

Functionality Determination of Hydroxyl-Terminated Butadiene Prepolymers*

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Synopsis

Functionality of hydroxyl-terminated butadiene prepolymers (HTPB) was determined from gel point measurements as described by Strecker and French.² Commercial HTPB samples had functionalities ranging from 1.9 to 2.6, with most of the material close to 2.0. In order to calculate functionality from gel point measurements, the hydroxyl content of the HTPB must be known. A method was developed which gave reproducible results. Curing agents used in the gel studies were viscous liquid polyfunctional isocyanates with functionalities of 2.00 and 2.50. An extensive study showed that no side reactions were occurring with the isocyanates at the temperatures employed. It is estimated that the precision of the method is $\pm 0.80\%$. Functionality calculated by dividing molecular weight by equivalent weight results in lower values in all cases when compared to gel point measurements.

INTRODUCTION

Functionally terminated low molecular weight polymers are currently used in sealants, adhesives, materials of construction, and as propellant binders. These materials are treated with reagents which react with and convert the prepolymers to three-dimensional structures whose properties are largely determined by the volume density of branch points in the polymer network. The branch point or crosslink density is determined by the number of branch points originally present in the prepolymer and the cross linking agent assuming complete reaction of all functional groups. Functionality is defined as the average number of reactive groups per molecule and thus becomes a most important property of the prepolymer.

Previously, functionality was calculated by dividing molecular weight by equivalent weight. However, it has been pointed out by Van Dam¹ that errors in molecular weight determination are not only due to impurities in the prepolymer, but also to the design and operation of the apparatus. Fluctuations in the temperature or solvent-polymer equilibrium will create an error. Additional errors can be due to association of polar molecules containing OH—, NH₂—, or COOH— groups when dissolved in a nonpolar

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solvent. Taking all these sources into consideration, molecular weights can be in error by as much as 5% and sometimes higher.

For this reason, Strecker and French² developed a method for the determination of functionality of prepolymers from gel point measurements. An equation for the weighted average functionality was obtained from the work of Stockmayer.^{3,4} The equation is as follows:

$$f_E = 1 + \frac{r}{p_A^2(g_E - 1)} = 1 + \frac{1}{rP_B^2(g_E - 1)}$$

where f_E and g_E are the weighted average functionality of the prepolymer A and the crosslinking agent B ; r is the ratio of the total number of B (isocyanate) groups to the total number of A (hydroxyl) groups initially present; P_A and P_B are the fractions of A and B groups initially present which have reacted at the gel point.

Strecker and French² worked mainly with carboxyl-terminated butadiene prepolymers (CTPB), while the present work establishes that the gel method is also applicable to hydroxyl-terminated butadiene prepolymers (HTPB)-isocyanate systems.

EXPERIMENTAL

Materials

The prepolymers used in the work were HTPB of molecular weights in the range of 1500-6000. Samples were obtained from Phillips Petroleum Company (Butarez HT series), General Tire and Rubber Company (Telagen HT series), and Sinclair Refining Company (R45M). These prepolymers were used without further purification. The crosslinking agents were polyfunctional isocyanates (Isonate 390P and Isonate 143L) obtained from the Upjohn Company. Some physical properties of the isocyanates are reported in Table II.

Determination of the Hydroxyl Content

The hydroxyl content of the prepolymers was determined by modifying a procedure of Smith and Bryant.⁵ Esterification of the HTPB was accom-

TABLE I
Hydroxyl Content of Various Prepolymers

Polymer	OH found, meq/g	Supplier's OH value, meq/g
HTPB A	0.33	0.36
HTPB B	0.31	0.35
HTPB C	0.99	1.05
HTPB D	0.96	0.98
HTPB E	1.02	0.99
HTPB F	0.93	0.91
HTPB G, I	0.35	0.32
HTPB H	0.77	0.7 to 0.8

plished by reacting the prepolymer with an excess of acetyl chloride at 60°C for 30 min. Water and pyridine were added to hydrolyze the excess acetyl chloride and this solution was then titrated with 0.5*N* sodium hydroxide, using phenolphthalein as the indicator. The difference between the amount of base required for a blank and a sample is a measure of the hydroxyl content. Results of the hydroxyl determinations for several HTPB prepolymers are shown in Table I.

Crosslinking Agents

Further work soon established that the originally recommended tricarballylic acid² was not suitable for routine use as a crosslinking agent in this system. Tricarballylic acid does not dissolve readily in the polymer below 145°C and also requires high temperatures of 150°–160°C for esterification.

Toluene diisocyanate was not used as crosslinking agent in the present work, as the two isocyanate groups have different reactivities due to the steric interference of the ortho methyl group. The different reactivities of the isocyanate groups results in an extremely slow viscosity increase, thus delaying gelation of the system. Therefore, the present study has concentrated on the use of other commercially available isocyanates.

The isocyanates that were used as curing agents in the functionality study were chosen for the following reasons: viscous liquids; low toxicity factor due to nonvolatile nature of isocyanates when used at room temperature or moderately low temperatures; reasonable time period for gelation of the mixture without the use of catalyst; elimination of side products inasmuch as the curing process involves an addition reaction; and low temperature curing.

The functionality of the isocyanates was calculated by dividing the molecular weight by the equivalent weight. Molecular weight determinations were made using the Hitachi Perkin Elmer Model 115 vapor pressure osmometer (see Table II). Equivalent weights were determined using the standard di-*n*-butylamine procedure.⁶

TABLE II
Functionalities (*f*) of the Isocyanates

Curing agent	Equivalent wt	Molecular wt	<i>f</i>
Isonate 390P	129	322	2.50
Isonate 143L	145	290	2.00

Functionality Determination From Gel Point Measurements

Except for the use of different crosslinking agents and temperatures, the procedure used to determine the functionalities of the various HTPB samples was identical to that outlined by Strecker and French.² After mixing an equivalent amount of the prepolymer and isocyanate, the viscosity of

the mixture was recorded, and the extent of reaction of the isocyanate was followed up to the gel point at 15-min intervals. Using the equation

$$f_E = 1 + \frac{1}{rP_B^2(g_E - 1)},$$

the functionalities of six prepolymers were determined and are reported in Table III. There is good agreement between the functionality of HTPB H as reported by Strecker and French² and the present work as illustrated in Table IV.

TABLE III
Functionalities of HTPB Prepolymers

Prepolymer	Func- tionality using Isonate 390P as curing agent		Func- tionality using Isonate 143L as curing agent		Func- tionality from mol wt/ equiv wt
	% reacted	% reacted	% reacted	% reacted	
HTPB C	1.94	84	1.99	94	1.58
HTPB D	1.95	83	1.94	96	1.64
HTPB F	1.96	82	1.99	94	1.59
HTPB G	1.99	82	2.06	91	1.76
HTPB H	2.54	65	2.63	72	2.42
HTPB I	2.03	78	2.10	91	1.76

TABLE IV
Functionality of HTPB H

Curing agent	Curing temp.	% Reacted	f_E
Tricarballic acid ^a	150°C	55.9	2.60
Toluene diisocyanate ^a	60°C	79.7	2.58
Isonate 390P	RT	65	2.54
Isonate 143L	RT	72	2.63

^a From Strecker and French.²

DISCUSSION

An interesting observation was made in the gel study of HTPB F and Isonate 390P. After stirring the isocyanate-HTPB mixture at room temperature for 0.5 hr, the isocyanate was 82% reacted and the degree of reaction remained constant for 2 hr, as shown in Figure 1. Even though the isocyanate content at the end of 0.5 hr and at the gel point is constant, it takes some 2 hr for the mixture to gel. This is the case for all the difunctional prepolymers that were studied in reaction with Isonate 390P; however, the initial reaction rate varies from prepolymer to prepolymer. The viscosity of the mixture at the end of 0.5 hr is low despite the high isocyanate conversion and remains relatively unchanged for approximately

$\frac{1}{2}$ hr, as shown in Figure 2. On heating a HTPB-isocyanate mixture at 70° – 90°C , the reaction is much more rapid than in the above cases, and the isocyanate content does not remain constant for a long period of time

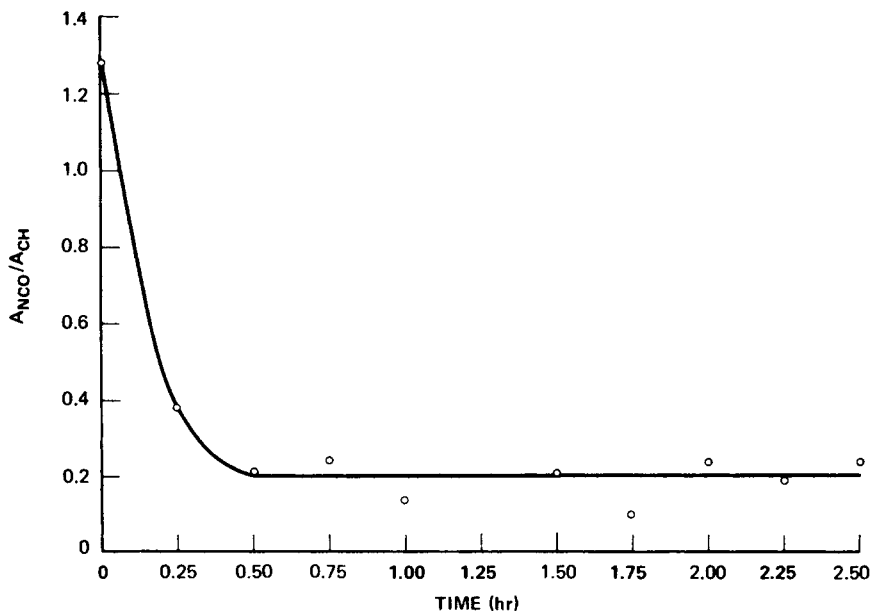


Fig. 1. Reaction of HTPB F and Isonate 390P at room temperature and under N_2 using the C—H band as reference.

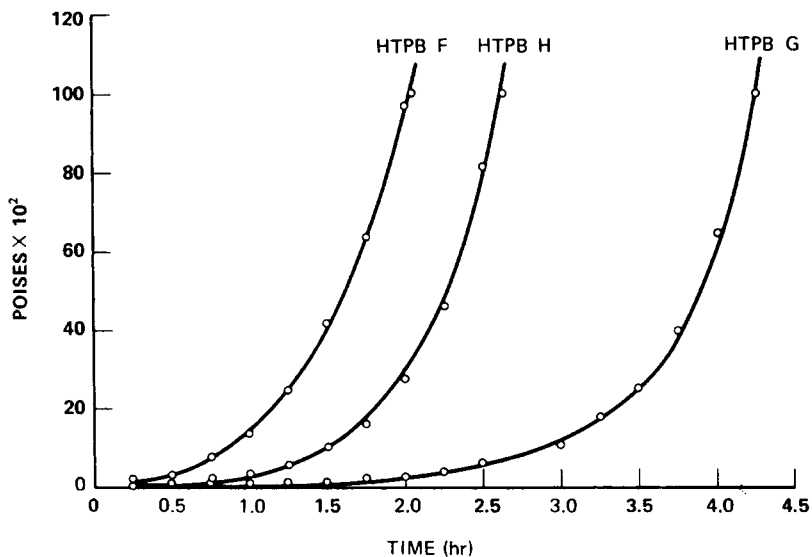


Fig. 2. Viscosity changes up to the gel point for HTPB and Isonate 390P systems.

before gelation occurs. Also, the viscosity increases more rapidly at the higher temperature.

HTPB F is lower in functionality than HTPB H, and therefore one would assume that a longer time for gelation would be necessary; but this is not the case. One can only assume that some impurity is catalyzing the reaction for HTPB F and Isonate 390P. Both HTPB F and G are similar in functionality and contain secondary hydroxyl groups, but HTPB G gel study was run at 90°C while HTPB F was run at room temperature. The difference in viscosity curves as shown in Figure 2 is further evidence for assuming that some impurity is catalyzing the reaction.

Precision of the Method

The precision of the functionality determination from gel measurements was obtained from a series of gel studies for HTPB H and Isonate 390P. The average as shown in Table V is $2.57 \pm 0.80\%$. In comparing the precision of molecular weight determinations to functionality determinations, a difference of greater than 4% is realized. Therefore, functionality calculated from gel measurements would be preferred over molecular weight/equivalent weight ratios.

TABLE V
Precision of Functionality Determination from Gel Measurements

f_E	Deviation from average
2.54	0.03
2.57	0.00
2.58	0.01
2.60	0.03
2.57 average	0.02 average

Functionality From Gel Measurements Versus Molecular Weight/ Equivalent Weight Ratio

Functionality calculated by dividing molecular weight by equivalent weight results in lower values in all cases, as shown in Table III. These lower values are the direct result of errors in molecular weight determinations, as discussed previously, and in equivalent weight values. All the prepolymers contain nonfunctional material, which is not taken into account when equivalent weights are determined. As a result of the nonfunctional material, the equivalent weights are higher than they should be, and thus the functionality is lower. With the gel method, the nonfunctional material does not affect the functionality because the results are dependent only on the reaction of the hydroxyl groups with the isocyanate.

Possibility of Side Reactions

There are undesirable side reactions that can occur when isocyanates are used as curing agents. Isocyanates can react with moisture from the

air, thus initiating side reactions. The use of catalysts such as amines or metal salts of carboxylic acids and heat can cause dimerization, trimerization, and allophanate formation.⁷⁻¹⁴ If any side reactions occur, an error will be introduced in the functionality determinations.

A study was made to see if the isocyanate curing agent was affected by atmospheric moisture. The isocyanate-HTPB mixture was reacted under the following conditions: (1) reaction mixture degassed under vacuum at room temperature and then allowed to react at room temperature under nitrogen; (2) reaction mixture degassed under vacuum at room temperature and then allowed to react at room temperature in a dry box; and (3) reaction mixture was not degassed and was allowed to react while exposed to the atmosphere at room temperature.

No difference was observed in the functionality values of the prepolymer. Also, if water was being absorbed, additional bands could appear in the infrared spectra due to the formation of an amine, an allophanate, or biuret linkages. Kogan¹⁰ reported that the allophanate and/or biuret reaction proceeds more readily in the presence of a urethane. On infrared analysis, using smears on sodium chloride plates, two peaks appear: one at 1735 cm^{-1} and the other at 1705 cm^{-1} . However, the infrared spectrum of a methylene chloride solution of the reacted polymer reveals only one peak¹⁵ at 1735 cm^{-1} . Thus, it can be concluded that the peaks at 1735 cm^{-1} and 1705 cm^{-1} correspond to a free and a bound urethane and that no side reactions due to water absorption are taking place.

Additional work was undertaken to determine what effect catalysts such as stannous octoate and heat would have on the functionality determination. Stannous octoate was added to the isocyanate curing agent, and the mixture was heated at 90°C. Gelation occurred in a relatively

TABLE VI
Prepolymer + Isocyanate System

Curing system ^a	Band used as standard	Curing temp.	% reacted	f_E
HTPB F + Isonate 390P	C—H at 2843 cm^{-1}	RT	82	1.96
HTPB F + Isonate 390P ^b	C—H at 2843 cm^{-1}	RT	85	1.89
HTPB F + Isonate 390P	C—H at 2843 cm^{-1}	75°C	84	1.93
HTPB F + Isonate 143L	C—H at 2843 cm^{-1}	85°C	94	1.99
HTPB F + Isonate 143L	C=C at 1595 cm^{-1}	85°C	95	1.97
HTPB H + Isonate 390P	C—H at 2843 cm^{-1}	RT	63.8	2.54
HTPB H + Isonate 390 P	CH ₂ at 1437 cm^{-1}	RT	65.3	2.52

^a Following the disappearance of isocyanate band.

^b Following the appearance of urethane band.

short period of time, thus indicating that the catalyst and heat were responsible for the homopolymerization of the isocyanate. Gel studies at room temperature and 70°–90°C were then run to see if heating, by itself, would catalyze side reactions. HTPB F was used as an illustration. This prepolymer was mixed with the isocyanate curing agent in approximately a 1:1 ratio and reacted at room temperature and at 75°C. There is a good correlation between the results, as shown in Table VI, thus indicating that the elimination of a catalyst and the use of low or moderate temperatures will not catalyze side reactions.

Different bands were used as a reference to see if there was any variation in the value for functionality. HTPB F-Isonate 143L and HTPB H-Isonate 390P systems were used as examples to determine if any variation would occur with a change in the internal standard. Changing the reference band had no effect on the functionality value, as shown in Table VI.

A further study was made on HTPB F to see if the rate of disappearance of the isocyanate could be correlated with the rate of formation of the urethane. The reaction was followed in the infrared by recording the absorbance of the isocyanate band at 2270 cm^{-1} , the urethane bands at 1735 cm^{-1} and 1705 cm^{-1} , and the C—H band at 2843 cm^{-1} . The value for 100% reaction of the HTPB prepolymer was determined by reacting the sample with phenyl isocyanate at room temperature and following the reaction in the infrared until there was no change in the absorbance of the urethane/C—H ratio. From the graph, $A_{\text{urethane}}/A_{\text{C-H}}$ versus time in hours, the extent of urethane formation at the gel point was determined. A good correlation was observed, as shown in Table VI.

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