The Cross-linking Reaction of the Polybutadiene Binder for Composite Propellants

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The monomer or prepolymer of the fuel binder should have a suitable fluidity at an ambient temperature in order to secure a high holding capacity of solid ingredients and a high castability. On the other hand, a propellant grain should have good mechanical and combustion characteristics. Polyurethane is an excellent binder, one which fulfills such requirements; its physical properties can be widely controlled by means of the reaction conditions and the type of starting materials.[1] Polybutadiene also seems to give a grain with a high ballistic performance and a good low temperature property due to its low heat of formation, its high hydrogen/carbon ratio and its low second-order transition point.

In view of these points, a polybutadiene fuel binder with good mechanical properties was studied using "telechelic polybutadiene" (carboxy-terminated polybutadiene) as the starting material.[2] "Telechelic polybutadiene" has a relatively uniform molecular weight distribution and is cross-linked with terminal groups, so that the resultant polymer network will be essentially uniform, containing no terminal sections. Unlike conventionally-vulcanized rubbers, which are randomly cross-linked, the strain would be distributed uniformly upon each elastic chain of the cross-linkage and the mechanical strength might be improved remarkably. Moreover, it is possible to control to some extent the reaction of the chain extension and the cross-linking because this compound functions as a dicarboxylic acid.

Tris[1-(2-methyl)aziridinyl] phosphine oxide [MAPO] was used as the cross-linking agent in this work.[3] Usually a curing temperature as high as 100—150°C is recommended; however, we preferred here to suppress the temperature as much as possible toward the ambient temperature in view of the volume contraction of the cured material and the inferior heat resistance of the additives. An effective accelerator was found which enables cross-linkage even at the relatively low temperatures of 50—70°C without the sacrifice of the properties of the cured products.

Raw Materials

"Telechelic polybutadiene" HC-434 (Thiokol Chem.) and Butarez CTL (Phillips Pet. Co.) were used as received. The number-average molecular weights were 3770 and 5500 respectively.

Experimental Results

An Accelerator for the Curing Reaction.—Reaction mixtures were poured into a 40×40×5 mm. glass cell, made of two 40×40 mm. glass plates standing face to face with a 5 mm. spacer with tin foils lining the inside surfaces; these plates served as a pair of electrodes. The loaded cell was put into a constant temperature oven, and the specific resistivity at 50°C was measured continuously. Figure 1 shows the curve of the specific resistivity versus the reaction time. The time required until the specific resistivity become constant is cut by the addition of the accelerator.

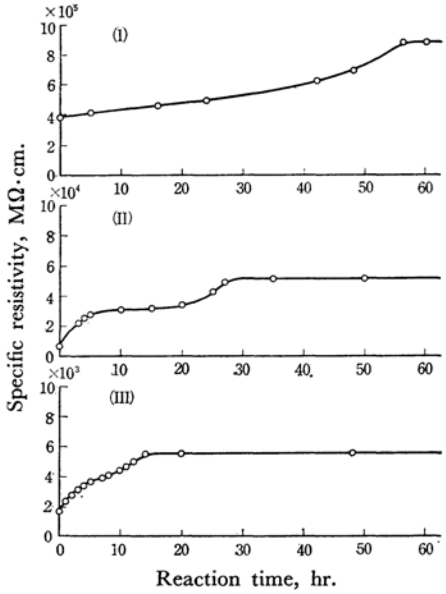

Fig. 1. Specific resistivity versus reaction time (50°C cure).
(I) HC-434 100 g.-MAPO 9.7 g.
(II) HC-434 100 g.-MAPO 9.7 g.-Accelerator 5 g.
(III) HC-434 100 g.-MAPO 9.7 g.-Accelerator 10 g.

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[1] K. Yamazaki, A. Iwama, S. Aoyagi, T. Sofue, M. Hayashi and K. Kishi, *J. Chem. Soc. Japan, Ind. Chem. Sec.* (*Kogyo Kagaku Zasshi*), **66**, 1630 (1963).

[2] C. A. Uraneck, H. L. Hsieh and O. G. Buck, *J. Pol. Sci.*, **46**, 535 (1960).

[3] U. S. Pat. 3087844.

TABLE I. PHYSICAL PROPERTIES OF HC-434 - MAPO - ACCELERATOR ELASTOMERS

Cross-linking agent [MAPO] (Equiv.)	Ultimate tensile strength kg./cm²	Elongation %	100% Modulus kg./cm²	300% Modulus kg./cm²	Hardness	M_c	Sol-fraction %
Accelerator 5 phr. 50°C cure							
2.0	10.9	360	5.1	10.0	34	9540	9.28
2.5	10.3	330	5.4	—	36	8140	8.46
3.0	13.8	400	5.8	11.5	38	7670	8.21
4.0	8.1	470	2.9	5.7	24	16890	21.12
Accelerator 10 phr. 50°C cure							
2.0	10.8	510	3.7	7.1	19	14640	31.1
2.5	16.7	510	5.5	10.5	28	13560	16.7
3.0	15.0	440	6.1	11.8	39	7680	18.1
4.0	13.9	450	4.9	10.1	42	7030	7.3
Accelerator 5 phr. 70°C cure							
1.0			(undercured)				
1.5	13.0	300	6.9	—	36	11540	8.14
2.0	14.0	260	7.8	—	43	5880	3.06
2.5	11.9	260	7.1	—	36	7030	5.19
3.0	11.3	310	5.7	—	33	6800	5.31
4.0	7.7	540	2.4	4.8	19	14900	14.91

TABLE II. PHYSICAL PROPERTIES OF BUTAREZ CTL-MAPO-ACCELERATOR ELASTOMER

Cross-linking agent [MAPO] (Equiv.)	Ultimate tensile strength kg./cm²	Elongation %	100% Modulus kg./cm²	300% Modulus kg./cm²	Hardness	M_c	Sol-fraction %
Accelerator 5 phr. 50°C cure							
2.0	7.0	730	—	—	12	14540	10.07
3.0	11.1	390	—	—	27	10900	8.87
4.0	—	—	—	—	—	14130	14.67

Even though the changes of the electric property could not indicate the degree of the chemical cross-linking exactly, it may be expected that the increase in specific resistivity is still be related to the process of the curing reaction; it is evident that the addition of the accelerator is very effective.

However, the time required for a perfect cure is remarkably affected by the type of vessel used for the curing. For example, the composition shown on Fig. 1 was cast and cured at 50°C in a 60 mm.$\phi\times$90 mm.H polyethylene cup, and the progress of the curing reaction was followed by hardness measurements with a durometer. The hardness increased as the reaction proceeded, but more than 2 weeks were required for a perfect cure. It is reasonable for the heat transfer to the inside of the reaction mixture in a large vessel to be slower than in a smaller one, but this difference alone can not explain the result. Although no decisive interpretation can yet be made, the difference may be attributed to the differences in the area of contact with the atmosphere from vessel to vessel. However, the addition of an accelerator was effective in both cases. In the end, for the purpose of lowering the curing temperature for the carboxy-terminated polybutadiene-MAPO system, some effective accelerators were found.

The Elastomer Preparation.—The required amounts of the ingredients were mixed manually at 75—80°C, degassed, and cast into the cavity formed by two parallel glass plates in order to form elastomer sheets about 2—3 mm. thick. After some preliminary tests, the curing time of 7 days was taken.

The Measuring Process.—The tensile stress-strain data were obtained using "Tensilon" with dumbbell-shaped specimens. Following the standard "Physical Testing Methods for Vulcanized Rubber" (JIS-K-6301), a strain rate of 500 mm./min., a cross-head distance of 50 mm. and No. 3 type dumbbell-shaped specimens die-cut from the elastomer were used.

The hardness was measured using an Asker durometer J.

All the experiments were performed in an air-conditioned room at a constant temperature of 20°C and at a constant relative humidity of 60%.

The data are shown in Tables I and II.

Equilibrium Swelling.—If a two-functional carboxy-terminated polybutadiene reacts quantitatively with an equivalent amount of a three-functional cross-linking agents [MAPO], the resultant network will have no terminal sections. In this case, each segment of the network structure acts in an elastic manner, and the length of each segment should be same as that of the initial two-functional polybutadiene molecule. However, the actual curing reaction will be more complicated because of some undesirable side reactions. The average molecular weight for the chain of the network and the degree of cross-linking are very important factors in describing a three-dimensional polymer network model; therefore, the equilibrium swelling was measured in order to clarify these indexes.

When the volume fraction, Q_m, of the polymer present in the swollen gel is rather small, it can be approximately represented by Eq. 1.[4]

$$Q_m=[(1/2-\mu)M_c/\rho_2 V_1]^{3/5} \tag{1}$$

where ρ_2 : the polymer density

V_1 : the molar volume of the solvent

μ : the polymer-solvent interaction constant

M_c : the average molecular weight between cross-links

Q_m can be determined directly by Eqs. 2 and 3.

$$W=W_1+W_2 \tag{2}$$

$$Q_m=1+(\rho_2/\rho_1)(W'/W_1-1) \tag{3}$$

where ρ_1 : the density of the solvent

W : the weight of the specimen before swelling

W_1 : the weight of gel in the specimen

W_2 : the weight of sol in the specimen

W' : the weight of the specimen on equilibrium swelling

The calibration term for terminal chains could be neglected because its fraction would be very small from the standpoint of the reaction scheme.

Small pieces of elastomers about 0.4—0.5 g. were immersed in carbon tetrachloride at 20°C. After 7 days, the swollen gel was removed from the solvent, quickly blotted with dry filter paper, and reweighed in a stoppered weighing bottle. The specimen was then transferred to an electric oven at 50°C in order to remove the imbibed solvent; the W_1 was thus determined. The weight difference, W_2, between W and W_1 was taken as the weight of the sol. It is impossible for all of the sol to be extracted by such a simple procedure; however, the measured value is useful as a semi-quantitative measure of the sol fraction.

The polymer density at 20°C was measured by the pycnometer method, using distilled water as the sealant.

The Q_m was determined from Eq. 3; then M_c was calculated by Eq. 1. The data obtained are shown in Table I and Table II, together with the sol fraction, which was measured by the procedure described.

The polymer-solvent interaction parameter, μ, was calculated as 0.264 (at 20°C) by means of the data shown by Shvarts.[5]

Discussion

From the data illustrated on Table I and Table II, it is evident that the chain length between cross-links, M_c, is strongly influenced by the cross-linking agent, the accelerator and the curing temperature. In general, as the addition of the cross-linking agent increases, the tensile strength and the modulus of the elastomer pass through a maximum. Namely, there is a peak in the curve of the tensile modulus versus the quantity of the cross-linking agent added. If this was due to only the "dilution effect" of an excess cross-linking agent, M_c would not decrease even if the tensile modulus decreased.

Though the data observed are negative for such a relation, M_c was inversely proportional to the tensile modulus; and this shows that the optimum molar ratio of the cross-linking agent should be determined with the maximum tensile modulus and it was found that a 100—200% excess of equivalence is required.

Assuming that the ideally cross-linked HC-434 polymer has a network model as has been described previously, its M_c should be same as the average molecular weight 3800 of the HC-434 polymer. However, the minimum M_c value obtained is about 6000, which is about one and a half times the chain length for an ideal network. Therefore, it is reasonable to assume that a considerable chain extending reaction occurs inevitably; this may be the reason why an excess of the cross-linking agent is required in order to obtain the maximum tensile modulus.

The kinetic theory of rubber elasticity predicts that the tensile stress-strain will be given by Flory's equation:

$$S=\nu \boldsymbol{R} T(\alpha-1/\alpha^2) \tag{4}$$

where S : the stress based on the original cross-sectional area

ν : moles of effective chain per unit volume

$\boldsymbol{R}$: the gas constant

T : the absolute temperature

α : the principal extension ratio

In Eq. 4 ν can be replaced by $1/M_c$, for the polymer density is almost equal to 1.00; the tensile stress, S, should then be inversely proportional to the chain length, M_c. As $\boldsymbol{R}$ and T are known quantities, the tensile stress at 100% elongation ($\alpha=2$) can be calculated by means of Eq. 5:

$$S_{100}=0.426\times 10^5(1/M_c)\ \text{kg./cm}^2 \tag{5}$$

Figure 2 shows the relationship between the tensile stress at 100% elongation and the chain length, M_c.

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[4] J. Furukawa and S. Yamashita, *J. Soc. Rubber Ind. Japan* (*Nippon Gomu Kyokai-shi*), **30**, 955 (1957).

[5] A. G. Shvarts, *Rubber Chem. and Tech.*, **31**, 691 (1958).

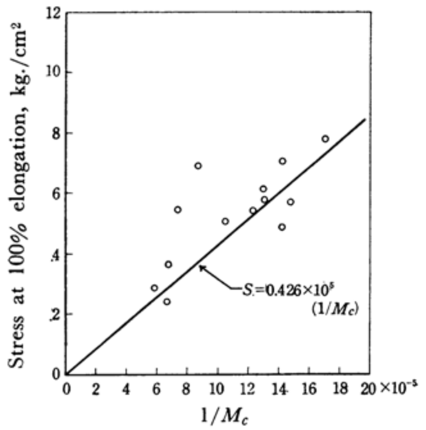

Fig. 2. Plot of tensile stress at 100% elongation versus M_c (HC-434 - MAPO - Accelerator).

Although there are a few exceptions, in general, the observed data agree well with the theoretical quantities.

It can readily be assumed that the quantity of an ingredient which makes no contribution to the cross-linking reaction (which would be proportional to the sol fraction) might be at a minimum at the optimum mixing ratio of the polybutadiene, the cross-linking agent and the accelerator for the maximum tensile modulus of an elastomer. The longer the chain length, the greater the quantity of the sol fraction. These relationships are illustrated in Fig. 3.

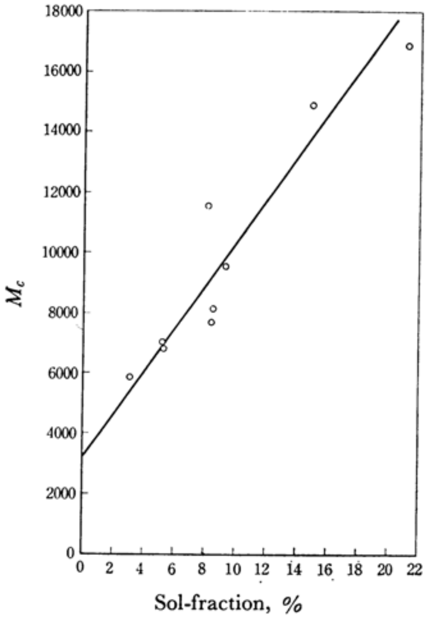

Fig. 3. Plot of sol fraction versus M_c (HC-434 - MAPO - Accelerator 5 phr.).

Figure 4 shows the chain length, M_c, versus the elongation at the break point of the elastomer.

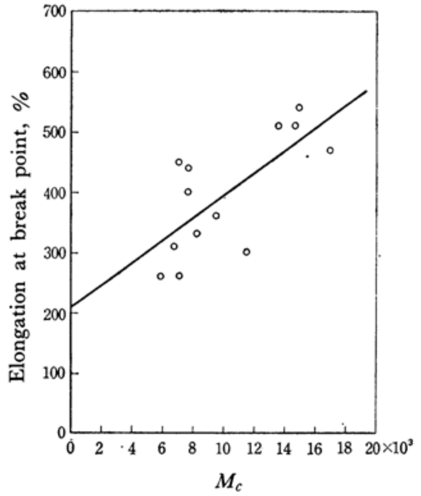

Fig. 4. Plot of elongation at break point versus M_c (HC-434 - MAPO - Accelerator).

Breaking phenomena can scarcely give reliable data, because they are strongly influenced by the internal defects in the molecular structure of the specimens. However, it is shown that the elongation at the break point increases with the chain length, M_c. As the cross-linking reaction proceeds so effectively that the chain length, M_c, becomes short, the internal stress per unit of the chain of the network should be increased; this may be what happens in the breaking of the elastomer.

Equation 4 shows that the stress, S, should be proportional to $(\alpha-1/\alpha^2)$ and that the slope of this line, $\nu\boldsymbol{R}T$, equals the shear modulus. These relationships are illustrated in Fig. 5 and Fig. 6; plots of S versus $(\alpha-1/\alpha^2)$ show a good linearity.

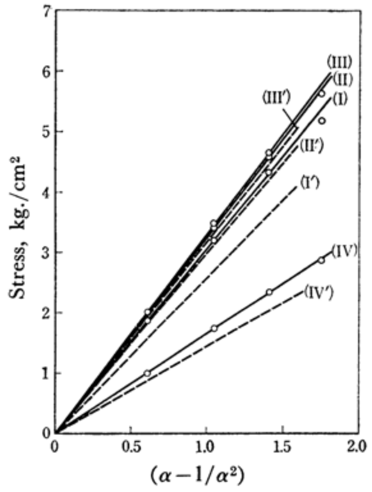

Fig. 5. Stress-strain data for some elastomers (HC-434 - MAPO - Accelerator 5 phr., 50°C cure).

(I) MAPO 2.0 eq. (III) MAPO 3.0 eq.
(II) MAPO 2.5 eq. (IV) MAPO 4.0 eq.

TABLE III. COMPARISON OF M_c AND SOL-FRACTION OF CURED BUTAREZ CTL AND HC-434

Cured condition	MAPO added	HC-434			Butarez CTL		
		M_c	M_c/M	Sol-fraction	M_c	M_c/M	Sol-fraction
50°C, 7 days	2.0 eq.	9540	2.53	9.28	14540	2.65	10.07
50°C, 7 days	3.0 eq.	7670	2.03	8.21	10900	1.98	8.87

(Accelerator 5 phr.)
M: Average molecular weight of raw materials

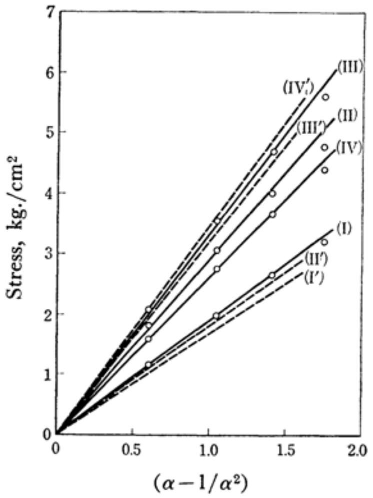

Fig. 6. Stress-strain data for some elastomers (HC-434 - MAPO - Accelerator 10 phr., 50°C cure).
(I) MAPO 2.0 eq. (III) MAPO 3.0 eq.
(II) MAPO 2.5 eq. (IV) MAPO 4.0 eq.

On the other hand, as M_c was determined from swelling data, the stress-strain data could be calculated by means of Eq. 4. These are represented in Fig. 5 and Fig. 6 with dotted lines. (The polymer density was assumed to be 1.00.)

Of course, there is a considerable amount of sol occluded in the network structure, and if the sol fraction has no role to play in the networks, the tensile stress can be calculated by considering the term of the "dilution effect" for the swelling data; however, the observed value is higher than that calculated from M_c. Therefore, a dilution effect of the sol fraction is not conceivable, while a reinforcing effect such as chain entanglement is plausible.

Table I shows the effects of the curing temperature. As is shown by the table, the increase in the temperature for the cross-linking reaction from 50°C to 70°C causes a decrease in the sol fraction, the chain length, M_c, and the quantity of cross-linking agent required for the maximum tensile modulus. These tendencies seem quite reasonable, since the reactivity and the mobility of the ingredients would increase with the reaction temperature.

Table III compares the cross-linking reactions of the Butarez CTL and HC-434 polymers. The average molecular weight of Butarez CTL is larger than that of HC-434, so the M_c of the cured products of the former is longer than that of those of the latter. However, not only are the ratios of M_c divided by the average molecular weight of respective raw materials almost the same; the sol fractions are also almost the same. Hence, it may be concluded that there is no noticeable difference between the reactivities of these two raw materials.

Conclusion

The cross-linking reactions of "telechelic polybutadiene" at relatively low temperatures have been studied, and some kinds of accelerator have been found to be effective.

In general, a 100—200% excess of cross-linking agent was required in order to obtain cured elastomers of the maximum tensile modulus.

As the curing temperature rose, the excess quantity of the cross-linking agent was diminished.

The measured stress-strain data of the elastomers closely fit Flory's equation for the rubber elasticity theory. The swelling data were in line with the stress-strain data.

Summary

The cross-linking reactions of carboxy-terminated polybutadiene with tris[1-(2-methyl)aziridinyl] phosphine oxide have been studied in order to obtain an excellent fuel binder of good mechanical properties as well as good combustion characteristics.

The tensile strength and elongation at the break point, as shown by the elastomer studied, were about 10—15 kg./cm.² and 250—500% respectively. For high tensile modulus of the elastomer, an 100—200% excess of the cross-linking agent over the equivalent ratio was required.

The reaction temperature for cross-linking was lowered to the 50—70°C range by the addition of a suitable accelerator.

The stress-strain curve of the elastomer closely fit the equation for the rubber elasticity theory, and these stress-strain data was in accordance with the measured swelling data.

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