

## The Effect of Varying Molecular Weight Distribution on the Properties of Binders

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### Synopsis

Work is reported on the effect of variation of molecular weight distribution on the properties of binder stocks. This work used three prepolymers (polypropylene glycol 1000, 2000, and 4000 and polypropylene glycol 400, 1000, and 2000) of different molecular weight and known molecular weight distribution. The prepolymer of the middle molecular weight was employed as standard, and stocks were prepared from it. To this prepolymer was added some of the high and low molecular weight prepolymers in proportions such that the crosslink density of stocks made from the mixture was the same as that of stocks made from the middle molecular weight prepolymer alone. Two series were prepared with different crosslinking agents. The proportions of high and low molecular weight prepolymer were successively increased until finally none of the middle molecular weight remained. Heterogeneity indexes of the glycols and their mixtures were measured by gel permeation chromatography. Elongation at break, modulus of elasticity, and extent of solvent swelling were determined on the crosslinked stocks. Properties which vary with crosslink density were found to show decreasing values with increasing heterogeneity index even though the stocks were formulated to a constant crosslink density. Narrow-distribution stocks reach the maximum degree of cure faster than the broader-distribution stocks. Infrared and thermal analysis confirm that monodisperse polymer has a greater extent of reaction than heterodisperse polymer. 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 the experimental variation in the elongation test below a heterogeneity index of 1.5. Above 1.5, however, if the effects observed are entirely due to variation in heterogeneity index, lot-to-lot variations in molecular weight distribution cannot be ignored. An explanation is presented based on the varying ability of prepolymer molecules of different size to diffuse through uniform mesh openings resulting in lower final extents of reaction for broad distribution material.

### INTRODUCTION

Information in the literature on the physical effects of varying molecular weight distribution of polymers is sparse and somewhat conflicting.<sup>1-6</sup> Work reported has been either on noncrosslinked material or random vulcanizates and has no direct bearing on the question of the properties of polymer networks where the sides of the mesh openings vary in uniformity of length. Such stocks may be prepared from commercially available prepolymers and crosslinking agents; and where a series of prepolymers is available, stocks may be formulated of constant crosslink density and varying distribution of mesh side lengths. Figure 1 illustrates mesh openings in

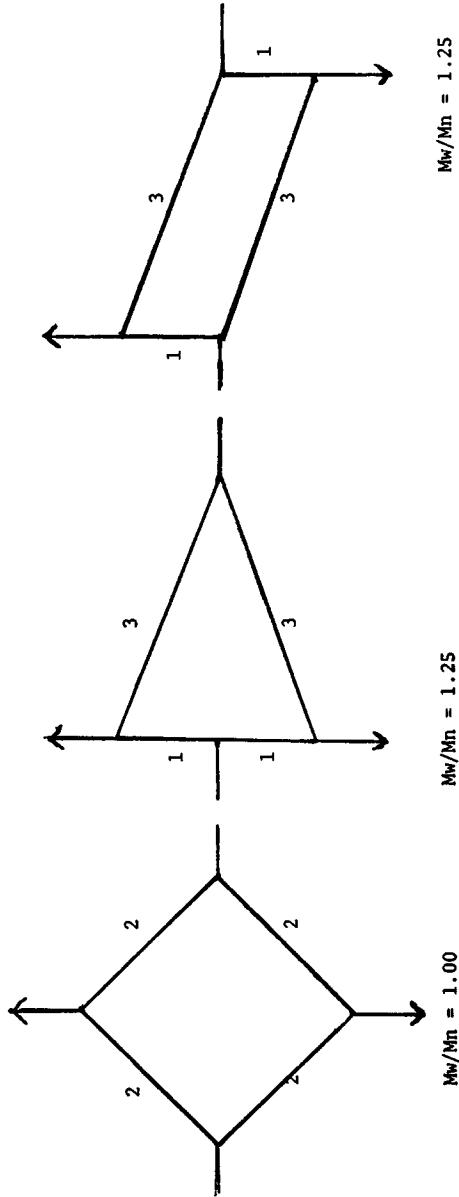


Fig. 1. Mesh openings in polymer networks of different molecular weight distribution, " $M_w = 2$ ."

TABLE I  
Properties of Materials

Abbreviation	Chemical name	Source	Active group cont., meq/g	Equiv. weight	Mol. weight	Functionality <sup>a</sup>	Terminal unsat., meq/g <sup>b</sup>
TMDI	trimethylhexamethylene diisocyanate	Hugo Stinnes	9.43	106	212 <sup>c</sup>	2.0	
CB-75	TDI on trimethylolpropane	Mobay	3.27	305		3.0	
TEA	triethanolamine		20.1	49.7	149 <sup>c</sup>	3.0	
PPG 400	polypropylene glycol OP1R-290-B	Wyandotte	4.58	218	423 <sup>d</sup>	1.94	0.008
PPG 1000	polypropylene glycol OPNQ-301-0	Wyandotte	1.91	525		2.0	0.022
PPG 2000	polypropylene glycol OP1R-142-H	Wyandotte	1.02	980	1981 <sup>d</sup>	2.02	0.033
PPG 4000	polypropylene glycol TB07150-497	Dow	0.51	1960	3793 <sup>d</sup>	1.93	0.074

<sup>a</sup> Two-figure values from structure; three-figure values from mol. wt./equiv. wt.

<sup>b</sup> Average of values from NAVORDSTA and from manufacturer.

<sup>c</sup> Calculated from structure.

<sup>d</sup> VPO.

polymer networks. On the left is a uniform distribution opening where we may regard the "heterogeneity index" as 1.0, while the other two illustrations will have a "heterogeneity index" of 1.25. In each case, the mesh opening is the same with a "molecular weight between crosslinks" of 2.

The question of the physical effect of such variations in molecular weight distribution has now become of importance since measurements of this property can be made with some precision by use of the gel permeation chromatograph. Molecular weight distribution is thus a variable which may now be tied down, and the question arises just how important is it to do so.

## EXPERIMENTAL

### Materials and Test Methods

Materials used in this study are described in Table I. Urethane cross-linked stocks were prepared from polypropylene glycols (PPG) of various molecular weights. Water contents of the glycols were in the range 0.02 to 0.05%. Hydroxyl content was determined by titration with acetyl chloride,<sup>7</sup> and isocyanate was determined using the standard di-*n*-butylamine procedure.<sup>8</sup> Molecular weights were measured in chloroform using a vapor pressure osmometer. Materials were first dried over molecular sieves and vacuum pumped. Results were corrected for any water then found to be present. Terminal unsaturation was determined by reaction with mercuric acetate and methanol.<sup>8,9</sup> Results of unsaturation are averages of those found by NAVORDSTA and those furnished by the manufacturers. The two sets of values were not far apart. Functionalities found for the polyols were always 1.9 or higher by molecular weight and equivalent weight. However, unsaturation in a terminal position lowers function-

TABLE II  
Characteristics of Uncured Mixtures

Stock	Heterogeneity index <sup>a</sup>	NCO/OH	Polyol funct. <sup>b</sup>	NCO funct.	System funct.	NCO content, meq/g
21	1.04	1.00	2.17	2.00	2.08	1.24
22	1.11	1.00	2.16	2.00	2.08	1.24
23	1.24	1.01	2.16	2.00	2.08	1.24
24	1.28	1.02	2.15	2.00	2.07	1.24
25	1.41	1.02	2.14	2.00	2.07	1.24
26	1.53	1.03	2.14	2.00	2.07	1.24
31	1.05	1.00	1.98	2.13	2.06	1.50
32	1.15	0.99	1.98	2.13	2.05	1.50
33	1.23	1.00	1.98	2.13	2.06	1.50
34	1.32	1.00	1.97	2.13	2.05	1.50
35	1.39	1.00	1.97	2.13	2.05	1.50
36	1.47	0.99	1.97	2.13	2.04	1.50

<sup>a</sup> From GPC.

<sup>b</sup> Calculated from terminal unsaturation and molecular weight.

TABLE III  
Calculated Dispersity of Polymer Mixtures, First Series

Polymers	Dispersity of polymers	Proportion	From composition		From GPC curves		Mixture dispersity (1) from compos.	Mixture dispersity from GPC
			$M_n$	$M_w$	$M_n$	$M_w$		
PPG 1000		100%	1030		1030	1082		1.05
PPG 2000		100%	2000		1935	2012		1.04
PPG 4000		100%	4000		4000	4120		1.03
PPG 1000	1.05	6.67%	2000	2200	1969	2185	1.10	1.11
PPG 2000	1.04	80.00%						
PPG 4000	1.03	13.33%						
PPG 1000	1.05	13.4%	2000	2400	1902	2350	1.20	1.24
PPG 2000	1.04	60.0%						
PPG 4000	1.03	26.6%						
PPG 1000	1.05	20.0%	2000	2600	2024	2598	1.30	1.28
PPG 2000	1.04	40.0%						
PPG 4000	1.03	40.0%						
PPG 1000	1.05	26.7%	2000	2800	1991	2816	1.40	1.41
PPG 2000	1.04	20.0%						
PPG 4000	1.03	53.3%						
PPG 1000	1.05	33.3%	2000	3000	1913	2922	1.50	1.53
PPG 2000	1.03	67.7%						

<sup>a</sup> Calculation assumes dispersity of each constituent is 1.00. However, see second column.

TALBE IV  
Comparison of Calculated and Measured Heterogeneity Indexes, Second Series

Polymers	Dispersity of polymers	Proportion	GPC $M_n$	GPC $M_w$	Mixture dispersity from compos. <sup>a</sup>	Mixture dispersity from GPC
PPG 423		100%	500	527		1.05
PPG 1000		100%	1030	1082		1.05
PPG 2000		100%	1935	2012		1.04
PPG 423	1.05	5.2%	1099	1259	1.12	1.15
PPG 1000	1.05	80.0%				
PPG 2000	1.04	14.8%				
PPG 423	1.05	10.4%	1096	1350	1.23	1.23
PPG 1000	1.05	60.0%				
PPG 2000	1.04	29.6%				
PPG 423	1.05	15.6%	1122	1476	1.34	1.32
PPG 1000	1.05	40.0%				
PPG 2000	1.04	44.4%				
PPG 423	1.05	20.8%	1164	1621	1.46	1.39
PPG 1000	1.05	20.0%				
PPG 2000	1.04	59.2%				
PPG 423	1.05	26.0%	1198	1756	1.57	1.47
PPG 2000	1.04	74.0%				

<sup>a</sup> Calculation assumes dispersity of each constituent is 1.00.

ality, and the true functionality of the PPG 4000 is certainly below 1.9. Functionalities of polyol mixtures used in experimental stocks were therefore computed from PPG functionalities calculated from the degree of unsaturation and the molecular weight. Results are shown in Table II.

Heterogeneity indexes of the polyol mixtures used in the work were determined by gel permeation chromatography (GPC) using a calibration curve measured on the materials listed in Table I plus an additional sample of PPG of molecular weight 770. The calibration curve was  $\log M_n = 6.87 - 0.138C$ , where  $C$  is the elution volume in 5 ml counts at  $M_n$ . The calibration curve was linear down to 600 molecular weight but fell off below this point. Heterogeneity indexes were calculated from the GPC curves using standard methods described elsewhere.<sup>10</sup> Results on the various polyol mixtures are shown in Tables III and IV. If one assumes that the heterogeneity indices of the PPG samples are 1.00, rather than their actual values of 1.03 to 1.05, then the indices of the mixtures may be calculated. Figure 2 shows a comparison of these calculated values with those measured by GPC.

### Composition and Preparation of Stocks

Two sets of three prepolymers were used in two series of stocks employing polypropylene glycol 1000, 2000, and 4000 and polypropylene glycol 400, 1000, and 2000 of different molecular weight and known molecular weight

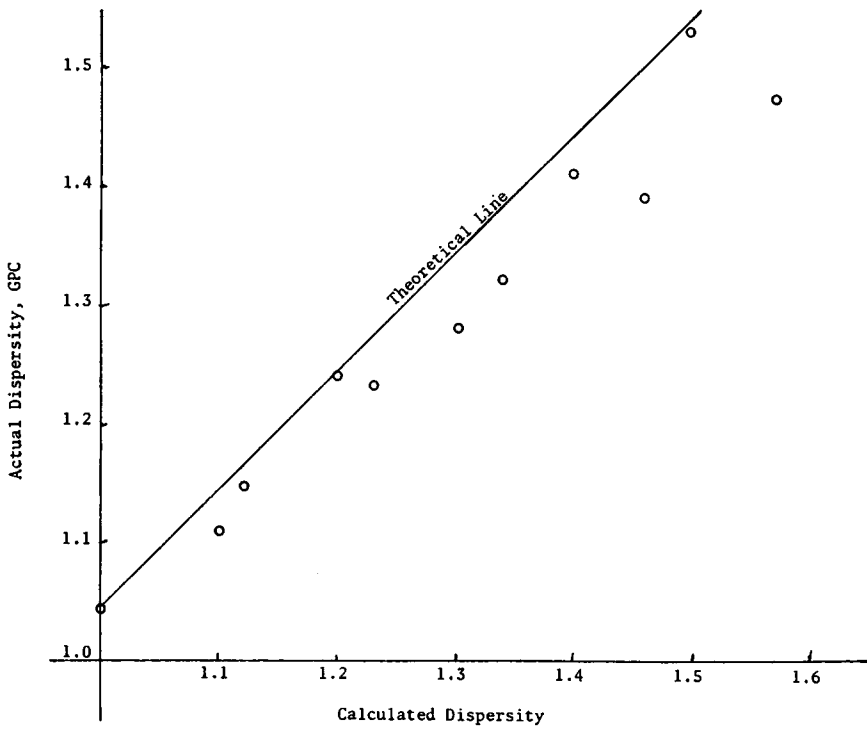


Fig. 2. Heterogeneity indexes of polyol mixtures.

TABLE V  
Composition of Polypropylene Glycol Gum Stocks.

Stock	First Series					
	P-1000, g	P-2000, g	P-4000, g	TEA, g	TMDI, g	FeAA, g
21		125		2.78	19.45	0.14
22	8.35	100	16.65	2.78	19.45	0.14
23	16.7	75	33.3	2.78	19.45	0.14
24	25.05	50	49.95	2.78	19.45	0.14
25	33.4	25	66.6	2.78	19.45	0.14
26	41.75		83.25	2.78	19.45	0.14

Stock	Second Series					
	P-400, g	P-1000, g	P-2000, g	TMDI, g	CB-75, g	FeAA, g
31		125		20.625	13.75	0.035
32	6.5	100	18.5	20.625	13.75	0.035
33	13	75	37	20.625	13.75	0.035
34	19.5	50	55.5	20.625	13.75	0.035
35	26	25	74	20.625	13.75	0.035
36	32.5		92.5	20.625	13.75	0.035

distribution. The prepolymer of the middle molecular weight was employed as standard, and stocks were prepared from it. To this prepolymer was added some of the high and low molecular weight prepolymers in proportions such that the crosslink density of stocks made from the mixture was the same as that of stocks made from the middle molecular weight prepolymer alone. In the first series, trimethylhexamethylene diisocyanate (TMDI) was used as curing agent, triethanolamine (TEA) was added as crosslinking agent. In the second series, a trimethylolpropane-tolyene diisocyanate adduct (CB-75) was employed as crosslinking agent. The proportions of high and low molecular weight prepolymer were successively increased until finally none of the middle molecular weight remained. The mixtures were poured into Teflon-coated molds, degassed, sealed, and cured 72, 96, 120, and 144 hr at 85°C to form slabs 0.075 in. thick. The composition of the stocks is shown in Table V.

Two factors only can determine the crosslink density of these stocks, the NCO content, which is constant in each series, and the system average functionality, which is 2.07 to 2.08 in the first series and 2.04 to 2.06 in the second series (see Table II).

## RESULTS

Results of elongation and tensile tests run on standard JANNAF specimens and of swelling tests in benzene are shown in Table VI.

TABLE VI  
Properties of Stocks from Prepolymers of Varying Polydispersity<sup>a</sup>

Stock	Elongation at break, %		Tensile strength, psi		Young's modulus, psi		RNB no. (benzene) <sup>b</sup> at 72 hr
	72 hr	144 hr	72 hr	144 hr	72 hr	144 hr	
First Series							
21	451	403	75	85	38	52	1.45
22	485	459	59	76	36	41	1.28
23	451	469	62	90	33	42	1.06
24	528	486	69	65	30	33	1.24
25	557	574	70	84	27	32	1.17
26	840	675	64	53	16	16	0.62
Second Series							
31	493		94		40		2.13
32	497		94		46		2.54
33	481		93		44		2.07
34	603		96		36		1.82
35	596		91		44		1.97
36	710		76		25		1.38

<sup>a</sup> Stocks cured 72 and 144 hr at 85°C.

<sup>b</sup> RNB no. is  $V_2^{5/3} \times$  per cent gel, where  $V_2$  is the volume fraction of polymer in the solvent-swollen gel.



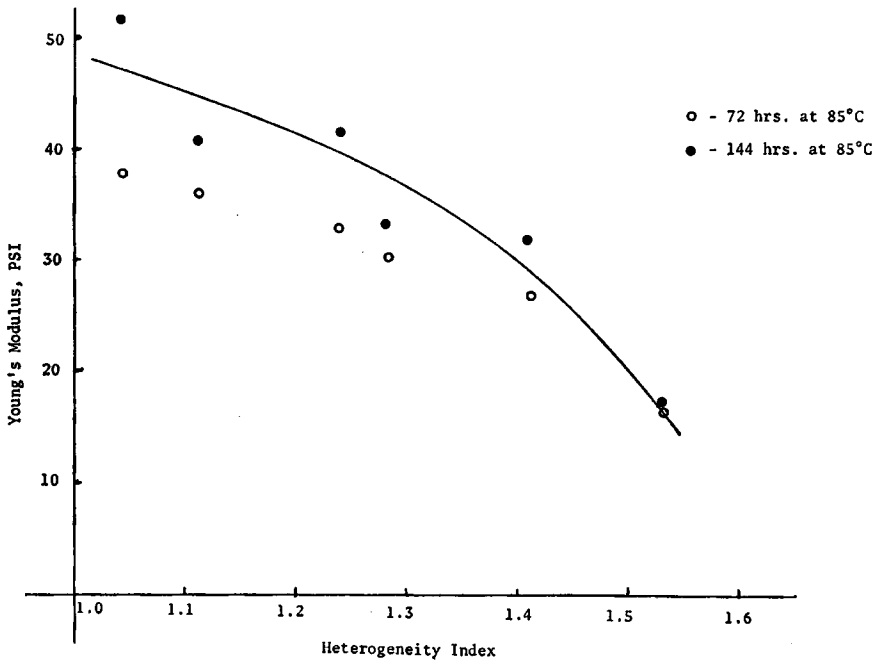


Fig. 3. Variation of Young's modulus with polydispersity.

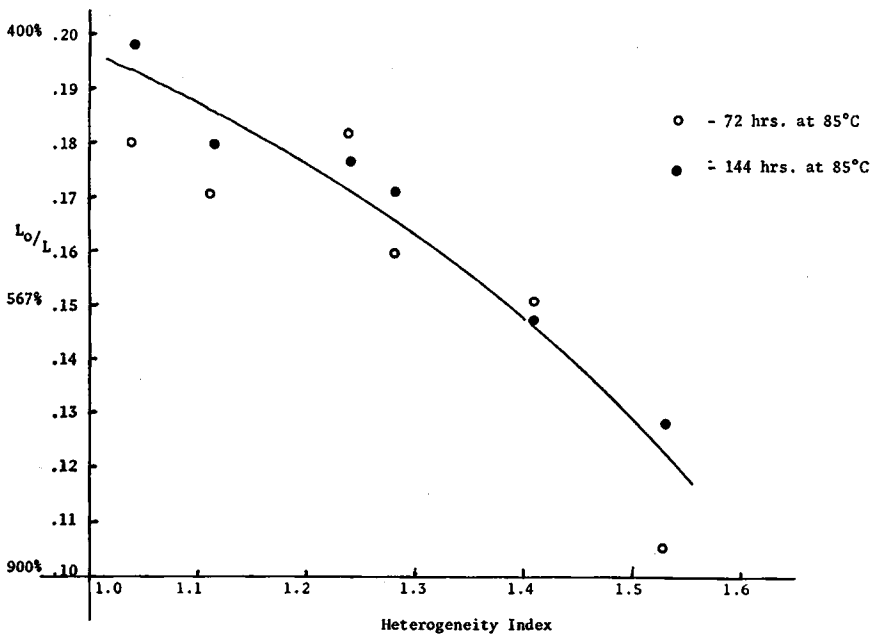


Fig. 4. Variation of elongation reciprocal with polydispersity.

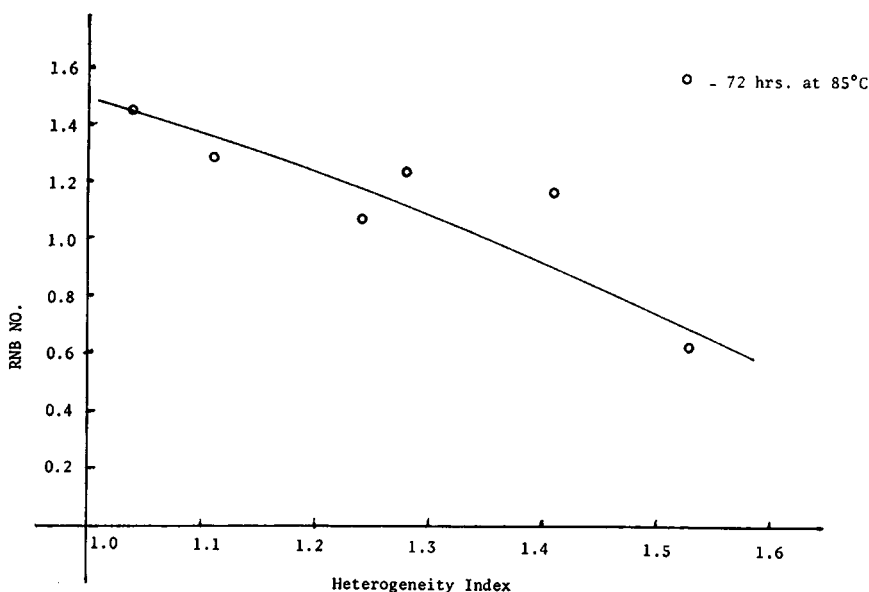


Fig. 5. Cure from solvent swelling vs. polydispersity.

Functions which vary with crosslink density for the first-series stocks are shown plotted against dispersity in Figures 3, 4, and 5. It is seen that the values of the functions decrease with increasing heterogeneity index although with considerable scatter even though the stocks were formulated to a constant crosslink density. The results may also indicate that the narrow-distribution stock reaches the maximum degree of cure faster than the broadest-distribution stock. The 72-hr cure at 85°C on stock 21 perhaps should be compared with the 144-hr cure at 85°C for stock 26. However, even 72 hr must be regarded as a very long time for cure of these stocks.

Variations in properties among the second-series stocks was not as regular as was found in the first series. However, stocks 35 and 36 of high heterogeneity index show a lower "degree of cure" than stocks 31 and 32, both when elongation at break and solvent swelling are considered. No significant variation was found in modulus except for stock 36. The results confirm and reinforce the results found on the first series.

## DISCUSSION

One may think about the effect of varying molecular weight distribution in several ways. An early idea was that short segments in a polymer network act as ties reducing elongation at break and increasing modulus of elasticity. This idea may be visualized by comparing the center mesh in Figure 1 with the uniform side mesh at the left in Figure 1. It should be observed in this figure that the circumference of the openings is the same in all cases.

On the other hand, the problem may be approached from a kinetic point of view. At the gel point, many monomer molecules remain unreacted. It follows that if the mesh size openings (crosslink density) are the same, broad-distribution material will contain large unreacted molecules unable to diffuse through the mesh openings, whereas narrow-distribution material will contain more diffusible molecules. The final extent of reaction in the broad-distribution material therefore should be less than in the narrow-distribution material since the molecules must be able to move around in order to react. The broad-distribution material should also require a longer time to reach the maximum degree of cure than the narrow-distribution material.

In order to test this idea, an attempt was made to determine the final extent of reaction in stocks 21 through 26 above, using attenuated total reflectance infrared techniques measuring the  $1717\text{ cm}^{-1}$  carboxyl band. A good reference point (at 100% reaction) was almost impossible to obtain. Consequently, results were only relative. The following conclusions were drawn:

1. Monodisperse polymer had a greater extent of reaction than heterodisperse polymer after 72 hours of cure at  $85^\circ\text{C}$ , about 70% as opposed to 66%.
2. Cures for 72 hr and 144 hr at  $85^\circ\text{C}$  for monodisperse polymer showed little change in extent of reaction, while heterodisperse showed an increase in extent of reaction.
3. The 144-hr cure showed that the extent of reaction was probably the same for monodisperse and heterodisperse. However, this statement is less certain than the first statement.

Thermal analysis (DSC and TGA) data confirmed the conclusions drawn from infrared data, namely: (a) monodisperse binder has a higher  $T_g$  ( $-59^\circ$  as compared to  $-62^\circ\text{C}$ ), indicating a higher extent of reaction; (b) TGA shows that a given weight loss comes at a higher temperature for monodisperse as compared to a heterodisperse binder cured for 72 hr (50% weight loss at  $380^\circ$  and  $371^\circ\text{C}$ , respectively), which indicates that the extent of reaction is greater in the monodisperse; and (c) after 144 hr, the weight loss-temperature relationship is the same, which indicates that the extent of reaction is the same.

The meaning of these results must now be considered. The data on elongation at break seem the most useful. Plotting all available elongations at break against heterogeneity index, a curve is obtained which shows a slow upward trend from 425% to 450% at low indexes but which rises rapidly above an index of 1.5, reaching 800% to 850% at a heterogeneity index of 1.6. Measurements on seven lots of carboxyl-terminated polybutadiene showed a total variation of 0.15 index value among all the lots, and measurements on seven lots of a hydroxyl-terminated polybutadiene showed a total variation of 0.11 index value. If the lot-to-lot variation in hydrocarbon prepolymers is considered to be 0.15 heterogeneity index units, one

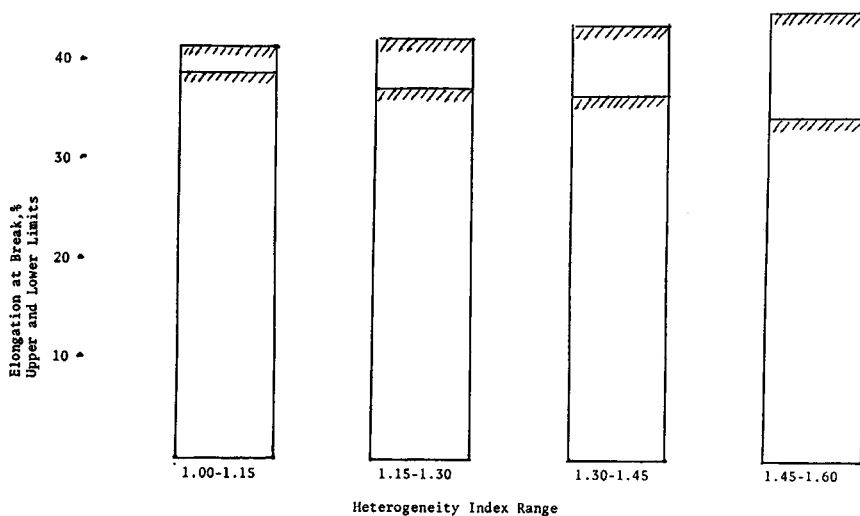


Fig. 6. Expected effect of variation in molecular weight distribution on elongation at break.

may calculate the percentage variation in elongation-at-break values for each 0.15 index range from the elongation at break curve. Results are:

$M_w/M_n$ range	Total variation in EB, % mean value
1.00-1.15	6.7
1.15-1.30	9.7
1.30-1.45	18.2
1.45-1.60	28.3

These results in terms of a filled stock of 40% elongation at break are shown graphically in Figure 6. The variation in elongation at break is to be expected because of lot-to-lot variations in heterogeneity index is probably not greater than the experimental variation in the elongation test below a heterogeneity index of 1.5. Above 1.5, however, lot-to-lot variations in molecular weight distribution cannot be ignored if our interpretation of the present work is correct.

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