The Maximum Extent of Reaction in Gelled Systems

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Synopsis

Just how far reactions can go after gelation during the cure of telechelic prepolymers has been a debatable point for some time. Utilizing a recently devised method,[7] the curing reactions of some telechelic prepolymers were followed after the gel point. Extents of reaction above 90% occurred only in systems of average functionality close to two, functionality being the average number of reactive groups per molecule. Among systems of higher functionality, maximum extents of reaction of about 70% were most common. The final extent of reaction was only a few per cent above the extent of reaction at the gel point. The maximum extent of reaction varied with the concentration of reactive species and the relationship was a linear one at each functionality of the system. The data were consistent with $P_A{}^2/r = \{0.88/[(h-1)(j-1)]\} + 0.10$ where P_A is the fraction of prepolymer reactive groups initially present which have reacted, r is the ratio of the initial number of crosslinking groups to prepolymer reactive groups, and h and j are weighted average functionalities of the two reactants. It is suggested that the limiting factor in defining the final extent of reaction in these systems is the accessibility of reactive groups as determined by solid geometry rather than thermodynamics or reaction kinetics. The final extent of cure is regularly dependent on functionality and one cannot regard functionality and maximum extent of reaction as ndependent variables.

INTRODUCTION

By the year 1940 it had been established and generally accepted that the laws governing the chemical reactions of polymers were essentially the same as those for low molecular weight species.[1] An apparent exception to this rule was expected and found in systems, including gels, where diffusion rates were low. Little work appears to have been done on the course of prepolymer reactions or condensation polymerizations beyond the gel point. It was found in industry and in the laboratory that difunctional polycondensations could be carried out to about 99% reaction when no gelation could occur. For instance, Flory[2] was able to react diethylene glycol with adipic acid in the presence of *p*-toluenesulfonic acid to 98.9% conversion corresponding to a degree of polymerization of 90. For systems with functionality greater than two, Flory,[1] Stockmayer,[3] and others[4–6] derived relationships giving the weight fraction of sol and gel at various degrees of reaction.[1] They tacitly assume that condensation polymerization in high functionality systems can be carried to completion.
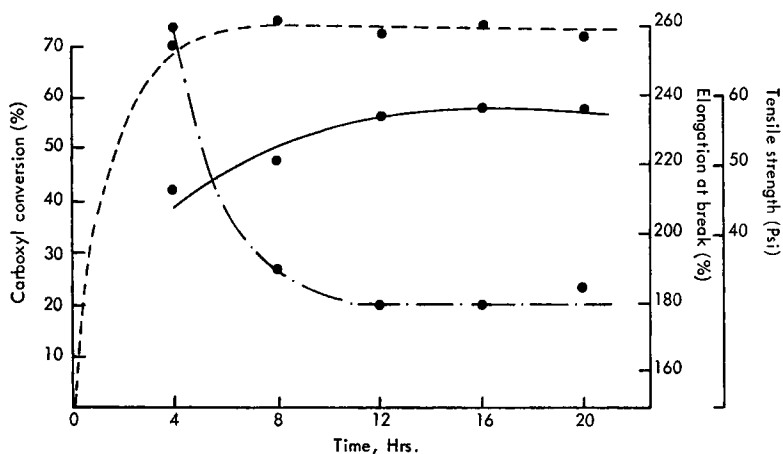
Fig. 1. Development of properties during cure of carboxyl-terminated polybutadiene:
(– – – –) conversion; (—) tensile; (–··–) elongation.

No firm conclusions can be drawn about the effect of prepolymer functionality and equivalent weight on network crosslink density unless either all the curing reactions go to the same extent in terms of reactive group content or unless the final extent of reaction is regularly dependent in some way on functionality or reactive group content.   Since one is able to detect correlations between prepolymer and cured stock properties, one or the other of these statements must be true.   Nevertheless, there has been no data to illuminate the matter.

Recently one of us[7] devised a method for following the curing reaction of certain prepolymers after the gel point.   It was found that many of these reactions proceeded only to about 70% conversion, a few per cent beyond the gel point.   Physical properties were found to develop mainly during the last few per cent reaction (see Fig. 1).

It is the purpose of the present work to see how the maximum extent of reaction occurring during the cure of prepolymers varies with the functionalities of the reactants and if any regular relationship determines this final extent of reaction.

Materials employed in the work were carboxyl and hydroxyl telechelic prepolymers which were crosslinked with epoxides and isocyanates to form elastomers of low tensile strength.

MATERIALS

Reactions were carried out using liquid carboxyl-terminated polybutadiene (CTPB) and liquid hydroxyl-terminated polybutadiene (HTPB) which were treated with polyfunctional epoxides and isocyanates, respectively.   The prepolymers had molecular weights ranging from 2000 to 6000.   They were obtained from Phillip's Petroleum Company, Thiokol Chemical Corporation, The General Tire and Rubber Company, and the

Sinclair Refining Company. They were used as received but were sometimes diluted with liquid polybutadiene of molecular weight 8000 obtained from the General Tire and Rubber Company.

Epoxides and isocyanates employed are shown in Table I. The functionality of these materials was determined from molecular weights ob-

TABLE I
Crosslinking Agents

Supplier	Trade name	Reactive group content, mEq/g	Functionality	Reactive groups
Shell	Epon X801[a]	9.10	2.86	Epoxide
Reichhold	Epotuf 427-60E[b]	6.10	2.73	Epoxide
Reichhold	Epotuf STF-6	6.95	2.52	Epoxide
Upjohn	Isonate 143L	7.25	2.10	Isocyanate
Upjohn	Isonate 390P	7.77	2.50	Isocyanate

[a] No longer manufactured.
[b] Original version of material now known as Epotuf STF-6.

tained using a vapor pressure osmometer and equivalent weights were obtained by standard analytical methods.[8,9]

The functionality of the prepolymers was determined by a gel point method[10] using a relationship developed by Stockmayer[11] and Kahn.[12] The equation is as follows:

$$h = 1 + \frac{r}{(P_A{}^2)_g (j - 1)} = 1 + \frac{1}{r(P_B{}^2)_g (j - 1)} \qquad (1)$$

where h = weighted average functionality of the prepolymer, j = weighted average functionality of the crosslinking agent, r = ratio of the total number of B (crosslinking) groups to the total number of A (prepolymer) groups initially present, and $(P_A)_g$, $(P_B)_g$ = fractions of A and B groups initially present 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 crosslinking groups to prepolymer reactive groups, (2) functionality of the crosslinking agent, and (3) extent of the reaction at the gel point.

The carboxyl content of the CTPB prepolymers was determined by titration with $0.1N$ sodium methylate to a thymol blue endpoint. The hydroxyl contents of the HTPB prepolymers were determined by esterification with an excess of acetyl chloride at 60°C for 30 min. Water and pyridine were added to hydrolyze the excess acetyl chloride. This solution was then titrated with $0.5N$ sodium hydroxide, using phenolphthalein as the indicator. The difference between the amount of base required for a blank and that of a sample is a measure of the hydroxyl content.[13]

Characteristics of the prepolymers are shown in Table II.

TABLE II
Maximum Extent of Reaction

Prepolymer	Reactive groups	Ostensible mol wt	Group content, mEq/g	Functionality h	Crosslinking agent	Functionality j	Prepolymer Total groups reacted, mEq/g	Total reaction, % of initial	$P_A{}^{2a}$	$\dfrac{1}{(h-1)\times(j-1)}$
FA2	COOH	5500	0.247	2.14	Epon X801	2.86	0.175	70.8	0.500	0.471
	COOH	5500	0.247	2.14	Epotuf 427-60E	2.73	0.180	72.6	0.527	0.508
FA3	COOH	5500	0.253	2.48	Epon X801	2.86	0.168	66.4	0.440	0.364
	COOH	5500	0.253	2.48	Epotuf 427-60E	2.73	0.176	69.7	0.486	0.391
FA5	COOH	5500	0.235	2.41	Epotuf STF-6	2.52	0.167	71.1	0.505	0.467
FB1	COOH	6000	0.338	2.29	Epon X801	2.86	0.254	75.4	0.568	0.417
FB3	COOH	6000	0.345	2.40	Epotuf 427-60E	2.73	0.248	72	0.52	0.414
FL1	COOH	3800	0.550	2.29	Epon X801	2.86	0.377	68.6	0.471	0.417
FL2	COOH	3800	0.512	2.72	Epotuf 427-60E	2.73	0.328	64	0.41	0.337
	COOH	3800	0.512	2.72	Epotuf STF-6	2.52	0.342	66.8	0.445	0.383
FR1	COOH	5000	0.379	2.37	Epon X801	2.86	0.244	64.5	0.416	0.392
FB2	COOH	6000	0.349	2.45	Epotuf 427-60E	2.73	0.234	67	0.45	0.398
FB2-30% NF	COOH	6000	0.244	2.45	Epotuf 427-60E	2.73	0.151	62	0.38	0.398
FB2-42% NF	COOH	6000	0.203	2.62	Epotuf STF-6	2.52	0.138	68	0.46	0.407
GC-1	OH	2000	0.98	1.95	Isonate 143L	2.10	0.96	98	0.96	0.96
FC-1	OH	5000	0.37	2.03	Isonate 143L	2.10	0.35	95	0.90	0.88
GG-1	OH	2000	0.92	1.99	Isonate 390P	2.50	0.76	83	0.69	0.675
GJ-1	OH	3000	0.77	2.53	Isonate 390P	2.50	0.52	68	0.46	0.43

^{a} $P_A{}^2$ is the square of the maximum or total reaction in terms of the fraction reacted of the amount initially present.

EXPERIMENTAL

Procedures used in the investigation of CTPB reactions were as follows. A prepolymer sample was mixed with an epoxide listed in Table I in 1:1 equivalent ratio, and 1% ferric acetyl acetonate (FeAA) was added. The mix was then evacuated at 60°–70°C, poured into a 3×3×0.075 in. mold, and cured 24 hr at 100°C. Two pieces, each large enough to cover one side of a Wilks Scientific Co. Model 12 ATR plate, were cut off and a
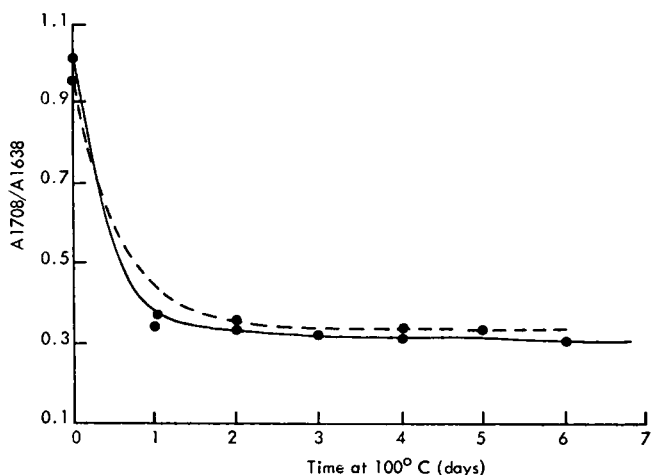
Fig. 2. Course of reaction between CTPB and Epon X801, ATR method: (—) FA2; (—-) FA3.
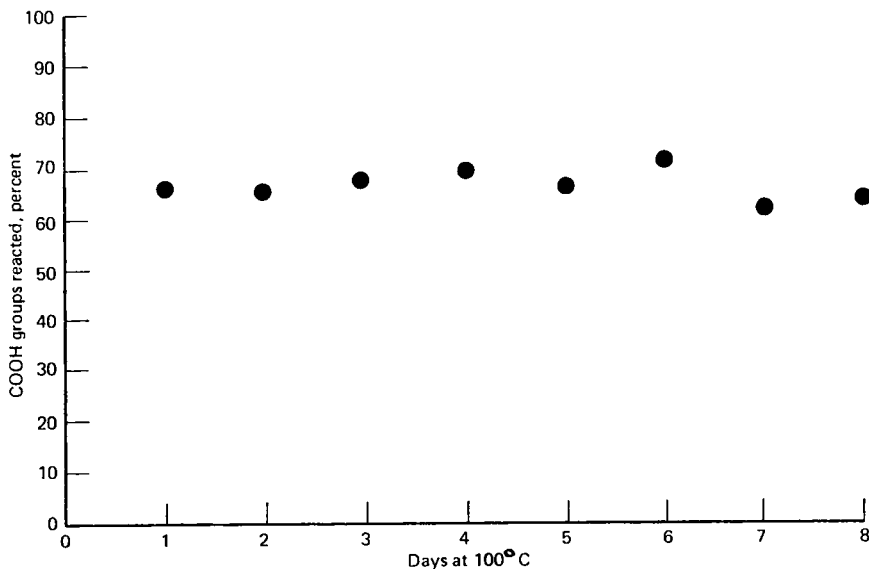
Fig. 3. Final extent of COOH reaction during heat aging.

spectrum was run by total internal reflection.   The sample was then placed
in an oxygen-free drybox (D. L. Herring Corp.) and heated at 100°C.   A
spectrum was run every 24 hr.   A sample of gas taken from the drybox
contained less than 0.01% oxygen as determined by a mass spectrograph.

In the infrared measurement, the ester peak at 1736 cm^{-1} was used and
compared with the olefin peak at 1638 cm^{-1} which served as an internal
standard.   A sample of the prepolymer was esterified with diazomethane
to 100% reaction and used as a comparison for the curing reaction (see
Fig. 2).

Measurements on the proportion of carboxyl groups reacted were taken
for as long as ten days at 100°C.   Figures 2 and 3 show the extent of reac-
tion of a CTPB sample as a function of time.   These results, which are
typical, indicate that little change occurs on prolonged heating in regard
to the proportion of carboxyl reacted and that results obtained in 24 to
72 hr at 100°C are in the plateau region for this cure.

Hydroxyl reactions in HTPB prepolymers, of which there were four, were
carried out using isocyanates as reactants (see Table I) at 80°C.   No cata-
lysts were employed.   The disappearance of the isocyanate infrared band at
2270 cm^{-1} was followed using the C—H band at 2843 cm^{-1} as an internal
standard.   When conversion versus time was plotted, it was found that
the curves leveled off while approaching the gel point, and the final extent
of these reactions was determined by extrapolation of the conversion–time
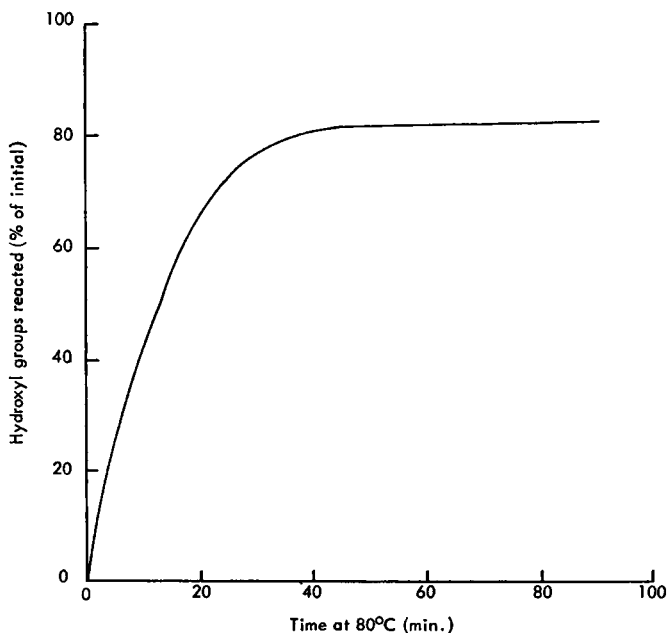curve as shown in Figure 4.

Fig. 4. Reaction of HTPB sample with isonate 390 P.

TABLE III

Maximum Extent of Reaction in Relation to Reactant Ratio

Prepolymer	Group content, mEq/g	Functionality h	Crosslinking agent	Functionality j	Ratio of reactants	Prepolymer Total groups reacted, mEq/g	Prepolymer Total reaction, % of initial	P_A^{2a}
FA2	0.252	2.14	Epotuf 427-60E	2.73	0.6	0.154	61	0.37
	0.250				0.8	0.167	67	0.45
	0.247				1.0	0.180	73	0.53
	0.245				1.2	0.196	80	0.64
	0.243				1.4	0.202	83	0.69
	0.241				1.6	0.205	85	0.72
FL2	0.520	2.72	Epotuf STF-6	2.52	0.67	0.277	53.2	0.283
	0.512				1.00	0.342	66.8	0.445
	0.497				2.00	0.381	76.6	0.586

[a] P_A^2 is the square of the maximum or total reaction in terms of the fraction reacted of the initial amount present.

RESULTS

Results for the maximum extent of reaction of carboxyl and hydroxyl groups on telechelic prepolymers are shown in Table II. Values are given as the total groups reacted in mEq/g and the final reaction as per cent of the reactive groups initially present. The crosslinking agent was used in a 1:1 equivalent ratio in each case. In Table III are shown maximum extents of reaction of CTPB prepolymers when the reactant ratio was varied.

It is evident that extents of reaction above 90% are found only in systems of average functionality close to two where elongations at break are high and tensile strengths are low. Among systems of higher functionality, maximum extents of reaction of 70% are most common. In fact, as shown in Table IV, the final extent of reaction is only a few per cent above the extent of reaction at the gel point.

TABLE IV
Final Extent of Reaction in Relation to the Gel Point

Pre-polymer	Funct. h	Crosslinking agent	Funct. j	Gel point, % of initial reacted	Final, % of initial reacted	Final % of initial, calc. from eq. (8)
FA2	2.14	Epon X801	2.86	69	71	72
FR1	2.37	Epon X801	2.86	63	65	67
FA2	2.14	Epotuf 427-60E	2.73	71	73	74
FB2	2.45	Epotuf 427-60E	2.73	63	67	67
FB3	2.40	Epotuf 427-60E	2.73	64	72	68
FL2	2.72	Epotuf 427-60E	2.73	58	64	63

DISCUSSION

One would expect that the final extent of a reaction should vary with the concentration of reactive species. Figure 5 shows a plot of reactive groups consumed against the initial reactive group concentration. It appears that the relationship is a linear one at each functionality of the system. Thus, as a working proposition one may say the proportion of groups consumed to initial amount present is constant for each functionality but increases as the system functionality decreases. We have already seen that this proportion is only slightly above the gel point. It is therefore reasonable to assume that the final extent of reaction is as given in Stockmayer's relationship, eqs. (1) and (3), plus a number whose magnitude diminishes as the average system functionality approaches two. Since a polymeric reaction in general goes no further than 99% at a functionality of two, this number will not decrease exactly to zero. It could be represented by $k[c - (P_A P_B)_g]$, where k and c are constants and $(P_A)_g$ and $(P_B)_g$ are the fractions of prepolymer and crosslinking reactive groups
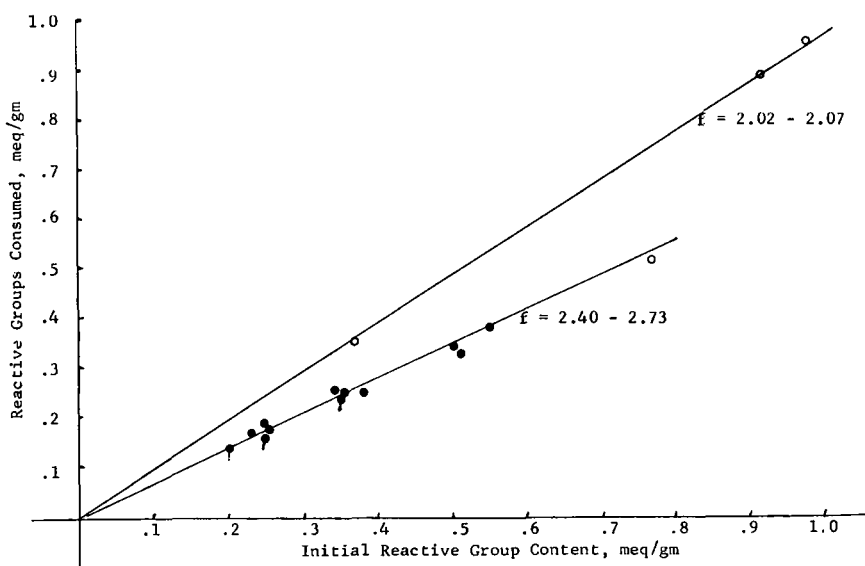
Fig. 5. Reactive groups consumed as a function of initial reactive group concentration: (O) HTPB; (●) CTPB; (◑) CTPB dilutions.

initially present which have reacted at the gel point. The final extent of reaction might then be represented by

$$P_A P_B = (P_A P_B)_g + k[c - (P_A P_B)_g] \tag{2}$$

where P_A and P_B are the fractions of prepolymer and crosslinking reactive groups initially present which have reacted at the end of the reaction.

Now Stockmayer's[8] and Kahn's[9] gel point relationship is

$$(P_A P_B)_g = \frac{(P_A{}^2)_g}{r} = (P_B{}^2)_g \, r = \frac{1}{(h-1)\,(j-1)} \tag{3}$$

where $r = B$ groups initially present (crosslinking)/A groups initially present (prepolymer), $h, j =$ weight-average functionality of A and B, and

$$P_A P_B = \frac{P_A{}^2}{r} = r \, P_B{}^2 \tag{4}$$

Substituting eqs. (3) and (4) in (2) and rearranging, we obtain

$$\frac{P_A{}^2}{r} = \frac{(1-k)}{(h-1)\,(j-1)} + kc \tag{5}$$

or
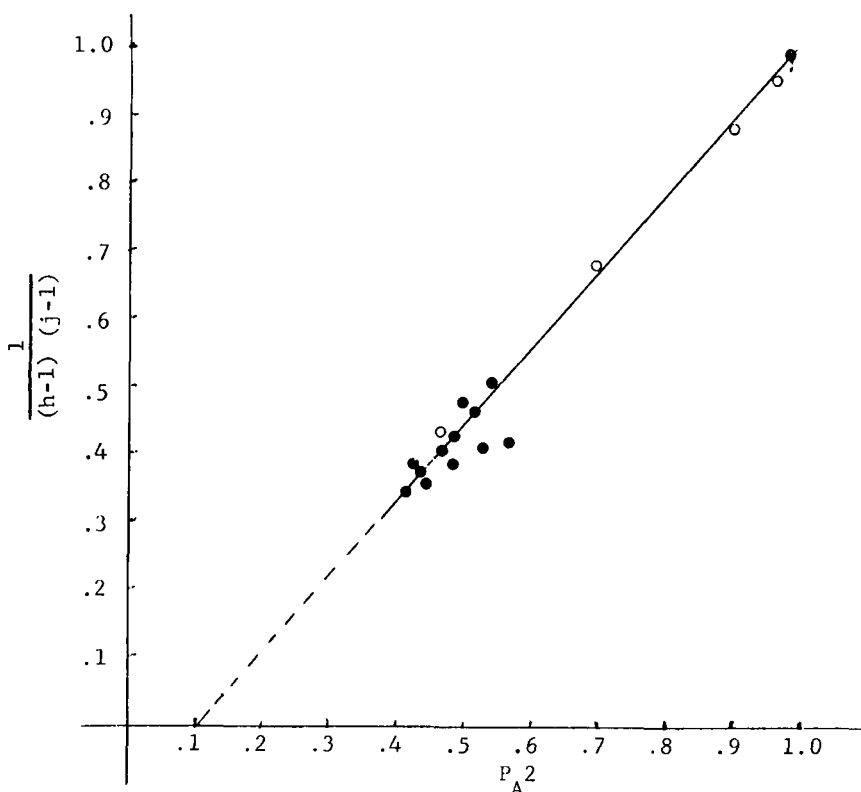
$$P_A{}^2 = (1-k)\,(P_A{}^2)_g + kcr \tag{6}$$

Fig. 6. Variation of square of maximum extent of reaction with Stockmayer's function: (O) HTPB; (●) CTPB; (⬤) max. reaction in polyesters.

At an average system functionality of two, $(P_A)_g = 1$ when $r = 1$ while P_A will be approximately 0.99. Substituting these conditions in eq. (6), obtain $c = 1 - (0.02/k)$ and $kc = k - 0.02$. Equation (5) then becomes

$$\frac{P_A{}^2}{r} = \frac{(1-k)}{(h-1)(j-1)} + (k-0.02).\tag{7}$$

This equation predicts that $P_A{}^2$ might be a linear function of $1/[(h-1)(j-1)]$ at a constant reactant ratio, while if the reactant ratio changes, $P_A{}^2$ should vary directly with r at a constant system functionality. Figure 6 shows $P_A{}^2$ plotted against $1/[(h-1)(j-1)]$ using the results in Table II. The plot indicates that a linear relationship does exist between the two quantities. Extrapolation of the line to the abscissa yields a value of 0.10 for $k - 0.02$ which makes eq. (7) become

$$\frac{P_A{}^2}{r} = \frac{0.88}{(h-1)(j-1)} + 0.10.\tag{8}$$

Figure 7 shows the maximum extent of reaction of two CTPB prepolymers plotted against the reactant ratio for two systems of average functionality 2.4 and 2.6. The $P_A{}^2$ is shown in Figure 8 as a function of the
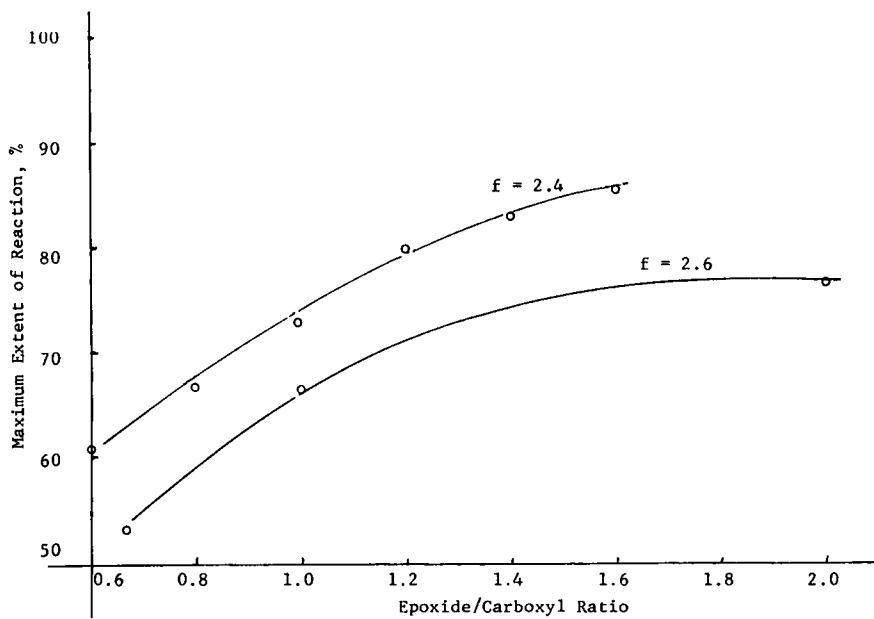
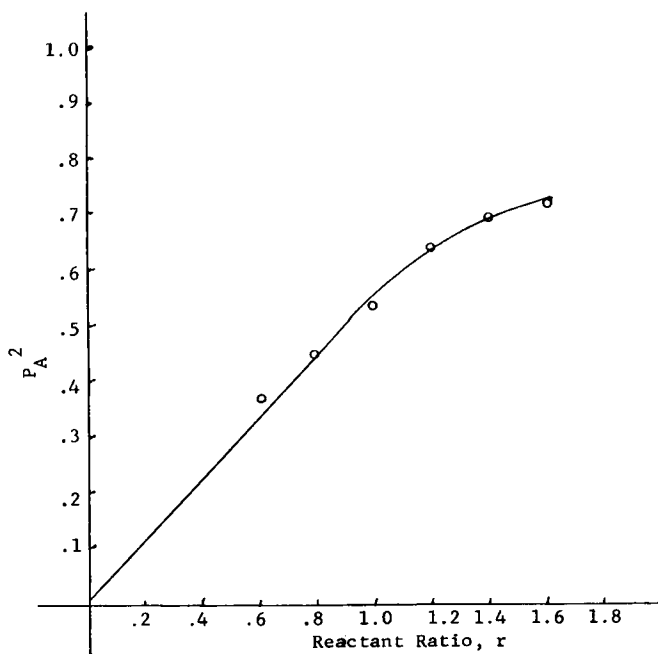Fig. 7. Final extent of reaction vs. reactant ratio.

Fig. 8. Variation of square of maximum extent of reaction with reactant ratio.

reactant ratio for one of these systems. When the slope of the initial part of this curve is used in conjunction with the values of the functionalities of the prepolymer and crosslinking agent, one can calculate the constant in eq. (7). The k value is found to be approximately 0.12, which again yields the constants given in eq. (8). It is evident that the relationship breaks down at values of r above 1.2 or 1.3.

It should be emphasized that the extent of reaction measured in this study and used to obtain eq. (8) is the average extent of reaction of all of the prepolymer reactive groups and not the extent of reaction of the prepolymer reactive groups in the gel phase only. The extent of reaction in the sol and gel phases is different, except at the gel point. More highly reacted sol molecules tend to bind to the gel before smaller molecules so that the sol becomes richer in less reacted material as time goes on.

In conclusion, data on the maximum extent of reaction occurring during the cure of telechelic prepolymers are consistent with eq. (8). It is suggested that the limiting factor in defining the final extent of reaction in these systems is the accessibility of reactive groups as determined by solid geometry rather than thermodynamics or reaction kinetics. The final extent of cure is regularly dependent on functionality so that one is justified in attempting prepolymer and cured stock correlation, and one cannot regard functionality and final extent of reaction as independent variables. The maximum extent of reaction is dependent on functionality and cannot vary at a given functionality.

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