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BDX-613-1867 (Rev.)

THE TIME-TEMPERATURE CORRESPONDENCE OF
THE DYNAMIC MECHANICAL PROPERTIES OF
HALTHANE 73-18 AND HALTHANE 87-1

by G. K. Baker

Published November 1978

Topical Report

Prepared for the United States Department of Energy
Under Contract Number DE-AC04-76-DP00613.

**Kansas City
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Project Team:
M. F. Radford

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PROPERTIES OF HALTHANE 73-18 AND HALTHANE 87-1

BDX-613-1867 (Rev.), Topical Report, Published November 1978

Prepared by G. K. Baker

The time-temperature correspondence of the storage shear modulus, loss shear modulus, and loss tangent of two urethane adhesives, Halthane 73-18 and Halthane 87-1, have been determined. Experimental determinations of the frequency dependence of the shear moduli were made from 0.01 to 3.0 Hz at various temperatures ranging from -60°C for Halthane 73-18 and -91.5°C for Halthane 87-1 to 25°C for both. The WLF equation was used to determine the frequency dependence of the shear moduli and loss tangent up to frequencies of 10 PHz.

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SUMMARY

Two new adhesives, Halthane 73-18 and Halthane 87-1, have been developed at Lawrence Livermore Laboratories (LLL) as potential substitutes for a polyurethane adhesive cured with 4,4'-methylenebis-orthochloroaniline (MOCA). As part of the general characterization of the properties of these adhesives, the time-temperature correspondence of the storage and loss shear moduli, and loss tangent of these adhesives have been determined. The data indicate the two adhesives exhibit reasonably low shear moduli, even up to 1 MHz. Halthane 87-1 has a higher modulus up to 100 MHz, but the rate of change of modulus with frequency is less compared to Halthane 73-18. The latter undergoes a change in modulus of about three decades, whereas the Halthane 87-1 exhibits a modulus change of only two decades.

DISCUSSION

SCOPE AND PURPOSE

Knowledge of the dynamic mechanical properties of materials is essential for the design and fabrication of nuclear weapons. Two adhesives, designated Halthane 87-1 and Halthane 73-18, have been developed at LLL for use in future weapons programs. They were developed to have better viscosity and potlife properties than a polyurethane adhesive cured with 4,4'-methylenebis-aniline (MDA) and better thermal stability than a polyurethane adhesive cured with a mixture of polyols. The latter two adhesives were the first substitutes for a polyurethane adhesive cured with 4,4'-methylenebis-orthochloroaniline (MOCA).

Because the Halthane adhesives are new, data on their chemical and mechanical properties are required to assess their value and potential application. In support of this endeavor during the last two years, the determination of the dynamic mechanical properties of the adhesives has been carried out at Bendix Kansas City for LLL.

All work prior to that discussed in this report has involved the determination of the storage shear modulus (G'), loss shear modulus (G''), and loss tangent ($\tan \delta$) as a function of temperature at a constant frequency of either 0.1 or 0.2 Hz.

The time-temperature correspondence of the dynamic mechanical properties of these adhesives was determined and is given in this report. Master curves of G' , G'' , and $\tan \delta$ have been prepared using the WLF equation to show the frequency response of the adhesives at 25°C over a broad frequency range.

ACTIVITY

Description of the Adhesives

The Halthane 73-18 system is a prepolymer terminated with 4,4'-methylenebis-phenyl isocyanate (MDI) and cured with a blend of diols and a small percent of a tetrafunctional alcohol. Halthane 87-1 is an isocyanate terminated prepolymer cured with a melting blend of aromatic amines. The detailed formulation and preparation of the adhesives may be found in reports by Hammon, Althouse, and Parker.^{1,2}

The adhesives were prepared at the Union Carbide Corporation, Y-12 Plant on January 5, 1976, and cured for 60 days at room temperature. They were shipped to Bendix in sealed moisture barrier bags for

chemical tests. The adhesives were stored in a refrigerator at 5°C, after receipt at Bendix.

Test Procedure

The dynamic mechanical test measurements were performed on test specimens 38.1 mm long by 12.7 mm wide and 3.18 mm thick using a mechanical spectrometer and fixed torsional pendulum geometry.

The storage shear modulus, loss shear modulus, and loss tangent were determined simultaneously by applying a torsional shear strain to the test specimen in a sinusoidal manner and measuring the resulting stress and phase angle at various temperatures and frequencies. The test specimen was first cooled to the lowest temperature of the test, and stress and phase angle measurements were made at frequencies of 0.01, 0.02, 0.05, 0.1, 0.2, 0.5, 1.0, 2.0, and 3.0 Hz. The sample was then heated several degrees and the measurements over the same frequency range were repeated. This was done for temperatures of from -60° to +25°C for Halthane 73-18 and -91.5° to +25°C for Halthane 87-1. The control for a given temperature was within $\pm 0.5^\circ\text{C}$. The sinusoidal angular displacement in these tests was held constant at each temperature at ± 0.042 radians.

Test Results

The data related to G' , G'' , and $\tan \delta$ for Halthane 73-18 and Halthane 87-1 at the various temperatures and frequencies employed in the experiments are summarized in Tables 1 and 2, respectively. The modulus values given in Tables 1 and 2 are actually the reduced variables (designated G'_r and G''_r) which have been calculated by multiplying the experimentally determined values of G' and G'' by the ratio of the reference temperature (T_0), which is 25°C in this work, to the test temperature (T). This has the effect of applying a slight vertical shift to the master curve to account for the temperature dependency. The method of reduced variables is described in detail by Ferry.³ If the actual values of G' and G'' at a given experimental temperature and frequency are desired, they can, of course, be obtained by multiplying G_r by $T/298$.

To obtain the horizontal shift, or frequency dependency, plots of G'_r versus the logarithm of the experimental frequency were made for each temperature. Such plots for Halthane 73-18 and Halthane 87-1 are shown in Figures 1 and 2, respectively. From these plots, the horizontal distance between each pair of adjacent temperature curves was measured and recorded as $\Delta \log a_t$. The values of $\Delta \log a_t$ were added progressively from the reference temperature 25°C to obtain the $\log a_t$ of each temperature. The

Table 1. Master Curve Data for Halthane 73-18

Temperature (°K)	Frequency (Hz)	$\log a_{tf}$	G'_r (MPa)	G''_r (MPa)	$\tan \delta$
213.0	0.01	12.6	583	106	0.183
	0.02	12.8	639	105	0.164
	0.05	13.2	685	94	0.138
	0.10	13.6	698	83	0.120
	0.20	13.8	724	78	0.108
	0.50	14.2	774	70	0.091
	1.00	14.6	818	62	0.076
	2.00	14.8	888	34	0.038
218.0	0.01	10.8	399	128	0.322
	0.02	11.1	424	119	0.280
	0.05	11.5	503	96	0.191
	0.10	11.8	535	106	0.198
	0.20	12.1	589	93	0.158
	0.50	12.4	624	88	0.140
	1.00	12.8	704	80	0.114
	2.00	13.1	751	60	0.079
223.0	0.01	9.3	245	27	0.111
	0.02	9.6	292	46	0.159
	0.05	10.0	337	95	0.284
	0.10	10.3	378	100	0.265
	0.20	10.6	394	98	0.249
	0.50	11.0	444	98	0.222
	1.00	11.3	483	94	0.194
	2.00	11.6	542	76	0.140
	3.00	12.1	619	36	0.058
225.5	0.01	8.6	140	71	0.506
	0.02	8.9	187	84	0.452
	0.05	9.3	243	92	0.378
	0.10	9.6	289	94	0.325
	0.20	9.9	325	96	0.296
	0.50	10.3	375	97	0.259
	1.00	10.6	422	98	0.231
	2.00	10.9	484	85	0.176
	3.00	11.1	558	49	0.088
228.5	0.01	7.8	97	54	0.558
	0.02	8.1	120	65	0.543
	0.05	8.5	158	73	0.463
	0.10	8.8	199	81	0.408
	0.20	9.1	227	86	0.381
	0.50	9.5	273	90	0.331

Table 1 Continued. Master Curve Data for Halthane 73-18

Temperature (°K)	Frequency (Hz)	$\log a_{tf}$	G'_r (MPa)	G''_r (MPa)	$\tan \delta$
228.5	1.00	9.8	314	91	0.290
	2.00	10.1	375	89	0.237
228.5	3.00	10.3	438	64	0.146
230.5	0.01	7.3	59	41	0.625
	0.02	7.6	71	43	0.605
	0.05	8.0	97	51	0.521
	0.10	8.3	120	59	0.495
	0.20	8.6	143	66	0.459
	0.50	9.0	175	74	0.421
	1.00	9.3	219	83	0.377
	2.00	9.6	271	85	0.315
230.5	3.00	9.8	330	71	0.216
233.5	0.01	6.7	33	22	0.662
	0.02	7.0	45	29	0.650
	0.05	7.4	63	40	0.625
	0.10	7.7	80	46	0.581
	0.20	8.0	105	53	0.502
	0.50	8.4	137	64	0.466
	1.00	8.7	166	70	0.421
	2.00	9.0	212	74	0.351
233.5	3.00	9.2	256	67	0.262
237.0	0.01	5.9	17	7	0.428
	0.02	6.2	22	13	0.589
	0.05	6.6	29	17	0.601
	0.10	6.9	36	24	0.662
	0.20	7.2	48	30	0.624
	0.50	7.6	67	40	0.593
	1.00	7.9	88	48	0.547
	2.00	8.2	117	56	0.481
237.0	3.00	8.4	146	56	0.384
240.0	0.01	5.2	12	4.5	0.364
	0.02	5.6	12	7.0	0.562
	0.05	6.0	19	10.5	0.570
	0.10	6.2	24	14.6	0.617
	0.20	6.6	31	20.0	0.641
	0.50	7.0	45	29.0	0.654
	1.00	7.2	59	37.0	0.625
	2.00	7.6	81	46.0	0.566
240.0	3.00	7.8	102	46.0	0.452

Table 1 Continued. Master Curve Data for Halthane 73-18

Temperature (°K)	Frequency (Hz)	$\log a_t f$	G'_r (MPa)	G''_r (MPa)	$\tan \delta$
248.0	0.01	3.8	4.9	1.6	0.319
	0.02	4.1	7.3	2.0	0.271
	0.05	4.5	8.7	2.9	0.338
	0.10	4.8	10.0	4.0	0.401
	0.20	5.1	11.4	5.2	0.463
	0.50	5.5	14.5	8.1	0.562
	1.00	5.8	18.6	11.2	0.605
	2.00	6.1	24.5	14.8	0.605
248.0	3.00	6.3	31.8	---	---
258.0	0.01	2.2	5.2	0.56	0.108
	0.02	2.5	5.4	0.41	0.076
	0.05	2.9	5.8	0.76	0.132
	0.10	3.2	5.9	0.86	0.146
	0.20	3.5	6.4	1.2	0.185
	0.50	3.9	7.2	1.7	0.240
	1.00	4.2	7.7	2.2	0.290
	2.00	4.5	9.6	3.1	0.322
258.0	3.00	4.7	11.6	3.3	0.284
273.0	0.01	0.3	4.0	0.6	0.155
	0.02	0.6	3.0	0.2	0.052
	0.05	1.0	4.4	0.11	0.026
	0.10	1.3	6.5	0.28	0.044
	0.20	1.6	4.5	0.23	0.052
	0.50	2.0	4.8	0.30	0.062
	1.00	2.3	5.0	0.48	0.096
	2.00	2.6	5.6	0.51	0.090
273.0	3.00	2.8	6.2	---	---
298.0	0.01	-2.0	3.7	0.99	0.268
	0.02	-1.7	3.7	0.04	0.113
	0.05	-1.3	3.7	0.08	0.023
	0.10	-1.0	3.5	0.06	0.018
	0.20	-0.7	3.8	0.02	0.006
	0.50	-0.3	3.7	0.11	0.029
	1.00	0.0	3.9	0.12	0.031
	2.00	0.3	3.9	0.11	0.029
298.0	3.00	0.5	4.2	---	---

Table 2. Master Curve Data for Halthane 87-1

Temperature (°K)	Frequency (Hz)	$\log a_t f$	G'_r (MPa)	G''_r (MPa)	$\tan \delta$
181.5	0.01	16.1	679	---	---
	0.02	16.4	738	---	---
	0.50	16.8	746	---	---
	0.10	17.1	806	---	---
	0.20	17.4	857	---	---
	0.50	17.8	953	---	---
	1.00	18.1	997	---	---
	2.00	18.4	1126	---	---
181.5	3.00	18.6	1278	---	---
193.0	0.01	12.7	326	86	0.265
	0.02	13.0	341	86	0.252
	0.05	13.4	395	96	0.243
	0.10	13.7	429	103	0.240
	0.20	14.0	464	106	0.228
	0.50	14.4	514	117	0.227
	1.00	14.7	566	120	0.213
	2.00	15.0	662	115	0.173
193.0	3.00	15.2	762	---	0.093
195.5	0.01	12.1	252	61	0.243
	0.02	12.4	265	63	0.237
	0.05	12.8	298	71	0.237
	0.10	13.1	286	64	0.225
	0.20	13.4	312	70	0.225
	0.50	13.8	355	80	0.225
	1.00	14.1	388	85	0.219
	2.00	14.4	453	85	0.188
195.5	3.00	14.6	522	61	0.150
198.0	0.01	11.5	170	40	0.237
	0.02	11.8	186	46	0.246
	0.05	12.2	213	48	0.225
	0.10	12.5	236	51	0.215
	0.20	12.8	253	55	0.215
	0.50	13.2	286	62	0.219
	1.00	13.5	325	70	0.216
	2.00	13.8	376	72	0.191
198.0	3.00	14.0	440	---	0.117
201.5	0.01	10.6	149	35	0.237
	0.02	11.0	161	37	0.228
	0.05	11.4	179	39	0.219
201.5	0.10	11.6	193	44	0.225

Table 2 Continued. Master Curve Data for Halthane 87-1

Temperature (°K)	Frequency (Hz)	$\log a_t f$	G'_r (MPa)	G''_r (MPa)	$\tan \delta$
201.5	0.20	12.0	208	43	0.206
	0.50	12.4	240	56	0.234
	1.00	12.6	277	58	0.210
	2.00	13.0	320	---	---
201.5	3.00	13.2	367	---	---
207.0	0.01	9.4	118	26	0.219
	0.02	9.7	123	28	0.231
	0.05	10.1	138	29	0.213
	0.10	10.4	149	31	0.206
	0.20	10.7	159	32	0.200
	0.50	11.1	175	36	0.206
	1.00	11.4	193	40	0.206
	2.00	11.7	220	40	0.179
	3.00	11.9	245	---	---
215.0	0.01	7.8	91	20	0.216
	0.02	8.1	98	21	0.213
	0.05	8.5	107	21	0.200
	0.10	8.8	110	20	0.185
	0.20	9.1	118	22	0.188
	0.50	9.5	130	24	0.185
	1.00	9.8	140	25	0.179
	2.00	10.1	159	26	0.164
	3.00	10.3	180	17	0.096
222.0	0.01	6.6	64	15	0.237
	0.02	6.9	68	18	0.271
	0.05	7.3	80	15	0.188
	0.10	7.6	84	19	0.225
	0.20	7.9	87	18	0.213
	0.50	8.3	92	19	0.198
	1.00	8.6	104	18	0.176
	2.00	8.9	117	---	---
	3.00	9.1	134	---	---
228.0	0.01	5.6	41	7.8	0.237
	0.02	5.9	44	6.8	0.179
	0.05	6.2	47	6.8	0.144
	0.10	6.6	50	7.6	0.138
	0.20	6.9	53	8.7	0.144
	0.50	7.3	57	9.5	0.153
	1.00	7.6	62	9.6	0.153
	2.00	7.9	70	---	---

Table 2 Continued. Master Curve Data for Halthane 87-1

Temperature (°K)	Frequency (Hz)	$\log a_t f$	G'_r (MPa)	G''_r (MPa)	$\tan \delta$
234.0	0.01	4.7	38	5.4	0.141
	0.02	5.0	39	5.5	0.141
	0.05	5.4	40	6.0	0.150
	0.10	5.7	42	6.4	0.153
	0.20	6.0	44	5.6	0.126
	0.50	6.4	49	6.8	0.141
	1.00	6.7	52	7.2	0.138
	2.00	7.0	58	6.6	0.114
234.0	3.00	7.2	66	---	---
243.0	0.01	3.4	29	3.8	0.132
	0.02	3.7	32	4.2	0.132
	0.05	4.1	34	4.3	0.126
	0.10	4.4	36	4.5	0.126
	0.20	4.7	37	4.3	0.117
	0.50	5.1	40	5.0	0.126
	1.00	5.4	42	5.0	0.120
	2.00	5.7	47	3.7	0.097
243.0	3.00	5.9	52	1.8	0.035
255.5	0.01	1.9	23	3.3	0.144
	0.02	2.2	24	3.2	0.129
	0.05	2.6	26	3.3	0.125
	0.10	2.9	28	3.5	0.125
	0.20	3.2	29	3.4	0.120
	0.50	3.6	30	3.6	0.117
	1.00	3.9	32	3.4	0.106
	2.00	4.2	36	2.9	0.082
255.5	3.00	4.4	40	---	---
273.0	0.01	0.1	16	1.5	0.093
	0.02	0.4	16	1.6	0.096
	0.05	0.8	17	1.6	0.093
	0.10	1.1	18	1.6	0.091
	0.20	1.4	19	1.7	0.091
	0.50	1.8	20	1.9	0.093
	1.00	2.1	21	1.7	0.082
	2.00	2.4	23	1.2	---
273.0	3.00	2.6	26	---	---
298.0	0.01	-2.0	10.6	1.0	0.093
	0.02	-1.7	12.1	0.9	0.076
	0.05	-1.3	12.2	0.9	0.073
298.0	0.10	-1.0	12.7	1.3	0.099

Table 2 Continued. Master Curve Data for Halthane 87-1

Temperature (°K)	Frequency (Hz)	$\log a_t f$	G'_r (MPa)	G''_r (MPa)	$\tan \delta$
298.0	0.20	-0.7	13.3	1.1	0.085
	0.50	-0.3	14.0	1.3	0.091
	1.00	0.0	14.9	---	---
	2.00	0.3	16.4	---	---
298.0	3.00	0.5	17.9	---	---

WLF equation (Equation 1) was then used to obtain the constants c_1 and c_2 for each adhesive.

$$\log a_t = c_1(T - T_0)/(c_2 + T - T_0) \quad (1)$$

This was done by plotting values of $T - T_0/\log a_t$ against $T - T_0$. The data for the plots are given in Table 3 and the plots to obtain c_1 and c_2 are given in Figure 3.

The value of c_1 was obtained from the negative reciprocal of the slope of the line, and c_2 was obtained from the value of the intercept divided by that of the slope. The values of c_1 and c_2 experimentally obtained for the adhesives are 12.5 (c_1) and 158 (c_2) for Halthane 73-18 and 16.8 (c_1) and 224 (c_2) for Halthane 87-1.

Finally, the constants c_1 and c_2 were used to prepare master curves of G'_r , G''_r , and $\tan \delta$ plotted against the $\log a_t f$ where f is the frequency in hertz. The master curves of G'_r , G''_r , and $\tan \delta$ are given in Figures 4, 5, and 6, respectively.

Evaluation of Data

As seen in Figure 3, the Halthane 87-1 adhesive has the higher storage shear modulus up to a frequency of about 10 MHz; however, the rate of change of modulus with frequency is less compared to the Halthane 73-18 adhesive. Over the entire frequency range, Halthane 87-1 undergoes a change in modulus of only two decades compared to a modulus change of three decades in the case of Halthane 73-18. The same general behavior is noted in the change of modulus of the two adhesives as a function of temperature. Plots showing the temperature dependency of these adhesives, obtained from previous work, are shown in Figure 7 of this report for reference. In the determination of the temperature dependency, a constant frequency of 0.2 Hz was employed. The test specimens were taken from the same slabs prepared at Y-12 that were used to determine the time-temperature correspondence in this study. The

Figure 1. Storage Modulus of Halthane 73-18 Versus Frequency at Indicated Temperatures

master curves show the moduli of both adhesives at room temperature to be relatively low over a wide frequency range. For example, at 1 MHz, Halthane 87-1 has a modulus of only 50 MPa and Halthane 73-18 has a modulus of 20 MPa.

The temperature dependency curves show Halthane 73-18 is essentially a brittle or elastic material below -80°C and has a shear modulus of about 800 MPa. The master curve of Halthane 73-18 indicates a modulus of 800 MPa is not reached until a frequency of 100 THz. Similarly, Halthane 87-1 adhesive is shown to be in the brittle state below -100°C with a shear modulus of 1500 MPa. The master curve shows a modulus of 1500 MPa corresponds to a frequency of about 10,000 THz. Such frequencies are extremely high and, in fact, are near or above that of the frequency of molecular vibrations. These high frequency data are probably unrealistic. Most of the data of a master curve is essentially extrapolated,

Figure 2. Storage Modulus of Halthane 87-1 Versus Frequency at Indicated Temperatures

and the further the extrapolation, the greater the error to be expected. Furthermore, the WLF time-temperature superposition treatment is not valid above the glass transition temperature, and since the lowest temperatures used in this work are close to the glass transition temperatures of the two adhesives, the errors in the data of the low temperatures (or high frequencies) are expected to be greater than at the higher temperatures (or low frequencies).

The upper limit for the experimentally determined frequency response with the instrumentation employed in this work is about 3 Hz. It would be good to be able to determine frequency responses at higher levels to check the master curve data in this work; however, such a capability is not available at the present.

Table 3. Data for the Determination of $\log a_t$ and the WLF Constants, c_1 and c_2 , for Halthane 73-18 and Halthane 87-1

Temperature					
(°C)	(°K)	$\Delta \log a_t(G'_r)$	$\Sigma \log a_t$	$T - T_0$	$T - T_0 / \Sigma \log a_t$
Halthane 73-18					
-50	223.0	1.19	11.83	-75.0	-6.3
-47.5	225.5	0.65	10.64	-72.5	-6.8
-44.5	228.5	0.88	9.99	-69.5	-7.0
-42.5	230.5	0.54	9.11	-67.5	-7.4
-40	233.5	0.94	8.57	-65.0	-7.6
-36	237.0	0.46	7.63	-61.0	-8.0
-33	240.0	1.27	7.17	-58.0	-8.1
-25	248.0	1.55	5.90	-50.0	-8.5
-15	258.0	2.00	4.35	-40.0	-9.2
0	273.0	2.35	2.35	-25.0	-10.6
25	298.0				
Halthane 87-1					
-91.5	181.5	2.36	17.96	-116.5	-6.5
-80.0	193.0	1.45	15.60	-105.0	-6.8
-77.5	195.5	0.78	14.10	-102.5	-7.3
-75.0	198.0	0.60	13.30	-100.0	-7.5
-71.5	201.5	1.00	12.70	-96.5	-7.6
-66.0	207.0	1.09	11.70	-91.0	-7.8
-58.0	215.0	1.30	10.60	-83.0	-7.9
-51.0	222.0	2.05	9.25	-76.0	-8.2
-45.0	228.0	0.90	7.20	-70.0	-9.7
-39.0	234.0	0.91	6.30	-64.0	-10.2
-30.0	243.0	1.42	5.39	-55.0	-10.2
-17.5	255.0	2.27	3.97	-42.5	-10.7
0	273.0	1.70	1.70	-25.0	-14.7
25	298.0

Figure 3. Plots of the WLF Equation to Determine the Constants, c_1 and c_2 , for Halthane 73-18 and Halthane 87-1

Experiments were not run above 25°C for two reasons. One reason is the magnitudes of the stress at the strain used in this work were quite low at 25°C and subject to considerable error. This problem would increase with increasing temperatures. The second and main reason is that at 25°C the change in modulus over the experimental frequency range is low and in the case of Halthane 73-18 is virtually zero. This means the shift factor, $\Delta \log a_f$, cannot be measured with any confidence.

The plots to determine the constant c_1 and c_2 for each adhesive (Figure 2) show reasonably good linearity, especially in the case of Halthane 73-18. The data points for Halthane 87-1 are more scattered and as a result more error is obtained in the determination of c_1 and c_2 . This is reflected in the less perfect continuity

Figure 4. Storage Modulus Master Curves for Halthane 73-18 and Halthane 87-1

of the data points in the G' and G'' master curves for Halthane 87-1 compared to Halthane 73-18. The greater scatter of data points for Halthane 87-1 is only a minor problem. Adjustments in the constants c_1 and c_2 could probably be made to obtain a better curve smoothing, but the overall result would not deviate significantly from that reported here.

The loss modulus master curve for Halthane 73-18 shows a maximum at 10 Hz, whereas the loss modulus for Halthane 87-1 simply increases gradually with frequency and shows no maximum. The rate of increase of both G' and G'' with frequency for Halthane 87-1 is

Figure 5. Loss Modulus Master Curves for Halthane 73-18 and Halthane 87-1

about the same. The result is the almost flat frequency response of $\tan \delta$. Such a result means the damping behavior of Halthane 87-1 is nearly the same over the entire frequency range.

The difference in the mechanical properties of the two adhesives is attributed to the difference in their structures. Past work at Bendix on numerous urethane adhesives has shown that isocyanate prepolymers cross-linked with polyols such as Halthane 73-18, exhibit a greater change in modulus with temperature, and have lower moduli at temperatures above the viscoelastic transition compared to those cross-linked with amines (Halthane 87-1).

Figure 6. Loss Tangent Master Curves for Halthane 73-18 and Halthane 87-1

The secondary bonding forces of the urea groups, obtained from the amine cured adhesives, are presumably greater than those of the urethane groups in the polyol cured systems. Some urethane adhesives cured with MOCA or with MDA also exhibit a relatively high $\tan \delta$ which changes only slowly with increasing temperature above the viscoelastic transition.

Figure 7. Temperature Dependence of the Storage Shear Modulus for Halthane 73-18 and Halthane 87-1

ACCOMPLISHMENTS

The time-temperature correspondence of the dynamic mechanical properties of Halthane 73-18 and Halthane 87-1 has been determined. Although the two materials were found to have different responses to frequency, they both exhibit good shear modulus and loss tangent properties at frequencies as high as 100 MHz. The difference in the frequency response is attributed to the difference in their chemical structure. Isocyanate prepolymers cured with

amines have greater secondary bonding forces than those cured with polyols and therefore have higher moduli and less change in moduli at elevated temperatures.

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