

## Properties of Elastomers Crosslinked by Bisglycidyl Ether of 2,2-Bis(*p*-hydroxyphenyl)-1,1,1-trichloroethane\*

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### Synopsis

Chlorobisphenolic epoxy resins in crystalline form, e.g., bisglycidyl ether of 2,2-bis(*p*-hydroxyphenyl)-1,1,1-trichloroethane (BGECBP) and the system sulfur-*N*-cyclohexyl-2-benzothiazolesulfonamide were used as crosslinking agents for vulcanization of butadiene-styrene and butadiene-acrylonitrile rubber. The density of crosslinking was determined by the equilibrium swelling method and on the basis of the Mooney-Rivlin equation which gives the relation between stress and elongation. The dynamic properties, namely,  $G'$  and  $G''$  and mechanical loss factor  $\delta$ , were determined. On the basis of these results, mechanisms for the crosslinking reaction were advanced, the activation energy was determined, and comparisons between crosslinking rates by different systems were made. It was found that vulcanizates crosslinked by BGECBP possess higher heat aging resistance and lower glass transition temperatures in comparison with those crosslinked by means of sulfur in the presence of *N*-cyclohexyl-2-benzothiazolesulfonamide.

### INTRODUCTION

A rapid development of technology in recent years has caused the demand for new, qualitatively better rubber articles. The properties of rubber depend, in fact, not only on the chemical structure of the elastomer but also on crosslinking and antiaging systems. Conventional sulfur systems currently used in vulcanization processes, which form polysulfide crosslinkages or even accelerated or peroxide systems (which give more stable C—C bonds), are in many cases unsatisfactory. A very important feature in elastomer processing is that antidegradants used in the process should have a protective effect, should not volatilize, and should not undergo extraction or cause staining. Unfortunately, effective protective agents from alkyl, aryl-substituted *p*-phenylenediamines possess these three fundamental faults.<sup>1</sup> Volatility of these substances can be reduced much by increasing their molecular weight<sup>2</sup> to above 300. Extractability, however, cannot be eliminated. Thus, the best method is by combining the antioxidant with the polymer chain. This can be done in two ways: during

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TABLE I  
Composition of Vulcanizates (phr)

|            | Composition of indicated vulcanizate, phr |     |     |     |     |     |      |     |     |      |     |     |
|------------|---|-----|-----|-----|-----|-----|------|-----|-----|------|-----|-----|
|            | A-1                                       | A-2 | A-3 | A-4 | A-5 | A-6 | B-1  | B-2 | B-3 | B-4  | B-5 | B-6 |
| <b>SBR</b> |   |     |     |     |     |     |      |     |     |      |     |     |
| BGECBP     | 1.0                                       | 2.0 | 4.0 | 6.0 | 8.0 | 3.0 | —    | —   | —   | —    | —   | —   |
| Thiohexame | —   | —   | —   | —   | —   | —   | 0.65 | 1.3 | 2.0 | 2.65 | 3.3 | 2.0 |
| Sulfur     | —   | —   | —   | —   | —   | —   | 0.35 | 0.7 | 1.0 | 1.35 | 1.7 | 1.0 |
| Others     | —   | —   | —   | —   | —   | a   | —    | —   | —   | —    | —   | b   |
|            | C-1                                       | C-2 | C-3 | C-4 | C-5 | C-6 | B-1  | B-2 | D-3 | D-4  | D-5 | D-6 |
| <b>NBR</b> |   |     |     |     |     |     |      |     |     |      |     |     |
| BGECBP     | 1.0                                       | 2.0 | 3.0 | 4.0 | 8.0 | 3.0 | —    | —   | —   | —    | —   | —   |
| Thiohexame | —   | —   | —   | —   | —   | —   | 0.65 | 1.3 | 2.0 | 2.65 | 3.3 | 2.0 |
| Sulfur     | —   | —   | —   | —   | —   | —   | 0.35 | 0.7 | 1.0 | 1.35 | 1.7 | 1.0 |
| Others     | —   | —   | —   | —   | —   | a   | —    | —   | —   | —    | —   | b   |

<sup>a</sup> Carbon black HAF, 50.0

<sup>b</sup> Stearic acid, 1.0; zinc oxide, 5.0

## EXPERIMENTAL

### Vulcanization Procedure

Blends of butadiene–styrene rubber Ker 1500 (SBR 1500) and butadiene–acrylonitrile rubber SKN-26 (NBR) containing various amounts of crosslinking substances were made by milling. As vulcanizing agents, the bisglycidyl ether of 2,2-bis(*p*-hydroxyphenyl)-1,1,1-trichloroethane (BGECBP), sulfur, and *N*-cyclohexyl-2-benzothiazolylsulfonamide (Tio-heksam) were used. The composition of the blends is given in Table I. These blends were crosslinked at 170° ± 1°C for 10, 22.5, 35, 47.5, and 60 min by BGECBP and for 5, 10, 22.5, 35, 47.5, and 60 min by sulfur in the presence of the sulfonamide.

### Crosslink Density

The effective crosslink density, taken as the number of network chains mole/cm<sup>3</sup> between effective bonds in space lattice, of vulcanizate was determined by two methods:

(a) From the relationship between elongation of the rubber sample and stress during stretching and the Mooney-Rivlin equation:<sup>12,13</sup> Constants  $C_1$  and  $C_2$  were determined graphically from the dependence

$$\frac{F}{2A_0(\lambda - \lambda^{-2})} = \lambda^{-1}$$

for nonswelled vulcanizates.

(b) By the equilibrium swelling method: Swelling carried out at 25° ± 1°C in *n*-decane in the case of SBR vulcanizates and in toluene in the case of NBR. The effective density of crosslinkage was determined from the Flory-Rehner equation.<sup>14</sup> Parameter  $\chi$  was determined using the Mooney-Rivlin equation.

TABLE II  
 Comparison of  $G'$ ,  $G''$ , and Loss Tangents (at 0.1 Hz) for Butadiene-Styrene Vulcanizates Crosslinked by BGECBP and Sulfur-Sulfonamide Systems

|  | 5 min | 10 min | 22.5 min | 35 min | 47.5 min | 60 min |
|--|-------|--------|----------|--------|----------|--------|
| <b>SBR + BGECBP</b>                          |       |        |          |        |          |        |
| (A-3)  |       |        |          |        |          |        |
| $G' \times 10^{-6}$ , dynes/cm <sup>2</sup>  | —     | 6.00   | 6.90     | 8.30   | 11.0     | 18.80  |
| $G'' \times 10^{-4}$ , dynes/cm <sup>2</sup> | —     | 59.70  | 54.86    | 59.76  | 63.8     | 99.64  |
| $\tan \delta \times 10^2$                    | —     | 9.95   | 7.95     | 7.20   | 5.80     | 5.30   |
| <b>SBR + S/P</b>                             |       |        |          |        |          |        |
| (B-3)  |       |        |          |        |          |        |
| $G' \times 10^{-6}$ , dynes/cm <sup>2</sup>  | 7.45  | 8.20   | 8.40     | 8.72   | 7.82     | 7.10   |
| $G'' \times 10^{-4}$ , dynes/cm <sup>2</sup> | 49.17 | 58.22  | 68.71    | 71.85  | 61.70    | 51.93  |
| $\tan \delta \times 10^2$                    | 6.60  | 7.10   | 8.18     | 8.24   | 7.89     | 7.30   |

### Investigation of Dynamic Properties

The dynamic properties were investigated on strand pendulum (method B) produced by Central Laboratory TNO at Delft. The measurements were carried at  $25^\circ \pm 0.1^\circ\text{C}$ . For the determination of dynamic modulus and mechanical loss factor in the vulcanizates, previously reported equations were used.<sup>15-17</sup> Values of  $G'$ ,  $G''$  and tangents for each of three moments of interio were interpolated to the free vibration frequency of 0.1 Hz (Table II). The reproducibility was  $\pm 1.4\%$  for  $G'$  and 1.8% for  $\tan \delta$ .

### Investigation of Static Properties

Investigation of static physical properties was carried out on an electronic ripper Instron. The results are presented as relationships between particular properties and vulcanization time (Fig. 7). In order to determine the resistance of the vulcanizates to thermal aging, samples were placed into a thermostat at  $150^\circ \pm 1^\circ\text{C}$  for 24 hr, and tensile strength, unit elongation under breaking, and hardness were then determined. Compositions of vulcanizates for which static physical properties were determined are given in Table II.

Furthermore, for NBR vulcanizates crosslinked by BGECBP (C-6) and by sulfur in the presence of sulfonamide (D-6), the glass transition temperature was determined.

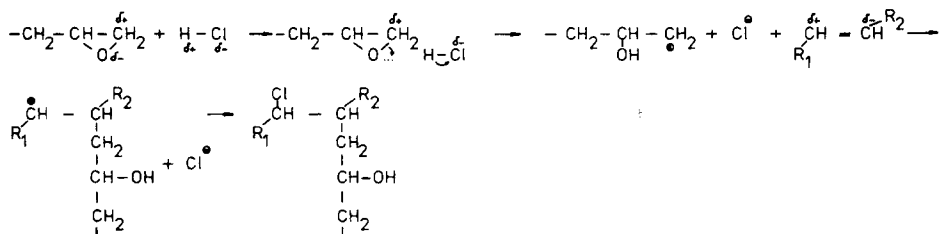
## RESULTS AND DISCUSSION

Measurements of effective crosslinkage density confirm that crosslinking of butadiene-styrene and butadiene-acrylonitrile copolymers occurs with BGECBP.

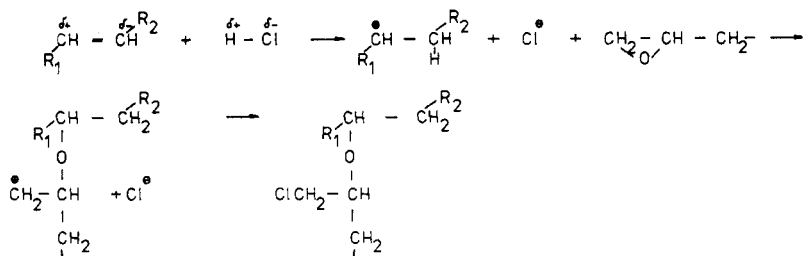
### Proposed Mechanism of Reaction

The lower glass transition temperature  $T_g$  for butadiene-acrylonitrile rubber crosslinked by BGECBP results in a higher elasticity of the network compared with vulcanizates crosslinked by sulfur-sulfonamide. It indicates the presence of long intermolecular bridges in the crosslinked elastomer, and linkage of two rubber chains by the bisglycidyl ether is presumed. The following mechanism is suggested:

Mechanism I



## Mechanism II



According to published work,<sup>19,20</sup> elimination of HCl from such chlorobisphenolic epoxy compounds occurs at vulcanization temperatures. The highly polar HCl molecule may initiate the reaction with the epoxy ring (mechanism I), as well as with the double bond of the elastomer (mechanism II). Because of a likely lower activation energy, it may be presumed that the reaction is predominantly mechanism I.

## Relationship Between Crosslink Density and Time

Figures 1, 2, 3, and 4 show the relationships between crosslink density and time. Each curve refers to a different concentration of crosslinking agent and may be used as a kinetic curve for vulcanization.

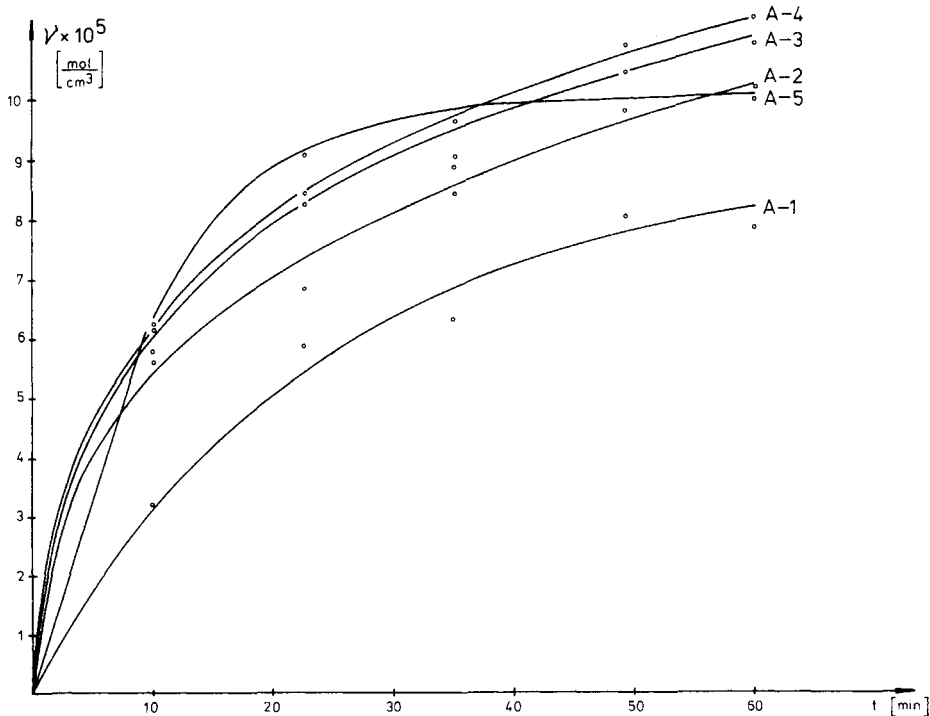


Fig. 1. Relationship between crosslink density and crosslinking time  $t$  for butadiene-styrene vulcanizates crosslinked by BGECBP.

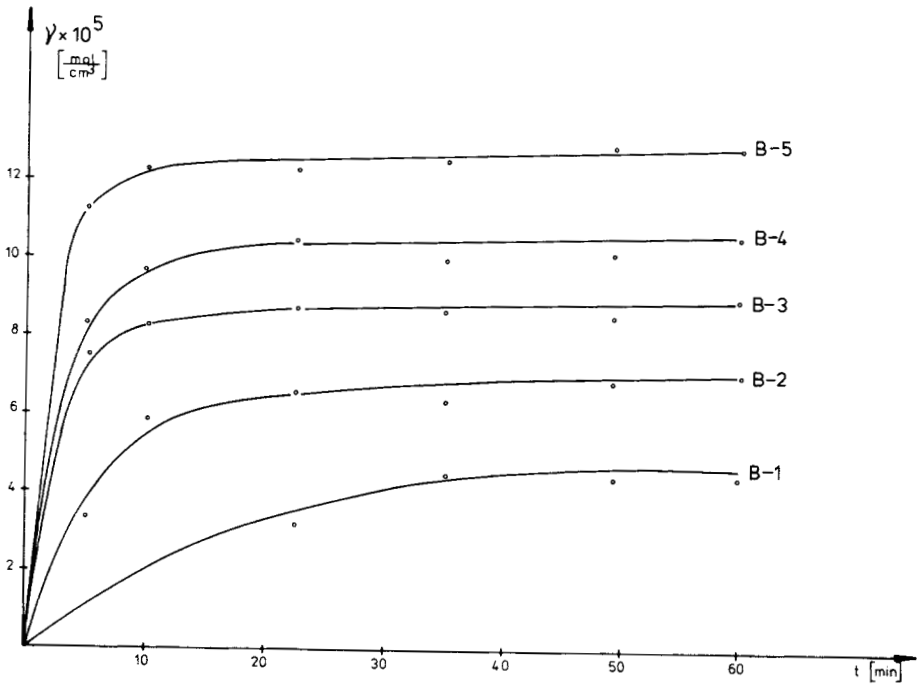


Fig. 2. Relationship between crosslink density and crosslinking time  $t$  for butadiene-styrene vulcanizates crosslinked by sulfur-sulfonamide.

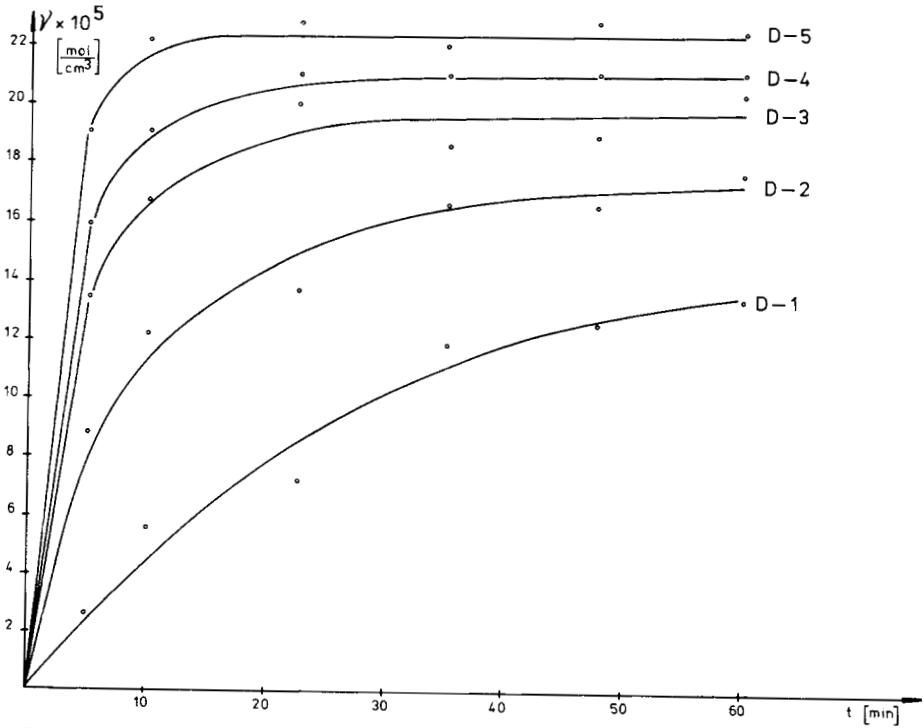


Fig. 3. Relationship between crosslink density and crosslinking time  $t$  for butadiene-acrylonitrile vulcanizates crosslinked by BGECBP.

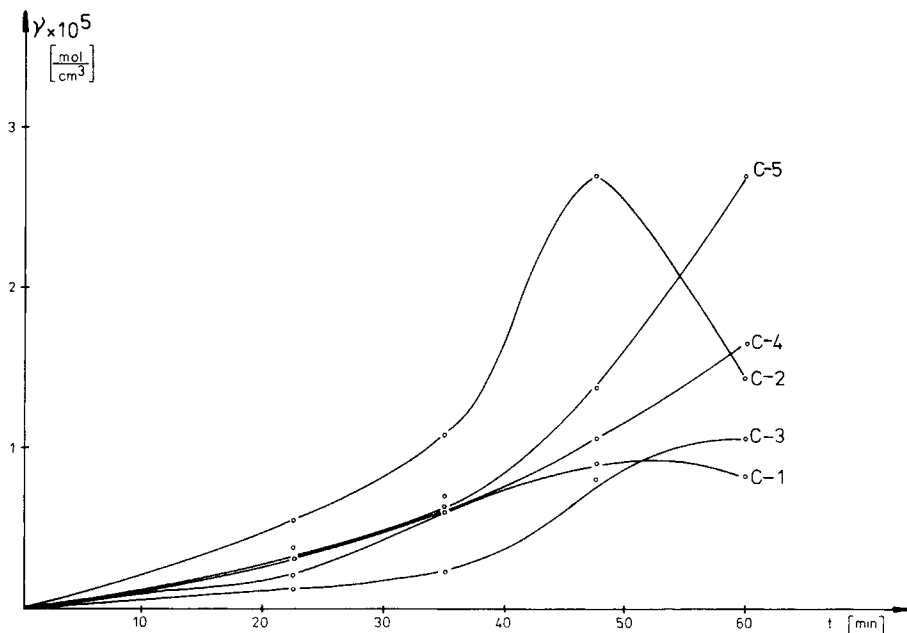


Fig. 4. Relationship between crosslink density and crosslinking time  $t$  for butadiene-acrylonitrile vulcanizates crosslinked by sulfur-sulfonamide.

Moreover, kinetic equations and activation energy values for crosslinking were determined. From Figures 1 and 2 it can be seen that crosslinking rates are higher for SBR vulcanized by means of sulfur in the presence of sulfonamide than in the case of BGECBP; however, the values of limiting density of crosslinkage are of the same order. It was found (Figs. 3 and 4) that the values of density and rate of crosslinkage are very small for NBR crosslinked by BGECBP in comparison with sulfur.

### Relationships Between Dynamic and Other Properties

Table II shows the relationship between the elastic component of dynamic modulus  $G'$  and crosslinkage time  $t$ . The different characters of the curves for vulcanizates obtained from butadiene-styrene rubber crosslinked by BGECBP (A-3) and by sulfur in the presence of sulfonamide (B-3) indicates their different space lattice structure, and hence different reaction mechanism, in agreement with results of experiments in which crosslink density was measured. Vulcanizates crosslinked by sulfur exhibit reversion unlike those in which BGECBP was used. A continuous increase of the real component of dynamic modulus  $G'$  with vulcanization time can be observed.

Table II shows also the relationship between  $G'$  and effective crosslink density for vulcanizates using BGECBP (A-3) and sulfur (B-3).

The shape of the curves also confirms the different mechanisms of crosslinking of butadiene-styrene copolymer using bisglycidyl ether of 2,2-bis(*p*-hydroxyphenyl)-1,1,1-trichloroethane or the sulfur-sulfonamide system. However, plastic properties, expressed by the log modulus  $G''$  or mechanical loss factor ( $\tan \delta$ ), depend less on crosslinkage density than does  $G'$ .



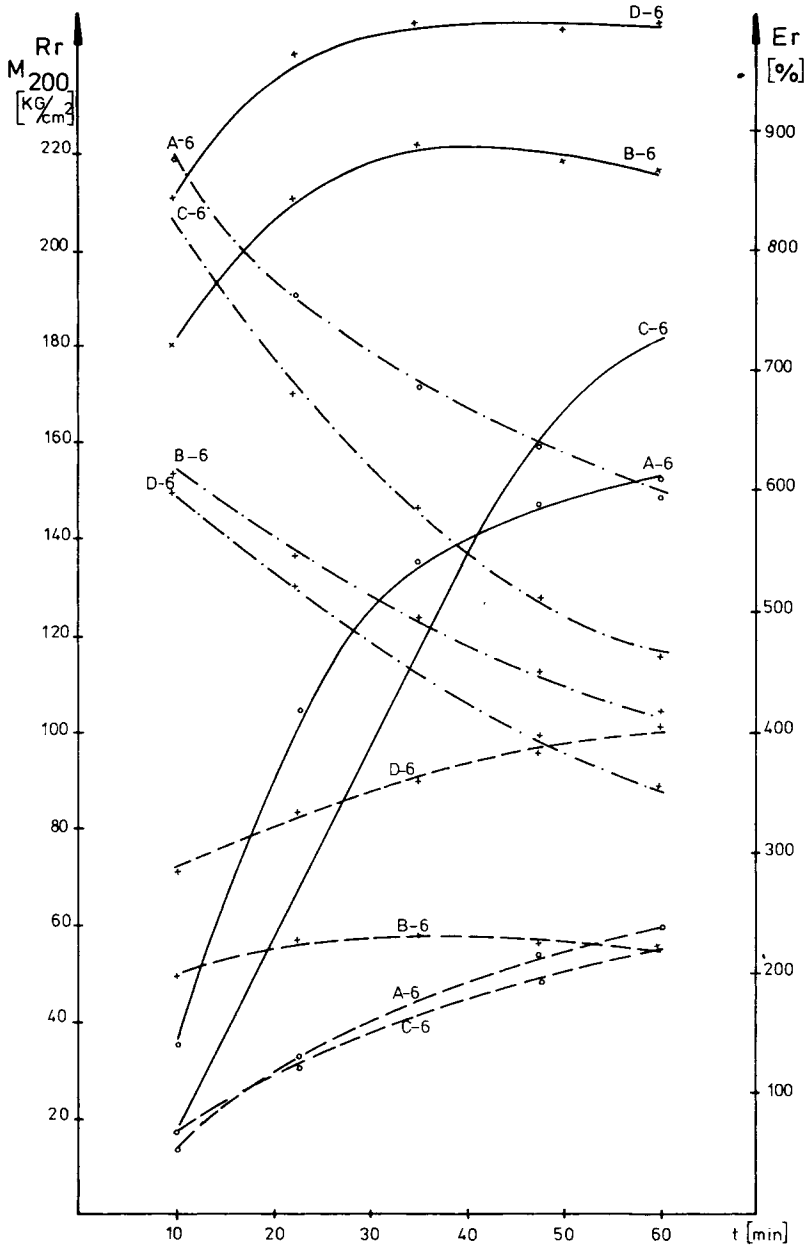


Fig. 5. Relationship between  $R_r$ ,  $E_r$ , and  $M_{200}$  and crosslinking time  $t$ . (—)  $R_r$ , (— · —)  $E_r$ , and (---)  $M_{200}$ .

In Figure 5 is shown the relationship between tensile strength ( $R_r$ ), unit elongation under breaking ( $E_r$ ), and 200% modulus ( $M_{200}$ ) and vulcanization time. It can be seen that higher values of tensile strength are obtained in shorter time for sulfur vulcanizates, both for SBR and NBR. In the case of elongations, the situation is reversed; for each vulcanization time, higher values of elongation were obtained for vulcanizates crosslinked by BGECBP than by sulfur-sulfonamide.

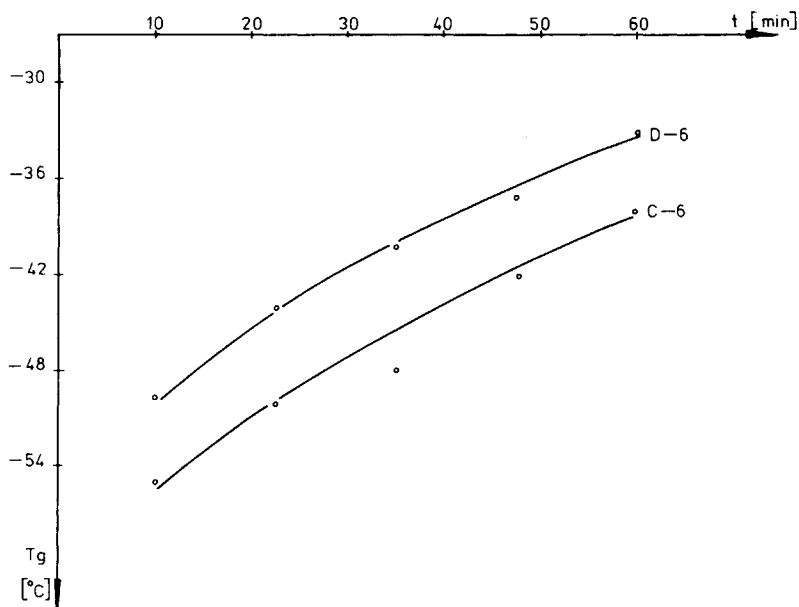


Fig. 6. Relationship between glass transition temperature  $T_g$  and crosslinking time  $t$ .

From the values of the 200% modulus, it is evident that considerably greater stresses are required for butadiene-styrene and butadiene-acrylonitrile vulcanizates crosslinked by sulfur than by BGECBP.

### Glass Transition Temperatures

The diagram showing dependence of glass transition temperature  $T_g$  and vulcanization time (Fig. 6) indicates that for NBR (BGECBP), vulcanizates have lower glass transition temperatures (the difference is about  $7^{\circ}\text{C}$ ) than when crosslinked by sulfur.<sup>18</sup> An increase in time results indicates that crosslinkages stiffen the linear chains of polymer.

### Thermal Aging

Vulcanizates crosslinked by BGECBP are more resistant to thermal aging, as indicated by change in hardness (+5% change for A-6 and C-6, compared with +25% change for B-6 and 21% for D-6), very high elongation at break (for A-6 and C-6), and small increase of modulus (Table III).

### CONCLUSIONS

1. Correlations have been found between crosslinkage density values determined by a rapid method from stress-strain measurements and those based on equilibrium swelling.
2. Higher resistance to air aging of vulcanizates from butadiene-styrene and butadiene-acrylonitrile rubbers crosslinked by BFECBP is evidence that the bisglycidyl ether of 2,2-bis(*p*-hydroxyphenyl)-1,1,1-trichloroethane acts not only as a crosslinking agent, but also as an effective antioxidant.

TABLE III  
Change (%) in Physical Properties of Vulcanizates After Aging at 150°C for 24 Hours

| Parameter <sup>a</sup>         | SBR + BGECBP<br>(A-6) | SBR + S/P<br>(B-6) | NBR + BGECBP<br>(C-6) | NBR + S/P<br>(D-6) |
|--------------------------------|-----------------------|--------------------|-----------------------|--------------------|
| $R_r$ , kg/cm <sup>2</sup>     | +3                    | -10                | +10                   | -10                |
| $E_r$ , %                      | -24                   | -40                | -13                   | -26                |
| $M_{100}$ , kg/cm <sup>2</sup> | +28                   | +213               | +50                   | +97                |
| $M_{200}$ , kg/cm <sup>2</sup> | +18                   | +1237              | +47                   | +67                |
| $M_{300}$ , kg/cm <sup>2</sup> | +8                    | —                  | +39                   | —                  |
| RHD Sh (A)                     | +5                    | +25                | +5                    | +21                |

<sup>a</sup> $R_r$ , Tensile strength;  $E_r$ , break elongation;  $M_{100,200,300}$ , modulus of 100, 200, 300 elongation; RHD, Shore hardness.

3. High resistance to thermo-oxidative aging has particular relevance to industrial practice because the bisglycidyl ether is chemically attached to the vulcanizate network and, unlike conventional antiagers such as the alkyl-aryl-*p*-phenylenediamines, does not undergo extraction, migration, or staining.

4. The lower  $T_g$  for butadiene-acrylonitrile rubber crosslinked by BGECBP indicates the presence of long intermolecular bridges in the crosslinked elastomer.

### References

1. J. Czyżewicz, *Polimery*, **13**, 68 (1968) (in Polish).
2. E. I. Latos and Sparks A. K., *Kaut. Gummi Kunstst.*, **23**(9), 41 (1970).
3. R. H. Kline, *Rev. Gen. Caoutch. Plast.*, **51**(7-8), 540 (1974).
4. R. Levy, *Rev. Gen. Caoutch. Plast.*, **51**(4), 243 (1974).
5. R. Fabre, *Rev. Gen. Caoutch. Plast.*, **48**(5), 501 (1971).
6. Brit. Pat. 1,577,770 (1968).
7. M. E. Cain, *Rubber J.*, **150**(11), 10 (1968).
8. Z. K. Brzozowski, *J. Fire Flamm. Fire Retardant Chem.*, Suppl. 1, 218 (Nov. 1974).
9. Z. K. Brzozowski, J. Kiełkiewicz, and A. Nessel, *Polimery*, **19**(12), 594 (1974) (in Polish).
10. Z. K. Brzozowski, M. Gajewski, and E. Jańczak, Pol. Pat. 72,319 (1974).
11. M. Gajewski, E. Jańczak, and B. Jankowski, *Gummiwerkstoffe für kältebeständige Dichtungen*, Vth International Conference on Sealings, Dresden, 1974.
12. M. Mooney, *J. Appl. Phys.*, **11**, 582 (1940).
13. R. S. Rivlin and D. W. Saunders, *Phil. Trans. Roy. Soc., London*, **A234**, 251 (1951).
14. P. J. Flory and J. Renner, Jr., *J. Chem. Phys.*, **11**, 512, 521 (1943).
15. J. Ruciński and M. Gajewski, *Polimery*, **17**(3), 145 (1972) (in Polish).
16. M. Gajewski and R. Chasset, *Rev. Gen. Caoutch. Plast.*, **44**, 187 (1968).
17. M. Gajewski, *Polimery*, **19**(6), 244 (1974) (in Polish).
18. J. P. Mercier, *Rev. Gen. Caoutch. Plast.*, **52**, 83 (1975).
19. Z. K. Brzozowski, T. Brzozowska-Janiak, S. Porejko, and T. Floriańczyk, *Polimery*, **17**, 419 (1972) (in Polish).
20. S. Porejko, T. Floriańczyk, Z. K. Brzozowski, *Polimery*, **18**, 132 (1973) (in Polish).

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