

Functionality Determination of Hydroxyl-Terminated Prepolymers

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Present methods to determine functionality of prepolymers are based upon a network theory proposed by Stockmayer. However, the Stockmayer functionality is weighted and becomes ambiguous for prepolymer mixtures with species of varying functionality. The number average functionality allows better prediction of the cure behavior of prepolymers. This paper presents a simple theory to obtain the number average functionality from gelation test data. This theory is shown to hold for pure compounds as well as for a mixture of prepolymers. The validity of the calculated functionality data is shown with well-characterized compounds.

Introduction

POLYURETHANE elastomers are obtained by reacting mixtures of one or more diols and a triol with a diisocyanate. The triol provides the necessary crosslinking, while the long-chain prepolymer diol gives the rubber its characteristic properties. Prepolymers abounding in species with only one hydroxyl group per chain, not only require high concentrations of crosslinker but yield rubbers of inferior mechanical strength. Conversely, if the prepolymer functionality is considerably in excess of 2, many of the OH-groups must remain unreacted, otherwise too highly crosslinked, brittle rubbers result. In either case semiconnected chains are the cause of inferior mechanical properties in the final product.^{1,2} Thus it is of prime importance to know the functionalities of prepolymers used in elastomer formulation.

Definition of Functionality

The number average functionality is defined by

$$f = \frac{\sum_{i=1}^n f_i A_i}{\sum_{i=1}^n A_i} \quad (1)$$

where A_i is the number of moles of reactant A bearing f_i functional groups. If zero-functional chains are excluded, f may be considered as an "effective" functionality.³ The effective functionality is best calculated from gelation test data. Strecker and French⁴ have applied a relation, initially proposed by Stockmayer,⁵ to determine effective functionalities of epoxides and various carboxylic acids from gel point determinations. The Stockmayer equation links functionalities of the reactants with the extent of reaction at gelation, i.e.,

$$(P_A P_B)_{\text{gel}} = (f_e - 1)^{-1} (g_e - 1)^{-1} \quad (2)$$

where P_A and P_B are the fractions of A and B groups that have reacted and f_e and g_e are "weighted" average functionalities of reactants A and B , respectively, defined as

$$f_e = \frac{\sum_{i=1}^n f_i^2 A_i}{\sum_{i=1}^n f_i A_i} \quad (3)$$

and g_e is similarly defined for the type B species. Fogiel³ has applied Stockmayer's equation to experimentally determine the effective functionalities of some polyisocyanates.

It is experimentally more convenient to adjust the proportion of the reactants such that one component (preferably the isocyanate) has completely reacted at the gel point. In this case $P_B = 1$ and P_A is the NCO/OH ratio at the start of the reaction. For pure compounds the Stockmayer functionality is identical with the number average functionality. Therefore, if a well-defined diisocyanate is used, Eq. (2) reduces to

$$(P_{\text{OH}})_{\text{gel}} = (\text{NCO})/(\text{OH}) = (f_e - 1)^{-1} \quad (2a)$$

Equation (2a) is meaningful only for values $f_e \geq 2$, since $(\text{NCO})/(\text{OH})$ cannot assume values greater than 1 under the constraint of complete reaction of isocyanate at the gel point.

For other than pure compounds, the use of f_e to define functionality causes ambiguity. For example, according to Eq. (3) a 30/70 mole mixture of a triol and a monol has about the same Stockmayer functionality (2.13) as a 10/90 mixture of triol and diol (2.14), whereas the number average functionalities are 1.6 and 2.1, respectively. The triol/monol mixture will not gel with a diisocyanate, but the latter yields a well-cured rubber. In general, it was found that f is a better criterion than f_e for the cure potential of a prepolymer.

Measurement of Functionality

To obtain f from gel point data one may follow the following considerations. A diol reacting with a diisocyanate will form infinitely long chains if no side reactions or cyclization stop this chain propagation. The reactant mixture eventually solidifies into something that resembles a rubber but differs from it by the absence of crosslinks. Unlike a crosslinked rubber, it will be completely soluble in a solvent and will melt at elevated temperatures. Essentially the same thing happens if only two functions of a triol react with a diisocyanate, except that in this case the resulting polymer contains pendant side chains. Hence, to obtain a crosslinked rubber the overall functionality f of the reactant mixture must be greater than 2. Every functional group that remains unreacted acts as a chain terminator, i.e., as if an equivalent number of moles of a monofunctional compound had been added to the mixture of reactants.

The generally adopted concept of gelation is that at the gel point only infinitely long chains but no crosslinks are present. Hence $\sum f_i = 2$ is the condition for gelation. Thus if $\sum f_i < 2$, a crosslinker must be added to achieve gelation. If e_1 denotes the equivalents per gram of reactant 1, e_2 the equivalents per gram of reactant 2, etc., then the overall crosslink density, X , expressed in moles branch points per gram of rubber, is given

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$$X = e_1(f_1 - 2)/f_1 + e_2(f_2 - 2)/f_2 + \dots = \sum_{i=1}^n e_i(f_i - 2)/f_i \quad (4)$$

Only reactants whose functionality differs from 2 need be considered because difunctional compounds neither add nor subtract crosslinks. If one of the components exhibits $f < 2$, chain termination will occur, which appears as a negative increment for X in Eq. (4). At the gel point the overall crosslink density is zero (by definition), i.e., crosslinking and chain termination, if present, must exactly cancel.

The determination of the effective functionality is based on analysis of the composition of the reactant mixture at the gel point. If the unknown polyol gels with a stoichiometric quantity of a diisocyanate its average functionality is greater than 2, if not, it is less than 2. Most commercial diols have a functionality slightly less than 2 and therefore require a triol for gelation. If the diol-to-triol ratio is varied such that the mixture will just gel when reacted with a stoichiometric quantity of a diisocyanate, Eq. (4) takes the following form:

$$e_p(f_p - 2)/f_p + e_x(f_x - 2)/f_x = 0 \quad (5)$$

where the subscript x refers to the crosslinker and the subscript p to the unknown prepolymer. If all other quantities are known, f_p can be calculated from Eq. (5).

The crosslinker in Eq. (5) can, of course, also be a polyisocyanate; however, in this case $e_x + e_{\text{diisocyanate}}$ must equal e_p .

It is more convenient to use a fixed diol/triol ratio and vary the diisocyanate level until gelation is just obtained. If Δe_{NCO} designates the equivalents of diisocyanate missing from cure stoichiometry, i.e., $\Delta e_{\text{NCO}} = e_x + e_p - e_{\text{NCO}}$, then Eq. (4) can be written as follows:

$$e_p(f_p - 2)/f_p + e_x(f_x - 2)/f_x - \Delta e_{\text{NCO}} = 0 \quad (6)$$

This assumes that every equivalent isocyanate missing from cure stoichiometry will cancel one crosslink. The same result is obtained if a monoisocyanate is used to cause termination, since $e_{\text{monoiso}} = \Delta e_{\text{NCO}}$. For a polyol ($f > 2$) which gels with a diisocyanate, Eq. (6) simplifies to

$$f_p = 2/(e_{\text{NCO}}/e_p) \quad (6a)$$

Equation (6) can also be used to determine the functionality of polyisocyanates.

For prepolymers whose functionality is much less than 2 it is advantageous to employ a polyisocyanate rather than a polyol as crosslinker to insure a large enough proportion of the unknown polyol in the reactant mixture. Equation (5) or (6) may be used depending on the reaction conditions. However, at high levels of monofunctionality corrections for the appearance of totally terminated species must be made.

When both reactants are still present at the gel point Eq. (4) may be written as follows:

$$e_p f'_p + e_{\text{NCO}} f'_{\text{NCO}} - \Delta e_{\text{NCO}} - \Delta e_p = 0 \quad (7)$$

where Δe_{NCO} refers to the equivalents of unreacted NCO and Δe_p denotes the equivalents of unreacted polyol at the gel point. f'_{NCO} and f'_p represent $(f_{\text{NCO}} - 2)/f_{\text{NCO}}$ and $(f_p - 2)/f_p$, respectively. In Eq. (7) it is again assumed that for each equivalent of unreacted material one crosslink vanishes.

The foregoing is obviously a very simplified treatment of network formation. In all derivations equal reactivity of all functional groups of one kind is assumed. Only a few commercial products will fall into this category. The problem of unequal reactivity can be minimized if complete reaction of all functional groups is forced by using stoichiometric quantities of reactants. It was assumed that each molecule of

chain terminator would cancel one crosslink. However, if the ratio of monoisocyanate to polyisocyanate becomes large, zero-functional species are formed for which corrections must be made. For example, a triol reacting with a monoisocyanate forms four species, namely, a completely reacted, a doubly reacted, a monoreacted, and an unreacted triol. The fully terminated triol can no longer partake in network formation. Moreover, it removes three equivalents of chain terminator per mole, which will not be available for termination, so that the net result is a gain of two crosslinks per mole of fully terminated triol. Similar considerations apply to isocyanate deficiency, only here the situation is reversed, the unreacted triol will not enter the network and, of course, eliminates three equivalents of "NCO deficiency" which otherwise would cause three dangling chains. There are higher order zero-functional compounds. For example, two moles triol may react with one mole HDI to form a tetrol which then may be completely terminated by monoisocyanate, etc. Their concentrations, however, will be small and are therefore ignored in the following treatment. To arrive at a more accurate value for f_p the equivalents of totally reacted (or totally unreacted) polyol must be deducted from e_p and may be calculated as follows. Let R denote the monoisocyanate/polyol equivalents ratio. Assuming equal reactivity, the probability that one group of an f -functional compound has reacted equals R , and the probability that it has not reacted is $1 - R$. The probability that a molecule is formed with a certain sequence of reacted (r) and unreacted ($f-r$) groups is $R^r(1-R)^{f-r}$. For all possible sequences the mole fraction P_r of an f -functional compound in which r functions have reacted is given by

$$P_r = f! R^r (1-R)^{f-r} / r! (f-r)! \quad (8)$$

The application of Eq. (8) will be discussed later.

Experimental

The materials used in this study are listed in Table I. Prior to use the commercial prepolymers, reagent grade n -octanol, n -amylalcohol, 3-pentanol, and the solvents were stored over $13 \times$ molecular sieve. The isocyanates HDI and butylisocyanate were distilled in vacuum, then freshly assayed by a method of Stagg.⁶ Desmodur N-75 was used as received. Because of their reactivity the isocyanates should never be used in stoichiometric excess. The preferred procedure was to weigh approximately 10 g of a prepolymer and the desired quantity of the isocyanate on an analytical balance into a small glass vial with a polyethylene snap cap. Two drops of a 5% solution of ferric acetyl acetate were added and the mixture was diluted with toluene to about 70% polymer. After thorough mixing the vials were placed into an oven at 55°C and cured for one day. Gelation was judged to have occurred when the mixture would not flow. By varying the NCO/OH ratio, crosslinker concentration, or polyisocyanate/monoisocyanate ratio, a condition was found where gelation would just occur. The method was quite precise; an NCO interval of less than one-half equivalent percent brought about transition from liquid to gel.

When conversion of the isocyanate was not complete at the gel point (condition to which Eq. (7) applies), residual NCO was analyzed either by the characteristic NCO band at 2270 cm^{-1} , or by quenching the reaction with dibutylamine and back titrating excess amine according to Stagg.⁶ The titrimetric method was experimentally easier and considerably more accurate than IR analysis because of the difficulty of dissolving a polymer close to the gel point.

The effective functionalities reported for the various prepolymers were based on the effective functionality of HDI which was taken to be 2. All of the HDI lots analyzed at Aerojet showed better than 99.3% activity. Because of the equal activity of the two NCO groups and the selectivity of the $\text{Fe}(\text{AA})_3$ catalyst for the urethane reaction, the general

Table 1 Materials used in study

	Type	Supplier
Polyols		
TP 4040	Poly (propylene oxide) triol	Wyandotte
TP 2540	Poly (propylene oxide) triol	Wyandotte
TP 340	Poly (propylene oxide) triol	Wyandotte
PCP 0310	Poly (caprolactone) triol	Union Carbide
GTRO	Glyceroltriricinoleate, triol	Baker, Castor Oil
R-18	Diethyleneglycoladipate polyester	Mobay
R-45M, or R-45HT	Polybutadiene, hydroxyl-terminated	ARCO
ARCO F	Special lots with lower functionality	ARCO
ARCO G		ARCO
ARCO R		ARCO
ARCO S		ARCO
Diols		
PTMEG 1000	Poly (tetramethylene oxide) diol	DuPont
PPG-P2025	Poly (propylene) glycol	Wyandotte
B-2000	Poly (1,2 butylene) glycol	Dow
NPGA	Neopentylazelaate polyesterdiol	Wittco
PCP 0240	Poly (caprolactone) diol	Union Carbide
Monols		
n-Octanol		Aldrich
n-Amylalcobol		Aldrich
3-Pentanol		Aldrich
Isocyanates		
Butylisocyanate		Eastman
HDI	Hexamethylene-diisocyanate	Mobay
Desmodur N-75	biuret triisocyanate	Mobay

reproducibility of the experiments was within 2%. As a secondary standard, DuPont's PTMEG 1000 a (polytetramethylene-oxide) diol was used. HDI and PTMEG reacted stoichiometrically (70% in toluene) will just fail to gel, while addition of one equivalent percent of triol will bring about gelation.

Results

Table 2 lists the effective number average functionalities of various prepolymers. Only prepolymers whose molecular weight is not too low can be tested. The high insolubility imparted by reaction with an isocyanate causes phase separation and precipitation of low-molecular-weight materials like hexanediol, trimethylolpropane, etc. TP 340, a propyleneglycol extended trimethylolpropane of approximately 340 molecular weight, showed crystallization during reaction and the data, therefore, must be used with caution. Where possible the determination of functionality was conducted in solution containing approximately 70% polymer. At this concentration there was comparatively little effect of small concentration changes on functionality.

The functionality of the triols was established by reacting with a deficient quantity of HDI. The experimentally found NCO/OH ratio is shown together with the corrected value for totally unreacted material obtained from Eq. (8). TP 4040, a high-molecular-weight poly (propylene oxide) triol, has a fairly high degree of terminal unsaturation (0.07 milliequivalents/g) which accounts for its lower functionality. Most triols have functionalities close to 3. There is, however, an apparent trend in that with decreasing molecular weight the functionality increases slightly. The reason is not known, but it may be that the entanglement density is much greater in the low-molecular-weight triols due to the higher degree of branching. The Stockmayer functionality may be obtained from the uncorrected NCO/OH ratio and Eq. (2a). Equating (2a) and (6a) gives a relation between the two functionalities, viz., $f_{ST} = 1 + f/2$, where f_{ST} is the experimentally determined Stockmayer functionality. Stockmayer functionalities are about 2.5 for triols.

Table 2 Number average functionality of some commercial prepolymers

Polymer and solvent, %	EW	Method	(NCO)/(OH)		f_{OH}^d
			Experimental	Corr.	
Polyols					
TP 4040, tol 30 ^a	1350	HDI def ^b	0.70	0.73	2.74
TP 4040, tol 30 ^a		HDI/BuI ^c	0.72	0.75	2.67
TP 4040, CH 30 ^a		HDI def	0.70	0.73	2.74
TP 2540, tol 30	873	HDI def	0.65	0.69	2.90
TP 2540, tol 30		HDI/BuI	0.66	0.70	2.86
TP 2540, CH 30		HDI def	0.65	0.69	2.90
TP 340, CH 30 ^f	101	HDI def	~0.57	0.64	(3.13) ^f
GTRO, tol 30	343	HDI def	0.62	0.67	2.99
		HDI/BuI	0.64	0.68	2.90
R-18, CH 30	876	HDI def	0.45	0.53	3.77
PCP 0310, CH 30	294	HDI def	0.57	0.64	3.13
Diols ($e_{NCO} = e_{OH}$)				e_x/e_p	f_{OH}^e
PTMEG 1000, tol 30	489	TP 2540 crosslinker		0.01	1.99
PPG-P2025, CH 30	910	TP 2540 crosslinker		0.15	1.91
B2000, CH 30	980	TP 2540 crosslinker		0.28	1.84
NPGA, CH 30	1025	TP 2540 crosslinker		0.55	1.71
PCP 0240, CH 50	1000	TP 2540 crosslinker		0.10	1.94
Isocyanates					
Butylisocyanate	101	Chemical analysis			1.0
HDI, Hexamethylene-diisocyanate	84	Chemical analysis			2.0
Desmodur N-75	~250	PTMEG 1000, $e_{NCO}/e_p = 0.45$			~4.2

^a Solvent is 30% of mixture; tol = toluene; CH = cyclohexanone. ^b def = NCO deficiency. ^c BuI = butylisocyanate. ^d Calculated from Eq. (6a). ^e Calculated from Eq. (5). ^f Turbidity develops during reaction.

Table 3 Gel point data of hydroxy-terminated polybutadiene prepolymers using various methods

Material	Lot	EW	Method 7 ^a	Method 6 HDI def		Method 6 HDI/BuNCO		
			Δe_{NCO}	f_{OH}^b	e_{NCO}/e_p	f_{OH}^b	e_{NCO}/e_p	f_{OH}^b
R-45 HT	111225	1183	0.21	3.45	0.59	3.39	0.61	3.28
R-45M	208155	1280	0.13	2.70	0.75	2.67	0.75	2.67
ARCO F	—	2000	0.11	2.56	0.78	2.56	0.79	2.53
ARCO G	—	1450	0.13	2.70	0.75	2.67	0.77	2.60
ARCO R	—	1429	0.12	2.63	—	—	—	—
ARCO S	206122	1449	0.05	2.22	0.90	2.20	0.91	2.20
Lithcoa ^c	—	2941	0.07	2.32	0.87	2.30	—	—
GTRO	—	343	0.19	3.22	0.62	3.23	0.66	3.03

^aMethod 7 refers to conditions for which Eq. (7) is applicable, i.e., the determination of residual NCO in reaction where originally $e_{\text{NCO}} = e_{\text{OH}}$. ^bFunctionalities are not corrected for totally unreacted (or fully terminated) polyol. ^cA Li-initiated PBD prepolymer.

Table 4 Observed NCO/OH ratios and calculated functionalities in the reaction of HDI with mixtures of polyols having an average functionality > 2. Polymer concentration approximately 70% in toluene; test method: HDI deficiency

Hydroxyl compound(s)	f^a	f_e^b	NCO/OH ^c	f_{ST}^d	f^e	f_{corr}^f
PTMEG 1000	2.0	2.0	1.0	2.0	2.0	2.0
GTRO	3.0	3.0	0.62	2.6	3.2	3.0
GTRO 3 moles, PTMEG 1 mole	2.75	2.82	0.69	2.45	2.9	2.74
GTRO 1 mole, PTMEG 1 mole	2.5	2.60	0.76	2.32	2.63	2.52
GTRO 1 mole, PTMEG 3 moles	2.25	2.33	0.87	2.15	2.30	2.24
GTRO 2 moles, 3-pentanol, 1 mole	2.33	2.72	0.84	2.19	2.38	2.32
GTRO 3 moles, 3-pentanol, 1 mole	2.50	2.80	0.77	2.30	2.60	2.50

^aNumber average functionality from Eq. (1). ^bStockmayer functionality from Eq. (3). ^cObserved (NCO)/(OH). ^dExperimental Stockmayer functionality, Eq. (2a). ^eExperimental number average functionality, Eq. (6a). ^fCorrected number average functionality [using Eq. (8)].

Table 5 Gel point data and calculated number average functionalities in reactant mixtures where $f_{\text{OH}} < 2$ (all quantities are equivalents)

f_{OH}^{a}	Composition of gelling mixture				Monoreacted HDI ^b	Octanol for DESM ^c	Fully term DESM ^c	ΣCT^* effective	Effective DESM ^e	$f_{\text{DESM}}^{\text{f}}$
	DESM	HDI	PTMEG	<i>n</i> -octanol						
System PMEG/ <i>n</i> -octanol/Desmodur/HDI 33% in cyclohexanone										
2.0	0.00	1.00	1.00	0.00	0.00	0.00	0.000	0.00	0.00	—
1.8	0.18	0.82	0.89	0.11	0.160	0.02	0.000	0.10	0.18	4.50
1.6	0.37	0.63	0.75	0.25	0.234	0.092	0.000	0.208	0.37	4.55
1.5	0.47	0.53	0.67	0.33	0.234	0.155	0.0014	0.26	0.465	4.55
1.4	0.62	0.38	0.57	0.56	0.186	0.267	0.021	0.34	0.60	4.65
1.3	0.83	0.17	0.46	0.59	0.084	0.465	0.082	0.43	0.75	4.65
1.24	1.00	0.00	0.39	0.61	0.00	0.61	0.138	0.47	0.86	4.41
System PTMEG/ <i>n</i> -octanol/Desmodur 33% in cyclohexanone										
f_{OH}	DESM ^g	Monoreacted		ΣCT	Fully term. DESM	Effective DESM	$\Sigma\text{CT}^{\text{d}}$ Effective	$f_{\text{DESM}}^{\text{f}}$		
		PTMEG	Octanol							
2.0	0.45	0.50	0.00	0.25	0.043	0.407	0.207	4.07		
1.8	0.49	0.46	0.05	0.28	0.052	0.438	0.228	4.17		
1.6	0.58	0.36	0.15	0.33	0.061	0.519	0.269	4.15		
1.5	0.63	0.34	0.21	0.38	0.083	0.547	0.297	4.37		
1.4	0.73	0.225	0.314	0.426	0.085	0.645	0.341	4.24		
1.3	0.89	0.09	0.50	0.545	0.125	0.765	0.420	4.43		

^aNumber average functionality as defined by Eq. (1). ^bFrom Eq. (8). ^cProportion of octanol in mixture that will react with Desmodur. ^d $\Sigma \text{CT}^* = 1/2$ of monoreacted PTMEG + octanol portion for DESM minus fully terminated Desmodur. ^eEffective Desmodur = Desmodur in gelling mixture minus fully terminated Desmodur. ^f $f_{\text{DESM}} = 2/(1 - (\Sigma \text{CT}/\text{DESM}) \text{ effective})$. ^gQuantity that causes gelation; PTMEG and octanol same as above. ^{*}CT is the chain terminator.

The functionality of the diols was determined by varying the diol/triol ratio at stoichiometric NCO level. PTMEG 1000 is the best defined diol. PPG-P2025 has terminal unsaturation of approximately 0.03 milliequivalents/g, which accounts for most of its lower functionality. Analytical data on other compounds are not available.

Table 3 presents data on various hydroxyl-functional hydrocarbon prepolymers tested by three different methods. The agreement between the methods is quite good. The functionalities predicted from Eq. (2) or (2a) show the above-mentioned relation to the number average functionality. To calculate the Stockmayer functionality, f_{ST} , from the data of

the third method, the weighted average functionality for the BuNCO/HDI mixture has to be used in Eq. (2). For this method $P_A P_B = 1$. For example, the weighted average functionality for the BuNCO-HDI combination $0.61e \text{ HDI}/0.39e \text{ BuNCO}$ according to Eq. (3) is 1.61. With this value Eq. (2) yields $g_e = f_{\text{ST}} = 1.61/0.61 = 2.64$, i.e., $(3.28/2 + 1)$.

Table 4 shows average functionalities of mixtures of hydroxyl compounds. For comparison the calculated theoretical, f_e , and experimental Stockmayer functionalities, f_{ST} , are included. For calculation of the theoretical functionalities f and f_e it was assumed that $f_{\text{GTRO}} = 3.0$; $f_{\text{PTMEG}} = 2.0$; and $f_{3\text{-pentanol}} = 1.0$.

Many experimental prepolymers exhibit functionalities much less than 2. The large fraction of monofunctional species present in such mixtures causes the appearance of zero-functional (i.e., fully terminated) products which, while not entering the network, have to be considered in order to arrive at the effective NCO/OH ratio of the species that do form the network. Two examples of such systems are shown in Table 5. In system A stoichiometric quantities of hydroxyl and isocyanate groups are reacted, while system B uses NCO deficiency. In both systems a mixture of PTMEG ($f=2.0$) and *n*-octanol ($f=1.0$) was used to produce a "prepolymer" of the desired average functionality. In system A the octanol will be distributed between Desmodur and HDI, forming mono to fully terminated Desmodur, half-terminated HDI, and fully terminated HDI. The half-terminated HDI becomes the effective chain terminator. There will also be higher order zero-functional compounds. For example, two molecules of semireacted HDI "neutralize" one molecule of PTMEG. The frequency of these higher order products decreases rapidly and has been ignored in this treatment. The species that form the gel are: nonreacted HDI, semireacted HDI, the octanol fraction for the Desmodur minus that part of it which is bound to the fully terminated Desmodur, and the remaining Desmodur. The results of such calculations are shown in Table 5. To arrive at the concentration of the Desmodur-octanol reaction products from Eq. (8), f of Desmodur has been assumed to be 4. In system B, due to isocyanate deficiency some of the octanol and PTMEG remain unreacted. In addition, a fraction of the PTMEG will react only at one end thus becoming a chain terminator.

Notwithstanding that the above is a rather simplified treatment, the agreement between the calculated values of f_{DESM} from the two systems is fairly good. In practice it is more convenient to construct a master curve of f_{OH} vs equivalent percent Desmodur, from which the unknown prepolymer functionality may be read, after the equivalent percent Desmodur necessary for gelation has been determined. Such a curve is shown in Fig. 1.

With the gel point data of the first reaction in system B, Eq. (2a) yields an experimental Stockmayer functionality, f_{ST} , of 3.22 for Desmodur, while from Eq. (6a) $f=4.44$, again showing the same relation between f_{ST} and f as noted previously.

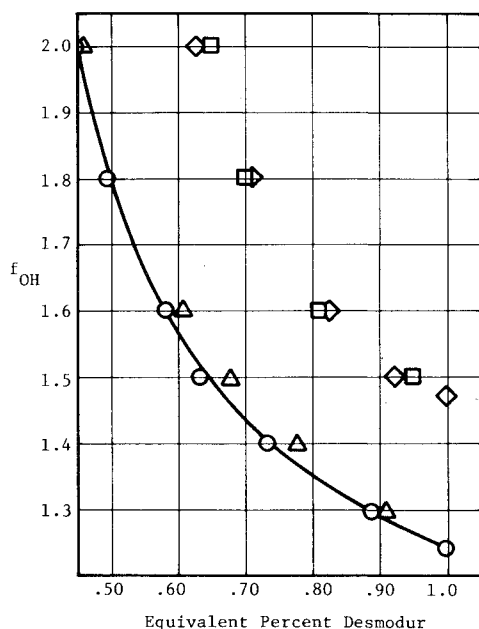


Fig. 1 Equivalent percent Desmodur necessary for gelation in various systems. \circ , PTMEG 1000/octanol; Δ , GTRO/3-pentanol; \diamond , GTRO/*n*-amylalcohol; \square , GTRO/*n*-octanol.

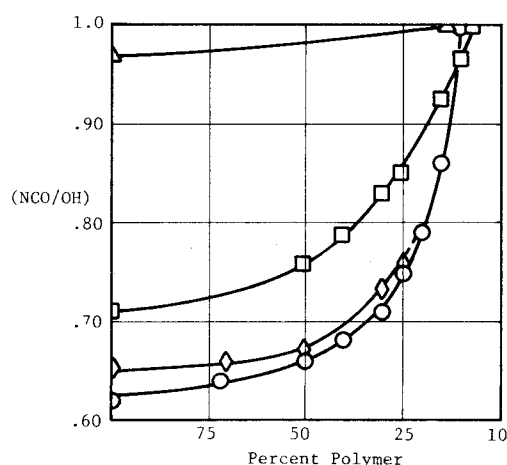


Fig. 2 Effect of dilution on the NCO/OH ratio at gelation. Method: NCO deficiency. \square , TP 4040; \diamond , TP 2540; \circ , GTRO; Δ , PTMEG 1000/TP 2540, $f_{\text{OH}}=2.07$.

Unequal reactivity of functional groups has a profound effect on the critical NCO/OH ratio, particularly in the case of NCO deficiency. Figure 1 shows that GTRO/*n*-octanol and GTRO/*n*-amylalcohol require much more Desmodur for gelation than GTRO/3-pentanol. In the former two examples the faster reacting primary hydroxyl groups of the monol will cause a higher degree of chain termination than in the GTRO/3-pentanol mixture. The effects of unequal reactivity on gelation can be minimized by choosing stoichiometric reaction conditions.

Effect of Dilution on Gelation

French and Strecker⁴ showed virtually no effect of dilution (between 100 and 33% polymer) for carboxy-terminated polybutadiene prepolymers reacted with epoxides. Fogiel³ found a strong dependence of dilution on the gelation of polyfunctional isocyanates, and most commercial triol-type prepolymers will not gel at concentrations less than 10% polymer (Fig. 2).

Fogiel presented a theory that accounts for the observed effects. Unfortunately some of the parameters necessary in his equation are experimentally inaccessible. Figure 2 shows the effect of dilution on the effective NCO/OH ratio at gelation for some triols. The results agree with those of Fogiel in that the effect increases with increasing functionality and is essentially nonexistent when the functionality approaches 2. The cause is generally attributed to intramolecular ring formation.⁷⁻⁹ At least qualitatively, the observed dependence on functionality is understandable. If a diol forms a ring, it becomes a zero-functional compound, no longer participating in network formation, but leaving the remainder undisturbed to form long chains. If two of the functions of a triol are short-circuited, it becomes, in effect, a monofunctional compound acting as chain terminator.

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References

- Flory, P. J., *Principles of Polymer Chemistry*, Cornell Univ. Press, Ithaca, N.Y., 1953, p. 458.
- Oberth, A. E., "Effect and Detection of Loose Chain Ends in Crosslinked Poly-Urethane Elastomers," *Rubber Chemistry and Technology*, Vol. 44, March 1971, pp. 152-165.
- Fogiel, A. W., "Effective Functionality and Intramolecular Reactions of Polyisocyanates and Polyols," *Macromolecules*, Vol. 2, Nov.-Dec. 1969, pp. 581-587.

⁴Strecker, R. A. H. and French, D. M., "The Determination of Reactive-Group Functionality from Gel Point Measurements," *Journal of Applied Polymer Science*, Vol. 12, July 1968, pp. 1697-1712.

⁵Stockmayer, W. H., "Molecular Distribution in Condensation Polymers," *Journal of Polymer Science*, Vol. 9, Jan. 1952, pp. 69-71.

⁶Stagg, H. E., "Method for the Determination of Isocyanates," *The Analyst*, Vol. 71, 1946, pp. 557-559.

⁷Jacobson, H. and Stockmayer, W. H., "Intra-Molecular Reaction in Polycondensations. I. The Theory of Linear Systems," *Journal of Chemical Physics*, Vol. 18, Dec. 1950, pp. 1600-1606.

⁸Harris, F. E., "Ring Formation and Molecular Weight Distributions in Branched-Chain Polymers," *Journal of Chemical Physics*, Vol. 23, Aug. 1955, pp. 1518-1525.

⁹Kilb, R. W., "Dilute Gelling Systems. I. The Effect of Ring Formation on Gelation," *Journal of Physical Chemistry*, Vol. 62, Aug. 1958, pp. 969-971.

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