalischen Tests einen hohen spezifischen Genauigkeitsgrad besitzen. Zur Vernetzung des untersuchten Vinylsilikonharzes wurde Dicumylperoxyd in einer optimalen Konzentration von 1,5 Gewichsprozenten verwendet. Der höchste Vernetzungsgrad wurde bei langsamem Verbrauch des Peroxyds bei tiefen Temperaturen während einer langen Behandlungsperiode erzielt. Bei einer vierstündigen Behandlungszeit lag die optimale Temperatur im Bereich von 125° bis 135°C.