

Determination of the Extent of Reaction for the System Carboxyl-Terminated Polybutadiene-Epoxy Beyond the Gel Point by Infrared Spectroscopy

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Synopsis

Curing reactions were investigated after the gel point, using infrared transmittance and reflection spectrophotometric techniques. In the system carboxyl-terminated polybutadiene (CTPB)/Epon X801 or Epotuf STF-6, catalyzed with Fe(III)-acetylacetonate (FeAA), at an equivalent ratio of carboxyl to epoxide groups, the final extent of reaction of COOH groups was found to be between 64% and 77% for eight CTPB samples. Increasing the ratio of epoxide to carboxyl groups (up to 1.6) resulted in an increase in the conversion, but the complete reaction of COOH groups could not be accomplished. The final extent of reaction also depends upon the functionality of the crosslinking agent. The lower the functionality of the epoxide, the higher the conversion of COOH groups. The use of chromium naphthenate as a catalyst for epoxide-COOH reactions gave higher conversions than FeAA. This result is related to side reactions catalyzed by the chromium naphthenate. The change in mechanical properties and the change in extent of reaction were followed simultaneously; it was found that no further development of mechanical properties occurred when the curing reaction between COOH and epoxide groups had ceased.

INTRODUCTION

In order to determine prepolymer functionality, it is only necessary to measure the extent of reaction up to the gel point.¹ It was observed that when the conversion versus time was plotted, the curves levelled off while approaching the gel point. This indicated that the crosslinking reaction would stop far short of the complete conversion of COOH and epoxide groups. Since no such investigation was found in the literature, it was thought of interest to see how far the crosslinking reaction would go beyond the gel point. Following the conversion by infrared transmittance or reflectance spectroscopy seemed to be the most promising approach.

MATERIALS

The prepolymers used were carboxyl-terminated polybutadienes (CTPB) of molecular weights in the range 4000-10000. The samples were obtained from Phillips Petroleum Company (Butarez CTL I and II), the General Tire and Rubber Company (Telagen CT), and the Thiokol Chemical Company (HC 434). The crosslinking agents were Epotuf STF-6 (formerly

427-60E) from Reichhold Chemicals, Inc., and Epon X801 from the Shell Development Company. The epoxide functionalities were 2.73 and 2.86, respectively. Epon X801 has been withdrawn from the market recently. The catalysts were Fe(III)-acetylacetonate (FeAA) from Aldrich Chemical Company and chromium naphthenate (4% solution in cyclohexane) from Harshaw Chemical Company. Prepolymers and crosslinking agents were used as received from the manufacturers. Diazomethane for the esterification of the CTPB samples was prepared from Diazald (N-methyl-N-nitroso-*p*-toluenesulfonamide) from the Aldrich Chemical Company.

EXPERIMENTAL

Preparation of Gum Stocks

Different samples of CTPB (30 g) were cured with Epon X801 and in two cases with Epotuf STF-6, using FeAA as the curing catalyst. The prepolymers were mixed mechanically with the curing agent at an equivalent ratio of epoxide to COOH groups and with 1% by weight FeAA and carefully degassed at 60°C in a vacuum oven. The mixture was then poured into Teflon-coated 3 in. × 6 in. molds, degassed again, and after closing the molds heated up to 100°C for various lengths of time.

Preparation of Samples for Infrared Analysis

The preparation and composition of the mixture of polymer, epoxide, and FeAA was the same as described above, only on the 5-g scale. A small sample was withdrawn from each mix and placed between NaCl windows, using a 0.025-mm polyethylene spacer. After placing the windows in a sample holder, the latter was transferred into a variable temperature cell. The cell was sealed and heated at 100°C.

Esterification of CTPB

Five-gram samples of CTPB were esterified with an ethereal solution of diazomethane, prepared from Diazald (N-methyl-N-nitroso-*p*-toluenesulfonamide).²

Mechanical Properties

The measurements of elongation and tensile strength were carried out on a Scott Tester, Model X5 (pulling speed 2 in./min), using the cured gum stocks stamped in the shape of standard dog bones. The hardness was determined with a Shore Durometer, Type A-2 (The Shore Instrument & Mfg. Co.).

DISCUSSION

The extent of reaction was determined by two different techniques: (a) determination of the extent of reaction by IR analysis when the sample was cured between NaCl windows and (b) determination of the extent of

reaction by internal reflection spectroscopy (ATR) attenuated total reflectance) when the sample was cured in Teflon-coated molds.

Determination of the Extent of Reaction by Infrared Analysis

The cure of the sample (preparation—see experimental part) was followed by scanning the spectrum between 1900 cm^{-1} and 1450 cm^{-1} at constant time intervals, and the relative carboxyl content was determined by the baseline method. The absorbance of the carboxyl band at 1708 cm^{-1} and of the C=C band at 1638 cm^{-1} , which served as a standard, was determined and the proportion A_{1708}/A_{1638} was computed. The ratio at zero time was obtained by taking the spectrum from a mixture of prepolymer and catalyst without crosslinking agent.

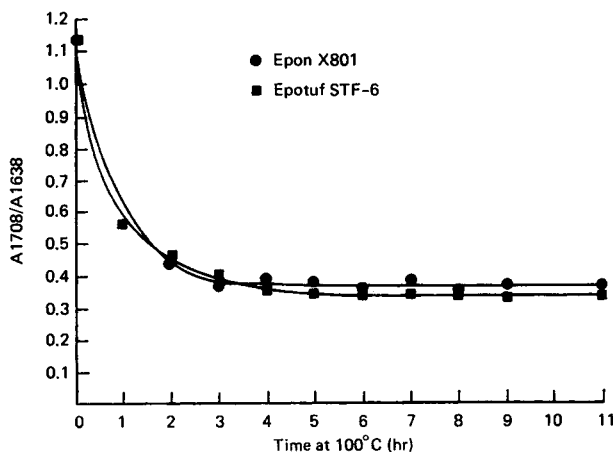


Fig. 1. Course of reaction between CTPB and two epoxides: infrared analysis method.

Figure 1 shows a typical run where the proportion A_{1708}/A_{1638} was plotted against time when a sample of CTPB was cured with Epon X801 and Epotuf STF-6. The difference in the two reactions is attributed to the different functionalities of the two curing agents ($f_{\text{Epon X801}} = 2.86$, $f_{\text{Epotuf}} = 2.72$). As can be seen from the diagram, the reaction is completed after 4 hr at 100°C . It was known, however, from previous experiments¹ that the gel time was 284 min with Epon X801 when the curing was carried out at 120°C in a glass tube. The faster reaction rate could be attributed to catalysis of the curing reaction by the NaCl windows.

Determination of Extent of Reaction by ATR

In order to avoid the possible catalytic effect of the NaCl windows, several samples were cured in Teflon-coated molds, using the same composition and temperature as in the infrared experiments. After one day, the molds were opened and two small pieces corresponding to the size of a reflector plate were cut from the cured gum stock. After obtaining the first

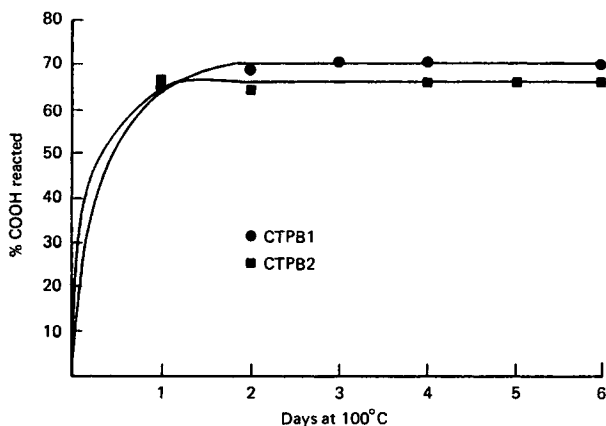


Fig. 2. Course of reaction between the CTPB samples and Epon X801: ATR method.

spectra from the two pieces, they were sealed in a glass tube, provided with a stopcock, flushed several times with dry nitrogen, and reheated in an oven at 100°C. Figure 2 shows that the reaction is completed after two to three days at 100°C.

The extent of reaction was determined by ATR technique, using a Model 12 internal reflection attachment (KRS5 reflector plate, 45° angle of incident) from Wilks Scientific Corp. and the spectra were scanned with a Perkin-Elmer 421 spectrophotometer between 1900 cm^{-1} and 1450 cm^{-1} . Table I shows good agreement between results from the transmittance and reflection technique.

TABLE I
Final Extent of Reaction of CTPB Samples Cured with Epon X801 at 100°C

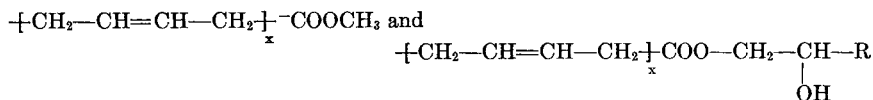
Sample no.	Method and frequency of determination		
	IR (1708 cm^{-1}), % COOH	ATR (1708 cm^{-1}), % COOH	ATR (1738 cm^{-1}), % COOH
1	70.8	71.8	—
2	68.0	66.4	—
3	77.0	—	75.4
4	64.3	—	64.7
5	65.0	65.6	65.1
6	67.6	—	68.6

Determination of Extent of Reaction by Means of the Formed Ester Groups

In the above cases the intensity of the COOH groups at 1708 cm^{-1} decreases continuously and the intensity of the ester groups at 1738 cm^{-1} increases as the reaction proceeds. After a certain amount of COOH

groups have reacted, only a shoulder is visible in the spectrum at 1708 cm^{-1} which prohibits an accurate determination of the carboxyl groups. In order to obtain a better procedure for the determination of the final extent of reaction, the possibility of determining the conversion from the intensity of the ester groups at 1738 cm^{-1} was investigated.

A very convenient method for the methylation of CTPB is available using an ethereal solution of diazomethane, and the only question is whether the molar extinction coefficients of the esters (obtained in the reaction with



an epoxide) are the same. According to Jones and Sandorfy³ and Bellamy,⁴ no change was obtained in the molar extinction coefficient with esters when the alcohol in the aliphatic series was changed. If the extinction coefficients are the same, it should be possible to determine the per cent of ester formed in the CTPB-epoxide reaction. This corresponds to the per cent of COOH groups which have reacted. One can relate this to the completely methylated CTPB ester which corresponds to 100% reacted CTPB. The final extent of reaction of the COOH groups therefore is calculated according to

% COOH reacted =

$$\left(\frac{A_{1738}}{A_{1638}} \text{ of the cured product} \times 100 \right) / \left(\frac{A_{1738}}{A_{1638}} \text{ of the methylated CTPB} \right).$$

As can be seen in Table I, last column, the results check well with those obtained from the previous determinations. As pointed out before, the results obtained from ester group determinations must be regarded as the most accurate.

Variation in Extent of Reaction with Epoxides of Different Functionalities

Because the crosslinking agent Epon X801 is no longer commercially available it was replaced in these experiments by Epotuf STF-6. The functionalities of these epoxides are 2.86 for Epon X801 and 2.73 for Epotuf STF-6 and therefore one would expect to obtain a slightly higher extent of reaction with Epotuf as curing agent. This was observed in Table II.

TABLE II
Variation in Extent of Reaction of CTPB Samples
with Epoxides of Different Functionalities

Sample no.	% COOH reacted with Epon X801	% COOH reacted with Epotuf STF-6
1	70.8	72.6
2	68.0	69.7

In these reactions FeAA was used as catalyst. However, with chromium naphthenate as catalyst, the conversion was always higher than in the reactions with FeAA.

Dependence of the Final Extent of Reaction on the Catalyst and Reactant Ratio

In order to elucidate the discrepancy found above and to investigate at the same time the extent of reaction when the ratio between carboxyl and epoxide groups was varied, two series were made with the same CTPB and epoxide but with different catalysts. Figure 3 shows the results obtained.

It may be observed that (1) complete reaction of all the carboxyl groups could not be obtained even at high ratios of epoxide to carboxyl groups; (2) the extent of reaction was always higher with chromium naphthenate than with FeAA; and (3) the curves converge at the higher equivalent ratios. This indicates that chromium naphthenate catalyzes two reactions with different rate constants: COOH-epoxide reaction and COOH-OH reaction. Hydroxyl groups are formed in the reaction between COOH and epoxide groups. At the higher epoxide/COOH ratios (1.2 to 1.6), the COOH-epoxide reaction predominates and the extent of reaction is nearly the same for both catalysts. At the ratio of 0.6 (maximum possible conversion of COOH groups through epoxide reaction is 60%), it was found that 60% of the COOH groups had reacted with FeAA as the catalyst, while 68% reacted using chromium naphthenate. A plausible explanation for this difference is that chromium naphthenate also catalyzes the COOH-OH reaction, thus leading to greater conversion of COOH groups.

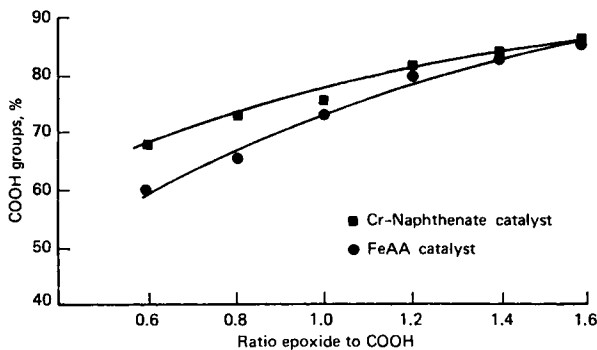


Fig. 3. Final state of cure at different equivalent rates.

Relationship between Extent of Reaction and Change in Mechanical Properties

CTPB-epoxide samples with chromium naphthenate (0.4% by weight) as catalyst were cured in Teflon-coated molds and samples were withdrawn periodically while the curing process was in progress. Samples for elongation and tensile strength measurements were cut in the shape of dog bones.

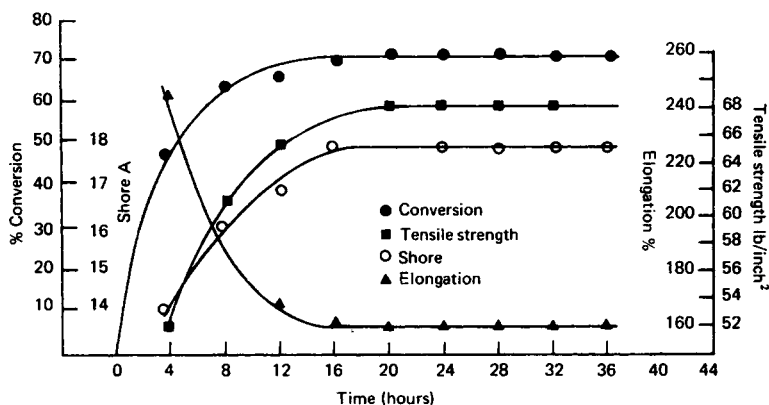


Fig. 4. Change in properties and conversion for a CTPB-epoxide system: chromium naphthenate catalyst; cured at 100°C.

After the first withdrawal, the remaining samples were sealed in glass tubes, flushed several times with nitrogen, and heated at 100°C. The measurements were taken at constant time intervals until constant results were obtained.

Typical data obtained are shown in Figure 4 where the per cent COOH conversion, Shore A, per cent elongation at break, and tensile strength at break in lb/in.² are plotted against time. No further development of mechanical properties can be noted when the curing reaction between COOH and epoxide groups has ceased.

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