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Network Structure in Terms of Prepolymer and Curative Parameters. II

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ABSTRACT

In previously reported work, an equation was developed relating the cross-link density of a network formed from telechelic polymers with properties of the prepolymer mix. The absolute value of the network cross-link density in moles/gram was found to be

$$2q\ (1 - 1/f_a - 1/f_p)(\mathrm{CDF})W_g$$

where q = equivalents of functional groups per gram of prepolymer, f_p = functionality of prepolymer, f_a = functionality of cross-linking agent, CDF = cross-link decrease factor, a nearly constant number now believed to have a value between 0.20 and 0.38, and W_g = weight fraction of gel. The CDF term is the factor by which the cross-link density in the gel is decreased because of failure of the reaction to go to completion at the maximum degree of cure.

A mistake made in the derivation of the equation is now corrected and the CDF term is shown to be in a different and simpler form than previously given. In additional work the reactant ratio, r, has been introduced into the relation which becomes:

$$X_d = 2q(BF)(CDF)W_g$$

where (CDF) is $(e - e_c)/(1 - e_c)$, (BF) or branching function is $(r - r/f_a - 1/f_p)$ when $r < 1$ and $(1 - r/f_a - 1/f_p)$ when $r > 1$, e is the final extent of reaction of the prepolymer functional groups, and e_c is their extent of reaction at the gel point.

For the case where r = 1, values of the branching function, the cross-link decrease factor, and the cross-link density per reactant equivalent were computed.

The degree to which the equation is followed by real stocks was examined. Young's modulus, the reciprocal of the elongation-at-break, the hardness, and solvent swelling data ($V_2^{5/3}$ × percent gel) were found to vary linearly with q(BF). When the crosslink decrease factor was given the value 0.25, agreement between the first equation above and crosslink density calculated from equilibrium modulus of elasticity and from the solvent swollen compression modulus was within a factor of 1.5 in three cases.

INTRODUCTION

Intermediate molecular weight prepolymers containing reactive groups are commonly converted to resinous or elastomeric materials by reaction with polyfunctional epoxides, isocyanates, or aziridines for use as adhesives, coatings, sealants, or propellant binders. A description of the network structures formed in terms of prepolymer and cross-linking agent parameters is needed. In a previous report [1] a relationship was presented between network cross-link density and properties of telechelic prepolymer mixes such as reactive group content, functionality, and including the maximum or final extent of reaction of the functional groups and the gel content of the cured stock. The effect of the ratio of the reactants was omitted from the discussion and no experimental evidence supporting the conclusions was presented.

In the present work the discussion is expanded to include the reactant ratio, a mistake in the previous reasoning is corrected, and experimental results are shown.

DISCUSSION

Recapitulation

In earlier work [1] an equation was developed relating the cross-link density of a network formed from telechelic polymers with properties of the polymer mix.

At an equivalent reactant ratio of 1.0 to 1.0 and with the branch points uniting no more than three chain ends, the cross-link density in the gel was found to be proportional to the product of a concentration term, q, and a geometrical term, $(1 - 1/f_a - 1/f_p)$, which is called the branching function. The absolute value of the network cross-link density in moles/g was found to be

$$2q(1 - 1/f_a - 1/f_p)(\mathrm{CDF})W_g \tag{1}$$

where q = equivalents of prepolymer functional groups per gram, f_p = functionality of prepolymer, f_a = functionality of cross-linking agent, CDF = cross-link decrease factor, a nearly constant number now believed to have a value between 0.20 and 0.38, and W_g = weight fraction of gel. The CDF term is the factor by which the crosslink density in the gel is decreased because of failure of the reaction to go to completion at the maximum degree of cure.

In the derivation of Eq. (1), the first step was the determination of the cross-link density of a stock formed from a telechelic prepolymer and a low molecular weight cross-linking agent at a 1 to 1 equivalent reactant ratio in which it was assumed that all functional groups had reacted. In the next step the condition of the gel was examined. It was assumed that all the prepolymer in the sample considered was tied to the gel but some functional groups remained unreacted. The cross-link density was taken as two-thirds of the number of chain segments in the volume of network divided by the molecular weight of that volume. From the total number of segments at the final reaction was subtracted the number of segments associated with the unreacted groups, and from the total molecular weight was subtracted the molecular weight associated with the unreacted groups. In order to calculate the number of segments associated with the unreacted groups, a parameter of unknown value was introduced which was evaluated by imposing the condition that the cross-link density at the gel point was zero and solving for the parameter in terms of the extent of reaction at the gel point.

A mistake was made. If the number of segments in the gel varies, the changed number of segments is still in the same volume or weight of material. Hence, the same molecular weight should be used and we should not subtract the weight associated with the unreacted groups. Making this change, the relation is simplified and the cross-link decrease factor becomes $(e - e_c)/(1 - e_c)$, where e is the final extent of reaction of the prepolymer functional groups and e_c is their extent of reaction at the gel point.

The third step in the derivation was to introduce the relative proportion of gel and sol into the relation

$$X_d = \frac{W_g X_g + W_s X_s}{W_g + W_s} = W_g X_g \tag{2}$$

where X_d = cross-link density of whole stock

X_g = cross-link density in gel

X_s = cross-link density in sol = 0

W_g = weight fraction of gel

W_s = weight fraction of sol

Then

$$X_d = 2q(1 - 1/f_a - 1/f_p)\left(\frac{e - e_c}{1 - e_c}\right)W_g \tag{3}$$

or

$$X_d = 2q(BF)(CDF)W_g$$

in abbreviated form where BF is the branching function $(1 - 1/f_a - 1/f_p)$ and q = equivalents of prepolymer functional groups per gram of undiluted prepolymer. Very approximately the weight fraction of gel was found by experiment to be expressed by

$$W_g = 1 - \frac{K}{q(1 - 1/f_a - 1/f_p)} = \frac{X_d}{X_d + 2K(CDF)} \tag{4}$$

where K was approximately 0.0067, q being expressed in milliequivalents/gram (see below). It is implied here that the stock contains some prepolymer not connected to the cross-linked network but no soluble diluent. If soluble diluent is present, q must be expressed in terms of the diluted stock when Eqs. (4), (5), (17), or (18) are employed.

The crosslink density relation becomes

$$X_d = 2\left(\frac{e - e_c}{1 - e_c}\right)[q(1 - 1/f_a - 1/f_p) - K] \tag{5}$$

Values of e_c for any set of values of f_a and f_p may be obtained from Stockmayer's [2] and Kahn's [3] gel-point relationship

$$e_c^2 = \frac{r}{(f_a - 1)(f_p - 1)} \tag{6}$$

The maximum extent of reaction, e, has been found to be determined by the following relation [4] for tribranched networks:

$$e^2 = 0.88e_c^2 + 0.10r \tag{7}$$

or with sufficient exactitude

$$e^2 = (1 - k)e_c^2 + kr \tag{8}$$

where $k = 0.10$.

It would seem that the CDF term could now be calculated. However, the extent of reaction used in determining the constants in Eq. (7) was the average extent of reaction of the whole system including sol and gel, whereas the extent of reaction needed in Eqs. (3) and (5) is the extent of reaction in the gel. It was assumed that the extent of reaction in the gel was determined by a relation similar to Eq. (8). It was found that the value of the constant k in Eq. (8) had to be between 0.10 and 0.37 with the most probable value between 0.19 and 0.37.

For the case where the reactant ratio is 1, values of the branching function, the cross-link decrease factor, and the cross-link density per reactant equivalent at three values of k have been computed for stocks of various functionalities and are shown in Table 1. The cross-link decrease factor, not quite constant, is shown plotted against functionality in Fig. 1. Although this factor varies, the change in its value over the functionality range of useful stocks is only ±4% at $k = 0.3$ and $r = 1$.

The variation of the cross-link density per reactant equivalent with the branching function is shown in Fig. 2 at three values of k. While not straight lines, the curvature is slight and for practical purposes the cross-link density can be taken as proportional to the branching function when $r = 1$.

Variation of Reactant Ratio

No definite conclusions were previously reached on the effect of variation of the reactant ratio on the form of Eqs. (3) and (5). Reviewing the

TABLE 1. Cross-link Density Functions

f_p or f_a	2.0	2.1	2.2	2.3	2.4	2.5	2.6	2.7	2.8	2.9	3.0	
f_a or f_p	2.0	2.1	2.2	2.3	2.4	2.5	2.6	2.7	2.8	2.9	3.0	
$(1 - 1/f_a - 1/f_p)$	0	0.048	0.091	0.130	0.167	0.200	0.231	0.259	0.286	0.310	0.333	
Cross-link decrease factor $k = 0.2$[a]	0.200	0.208	0.215	0.226	0.230	0.236	0.242	0.248	0.258	0.263	0.265	
$k = 0.3$	0.300	0.310	0.310	0.325	0.337	0.345	0.354	0.368	0.366	0.376	0.378	
$k = 0.4$	0.400	0.411	0.422	0.430	0.441	0.449	0.453	0.461	0.467	0.475	0.483	
Cross-link density per reactant equivalent[b] $k = 0.2$	0	0.020	0.039	0.059	0.077	0.094	0.115	0.132	0.147	0.163	0.177	
$k = 0.3$	0	0.030	0.058	0.085	0.113	0.138	0.163	0.191	0.214	0.233	0.252	
$k = 0.4$	0	0.039	0.077	0.112	0.147	0.180	0.209	0.239	0.267	0.295	0.322	
f_p or f_a	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	
f_a or f_p	2.0	2.1	2.2	2.3	2.4	2.5	2.6	2.7	2.8	2.9	3.0	
$(1 - 1/f_a - 1/f_p)$	0	0.024	0.046	0.065	0.083	0.100	0.115	0.130	0.143	0.155	0.167	
Cross-link decrease factor $k = 0.3$	0.300	0.306	0.310	0.314	0.317	0.319	0.326	0.328	0.332	0.336	0.338	
f_p or f_a	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0
f_a or f_p	1.5	1.6	1.7	1.8	1.9	2.0	2.1	2.2	2.4	2.6	2.8	3.0
$(1 - 1/f_a - 1/f_p)$	0	0.042	0.079	0.111	0.140	0.167	0.191	0.212	0.250	0.282	0.310	0.333
Cross-link decrease factor $k = 0.3$	0.300	0.310	0.322	0.323	0.325	0.338	0.344	0.349	0.358	0.366	0.374	0.378

[a] The constant in $e^2 = (1 - k)e_c^{\,2} + kr$, where $e_c^{\,2} = r(f_a - 1)^{-1}(f_p - 1)^{-1}$ and $r = 1$.

[b] $2(1 - 1/f_a - 1/f_p) \times$ cross-link decrease factor.

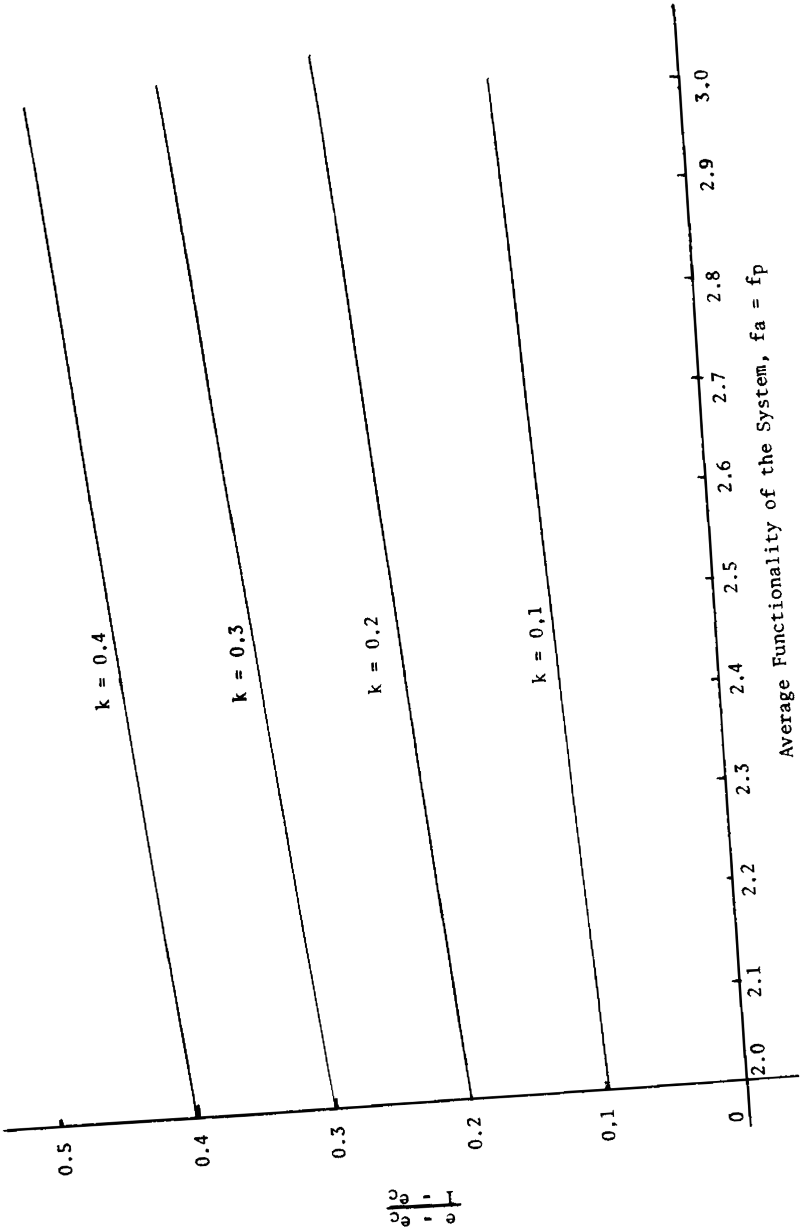

FIG. 1. Cross-link decrease factor vs functionality.

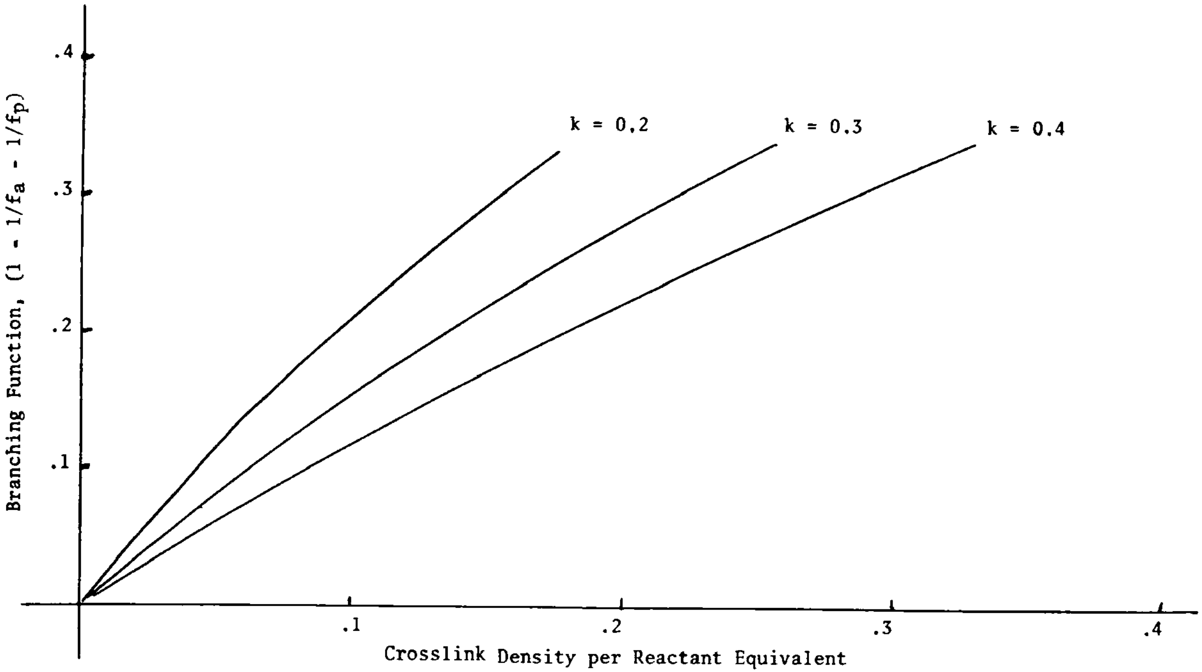

FIG. 2. Variation of the cross-link density with the branching function.

derivation of these equations, it is found that they were derived on the initial basis that all functional groups were reacted, which requires that the reactant ratio is 1. The opinion is advanced that Eqs. (3) and (5) should not employ the reactant ratio except as it changes the effective functionality of the two reactants and except as it changes the extent of reaction.

Define the reactant ratio, r, as the ratio of the number of cross-linker reactive groups to the number of prepolymer reactive groups. Then:

$$r = n_a f_a / n_p f_p$$

where n_a = moles of cross-linking agent

f_a = functionality of cross-linking agent

n_p = moles of prepolymer

f_p = functionality of prepolymer

When r is greater than 1, we have a deficiency of prepolymer and an excess of cross-linking agent. The number of groups on the cross-linking agent which will be capable of reaction will be equal to the number of reactive groups on the prepolymer, $n_p f_p$. Hence the effective functionality of the cross-linking agent will be $n_p f_p / n_a$. But $n_p f_p = n_a f_a / r$, or the effective functionality of the cross-linking agent will be f_a / r.

When r is less than 1, we have an excess of prepolymer and a deficiency of cross-linking agent. The number of groups on the prepolymer which will be capable of reaction will be equal to the number of reactive groups on the cross-linking agent $n_a f_a$. The effective functionality of the prepolymer will be $n_a f_p / n_p = r f_p$.

As the reactant ratio varies, the number of chain segments varies and we must substitute in the expression for the number of segments f_a / r for f_a or $r f_p$ for f_p as the case may be. However, as r varies, the number of chain segments is still in the same volume or weight of material. Hence we leave the molecular weight the same.

Carrying through these operations, the cross-link density becomes:

$$X_d = 2_q (BF)(CDF) W_g \tag{9}$$

where (CDF) is as above and (BF) or branching function is

$(r - r/f_a - 1/f_p)$ when $r < 1$ and

$(1 - r/f_a - 1/f_p)$ when $r > 1$.

When we consider the effect of variation in reactant ratio, r, on cross-link density, the situation becomes complicated. The cross-link decrease factor increases with increasing reactant ratio and also varies with changing prepolymer functionality. It is no longer possible to consider it approximately constant, and each case must be separately calculated. Figure 3 shows the theoretical variation with reactant ratio according to Eq. (9) of the branching function and the cross-link density per polymer equivalent for a two-functional prepolymer reacted with a three-functional cross-linking agent. The extents of reaction were calculated using a value of k of 0.3.

Materials, Methods and Results Obtained

The experimental data in support of the above relations were not obtained as a single effort on one project but resulted from work on five projects by eight different persons over a period of years. Four types of binders were employed including 11 prepolymers with 11 "cross-linking agents." Rubber stocks were prepared using liquid prepolymers: carboxyl-terminated polybutadiene (CTPB), hydroxyl-terminated polybutadiene (HTPB), carboxyl-terminated polyesters, and an hydroxyl-terminated polyether which were treated with aziridines, epoxides, and isocyanates. The prepolymers had molecular weights ranging from 1500 to 6000. They were obtained from Phillip's Petroleum Company, Thiokol Chemical Corporation, the General Tire and Rubber Company, the Arco Chemical Company, the Witco Chemical Company, and the BASF-Wyandotte Corporation.

The prepolymers and cross-linking agents employed are listed in Table 2. Reactive group contents were determined using standard analytical methods [5-8]. Functionality values, the number of reactive groups per molecule for Epotuf STF-6, RDR701, and Isonate 390P, were obtained from molecular weights determined using a vapor pressure osmometer and the equivalent weights. The functionality value of GP1530 was calculated using terminal unsaturation measurements [7, 9].

The functionality of the CTPB, HTPB, and Mapo was determined by a gel point method [10] using a relationship developed by Stockmayer [2] and Kahn [3]. The equation is

$$f_p = 1 + \frac{r}{e^2(f_a - 1)} = 1 + \frac{1}{re_a^{\,2}(f_a - 1)}$$

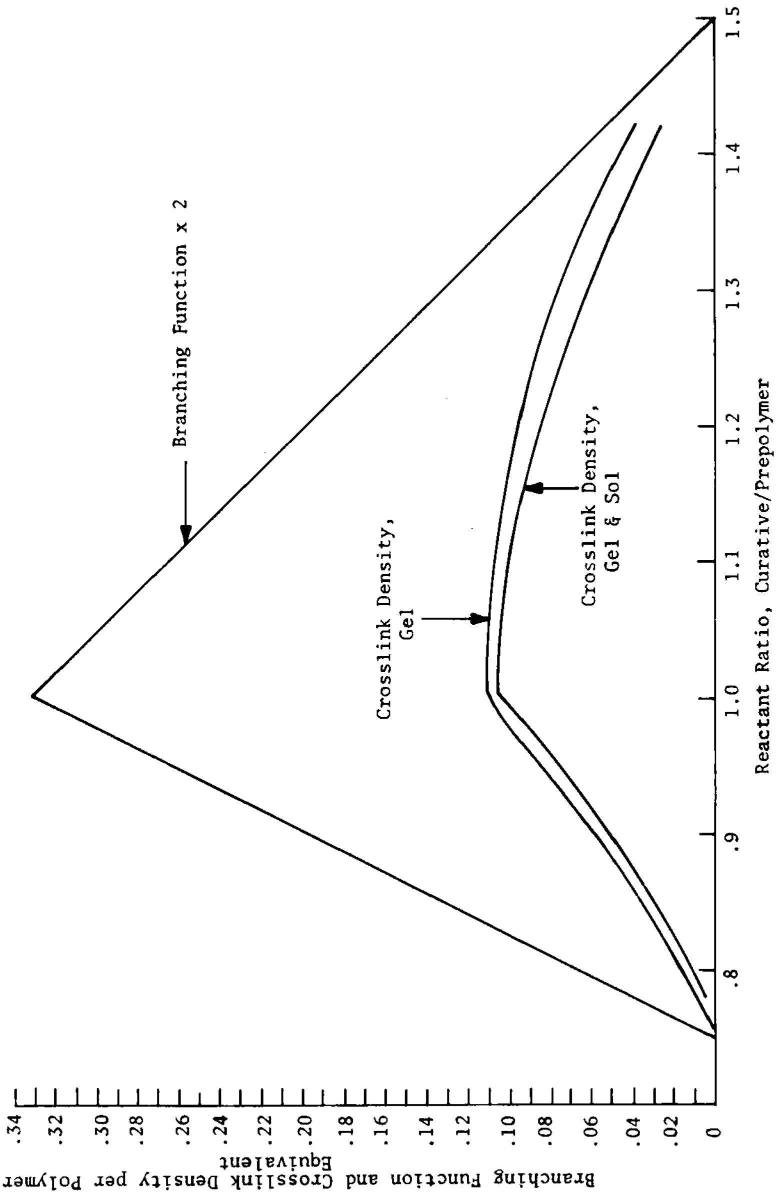

FIG. 3. Theoretical relation between cross-link density and reactant ratio (average functionality = 2.4, k = 0.3).

TABLE 2. Materials Employed

Description	Trade name	Source	Reactive group content (meq/g)	Functionality
Carboxyl-terminated polybutadiene	Butarez CTL-I	Phillips Petroleum Co.	Various	Various
	Butarez CTL-II	Phillips Petroleum Co.	0.34, 0.35	2.29, 2.62
	Telagen CT	General Tire & Rubber Co.	Various	Various
	HC 434	Thiokol Chemical Co.	0.53, 0.51	2.38, 2.72
Hydroxyl-terminated polybutadiene	Butarez HTS	Phillips Petroleum Co.	0.32	2.03
	Telagen HTS	General Tire & Rubber Co.	0.92	1.99
	R45M	Arco Chemical Co.	0.77	2.53
Carboxyl-terminated polyesters	F17-47	Witco Chemical Co.	0.89	2.2
	F17-80[a]	Witco Chemical Co.	1.28	2.2
	F17-84[a]	Witco Chemical Co.	1.55	2.2
Hydroxyl-terminated polyether	GP-1530	BASF-Wyandotte Corp.	1.89	2.97
Tris[1-(2 methyl)-aziridinyl]phosphine oxide	Mapo	Interchemical Corp.	13.3	3.3
Phenyl bis[1-(2 methyl)-aziridinyl)] phosphine oxide	Phenyl Mapo	Interchemical Corp.	8.5	2.0
Glyceryl glycidyl ether	Epon 812	Shell Chemical Co.	6.6	2.2
Trimethylol propane triglycidyl ether	Epotuf STF-6[a]	Reichhold Chemicals	6.95	2.52
Polyphenyl glycidyl ether	RDR 701[a]	Koppers Co.	7.0	2.7
Isocyanate	Isonate 143L	Upjohn Co.	8.00	2.1
Isocyanate	Isonate 390P	Upjohn Co.	7.77	2.50
Polymethylene polyphenylisocyanate	PAPI	Upjohn Co.	7.5	3
Isophorone disocyanate	IPDI	Thorson Chemical Corp.	9.02	2.00
Trimethyl hexamethylene diisocyanate	TMDI	Thorson Chemical Corp.	9.43	1.98
Phenyl isocyanate	PI		8.39	1.00

[a] Product discontinued or not generally available from manufacturer.

where f_p = weighted average functionality of the prepolymer, f_a = weighted average functionality of the cross-linking agent, r = ratio of the total number of cross-linking groups to the total number of prepolymer groups initially present, and e and e_a = fractions of prepolymer and cross-linking groups initially present, respectively, which have reacted at the gel point. To determine the functionality of the prepolymer, the following three quantities must be known: 1) initial ratio of the cross-linking groups to prepolymer reactive groups, 2) functionality of the cross-linking agent, and 3) extent of the reaction at the gel point.

Ferric acetyl acetonate, FeAA, and dimethyl benzyl amine were employed as catalysts in epoxide and some isocyanate reactions. The plasticizers used were liquid polybutadiene, dioctyl sebacate, and triethylene glycol di(2-ethyl butyrate)(Flexol 3GH). The filler system employed was principally ammonium perchlorate at a high solids loading.

Stocks were cured in closed molds for 72 hr at 80 or 95°C. Properties of the gum stocks prepared are given in Tables 3-7, while the filled stocks are described in Tables 8-10. Unfortunately, complete information was not available on many of the stocks. Young's modulus and elongation at break were determined using an Instron instrument or in some cases a Scott L-6 or X-5 tester at 12 or 20 in./min.

The dynamic modulus of elasticity was obtained on a few samples from the vibrational resonance frequency using the method of Hanson et al. [11]. The modulus is obtained from

$$E = \frac{16\pi^2 Pl^3 Fe^2 Ft^2}{g}$$

where E = modulus of elasticity (dynes/cm^2)
P = density (g/ml)
l = length of sample (cm)
g = acceleration due to gravity
Fe = longitudinal resonance frequency (cycles/sec)
Ft = transverse resonance frequency (cycles/sec)

Strips of stock 2 mm × 2 mm × 6 cm were used.

Although these measurements are called "dynamic," they are not instantaneous measurements. In practice, the operator sets the sample into vibration and changes the frequency until he obtains a standing wave. The sample is in vibration from 1 to 3 min and the resonance frequency decreases with time. The modulus is closer to an equilibrium value than to an instantaneous one.

A number of values of the dynamic modulus of a single sample were obtained. Values obtained on repeating the measurement four times on the same strip of material were 313, 387, 410, and 420 psi. Six values

TABLE 3. Polypropylene Oxide and Polyester Gum Stocks

Binder[a]	PU-1	PU-2	PU-3	PE-1	PE-1	PE-1	PE-2	PE-3
Binder, reactive group content (meq/g)	1.57	0.701	1.18	0.83	0.83	0.78	1.07	1.25
Binder functionality	3.00	2.97	2.97	2.2	2.2	2.2	2.1	2.2
Cross-linker[b]	PI, TMDI	TMDI	TMDI	Mapo	Mapo	RDR701	RDR701	RDR701
Cross-linker functionality	1.68	1.98	1.98	3.3	3.3	2.7	2.7	2.7
Reactant ratio[c]	0.98	0.99	0.99	0.92	1.02	1.00	1.00	1.00
Branching function[d]	0.063	0.153	0.153	0.187	0.236	0.178	0.156	0.178
Cure function[d]	0.100	0.107	0.181	0.155	0.196	0.139	0.167	0.223
Young's modulus (psi)	97	66	216	98	216	110	135	209
Elongation-at-break (%)	107	50	39	-	75	117	117	87
Hardness, Shore A	30	23	40	30	34	27	-	-
Gel content (%)	93.4							

[a] PU = polyurethane, propylene oxide; PE = polyester, COOH terminated.

[b] PI = phenyl isocyanate; TMDI = trimethyl hexamethylene diisocyanate; RDR701 = epoxide, Kopper's Co, discontinued; Mapo = tris(1-(2 methyl)-aziridinyl) phosphine oxide.

[c] Cross-linker to binder equivalent ratio.

[d] See text.

TABLE 4. Hydroxyl-Terminated Polybutadiene Gum Stocks

Binder	GJ	GJ	GJ	GJ	GJ	GG	GG	FC
Binder, reactive group content (meq/g)	0.700	0.703	0.709	0.700	0.700	0.85	0.85	0.30
Binder functionality	2.53	2.53	2.53	2.53	2.53	1.99	1.99	2.03
Cross-linker[a]	PAPI	390P	1PDI	390P PAPI	390P	143L	PAPI	143L
Cross-linker functionality	3	2.50	2.00	2.7	2.50	2.1	3	2.1
Reactant ratio[b]	1.00	0.97	1.00	1.00	1.00	1.00	1.00	1.00
Branching function[c]	0.272	0.217	0.105	0.235	0.205	0.021	0.165	0.031
Cure function[c]	0.190	0.153	0.074	0.165	0.144	0.018	0.140	0.009
Elongation-at-break (%)	175	198	-	-	90	665	250	>1000
RNB No., xylene[d]	5.75	4.31	2.37	5.29	5.58	0.34	-	<0.10
Hardness, Shore A	-	-	-	-	-	-	24	-
Gel content (%)	-	-	-	-	97.5	36.7	-	3.8

[a] 390P and 143L = Isonate 390P and 143L, Upjohn; IPDI = isophorone dissocyanate; PAPI = polymethylene polyphenyl isocyanate.

[b] Cross-linker to binder equivalent ratio.

[c] See text.

[d] $V_2^{5/3}$ × percent gel, V_2 = volume function polymer in xylene swollen gel.

TABLE 5. Carboxyl-Terminated Polybutadiene Gum Stocks

Binder	FA-1	FA-1	FA-2	FA-3	FA-3	FV-1	FW-1	FV-1
Binder, reactive group content (meq/g)	0.230	0.235	0.266	0.214	0.209	0.426	0.248	0.424
Binder functionality	2.33	2.33	2.18	2.03	2.03	2.40	2.95	2.40
Cross-linker[a]	Mapo Epon	Mapo	Mapo Epon	Mapo	Mapo Epon	Mapo	Mapo	Mapo Ph Mapo
Cross-linker functionality	3.0	3.3	3.0	3.3	3.0	3.3	3.3	2.84
Reactant ratio[b]	1.10	1.00	1.00	1.00	1.00	1.00	1.00	1.00
Branching function[c]	0.204	0.267	0.208	0.204	0.174	0.280	0.358	0.231
Cure function[c]	0.047	0.063	0.055	0.044	0.036	0.119	0.089	0.098
Young's modulus (psi)	-	45	37	-	-	102	-	78
Elongation-at-break (%)	307	275	329	-	-	215	215	-
RNB No., xylene[d,e]	0.93	1.1	0.84	1.35	1.19	-	-	-
Hardness, Shore A	6	7	6	-	-	17	14	-
Gel content (%)[e]	89	-	88	86	81	-	-	-

[a] Mapo = tris(1-(2-methyl)-aziridinyl) phosphine oxide; Epon = Epon 812, Shell; Ph Mapo = phenyl Mapo difunctional.

[b] Cross-linker to binder equivalent ratio.

[c] See text.

[d] $V_2^{5/3}$ × percent gel, V_2 = volume fraction polymer in xylene swollen gel.

[e] RNB No. and gel content of FA stocks have been corrected for 30% plasticizer content.

TABLE 6. Carboxyl-Terminated Polybutadiene Gum Stocks

Binder	FB-1	FB-1	FB-2A	FB-2A	FB-2A	FL-1	FL-2	FL-2
Binder, reactive group content (meq/g)	0.317	0.328	0.340	0.331	0.322	0.513	0.493	0.499
Binder functionality	2.53	2.53	2.62	2.62	2.62	2.38	2.72	2.72
Cross-linker[a]	Mapo Epon	Mapo	Mapo	Mapo Epon	STF-6	Mapo	STF-6	STF-6
Cross-linker functionality	3.0	3.3	3.3	3.0	2.52	3.3	2.52	2.52
Reactant ratio[b]	1.10	1.10	1.00	1.00	1.00	1.00	1.00	0.67
Branching function[c]	0.238	0.272	0.315	0.286	0.222	0.277	0.237	0.036
Cure function[c]	0.075	0.089	0.107	0.094	0.071	0.142	0.117	0.018
Young's modulus	-	-	-	-	-	100	-	-
Elongation-at-break (%)	260	200	127	145	-	160	136	-
RNB No., xylene[d]	-	-	3.39	3.53	2.99	-	3.42	0.66
Hardness, Shore A	-	-	-	-	-	33	-	-
Gel content (%)	-	-	92.2	89.8	93.5	-	93.5	73.3

[a] Mapo = tris[1-(2-methyl)-aziridinyl] phosphine oxide; Epon = Epon 812, Shell; STF-6 = Epotuf STF-6, Reichhold.

[b] Cross-linker to binder equivalent ratio.

[c] See text.

[d] $V_2^{5/3}$ × percent gel, V_2 = volume fraction polymer in xylene swollen gel.

TABLE 7. Carboxyl-Terminated Polybutadiene Gum Stocks

Binder	FR-1	FR-1	FR-1	FR-1	FR-2	FR-2
Binder, reactive group content (meq/g)	0.345	0.344	0.343	0.342	0.338	0.331
Binder functionality	2.1	2.1	2.1	2.1	2.60	2.60
Cross-linker[a]	Mapo	Mapo Ph Mapo	Mapo Ph Mapo	Mapo Ph Mapo	Mapo	Mapo Epon
Cross-linker functionality	3.3	2.9	2.7	2.4	3.3	3.0
Reactant ratio[b]	1.00	1.0	1.0	1.0	1.10	1.10
Branching function[c]	0.275	0.226	0.176	0.123	0.282	0.246
Cure function[c]	0.102	0.084	0.065	0.046	0.095	0.081
Young's modulus (psi)	74	51	-	21	-	-
Elongation-at-break (%)	250	300	630	800	230	280
Hardness, Shore A	13	-	-	-	-	-

[a] Epon = Epon 812, Shell; Mapo = tris[1-(2-methyl)-aziridinyl] phosphine oxide; Ph Mapo = phenyl Mapo difunctional.

[b] Cross-linker to binder equivalent ratio.

[c] See text.

TABLE 8. Formulations of Filled Stocks

	I	II	III	IV	V
CTPB FA	17.18	-	-	-	-
CTPB FB	-	17.35	12.14	-	-
CTPB FR	-	-	-	17.35	12.14
Liquid polybutadiene	-	-	5.21	-	5.21
Mapo	0.38	0.45	0.33	0.46	0.37
Epon 812	0.43	0.43	0.43	0.43	0.43
Filler	82.0	82.0	82.0	82.0	82.0
	99.99	100.23	100.11	100.24	100.15

TABLE 9. CTPB FA and FB Filled Stocks

Stock	Functionality, weight average	Reactive group content (meq/g)	Cure function (meq/g)	Log cure function $\times 10^3$	Elongation-at-break (%)	Dynamic modulus, (psi)	RNB No., Xylene	Hardness Shore A
A	2.14	0.246	0.0491	1.691	33	410	11.9	66
B-C	2.14	0.240	0.0479	1.680	30	-	-	67
D	2.28	0.235	0.0536	1.729	24	-	12.9	66
E	2.11	0.253	0.0488	1.688	23	-	12.1	65
F	2.22	0.246	0.0532	1.726	24	480	12.7	66
G	2.14	0.253	0.0505	1.703	21	-	12.6	66
H	2.35	0.250	0.0603	1.780	24	-	13.3	67
3H-J	2.40	0.251	0.0628	1.798	22	-	-	66
H-J	2.45	0.252	0.0651	1.814	19	585	13.3	75
J	2.55	0.253	0.0694	1.841	16	850	15.4	77
K	2.29	0.339	0.0780	1.892	12	-	-	-

TABLE 10. CTPB FR Filled Stocks

Stock	Functionality, weight average	Reactive group content (meq/g)	Cure function (meq/g)	Log cure function × 10^3	Elongation-at-break (%)
L	2.60	0.347	0.0979	1.991	12
M	2.60	0.278	0.0784	1.894	24
N	2.60	0.260	0.0733	1.865	28
P	2.69	0.242	0.0714	1.854	33
Q	2.64	0.246	0.0708	1.850	32
R	2.60	0.245	0.0691	1.839	32
S	2.53	0.244	0.0664	1.822	33
T	2.60	0.226	0.638	1.805	38
U	2.60	0.208	0.0587	1.769	40
V	2.34	0.239	0.0574	1.754	39

obtained on different strips cut from one sheet were 475, 553, 339, 309, 440, and 364 psi. Variation appears to be too great for strictly quantitative comparisons. However, the data does show a pronounced increase at higher calculated cross-link density in Table 9.

Hardness was measured with a Shore durometer, type A at 5 sec time. Gel content was determined in Soxhlet extractors with methylene chloride, the extraction time being 72 hr. A solvent swelling test was run in mixed xylene which was reported as the RNB number, defined as $V_2^{5/3}$ × percent gel, where V_2 is the volume fraction of polymer in the xylene swollen gel and the percent gel is as determined in the swelling test. The RNB number, the modulus, and the elongation at break served as experimental definitions of the state of cure.

Results on Gum Stocks

One needs now to examine the degree to which the cross-link density, Eqs. (3) and (5) above, are followed by the real stocks described in the last section. For this purpose Young's modulus, the reciprocal of the elongation-at-break, and the RNB number as defined above will be used as measures of the cross-link density while the cross-link decrease factor and usually the gel content will be regarded as approximately constant in the equations.

From classical network theory one predicts to a first approximation that the cross-link density for three-branched networks can be expressed by

$$X_D = \frac{2}{3}\left(\frac{E_0}{3RTPV_2^{2/3}}\right) \tag{10}$$

or

$$X_D = \frac{2}{3}\left[\frac{\tau}{RTPV_2^{2/3}(\alpha - \alpha^{-2})}\right] \tag{11}$$

where E_0 = equilibrium value of Young's modulus

τ = equilibrium stress at relative elongation α

$R = 1206 \dfrac{\text{lb cm}^{-3}}{\text{in.}^2, \,°\text{K, mole}}$

T = absolute temperature

P = binder density

V_2 = volume fraction of network polymer in binder phase

We have also expressed the cross-link density in the gel as $q(1 - 1/f_a - 1/f_p)$, the cure function (CF) multiplied by the cross-link decrease factor (CDF), which can be regarded as nearly constant and having a value between 0.20 and 0.38. The cure function and Young's modulus should therefore vary linearly with each other. The little data available for CTPB is shown plotted in this way in Fig. 4.

$E = 740 \times \text{CF}$ (meq/g), where E is the first-pull value of Young's modulus at a jaw separation rate of 20 in./min.

Treloar [12] predicted that the elongation of break (relative elongation minus one) should be proportional to the square root of the average number of "freely orienting segments" per network chain. The length of such a segment could not be specified, but the number of such segments per chain would have to be proportional to the molecular weight between cross-links and inversely proportional to the cross-link density or to the equilibrium value of Young's modulus. A plot of log E against log ϵ_β, where ϵ_β is elongation-at-break in percent given in Fig. 5, reveals the proportionality

$$\epsilon_\beta = 5220/E^{0.77} \qquad \text{or} \qquad E = 67{,}600/\epsilon_\beta^{1.3}$$

Crystallization of the binder during stretching or introduction of reinforcing fillers changes the relationship between the initial and final

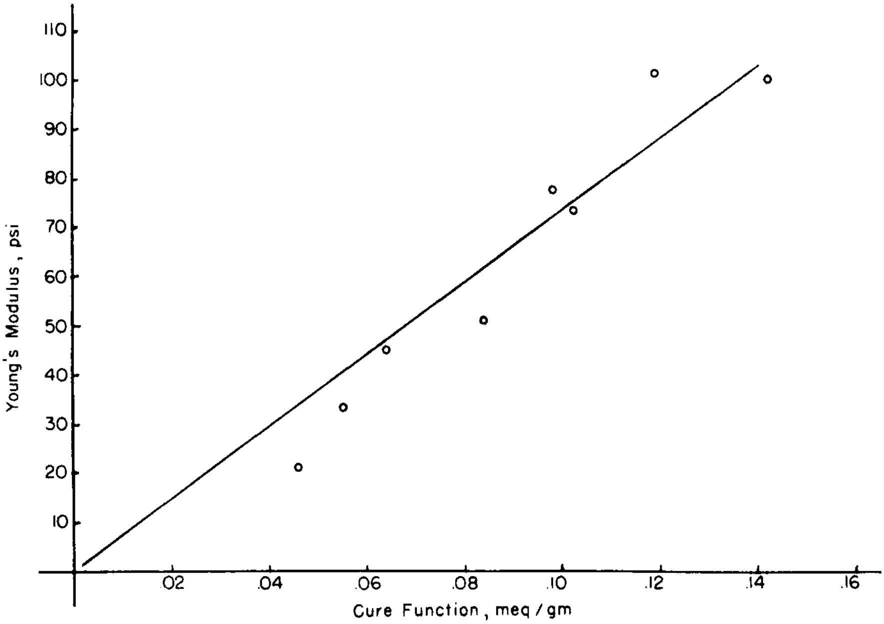

FIG. 4. Variation of Young's modulus with cure function (CTPB).

states of the elastomers during the stretching process and increases the modulus corresponding to a given elongation at break. The data in Fig. 5 can almost as well be described by the linear relation

$$\frac{1}{\epsilon_\beta} = 5 \times 10^{-5}\ E + 0.001$$

or

$$E = 20 \left(\frac{1000}{\epsilon_\beta} - 1\right)$$

This relation is followed fairly well up to a modulus of 700 psi but not above this point (see Fig. 6). Failure of the data to follow Treloar's prediction exactly could be due to the use of first-pull Young's modulus rather than equilibrium values.

Since the modulus varies with the cross-link density, it follows that the cure function should vary with the elongation at break in the same

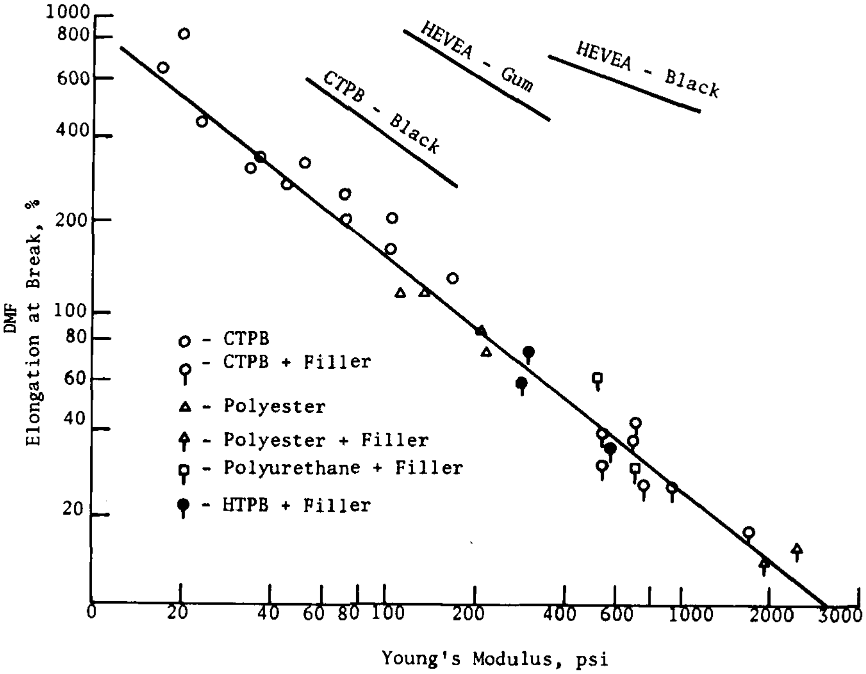

FIG. 5. Elongation at break vs Young's modulus for gum stocks and filled stocks.

manner as the modulus. Figure 7 shows an apparent linear variation of $1/\epsilon_\beta$ with the cure function where $\epsilon_\beta = 17.7/\text{CF}$. ϵ_β is expressed in percent and CF in meq/g. HTPB stocks are hydrogen bonded and are not included. As in the case of ϵ_β vs modulus, the data can also be represented by $\epsilon_\beta = 35/\text{CF}^{0.77}$ or $\text{CF} = 100/\epsilon_\beta^{1.3}$. Placing the value CF/100 for $\epsilon_\beta^{-1.3}$ in $E = 67{,}600\epsilon_\beta^{-1.3}$, we obtain $E = 676(\text{CF})$, in reasonable agreement with $E = 740(\text{CF})$ found above.

Summarizing the more precise exponential relationships:

$$X_D\ (\text{meq/g}) = \frac{2}{3}\left(\frac{1000E_0}{3RTPV_2}\right) = \frac{E_{0,\text{psi}}}{1455} \qquad (12)$$

but

$$E = 67{,}600\epsilon_\beta^{1.3} \qquad (13)$$

$$X_D \cong \frac{67{,}700\epsilon_\beta^{-1.3}}{1455} = 46\epsilon_\beta^{-1.3} \tag{14}$$

also

$$X_D \cong (\mathrm{CDF})(\mathrm{CF})$$

but

$$\mathrm{CF} = 100\epsilon_\beta^{-1.3} \tag{15}$$

$$X_D \cong 100(\mathrm{CDF})\epsilon_\beta^{-1.3} \tag{16}$$

If the CDF turn has a value between 0.20 and 0.38 and we regard Eq. (14) as most correct, then Eq. (16), neglecting sol rubber, expresses the cross-link density to within a factor of 1.5.

The fraction of sol rubber is shown plotted against the cure function on log-log paper in Fig. 8, with fraction sol = $0.0028(\mathrm{CF})^{-1.3}$. With less precision the approximate linear relation is fraction sol = 0.0067/(CF).

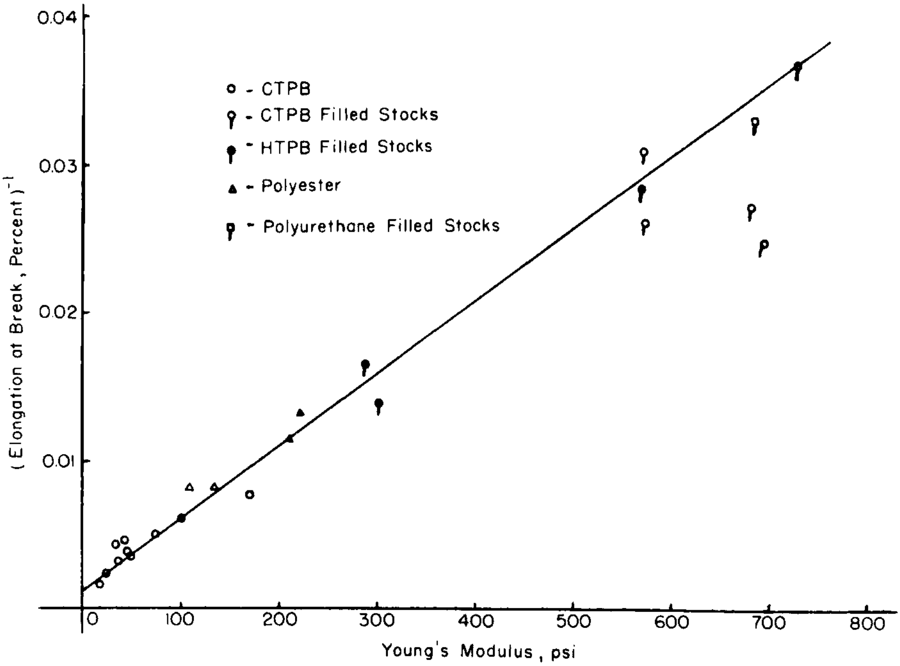

FIG. 6. Variation of reciprocal elongation with Young's modulus.

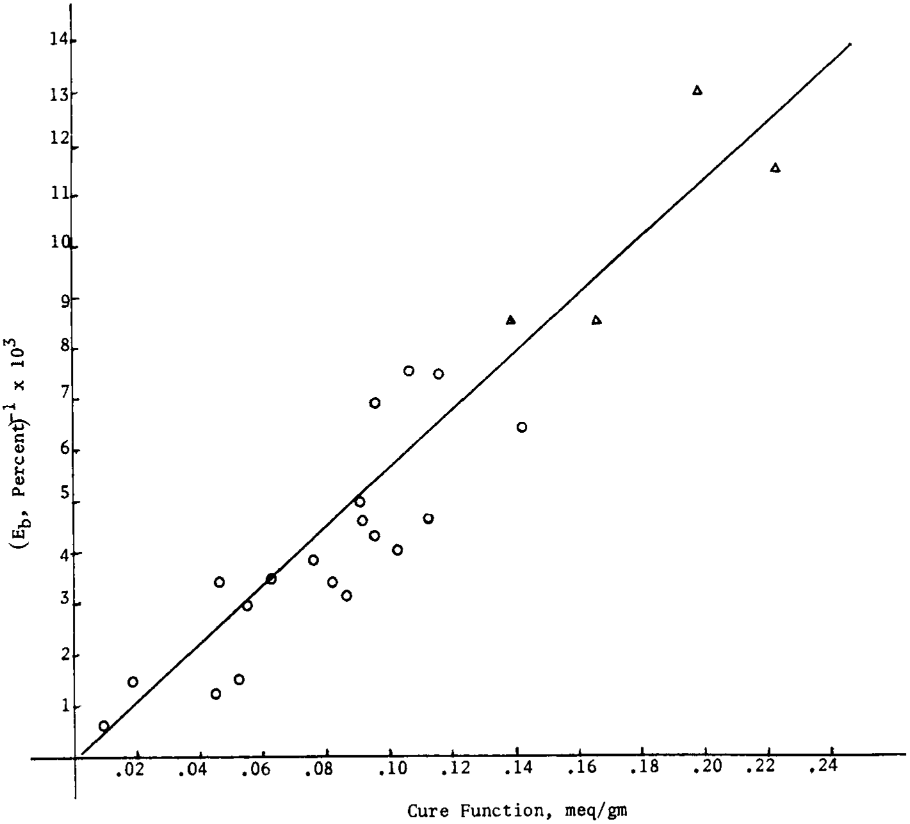

FIG. 7. Variation of elongation reciprocal with cure function.

The absolute value of the cross-link density was checked on three CTPB stocks using the results of Mosher and Tuono [13]. Cross-link density was measured by equilibrium modulus in tension (Eq. 11) and from the swollen compression modulus using the method of Cluff, Gladding, and Pariser [14]. Comparative values are shown in Table 11.

A value of 0.25 was used for the cross-link decrease factor in calculating the cross-link density in Table 11. Equation (5) was used for the calculation.

$$X_d = 2q(\text{CDF})(\text{BF}) - 2 \times 0.0067(\text{CDF}) \tag{17}$$

$$= 0.5q(\text{BF}) - 0.0033 \tag{18}$$

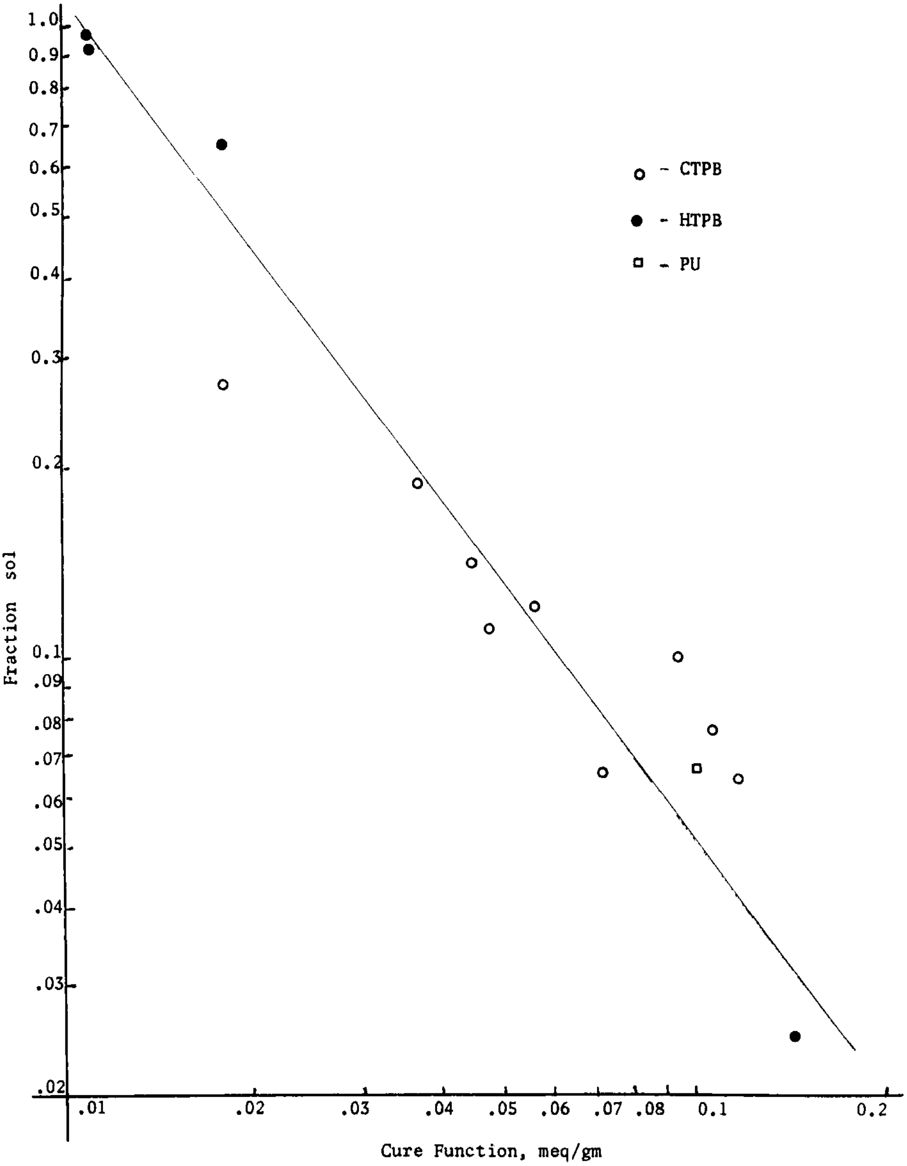

FIG. 8. Variation of sol content with cure function.

TABLE 11. Comparison of Calculated with Measured Values of Cross-link Density

	Reactive Group content, (meq/g)	Binder functionality	Branching function	Cross-link density (meq/g)		
					Measured	
				Calculated	Tension	Compression
CTPB-FA4[a]	0.243	2.14	0.230	0.025	0.025	0.017
CTPB-FA5[b]	0.245	2.52	0.270	0.030	0.035	-
CTPB-FA6[b]	0.228	2.26	0.225	0.022	0.017	-

[a] Mapo cured.
[b] Mapo + Epon 812 cured.

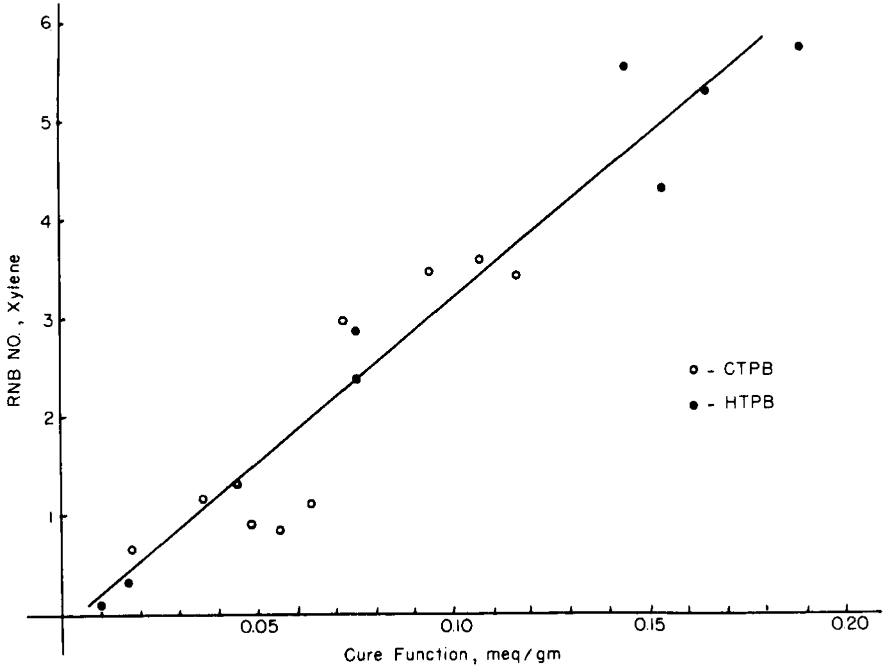

FIG. 9. Cure function vs swelling results, CTPB and HTPB.

Agreement between measured and calculated values is an argument in favor of the method of calculation, while the excellent agreement within factors of 0.85 to 1.5 as found here indicates that a use of 0.25 for the CDF term is not far wrong.

Absolute or relative cross-link density values may also be obtained from solvent swelling measurements. Figure 9 shows the cure function plotted against the RNB number determined in xylene for the CTPB and HTPB gum stocks cured at a 1.0 to 1.0 reactant ratio. The RNB number is $V_2^{5/3}$ × percent gel, where V_2 is the volume fraction of polymer in the solvent swollen stock. The RNB value increases with cure from zero to 100 and at low values would be linear with respect to cure. Experience has shown that the hydrogen bonding in HTPB stocks is broken during swelling. The scatter in Fig. 9 is greater than the error in the swelling measurements.

Figure 10 shows Shore A hardness of the gum stocks plotted against the cure function. Since a linear relation would be expected only over the lower portion of the curve, values of hardness over 35 have been omitted.

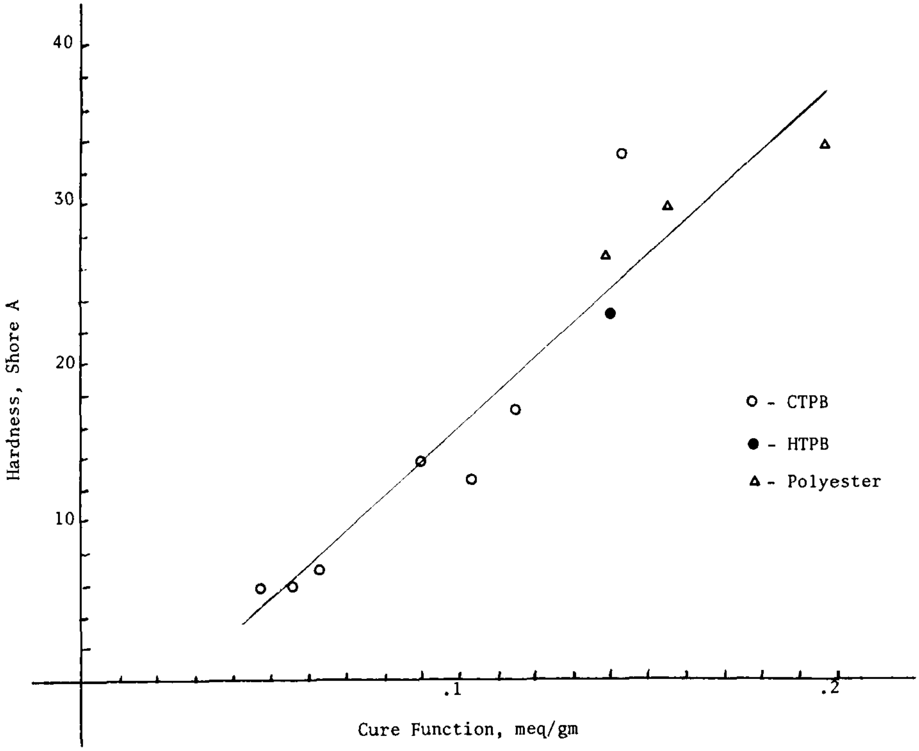

FIG. 10. Cure function vs hardness for CTPB, HTPB, and polyester stocks.

Filled Stocks

Correlation was extended to filled stocks formulated as in Table 8. Various lots of three prepolymers were employed with different functionalities. In addition to the 30% polybutadiene plasticizer employed in Stock V, other concentrations, 20, 25, 35, and 40%, were also used. Parameters of the stocks are listed in Tables 9 and 10. These include the weight-average prepolymer functionality f_p, determined by gel point measurements, the carboxyl group content q, and the cure function $q(1 - 1/f_a - 1/f_p)$.

It was shown above that the cure function for gum stocks varied as $\epsilon_\beta^{-1.3}$, where ϵ_β is the elongation-at-break in percent. The cure function refers to the state of the binder alone. The effective cross-link density of a filled stock will be higher than that of a gum stock because of binder-filler adhesion. This adhesion may vary with the cure of the binder. Thus, to extend the same relation between cure function and elongation to filled stocks, one should add an unknown quantity to the cure function representing the effective cross-links contributed by the presence of filler. In actual fact, a plot of log ϵ_β vs the logarithm of the cure function as in Fig. 11 yields rough relations, peculiar to each of two brands of prepolymers, which have the form $q(1 - 1/f_a - 1/f_p) = \text{const}/\epsilon_\beta^{0.4}$. The scatter of the points is believed to be greater than experimental error, and certainly the displacement of the two curves in Fig. 1 is greater than experimental error. An uncontrolled variable is operating.

Two such variables are the distribution of molecular weights and the functionality distribution. The effect of varying molecular weight distribution on the properties of binders has been studied at this laboratory [15]. The results showed that the variation in elongation-at-break to be expected because of lot to lot variations in heterogeneity index is probably not greater than experimental variation in the elongation test below a heterogeneity index of 1.5, which we have in the prepolymers used here.

Examination of the functionality distribution of a CTPB-FA lot, Stock H, Table 9, and a CTPB-FR lot, Stock L, Table 10, by silica gel elution and by analysis of gel permeation chromatography fractions [16] shows the results as given in Table 12.

In the case of these two prepolymers at least enough tetra- and pentafunctional moles are present in one of them to account for the difference between them. It is suggested that the scatter in Fig. 11 may be accounted for by differences in functionality distribution. Such an explanation means that although the state of cure of prepolymer stocks increases as the average functionality rises from two to three, if material of functionality greater than three is present, the extent of cure will be less than expected when the reactant proportions are based on all the prepolymer functional groups present.

CONCLUSION

The relation describing the value of the cross-link density in telechelic stocks has been separated into four factors: 1) the reactive group content q; 2) the proportion of prepolymer reactive groups which

TABLE 12. Functionality Distribution

Functionality	CTPB-FA	CTPB-FR: From GPC fractions	CTPB-FR: From SiO_2 column
0	26.6	7.1	6.5
1	0	0.3	0
2	48.5	52.8	66.7
3	18.3	28.8	12.0
4	-	7.6	9.8
5	-	3.3	-
	93.4	99.9	95.0

because of the presence or absence of polyfunctionality can form branch points at complete reaction, branching function (BF) = $(1 - 1/f_a - 1/f_p)$; 3) the factor by which the cross-link density is decreased because of failure of the curing reaction to go to completion, CDF factor (geometrical considerations prevent complete reaction); and 4) the gel content of the stock, which was related empirically to the reactive group content and the branching function.

Since the objective of the experimental work was to establish general trends, approximations were made which are only partly true. For instance, cross-link density was taken as proportional to the first-pull value of Young's modulus whereas the equilibrium value should have been used. The cross-link decrease factor was regarded as constant and the sol rubber content was often neglected. The nature of the test methods, gel-point determinations, and stress-strain and solvent swelling measurements is such that some error is present. Of equal importance, the properties considered are known not to include all the variables. In important source of error is probably polymerization of cross-linking agents so that the final reactant ratio after cure is not the same as that of the initial mix. This polymerization also increases the functionality of the cross-linking agent.

In spite of these shortcomings it is believed that the results show the essential correctness of the cure function, $q(1 - 1/f_a - 1/f_p)$, in describing the variation of cross-link density of prepolymer stocks derived from two- and three-functional reactants. That is, one may regard the cross-link decrease factor as sufficiently constant for many purposes. When the cross-link decrease factor was given the value 0.25, the absolute value of the cross-link density became $0.50q(BF) - 0.0033$. Agreement between this relation and cross-link density calculated from equilibrium modulus of elasticity and from the solvent swollen compression modulus was excellent in three cases.

SYMBOLS

n_p = moles of prepolymer

f_p = functionality of prepolymer, average number of reactive groups per molecule. The word functionality as used here does not refer to the number of chain ends united at branch points in polymer networks.

q = equivalents of prepolymer reactive groups per gram. See also statement following Eq. (4)

n_a = moles of cross-linking agent

f_a = functionality of cross-linking agent

X_d = moles of branch points/gram, cross-link density

X_g = cross-link density in the gel

X_s = cross-link density in the sol

M_c = molecular weight between cross-links

r = ratio of number of cross-linking groups to prepolymer reactive groups

e = extent of reaction of the prepolymer in terms of 1 for complete reaction

e_c = extent of reaction of the prepolymer at the gel point

e_a = extent of reaction of the cross-linking groups at the gel point

W_g = weight fraction of gel

W_s = weight fraction of sol

BF = branching function; the proportion of prepolymer reactive groups (q) which can form branch points at complete reaction

CDF = cross-link decrease factor; the factor by which the cross-link density is decreased because of failure of the curing reaction to go to completion at the final and maximum degree of cure

CF = cure function; the product of q and BF

τ = equilibrium stress

E_0 = equilibrium value of Young's modulus, psi

E = first-pull value of Young's modulus, psi

ϵ_β = elongation-at-break expressed in percent

α = relative elongation

R = gas constant, 1206 lb cm^3/in.^{2}, °K, mole

T = absolute temperature, °K

P = binder density, grams/milliliter

V_2 = volume fraction of network polymer in the binder or in the solvent swollen binder

RNB = relative number of cross-linking bonds = $100\ W_g V_2^{5/3}$

ℓ = length

F_e = resonance frequency, longitudinal

F_t = resonance frequency, transverse

g = acceleration due to gravity

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