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**BOND STRENGTH OF URETHANE AND
EPOXY-MODIFIED ADHESIVES**

**F. G. Childress
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April 1976

**OAK RIDGE Y-12 PLANT
OAK RIDGE, TENNESSEE**

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ABSTRACT

A number of urethane and epoxy-modified urethane systems were evaluated as room-temperature-curing adhesives. The systems were formulated to yield a variety of modulus levels and to be compatible with certain chemically sensitive materials.

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SUMMARY

A number of urethane and epoxy-modified urethane systems were evaluated as room-temperature-curing adhesives suitable for bonding chemically sensitive materials.

Cure time was evaluated as functions of viscosity, hardness, adhesive tensile strength, and T-peel strength.

All systems except one were based on Du Pont Adiprene prepolymers (L-100, L-315, LW-520) cured with polyols or aromatic diamines. The Adiprenes are reaction products of polybutylene ether glycol and toluene diisocyanate (L-100 and L-315) or dicyclohexyl methane-4,4'-diisocyanate (LW-520). One system was based on a polyol-cured polybutadiene-based elastomer.

The data provide means for adhesive selection or further modification according to use or end-product properties.

INTRODUCTION

Adhesive bonding of a number of chemically sensitive materials has been accomplished in the recent past with urethane adhesives. Additional urethane formulations are being evaluated at the Oak Ridge Y-12 Plant^(a) in order to provide a series of systems with a variety of properties.

(a) Operated by the Union Carbide Corporation's Nuclear Division for the US Energy Research and Development Administration.

BOND STRENGTH OF ADHESIVES

Two series of comparative studies have evolved as a result of the need for selectivity in adhesive properties. Adhesive systems were formulated primarily from commercially recommended or available resins and curing agents to provide products of varying moduli. The first series of tests involved adhesive T-peel evaluation (with aluminum) as a function of the cure time with nine formulations. The second series of eight formulations included T-peel evaluation with aluminum and carbon steel and tensile with aluminum. Four adhesives of the first series were further evaluated in the second series, making a total of 13 systems under consideration. These systems are listed in Table 1 and further identified in Table 2. The room-temperature modulus order for fully cured systems is shown in Table 3. This information should be used with caution due to variation in rate sensitivity of the various systems.

Table 1
ADHESIVE SYSTEMS

Adhesive System	Components	Weight Ratios
A	L-100/MOCA	100/13
B	L-100/Polyol/FAA	100/4.3/0.01
C	L-315/Polyol/FAA	100/9.2/0.03
D	L-315/Polyol/FAA	100/10/0.03
E	LW-520/Eutectic	100/7.5
F	LW-520/BDO/FAA	100/6.1/0.005
G	EN-7(A)/EN-7(B)	100/17.5
H	LW-520/ER-508/Eutectic	60/40/12
J	LW-520/ER-508/Eutectic	40/60/14
M	L-315/Polyol/Dabco	100/9.2/0.02
N	LW-520/ER-508/Eutectic	100/20/11
P	LW-520/ER-508/Eutectic	50/50/13
R	L-100/Polyol/Dabco	100/4.3/0.01

Cure rate as a function of viscosity was determined for all the systems in the second series and two from the first series. System D was not tested since it was not significantly different from System C. Systems H and J were not significantly different from System P and, likewise, were not tested.

Typical viscosity curves are presented in Figure 1. Both formulations of polyol-cured Adiprene L-100 (Systems B and R) exhibited the slowest cure rates. There was no significant difference in the catalytic effect of ferricacetylacetonate (FAA) and 1,4-diazabicyclo [2.2.2] octane (Dabco)

Table 2
COMPONENT IDENTIFICATION FOR ADHESIVE SYSTEMS

Components	Identification
L-100, L-315, LW-520 ⁽¹⁾	Adiprene (Dupont)
MOCA	4,4'-Methylene-bis-2-chloroaniline (Dupont)
Polyol (7/2 ratio)	1,4-Butanediol (BDO)/trimethylolpropane (TMP)
FAA	Ferricacetylacetonate
Eutectic (40/60 ratio)	Methylenedianiline (MDA)/metaphenylenediamine (MPDA)
BDO	1,4-Butanediol
EN-7(A) ⁽²⁾	Conathane (Conap, Inc)
EN-7(B)	FAA-catalyzed blend of polyols
ER-508 ⁽³⁾	Epi-Rez epoxy (Celanese)
Dabco	1,4-Diazabicyclo [2.2.2] octane (Houdry)

(1) L-100 and L-315—Reaction products of polybutylene ether glycol and toluene diisocyanate. LW-520—Reaction product of polybutylene ether glycol and dicyclohexyl methane-4,4'-diisocyanate.

(2) EN-7—Polybutadiene-based elastomer.

(3) ER-508—High-purity diglycidyl ether of Bisphenol A.

Table 3
MODULUS RATING ORDER

Adhesive	Type	Modulus
J	Urethane-epoxy	Highest
P	Urethane-epoxy	
H	Urethane-epoxy	
N	Urethane-epoxy	
A,E	Amine-cured urethane	
C,D,M	Urethane-polyols ⁽¹⁾	
F	Urethane-diol	
G,R,B	Urethane-polyols	Lowest

(1) These systems exhibit high creep with the modulus being highly rate sensitive.

with this prepolymer. In contrast, the L-315 prepolymer cures much more rapidly with the Dabco catalyst (System M) than with the FAA catalyst (System C). These systems were recommended by H. G. Hammon of the Lawrence Livermore Laboratory. Systems containing LW-520 exhibited the highest initial viscosities, with the eutectic amine-cured formulation (System E) being the most viscous.

Cure rate as a function of Shore A hardness was determined for nine of the adhesives.

Systems B, D, H, and J were not tested since they were not significantly different from the other systems. Typical hardness curves (Figure 2) are shown for the immediate reading and for that observed after a one-minute indentation. System M (L-325/polyol/Dabco) appears, from these data, to attain a useable hardness level at the earliest cure time. System F (LW-520/BDO/FAA), though not tested at an eight-hour cure level, may be as rapid in cure. Its creep resistance, as determined by the one-minute indentation readings, is acquired at the earliest cure time.

The first series of bond-strength tests were performed with T-peel specimens per a modified procedure of ASTM D-1876. A constant head speed of 50 mm/min was used rather than the prescribed 250 mm/min. Bonding, aging, and testing were performed at 20°C in a controlled-humidity environment (10% rh). Specimens were fabricated from 600- μ m-thick aluminum sheet (AA-1100-H14) and were sheared to width (25 mm) after bonding. Bondline thicknesses of approximately 380 μ m were employed. Aluminum was prepared for bonding by etching in a solution of sodium dichromate and sulfuric acid.

Specimens were tested at cure-time intervals of 4, 7, 14, 30, 60, 120, and 240 days at a 20°C aging temperature. Two specimens of each adhesive were postcured for 3 hours at 90°C after curing 7 days at 20°C. These specimens were not aged. The results of these tests are shown, graphically, in Figure 3. Maximum strength over the time period involved was attained with Systems C and D. There was no significant difference in these systems. Though strengths of approximately 90 N/cm width were noted after a 7-day cure, final strength appears to have stabilized at approximately 60 N/cm width. This value is better than twice the strength of the next best system, System G.

Correlation of hardness and peel-strength data indicates a possible relationship between strength and creep, with creep being determined by observing the difference in hardnesses from the immediate to one-minute indentation readings. System C demonstrates the most creep per this test. Another correlation appears to be that maximum peel strength is attained well before maximum hardness is reached.

Strengths of postcured specimens were greater than respective stabilized strengths (8-month cure). Postcured specimens were not aged, however. On the average, these strengths are not significantly different from the 7-day-cured groups, which represent similar aging (see Table 4).

Figure 1. TYPICAL VISCOSITY CURVES. (See Table 1 for Adhesive Formulations)

Figure 2. TYPICAL HARDNESS CURVES. (See Table 1 for Adhesive Formulations)

Figure 3. T-PEEL AS A FUNCTION OF THE CURE TIME. (Series 1; for Adhesive Identification, See Table 1)

Table 4
T-PEEL STRENGTH⁽¹⁾
(Series 1)

Adhesive System ⁽²⁾	Cure Time in Days at 20° C (N/cm of width)							
	4	7	14	30	60	120	240	7+ Postcure ⁽³⁾
A	38	35	19	10	7	7	9	15
B	33	23	10	4	2	3	3	9
C	79	88	79	75	68	59	68	87
D	82	89	68	79	61	58	60	76
E	56	39	13	7	5	4	5	31
F	35	32	28	14	16	15	21	41
G	39	53	54	38	34	26	26	58
H	82	18	2	2	3	1	2	3
J	2	2	4	4	6	4	4	3

(1) ASTM-D1876, modified, aluminum (0.66-mm-thick AA-1100-H14, ASTM B209).

(2) See Table 1 for adhesive formulations.

(3) Postcured 90° C/3 hr after curing 7 days at 20° C.

Additional tests were initiated to determine whether strength reduction with time was a function of bond deterioration, or a change in physical properties (modulus or creep). Peel strengths with carbon steel and aluminum (Table 5) and tensile strengths with aluminum (Table 6) are reported graphically in Figures 4 through 11. Tensile strengths tended to increase in strength through the first 60 days of cure and experienced little change

Table 5
T-PEEL STRENGTH⁽¹⁾
(Series 2)

Adhesive System ⁽²⁾	Specimen Type ⁽³⁾	Cure of Age ⁽⁴⁾ Time in Days at 20° C (N/cm of width)						
		3	7	14	30	60	140	240
C	Al	89	72(93)	74	74(105)	79(88)	74(103)	60(77)
	Fe	60	63(102)	72	84(105)	79(86)	79(91)	68(86)
E	Al	51	38(52)	33	21(61)	12(60)	5(58)	5(56)
	Fe	65	58(102)	47	35(74)	44(88)	30(70)	37(77)
F	Al	56	63(94)	61	51(86)	49(77)	44(65)	32(40)
	Fe	30	32(60)	24	28(60)	24(30)	30(40)	21(38)
G	Al	51	54(68)	52	46(66)	47(63)	42(60)	40(66)
	Fe	49	56(94)	66	93(89)	52(84)	51(79)	52(77)
M	Al	84	82(102)	72	79(91)	72(105)	58(91)	58(74)
	Fe	91	80(116)	93	108(117)	79(107)	98(108)	68(89)
N	Al	70	54(32)	42	28(40)	21(37)	18(28)	12(30)
	Fe	79	80(56)	63	66(66)	46(49)	37(54)	47(52)
P	Al	4	5(7)	7	5(7)	2(5)	4(7)	4(5)
	Fe	14	14(37)	5	7(26)	7(28)	4(28)	4(19)
R	Al	46	40(49)	21	16(37)	12(26)	5(19)	4(18)
	Fe	46	42(38)	37	35(32)	19(21)	4(14)	4(12)

(1) ASTM-D1876, modified.

(2) See Table 1 for adhesive formulations.

(3) Al - 0.6-mm-thick AA-1100-H14, ASTM B209.

Fe - 0.45-mm-thick cold finished carbon steel, ASTM A366.

(4) Strengths shown in parentheses are of specimens cured at 20° C for 3 to 7 days, postcured 4 hrs at 90° C. Time is sum of 20° C cure and post aging times.

Table 6
ADHESIVE TENSILE STRENGTHS⁽¹⁾
(All Values in MPa)

Adhesive System ⁽²⁾	Cure Time (days at 20° C)							Postcured (90° C - 4 hrs)
	3	7	14	30	60	128	240	
C ⁽³⁾	6.1 ⁽⁴⁾	8.8	12.1	13.4	17.3	17.1	18.4	-
E ⁽³⁾	7.2 ⁽⁴⁾	13.2	15.3	16.6	17.0	12.9	13.4	-
F	9.3 ⁽⁴⁾	10.1	12.2	11.9	10.5	10.7	12.3	8.3
G	1.7	3.7	6.9	8.5	9.9	11.4	11.3	6.5
M	8.5	11.1	15.1	11.7	12.1	13.2	10.7	12.4
N	5.2	10.4	16.0	15.1	19.9	23.1	21.2	23.6
P	10.8	19.6	19.8	17.0	20.5	20.4	21.6	27.7
R	0.5	1.8	3.2	2.9	3.0	2.9	2.9	1.8

(1) Aluminum to aluminum (2024-T3), average of 3 specimens each.

(2) See Table 1 for adhesive formulations.

(3) Included for comparison from previous data, approximate cure times.

(4) Four-day cure at 20° C.

Figure 4. ADHESIVE STRENGTH AS A FUNCTION OF THE CURE TIME. (System C)

Figure 5. ADHESIVE STRENGTH AS A FUNCTION OF THE CURE TIME. (System E)

Figure 6. ADHESIVE STRENGTH AS A FUNCTION OF THE CURE TIME. (System F)

Figure 10. ADHESIVE STRENGTH AS A FUNCTION OF THE CURE TIME. (System P)

Figure 11. ADHESIVE STRENGTH AS A FUNCTION OF THE CURE TIME. (System R)

thereafter. Systems C and N increased slightly, while System E declined. Maximum tensile strength with cure at 20° C was achieved with System N (23.1 MPa). System P had the highest strength of all systems when postcured for 4 hours at 90° C (27.7 MPa). In contrast, this system had the lowest peel strength in each aging group.

Maximum peel strengths of the Series 2 specimens were achieved with System M—Dabco-catalyzed, polyol-cured L-315 (Figure 8). There is probably no significant difference, however, in these results and those shown for System C (Figure 4)—the FAA-catalyzed formulation. Bondlines of the Series 2 peel specimens were approximately 250 μ m thick.

CONCLUSIONS

Postcured and aged peel specimens yielded higher strengths in almost all cases than respective specimens aged at 20° C. In seven of the eight systems, tested in Series 2, peel strengths were greater with the sand-blasted steel than with the etched aluminum. An exception was noted with System F (Figure 6) which had a significantly greater strength with aluminum.

Degradation of peel strength with time appears generally less severe in the Series 2 study than in the prior tests. It is still quite pronounced, however, with Systems E, N, and R, especially with aluminum specimens.

Comparative T-peel tests were made with two commercial adhesives using the same test procedures. A nitrile epoxy,^(b) structural adhesive yielded an average strength of 72 N/cm width; whereas, an epoxy^(c) adhesive averaged only 4 N/cm width.

Under the noted conditions of bonding, aging, and testing (20° C at 10% rh), bond deterioration with either aluminum or steel is not believed to be significant. Changes in strength with time are more likely the result of changes in the physical properties of the adhesive (modulus and creep). These conclusions seem reasonable in view of the fact that most of the systems, when postcured, exhibited no significant change in strength with time. There were anomalies, however, such as those exhibited by Systems F (Figure 6) and R (Figure 11). Tensile-strength results tend to further reinforce these conclusions.

Within limits, peel strength and tendency to creep under load appear to be directly proportional. The highest peel strengths were observed with those systems with the greatest creep.

(b) Cyanamid—FM-123-2 film adhesive.

(c) Woodhill Chemical Sales—E-Pox-E.

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