

Peroxide- and Radiation-Cured Compounds Filled with Reinforcing Fine-Particle Silica*

J. W. SELLERS, M. P. WAGNER, B. J. DEWITT, C. C. STUEBER, and J. H. BACHMANN†
Barberton Research Laboratories, Chemical Division, Pittsburgh Plate Glass Company, Barberton, Ohio

INTRODUCTION

The hydrated fine-particle silica Hi-Sil 233 has particle dimensions characteristic of a fully reinforcing filler^{1,2} and undergoes chemical filler-polymer interactions similar to those of a typical HAF carbon black, Philblack O.³ Initial evidence for the ability to undergo filler-polymer interactions appears in the formation of filler-polymer gel (bound rubber) during the mixing or heating of simple filler-elastomer mixtures. Data have been presented which show that, similar to the HAF black, the fine-particle reinforcing silica forms significant amounts of bound rubber by a process which is substantially chemical and proceeds by a free-radical mechanism.³ A mechanism by which reactive polymer chain fragments can be accepted for crosslinking purposes by reinforcing fillers of dissimilar surface chemistry has been proposed.³

Although the fine-particle silica reinforces common elastomers crosslinked by the usual sulfur vulcanizing systems, the high potential suggested by its bound rubber behavior remains to be fully realized. A valid measure of the degree to which the reinforcing potential of a filler is utilized is the value of the ratio η/η_0 , the crosslink density of the cured, filled compound divided by that of the similarly cured, unfilled control. For Hi-Sil 233-filled SBR and Hevea vulcanizates, the value of this ratio seldom exceeds one at practical loadings, despite the combination of over 85% of the sulfur.^{4,5}

Mixtures vulcanized by means of dicumyl peroxide or radiation provide ideal model systems for the study of the η/η_0 ratio. Crosslinking is reported to proceed in each for both filled and unfilled mixtures by a relatively uncomplicated free-radical mechanism.⁶⁻⁸ Also, the use of such

curing systems permits more direct association of any filler-polymer activity with bound rubber development occurring by a free-radical mechanism.

EXPERIMENTAL

The type of natural rubber used in this study was No. 1-ribbed smoked sheet. The fillers were two fine-particle reinforcing silicas made by Chemical Division, Pittsburgh Plate Glass Co., Southern Chemical Corp., Hi-Sil 101 (no longer produced) and Hi-Sil 233, and a high-abrasion furnace (HAF) carbon black, Philblack O, made by Phillips Petroleum Co. Other curing ingredients were common rubber-grade products obtained from a variety of sources. The filler and rubber were mixed in an internal mixer (Banbury, size B). In the peroxide study, dicumyl peroxide was added on the mill to the masterbatch and the stock was sheeted out for curing. For the radiation study, the filler-rubber masterbatch was divided into two portions: One aliquot was sheeted out and submitted to radiation, and to the second portion the conventional sulfur curing ingredients were added on a mill and the mixture was sheeted out for curing. All sheets were of 0.075 in. gage.

The peroxide- and sulfur-vulcanized compounds were cured between aluminum foil in preheated laboratory presses at 2000 psi and 153°C. and 142°C., respectively. Rubber-filler slabs were irradiated in air at the Stanford Research Institute under the direction of Dr. Richard Glass, with the use of a 1-m.e.v. resonant transformer, at the rate of 7×10^6 rep/min. Half of the total radiation dose was applied to each side of the slab.

Physical testing of vulcanizates was carried out by customary procedures. Crosslink densities η were determined from equilibrium swelling.^{9,10}

For the peroxide study, the compounds were cured with 1.8 phr dicumyl peroxide (90% purity,

* Presented before the Division of Rubber Chemistry at the 138th meeting of the American Chemical Society, New York, September 1960.

† Present address: Department of Chemistry, The University of Akron, Akron, Ohio.

TABLE I
Formulations for Radiation Cure

| | A-R | B-R | C-R | D-R | E-R | F-R |
|--------------------------|-----|-----|------|------|------|------|
| No. 1-RSS | 100 | 100 | 100 | 100 | 100 | 100 |
| Antioxidant ^a | — | 2 | — | — | 2 | — |
| Hi-Sil 233 | — | — | 29.3 | 58.5 | 58.5 | — |
| Phlblack O | — | — | — | — | — | 54.0 |

^a American Cyanamid Antioxidant 2246: 2,2'-methylenebis(4-methyl-6-*tert*-butylphenol)

TABLE II
Formulations for Sulfur Cure

| | A-S | B-S | C-S | D-S | E-S | F-S |
|--------------------------|-----|-----|------|------|------|------|
| No. 1-RSS | 100 | 100 | 100 | 100 | 100 | 100 |
| Antioxidant ^a | — | 2 | — | — | 2 | — |
| Hi-Sil 233 | — | — | 29.3 | 58.5 | 58.5 | — |
| Phlblack O | — | — | — | — | — | 54.0 |
| Curative ^b | 16 | 16 | 16 | 16 | 16 | 16 |

^a American Cyanamid Antioxidant 2246: 2,2'-methylenebis(4-methyl-6-*tert*-butylphenol)

^b Curatives, phr: Antioxidant 2246, 1.0; 2,2'-dithiobisbenzothiazole, 0.8; di-*o*-tolylguanidine, 1.2; triethanolamine, 2.0; sulfur, 3.0; stearic acid, 3.0; zinc oxide, 5.0.

Hercules), and contained either no filler or 50 phr of filler as noted. In the radiation work, the compounds were formulated as shown in Table I. The respective sulfur-cured controls were compounded as shown in Table II.

DISCUSSION OF RESULTS

Peroxide Cure

In Figure 1 is shown the development of crosslinking as a function of time of cure. The curves indicate that the optimum time of cure is similar for all compounds, and that the contribution of filler to crosslink density is substantial for all fillers. The extent of the contribution of the fillers becomes more apparent upon consideration of the value of the crosslinking ratios η/η_0 (Table III). These ratios reveal that the filler contribution to crosslinking in the Hi-Sil 101-filled dicumyl peroxide-cured compound, where the decomposition of the curing agent took place in a favorable environment, approaches that of HAF black. Kraus⁵ in his work found only a 20% "black contribution" ($\eta/\eta_0 = 1.2$) for an HAF black-filled, dicumyl peroxide-cured SBR compound. In a neutral or alkaline environment, dicumyl peroxide decomposes thermally in a homolytic manner to free-radical fragments which initiate the crosslinking process during cure.⁷ Acid-catalyzed decomposition, however, yields ionic intermediates which do not promote crosslinking.¹¹ Apparently, the more neutral Hi-Sil 233 contains a few acid sites on its

TABLE III
Filler Contribution to Crosslinking in Hevea at Optimum Peroxide Cure^a

| Filler | Filler pH | Crosslinks $\times 10^4$, moles/g. | η/η_0 |
|-------------------------|-----------|-------------------------------------|---------------|
| None | — | 0.56 | — |
| Hi-Sil 233 ^b | 7.0 | 0.88 | 1.6 |
| Hi-Sil 101 ^b | 9.0 | 1.06 | 1.9 |
| Phlblack O ^b | 8.8 | 1.16 | 2.1 |

^a 120 min. at 153°C.

^b 50 phr.

surface. In the vicinity of these sites, the peroxide decomposes ineffectually.

A simple calculation shows that the amount of peroxide used should yield 0.6×10^{-4} mole of crosslinks per gram of rubber, assuming that one crosslink is formed per molecule of peroxide. On this basis, the efficiencies of crosslinking for the unfilled, the Hi-Sil 233-filled, and the Hi-Sil 101-filled compounds are 100%, 160%, and 190%, respectively.

Radiation Cure

The number of crosslinks produced in radiation cure is a linear function of dosage, regardless of whether the elastomer is unfilled or filled with fine-particle silica or carbon black (Fig. 2). Arnold and co-workers¹² reported a similar result for compounds of HAF black in SBR or Hevea irradiated by spent-fuel elements. As shown by the values of the η/η_0 ratios, the filler contribution to crosslink density increases with silica loading, as is desirable in a fully reinforcing filler (Table IV). Such behavior is common with highly reinforcing blacks in conventional curing systems. As usual, however, the η/η_0 value for sulfur-cured compounds filled with the silica did not change with loading.

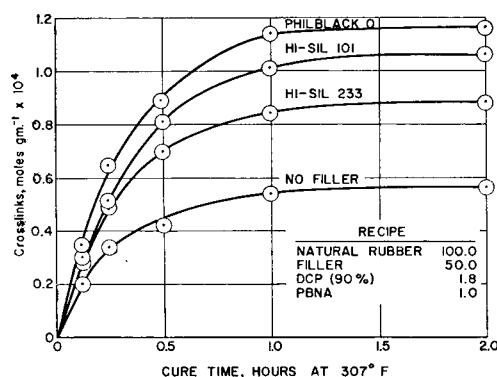


Fig. 1. Effect of fillers on crosslinking in dicumyl peroxide-cured natural rubber.

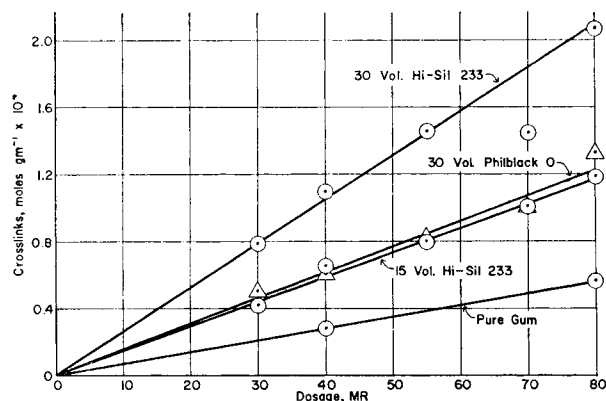


Fig. 2. Effect of fillers on crosslinking in radiation-cured natural rubber.

The contribution to reinforcement by Hi-Sil 233 in the radiation-cured compounds is large as compared with that found in the usual sulfur vulcanizates. It is also much higher than the filler contributions in the radiation-cured black mixture (Table V). Lamm and Madelaine¹⁴ recently reported a similar observation based on 100% modulus values from their work on the irradiation in air of Philblack O- and Hi-Sil 233-natural rubber mixtures by a Co⁶⁰ source. In a compatible curing system, therefore, the potential of silica as an elastomer reinforcer equivalent to the most efficient blacks appears unequivocal.

To diminish possible oxidation effects during irradiation in air, 2-phr portions of a sterically hindered phenol, 2,2'-methylenebis(4-methyl-6-*tert*-

TABLE IV
Contribution of Hi-Sil 233 Filler to Crosslinking in Sulfur- and Radiation-Cured Rubber

| Loading volume | η/η_0 at optimum cure | |
|----------------|-------------------------------|-----------------------------|
| | Sulfur cure ^a | Radiation cure ^b |
| 15 | 1.1 | 2.0 |
| 30 | 1.1 | 3.6 |

^a 30 min. at 142°C.

^b 8×10^7 rep.

TABLE V
Contribution of Filler to Crosslinking in Radiation-Cured Compounds

| Filler ^a | η/η_0 at optimum cure ^b |
|---------------------|--|
| Hi-Sil 233 | 3.6 |
| Philblack O | 2.3 |

^a 30 vol.

^b 8×10^7 rep.

TABLE VI
Effect of Free-Radical Scavenger^a on Crosslinking in Radiation Cure^b

| Filler | $G, \eta/100$ e.v. | | F^c |
|-------------------------|--------------------|--------------|-------|
| | No additive (0) | Additive (1) | |
| None | 0.74 | 0.35 | 0.50 |
| Hi-Sil 233 ^d | 2.7 | 1.4 | 0.48 |

^a 2,2'-methylenebis(4-methyl-6-*tert*-butylphenol), 2 phr.

^b Dose: 8×10^7 rep.

^c Fraction of crosslinks stopped = $1 - (G_0/G_1)$.

^d 30 vol.

butylphenol) were added to a sample of unfilled rubber (compound B-R) and to a sample containing 30 vol. of silica (compound E-R). The results are summarized in Table VI.

The silica increases the efficiency of the crosslinking reaction initiated by radiation by a factor of about 4 whether the antirad is present or not. The magnitude of constancy of the efficiency factor F for this antirad was surprising in view of the limited resonance structures for the molecule. The G values for crosslinking found here for irradiation of the unfilled sample in air are in excess of those generally reported in the literature.¹³

The silica vulcanizates for this study were prepared chiefly for structural studies and no attempt was made to obtain an optimum balance of physical properties. In general, however, properties such as tensile strength were lower in the radiation-cured than in the sulfur-cured samples. These differences are shown in Table VII and compared with similar results reported by other investigators.^{12,14,15}

For the fact that the tensile strengths of peroxide- and radiation-cured materials were lower than those of similarly filled sulfur-vulcanized compounds Pinner^{15c} blamed the relatively rigid C—C linkages between polymer chains. He advanced the concept

TABLE VII
Tensile Strength in Radiation-Cured and Sulfur-Cured Rubber

| Filler | Loading, phr | Tensile strength, optimum cure, psi | | Reference |
|---------------|--------------|-------------------------------------|--------------------------|---------------|
| | | Radiation cure ^a | Sulfur cure ^b | |
| Hi-Sil 233 | 58 | 2830 | 3890 | This work |
| Hi-Sil 233 | 60 | 4050 | 3510 | Reference 12 |
| Philblack O | 45 | 1950 | 4150 | Reference 14 |
| Furnace black | 40 | 2230 | 4560 | Reference 15a |
| None | — | 1900 | 3700 | Reference 15d |

^a 8×10^7 rep.

^b 30 min. at 142°C.

that the sulfide bonds present in sulfur cures are more easily broken on stress, permitting chain alignment before reforming. Thus the crystallization necessary for high stress occurs.

The assistance of Mr. Gerald Humes in this investigation is gratefully acknowledged.

References

1. Studebaker, M. L., *Rubber Chem. and Technol.*, **30**, 1400 (1957).
2. Bachmann, J. H., J. W. Sellers, M. P. Wagner, and R. F. Wolf, *Rubber Chem. and Technol.*, **32**, 1286 (1959).
3. Wagner, M. P., and J. W. Sellers, *Ind. Eng. Chem.*, **51**, 961 (1959).
4. Laning, S. H., M. P. Wagner, and J. W. Sellers, *J. Appl. Polymer Sci.*, **2**, 225 (1959).
5. Kraus, G., *Rubber World*, **135**, 67, 254 (1956); *Rubber Chem. and Technol.*, **30**, 928 (1957).
6. Bueche, A. M., *J. Polymer Sci.*, **15**, 105 (1955); *Rubber Chem. and Technol.*, **28**, 865 (1955).
7. Dannenberg, E. M., M. E. Jordan, and H. M. Cole, *J. Polymer Sci.*, **31**, 127 (1958); see also C. R. Parks and O. Lorenz, paper presented at the meeting of the Division of Rubber Chemistry of the American Chemical Society, Buffalo, N. Y., May 1960.
8. Charlesby, A., *Atomic Radiation and Polymers*, Pergamon Press, New York, 1960.
9. Flory, P. J., and J. Rehner, *J. Chem. Phys.*, **11**, 521 (1943).
10. Adams, H. E., and B. L. Johnson, *Ind. Eng. Chem.*, **45**, 1539 (1953); *Rubber Chem. and Technol.*, **26**, 741 (1953).
11. Kharasch, M. S., A. Fono, and W. Nudenberg, *J. Org. Chem.*, **15**, 748 (1950).
12. Arnold, P. M., G. Kraus, and H. R. Anderson, Jr., *Kautschuk u. Gummi*, **12**, WT 27 (1959); *Rubber & Plastics Age*, **40**, 836 (1959); G. Kraus, U.S. Pat. 2,964,457 (1960) (to Phillips Petroleum Co.).
13. Bauman, R. G., *J. Appl. Polymer Sci.*, **2**, 328 (1959); D. T. Turner, *J. Polymer Sci.*, **27**, 503 (1958); *Rubber Chem. and Technol.*, **31**, 737 (1958).
14. Lamm, G., A. Lamm, and H. Madelaine, *Kautschuk u. Gummi*, **13**, WT 80 (1960).
15. (a) Dogadkin, B. A., Z. N. Tarasova, M. Kaplunov, V. Karpov, and N. Klauzen, *Kolloid Zhur.*, **20**, 260 (1958); *Rubber Chem. and Technol.*, **32**, 785 (1959); (b) T. S. Nikitina, A. S. Kuzminskii, L. A. Oksentevich, and V. L. Karpov, *Proc. First All-Union Conf. Radiation Chem.* 1957, p. 275; (c) B. L. Johnson, H. E. Adams, and M. Barzan, *Rubber World*, **137**, 73 (1957); (d) S. D. Gehman, and I. Auerbach, *Intern. J. Appl. Radiation and Isotopes*, **1**, 102 (1956); (e) S. H. Pinner, *ibid.*, **5**, 121 (1959).

Synopsis

There are indications that the chemical reaction involved in bound rubber formation proceeds via a free-radical mechanism for compounds filled with reinforcing hydrated fine-particle silica, as well as in the case of carbon black as filler. The high potential of silica as a rubber reinforcer is indicated by its bound rubber formation. This potential was realized by the extent of filler-polymer interaction developed in silica-filled vulcanizates cured by peroxide and by high-energy radiation, respectively. Both these relatively simple curing systems are postulated to effect crosslink for-

mation via a free-radical mechanism. The value, after cure, of the ratio of the crosslink density of the filled compound to the crosslink density of the respective unfilled compound, η/η_0 , was taken to be a logical measure of the ability to reinforce. In natural rubber compounds filled with silica (30 vol.), the values of η/η_0 obtained were 1.6-1.9 for peroxide-cured material, and 3.6 for radiation-cured material. Comparisons are made with similarly cured HAF black-filled stocks. Sulfur-cured natural rubber stocks filled with HAF black (30 vol.) generally exhibit η/η_0 values in the range of 1.5 to 2.0. Comparative effects of antioxidants are described.

Résumé

Il y a des indications que la réaction chimique, qui se passe durant la formation de caoutchouc, résulte d'un mécanisme radicalaire pour des produits chargés de fines particules hydratées de silice, de même que dans le cas du carbone. Un haut potentiel de la silice dans le renforcement est indiqué par suite de l'étendue de l'interaction charges-polymère, développée dans un produit contenant de la silice et vulcanisé respectivement à l'aide de peroxyde et de radiation de haute énergie. Chacun de ces systèmes relativement simples de vulcanisation peuvent donner lieu à la formation de ponts par un mécanisme radicalaire. Comme mesure logique de la possibilité de renforcement on a pris la valeur, après vulcanisation, du rapport de densité de pontage du composé avec charges et de la densité de pontage du composé sans charges η/η_0 . Dans des composés de caoutchouc naturel contenant de la silice des valeurs η/η_0 ont été obtenues: vulcanisation par peroxyde 1.6 à 1.9, vulcanisation par radiation 3.6. Des comparaisons ont été faites avec des matières remplies de noir HAF vulcanisés par la même voie. Du caoutchouc naturel vulcanisé avec du soufre et rempli de noir HAF (30 vol) est généralement caractérisé par des valeurs η/η_0 de 1.5 à 2.0. Des effets comparatifs d'antioxydants ont été décrits.

Zusammenfassung

Es bestehen Anzeichen dafür, dass die chemische Reaktion (Bound-Rubberbildung) zwischen Kautschuk und feinteiliger, hydratisierter Kieselsäure, ebenso wie im Falle von Russ, über einen Radikalmechanismus verläuft. Ein hohes Verstärkungspotential der Kieselsäure zeigt sich in der Bound-Rubberbildung. Dieses Potential äussert sich in dem Ausmass der Füllstoff-Polymerwechselwirkung, die in kieselsäuregefüllten Vulkanisaten nach der Vulkanisation mit Peroxyden bzw. hochenergetischer Strahlung auftrat. Von beiden verhältnismässig einfachen Vulkanisationssystemen wird angenommen, dass sie Vernetzung über einen Radikalmechanismus liefern. Als sinngemässes Mass für die Verstärkungsfähigkeit wurde der Wert des Verhältnisses Vernetzungsdichte der gefüllten Mischung zu dem der entsprechenden ungefüllten Mischung nach der Vulkanisation, η/η_0 , genommen. Bei kieselsäuregefüllten Naturkautschukmischungen (30 Vol.) wurden folgende Werte für η/η_0 erhalten: Peroxydvulkanisation 1,6 bis 1,9; Bestrahlungsvulkanisation 3,6. Vergleiche mit ähnlich vulkanisiertem HAF-russgefülltem Rohkautschuk werden angestellt. Schwefelvulkanisierter, mit HAF-Russ gefüllter (30 Vol.) Naturkautschuk zeigt im allgemeinen η/η_0 -Werte im Bereich von 1,5 bis 2,0. Vergleichbare Einflüsse von Antioxydantien werden beschrieben.

Received September 12, 1960