

Effect of Peroxide Crosslinking on the Dynamic Modulus of Silicone Rubber

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Received 23 August 2003; accepted 28 December 2004

DOI 10.1002/app.21903

Published online in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: The effect of peroxide crosslinking on the dynamic modulus of a silica-reinforced silicone [poly(dimethylsiloxane)] elastomer was investigated. Three different peroxides (*t*-butyl peroxide, *t*-butyl perbenzoate, and benzoyl peroxide) were employed at various practical loadings and differences in the nonlinear behavior of the dynamic modulus were found. Results are discussed with respect to

changes in crosslinking density and the identity of the peroxide. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 97: 1504–1512, 2005

Key words: silicones; elastomers; modulus; crosslinking; Payne effect

INTRODUCTION

The dynamic mechanical properties of elastomers that are reinforced with particulate materials, such as carbon black or fumed process silica, generally exhibit a very nonlinear response in the low strain region. This is called the Payne¹ effect and is normally demonstrated by showing a dynamic elastic shear modulus $G'(\gamma)$ that decreases markedly with increasing strain in the small strain region (0.1–10%). This phenomenon is usually attributed to the behavior of the particulate reinforcement used in the elastomer formulation. Two recent reviews^{2,3} summarize the current understanding of this phenomenon.

The Payne effect in elastomers is generally undesirable in that it complicates the design and performance prediction of vibration isolators.⁴ The static strain on the isolator is often significantly larger than the dynamic strains and thus the static stiffness of the isolator will be lower than the dynamic stiffness. This often constrains the isolator design and isolation performance.

Recent work^{5,6} has shown the importance of the behavior of the polymer phase as it pertains to the Payne effect. The choice of the peroxide used to crosslink a silicone elastomer is often made on the basis of the normal use temperature of the particular peroxide relative to the capability of the processing equipment available to the manufacturer of the prod-

uct. The objective of this work is to investigate the effect of the peroxide type on the resulting dynamic properties of the crosslinked elastomer and to gain insight into the subtle factors affecting the Payne effect. In this work we examine the effect of the polymer crosslinking system on the Payne effect in silicone elastomers.

EXPERIMENTAL

Raw materials

The silicone polymer used was SE-54 PVMQ silicone gum (GE Silicones, Waterford, NY). The peroxides were benzoyl peroxide, *t*-butyl perbenzoate, and *t*-butyl peroxide (Atochem NA). All materials were used as received. The silica used was TS-500 (Cabot, Tuscola, IL) which is treated with hexamethyl disilazane (HMDS) to replace surface silanol groups with $(\text{CH}_3)_3\text{Si}$ - groups.

Masterbatch and compound preparation

These formulations (Table I) were designed to have a high silica loading to impart significant strain dependence of $G'(\gamma)$ and also to provide a large number of silica particles to allow interaction with the crosslinking system. The silica used is treated with HMDS, which attaches trimethyl silyl groups on the surface. The CH_3 groups are capable of entering into the crosslinking chemistry through hydrogen atom abstraction. In this way, the possibility of crosslinking between polymer and silica is present.

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TABLE I
Formulations Used

| | P1 | P2 | P3 | P4 | P5 | P6 | P7 | P8 | P9 |
|--|------|------|------|------|------|------|------|------|------|
| SE-54 (phr) | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 |
| TS-500 (phr) | 75 | 75 | 75 | 75 | 75 | 75 | 75 | 75 | 75 |
| <i>t</i> -Butyl peroxide (mmol/100 g) | 1.61 | 7.26 | 12.8 | | | | | | |
| <i>t</i> -Butyl perbenzoate (mmol/100 g) | | | | 1.61 | 7.26 | 12.8 | | | |
| Benzoyl peroxide (mmol/100 g) | | | | | | | 1.61 | 7.26 | 12.8 |

The (SE-54/TS-500) masterbatch was mixed in a 95-L Baker-Perkins sigma blade mixer by adding proportions of the TS-500 to the SE-54 at a mixer temperature of 150°C followed by mixing for 1 h under vacuum after all of the silica was incorporated. The total mixing time was 6 h. The masterbatch was aged for a minimum of 3 weeks (maximum of 10 months) prior to adding peroxide on a two-roll mill at room temperature in approximately 1-kg batches. The silica volume fraction is 0.247 assuming a polymer density of 0.96 g/cm³ and a silica density of 2.2 g/cm³.

Dynamic modulus measurement

Dynamic property measurement was done using a double lap simple shear test. Specimens consisted of two blocks of rubber approximately 5 mm in thickness (16 mm width × 41 mm length) bonded between three steel supporting members using a silane adhesive during molding and vulcanization. The correction⁷ for the bending component of the deformation in this specimen is only 0.52% and is neglected. Prior to molding, the rubber was freshened on a two-roll mill to remove crepe hardening. The specimens were molded in a six-cavity steam-heated transfer mold, which fills each side of the specimen with a separate sprue with a gate of approximately 1.6 mm in diameter. Specimens were cured for 20 min at 171, 149, or 127°C (for di-*t*-butyl peroxide, *t*-butyl perbenzoate, and benzoyl peroxide, respectively). This was followed by a 24-h post cure in a circulating air oven at 177°C. The time to fill the mold cavity was on the order of 20 s at an approximate pressure in the transfer pot of 13.5 MPa.

The molded specimens are inserted in a servo-hydraulic test stand by attaching the inner member to a 22-kN load cell through a barrel nut and the outer members are clamped symmetrically to a fixture attached to the hydraulic actuator. The rubber wall thickness is thus constrained to remain constant throughout the test.

The periodic force and displacement time domain signals are decomposed through an FFT algorithm. The complex modulus $G^*(\gamma)$ is calculated as the ratio of the amplitudes of the fundamental force and displacement sinusoids. Also, δ is defined as the phase angle between the force and displacement fundamen-

tal sinusoids. The dynamic elastic modulus $G'(\gamma)$ and dynamic loss modulus $G''(\gamma)$ are calculated from these measured quantities. Unless otherwise specified each rubber specimen was tested only once and discarded. Since the goal of this work was to assess the effect of strain magnitude on the variation of the dynamic modulus with strain, the moduli at $\gamma = 0.1\%$ and $\gamma = 52.5\%$ were used to represent the low strain and high strain values of G' .

Crosslink density determination

The crosslink density of the vulcanized rubber was determined by the equilibrium swelling technique using the Flory-Rehner equation:

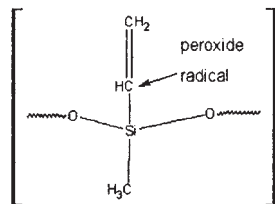
$$v = \frac{-[\ln(1 - v_2) + v_2 + \chi v_2^2]}{2V_1(v_0^{2/3}v_2^{1/3} - v_2/2)} \quad (1)$$

where v is the moles of crosslinks per unit volume of polymer, v_2 is the volume fraction of polymer in the swollen sample, V_1 is the molar volume of the solvent, and v_0 is the volume fraction of polymer at the time of crosslinking. The v_0 term is used to correct for material that is extracted by the solvent. The two-solvent method⁸ was used to provide a determination of the polymer-solvent interaction parameter χ . This technique requires a set of compounds that differ only in crosslink density to be separately swollen in two different solvents. The Flory-Rehner equation is written separately for each solvent. For each crosslink density the two expressions are equated since they must have the same value calculated by the equation. This is done for all of the samples in the set and the two independent values for χ are determined by linear regression:

$$y = \chi_b x + \chi_a \quad (2)$$

where the y and x values correspond to

$$x = \frac{V_{1a}v_{2b}^2(v_{0a}^{2/3}v_{2a}^{1/3} - v_{2a}/2)}{V_{1b}v_{2a}^2(v_{0b}^{2/3}v_{2b}^{1/3} - v_{2b}/2)} \quad (3)$$



Scheme 1

$$y = \frac{\ln(1 - v_{2a}) + v_{2a}}{v_{2a}^2} \times \left[1 - \frac{V_{1a}(v_{0a}^{2/3}v_{2a}^{1/3} - v_{2a}/2) \ln(1 - v_{2b}) + v_{2b}}{V_{1b}(v_{0b}^{2/3}v_{2b}^{1/3} - v_{2b}/2) \ln(1 - v_{2a}) + v_{2a}} \right] \quad (4)$$

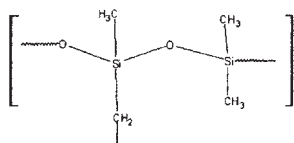
Values for y and x are computed for each sample of varying crosslink density and a plot is generated. The values for χ_a and χ_b are then determined from linear regression.

Peroxide crosslinking chemistry

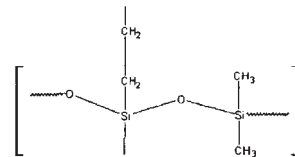
Peroxides such as *t*-butyl peroxide will only produce a practical number of crosslinks with vinyl-containing silicone copolymers since the peroxide radical is not of sufficient energy to efficiently abstract a hydrogen atom from a pendant methyl group. A typical concentration of vinyl copolymer units is 0.25% on a molar basis. One proposed mechanism⁹ for crosslinking silicone rubber with these peroxides is that the peroxide radical adds to the vinyl group attached to the backbone as seen in Scheme 1.

The resulting polymer radical abstracts a hydrogen atom from a methyl group attached to a polymer chain. This methyl radical then combines with a substituted ethyl group containing the peroxide fragment, thus releasing the peroxide radical. The result (Scheme 2) is a three carbon bridge and (Scheme 3) a regeneration of the peroxide radical.

Two-carbon bridges are formed when the peroxide radical is capable of abstracting a hydrogen atom from a methyl group on the polymer. The radical thus formed will combine with another methyl polymer radical to form a crosslink. Benzoyl peroxide is an example of a peroxide that is capable of crosslinking silicone polymer without the need for vinyl functionality on the polymer. Of course, in a vinyl containing



Scheme 2



Scheme 3

copolymer, benzoyl peroxide can form three-carbon bridges as well. Thus, the set of peroxides, *t*-butyl peroxide, *t*-butyl perbenzoate, and benzoyl peroxide, form an interesting series in which to explore the effects of different types of peroxide on the resulting dynamic properties. Homolytic cleavage of *t*-butyl peroxide will yield two radicals that have affinity primarily for vinyl groups, benzoyl peroxide will form two radicals capable of abstracting a hydrogen atom, and *t*-butyl perbenzoate will form one radical of each type. The benzoyl radicals formed by homolytic cleavage of benzoyl peroxide are likely to decarboxylate to yield a phenyl radical and CO₂.

RESULTS AND DISCUSSION

Figure 1 shows the data used to determine the polymer-solvent interaction parameters (χ) for the compounds and solvents used in this work plotted according to Eq. (2).

The values of χ for toluene and *n*-decane were determined to be 0.499 and 0.573, respectively. The plot is quite linear over the relatively large range of crosslink densities obtained. It should be noted that the two-solvent technique implicitly requires that both solvents should swell the network to roughly the same degree. This avoids errors due to the crosslink density being a function of the degree of swelling of the network since the material is certainly nonlinear in response to strain. This condition is approximately satisfied with the solvent pair used in this work.

Figure 2 shows the crosslink density values deduced from the swelling experiments. These data are reasonable in that the efficiency of benzoyl peroxide has been found⁹ to change with increased concentration in silicone rubber.¹⁰ The difference in physical properties of silicone rubber vulcanizates crosslinked with 2,5-dimethyl-2,5-di(*tert*-butylperoxy)hexane and α, α' -di(*tert*-butylperoxy)-*m*/*-p*-diisopropylbenzene has been attributed¹¹ to differences in the tendency of the peroxide radical to abstract a hydrogen atom from a neighboring peroxide molecule. Evidently there is sufficient peroxide to react a significant fraction of the vinyl groups with the lowest concentration of *t*-butyl peroxide. This could be the reason for the very weak increase in crosslink density with higher loadings of *t*-butyl peroxide. Of course all of the curves in Figure 2 must intersect the origin of the plot as the loading is

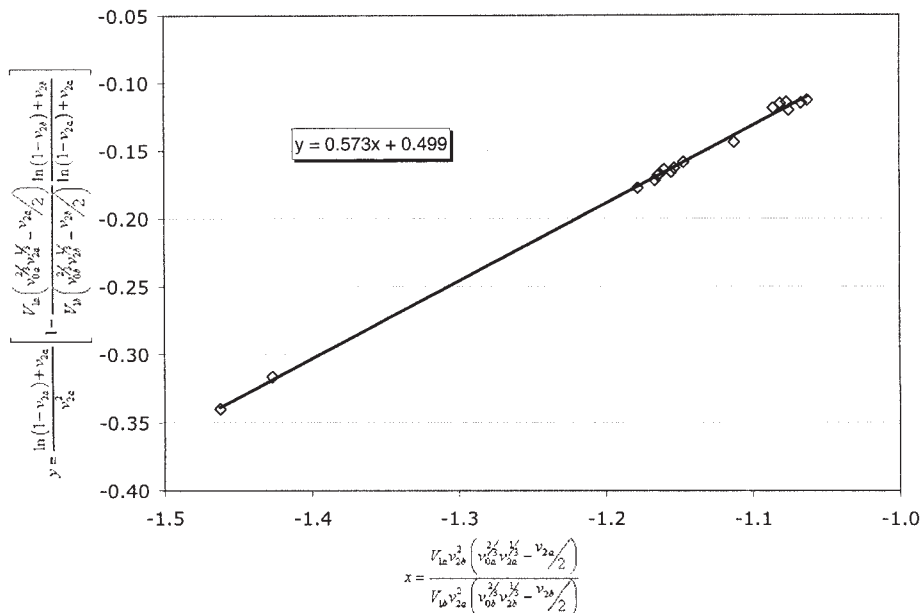


Figure 1 Determination of polymer–solvent interaction parameters by the two-solvent method using toluene and *n*-decane, where *y* and *x* are defined by Eqs. (4) and (3), respectively, and $y = \chi_b x + \chi_a$.

decreased. The curve for benzoyl peroxide appears to be approaching the origin as anticipated, whereas the other two curves would not extrapolate to the origin. A peroxide radical that is formed can generate many crosslinks due to the chain nature of the crosslinking reaction. Apparently the *t*-butyl peroxide and *t*-butyl perbenzoate are more efficient at low loadings such that significantly more crosslinks are formed at a given (low) loading. Clearly at a peroxide concentration of 0 phr the crosslink density would be zero for

any peroxide. The relative behavior of the curves in Figure 2 is in accord with what is expected based on the discussion of the crosslinking chemistry.

Figure 3 shows that the large strain dynamic elastic modulus G' (52.5%) is correlated with crosslink density within the constraints of this experiment. Thus, G' (52.5%) depends only on the crosslink density and is independent of the chemical identity of the peroxide used to crosslink the elastomer. This is perhaps not too surprising since the strain on the network at equilib-

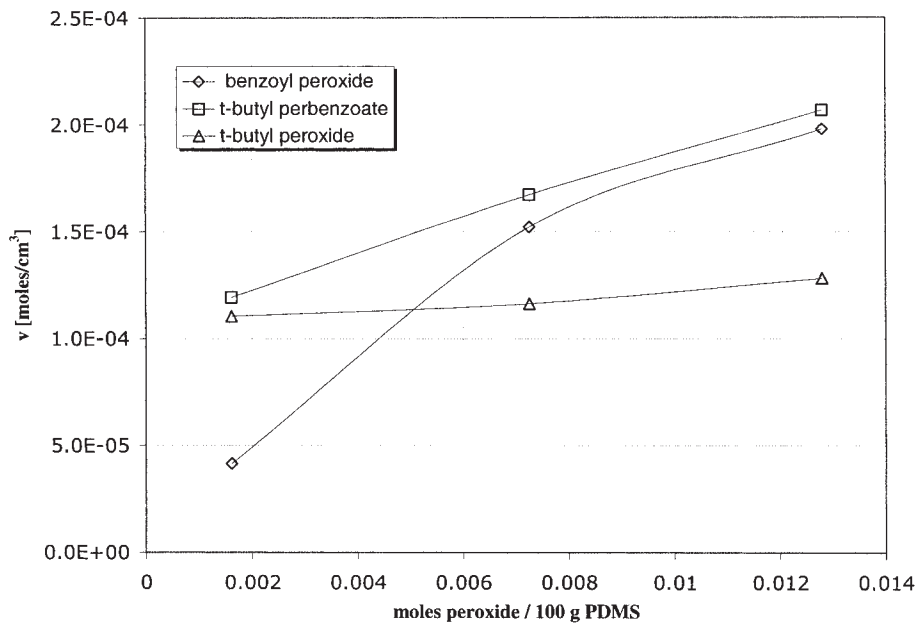


Figure 2 Crosslink density *v* as a function of the concentration of peroxide [mol peroxide/100 g polymer].

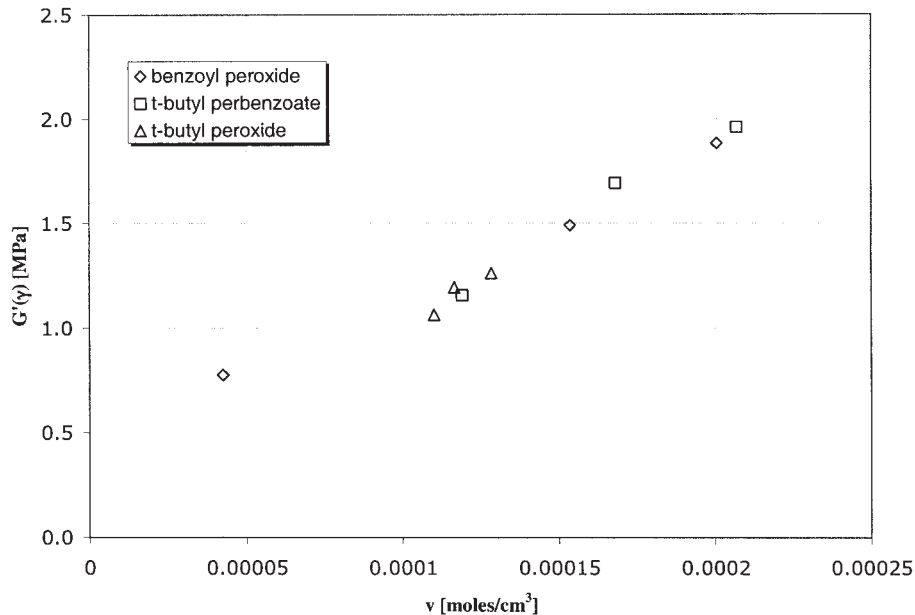


Figure 3 Dynamic storage modulus $G'(\gamma)$ [MPa] (23°C, 1 Hz, 52.5% SSA) versus crosslink density [mol/cm³].

rium swell (~ 50% by volume) will be relatively large with these solvents. Since the crosslink density measurement depends on the strain energy in the material at equilibrium swell, it is reasonable that it would correlate with a modulus measurement at large strains.

The value of G' (0.1%) at small strain is not determined solely by the crosslink density (Figure 4). At the same crosslink density there is a considerable difference in the value of G' (0.1%) among the different

peroxide types. The rates of increase in G' (0.1%) with crosslink density in Figure 4 for the three individual peroxides are similar but it is clear that the variation of $G'(\gamma)$ with strain is different for the different peroxide types. Since the benzoyl peroxide compounds exhibit the lowest G' (0.1%) values at a given crosslink density, these compounds would have the lowest magnitude Payne effect at a given crosslink density as well.

One possible interpretation of the small strain $G'(\gamma)$ data is that perhaps some crosslinks are formed such

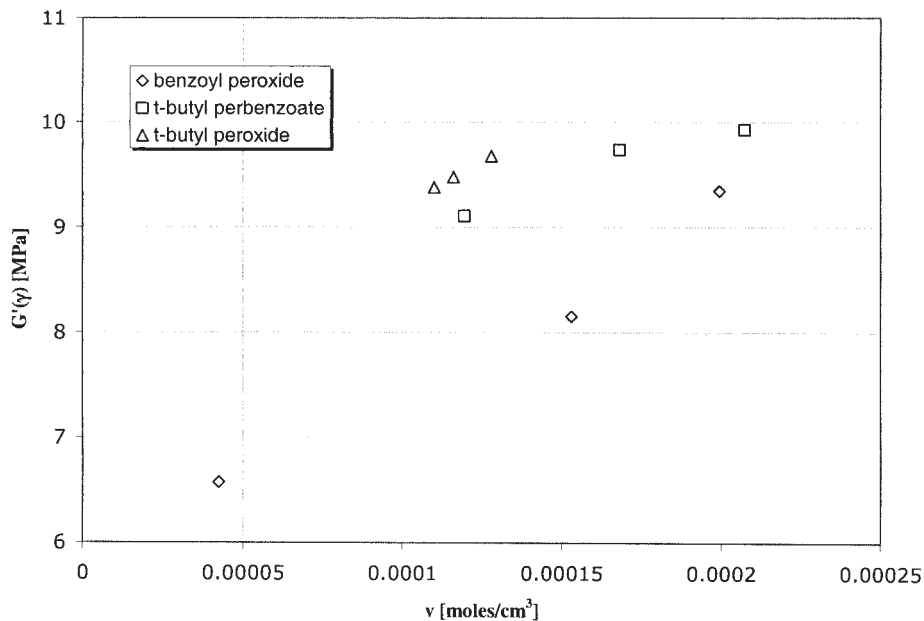


Figure 4 Dynamic storage modulus $G'(\gamma)$ [MPa] (23°C, 1 Hz, 0.1% SSA) versus crosslink density [mol/cm³].

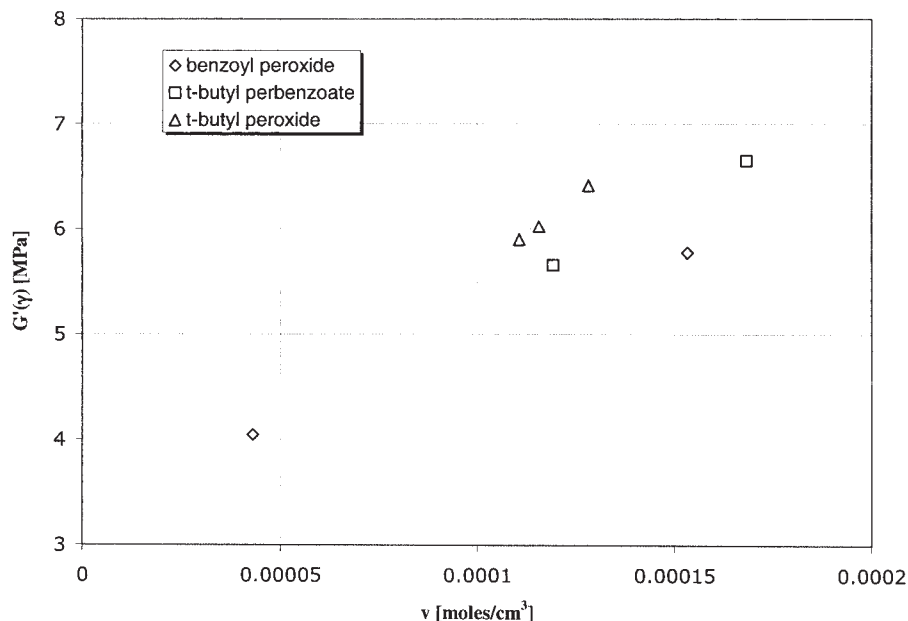


Figure 5 Dynamic storage modulus $G'(\gamma)$ [MPa] (23°C, 1 Hz, 0.1% SSA, after cycling to 100% SSA) versus crosslink density [mol/cm³].

that as the strain is increased those links are stressed more than the network average and are broken at some intermediate strain. This type of strain-intolerant structure might be expected to exist as short crosslinks between chains attached to adjacent silica particles would break easily as the first strain cycle to large deformations is imposed. This mechanism has been also proposed to explain strain softening of unreinforced rubber due to deformation.¹² If the difference in the low strain value of $G'(\gamma)$ for the different peroxides was due to this type of structure formed during crosslinking, a moderate strain prefix should be able to remove the difference entirely since compounds with the same crosslink density have the same value of $G'(\gamma)$ at large strain. Stated another way, if the equality of the large strain value of $G'(\gamma)$ at the same crosslink density was explained in terms of a strain-intolerant structure that is destroyed by the time the large strain measurements are performed, then cycling to the large strain prior to making the low strain measurements should remove the dependence of the low strain values of $G'(\gamma)$ on peroxide type.

Figure 5 shows that, although the $G'(0.1\%)$ values are reduced, the dependence of $G'(0.1\%)$ on the peroxide type remains after cycling the specimen to $\pm 100\%$ strain. The reduction in $G'(0.1\%)$ values is an expected consequence of the strain history. The correlation of $G'(52.5\%)$ with crosslink density persists after the large strain prefix as well (Figure 6). Figure 7 shows the effect of crosslink density on the strain dependence of $G'(\gamma)$ expressed as $G'_{rel} = G'(0.1\%)/G'(52.5\%)$, both measured at 1 Hz.

Increasing the crosslink density via peroxide concentration causes a decrease in magnitude of the

Payne effect. Representing the strain dependence in this way is useful for evaluating the suitability of a compound for a mechanical component design. In Figure 8 we see that, for *t*-butyl peroxide and *t*-butyl perbenzoate, there is a nearly constant value of $\Delta G' = G'(0.1\%) - G'(52.5\%)$ with increasing crosslink density. This is the trend that one might expect for the simple additive relationship¹ between the response of the polymer and the response of the phenomenon responsible for the Payne effect. Payne envisioned that the modulus of the polymer was embodied in the high strain modulus and that the "filler network" increased the modulus of the composite such that the two effects were noninteracting and additive. If we take $G'(52.5\%)$ as approximately representative of the polymer modulus and the difference $\Delta G' = G'(0.1\%) - G'(52.5\%)$ as being representative of the filler network then a constant value of $\Delta G'$ would indicate that the mechanism producing the Payne effect is independent of the crosslink density.

The benzoyl peroxide compounds behave differently wherein the $\Delta G'$ is not constant but increases with increased peroxide loading and hence increasing crosslink density. This would suggest that the benzoyl peroxide crosslinking is affecting the phenomenon responsible for the Payne effect as well as increasing the modulus of the polymer phase. The decreasing trend of G'_{rel} with increasing crosslink density in Figure 7 is seen to be due to the relatively constant value of $\Delta G' = G'(0.1\%) - G'(52.5\%)$ (Figure 8) accompanied by an increase in $G'(52.5\%)$ with increasing crosslink density (Figure 3).

It is unexpected that changing the crosslink density through a change in peroxide concentration should

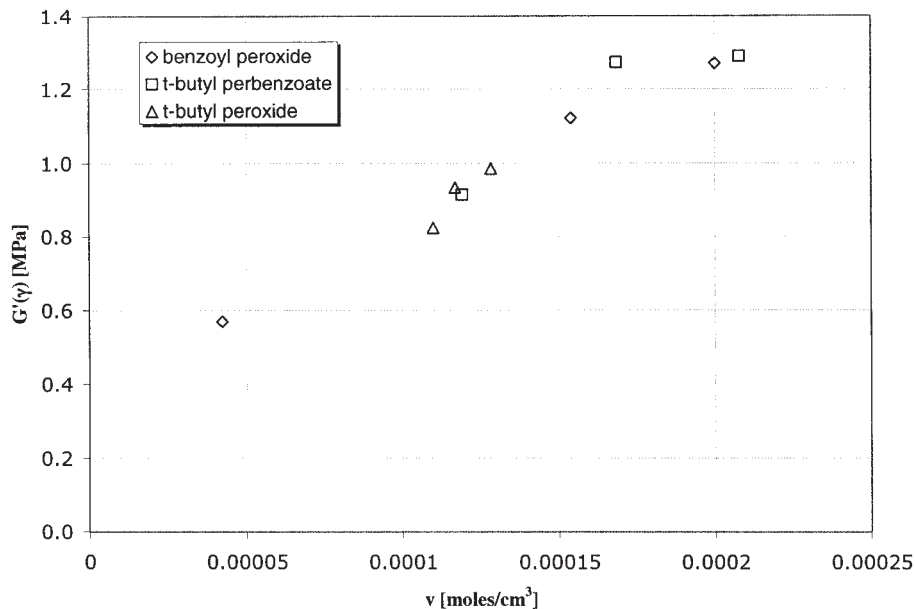


Figure 6 Dynamic storage modulus $G'(\gamma)$ [MPa] (23°C, 1 Hz, 52.5% SSA, after cycling to 100% SSA) versus crosslink density [mol/cm³].

affect the $\Delta G'$. The peroxide concentration will not affect the traditional network variables that are used to describe the effect of reinforcing fillers on elastomer properties, such as dispersion of the silica, silica agglomeration, bound rubber, or the physical state of the polymer that is adsorbed to the silica surface. There is no reason to expect that a change in the peroxide concentration would induce a change in the state of mixing of the composite since all of the compounds in this work were made from the same polymer/silica

masterbatch. The most striking observation is that the peroxide that does not rely at all on the presence of vinyl functionality on the polymer is the one that stands out the most among the materials considered.

It is tempting to describe these results in terms of polymer-silica bonds preventing desorption of the polymer from the silica at higher strains. If ideal mixing is assumed, a given polymer and volume fraction of silica will yield a constant value for the number of vinyl groups in the vicinity of the silica surface. The

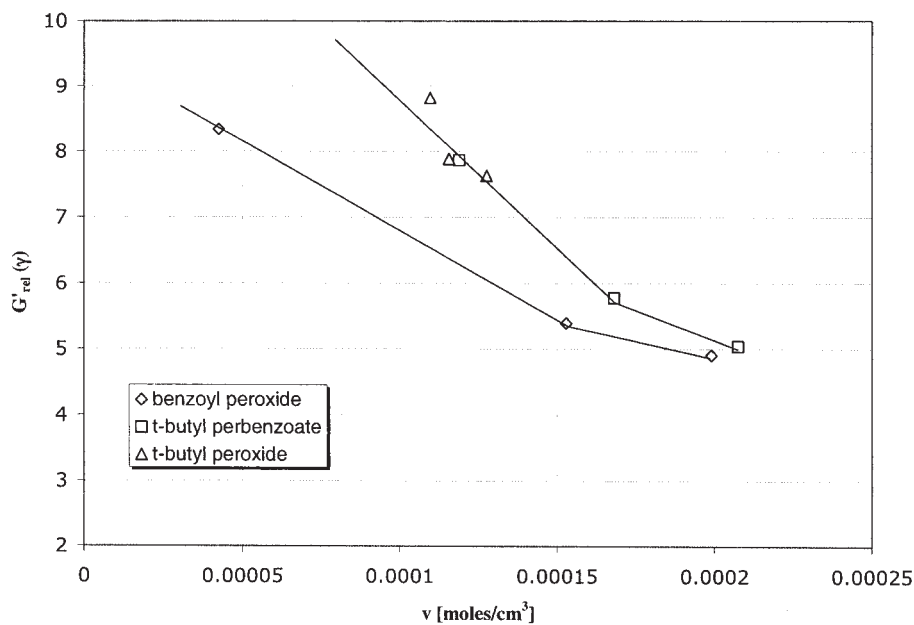


Figure 7 Normalized storage modulus $G'_{rel}(\gamma) = G'(0.1\%)/G'(52.5\%)$ (at 1 Hz, 23°C) versus crosslink density.

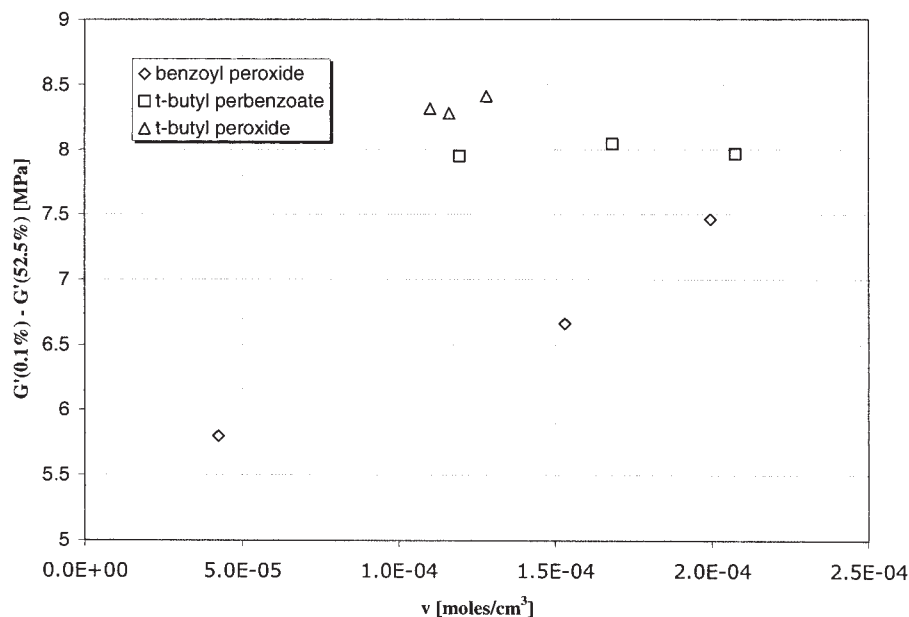


Figure 8 $\Delta G' = G'(0.1\%) - G'(52.5\%)$ (at 1 Hz, 23°C) as a function of crosslink density.

peroxides would have different limitations on the number of potential crosslinks between the silica and adsorbed polymer due to differing dependences on the availability of vinyl groups. Since benzoyl peroxide does not require vinyl groups one would speculate that benzoyl peroxide compounds would have the highest values of $G'(0.1\%)$, which is the opposite of the observations.

If the results were viewed in terms of desorption from the silica then there should be little effect on $G'(\gamma)$ at the lowest strains since at very low strains the driving force to desorb is small. There should also be a progressive increase in $G'(\gamma)$ at higher strains as the crosslink density is increased since the polymer-silica bond would be expected to be more important at higher strains. This is clearly not true since to a first approximation the $G'(\gamma)$ at low strains is affected more by the peroxide concentration than is the large strain value of $G'(\gamma)$. In fact, the opposite behavior is observed since at a given crosslink density, the large strain value of $G'(\gamma)$ is essentially the same for the different peroxides. From Figure 5 it is evident that the highest value for $G'(\gamma)$ at small strains is for the peroxide that should introduce the fewest polymer-silica bonds. It seems likely, then, that the change in behavior is due to changes in the polymer phase.

The ring-opening polymerization that is used to manufacture the polymer is an equilibrium polymerization.¹² Some of the decomposition products from benzoyl peroxide and *t*-butyl perbenzoate would be expected to be carboxylic acids which might serve as catalysts in a reequilibration of the polymer, since both acids and bases can be used to initiate polymerization. Another possibility for changes in the polymer phase

is a rearrangement of the polymer due to the crosslinking chemistry. Stabilization of β -carbon-centered radicals by Si-C hyperconjugation is well known.¹³ Perhaps this stabilization might be involved in a rearrangement of the silicone polymer during the crosslinking phase.

A more tangible effect of the different peroxide types is a difference in the distribution of the chain lengths of polymer between crosslinks. In the case of *t*-butyl peroxide, where crosslinks are initiated at pendant vinyl groups, the distribution of crosslinks will be substantially dependent on the sequence distribution of the vinyl-containing copolymer units. Once a polymer radical is formed the creation of a crosslink via hydrogen abstraction should be a random process dependent only on the lifetime of the radical and the proximity of an available CH_3 group. In the case of benzoyl peroxide, the distribution of crosslinks might be more uniform (to the extent that the dispersion of the peroxide itself is uniform) since CH_3 groups are available at each repeat unit. This would impart a nonrandom distribution of crosslinks to the polymer network, at least in the case of *t*-butyl peroxide, since the *t*-butyl peroxide radicals will produce crosslinks predominantly via pendant vinyl-containing repeat units on the polymer, which are in low concentration. The effect of this hypothetical nonrandom distribution of crosslinks would be expected to decrease as the crosslink density is increased past the level where there is a low concentration of residual vinyl groups. In this scenario the fraction of the crosslinks that were initiated via vinyl groups decreases with each incremental (random) crosslink presuming a low concentration of unreacted vinyl groups. This is difficult to

interpret quantitatively in this type of experiment since the peroxide radical is returned upon formation of a crosslink.

It should be noted that, due to the nature of the peroxides used in this experiment, the temperature used in the crosslinking varied considerably for the different peroxide types. This was necessary to control the molding time for the different specimens. The temperatures were chosen such that the peroxides would each decompose at approximately the same rate at the molding temperature. Since the mixing temperature for the masterbatch was above the molding temperature in all cases, no changes in the polymer-silica interaction are expected to occur due to the difference in molding temperature. One caveat is, since silica-reinforced silicone polymers are known to be thixotropic in the unvulcanized condition, an increase in the molding temperature will also increase the rate of recovery from the shear history encountered by the unvulcanized elastomer when the mold cavity was filled. This effect is inseparable from the effect of changing the peroxide types in this work, but it seems unlikely that this could be responsible for the behavior of the benzoyl peroxide compounds.

CONCLUSIONS

These results are consistent with previous work⁵ that concluded, although the crosslinked polymer in the

absence of silica showed no variation in $G'(\gamma)$ with strain, the behavior of $G'(\gamma)$ of silica-filled silicone rubber is at least partially responsive to the behavior of the polymer phase in the presence of silica. Benzoyl peroxide appears to be advantageous from the viewpoint of minimization of the Payne effect in silicone elastomers at a given level of crosslink density.

The authors thank Lord Corp. (Cary, NC) for their support of this work. Gary Jackson deserves special thanks for his meticulous execution of the dynamic property measurements.

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