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Final Summary Report

EXPLORATORY STUDY ON THE EFFECTS OF NOVEL DIAMINE CURING AGENTS AND ISOCYANATE PRECURSORS ON THE PROPERTIES OF NEW EPOXY AND URETHANE ADHESIVES

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by

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Prepared under Contract No. NAS1-13982
Modification No. 1

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For

National Aeronautics and Space Administration
Langley Research Center
Hampton, VA 23665

May 1977

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ABSTRACT

This report covers the results of investigations directed toward studying the effects of novel aromatic diamine structures on epoxy adhesive properties and includes work done under a modification to the original contract. The results accomplished under the original contract have been reported in NASA CR-145022.

Three aromatic diamines based on diphenylsulfone and benzophenone were studied as epoxy adhesive curing agents. Previously found differences in adhesive strengths for meta vs para orientation were not found in these series.

The use of aluminum and alumina as fillers in a *m,m'*-methylene dianiline-cured epoxy adhesive was not found to be beneficial to adhesive strength. Alumina filled adhesives had much lower strength than unfilled adhesives. The unfilled *m,m'*-methylenedianiline-based epoxy adhesive had excellent resistance to moisture relative to a *p,p'*-methylenedianiline-based adhesive and maintained good strengths up to 250°F.

A glass fiber composite based on a *m,m'*-methylenedianiline-cured epoxy appeared to be equivalent to the *p,p'*-methylenedianiline-cured epoxy as judged by short beam shear tests.

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FOREWORD

This report was prepared by Monsanto Research Corporation, Dayton Laboratory, under Contract No. NAS1-13982, Modification No. 1, "Exploratory Study on the Effects of Novel Diamine Curing Agents and Isocyanate Precursors on the Properties of New Epoxy and Urethane Adhesives", for the Langley Research Center of the National Aeronautics and Space Administration. Dr. Vernon L. Bell served as project manager.

The work was performed at the Dayton Laboratory of Monsanto Research Corporation by Dr. D. G. Glasgow, project leader.

The authors are indebted to Dr. J. M. Butler for his many helpful suggestions and stimulating discussions. Also, the capable assistance of Mrs. C. Fritsch and Mr. D. L. Sheppard, who conducted the physical tests, is appreciated.

EXPLORATORY STUDY ON THE EFFECTS OF NOVEL DIAMINE CURING AGENTS AND ISOCYANATE PRECURSORS ON THE PROPERTIES OF NEW EPOXY AND URETHANE ADHESIVES

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SUMMARY

Task A

The effect on adhesive strengths of meta vs para orientation of amine substituents for two aromatic diamine pairs was examined. The tensile shear and T-peel strengths of *m*,*m*'-diaminodiphenylsulfone (*m*,*m*'-DADPS) and *p*,*p*'-diaminodiphenylsulfone (*p*,*p*'-DADPS) were found to be very comparable under the cure conditions used. The occurrence of cohesive failure in both systems suggests it may be possible to obtain still greater strengths than were found in this brief study. The handling characteristics of adhesive formulations based on these two diamines were very similar. The amines dissolved at 135°C readily. The mixtures were processed at 100°C to obtain formulations fluid enough to permit easy spreading.

A comparison of *m*,*m*'-diaminobenzophenone (*m*,*m*'-DABP) and *p*,*p*'-diaminobenzophenone (*p*,*p*'-DABP) was not possible. Attempts to incorporate *p*,*p*'-DABP in an epoxy resin with the use of heat only resulted in rapid curing once the amine dissolved. Efforts to prepare a B-stage resin through the use of a solvent (e.g. dimethylacetamide) were successful but solvent traces caused bubble formation in the bond line and consequently low adhesive strengths were found.

Task B

Optimization studies begun under the first phase of this project were continued with examination of the effect of alumina and aluminum fillers, primers, a study of the moisture resistance of *m,m'*- and *p,p'*-methylenedianiline (*m,m'*-MDA and *p,p'*-MDA) adhesively bonded structures, and a determination of the effect of temperature on adhesive strength of the same two adhesives.

It was found that use of twenty weight percent alumina filler reduces bond strength almost fifty percent in a *m,m'*-MDA cured epoxy adhesive. The relationship between alumina content and tensile shear strength is not linear and only slightly greater strength losses are noted at the fifty weight percent level. The use of epoxy and aminofunctional silane primers for the alumina results in only about a thirty-five percent loss in tensile shear strength relative to an unfilled system. However, somewhat surprisingly use of primer on the adherend is not beneficial.

The use of twenty weight percent aluminum powder as a filler gave a slight reduction in tensile shear strength relative to an unfilled system. The use of primers was beneficial when they were applied to either the adherend or filler with the best strengths being obtained when primers were present on both. However, the best combination of primers for aluminum filler and adherend did not increase the tensile shear strength significantly over an unfilled system.

The moisture resistance of a *m,m'*-MDA-cured Epon 828 adhesive was shown to be quite good. Aging for thirty days at 120°F/95% RH resulted in less than 10% decrease in tensile shear strength and no loss in T-peel strength. In contrast a *p,p'*-MDA-cured Epon 828 lost 35% of its tensile shear strength in the same period.

Determination of the tensile shear and T-peel strengths of *m,m'*-MDA and *p,p'*-MDA-based adhesives vs temperature showed the *m,m'*-MDA system lost strength more rapidly but still had strength comparable to the *p,p'*-MDA system at 250°F.

Task E

The effect of meta vs para orientation of amine functions on composite strengths was studied briefly by preparation of 13 ply composites. Short beam shear strengths of 31.6 x 10^6 N/m^2 and 28.5 x 10^6 N/m^2 were obtained for *m,m'*-MDA and *p,p'*-MDA-based composites respectively. It is doubtful that this difference can be considered significant.

INTRODUCTION

The objective of this research program was to determine the effects of novel aromatic diamine curing agents and isocyanate precursors on the properties of new epoxy and polyurethane adhesives. The original program had four tasks, two dealing with epoxy and two with polyurethane adhesives. In Task A the effectiveness of five novel aromatic diamines as curing agents for epoxies was investigated. In Task B a particular diamine curing agent was chosen for additional study to optimize an epoxy adhesive formulation based on that diamine. The effectiveness of three novel aromatic diamines as a curing agent for polyurethane adhesives was investigated under Task C. Two experimental aromatic diamines were converted to diisocyanates and studied in conventional polyurethane adhesive formulations in Task D.

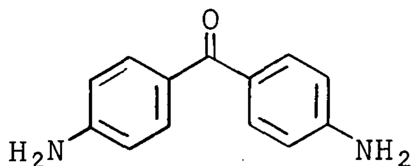
The modified contract expanded Task A to include three more aromatic diamines. Task B was expanded to cover more optimization work and property characterization. A new Task E was included to briefly study an epoxy/glass composite based on the resin chosen in Task B.

This report covers work performed during the period 28 September 1976 to 31 March 1977.

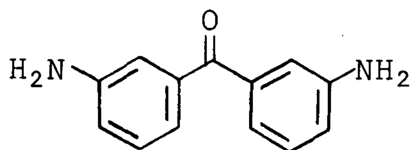
RESULTS AND DISCUSSION

Task A. Screening of Epoxy Adhesives

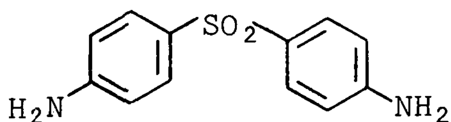
The objective of this task was to expand the evaluation work done on Task A of the initial project and study the effect of structure on adhesive properties of two more *p,p'-m,m'* diamine pairs. Work at NASA Langley and under the initial phases of this contract had shown that some *m,m'*-aromatic diamines consistently gave higher adhesive strengths in polyimide and epoxy adhesives than their *p,p'* counterparts. The two additional diamine pairs illustrated below were therefore studied.



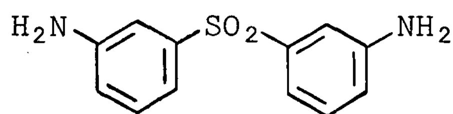
p,p'-DABP



m,m'-DABP



p,p'-DADPS



m,m'-DADPS

Reactivity and Pot Life

The handling characteristics of the above diamines were determined in the same manner as reported previously (Ref. 1). The data obtained are given in Table I and compared to *p,p'*-methylene dianiline (*p,p'*-MDA) and *m,m'*-methylenedianiline (*m,m'*-MDA). These latter two diamines represent the state-of-the-art and the best diamine from the previous work on Task A respectively.

Table I

PROCESSING CHARACTERISTICS OF AROMATIC DIAMINE/EPON 828 MIXTURES[a]

Diamine	Mixing Temp. °C	Viscosity at Temp.	Spreadability at Room Temp.	Diamine Crystallization at Room Temp.
p,p'-MDA	100	low	good	no
m,m'-MDA	100	low	good	no
p,p'-DABP	[b]185	--	--	--
m,m'-DABP	125	low	poor	yes[c]
p,p'-DADPS	135	low	none[d]	no
m,m'-DADPS	135	low	none	no

[a]Stoichiometric mixtures
[b]Set up before all diamine went into solution
[c]Crystals formed at 80°C
[d]Formulation handled at 100°C

The *p,p'*-DABP based formulation required very high temperatures to obtain a solution. At temperatures of 200°C it dissolved readily but also set up much too rapidly to be useful. Attempts to utilize lower temperatures resulted in the formulation setting up prior to complete solution of the diamine. Several attempts were made to B-stage the *p,p'*-DABP formulation at a lower temperature in a solvent and so achieve solubility of the diamine without having the mixture set up. The formulation is soluble in dimethylformamide, dimethylacetamide (DMAC) and N-methylpyrrolidone. Less polar solvents were evaluated

but none were effective. The formulation was successfully B-staged in DMAC but we were unable to remove enough of the solvent to allow preparation of bubble free adhesive joints. The limited success achieved indicated that a technique for preparation of a solvent free system could be developed but the necessary time was not available in this project.

The *m,m'*- and *p,p'*-isomers of DADPS had very similar handling characteristics. Resin temperatures of 135°C were required to dissolve them and no crystallization occurred on cooling to room temperatures. The mixtures were much too viscous to be spread at room temperature and temperatures of 100°C were used to permit easy spreading.

The pot lives of the *m,m'*- and *p,p'*-DADPS systems were compared at 100°C using the apparent viscosity vs time technique described in Ref. 1. The data obtained are presented graphically in Figure 1. Note the very definite structural influence on reactivity. This is undoubtedly a reflection of the difference in basicities between the two amines caused by the more powerful electron withdrawing effect of a para vs a meta sulfonyl group. The data for *p,p'*-DADPS indicate a pot life at 100°C in excess of six hours whereas the literature quotes a value of three hours at 100°C (Ref. 2). The reason for the discrepancy is not known. The instrument used for the viscosity measurements was checked and found to be functioning properly Also the formulation used for the viscosity measurements was used to make adhesive samples and these gave the expected strength values indicating no problems in stoichiometry.

Adhesive Properties

The stoichiometry suggested in the literature for *p,p'*-DADPS-cured Epon 828 type formulations varies from 20-30 phr (Ref. 2) to 33-38 phr (Ref. 3). A significant difference in reactivity had been noted between the meta and para isomers. Based on these two items it was felt that a brief study of the effect of stoichiometry on a *m,m'*-DADPS/Epon 828-based adhesive system was in order. Lap shear specimens were used to study the effect. The data obtained are given in Table II. These data indicate that comparable adhesive strengths are obtained over a wide range of *m,m'*-DADPS concentrations and that *m,m'*-DADPS acts very similar to *p,p'*-DADPS in this respect. (See Ref. 2, p.8-8 for the effect of *p,p'*-DADPS concentration on properties.)

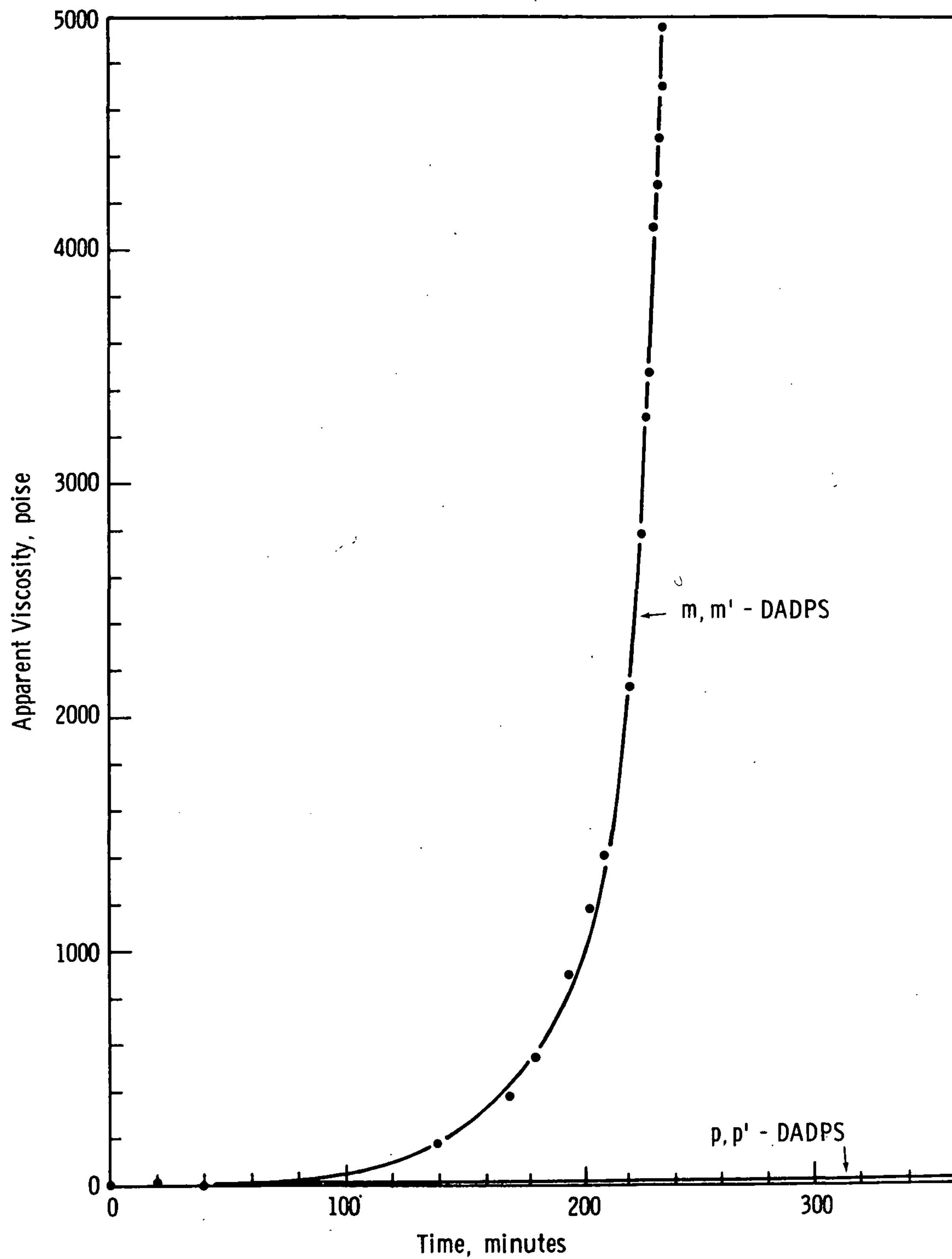


Figure 1. Apparent Viscosity vs Time at 100°C for Epoxy Adhesive Formulations

Table II

EFFECT OF STOICHIOMETRY ON TENSILE SHEAR STRENGTH OF *m,m'*-DADPS/EPON 828-BASED ADHESIVES[a]

Sample No.	Stoichiometric Level, %	Diamine, phr	Tensile Shear Strength,		Failure Mode
			$N/m^2 \times 10^{-6}$	psi	
191890-1	72	25	16.7	2420	cohesive
-2	80	28	21.8	3160	cohesive
-3	89	31	20.0	2900	cohesive
-4	98	33	22.2	3220	cohesive
191896-1	95	33	20.5	2970	cohesive
-2	98	34	20.8	3020	cohesive
-3	101	35	21.9	3180	cohesive
-4	103	36	21.1	3060	cohesive

[a]Cure cycle was 1.8×10^4 sec (5 hr) at 400°K (127°C) followed by 3.6×10^2 sec (1 hr) at 473°K (200°C)

Adhesive test specimens were prepared to directly compare *m,m'*- and *p,p'*-DADPS using the same cure cycle. The data given in Table III indicate that the two systems have very comparable strengths. Note that both systems failed cohesively indicating that optimization of the cure could potentially lead to still higher strengths.

Table III

ADHESIVE STRENGTHS OF AROMATIC DIAMINE/EPON 828-BASED ADHESIVES

Sample No.	Diamine	Cure Cycle[a]				Tensile Shear Strength,		Failure Mode	T-Peel Strength,		Failure Mode	Approximate Pot Life at 100°C, hr
		Temp		Time								
		°K	°C	sec x 10^{-3}	hr	$N/m^2 \times 10^{-6}$	psi		N/m	piw		
202516	*m,m'*-DADPS	473	200	3.6	1	22.4±1.7	3250	cohesive	245±5	1.4	cohesive	3.9
202511	*p,p'*-DADPS	473	200	3.6	1	21.2±1.2	3020	cohesive	270±15	1.5	cohesive	>5.2
191823	*m,m'*-DABP	473	200	7.2	2	30.4±1.6	4410	cohesive	245±15	1.4	cohesive	0.60
202523	*m,m'*-DABP	473	200	7.2	2	28.0±0.8	4060	cohesive	--	--	--	--

[a] Cure at designated temperature was preceeded by 1.8×10^3 sec (0.5 hr) cure at 388°K (115°C) for samples 191823 and 202523 and 1.8×10^4 sec (5 hr) cure at 400°K (127°C) for samples 202511 and 202516.

The tensile shear strength of a *m,m'*-DABP-based system is shown in Table III and compared with a comparable system prepared during the first phase of this project. Good reproducibility is indicated. These samples were prepared in anticipation of doing a comparison with a *p,p'*-DABP-cured epoxy adhesive.

The glass transition temperatures of the *m,m'*- and *p,p'*-DADPS-based epoxies were measured via the Clash-Berg technique. The data given in Figure 2 show the glass transition temperatures of the *m,m'*- and *p,p'*-systems to be 165°C and 200°C respectively.

Task B. Optimization of Epoxy Adhesives

The work begun under the first phase of this project was expanded to include determination of the effect of fillers, study of the moisture resistance of adhesive specimens and the effect of temperature on lap shear strength. The adhesive used for these studies was *m,m'*-MDA-cured Epon 828. Where appropriate it was compared with a similar *p,p'*-MDA cured system.

Prior to beginning the optimization studies standard *m,m'*-MDA-cured Epon 828 adhesive test specimens were made to insure that the adhesive strengths found in earlier work could be reproduced. A tensile shear strength of 29.6×10^6 N/m^2(4290 psi) (sample 191854, Table IV) was obtained under the same conditions where previous work had given values of $35\text{-}36 \times 10^6$ N/m^2 (5100-5200 psi). This result initiated a study to determine the cause for the lack of reproducibility.

A *p,p'*-MDA cured adhesive similarly gave a low tensile shear strength (22.5×10^6 N/m^2) relative to previously obtained values of 26.8×10^6 N/m^2. Both samples exhibited cohesive failure. The fact that cohesive failure was observed indicated that the problem is concerned with the bulk properties of the adhesive rather than the metal-adhesive interface. This suggests problems in stoichiometry or cure cycle. These variables were studied further. An adhesive prepared from freshly purified *m,m'*-MDA compared with as received *m,m'*-MDA showed only a 1.3×10^6 N/m^2 difference in tensile shear strength (see samples 191888-1 and 2 of Table IV). This variation was not sufficient to account for the problem.

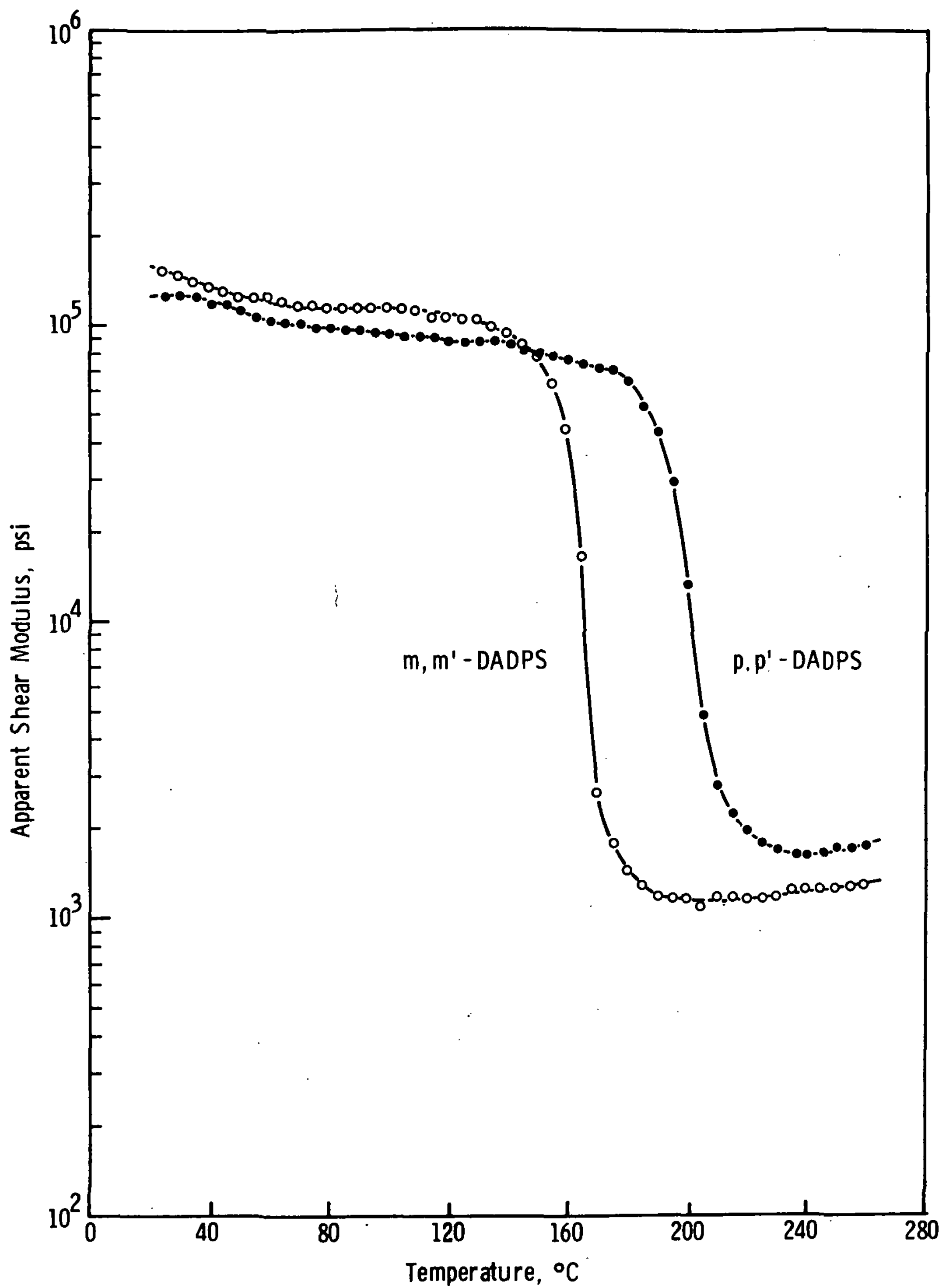


Figure 2. Apparent Shear Modulus vs Temperature for Aromatic Diamine-Cured Epon 828

Determination of the equivalent weight of the epoxy resin gave a value of 189, only 3 units different from that obtained during the first phase of the project. These data indicated that stoichiometry was not the cause of the low strengths. To confirm this, lap shear specimens were prepared on different days using amine levels that varied between 98 and 102% of theoretical. The tensile shear strengths obtained did not show any consistent variation with stoichiometry but appeared to depend more on the day in which they were prepared. The data for samples 191856 thru 191865 in Table IV illustrate this point.

The entire process of adhesive specimen preparation and testing was reviewed to determine if any uncontrolled variables could be identified or if any of the controlled variables had changed relative to the prior work. The review determined the following items:

1. The aluminum being used came from the same 4' x 8' sheet as used previously and the grain of the lap shear specimens ran in the same direction.

2. The experimental work was done by the same individual in the same laboratory and using the same lots of chemicals, water, diamines and Epon 828 as had been used previously. No variation in experimental technique could be found.

3. The curing and drying ovens used were the same and recalibration showed no difference in temperature profile relative to prior work.

4. The test equipment was the same and the tests were done by the same inidividual as previously. Recalibration of the test equipment showed no variation.

In summary no controlled or uncontrolled variable could be found that would account for the observed variations in tensile shear strength.

The cure cycle study performed previously was redone using a single adhesive mixture. Cure time variations of 0.5 hr to 3.5 hr were used. The specimens cured at 200°C for 3.0 hr gave a tensile shear strength value of 35.2×10^6 N/m^2, a value very comparable to those obtained previously. The strengths obtained are given in Table IV, samples 202509-1 thru 7. An attempt to repeat

this high strength in a subsequent preparation gave a value of 29.1 x 10^6 N/m^2 (sample 202522) suggesting that perhaps adhesive bulk strength was being influenced by more than one variable. These studies did not result in any definite conclusion concerning the problem.

Some variations in surface treatment were studied (sample 191867-1 thru 202508-3) prior to recognizing that the problem could not be the interface. No significant variables were found.

A possible explanation for the problem which could not be studied in the short time available on the project is the influence of adherend thickness. Guess, *et al.* (Ref. 4) among others have shown that using an adherend that is too thin can result in significant peel forces during tensile shear testing with resultant lowering of the tensile shear value obtained. This could potentially be happening with the high strength adhesives being sutdied in this project if small variations in adherend thickness or strength occurred.

Effect of Fillers

A study of the effect of fillers was carried out in spite of the fact that reproducible adhesive strengths could not be obtained. It was felt that significant influences of fillers would still be detectable. Aluminum and alumina were studied.

An alumina filled *m,m'*-MDA-cured epoxy adhesive containing 50 weight percent Al_2O_3 gave tensile shear strengths considerably lower than an unfilled adhesive. Tensile shear strength values of 13 to 16 x 10^6 N/m^2 (1860 to 2300 psi) were obtained in spite of variations in stoichiometry, adherend surface roughness and use of a primer for the aluminum adherend (see samples 191866 thru 191876-4 of Table V). In all cases adhesive failure was found indicating that bulk adhesive is considerably higher modulus than the unfilled adhesive therefore forcing failure to occur at the interface.

It was shown that decreasing strengths were obtained with increasing filler levels. Alumina levels above about 30 weight percent gave somewhat comparable strengths as shown by the data for samples 191889-2 thru 191889-3.

Table IV

ADHESIVE STRENGTHS OF *m,m'*-MDA/EPON 828-BASED ADHESIVES

Sample No.	Stoichio-metric Level, %	Cure Cycle (a)				Tensile Shear Strength (b)		Failure Mode	Surface Roughness, μin.
		Temp.		Time					
		°K	°C	sec x 10^{-3}	hrs	N/m² x 10^{-6}	psi		
191856	98	473	200	12.6	3.5	21.0±1.5	3050	cohesive	60-75
191854	100	473	200	12.6	3.5	29.6±1.4	4290	cohesive	60-75
191855	102	473	200	12.6	3.5	27.7±1.7	4020	cohesive	60-75
191875-1	99	473	200	12.6	3.5	31.3±1.4	4540	cohesive	60-75
191875-2	101	473	200	12.6	3.5	32.6±0.3	4730	cohesive	60-75
191865	100	473	200	12.6	3.5	29.3±0.9	4250	cohesive	60-75
191888-1	100	473	200	12.6	3.5	27.8±0.7	4030	cohesive	60-75
[c]191888-2	100	473	200	12.6	3.5	29.1±1.1	4220	cohesive	60-75
202509-1	100	473	200	1.8	0.5	31.1±1.6	4510	cohesive	60-75
202509-2	100	473	200	3.6	1.0	29.8±3.6	4320	cohesive	60-75
202509-3	100	473	200	5.4	1.5	33.5±0.6	4860	cohesive	60-75
202509-4	100	473	200	7.2	2.0	30.3±5.1	4390	cohesive	60-75
202509-5	100	473	200	9	2.5	33.0±0.7	4790	cohesive	60-75
202509-6	100	473	200	10.8	3.0	35.2±0.2	5100	cohesive	60-75
202509-7	100	473	200	12.6	3.5	33.4±1.7	4840	cohesive	60-75
202522	100	473	200	10.8	3.0	29.1±0.8	4220	cohesive	60-75
[d]191867-1	100	473	200	12.6	3.5	29.4±1.3	4260	cohesive	60-75
191867-2	98	473	200	12.6	3.5	30.8±0.3	4470	cohesive	60-75
[e]191867-3	98	473	200	12.6	3.5	31.6±0.4	4580	cohesive	60-75
[f]191874	100	473	200	12.6	3.5	32.3±0.7	4680	cohesive	60-75
202508-1	100	473	200	12.6	3.5	31.2±0.7	4520	cohesive	50-65
202508-2	100	473	200	12.6	3.5	30.3±1.4	4390	cohesive	60-75
202508-3	100	473	200	12.6	3.5	27.7±2.5	4020	cohesive	70-90

[a]Cure at designated temperature preceeded by 1.8 x 10^3 sec (0.5 hr) cure at 388°K (115°C)

[b]Average of 8 specimens

[c]*m,m'*-MDA recrystallized from ethanol

[d]Aluminum specimens subjected to extensive degreasing relative to those used for sample 191865

[e]Aluminum specimens sand blasted, degreased and stored for 10 months prior to use

[f]Aluminum specimens sand blasted, degreased and used immediately

Table V

ADHESIVE STRENGTHS OF *m,m'*-MDA/EPON 828-BASED ADHESIVES

Sample No.	Diamine	Stoichio-metric Level, %	Weight Percent Al_2O_3 (a)	Cure Cycle (b) Temp. °K	°C	Time sec x 10^{-3}	hrs	Tensile Shear Strength (c) N/m² x 10^{-6}	psi	Failure Mode	Surface Roughness, µin.
191866	*m,m'*-MDA	102	50	473	200	12.6	3.5	15.1±0.9	2190	adhesive	60-75
191868	*m,m'*-MDA	98	50	473	200	12.6	3.5	16.0±0.3	2320	adhesive	60-75
191876-1	*m,m'*-MDA	100	50	473	200	12.6	3.5	12.8±0.6	1860	adhesive	10-20
191876-2	*m,m'*-MDA	100	50	473	200	12.6	3.5	15.5±0	2250	adhesive	60-75
[d]191876-3	*m,m'*-MDA	100	50	473	200	12.6	3.5	13.6±0.7	1970	adhesive	10-20
191876-4	*m,m'*-MDA	100	50	473	200	12.6	3.5	14.7±0.3	2130	adhesive	60-75
191894-1	*m,m'*-MDA	100	5	473	200	12.6	3.5	23.5±0.1	3410	adhesive	60-75
191894-2	*m,m'*-MDA	100	10	473	200	12.6	3.5	20.9±0.6	3030	adhesive	60-75
191894-3	*m,m'*-MDA	100	15	473	200	12.6	3.5	15.8±0.7	2290	adhesive	60-75
191889-1	*m,m'*-MDA	100	20	473	200	12.6	3.5	17.2±0.2	2490	adhesive	60-75
191889-2	*m,m'*-MDA	100	30	473	200	12.6	3.5	13.6±0.3	2260	adhesive	60-75
191889-3	*m,m'*-MDA	100	40	473	200	12.6	3.5	14.7±0.2	2130	adhesive	60-75

[a] Al_2O_3 was Alcoa Alumina T-61
[b] Cure at designated temperature preceeded by 1.8 x 10^3 sec (0.5 hr) cure at 388°K (115°C)
[c] Average of 8 specimens
[d] Al surface primed with 1% ethanolic solution of 3-aminopropyltriethoxysilane

These data prompted a more thorough study of the effect of primers on adhesion in the alumina filled systems. The primers chosen were the functional silanes and they were used on both the filler and adherend. A filler level of 20 weight percent was chosen for the study.

Three functional silanes capable of reacting with an epoxy adhesive, γ-aminopropyltriethoxysilane (A-1100), γ-glycidoxypropyltrimethoxysilane (A-187) and β-(3,4-epoxycyclohexyl)ethyltrimethoxysilane (A-186), were evaluated as primers for the adherend in an unfilled system to establish baselines for the filler study. The data show very little difference in tensile shear strengths but suggest the use of A-1100 or no primer to be slightly better than the epoxy primers. These data are given in Table VI, samples 202528-1 thru 4. The same batch of adhesive was used for all four samples.

When 20 weight percent alumina was included in the adhesive formulation, the use of adherend primers did not show any benefit. In addition the tensile shear strengths dropped from the 29-32 x 10^6 N/m^2 (4200-4600 psi) range to 16-17 x 10^6 N/m^2 (2300-2450 psi). These data are given in samples 202530-1 thru 4 of Table VI.

Addition of primers on the surface of the alumina filler increased the tensile shear strengths to 20-22.5 x 10^6 N/m^2 (2900-3300 psi) as shown by the data for samples 202527-1 thru 6, Table VI. All three primers, A-1100, A-187 and A-186, resulted in increased strengths when used as filler surface treatments with the use of A-187 showing slightly more increase ($\sim$6 x 10^6 N/m^2) than the other two. A comparison of samples 202530-4, 202530-1, 202527-1 and 202527-2 shows that use of primer on the filler increases the tensile shear strength about 4 x 10^6 N/m^2 irregardless of whether primer is used on the adherend. The same type of result is true for the other two primers also. Since adhesive failure is noted in all cases, it is not readily understood why the increased adhesion between the resin and filler that is probably obtained should effect the adhesion of the epoxy to the adherend. It is possible that cohesive failure is occurring and our visual examinations do not detect it.

The use of aluminum powder as a filler was studied in the same manner as the alumina using primer on both the filler and adherend. In the case of this filler slightly better tensile shear strengths were obtained using

primers on the adherend with A-1100 being the best primer. Also the strengths of the adhesives containing 20 weight percent aluminum were only 3 to 5 x 10^6 N/m^2 less than unfilled adhesives in contrast to the 13 to 15 x 10^6 N/m^2 decrease found with Al_2O_3 filler. These data are shown in samples 202530-5 thru 8 of Table VI.

Use of primed aluminum filler gave a slight increase in tensile shear strength when any of the three primers were used, with A-186 giving the greatest increase in strength. This can be determined by comparing sample 202530-5 with 202529-1, 3 and 5 and sample 202530-8 with 202529-2, 4 and 6 as presented in Table VI. Cohesive failure was noted for all the aluminum filled adhesives.

The effect of increasing the aluminum content to 35 and 50 weight percent was slight. The tensile shear strengths dropped to about 27.5 x 10^6 N/m^2 (4000 psi) as shown by the data for samples 202532-1 and 2 of Table VI.

The effect of curing agent structure on an aluminum filled adhesive was evaluated using 20 weight percent A-186 primed aluminum and A-1100 as the adherend primer. The tensile shear strength of the *m,m'*-MDA-based adhesive was 6.7 x 10^6 N/m^2 (1000 psi) more than the *p,p'*-MDA-based adhesive. The T-peel strengths were 250 N/m (1.4 piw) and 405 N/m (2.3 piw) respectively. The difference in tensile shear strengths is about the same as found previously for an unfilled, unprimed system (i.e., 8.3 x 10^6 N/m^2, 1200 psi).

Moisture Resistance

The moisture resistance of a *m,m'*-MDA-cured Epon 828 and *p,p'*-MDA-cured Epon 828 was determined at 120°F and 95% RH over a thirty (30) day period. The *m,m'*-MDA-cured adhesive system was run in duplicate. This study was initiated at a time when we were having problems duplicating previously obtained tensile shear strengths so the values are lower than might be expected. The data given in Table VII show that the *m,m'*-MDA-cured adhesive maintains both its tensile shear and T-peel strengths fairly well over the 30 day test period. Tensile shear strength decreases of only 200 to 300 psi (less than 10%) were noted for the *m,m'*-MDA-cured adhesive, while the moisture-induced decrease in tensile shear strength of the *p,p'*-MDA-cured adhesive was 1130 psi, or over 35% of the initial strength. Slight increases in peel strength were observed for both adhesive systems. These data demonstrate that the *m,m'*-MDA-cured system has considerably more moisture resistance than the *p,p'*-MDA system.

Table VI

EFFECT OF FILLERS AND PRIMERS ON EPOXY ADHESIVE STRENGTHS[a]

		Filler				Tensile Shear Strength (b)			T-Peel Strength (b)		
Sample No.	Diamine	Type	Wt %	Primer	Substrate Primer	$N/m^2 \times 10^{-6}$	psi	Failure Mode	N/m	piw	Failure Mode
202528-1	*m,m'*-MDA	--	--	--	A-1100[c]	31.8±0.7	4610	cohesive	--	--	--
-2	*m,m'*-MDA	--	--	--	A-187[d]	29.2±0.9	4230	cohesive	--	--	--
-3	*m,m'*-MDA	--	--	--	A-186[e]	29.2±0.6	4230	cohesive	--	--	--
-4	*m,m'*-MDA	--	--	--	--	30.4±0.9	4410	cohesive	--	--	--
202530-1	*m,m'*-MDA	Al_2O_3[f]	20	--	A-1100	16.5±0.2	2390	adhesive	--	--	--
-2	*m,m'*-MDA	Al_2O_3	20	--	A-187	16.6±0.3	2410	adhesive	--	--	--
-3	*m,m'*-MDA	Al_2O_3	20	--	A-186	16.0±0.3	2320	adhesive	--	--	--
-4	*m,m'*-MDA	Al_2O_3	20	--	--	16.9±0.8	2450	adhesive	--	--	--
202527-1	*m,m'*-MDA	Al_2O_3	20	A-1100	A-1100	20.3±0.8	2940	adhesive	--	--	--
-2	*m,m'*-MDA	Al_2O_3	20	A-1100	--	20.3±0.8	2940	adhesive	--	--	--
-3	*m,m'*-MDA	Al_2O_3	20	A-187	A-1100	22.6±2.0	3280	adhesive	--	--	--
-4	*m,m'*-MDA	Al_2O_3	20	A-187	--	22.6±1.9	3280	adhesive	--	--	--
-5	*m,m'*-MDA	Al_2O_3	20	A-186	A-1100	20.6±2.9	2900	adhesive	--	--	--
-6	*m,m'*-MDA	Al_2O_3	20	A-186	--	20.8±1.9	3020	adhesive	--	--	--
202530-5	*m,m'*-MDA	Al[g]	20	--	A-1100	28.7±1.4	4160	cohesive	--	--	--
-6	*m,m'*-MDA	Al	20	--	A-187	26.4±0.1	3830	cohesive	--	--	--
-7	*m,m'*-MDA	Al	20	--	A-186	24.4±0.6	3540	cohesive	--	--	--
-8	*m,m'*-MDA	Al	20	--	--	24.8±0.1	3600	cohesive	--	--	--
202529-1	*m,m'*-MDA	Al	20	A-1100	A-1100	30.5±0.6	4420	cohesive	--	--	--
-2	*m,m'*-MDA	Al	20	A-1100	--	26.8±1.0	3890	cohesive	--	--	--
-3	*m,m'*-MDA	Al	20	A-187	A-1100	29.5±0.9	4280	cohesive	--	--	--
-4	*m,m'*-MDA	Al	20	A-187	--	27.7±0.4	4020	cohesive	--	--	--
-5	*m,m'*-MDA	Al	20	A-186	A-1100	32.2±0.3	4670	cohesive	--	--	--
-6	*m,m'*-MDA	Al	20	A-186	--	28.4±0.4	4120	cohesive	--	--	--
202532-2	*m,m'*-MDA	Al	35	A-186	A-1100	27.4±0.7	3970	cohesive	--	--	--
-1	*m,m'*-MDA	Al	50	A-186	A-1100	27.9±0.5	4050	cohesive	--	--	--
[h]202533-1	*p,p'*-MDA	Al	20	A-186	A-1100	24.4±1.0	3540	cohesive	405±45	2.3	cohesive
[h]202533-2	*m,m'*-MDA	Al	20	A-186	A-1100	31.1±1.1	4510	cohesive	250±20	1.4	cohesive

[a] Cure cycle is 1.8×10^3 sec (0.5 hr) at 388°K (115°C) followed by 12.6×10^6 sec (3.5 hrs) at 473°K (200°C)
[b] Average of 3 specimens except as noted
[c] A-1100 is γ-aminopropyltriethoxysilane
[d] A-187 is γ-glycidoxypropyltrimethoxysilane
[e] A-186 is β-(3,4-epoxycyclohexyl)ethyltrimethoxysilane
[f] Al_2O_3 was Alcoa Alumina T-61, average particle size is 6-13μ
[g] Al was Alcoa Atomized Powder No. 123, average particle size is 15-19μ
[h] Average of 8 specimens

Table VII

MOISTURE RESISTANCE OF EPOXY ADHESIVES[a]

Sample No.	Diamine	Storage Time, Days	Tensile Shear Strength			T-Peel Strength		
			$N/m^2 \times 10^{-6}$	psi	Failure Mode	N/m	psi	Failure Mode
191879	*m,m'*-MDA	0	24.2±1.1	3510	cohesive	240±5	1.4	cohesive
		6	26.7±1.8	3870	cohesive	240±5	1.4	cohesive
		15	24.0±1.3	3480	cohesive	240±10	1.4	cohesive
		22	22.9±1.7	3320	cohesive	240±10	1.4	cohesive
		30	22.9±2.1	3320	cohesive	270±25	1.5	cohesive
191899	*m,m'*-MDA	0	27.6±1.7	4000	cohesive	--	--	--
		7	27.1±1.5	3930	cohesive	--	--	--
		15	28.5±1.9	4130	cohesive	--	--	--
		22	29.1±1.0	4220	cohesive	--	--	--
		30	26.0±1.6	3770	cohesive	--	--	--
191882	*p,p'*-MDA	0	21.5±1.4	3120	cohesive	320±5	1.8	cohesive
		6	20.1±1.0	2910	cohesive	320±25	1.8	cohesive
		15	16.1±1.7	2330	cohesive	320±25	1.8	cohesive
		22	14.9±1.0	2160	cohesive	335±40	1.9	cohesive
		30	13.7±1.7	1990	cohesive	360±30	2.1	cohesive

[a]Samples aged at 120°F and 95% relative humidity

Strength at Elevated Temperatures

The tensile shear and T-peel strengths of *m*,*m*'-MDA and *p*,*p*'-MDA-cured adhesives were determined at 72, 150 and 250°F. The data show that the *m*,*m*'-MDA-based adhesive has lower modulus than the *p*,*p*'-MDA adhesive. The tensile shear strength decreases more and the T-peel strength increases more for the *m*,*m*'-MDA-based adhesive than the *p*,*p*'-MDA-based adhesive as shown by the data in Table VIII. However, the *m*,*m*'-MDA-based adhesive still has a tensile shear strength equivalent to the *p*,*p*'-MDA-based adhesive at 250°F since it has higher initial strength. The difference in modulus of these two systems at elevated temperatures can also be seen by examination of Figure 3 in Ref. 1.

Table VIII

EFFECT OF TEMPERATURE ON EPOXY ADHESIVE STRENGTHS

Sample No.	Diamine	Tensile Shear Strength $N/m^2 \times 10^{-6}$			T-Peel Strength N/m		
		72°F	150°F	250°F	72°F	150°F	250°F
202501	*m*,*m*'-MDA	26.5±3.5	28.4±2.3	22.3±1.2	250±10	330±15	670±90
202507	*p*,*p*'-MDA	18.5±2.7	16.1±2.0	21.2±0.8	300±45	370±50	450±80

Task E. Effect of Structure on Composite Strength

The objective of this task was to establish the effect of diamine structure on the strength of an epoxy composite. The diamine used in optimization studies, *m*,*m*'-MDA, was used as the curing agent and compared with a *p*,*p*'-MDA-cured system. Short beam shear strength was chosen as the comparison test using a 13 ply composite.

The composite layups were prepared by impregnating four inch wide glass cloth in the holder shown in Figure 3 while holding the resin mixture at 100°C. The impregnated cloth was then cut into four inch squares and assembled into the composite as shown in Figure 4. The composite was vacuum degassed for 30 minutes in a vacuum

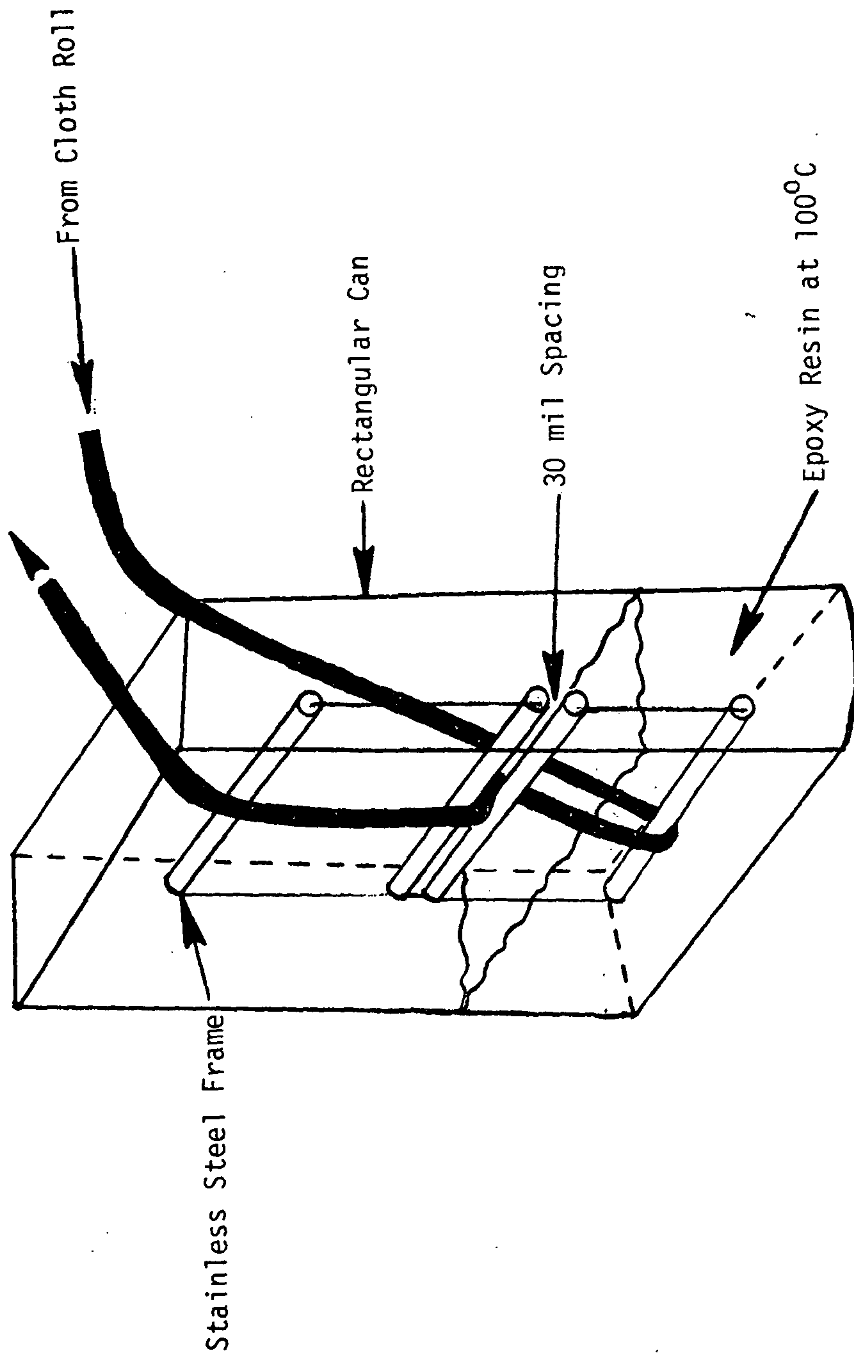


Figure 3. Glass Cloth Impregnation Device

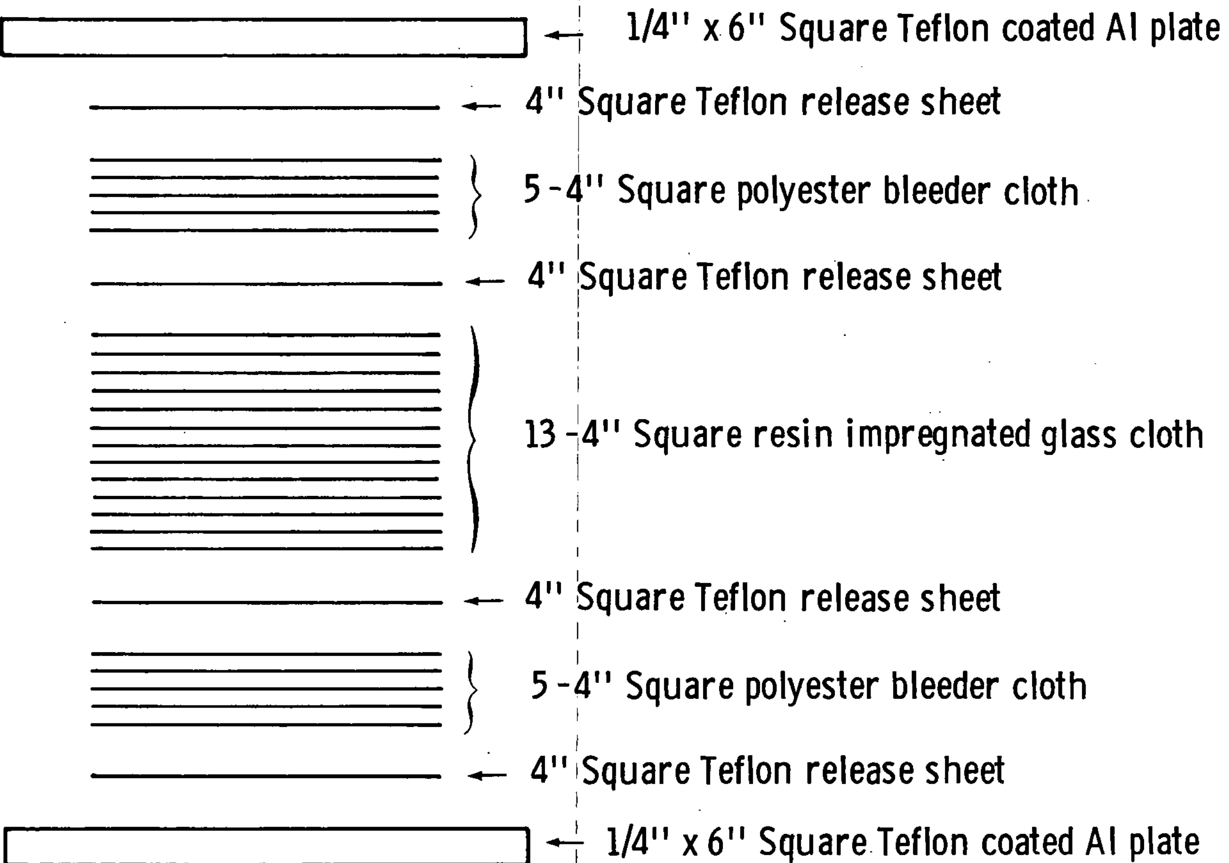


Figure 4. Composite Layup Assembly

bag and cured using the same cure schedule as employed for preparation of adhesive specimens of the particular diamine being used. Cure pressure was 0.5 psi. A separate B-staging of the resin was found not to be necessary using this layup procedure since sufficient time at 100°C was employed to give the necessary viscosity increase. The procedure from initial mixing of the epoxy and diamine through impregnation of the cloth was done within 20 minutes since rapid viscosity buildup occurs if the diamine/epoxy mixtures are held at 100°C for much longer than 30 minutes as shown by the data in Figure 5.

Table IX gives the data obtained on the *m,m'*-MDA and *p,p'*-MDA-cured epoxy systems. As can be seen the *m,m'*-MDA-cured system has a little more short beam shear strength than the *p,p'*-MDA-cured system. These differences may not be real since the other data in Table IX indicate slight differences in the two composites. In particular the high void content makes it difficult to assign any significance to the slight differences obtained. Microscopic examination of the composites revealed that the voids were present in the fiber bundles. Therefore these high void levels could probably have been avoided if the system could have been cured under vacuum. Figure 6 is a photomicrograph of the *m,m'*-MDA-cured system.

Table IX

COMPOSITE DATA ON *p,p'*-MDA AND *m,m'*-MDA-CURED COMPOSITE[a]

Sample No.	Curing Agent	Density (g/cc)	Fiber Content (wt %)	Resin Content (wt %)	Average Thickness (inches)	Void Volume %	Short Beam Shear Strength $N/m^2 \times 10^{-6}$
202520	*p,p'*-MDA	1.51	65.2	34.8	0.159±0.004	14.4	28.5±2.1
202521	*m,m'*-MDA	1.59	65.9	34.1	0.154±0.004	14.0	31.6±1.5

[a]Tests performed as per ASTM D2344-72, using 12 specimens

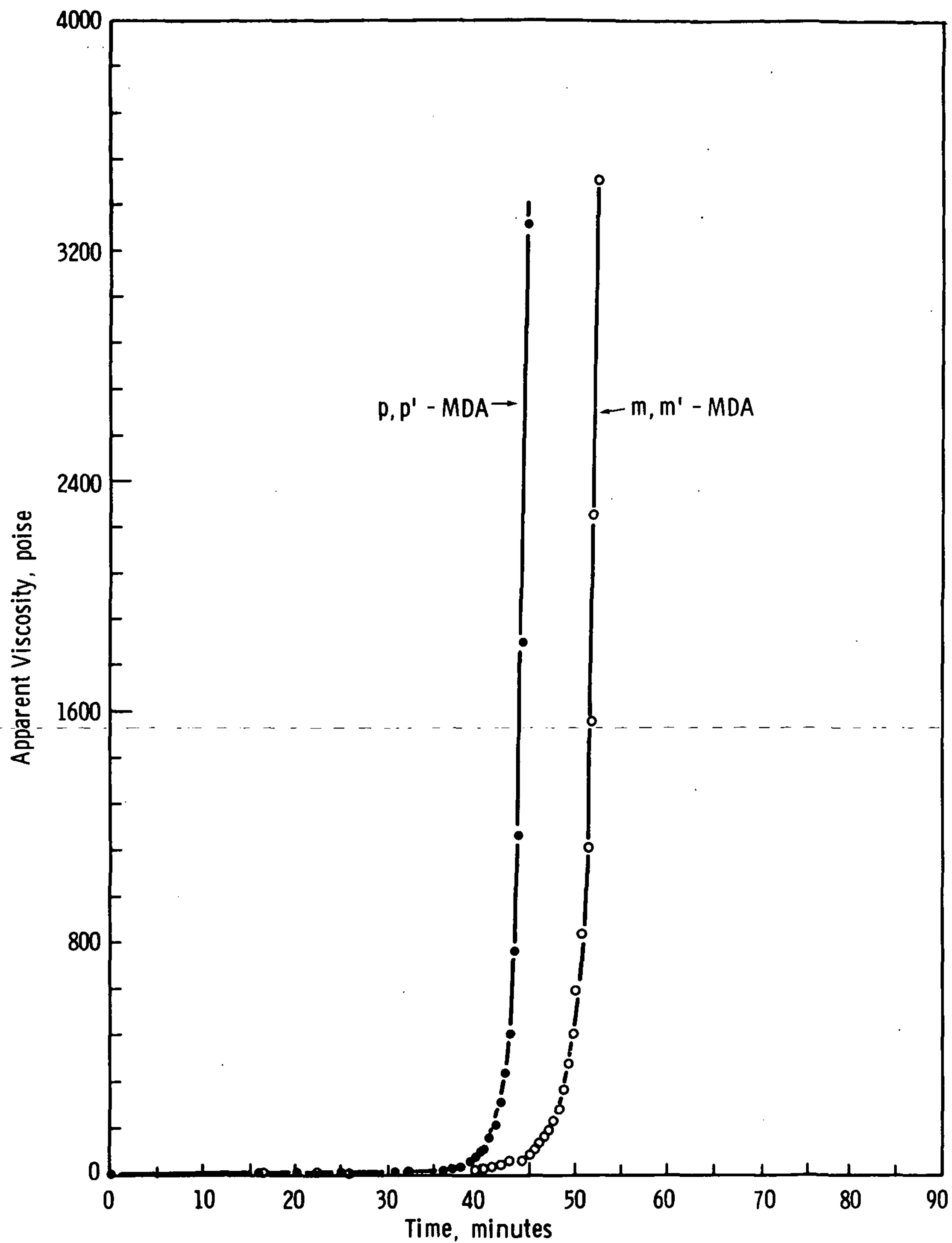


Figure 5. Apparent Viscosity vs Time at 100°C for Diamine/Epoxy Mixtures

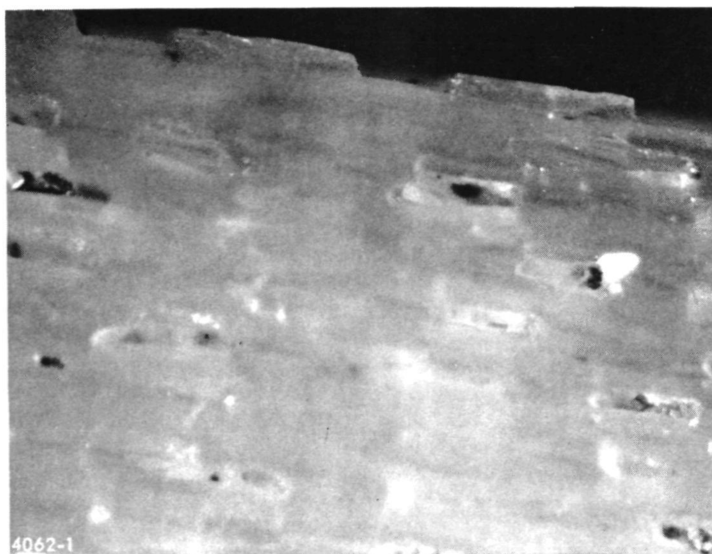


Figure 6. Photomicrograph of *m,m'*-MDA Cured Epon 828

CONCLUSIONS

The significant increases in tensile shear strength of *m,m'*-MDA vs *p,p'*-MDA found in the first phase of this project were not found in the *m,m'*-DADPS vs *p,p'*-DADPS series as studied here. However, the occurrence of cohesive failure in these adhesives suggests still greater strengths could potentially be found through optimization of cure.

The high melting point and solubility characteristics of *p,p'*-DABP make it difficult to prepare adhesive specimens for obtaining a comparison with the corresponding meta isomer.

Problems found in obtaining reproducible tensile shear strengths for the *m,m'*-MDA and *p,p'*-MDA systems suggest that future studies of these adhesives should include an investigation of the effect of adherend thickness.

Adhesive strengths of *m,m'*-MDA-based adhesives decreased slightly by use of aluminum as a filler relative to an unfilled system. Use of primers on the filler and adherend were beneficial but the increases in strength were only a few hundred psi. The use of alumina as a filler was very detrimental to bond strength although alumina responded to primers on the filler better than aluminum.

The *m,m'*-MDA-based epoxy adhesive has very good resistance to moisture losing very little strength ($\sim$10%) over a 30 day test period while a comparable *p,p'*-MDA system lost 35% of its strength. The resistance of the *m,m'*-MDA system to temperature is good although not quite as good as the *p,p'*-MDA system probably because of the difference in modulus.

In addition to the generally beneficial effects of using *m,m'*-MDA to cure epoxy adhesives, the use of *m,m'*-MDA as a curing agent for epoxy resin resulted in glass fiber composites with strengths comparable to those using *p,p'*-MDA as the curing agent.

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