

Influence of Hydrofuranide on Network Structure and Kinetics of Thiuram Vulcanization

B. BANERJEE,* S. N. CHAKRAVARTY,** and A. B. BISWAS,
*Department of Chemistry, Indian Institute of Technology, Bombay-400076,
India*

Synopsis

The influence of hydrofuranide (a reaction product of furfural and ammonia) on the network structure and overall kinetics of thiuram vulcanization of natural rubber is reported. The nature of the network structure of the thiuram vulcanizates in the presence and absence of hydrofuranide was determined using triphenyl phosphine (Ph_3P) as a chemical probe. The presence of hydrofuranide produces structural complexity of the vulcanizate. The overall kinetics of thiuram vulcanization follows a first-order-rate law in the presence as well as in the absence of hydrofuranide. The rate constant increases while the energy of activation decreases in the presence of hydrofuranide.

INTRODUCTION

The influence of hydrofuranide as a booster for thiazole-accelerated vulcanization has been reported earlier.¹ In thiuram vulcanization, the presence of hydrofuranide causes an increase in cure rate but a decrease in crosslink density.^{2,3} This type of negative effect of accelerator combination on crosslink density has not been observed previously. The influence of amines on thiuram vulcanization is related³ to the basicity of the amines: the higher the basicity of the amine, the greater the cure rate, but the lower the crosslink density. The decrease in crosslink density of thiuram vulcanizate in the presence of amines is due to interaction of thiuram disulfide and amine resulting in a noncrosslinking reaction.⁴ The course of the reaction between thiuram disulfide and amine has been studied⁴ using various analytical tools such as thermogravimetric analysis (TGA), gas-chromatographic analysis, and infrared spectroscopy (IR).

This paper reports the role of hydrofuranide on the network structure and the overall kinetics (reaction order, rate constant, energy of activation) of thiuram vulcanization.

EXPERIMENTAL

The preparation of hydrofuranide, the quality of natural rubber (NR), the compounding ingredients and the mixing and vulcanization procedure has been reported earlier.¹⁻³ The compounds were cured (vulcanized) at 150°C.

* Present address: IRMRA, Bombay, India.

** Present address: Modi Rubber Ltd., Modipuram, Meerut, U.P., India.

Determination of Energy of Activation

The cure characteristics of compounds were studied with the Monsanto rheometer (model R-100) fitted with a micro die. The apparent energy of activation was determined from the slope of straight-line plots of $\log t_{90}$ (t_{90} = time required to attain 90% of maximum torque) against reciprocal of absolute temperature using the following equation^{5,6}:

$$\text{slope} = \frac{E}{2.303R} \quad (1)$$

where E = apparent energy of activation and R = gas constant (1.987 cal/deg mole).

Kinetics Study of Vulcanization Reaction

For a first-order reaction the kinetic equation is as follows⁵:

$$\ln(a - x) = -kt + \ln a \quad (2)$$

where k = reaction rate constant, a = the initial concentration, and x = the reacted quantity at time t . In vulcanization, a physical property such as modulus is taken as the measure of the extent of reaction rather than the change of reactant concentration. The above equation can be written in a modified form as

$$\ln(F_{\infty} - F) = -kt + \ln(F_{\infty} - F_0) \quad (3)$$

where F_{∞} is the maximum modulus when the reactants are consumed, F is the modulus at time t , and F_0 is the modulus at zero time.

For a second-order reaction, the equation is

$$\frac{1}{F_{\infty} - F} = kt + \frac{1}{F_{\infty} - F_0} \quad (4)$$

In this study, the values of F_{∞} , F , and F_0 were determined from the rheometric torque, which reflects the shear modulus. This can be considered a satisfactory measure of cure.⁶

In the thiuram vulcanization system, the cure curve after the attainment of maximum torque follows a plateau pattern (as these compounds are reversion resistant). So the value of t_{\max} was taken as the value of F_{∞} . Thus, the value of $F_{\infty} - F$ was determined by subtracting from t_{\max} the torque values at different time of cure.

Determination of Combined Sulfur

The combined sulfur S_c in the vulcanizate was determined by the zinc-nitric acid method in accordance with standard ASTM procedure.⁷ The acetone-extracted vulcanizates were digested with zinc-nitric acid solution, followed by oxidation with concentrated fuming nitric acid. The sulfur in the vulcanizate was oxidized to sulfate, which was estimated gravimetrically. Corrections were made for the presence of sulfidic sulfur.

Determination of Crosslink Density and Crosslink Efficiency

The physical crosslink density of the vulcanizates was determined by the equilibrium swelling method using the Flory–Rehner equation.^{1-3,6,8} The chemical crosslink density was computed by the Mullins equation⁹ from the value of elastic constant C_1 and physical crosslink density. The Mullins equation for elastic constant is

$$C_1 = [\rho RT(2Mc_{\text{chem}})^{-1} + 0.78 \times 10^6] \times [1 - 2.3(mc_{\text{chem}}) \bar{M}_n^{-1}] \text{ dyn/cm}^2 \quad (5)$$

where ρ is the vulcanizate density, R is the molar gas constant, T is the absolute temperature, \bar{M}_n is the initial molecular weight of rubber hydrocarbon in the mixture, and $(2Mc_{\text{chem}})^{-1}$ is the density of chemical crosslinks and is reported as g mole/g rubber hydrocarbon (RH). C_1 is the elastic constant pertinent to rubber hydrocarbon in the vulcanizate which was calculated from the following relationship¹⁰:

$$-[\ln(1 - V_r) + V_r + XV_r^2] = 2C_1 V_0 \left(V_r^{1/3} - \frac{V_r}{2} \right) / RT \quad (6)$$

where V_r = volume fraction of rubber in swollen vulcanizate (using the equilibrium swelling method), V_0 = molar volume of the solvent, and X = solvent–polymer interaction constant (0.437 for natural rubber vulcanizate swollen in benzene at $25 \pm 1^\circ\text{C}$).

The value of \bar{M}_n of natural rubber was determined by the intrinsic viscosity method using the equation

$$[\eta]_{\text{benzene}} = 2.29 \times 10^{-7} \bar{M}_n^{1.33} \quad (7)$$

The crosslink efficiency is defined as the number of atoms of sulfur combined in the vulcanizate network per chemical crosslink. Hence, crosslink efficiency was computed by dividing combined sulfur by chemical crosslink density.

Structural Characterization of Vulcanizates

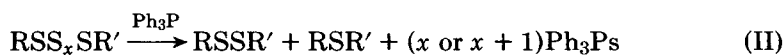
In this study, triphenyl phosphine in benzene is used as a chemical probe for elucidating the network structure. The reactions of triphenyl phosphine with organic polysulfides are as follows:

(1) Simple alkyl and benzyl polysulfides are smoothly desulfurized to disulfides according to the following equation:



where $\text{R} = \text{R}' = \text{alkyl}$, $\text{Ph} = \text{phenyl}$.

(2) Di(2-alkenyl) di- and polysulfides are desulfurated to disulfides and to monosulfides according to the reaction time, temperature, and detailed structure. A typical equation is as follows:



Thus, unsaturated polysulfides $\text{RSS}_x\text{SR}'$ in networks are expected to lose at least x and not more than $x + 1$ atoms of sulfur per molecule of triphenyl phosphine.

Moore and Trego¹¹ also introduced a parameter E' which they define as the number of gram-atoms of sulfur remaining in the network per chemical crosslink originally present after treatment with triphenyl phosphine. A comparison of E value (number of atoms of sulfur per chemical crosslink before treatment with triphenyl phosphine) with E' shows the extent of main chain modification and polysulfide crosslinks.

In this study, the experimental method is the same as that used by Moore and Trego.¹² The vulcanizate was extracted with acetone in a Soxhlet for 96 hr. A weighed portion (1 g) of the extracted vulcanizate was allowed to swell overnight in a solution (20 ml) of triphenyl phosphine in dry benzene under nitrogen, and the solvent was removed at room temperature *in vacuo*. The concentration of the solution was calculated from the predetermined degree of swelling of the vulcanizate in benzene such that 1 g-mole triphenyl phosphine per g-at. network combined sulfur was retained in the dried vulcanizate. The dried vulcanizate was weighed and then heated in a glass ampoule *in vacuo* for 96 hr at 80°C. The treated sample was then extracted continuously with cold benzene for 24 hr under nitrogen in the dark to remove any excess triphenyl phosphine and triphenyl phosphine sulfide.

The combined sulfur in the original and triphenyl phosphine-treated sample was determined by the zinc-nitric acid method. The parameters E and E' were determined by chemical crosslink density and the combined sulfur of the original and triphenyl phosphine treated sample.

RESULTS AND DISCUSSION

Kinetics of Thiuram Vulcanization (Influence of Hydrofuramide)

The plots of $\log (F_{\infty} - F)$ versus time of cure is shown in Figure 1. All the plots

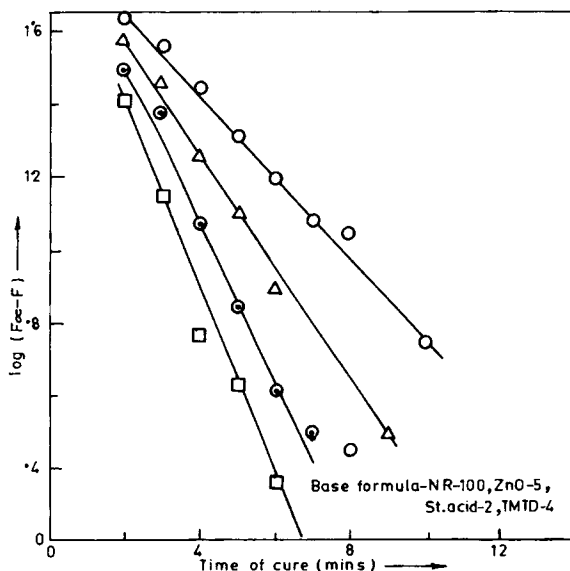


Fig. 1. Influence of hydrofuramide on kinetics of thiuram vulcanization: (O), no hydrofuramide, (Δ), 1 phr hydrofuramide; (\odot), 2 phr hydrofuramide; (\square), 3 phr hydrofuramide.

show a straight-line pattern, indicating that the thiuram vulcanization follows a first-order-rate law up to the level of 3 phr (parts per hundred rubber) of hydrofuramide. The reaction rate constant k , calculated from the slope of these plots, is plotted against the hydrofuramide concentration (Fig. 2). The value of k increases with increasing levels of hydrofuramide, from 0.28 (for the control compound containing no hydrofuramide) to 0.53 by inclusion of 2 phr hydrofuramide. Beyond 2 phr, k increases further with increasing levels of hydrofuramide, but the rate is slower.

Energy of Activation

The Arrhenius plots of thiuram vulcanization are shown in Figure 3. Plots of $\log t_{90}$ versus the reciprocal of absolute temperature follow a linear relationship in all cases, suggesting that the Arrhenius equation holds in the range studied. The apparent energy of activation (E) calculated from the slope of the straight-line plots is shown on the graphs; E is reduced by about 12.0% by incorporation of 2 phr hydrofuramide. The increase in cure rate and the reduction of energy of activation suggest that hydrofuramide promotes the rate-determining step of thiuram vulcanization.

Structural Characterization of Vulcanizates

The influence of hydrofuramide on the structural pattern of thiuram vulcanizate has been studied using triphenyl phosphine as the chemical probe. The formulation of compounds A and B is given in Table I, and results of this study are represented in Table II.

Table II shows the change of S_c^a (combined sulfur in the vulcanizate before treatment with Ph_3P) and $S_c'^b$ (combined sulfur after treatment with Ph_3P) as

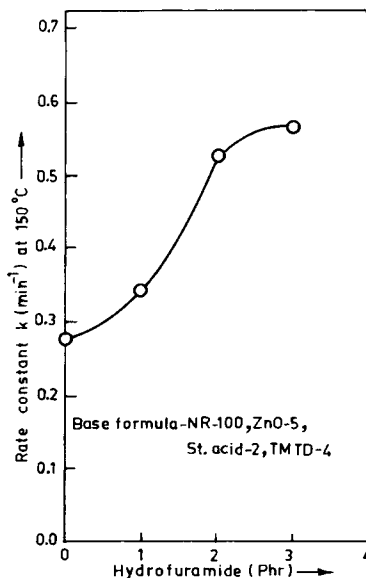


Fig. 2. Influence of hydrofuramide on rate constant of thiuram vulcanization.

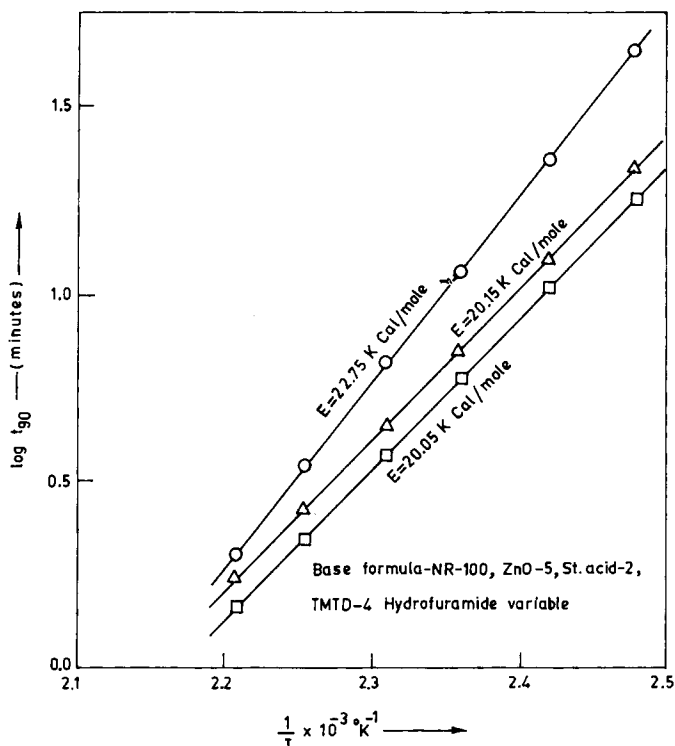


Fig. 3. Influence of hydrofuramide on activation energy of thiuram vulcanization system: (O), no hydrofuramide; (Δ), 2 phr hydrofuramide; (\square), 3 phr hydrofuramide.

a function of cure time. S_c^a decreases with time of cure in case of compound A, while the trend is reversed for compound B (Table II).

As the cure time increases, both the values of E^a (g-at. of combined sulfur in the network before treatment with Ph_3P) and E'^b (g-at. of combined sulfur in the network after treatment with Ph_3P) decrease in the case of mix A. In the case of mix B, E^a and E'^b increase with cure time.

At a particular cure time, the values of E^a and E'^b are higher with mix B than with mix A. These observations indicate less efficient utilization of sulfur in the formation of crosslink and increased modification of the main chain in mix B, i.e., addition of hydrofuramide increases the structural complexity in the vulcanizates.

The gradual decrease in combined sulfur S_c^a and $S_c'^b$ with increasing cure time in the case of compound A can be explained in the following way: According to Bateman and co-workers,¹³ thiuram vulcanization in the presence of zinc oxide

TABLE I
Composition of the Mixes

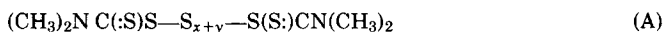
	Mix A	Mix B
Natural rubber	100	100
ZnO	5	5
Stearic acid	2	2
TMTD	4	4
Hydrofuramide	—	1.5

TABLE II
Chemical Characterization of Vulcanizate Networks

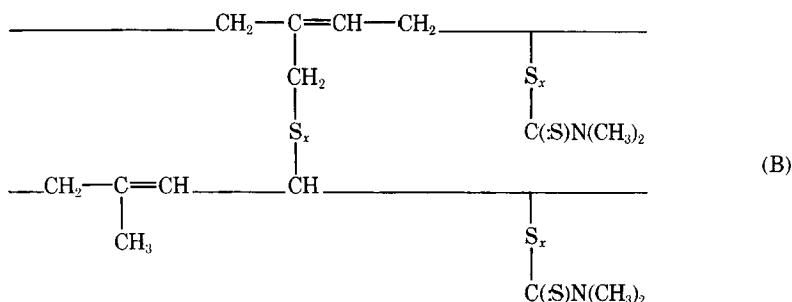
Mix	Cure time, min	Total chemical crosslink density ($2M_c \text{chem}$) ⁻¹ × 10 ⁵ , g mole/g RH	Network combined sulfur × 10 ⁴ ,		Sulfur efficiencies, atom/chemical crosslink $\frac{E^a}{E^b}$	S_c removed by Ph ₃ P treatment, %
			S_c^a g-at./g RH	S_c^b		
A	10	3.72	3.46	2.16	9.3	37.6
	20	4.05	2.79	1.98	6.9	29.0
	120	4.00	2.52	1.88	6.3	25.4
	240	3.50	1.89	1.42	5.4	24.9
B	10	3.15	3.62	1.94	11.5	46.0
	20	3.03	3.88	2.18	12.8	43.8
	120	2.80	4.03	2.60	14.4	35.4
	240	2.55	3.95	2.68	15.5	32.0

^a Superscript "a" = before Ph₃P treatment; superscript "b" = after Ph₃P treatment.

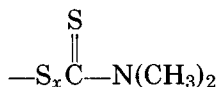
proceeds according to an ionic mechanism. A polysulfide of the type^{4,13}



is first formed and yields active sulfur for crosslinking and a fragment of the polysulfide appears as a pendent group. The network structure of thiuram vulcanizate can be represented as follows^{6,13}:



Thus, in thiuram vulcanization some of the sulfur is present in the crosslink, but the rest is located in pendent groups of the type



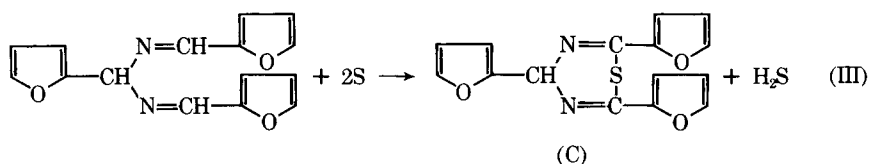
which are situated at the α -CH₃ and α -CH₂ groups along the main polyisoprene chain. The number of these groups decreases relative to the crosslinks as the cure proceeds and the average value of x in $\text{S}_x\text{C}(\text{S})\text{N}(\text{CH}_3)_2$ decreases so that only $\text{---S---C}(\text{S})\text{N}(\text{CH}_3)_2$ groups survive in a fully cured vulcanizate. Thus, the pendent groups where $x \geq 2$ are believed to be the precursors of actual crosslinks. These can be identified with a rubber-bound intermediate compound that undergoes subsequent reaction to yield crosslinks and the zinc salt of dimethyl dithiocarbamic acid.

The above line of argument also explains the decrease of E^a and E'^b values (in case of compound A) with increasing cure time.

In the case of compound B, S_c^a and $S_c'^b$ increase with increasing cure time up to 120 min, beyond which the values remain almost constant. The values of E^a and E'^b also increase with cure time. Structural complexity increases considerably with incorporation of hydrofuramide. This is probably due to an interaction of tetramethylthiuram disulfide (TMTD) and amine.⁴ Such interaction of TMTD and hydrofuramide⁴ results in gaseous products consisting chiefly of hydrogen sulfide and a thiol. Hydrogen sulfide results from thermal reaction of active sulfur (produced from thiuram trisulfide as proposed by Craig¹⁴ or from the so-called polysulfide as proposed by Bateman¹³) with hydrofuramide. Thus, in the presence of hydrofuramide, the sulfur donated by thiuram disulfide is consumed by both rubber and hydrofuramide. This will eventually decrease the value of x in the pendent group $\text{---S}_x\text{C}(\text{S})\text{N}(\text{CH}_3)_2$ known to be the precursor of crosslinks.

Alternatively, the consumption of sulfur from the polysulfide (A) by both rubber and hydrofuramide may result in a residue which will contribute only $\text{---SC}(\text{S})\text{N}(\text{CH}_3)_2$ as the pendent group to the main chain.

The thermal reaction of active sulfur and hydrofuramide is as follows⁴:



The IR spectra of reaction product of hydrofuramide and sulfur shows a band around 850 cm^{-1} corresponding to a C-S linkage which supports the formation of compound C.

If the pendent group of the type $-\text{SC}(\text{S})\text{N}(\text{CH}_3)_2$ is formed, the crosslink density will not increase with time of cure, while the combined sulfur and efficiency values will increase as is observed in the case of compound B. Thus, the interaction of TMTD/hydrofuramide, which was reported⁴ to be responsible for a decrease in the crosslink density, is also responsible for increasing the structural complexity and main chain modification of the vulcanizate.

References

1. B. Banerjee, *Angew. Makromol. Chem.*, to appear.
2. B. Banerjee, *Kautschuk Gummi Kunstst.*, **32**, 13 (1979).
3. B. Banerjee, First Dunlop Award for best fundamental research in rubber in India in 1977-78.
4. B. Banerjee, S. N. Chakravarty, B. V. Kamath, and A. B. Biswas, *J. Appl. Poly. Sci.*, **24**, 683 (1979).
5. A. E. Juve, "Rate of Cure and Related Matters," in *Vulcanization of Elastomers*, G. A. Alliger and I. J. Sjothun, Eds.
6. B. Banerjee, Ph.D. thesis, University of Calcutta, January 1979.
7. ASTM, D-297, American Standard for Testing of Materials, Part 28, 1971.
8. P. J. Flory and R. Rehner, *J. Chem. Phys.*, **11**, 512 (1943); **11**, 521 (1943).
9. L. Mullins, *J. Appl., Poly. Sci.*, **2**, 1 (1959).
10. P. J. Flory, *J. Chem. Phys.*, **18**, 108 (1950).
11. C. G. Moore and B. R. Trego, *J. Appl. Poly. Sci.*, **8**, 1957 (1964).
12. C. G. Moore and B. R. Trego, *J. Appl. Poly. Sci.*, **5**, 299 (1961).
13. L. Bateman, C. G. Moore, B. Saville, and M. Porter, "Chemistry of Vulcanization," in *Chemistry and Physics of Rubberlike Substances*, L. Bateman, Ed., Maclaren, London, Wiley, New York, 1963, p. 525.
14. D. Craig, A. E. Juve, and W. L. Davidson, *J. Polym. Sci.*, **5**, 709 (1950).

Received August 6, 1979

Revised October 3, 1979