Chemorheological Study of Cured Polysulfide Liquid Polymers*

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INTRODUCTION

The chemorheology of polysulfide rubbers had previously been investigated by Stern,[1] Mochulsky and Tobolsky.[2] It was determined that the stress relaxation of these materials was due to an interchange reaction occurring amongst the disulfide linkages and between these groups and free mercaptan terminals located on adjacent polymer chains. Such reactions would have remained undetected as long as the samples were maintained in an unstrained condition. Upon the application of a strain, these exchange reactions would allow the internal structure to come to equilibrium with the newly imposed dimensions without causing any change in the physical or chemical properties of the system. It was also noted that the introduction of excess free mercaptan groups, sulfur, or ultraviolet radiation had a noticeable accelerating effect on the relaxation process while the inclusion of reagents which combined with free mercaptans had a retarding effect on the rate of stress decay.

This mechanism has been confirmed chemically by the observed interchange of disulfides with other disulfides or with mercaptans[3-8] and the formation of a copolymer when two polysulfide latices of different structure were mixed under suitable catalytic conditions.[9]

In this study the effects of curing agents and their reaction products upon the stress relaxation properties of cured polysulfide liquid polymers were investigated. These liquid polymers were prepared by the condensation of organic dihalides with sodium polysulfide resulting in the formation of a latex which was then controllably cleaved at the disulfide links by their reduction with sodium hydrosulfide and sodium sulfite.[10] The resulting liquid polymer can be readily cured to a rubber

upon the oxidation of the mercaptan terminals to disulfide linkages or by the reaction of these end groups with some polyfunctional reagent. Oxidizing agents by which cures were obtained or attempted included PbO_2, MnO_2, organic peroxides, and hydroperoxides, and p-quinonedioxime. Other cures were performed by reacting the mercaptan terminals with diisocyanates and further attempts were made by the use of ozone, high energy radiation, and catalyzed air oxidation.[11-13]

EXPERIMENTAL

Material

The polysulfide liquid polymer used in this study was a special laboratory batch of the Thiokol LP-2 prepared by the condensation of a mixture of 98 mole-% bis-β-chloroethyl formal and 2 mole-% of 1,2,3-trichloropropane with sodium polysulfide. Excess alkali and polysulfide were removed from the latex by 30 washings with water after which the latex was reduced to the liquid polymer by treatment with NaSH and Na_2SO_3. From mercaptan end group analysis, the equivalent weight of the liquid polymer was found to be 1710. The viscosity was measured by means of a Brookfield viscometer and found to be 560 poises at 30°C.

p-Quinonedioxime Cures

The curing formulations using p-quinonedioxime as an oxidizing agent are tabulated in Table I. The components were weighed out and mixed together with a spatula. This mixture was transferred to a three-roller paint mill through which it was given three passes with the rolls set for fine grinding. The mixture was cured in bulk for 16 hr. at 70°C. The cured samples were then crumbled on a rubber mill and molded in a press for 10 min. at 140°C. Sample IIB had been extracted with a 50% mixture of acetone and toluene followed by drying for 48 hr. under vacuum.

TABLE I						
p-Quinonedioxime Curing Formulations						
	Samples					
	I	II	III	IV	IX	IIB
LP-2	100	100	100	100	100	100
Pelletex	30	30	30	30	30	30
p-Quinonedi-oxime	2.5	2.5	2.5	2	2.5	2.5
Diphenylguani-dine	—	1.5	1.5	1	—	1.5
Sulfur	1.5	0.3	—	0.1	—	0.3
ZnO	—	—	—	5	—	—
Stearic acid	—	—	—	0.5	—	—
τ 80°C.	4.2	52	34	24	25	39

TABLE II					
Organic Peroxide Curing Formulations					
	Samples				
	VII	X	XI	XII	XV
LP-2	100	100	100	100	100
MgO	1.5	1.5	1.5	1.5	—
Stearic acid	1	1	1	1	—
MEKP[a]	—	—	8	—	—
DTBP[b]	—	—	—	8	—
CHP[c]	5	—	—	—	—
Co naphthenate	—	—	—	—	0.6
t-BHP[d]	—	6	—	—	6
τ 80°C.	38	50	—	—	2.7

[a] MEKP, methylethylketone peroxide.
[b] DTBP, di-tert-butylperoxide.
[c] CHP, cumene hydroperoxide.
[d] t-BHP, tert-butylhydroperoxide.

Organic Peroxide Cures

The organic peroxide curing formulations are listed in Table II. In these cures the liquid polymer, MgO, and stearic acid were mixed together with a spatula and finally blended by three passes through the paint mill. The peroxide was then added to the mixture and worked in by means of a spatula. In sample XV, the cobalt naphthenate was added and similarly mixed. Samples VII, X, and XV gave good cures at room temperature within 24 hr. Sample XI gave a rather violent reaction which resulted in a poor cure while XII gave only a partial cure. The cured samples were then crumbled on a rubber mill and molded in a press for 10 min. at 140°C.

Attempts were made to cure the liquid polymer using tert-butylhydroperoxide (t-BHP) and di-tert-butylperoxide (DTBP) with visible and ultraviolet radiation[14] to initiate the reaction without including

MgO to serve as an activator. Mixtures consisting of 6 g. LP-2 with 0.7 g. DTBP and 6 g. LP-2 with 0.6 g. t-BHP were poured into 150 mm. crystallizing dishes to give films of 10 mils thickness. One sample of each was irradiated with a G.E. RS sunlamp and a G.E. ultraviolet germicidal lamp. No appreciable amount of curing was noticed in either case after two weeks of irradiation at room temperature.

Diisocyanate Cures

The formulation for the diisocyanate cures are listed in Table III. In samples XIX, XX, and XXI the components were mixed directly while in XXII, XXIII, and XXIV the Pelletex and LP-2 were first blended by three passes through the paint

TABLE III							
Diisocyanate Curing Formulations							
	Samples						
	XIX	XX	XXI	XXII	XXIII	XXIV	XXV
LP-2	100	100	100	100	100	100	100
Pelletex	—	—	—	30	30	30	—
MDI[a]	—	—	—	10	10	—	—
MDI-50[b]	20	20	20	—	—	20	—
NMP[c]	—	—	1	1	—	1	0.5
Pyridine	0.5	—	—	—	1	—	—
NDA[d]	—	0.3	—	—	—	—	—
TDI[e]	—	—	—	—	—	—	7
τ 80°C.	—	—	120	64	52	82	(200)[f]

[a] MDI, diphenylmethane 4,4'-diisocyanate.
[b] MDI-50, 50% MDI in o-dichlorobenzene.
[c] NMP, N-methyl-2-pyrrolidone.
[d] NDA, N,N-dimethylaniline.
[e] TDI, 2,4-toluene diisocyanate.
[f] Extrapolated from Figure 6.

mill after which the diisocyanate and catalyst were mixed in with a spatula. All samples cured within 24 hr. at 70°C. The cures were crumbled by a rubber mill and molded for 10 min. at 140°C.

In sample XXV the components were mixed and poured directly into a hot mold in a vacuum oven at 70°C. The material cured completely within 24 hours. The sample was then post cured at 100°C. for 1 week.

Other cures were attempted using M-methylmorpholine, methylbenzyldimethylamine, and N,N-diethylcyclohexylamine as catalysts which caused very high reaction rates resulting in poor cures. Iron 2,4-pentanedione[15] showed only a slight degree of cure after 27 hr. at 70°C.

Metallic Oxide Cures

The metallic curing formulations are listed in Table IV. In samples V and VB, the LP-2, and Pelletex were first blended by three passes through the paint mill. A paste was prepared by dissolving the stearic acid in toluene at 70°C. and adding the PbO₂. This was mixed in a ball mill for 16 hr. before it was added to the LP-2 and Pelletex. The samples cured within 24 hr. at room temperature. These were then crumbled by a rubber mill and molded for 10 min. at 140°C. Sample VB was post cured for 5 days at 75°C. In sample VI, the LP-2 and Pelletex were blended as in V and a paste of PbO₂, stearic acid, and dibutyl phthalate was similarly prepared. These two mixtures were then combined and mixed together with a spatula. The curing and molding of sample VI were identical to V. In sample VIII, all the components except morpholine were blended on the paint mill after which the morpholine was mixed in with a spatula. This cured within 24 hr. at 70°C. and was then crumbled and molded for 10 min. at 140°C.

TABLE IV
Metallic Oxide Curing Formulations

	Samples			
	V	VI	VIII	VB
LP-2	100	100	100	100
Pelletex	30	30	30	30
Stearic acid	1.9	1.9	—	1.9
PbO₂	7.3	7.3	—	7.3
Dibutylphthalate	—	6	—	—
Toluene	5	—	—	5
MnO₂	—	—	18.9	—
Mn acetate	—	—	2	—
Morpholine	—	—	2	—
τ 80°C.	0.68	0.17	32	15

High-Energy Irradiation

A sample of LP-2 contained in a Pyrex test tube was placed in an aluminum cylinder which was then lowered into the center of the 3200 curie Co⁶⁰ source at the Esso Research Center.‡ The sample was irradiated for 60 hr. at a temperature of 40–45°C. for a total dosage of 73,300,000 roentgens. Not only was there no indication of a cure but the viscosity dropped from 560 to 328 poises. There was no noticeable change in the infrared spectrum of the irradiated LP-2.

Oxidation of Mercaptan Terminals with Ozone

A film of 6 g. LP-2 was cast in a 150 mm. crystallizing dish to give a film of 10 mils thickness. This was placed in a closed chamber under a flow of oxygen containing approximately 2% ozone. The sample was inspected after 6, 18, 33, 57, and 70 hr. exposure to ozone. At no time was there any evidence of cure. There was also no apparent change in the infrared spectrum of the exposed material.

Catalyzed Air Oxidation of Mercaptan Terminals

Ten grams of LP-2, 0.4 g. NaOH, and 1 g. β-napthol were thoroughly ground and the resulting mixture poured into a 150 mm. crystallizing dish to form a film of 15 mils thickness. The film cured to a weak sheet in 5 hr. at room temperature.

Ten grams of LP-2, 0.4 g. NaOH, and 0.6 g. phenol were mechanically mixed and then placed in a 150 mm. crystallizing dish to form a similar film. This film required 5 days for a complete cure at room temperature.

Two 10-mil films containing 6 g. LP-2 with 1.5 and 1.0 g. 2,4,6-tris(dimethylaminomethyl) phenol were cast in 150 mm. crystallizing dishes. The first cured after 3 weeks and the second after 5 weeks at room temperature.

Stress-Relaxation Measurements

All measurements were made on Firestone relaxometers[16] which had been modified for strip samples.[17] The data have been plotted as relative stress, f/f_0, as a function of logarithmic time. The reference stress, f_0, was determined by graphical interpolation for the time 0.01 hr. The stress decay at constant strain and temperature has been found to obey approximately the equation, $f/f_0 =$

‡ We are indebted to Drs. Black and Guthrie of the Esso Research Center for their cooperation with this phase of the work.

$e^{-t/\tau}$, where τ is the relaxation time of the sample at the specified temperature. The relaxation time, τ, is equal to the time required for the stress to decay to $1/e$ or 36.8% of its reference value. As τ may be considered to be the reciprocal of a reaction rate constant, it is possible to calculate an activation energy for the process from the slope of a plot of $\log \tau$ vs. $1/T$.

RESULTS AND DISCUSSION

The stress-relaxation data at 80°C. for the p-quinonedioxime cures of the liquid polymer are presented in Figures 1 and 2 and the relaxation times of the various samples are included in Table I. The curing action is due to the oxidation of the mercaptan terminals to disulfide linkages while the p-quinonedioxime is reduced to p-phenylenediamine:

—ᴡᴡ—SH + HON= ⬡ =NOH + HS—ᴡᴡ—

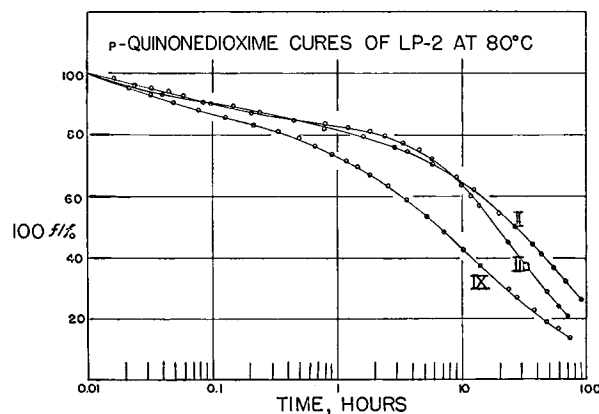⟶ —ᴡᴡ—S—S—ᴡᴡ— + H₂N⬡NH₂
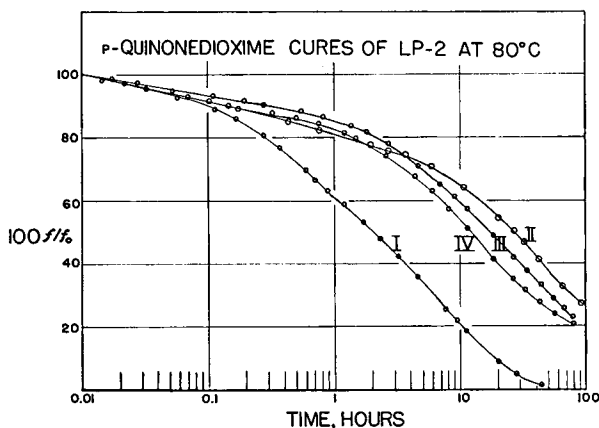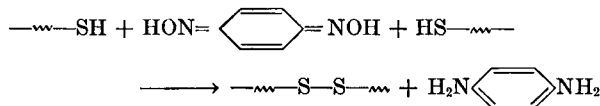
Figure 1.

Figure 2.

The effect of sulfur on the relaxation rate is shown in Figure 1. Small amounts of sulfur (II) are seen to cause a retarding effect upon the relaxation rate while large amounts (I) greatly accelerate the rate of stress decay. It had been previously observed that in the absence of ionic catalysts the disulfide-disulfide and disulfide-mercaptan interchange reactions proceed very slowly[3,4,8,18] compared to the rate of the catalyzed reaction. This can explain the retarding effect of small amounts of sulfur included in the curing formulation by their combining with ionic impurities present and thus rendering them harmless as to their catalytic activity. In the case where a large excess of sulfur is added it is probable that appreciable amounts of higher sulfides are formed under the conditions prevailing

—ᴡᴡ—S—S—ᴡᴡ— + S₈ ⟶ —ᴡᴡ—Sₓᴡᴡ—
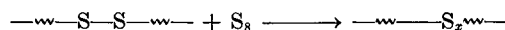
during the curing process. It had been shown that while disulfide-disulfide exchange proceeds slowly in the absence of ionic material, the trisulfide-trisulfide and trisulfide-disulfide interchange reactions occur readily.[7,19,20] This could well account for the increase observed in the relaxation rate.

It had also been observed that the exchange rate is greatly accelerated by increasing the pH[4,21,22] of the system. To observe this effect a cure was performed, IX, omitting the accelerator, diphenylguanidine. The cure obtained was rather poor and the rate of stress relaxation was quite high. As the reduced form of the oxidizing agent, p-phenylenediamine, is also quite basic and could similarly affect the exchange rate. The sample IIB, identical with II, was extracted with a mixture of acetone and toluene to remove the p-phenylenediamine, diphenylguanidine, and the unreacted p-quinonedioxime. The observed relaxation time for this sample was noticeably lower than the original, II, which indicates that these organic bases probably have little accelerating effect on this exchange reaction.

The data for the cures effected by organic peroxides are given in Figure 3 and Table II. Attempts to cure the liquid polymer with only the peroxide and without the inclusion of an activator were unsuccessful. Further attempts to decompose the peroxide photochemically[13] by the use of visible and ultraviolet radiation to obtain a cure were also without success. Curves were obtained using tert-butylhydroperoxide and cobalt[23] naphthenate as an activator. However, due to the catalytic effect of the cobalt ions upon the rate of the disulfide interchange reaction, the decay time of
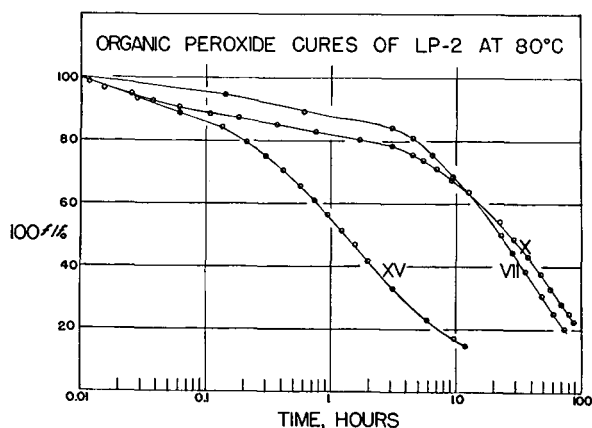
Figure 3.

this sample at 80°C. was extremely short. Good cures were obtained using magnesium oxide as an activator with both *tert*-butyl and cumene hydroperoxides but no cure resulted from di-*tert*-butylperoxide and a poor cure from methylethylketone peroxide. The mechanism for this reaction, whether it is free radical or ionic, is not known. An attempt to polymerize styrene using the *tert*-butylhydroperoxide–magnesium oxide system was unsuccessful. The decomposition of tertiary hydroperoxides in the presence of alkali[24] has been observed to proceed rapidly at elevated temperature with the evolution of oxygen by what is believed to be an ionic mechanism. The difference in relaxation rates between the *tert*-butyl and cumene hydroperoxide cures may be due to the substantial amount of benzoic acid formed by the basic decomposition of the cumene hydroperoxide. The benzoic acid once formed can then attack the formal linkages along the network chains of the elastomer
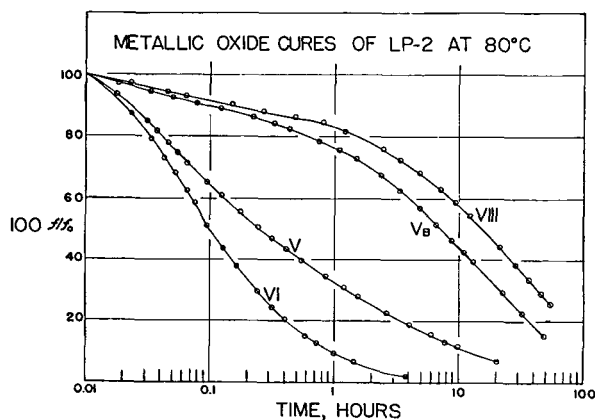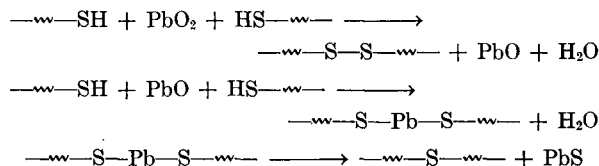

Figure 4.

thus increasing the total rate of effective chain cleavage.

Data for cures of the liquid polymer with the metallic oxides, PbO_2 and MnO_2, are given in Figure 4 and Table IV. From Figure 4 the PbO_2 curves, samples V and VI, are seen to decay at an exceedingly high rate such as to suggest molecular flow due to incomplete curing of the samples as the cause of the stress relaxation. Sample VB, identical with V except that it was post cured at 80°C. for one week, had a relaxation time twenty times that of V which was not post cured. However, the initial moduli at 80° of these two samples were comparable, thus indicating that the extent of cure in both cases was about the same. The following mechanism for the curing reaction had been proposed:[25]

$$—\text{\small www}—SH + PbO_2 + HS—\text{\small www}— \longrightarrow$$
$$—\text{\small www}—S—S—\text{\small www}— + PbO + H_2O$$
$$—\text{\small www}—SH + PbO + HS—\text{\small www}— \longrightarrow$$
$$—\text{\small www}—S—Pb—S—\text{\small www}— + H_2O$$
$$—\text{\small www}—S—Pb—S—\text{\small www}— \longrightarrow —\text{\small www}—S—\text{\small www}— + PbS$$

From work done on other types of metallic sulfide compounds,[18] it is apparent that the lead dimercaptide groups present to a great extent in V would undergo exchange reactions quite readily. From the observation of PbS diffusing to the surface of the sample during the post curing process, it was evident that a great portion of these lead dimercaptide groups were converted to monosulfide linkages. As it had been previously shown that monosulfides do not participate in interchange reactions,[6,9] the removal of these exchanging dimercaptide groups increased the relaxation time by a factor of twenty.

The overall reaction of the MnO_2 cure may be given

$$—\text{\small www}—SH + MnO_2 + HS—\text{\small www}— \longrightarrow$$
$$—\text{\small www}—S—S—\text{\small www}— + H_2O + MnO$$
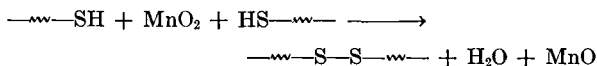
However, the reaction of the liquid polymer and MnO_2 alone proceeds quite slowly in the absence of an activator, such as the manganous ion, or in an acidic medium. It is thus probable that the curing reaction consists of an elaborate mechanism involving a number of oxidation states of manganese. As can be seen from Figure 4 and Table IV, the relaxation time for this cure is much greater than for the PbO_2 cures. This perhaps indicates that the dimercaptide either is converted to the monosulfide much more easily than in the case for PbO_2 or is not formed at all. Also, the added manganous ion probably undergoes some disproportionation
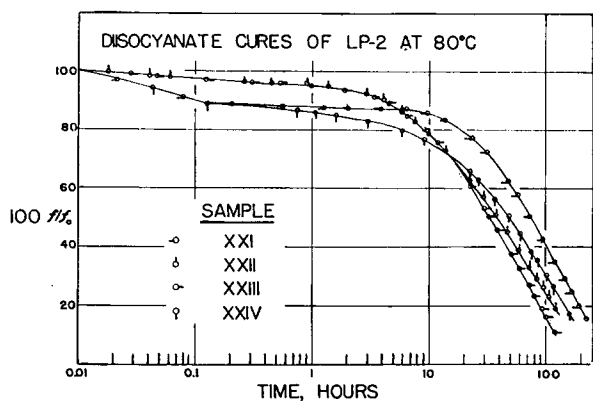
Figure 5.

reaction with the higher oxidation states of manganese to form nonionic oxides thus rendering it unable to catalyze the disulfide interchange.

Table III and Figures 5 and 6 contain data concerning diisocyanate cures of the liquid polymer. The curing process consists of the reaction of the mercaptan terminals of the liquid polymer with isocyanate groups resulting in the formation of isothiourethane linkages:

—ww—SH + OCN—R—NCO + HS—ww— ———→

—ww—S—CO—NH—R—NH—CO—S—ww—
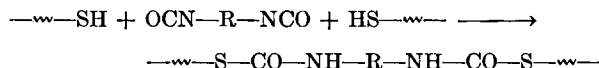
This reaction is also base catalyzed.[14] It is seen that the relaxation rate is dependent upon the diisocyanate, catalyst, and filler used in the cure. However, the relaxation times for this type of cure are seen to be far greater than that of any others, primarily due to the absence of ionic materials and reaction products of the curing process. The activation energy for the stress decay was found to be 36.6 kcal. from the plot in Figure 6. This differs greatly from the value of 24 kcal.[1,2] found for
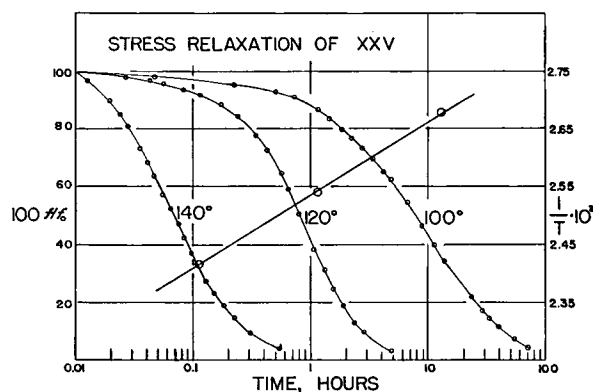

Figure 6.

other types of cures. The possibility thus arises that in the absence of ionic material the disulfide interchange occurs by a different mechanism or that the disulfide exchange reaction proceeds so slowly that the rate determining step of the decay process is the cleavage of the isothiourethane linkages.

Attempts to cure the liquid polymer without the addition of curing agents were totally unsuccessful. The effect of the gamma radiation from a Co[60] source led to a decrease in viscosity of the liquid polymer which is in agreement with the previous observation that cured rubbers of this type are degraded by high-energy radiation.[26] The attempt to oxidize the mercaptan terminals of a thin film of the material by its exposure to ozone also ended in failure. If either method had succeeded, it would then have been possible to measure the rate of interchange in the absence of all extraneous material.

The stress at constant elongation of the samples prepared by catalyzed air oxidation[11-13] decayed extremely rapidly. As the catalyst consisted of a suspension of a phenol type compound and sodium hydroxide, the cause of the short relaxation time is the action of this same catalyst system upon the disulfide interchange reaction.

It thus appears that the exchange reaction occurs predominantly by an ionic mechanism as it is seen to be both catalyzed by ionic material and also highly pH dependent. However, it is also apparent that the interchange can occur by a free radical mechanism as evidenced by the increase in relaxation rate of samples undergoing ultraviolet irradiation[2] and the photochemical redistribution of RS groups between disulfides and thiols or other disulfides.[5,7] Also, the mercaptyl radical, prepared by the photochemical dissociation of disulfides, has been used to initiate the polymerization of butadiene and styrene.[27,28] The total relaxation process may proceed by both these mechanisms. In the presence of ionic salts or an alkaline medium, the ionic mechanism would proceed at a high rate such as to overshadow the free radical contribution. In the absence of these catalysts, such as in the isocyanate cures, the free radical mechanism would account for a significant portion of the interchange reaction.

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Synopsis

The effect of curing agents and their reaction products upon the disulfide interchange reaction of cured liquid polysulfide polymers was studied. The curing process involved the oxidation of the mercaptan terminals of the liquid polymer to disulfide linkages or the reaction of these end groups with some polyfunctional reagent. Several different types of cure were attempted on the same batch of the liquid polymer including oxidation by metallic oxides, organic peroxides, and hydroperoxides, p-quinonedioxime, and catalyzed air oxidation. Cures were also obtained by the use of diisocyanates. The disulfide interchange was studied by means of stress relaxation. It was found that the rate of exchange was greatly accelerated by the presence of ionic or alkaline materials. In their absence the exchange reaction proceeded quite slowly. The incorporation of excess sulfur also increased the reaction rate. The mechanism of the reaction is believed to be predominantly ionic.

Résumé

L'effet d'agents de traitement et de leurs produits de réaction sur la réaction d'échange de disulfure a été étudié dans le cas de polymères polysulfures liquides. Le traitement comporte l'oxydation des extrémités mercaptans du polymère liquide en liaisons disulfures ou la réaction de ces fins de chaîne avec une réactif polyfonctionnel. De nombreux types différents de traitement ont été essayés sur le même polymère liquide, y compris l'oxydation par les oxydes métalliques, les peroxydes organiques et hydroperoxydes, la p.quinone dioxime et l'oxydation catalytique à l'air. Les traitements ont été effectués également au moyen de diisocyanates. L'échange des disulfures a été étudié par des mesures de relaxation à la tension. On a trouvé que la vitesse d'échange était considérablement accélérée par la présence de matériaux ioniques ou alcalins. En leur absence la réaction d'échange n'avance que bien lentement. L'incorporation d'un excès de soufre accroît également la vitesse de réaction. Le mécanisme de la réaction est principalement ionique.

Zusammenfassung

Es wurde der Einfluss von Vulkanisationsmitteln und ihren Reaktionsprodukten auf die Disulfidaustauschreaktion von vulankisierten, flüssigen Polysulfidpolymeren untersucht. Der Vulkanisationsvorgang erfolgte in Form einer Oxydation der Merkaptanendgruppen des flüssigen Polymeren zu Disulfidbindungen oder in Form einer Reaktion dieser Endgruppen mit gewissen polyfunktionellen Reagenzien. Einige verschiedene Vulkanisationsverfahren wurden an ein und derselben Probe des flüssigen Polymeren durchgeführt und zwar Oxydation durch Metalloxyde, organische Peroxyde und Hydroperoxyde, p-Chinondioxim und katalytische Oxydation mit Luft. Bei Anwendung von Diisocyanaten wurden gleichfalls Vulkanisate erhalten. Der Disulfidaustausch wurde mittels der Spannungsrelaxation untersucht. Es wurde gefunden, dass die Austauschgeschwindigkeit durch die Anwesenheit von Ionen oder Alkalien stark beschleunigt wurde. In Abwesenheit dieser Stoffe ging die Austauschreaktion sehr langsam vor sich. Die Anwendung eines Schwefelüberschusses erhöhte ebenfalls die Reaktionsgeschwindigkeit. Es wird angenommen, dass es sich um einen vorwiegend ionischen Reaktionsmechanismus handelt.