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Poly-2-oxazolidones as Cryogenic Adhesives

STANLEY R. SANDLER, *Central Research Laboratory, Borden Chemical, Division of Borden, Inc., Philadelphia, Penna. 19124*

Synopsis

Adhesives data are presented at −320° to +400°F for adhesion to aluminum or stainless steel to indicate that poly-2-oxazolidone-type adhesives give poor results when conpared to epoxy amine, polyurethane prepolymer amine, or a mixture of the latter two resins.

INTRODUCTION

In an earlier investigation it was shown that polyurethanes[1] containing the polyether backbone gave superior adhesives at cryogenic temperatures (−453°F) as compared to epoxy resins.[2,3] However, these adhesives showed poor performance at +400°F. In later investigations it was shown that epoxy resins react with polyurethane prepolymers in the presence of catalysts at 120°–160°C to give poly-2-oxazolidones [eq. (1)].[4,5]

The object of this program was to develop an adhesive for aluminum or stainless steel which incorporates the good low-temperature adhesive properties of the polyether polyurethane resin and the good high-temperature properties of the epoxy resin.

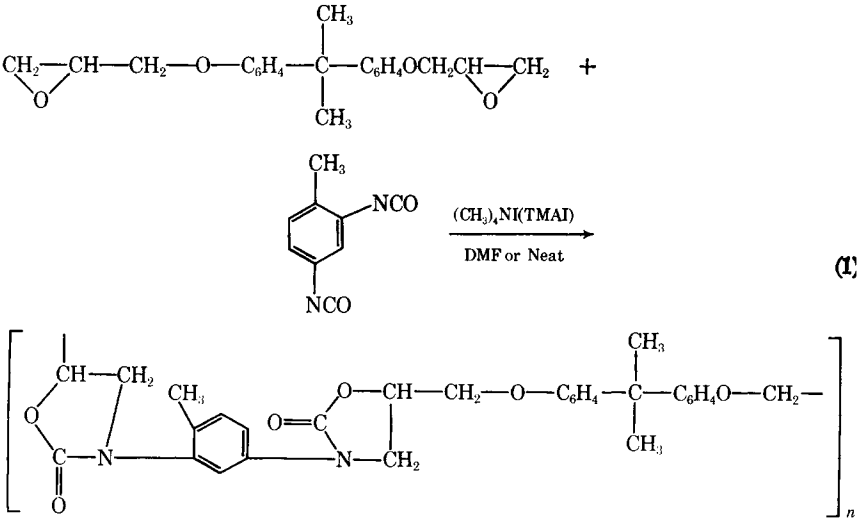


TABLE I
Physical Evaluation of Poly-2-oxazolidone Adhesives on Stainless Steel and Aluminum

Sample no.	Composition[a]	Tensile shear strength, psi							
		Aluminum				Stainless Steel			
		−320°F	73°F	250°F	400°F	−320°F	73°F	250°F	400°F
1	Adiprene L315 + MOCA (5/2)	6500	4085	1315	40	—	—	—	—
2	Same (5/2)	6430	4580	1365	25	—	—	—	—
3	Der 332 or EPON828 + MDA (5/1.4)	3540	2430	1177	556	4090	2690	1931	—
4	EPON828 + Adiprene L315 (1.9/3.7) (and other ratios)	Did not cure							
5	DER332 + Adiprene L315 (5.0/5.3) (and other ratios)	Did not cure							
6	DER332 + Adiprene L315 + $(CH_3)_4NI$ (5./5.3/0.02)	3570	407	—	—	100	40	—	—
7	DER332 + Adiprene L315 + $(CH_3)_4NI$ (3.0/7.8/0.06)	5520	117	—	—	80	80	—	—
8	DER332 + Adiprene L315 + pyridine (5.0/2.0/1 drop)	4380	637	—	—	5860	597	—	—
9	DER332 + Adiprene L315 + MDA (5.0/2.0/1.8)	3640	3750	1580	—	4410	2840	1113	—
10	DER332 + Adiprene L315 + MDA + pyridine (5.0/2/1.8/1 drop)	—	—	—	—	3270	3290	760	—
11	DER332 + Adiprene L315 + MDA + TMAI (5/2.0/1.8/0.08)					2590	2250	1180	250
12	Adiprene L315 + 428-30 + TMAI (1.4/0.5/1.08)					3240	715	—	—
13	Adiprene L315 + 409-123 + TMAI (4.5/1.7/0.08)					3040	483	—	—

14	428–43 + 409–123 + TMAI (6.2/0.8/0.08)				2830	40	—	—
15	428–43 + 409–123 + TMAI (6.2/0.8/0.08)				7600	268	—	—
16	428–43 + Epiphen 825 + TMAI (10/1.8/0.08)				6700	343	—	—
17	428–53 + Epiphen 825 + TMAI (6.4/1.8/0.08)				5460	901		
18	Epiphen 825 + Adiprene L315 + MDA + TMAI (8.8/2.0/1.7/0.08)	1930	2980	1050				
19	Epiphen 825 + Adiprene L315 + MDA (8.8/2.0/1.7)	2310	3080	757				
20	Epiphen 825 + Adiprene L315 + TMAI (3.2/7.8/0.08)	4466	1216	137				
21	Epon 812 + 428–47 + TMAI (0.5/4.5/0.1)	5580	2870	135				
22	Epon 812 + Adiprene L315 + MOCA + TMAI (0.5/4.5/1.4/0.1)	3000	3300	739				
23	Epon 812 + Adiprene L315 + TMAI (0.5/4.5/0.1)	5640	1150	130				
24	Epon 812 + Adiprene L315 + TMAI (1.0/3.0/0.08)	1740	198	—				

[a] DER 332 = Dow diglycidyl ether of bisphenol A; Adiprene L315 = du Pont polyurethane with reactive isocyanate groups; MDA = 4,4′-diaminodiphenylmethane; TMA = tetramethylammonium iodide; Epiphen 825 = Borden glycidyl ether-type epoxy resin; 428–53 = 2 moles 3,3′-dimethyldiphenylmethane 4,4′-diisocyanate reacted with 1 mole of Pluracol P710 (1 drop ortho-chlorobenzoyl chloride) to give a prepolymer, % NCO = 7.0% 428–43 = 3 moles TDI reacted with 2 moles Pluracol P710 to give a prepolymer with 4% NCO; 409–123 = diglycidyl phthalate; 409–134 = diglycidyl isophthalate; 428–30 = diglycidyl terephthalate; Epon 828 = Shell diglycidyl ether of bisphenol A; Epon 812 = glycerol triglycidyl ether (Shell); MOCA = 3,3′-dichloro-4,4′-diaminodiphenylmethane (du Pont); 428–47 = TDI adduct of Pluracol P-410 (TDI/P410 = 1.86/1).

EXPERIMENTAL AND RESULTS

The methods of preparing the polyurethane and epoxy resins are described in detail in earlier investigations.[1-3]

Adhesive Preparation

The adhesive was applied with a spatula to both freshly etched surfaces to be bonded. One panel was placed on a jig designed to allow 0.50 in. overlap of the 1 × 3 in. panels. The second panel was put in place and the 0.50 in. bonded area was clamped at each edge with a small spring clip.

Physical Testing

The physical testing data are presented in Table I. In most cases the adhesives were tested at 400°, 250°, 73°, and −320°F using 0.064-in. thick Alclad aluminum 2014-T6, Federal Specification QQ-A-255. Some adhesives were tested on #321 stainless steel, 0.064-in. thick, Federal Specification QQ-S-766. The stainless was etched with sulfuric acid–dichromate according to a procedure described earlier.[2] The samples were cured at 100°C for 2 hr, unless otherwise specified, and equilibrated before testing for seven days at room temperature (73°F) in a constant temperature–humidity room. The tensile shear strength was determined by using a Tinius Olsen Electromatic universal testing machine. An average of three determinations is shown. The cryostat was obtained from Hofman Laboratories, Inc., Newark, New Jersey, and is described by Sandler and Berg.[1]

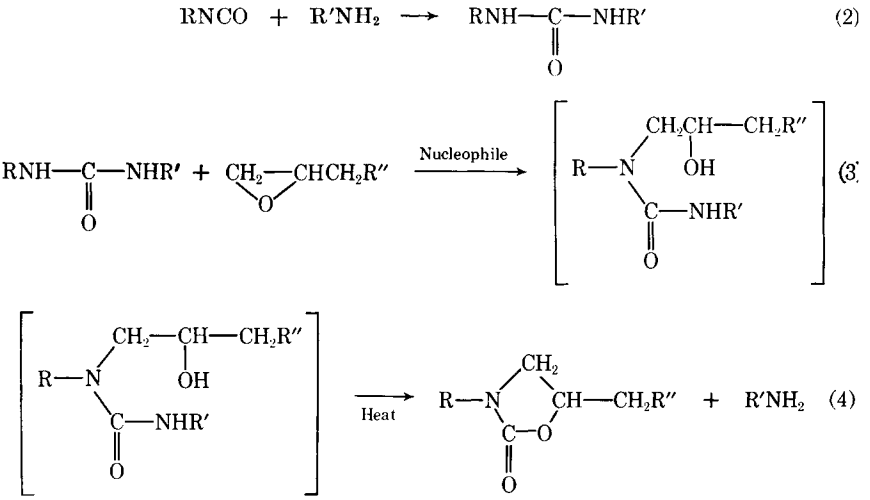
DISCUSSION

Poly-2-oxazolidones can be produced by either reacting diepoxides with diisocyanates,[4-6] bisurethanes,[7,8] or bisureas[7] in the presence of a nucleophilic reagent such as triethylamine, pyridine, or tetramethylammonium iodide.

In the present investigation the effectiveness of poly-2-oxazolidone adhesives produced from diepoxides with diisocyanates in the presence of a nucleophile is compared to that of polymers produced by curing the mixture of diepoxide and diisocyanate with only a diamine [eqs. (2) and (3)]. In the latter case, a poly-2-oxazolidone is not likely unless an additional nucleophile is also present.[7] The nucleophile is necessary to catalyze the newly formed polymer resin with epoxy groups [eq. (4)].[7]

The resulting free amine, $R'NH_2$, can react with either remaining isocyanate or epoxy groups.

As described in Table I, the addition of TMAI or pyridine to a mixture of DER332 and Adiprene L315 or other similar combination produced a polymer with poor adhesive strength at 73°F. Varying the ratio of epoxy resin to polyurethane prepolymer or adding more nucleophile did not significantly alter these results. However, when MDA is added, as in sample 11,



the adhesive acquires adhesive strength at 73°F and 250°F equivalent to a straight epoxy resin cured with MDA. The adhesive results at 400°F appear to be a compromise between the poor results obtained with the straight polyurethane resin samples 1 and 2. Omission of the TMAI entirely gives even a further increase in strength at 73°F and 250°F, as seen in sample 9. The conclusion is that TMAI or pyridine cause a lowering of properties and that an amine-cured resin mixture gives a compromise of properties. Similar results are obtained with Epiphen 825 and other epoxy resins.

Whether the resins cured with only the amine have some polyoxazolidone-type structures is not known but may be likely since the starting amine or epoxyamine product may catalyze oxazolidone formation. A likely possibility would be that this resin is composed of a mixture of polymers with urea, hydroxypropyl groups, and some oxazolidone groups. The high reactivity of the epoxy and isocyanate groups of these resins for amine groups at 100°C lends support to this suggestion. Further data are required to determine the structure of this complex crosslinked polymer.

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