MRC-DA-555

NASA CR-145022

Annual Summary Report

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

Author

D. Gerald Glasgow

18 June 1975 — 17 March 1976

Prepared under Contract No. NAS1-13982

By

MONSANTO RESEARCH CORPORATION
Dayton Laboratory
Dayton, Ohio 45407

For

NASA
National Aeronautics and
Space Administration

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Langley Research Center
Hampton, VA 23665

May 1976

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EXPERIMENTAL (cont'd)

ABSTRACT

This report consists of the results of investigations directed toward determining the effects of novel aromatic diamine structures on the adhesive properties of epoxy and polyurethane adhesives.

Three aromatic diamines based on benzophenone and diphenylmethane isomers were evaluated as curing agents for epoxy resins. Tensile shear strengths in excess of comparable state-of-the-art adhesives were obtained with all three new curing agents. An adhesive based on *m*,*m*'-methylenedianiline had a tensile shear strength about thirty-three percent greater than the state-of-the-art. T-peel strengths of adhesives based on the new diamines were slightly less than the state-of-the-art values.

Three benzophenone and diphenylmethane-based diamine isomers were evaluated as curing agents for polyurethane adhesives. The benzophenone-based isomers gave low strength adhesives and the reactivity of the diphenylmethane isomer was too fast for practical use.

Polyurethane adhesives were prepared based on *m*,*m*'-diisocyanatodiphenylmethane and *m*,*m*'-diisocyanatobenzophenone. The *m*,*m*'-diisocyanatodiphenylmethane-based adhesive had properties comparable to state-of-the-art adhesives. The *m*,*m*'-diisocyanatobenzophenone-based adhesive was extremely reactive.

FOREWORD

This report was prepared by Monsanto Research Corporation, Dayton Laboratory, under Contract No. NAS1-13982, "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 author is indebted to Dr. J. M. Butler for his many helpful suggestions and stimulating discussions. Also, the capable assistance of Mr. C. Garthwait, who prepared the adhesive samples, and 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

By

D. G. Glasgow
Monsanto Research Corporation
Dayton Laboratory
Dayton, Ohio 45407

SUMMARY

Task A

The effect of aromatic diamine curing agent structure on epoxy adhesive properties was determined using three novel diamines supplied by NASA Langley. All three diamines, *m,m'*-methylenedianiline (*m,m'*-MDA), *o,p'*-methylenedianiline (*o,p'*-MDA) and *m,m'*-diaminobenzophenone (*m,m'*-DABP), gave epoxy adhesives having tensile shear strengths greater than a comparable state-of-the-art adhesive based on *p,p'*-methylenedianiline (*p,p'*-MDA). T-peel strengths of these adhesives were slightly less than state-of-the-art values. The best values obtained are summarized below. Cohesive failure was obtained in each case. The *m,m'*-MDA cured adhesive shows a significant advancement in the state-of-the-art.

	Tensile Shear Strength		T-Peel Strength		Approximate Pot Life at Room
Diamine	N/m^2 x 10^{-6}	psi	N/m	piw	Temperature
m,m'-MDA	35.9 ± 0.8	5200	275 ± 35	1.6	14-17 hr
o,p'-MDA	27.7 ± 2.1	4020	250 ± 10	1.4	22-24 hr
m,m'-DABP	30.4 ± 1.6	4410	245 ± 15	1.4	2 hr[1]
p,p'-MDA	26.8 ± 1.0	3890	305 ± 25	1.7	4 hr

[1] at 90°C

The MDA isomers had handling characteristics very similar to *p,p*'-MDA in that they dissolved readily in the epoxy resin at 90°C, were low viscosity and spread readily and cooled to room temperature without crystallizing. The diamine precipitated from the *m,m*'-DABP-based formulation on cooling and the mixture was quite viscous unless held at 90°C or above. The approximate pot lives are shown in the table above.

Apparent shear modulus vs temperature measurements suggest that all four diamine-cured epoxy adhesive would have similar lap shear strength vs temperature curves up to 120°C. Glass transition temperatures ranged from 140 to 156°C.

Task B

Optimization studies of a *m,m*'-MDA-based epoxy adhesive were carried out under this task. The effect of stoichiometry, cure cycle, fillers, reactive diluents, glass fabric supports and adherend surface preparation were studied. It was found that 100% stoichiometry and a cure of 200°C for 3.5 hours gave the optimum tensile shear strength on aluminum substrates that had been sand blasted to a surface roughness of 60-75 µin. prior to etching. (These conditions were used to prepare the adhesives listed in the above table). Adhesive strengths were lowered by using aluminum powder or mica as a filler, a high molecular weight epoxy resin or a carboxy-terminated polybutadiene as a reactive diluent and glass fabric supports. Use of an aminosilane surface primer did not alter the adhesive properties.

Task C

Three novel diamines, *o,p*'-methylenedianiline (*o,p*'-MDA), *o,p*'-diaminobenzophenone (*o,p*'-DABP) and *m,p*'-diaminobenzophenone (*m,p*'-DABP), were evaluated as curing agents for polyurethane adhesives with 4,4'-methylenebis(*o*-chloroaniline) (MOCA) used as the standard. The DABP-based adhesives had pot lives similar to MOCA-cured adhesives but their lap shear and T-peel strengths were much lower. Adhesives based on *o,p*'-MDA had adhesive strengths similar to MOCA-cured polyurethanes but the high reactivity of the *o,p*'-MDA-based formulations make it an impractical system with which to work.

Task D

The effects of two new diisocyanates based on novel diamines on polyurethane adhesive properties were evaluated. The diisocyanates, *m,m'*-diisocyanatodiphenylmethane (*m,m'*-MDI) and *m,m'*-diisocyanatobenzophenone (*m,m'*-DIBP), were prepared from the corresponding amines and phosgene and then converted to isocyanate-terminated 2000 molecular weight poly(oxytetramethylene)glycol-based prepolymers.

The *m,m'*-MDI based prepolymer reacted somewhat more rapidly than a 2,4-tolylene diisocyanate-based prepolymer when mixed with molten MOCA. Comparable tensile shear strengths were obtained. The *m,m'*-DIBP-based prepolymer reacted so rapidly with molten MOCA that adhesive test specimens could not be prepared.

INTRODUCTION

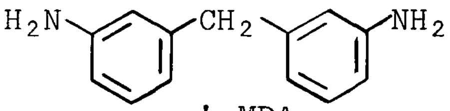
The objective of this research program was to determine the effects of novel aromatic diamine curing agents and isocyanate precursors on the properties of new epoxy and polyurethane adhesives. The program had four tasks, two dealing with epoxies and two with polyurethane adhesives. In Task A the effectiveness 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.

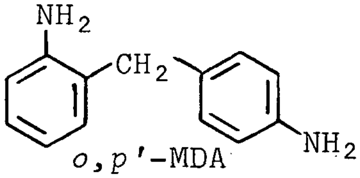
This report covers work performed during the period 18 June 1975 to 17 March 1976.

RESULTS AND DISCUSSION

Task A. Screening of Epoxy Adhesives

The objective of this task was to evaluate the effect of the three novel diamines shown below on adhesive properties of epoxy adhesives and compare these properties with the state-of-the-art. A *p,p'*-MDA cured Epon 828 was used as the state-of-the-art standard. The effects of cure cycle and surface preparation on adhesive properties were determined as were the pot lives and reactivities of the various formulations.


m,m'-MDA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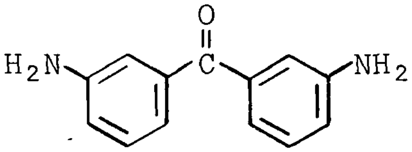
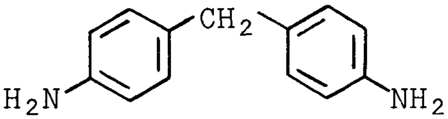

m,m'-DABP


p,p'-MDA

<u>Reactivity and pot life.</u> - It was important to know the handling characteristics of the aromatic diamine/epoxy mixture prior to making up adhesive test specimens. This was done by preparation of small quantities of stoichiometric mixtures of diamine/Epon 828 and observing diamine solution temperature and occurrence of crystallization on cooling of the mixture. In addition, an estimate of viscosity relative to a similar *p,p'*-MDA based formulation was made to get an estimation of the potential difficulties that might be encountered in spreading a particular formulation on an aluminum substrate. Data obtained are shown in Table I.

The three MDA isomers all dissolved readily at 100°C, had low viscosity on cooling to room temperature and showed no indication of crystallization.

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.
m,m'-MDA	100	low	good	no
o,p'-MDA	100	low	good	no
m,m'-DABP	125	low	poor	yes[b]
p,p'-MDA	100	low	good	no

[a] Stoichiometric mixtures
[b] Crystals formed at about 80°C

The *m,m'*-DABP based formulations required 125°C to dissolve the diamine. Also this diamine crystallizes in the mixture at about 80°C, thus requiring that the mixture be handled hot. It was noted that if the formulation was kept at about 100°C for 10-15 minutes, the diamine did not crystallize on cooling to room temperature. Evidently it had reacted sufficiently to prevent crystallization. However, this formulation was quite viscous and considerable difficulty was encountered in attempting to apply it to aluminum substrates. Rapid cooling occurred causing increase in viscosity and therefore poor spreading characteristics. These data suggest that the *m,m'*-DABP/epoxy formulation would be more suited for use as a B-staged resin.

The reactivity of *m,m'*-DABP/epoxy mixture is considerably less than that of the MDA-based formulations. After 18 hours at room temperature a DABP/epoxy mixture still flowed when it was reheated to 100°C whereas the MDA/epoxy mixtures would not flow. The viscosity of the *m,m'*-DABP/epoxy mixture after 18 hours at room temperature was much too high for it to be useful as an A-stage formulation however.

The reaction of these systems was followed by determining the change in apparent viscosity versus time. Approximately 3 grams of the reacting mixture was placed in a 10 x 75 mm test tube centered around a #7 spindle of a Brookfield Viscometer running at 10 rpm. The data obtained are shown in Figures 1 and 2. These viscosities cannot be considered true viscosities due to the shape of the container. Part of the initial rapid increase in viscosity occurs as the sample cools from the mix temperature to room temperature (approximately 15 minutes). Zero time was the point at which the diamine was added to the hot epoxy resin. The *m,m'*- and *o,p'*-MDA/epoxy mixtures all showed the same type curve indicating a long pot life.

An estimate of spreadability vs time of each adhesive formulation was obtained by periodically spreading the formulation on aluminum as if adhesive specimens were being prepared. The time at which each formulation became difficult to spread is noted on the curves. Of the three MDA/epoxy formulations only the *p,p'*-MDA-based formulation became unusable in the time period studied. The *o,p'*-MDA/epoxy formulations could still be spread with some difficulty after 23 hours when the viscosity is >4000 poise. The *m,m'*-MDA/epoxy system cannot be spread after 17 hours. The *m,m'*-DABP/epoxy formulation did not show very good reproducibility with respect to viscosity vs time measurements as shown in Figure 2. A third measurement of viscosity vs time fell between the two curves in Figure 2 but closer to the curve on the right side of the graph. The maximum pot life expected is probably close to two hours at 90°C.

It was of interest to determine the pot life of the *m,m'*- and *o,p'*-MDA mixtures by actual sample preparation as well as by the spreadability and viscosity techniques discussed above. Adhesive mixtures were made up and stored overnight at 22°C. Tensile shear specimens were made up the following day on freshly etched metal. The results, shown below, demonstrate the very long pot life that can be expected using these adhesives.

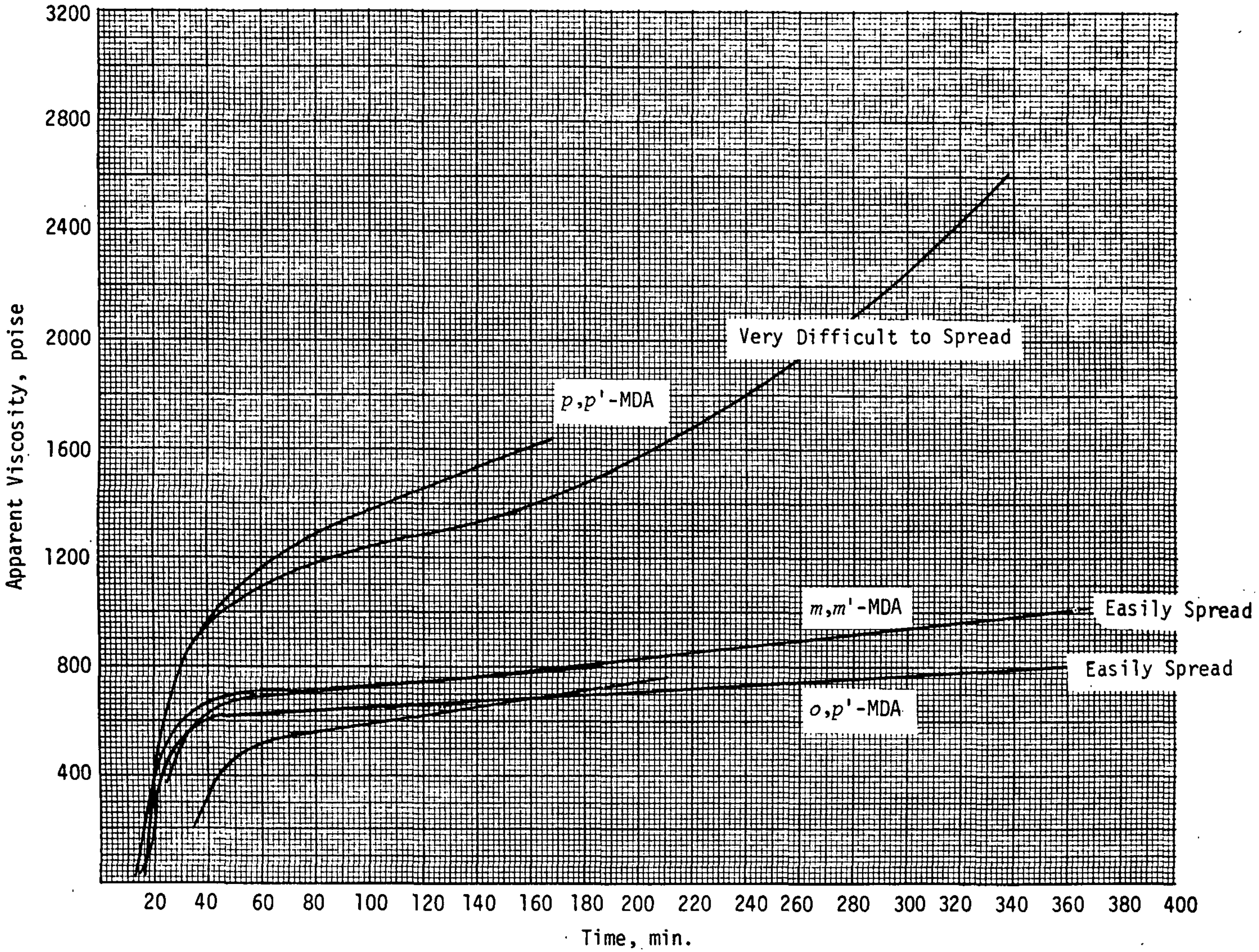


Figure 1. Apparent Viscosity vs Time at Room Temperature for Epoxy Adhesive Formulations (curing agent shown on graph)

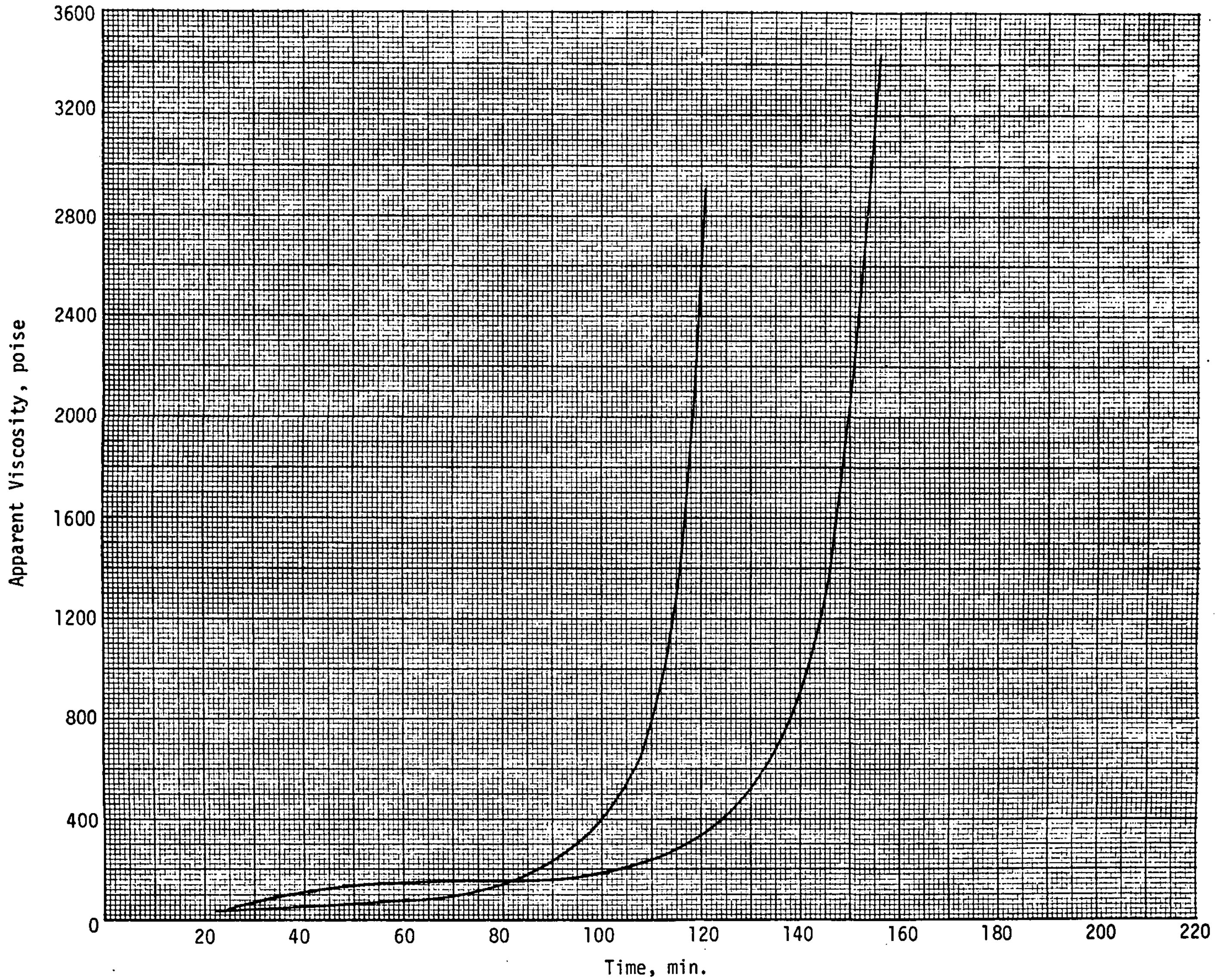


Figure 2. Apparent Viscosity vs Time for Epon 828/*m*,*m*'-DABP (data obtained at 90°C on two separate runs)

Diamine	Time From Preparation of Adhesive, hrs	Tensile Shear Strength, $N/m^2 \times 10^{-6}$	psi
m,m'-MDA	0	16.3	2360
	13.3	15.0	2180
	14.2	15.3	2220
o,p'-MDA	0	15.2	2200
	13.3	14.2	2060
	16.9	14.7	2130
	20.9	14.4	2090
	22.6	13.9	2020

Cure cycle studies. - The cycle of *p,p'*-MDA cured epoxies reported in the literature (Ref. 1) is one half hour at 115°C followed by two and one half hours at 177°C. Consequently this cure cycle with variations in time at 177°C was studied initially for the MDA-based adhesives. Initially a different cure cycle was used for the *m,m'*-DABP-based adhesive in anticipation of having to cure this adhesive for a considerable length of time. Its qualitative handling characteristics (discussed above) were similar to *p,p'*-diaminodiphenylsulfone, whose epoxy formulations require considerably more cure than *p,p'*-MDA based adhesives.

IR spectroscopy was used to follow cure by observing the disappearance of the epoxy band at 10.96 microns in the curing mixture between salt plates using the technique of Ref. 1 p. 6-9. This technique showed that the *m,m'*-DABP based epoxy cured at least 50% slower than the MDA based epoxies. In all cases this epoxy vibration decreased to a constant level before the 177°C cure temperature was reached.

The adhesive strengths obtained during these initial cure cycle studies are given in Table II. All three NASA-supplied diamines gave adhesives with considerably greater shear strength and slightly less peel strength when compared to the *p,p'*-MDA standard. These data cannot be considered optimum since adhesive failure occurred during the lap shear tests indicating less than optimum bonding. Comparison of the effect of structure on strength can only be done if cohesive failure is obtained in the lap shear test.

Table II

ADHESIVE STRENGTHS OF AROMATIC DIAMINE/EPON 828-BASED ADHESIVES[a]

Sample No.	Diamine	Cure Time at 450K sec x 10^{-3} (hrs) (b)	Tensile Shear Strength, (c) N/m² x 10^{-6}	Tensile Shear Strength, (c) psi	Failure Mode	T-Peel Strength, (c) N/m	T-Peel Strength, (c) piw	Failure Mode
185829	*p,p'*-MDA	5.4 (1.5)	[d]10.9	1580	adhesive	--	--	--
185832		9.0 (2.5)	[d]12.8	1860	adhesive	[d]460	2.6	cohesive
185831		14.4 (4.0)	[d]9.8	1420	adhesive	--	--	--
185854		7.2 (2)	15.6	2260	adhesive	360	2.1	cohesive
		9.0 (2.5)	16.9	2450	adhesive	380	2.2	cohesive
		10.8 (3)	15.4	2230	adhesive	370	2.1	cohesive
		12.6 (3.5)	14.3	2070	adhesive	350	2.0	cohesive
		14.4 (4)	15.9	2300	adhesive	290	1.7	cohesive
185878		9.0 (2.5)	[d]13.7±0.4	1990	adhesive	[d]260±15	1.5	adhesive
185839	*m,m'*-MDA	9.0 (2.5)	[d]18.1	2620	adhesive	[d]280	1.6	cohesive
185856		7.2 (2)	18.6	2700	adhesive	280	1.6	cohesive
		9.0 (2.5)	18.4	2670	adhesive	310	1.8	cohesive
		10.8 (3)	18.6	2700	adhesive	300	1.7	cohesive
		12.6 (3.5)	20.1	2910	adhesive	300	1.7	cohesive
		14.4 (4)	17.9	2600	adhesive	260	1.5	cohesive
185880		12.6 (3.5)	[d]20.6±0.9	2990	adhesive	[d]270±5	1.5	cohesive
185841	*o,p'*-MDA	9.0 (2.5)	[d]16.3	2360	adhesive	[d]240	1.4	cohesive
185861		7.2 (2)	18.3	2650	adhesive	290	1.7	cohesive
		9.0 (2.5)	19.9	2890	adhesive	300	1.7	cohesive
		10.8 (3)	18.2	2640	adhesive	280	1.6	cohesive
		12.6 (3.5)	18.5	2680	adhesive	270	1.5	cohesive
		14.4 (4)	18.1	2620	adhesive	260	1.5	cohesive
185882		9.0 (2.5)	[d]17.3±0.6	2510	adhesive	[d]250±10	1.4	cohesive
185843	*m,m'*-DABP	3.6 (1.0)	20.8	3020	adhesive	325	1.9	cohesive
		7.2 (2.0)	21.8	3160	adhesive	300	1.7	cohesive
		14.4 (4.0)	21.1	3060	adhesive	[e]255	1.5	cohesive
185863		7.2 (2)	21.3	3090	adhesive	310	1.8	cohesive
		14.4 (4)	20.9	3030	adhesive	270	1.5	cohesive
		21.6 (6)	18.5	2680	adhesive	290	1.7	cohesive
		28.8 (8)	18.5	2680	adhesive	260	1.5	cohesive
185884		7.2 (2)	[d]19.8±0.7	2870	adhesive	[d]270±10	1.5	cohesive

[a] Stoichiometric mixtures

[b] Cure at 450K (177°C) was preceeded by 1.8 x 10^3 sec (0.5 hr) cure at 388K (115°C) except for sample 185843 which was cured at 393K (120°C) for 7.2 x 10^3 sec (2.0 hr) prior to cure at 450K (177°C)

[c] Average of 2 specimens except as noted

[d] Average of 8 specimens

[e] Average of 4 specimens

During a discussion of the above results with NASA Langley personnel the author was informed of a method of surface preparation that resulted in cohesive failure of epoxy adhesives of the type under study in this task. Subsequently, this method was successfully utilized. The surface preparation involves the following steps; sand blasting, degreasing, chromic acid etch, rinsing and drying. (See the experimental section for details).

Initially two epoxy adhesives were used to evaluate the effect of the above surface preparation, a *p*,*p*'-MDA and a *m*,*m*'-MDA cured Epon 828. Using cure cycles established previously for each system the results shown for the first three samples in Table III were obtained. Both adhesives exhibited cohesive and adhesive failure. These results show that the *m*,*m*'-MDA cured epoxy adhesive has approximately 33% more tensile shear strength than the comparable *p*,*p*'-MDA cured system.

All four aromatic diamine cured systems were then prepared and the results shown in the second set of samples in Table III were obtained. A significant drop in strength was found and the failure mode returned to total adhesive failure. Surface roughness measurements were then made and the results (shown in Table III) suggest that a minimum surface roughness is needed if cohesive failure is to be obtained. Examination of the grit used for sand blasting established that a significant reduction in particle size had occurred between sand blasting the first and second set.

The third set of data in Table III was obtained using specimens that were not sand blasted. These data further support a surface roughness-tensile shear strength relationship for these adhesives. It should be noted that in all three sets the *p*,*p*'-MDA-based adhesive shows the lowest tensile shear strength.

This improved surface preparation technique was utilized in conjunction with the four aromatic diamine-cured epoxy adhesives along with increased cure temperatures. Cohesive failure was then obtained in all systems.

Utilization of the improved surface preparation along with cure at 200°C resulted in increased tensile shear strengths and cohesive failure for the epoxy adhesives. Interestingly the relative strengths of the four adhesives did not change significantly as compared with results reported previously

Table III

ADHESIVE STRENGTHS OF AROMATIC DIAMINE/EPON 828-BASED ADHESIVES[a]

Sample No.	Diamine	Cure Time at 450K, sec x 10^{-3} (hrs) (b)	Tensile Shear Strength, (c)		Failure Mode	Aluminum Surface Sand Blasted	Surface Roughness, microinches
			$N/m^2 \times 10^{-6}$	psi			
189666	*p,p'*-MDA	9.0 (2.5)	21.7±0.3	3150	cohesive/adhesive	yes	60-75
189670-5	*p,p'*-MDA	9.0 (2.5)	[d]20.1±2.0	2910	cohesive/adhesive	yes	60-75
189670-1	*m,m'*-MDA	12.6 (3.5)	[d]27.5±0.4	3990	cohesive/adhesive	yes	60-75
189673	*p,p'*-MDA	9.0 (2.5)	16.0±0.6	2320	adhesive	yes	20-50
189672	*m,m'*-MDA	12.6 (3.5)	22.1±0.7	3200	adhesive	yes	20-50
189675	*o,p'*-MDA	9.0 (2.5)	20.1±0.9	2910	adhesive	yes	20-50
189674	*m,m'*-DABP	7.2 (2.0)	20.5±1.0	2970	adhesive	yes	20-50
189628	*p,p'*-MDA	9.0 (2.5)	13.1±0.6	1900	adhesive	no	10-20
189630	*m,m'*-MDA	12.6 (3.5)	16.3±0.7	2360	adhesive	no	10-20
189629	*o,p'*-MDA	9.0 (2.5)	15.2±0.9	2200	adhesive	no	10-20
189631	*m,m'*-DABP	7.2 (2.0)	15.4±1.5	2230	adhesive	no	10-20

[a] Stoichiometric mixtures

[b] Cure at 450K (177°C) was preceeded by 1.8 x 10^3 sec (0.5 hr) cure at 388K (115°C)

[c] Average of 8 specimens except where noted

[d] Average of 2 specimens

when adhesive failure was observed. (Compare the results in Tables II and IV).

The most significant result was the large increase in tensile shear strength of the *m,m'*-MDA-cured adhesive. Tensile shear strength as high as 35.9×10^6 N/m^2 (∿5200 psi) were obtained as compared to 26.8×10^6 N/m^2 (∿3900 psi) for a comparable cured *p,p'*-MDA-based adhesive, i.e. state-of-the-art adhesive. In addition there was relatively little difference in the T-peel strengths. These results can be seen by examining the data for the first two groups of samples in Table IV. Note that the high tensile shear strength of the *m,m'*-MDA cured epoxy adhesive was reproducible.

The occurrence of cohesive failure with these adhesives is difficult to detect with the MDA-based adhesives but very readily detectable with the DABP-based adhesives. The DABP-based adhesives absorb quite strongly in the 366 mμ region of the UV spectrum so that thin layers are readily visible on the metal after failure. The MDA-based adhesives absorb rather weakly relative to the DABP-based adhesives and detection under UV light is not possible. In the case of MDA-based adhesives cohesive failure was determined by microscopic examination of failure surfaces for bulk adhesive.

NASA Langley research on polyimide adhesives (Ref. 2) has shown that the DABP-based adhesives are significantly stronger than comparable MDA-based adhesives. In Task C of this project two diaminobenzophenone isomers, i.e. *m,p'*-DABP and *o,p'*-DABP, were used as polyurethane curing agents. These diamines were also tested as epoxy curing agents to determine if any benefit could be found. Tensile shear strengths comparable to those obtained with present state-of-the-art epoxy adhesives were found. The T-peel strengths were somewhat lower. These data are given in the last three samples in Table IV.

The glass transition temperatures of the four aromatic diamine-cured epoxy adhesives cured at 177°C were measured via the Clash-Berg technique. These data (Figure 3) also indicate the relative modulii of the different polymers. The glass transition temperatures derived from these curves are listed below. The modulus vs temperature curves for the *m,m'*-MDA and *o,p'*-MDA-cured epoxies are so nearly superimposable that only one curve was drawn. The glass

Table IV

ADHESIVE STRENGTHS OF AROMATIC DIAMINE/EPON 828-BASED ADHESIVES[a]

Sample No.	Diamine	Cure Cycle (b)		Tensile Shear Strength (c)		Failure Mode	T-Peel Strength (c)		Failure Mode
		Temp °C	Time hr	$N/m^2 \times 10^{-6}$	psi		N/m	piw	
191805	*p,p*'-MDA	177	2.5	22.9±2.2	3320	adhesive	--	--	--
191812	*p,p*'-MDA	200	2.5	24.1±0.6	3490	adhesive	--	--	--
191820	*p,p*'-MDA	200	2.5	24.4±1.1	3540	cohesive	355±20	2.0	cohesive
191827	*p,p*'-MDA	200	3.5	26.8±1.0	3890	cohesive	305±25	1.7	cohesive
189672	*m,m*'-MDA	177	3.5	22.1±0.7	3200	adhesive	245±10	1.4	cohesive
191807	*m,m*'-MDA	200	3.5	35.9±0.8	5200	cohesive	275±35	1.6	cohesive
191821	*m,m*'-MDA	200	3.5	35.1±1.5	5090	cohesive	--	--	--
191811	*o,p*'-MDA	177	2.5	24.4±1.4	3540	adhesive	--	--	--
191819	*o,p*'-MDA	200	2.5	27.7±2.1	4020	cohesive	--	--	--
191810	*m,m*'-DABP	177	2	24.6±1.9	3570	adhesive	--	--	--
191823	*m,m*'-DABP	200	2	30.4±1.6	4410	cohesive	245±15	1.4	cohesive
191813	*m,p*'-DABP	200	3.5	21.2±3.0	3070	cohesive	255±10	1.5	cohesive
191816	*m,p*'-DABP	200	3.5	20.8±3.5	3010	cohesive	255±20	1.5	cohesive
191828	*o,p*'-DABP	200	3.5	24.7±1.2	3580	cohesive	205±15	1.2	cohesive

[a] Stoichiometric mixtures
[b] Cure preceeded by 1.8×10^3 sec (0.5 hr) cure at 388K (115°C)
[c] Average of 8 specimens

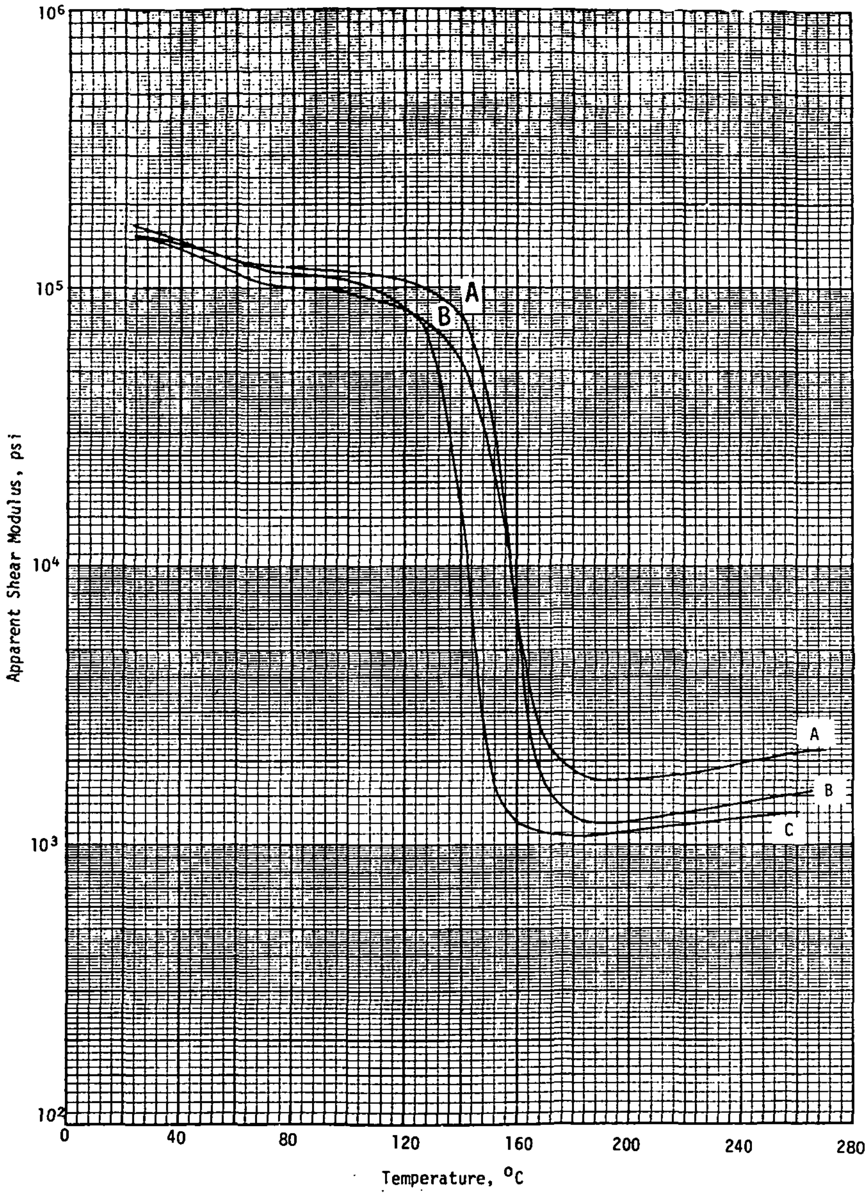


Figure 3. Apparent Shear Modulus vs Temperature for Aromatic Diamine-Cured Epon 828

Curve	Curing Agent
A	*p*,*p*'-MDA
B	*m*,*m*'-DABP
C	*m*,*m*'-MDA
C	*o*,*p*'-MDA

Curing Agent	T_g, °C
p,*p*'-MDA	156
m,*m*'-MDA	156
o,*p*'-MDA	140
m,*m*'-DABP	140

transition temperature was taken as the inflection point on the curve. The epoxy resins cured with the NASA-supplied diamines all give adhesives with comparable modulii up to about 120°C. This would indicate that probably such formulations would have comparable lap shear strength vs temperature curves.

The glass transition temperatures for the *m*,*m*'-MDA and *m*,*m*'-DABP-based adhesives cured at 200°C were also obtained to establish if any significant changes had resulted from use of higher cure temperatures. The curves obtained are superimposable with those shown in Figure 3.

Task B. Optimization of Epoxy Adhesives

This task involved optimization of an adhesive system based on either *m*,*m*'-MDA or *m*,*m*'-DABP, the particular diamine to be selected based on the results found in Task A. Optimization included studies of the effect of cure cycles, stoichiometry, fillers, reactive diluents and modifiers.

Based on the work done under Task A *m*,*m*'-MDA was chosen over *m*,*m*'-DABP as the diamine to be used in this task. The adhesive strengths obtained using either curing agent were comparable at the time the choice was made but the processing characteristics of the *m*,*m*'-MDA-based system made it much easier to handle and more amenable to addition of various additives and modifiers. The effects of cure temperature, stoichiometry, and two reactive diluents were studied initially using test specimens that were not sand blasted so ultimate strengths were not obtained. However, the trends found are probably realistic.

The data for the first three samples in Table V show that 180°C is the best of the three cure temperatures studied. This series was extended to 220°C cure temperatures when remade on sand blasted metal as discussed below.

Table V

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

Sample No.	Diamine	Stoichio-metric Level, %	Additive		Cure Cycle (b)		Tensile Shear Strength, (c)		Failure Mode	T-Peel Strength, (c)		Failure Mode
			Type	%	Temp K	Time, sec x 10^{-6} (hrs)	N/m^2 x 10^{-6}	psi		N/m	piw	
189649	*m*,*m*'-MDA	100	--	--	413	12.6 (3.5)	14.4±0.2	2090	adhesive	265±5	1.5	cohesive
189651	*m*,*m*'-MDA	100	--	--	433	12.6 (3.5)	13.3±0.5	1930	adhesive	280±20	1.6	cohesive
189653	*m*,*m*'-MDA	100	--	--	453	12.6 (3.5)	16.9±0.7	2450	adhesive	250±10	1.4	cohesive
189650	*m*,*m*'-MDA	90	--	--	450	12.6 (3.5)	15.2±0.9	2200	adhesive	265±35	1.5	cohesive
189652	*m*,*m*'-MDA	95	--	--	450	12.6 (3.5)	13.7±0.9	1990	adhesive	265±15	1.5	cohesive
189654	*m*,*m*'-MDA	105	--	--	450	12.6 (3.5)	14.8±0.6	2150	adhesive	320±25	1.8	cohesive
189664	*m*,*m*'-MDA	100	Epon 1010[d]	10	450	12.6 (3.5)	16.3±0.9	2360	adhesive	305±15	1.7	cohesive
189661	*m*,*m*'-MDA	100	Epon 1010	20	450	12.6 (3.5)	14.0±0.8	2030	adhesive	325±15	1.9	cohesive
189663	*p*,*p*'-MDA	100	Epon 1010	10	450	9 (2.5)	11.1±0.5	1610	adhesive	325±5	1.9	cohesive
189660	*p*,*p*'-MDA	100	Epon 1010	20	450	9 (2.5)	13.4±0.5	1940	adhesive	365±15	2.1	cohesive
189659	*m*,*m*'-MDA	100	CTBN[e]	10	450	12.6 (3.5)	4.2±0.3	610	adhesive	195±20	1.1	adhesive
189658	*p*,*p*'-MDA	100	CTBN	10	450	9 (2.5)	4.4±0.2	640	adhesive	165±15	1.0	adhesive

[a] Aluminum surfaces were not sand blasted, i.e. surface roughness was 10-20 μin.
[b] Cure at designated temperature was preceeded by 1.8 x 10^3 sec (0.5 hr) cure at 388K (115°C)
[c] Average of 8 specimens
[d] Shell Chemical Co. epoxy resin with equivalent weight of 4000 to 6000
[e] B. F. Goodrich Hycar CTBN 1300X8 carboxy-terminated polybutadiene:acrylonitrile

No significant differences were noted in tensile shear strength when the stoichiometric level of amine was varied from 90 to 105%. However, a slight increase in T-peel strength was found at 105% amine stoichiometry. These data are given in the second set of samples in Table V.

Addition of a 5000 equivalent weight epoxy resin did not alter the tensile shear or T-peel strength significantly at additive levels up to 20 weight percent using either *m,m'*-MDA or *p,p'*-MDA as curing agent. (See Table V, samples 189660-189664 for data).

Addition of a low molecular weight carboxy-terminated polybutadiene:acrylonitrile resin resulted in a brittle polymer (samples 189658 and 189659, Table V). This resin often acts as a toughening agent for epoxy resins. In this instance the cured polymers were opaque, a condition that usually indicates that the epoxy resin is the discontinuous phase. If true, this would account for the brittle nature of the product.

Further optimization of the epoxy adhesive based on *m,m'*-MDA was done by determining the effects of adherend surface preparation, cure temperature, stoichiometry, fillers and glass fabric supports. Some of the data reported below was obtained on surfaces inadvertently sand blasted with the wrong size grit so that some work had to be repeated. All the data are presented and the surface roughness of each sample noted.

The effect of cure temperature was studied utilizing surfaces of two different roughnesses with the same trends being found. Increasing the cure temperature up to 200°C increased tensile shear strengths without significantly changing T-peel strength. Using a substrate surface of 60-75 μin. roughness cohesive failure was obtained at 200 and 220°C with the maximum tensile shear strength of 35.9 x 10^6 N/m^2 (5200 psi) being found with 200°C cure temperatures. Tensile shear strengths dropped when a 220°C cure temperature was used. These data are presented in the first two groups of data in Table VI.

Variations in the diamine level in 5% increments between 90 and 105% of stoichiometry established that the 100% level is the optimum of those studied. The data suggest that the true optimum level lies between 95 and 100%. These data are presented in the third group of data in Table VI.

Table VI

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

Sample No.	Diamine	Stoichiometric Level, %	Additive		Cure Cycle (a)				Tensile Shear Strength (b)		Failure Mode	T-Peel Strength (b)		Failure Mode	Surface Roughness, μin.
					Temp		Time								
			Type	%	K	°C	sec x 10^{-6}	hrs	N/m² x 10^{-6}	psi		N/m	piw		
189682	*m,m'*-MDA	100	--	--	433	160	12.6	3.5	20.8±0.5	3020	adhesive	265±0	1.5	cohesive	20-50
189672	*m,m'*-MDA	100	--	--	450	177	12.6	3.5	22.1±0.7	3200	adhesive	245±10	1.4	cohesive	20-50
189681	*m,m'*-MDA	100	--	--	463	190	12.6	3.5	22.3±0.6	3230	adhesive	255±10	1.5	cohesive	20-50
189683	*m,m'*-MDA	100	--	--	473	200	12.6	3.5	24.8±0.7	3600	adhesive	220±20	1.3	cohesive	20-50
191802	*m,m'*-MDA	100	--	--	433	160	12.6	3.5	19.8±1.3	2870	adhesive	265±20	1.5	cohesive	60-75
189692	*m,m'*-MDA	100	--	--	450	177	12.6	3.5	22.7±0.7	3290	adhesive	--	--	--	60-75
189691	*m,m'*-MDA	100	--	--	463	190	12.6	3.5	25.4±1.5	3680	adhesive	200±30	1.1	cohesive	60-75
191807	*m,m'*-MDA	100	--	--	473	200	12.6	3.5	35.9±0.8	5200	cohesive	275±35	1.6	cohesive	60-75
191821	*m,m'*-MDA	100	--	--	473	200	12.6	3.5	35.1±1.5	5090	cohesive	--	--	--	60-75
191825	*m,m'*-MDA	100	--	--	493	220	12.6	3.5	32.7±1.0	4740	cohesive	235±15	1.3	cohesive	60-75
191832	*m,m'*-MDA	90	--	--	473	200	12.6	3.5	28.7±2.8	4160	cohesive	245±15	1.4	cohesive	60-75
191831	*m,m'*-MDA	95	--	--	473	200	12.6	3.5	32.7±2.5	4740	cohesive	250±10	1.4	cohesive	60-75
191821	*m,m'*-MDA	100	--	--	473	200	12.6	3.5	35.1±1.5	5090	cohesive	--	--	--	60-75
191833	*m,m'*-MDA	105	--	--	473	200	12.6	3.5	29.7±1.5	4310	cohesive	270±15	1.5	cohesive	60-75
191827	*p,p'*-MDA	100	--	--	473	200	12.6	3.5	26.8±1.0	3890	cohesive	305±25	1.7	cohesive	60-75
[c]189699	*m,m'*-MDA	100	--	--	450	177	12.6	3.5	22.8±0.7	3300	cohesive	280±10	1.6	cohesive	60-75
[c]191826	*m,m'*-MDA	100	--	--	473	200	12.6	3.5	36.2±1.6	5250	cohesive	215±15	1.2	cohesive	60-75
189672	*m,m'*-MDA	100	--	--	450	177	12.6	3.5	22.1±0.7	3200	cohesive	245±10	1.4	cohesive	20-50
189679	*m,m'*-MDA	100	Al	50	450	177	12.6	3.5	20.5±0.5	2970	cohesive	330±20	1.9	cohesive	20-50
189680	*m,m'*-MDA	100	mica	33	450	177	12.6	3.5	11.8±0.6	1710	cohesive	405±15	2.3	cohesive	20-50
189673	*p,p'*-MDA	100	--	--	450	177	9	2.5	16.0±0.6	2320	adhesive	265±45	1.5	cohesive	20-50
189678	*p,p'*-MDA	100	Al	50	450	177	9	2.5	17.6±0.6	2550	adhesive	370±60	2.1	cohesive	20-50
189685	*p,p'*-MDA	100	mica	33	450	177	9	2.5	12.3±0.3	1780	cohesive	460±10	2.6	cohesive	20-50
189694	*m,m'*-MDA	100	Al	50	450	177	12.6	3.5	21.0±0.9	3050	adhesive	325±20	1.9	cohesive	60-75
191829	*m,m'*-MDA	100	Al	50	473	200	12.6	3.5	22.3±1.1	3230	adhesive	400±40	2.3	cohesive	60-75
189690	*p,p'*-MDA	100	Al	50	450	177	9	2.5	21.6±0.8	3130	adhesive	335±45	1.9	cohesive	60-75
191824	*p,p'*-MDA	100	Al	50	473	200	9	2.5	22.6±1.3	3280	adhesive	495±30	2.8	cohesive	60-75
191808	*m,m'*-MDA	100	glass tape[d]		473	200	12.6	3.5	25.0±0.8	3630	cohesive	--	--	--	60-75
191822	*m,m'*-MDA	100	glass tape[d]		473	200	12.6	3.5	27.2±1.1	3940	cohesive	--	--	--	60-75

[a] Cure at designated temperature preceeded by 1.8 x 10^3 sec (0.5 hr) cure at 388K (115°C)
[b] Average of 8 specimens
[c] Al surface primed with 1% ethanolic solution of 3-aminopropyltriethoxysilane
[d] 4 mil tape obtained from Carolina Narrow Fabric Co., Inc., Winston-Salem, NC

An aminosilane surface treatment (primer) was utilized but no change in tensile shear or T-peel strength was noted. This was expected since cohesive failure had already been obtained without primer. These primers would probably be beneficial for improving moisture resistance of the bonded system. These data are given in Table VI, samples 189699 and 191826.

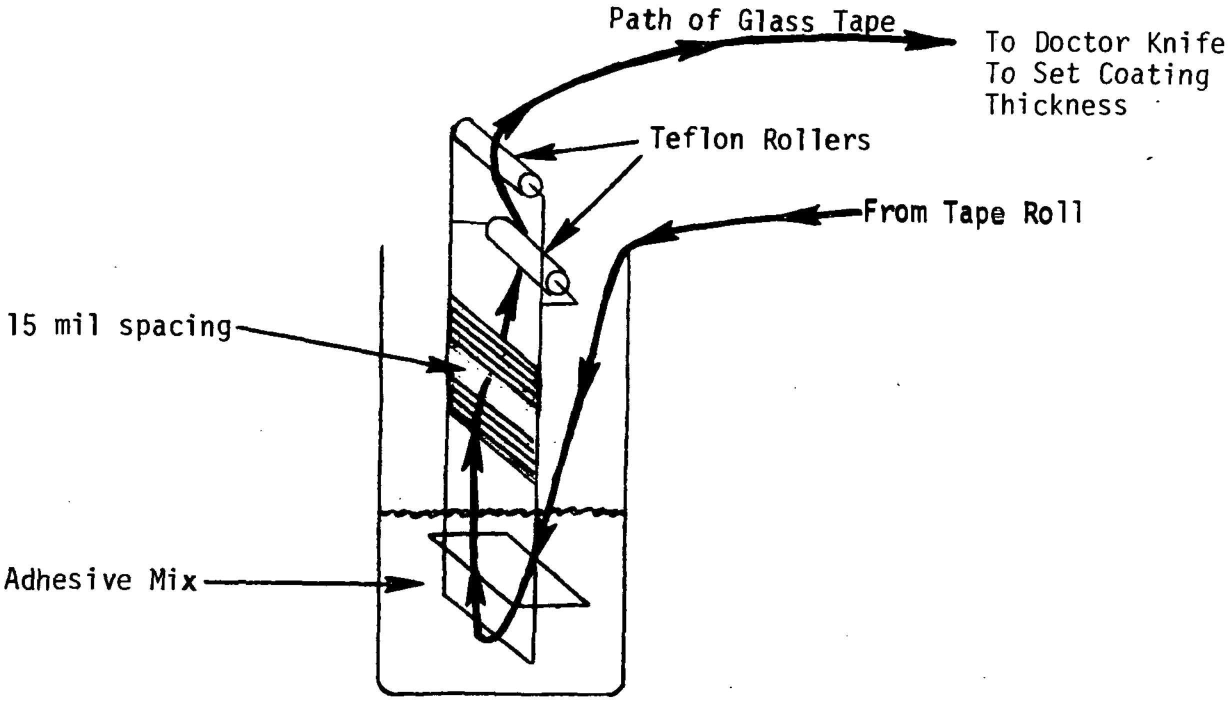
The use of aluminum filler in *m,m'*-MDA-cured adhesives produced about the expected decrease in tensile shear strength (35.9×10^6 N/m^2 to 22.3×10^6 N/m^2, samples 191807 and 191829, Table VI) based on known reductions in bulk tensile strength of aluminum filled, amine cured epoxies (Ref. 1, p. 14-16, 17). However, the slight increase in T-peel strength was not expected. The changes were not nearly so significant with the *p,p'*-MDA-cured adhesives, samples 191827 and 191824, Table VI. The occurrence of adhesive failure in the aluminum filled system raises some doubt concerning the completeness of cure.

Use of mica as a filler resulted in significant weakening of the adhesive with cohesive failure being observed in the tensile shear strength measurements at about 12×10^6 N/m^2 (1750 psi).

The use of a 4 mil glass cloth carrier for the *m,m'*-MDA-cured Epon 828 adhesive system was evaluated. The tape, obtained with an aminosilane surface treatment from the manufacturer, was impregnated with the resin immediately prior to use to avoid problems associated with development of storage system. Impregnation was accomplished using the device shown below with the resin maintained at 25-30°C.

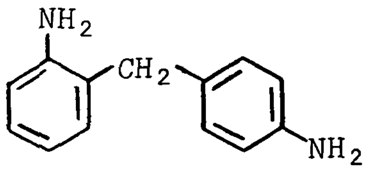
The tensile shear strengths obtained ($25\text{-}27 \times 10^6$ N/m^2) were similar to those obtained using commercial supported adhesives, e.g. 3M's AF-143 develops a tensile shear strength of 25×10^6 N/m^2 according to the product bulletin.

Volume shrinkage was determined for the *m,m'*-MDA and *p,p'*-MDA-cured Epon 828-based epoxies to obtain a comparison of this property with the state-of-the-art material. A value of 3.22 volume % was obtained for the *m,m'*-MDA based system as compared to 3.38% for the comparable *p,p'*-MDA based system.

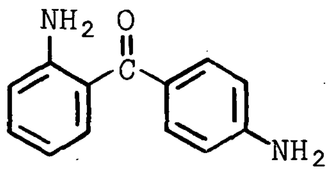


Task C. Effects of Diamine Curing Agents on Polyurethane Adhesive Properties

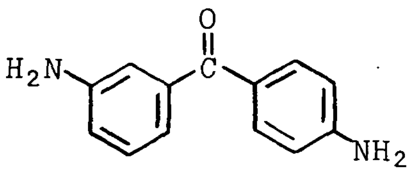
The objective of this task was to establish the effect of the three aromatic diamines shown below on adhesive properties of polyurethane adhesives. A 4,4'-methylenebis(*o*-chloroaniline)(MOCA) cured adhesive was used as a standard.



o,*p*'-MDA



o,*p*'-DABP



m,*p*'-DABP

Prior to preparation of adhesives we evaluated techniques for preparation of the necessary formulations to insure adequate mixing and to obtain a qualitative estimate of the pot-life of each formulation. None of the diamines were soluble enough in the polyurethane prepolymer to permit use of room temperature mixing of components. It was also noted the *o,p*'-MDA reacted very rapidly with the prepolymer even when added as a fine powder. Addition of the diamines as melts to the prepolymer at the lowest possible temperature to prevent amine crystallization was chosen as the most practical method. When using *o,p*'-DABP the prepolymer had to be heated to 50°C to insure that the curing agent did not crystallize prior to reacting. Prepolymer temperature for *m,p*'-DABP had to be 100°C. Lower prepolymer temperatures results in diamine solidification and encapsulation of the diamine preventing further reaction.

The very rapid gelation of the *o,p*'-MDA-based polyurethane formulation made it difficult to get an adequate number of test specimens particularly T-peel specimens. This formulation gelled in from five to eight minutes after the molten curing agent was added to the prepolymer.

The pot life of the MOCA-cured and *o,p*'-DABP-cured polyurethanes was evaluated via the viscosity vs time technique (see experimental section). The data obtained are presented in Figures 4 and 5. It appears that the *o,p*'-DABP system reacts slightly more rapidly than the MOCA system. The large differences between the curves for the *o,p*'-DABP systems may be due to small initial temperature differences of the prepolymer as well as differences in stoichiometry. Formulations containing either MOCA or *o,p*'-DABP can be spread even at the maximum time at which the viscosity measurements were taken indicating very desirable pot lives for both.

In order to prepare a polyurethane adhesive using *m,p*'-DABP it was necessary to preheat the prepolymer to 100°C and add molten *m,p*'-DABP. Once properly mixed the formulation had extremely high viscosity but was still spreadable. An attempt to measure viscosity gave a value greater than the maximum that could be read on our equipment, i.e. >20,000 poise.

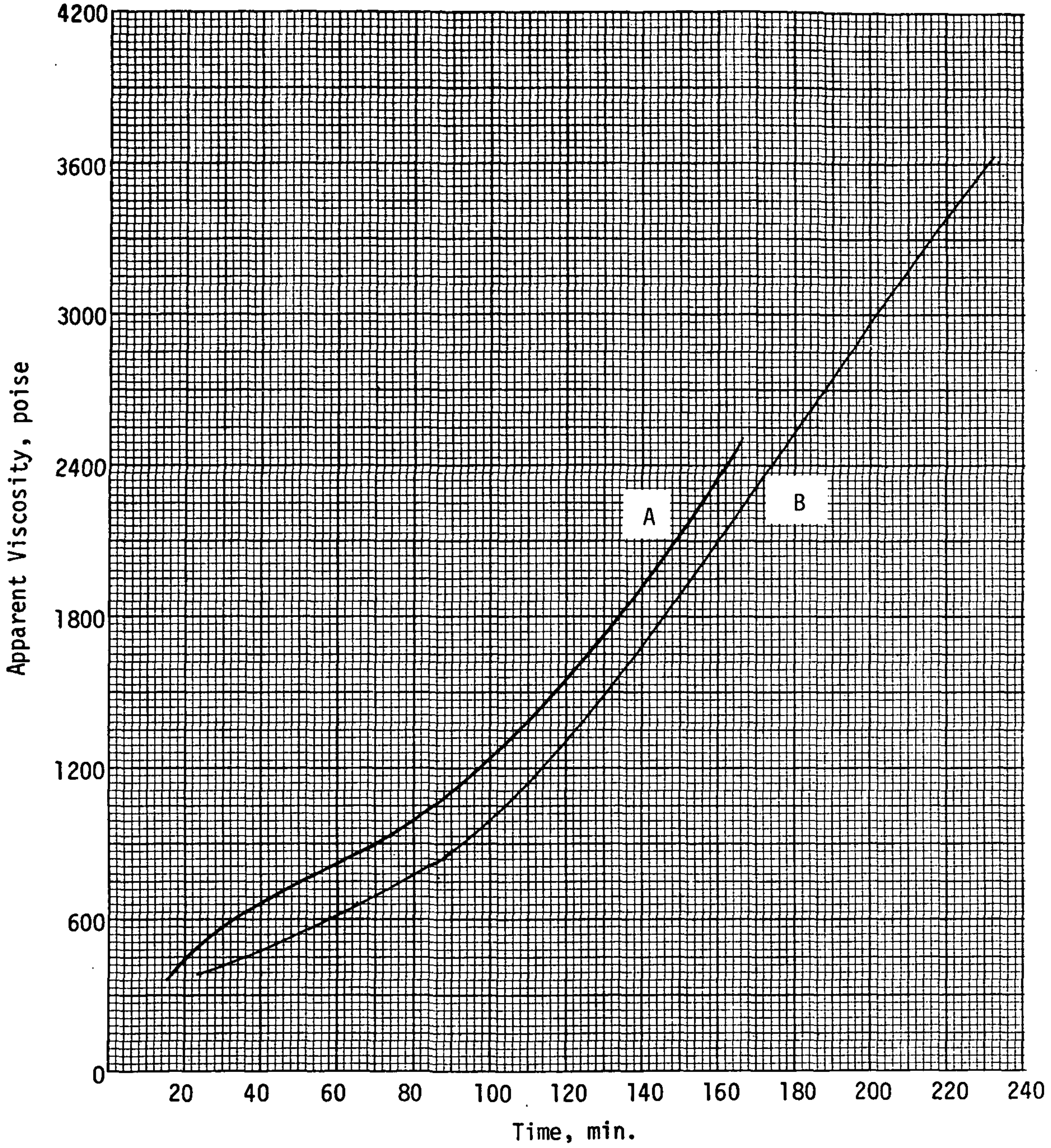


Figure 4. Apparent Viscosity vs Time at Room Temperature for MOCA-Cured 2,4-TDI-Terminated Polymeg 2000

Curve	Stoichiometric Amount of Diamine, %
A	98
B	82

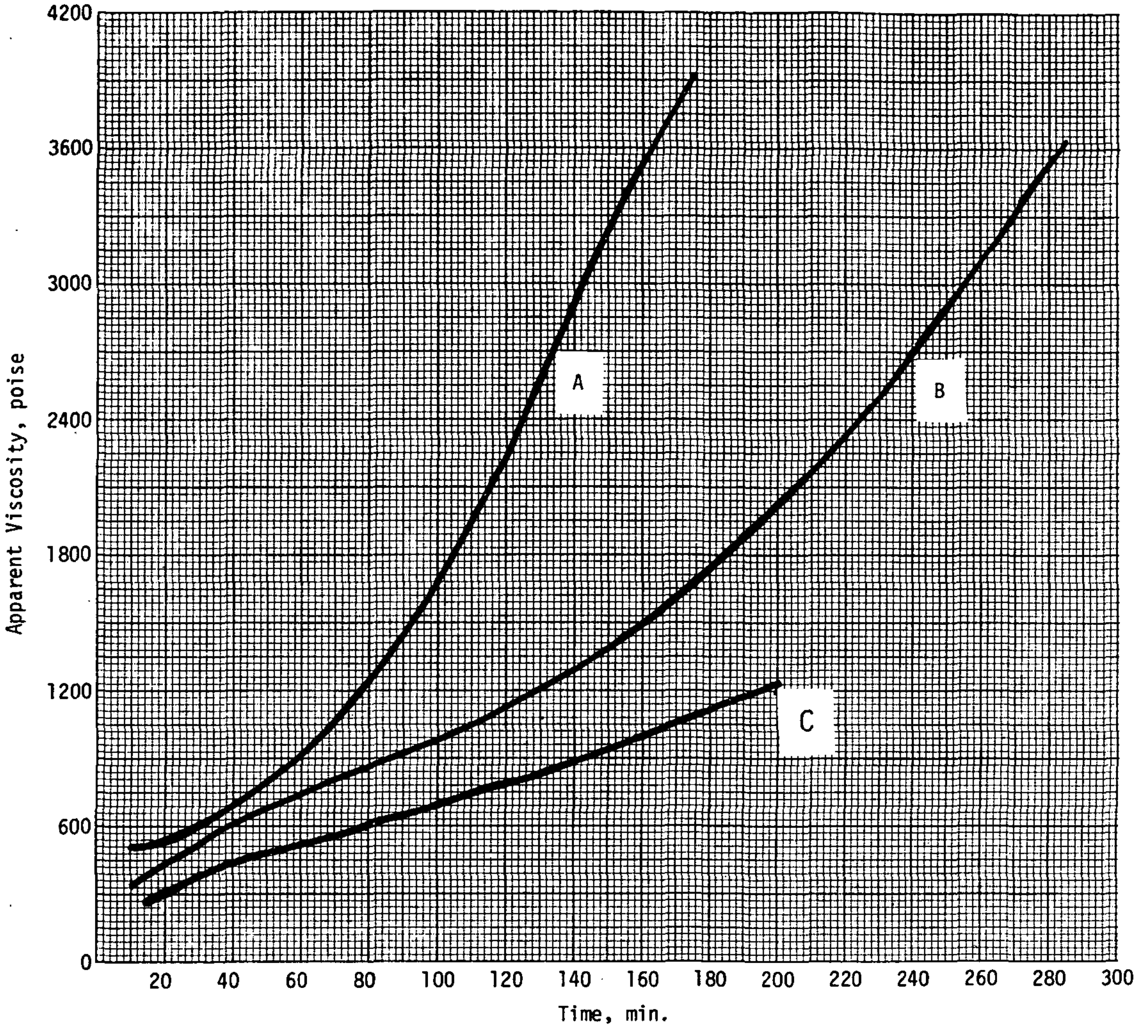


Figure 5. Apparent Viscosity vs Time at Room Temperature for *o,p'*-DABP-Cured 2,4-TDI-Terminated Polymeg 2000

Curve	Stoichiometric Amount of Diamine, %
A	101
B	86
C	100

Test samples were made up at various periods after mixing to obtain an estimate of pot life. The formulation was held at 25°C after mixing. The results are shown below. No T-peel specimens were made at 3 hours after mixing as the adhesive was too viscous to spread. These data indicate that *m,p'*-DABP-based polyurethanes have shorter pot lives than comparable MOCA-cured systems, possibly due to the extremely high initial viscosity.

Time From Preparation of Adhesive, hrs	Tensile Shear Strength		T-Peel Strength	
	$N/m^2 \times 10^{-6}$	psi	N/m	piw
0	1.7	245	3900	22
1	1.8	260	2900	17
2	1.6	245	3570	20
3	1.7	230	--	

An attempt to utilize *m,m'*-DABP (an epoxy curing agent) as a polyurethane curing agent resulted in rapid gellation of the formulation on addition of molten diamine. Apparently at least one amine group ortho to the carbonyl function is needed to obtain the low reaction rates needed to get long pot life.

The adhesive strengths obtained using these diamines as polyurethane curing agents are shown in Table VII. As can be seen the DABP-based formulations have much lower tensile strength than the MOCA-cured standard. In one preparation an *o,p'*-MDA-based adhesive gave tensile shear and T-peel strengths that compared favorably with the MOCA-cured standard. However, this formulation has such a short pot life that it would not be practical to use.

Task D. Effect of Isocyanate Structure on PTMG-Based Polyurethanes

The objective of this task was to examine the structural effects of two new diisocyanates on polyurethane adhesive properties. The two diisocyanates, shown below, were prepared and converted to isocyanate-terminated 2000 molecular weight poly(oxytetramethylene glycol)-based prepolymers

Table VII

ADHESIVE STRENGTHS OF AROMATIC DIAMINE-CURED POLYURETHANE ADHESIVES[a]

Sample No.	Diamine	Stoichiometric Level, %	Cure Cycle (b)		Tensile Shear Strength, (c)		Failure Mode	T-Peel Strength, (c)		Failure Mode
			Temp K	Time, sec x 10^{-3} (hrs)	N/m^2 x 10^{-6}	psi		N/m	piw	
185886	MOCA	100	348	86.4 (24)	6.0±0.9	870	adhesive	3810±235	22	adhesive
189604	MOCA	98	348	86.4 (24)	6.9±0.6	1000	adhesive	2950±240	17	adhesive
189620	MOCA	99	373	10.8 (3)	5.8±0.7	840	adhesive	2430±210	14	adhesive
185898	*o,p*'-DABP	86	348	86.4 (24)	2.5±0.5	360	adhesive	2530±215	14	adhesive
189621	*o,p*'-DABP	100	373	10.8 (3)	2.9±0.5	420	adhesive	2580±180	15	adhesive
189625	*o,p*'-DABP	100	393	10.8 (3)	2.7±0.6	390	adhesive	2160±170	12	adhesive
189643	*m,p*'-DABP	100	393	10.8 (3)	2.2±0.4	320	adhesive	1650±110	9	adhesive
189645	*m,p*'-DABP	100	393	10.8 (3)	1.7±0.3	245	adhesive	2950±350	17	adhesive
189646	*m,p*'-DABP	100	393	10.8 (3)	2.0±0.2	290	adhesive	2310±165	13	adhesive
189647	*m,p*'-DABP	100	393	10.8 (3)	1.7±0.2	245	adhesive	3900±440	22	adhesive
185893	*o,p*'-MDA	100	348	86.4 (24)	[d]4.5±1.2	650	adhesive	[e]1030±175	6	adhesive
189608	*o,p*'-MDA	89	373	86.4 (24)	6.5±0.4	940	adhesive	[f]5760±200	33	adhesive
189613	*o,p*'-MDA	112	373	86.4 (24)	5.4±0.4	780	adhesive	1790±280	10	adhesive
189617	*o,p*'-MDA	99	373	86.4 (24)	4.9±0.8	710	adhesive	1110±160	6	adhesive
189624	*o,p*'-MDA	100	393	10.8 (3)	--	--	--	1130±160	6	adhesive
189635	*o,p*'-MDA	100	393	10.8 (3)	4.1±0.5	595	adhesive	970±115	6	adhesive

[a] A 2,4-tolylene diisocyanate-terminated 2000 molecular weight poly(oxytetramethylene)glycol was used as the prepolymer (% NCO = 3.27)

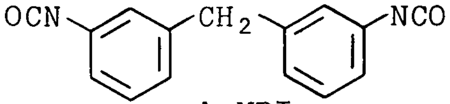
[b] Samples 185886, 189604, 185898 and 185893 were cured for 86.4 x 10^3 sec (24 hrs) at room temperature prior to heat cure. All other samples had no room temperature cure.

[c] Average of 8 specimens except as noted

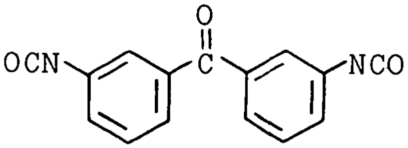
[d] Average of 7 specimens

[e] Average of 6 specimens

[f] Average of 4 specimens



m,m'-MDI



m,m'-DIBP

which were in turn cured with 4,4'-methylenebis(2-chloroaniline)(MOCA).

The preparation of the above diisocyanates presented no difficulty. (The details are given in the experimental section.) The corresponding 2000 molecular weight poly(oxytetramethylene glycol)-based prepolymers were extremely viscous especially the *m,m'*-DIBP terminated prepolymer which was a soft wax-like solid at room temperature. Both prepolymers had to be heated to 100°C to get liquids that were fluid enough to permit liquid MOCA to be stirred in without entrapping significant quantities of gas. For this reason the adhesive formulations were quite reactive. The *m,m'*-DIBP-based adhesive mixture gelled in about 1.5 minutes preventing any adhesive test specimens from being prepared. The high reaction rate of the *m,m'*-DIBP-based formulation is not unexpected based on literature data. Electron withdrawing substituents on an aromatic ring are known to significantly accelerate the reaction rate of the isocyanate function (Ref. 3).

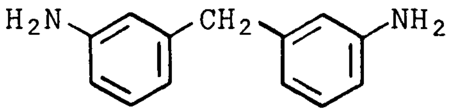
A bulk polymer sheet was prepared by hot pressing the gelled mixture and curing at 120°C for 3 hours. The polymer was quite tough and appeared to be comparable to conventional polyurethanes of similar structure.

The *m,m'*-MDI-based adhesive formulation was not nearly so reactive even though it was mixed at 100°C. Adhesive test specimens were successfully prepared in the 6.5 minute period that was available prior to gellation of the reaction mixture. The adhesive strengths are shown below in comparison to a similarly prepared and cured TDI-based adhesive. Note the high T-peel strength and comparable tensile shear strength relative to the standard.

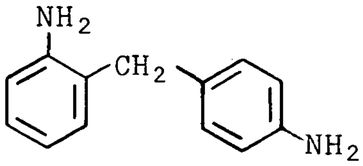
		Isocyanate	
		m,m'-MDI	TDI
Tensile Shear Strength	$N/m^2 \times 10^{-6}$	5.3±0.5	5.8±0.7
	psi	770	840
T-Peel Strength	N/m	6210±840	2430
	piw	35	14
Approximate gel time at 100°C	min	6.5	12

Characterization of Raw Materials

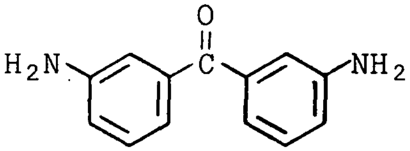
NASA Langley supplied the five aromatic diamines shown below along with differential thermal analysis (DTA) curves for each.



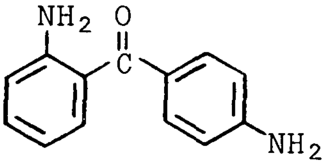
m,m'-MDA



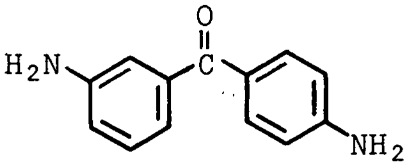
o,p'-MDA



m,m'-DABP



o,p'-DABP



m,p'-DABP

As the DTA curves indicated various purity levels further characterization was undertaken via determination of equivalent weight by titration with perchloric acid in acetic acid. The *m,p'*-DABP was dried prior to analysis by azeotropic distillation of water with benzene at the suggestion of V. L. Bell (NASA). In those cases where DTA and/or titrations indicated purity levels lower than desired characterization by NMR was undertaken. Equivalent weights obtained by titration are shown in the following table for these diamines and *p,p'*-methylenedianiline (*p,p'*-MDA) that was used as a standard for the epoxy adhesives.

Diamine	Equivalent Weight Theory	 Found
m,m'-MDA	99.1	98.9
m,m'-DABP	106.1	106.6
o,p'-MDA	99.1	99.0
o,p'-DABP	106.1	110.1
m,p'-DABP	106.1	111.8
p,p'-MDA	99.1	99.1

The *o,p'*-DABP and *m,p'*-DABP gave values indicative of low purity. The high equivalent weights indicated presence of monofunctional or inert impurities. Purification of *o,p'*-DABP was accomplished by recrystallization from toluene and *m,p'*-DABP by recrystallization from methanol followed by benzene.

NMR analysis of *m,m'*-MDA, *m,m'*-DABP, *o,p'*-MDA and *o,p'*-DABP utilizing ^{13}C and ^{1}H NMR showed impurities present in the *m,m'*-MDA and *o,p'*-MDA whose structures could not be determined due to lack of suitable reference spectra particularly for the ^{13}C NMR patterns.

Characterization of these diamines by ^{13}C NMR was discontinued as initial studies indicated considerable effort would be required to establish impurity structures and levels and since purification of the impure amines was accomplished. The final conclusions from NMR analyses are given below.

Diamine	NMR Analysis Results
m,m'-MDA	no impurities detected
m,m'-DABP	no impurities detected
o,p'-MDA	possible -CHOH- containing impurity
o,p'-DABP	impurity peaks could not be readily identified

The Epon 828 used as the epoxy resin for Tasks A and B was analyzed for oxirane content via the pyridine/pyridinium chloride method. An epoxy equivalent weight of 186.2 was obtained.

EXPERIMENTAL

Bonding Procedure

Surface Preparation.

Sand Blasting: The aluminum (2024-T3) panels were cleaned with acetone to remove all visible markings and dirt. The panels were then sand blasted using glass beads (0.074 to 0.149 mm diameter, 100-200 mesh) using a Trinico Dry Blast (model 30). After sand blasting the panels were vapor degreased in trichloroethylene.

Chromic Acid Etch: The degreased panels were then etched for 10 minutes at 70°C in the solution given below:

10 pbw Sodium dichromate dihydrate
300 pbw Distilled water
100 pbw Concentrated sulfuric acid

After removal from the etching bath the panels were rinsed in deionized water by immersion to remove the acid and then soaked in tap water (see ref. 4) at 60°C for 30 minutes. The panels were allowed to drain dry briefly and then placed in an air circulating oven at 150°F for 30 minutes.

Adhesive Preparation.

Epoxy: The epoxy resin was carefully weighed into a clean, degreased four ounce bottle, heated to 100°C and degassed. The diamine curing agent was added to the epoxy resin at 100°C with slow stirring to prevent air entrapment using a marine type blade for mixing. Immediately after all the diamine had dissolved the source of heat was removed and the mixture degassed again.

Polyurethane: The polyurethane prepolymer was degassed (application of heat was used to decrease degassing times). Molten curing agent was then added to the prepolymer under nitrogen with slow stirring to avoid gas entrapment using a marine type blade. The 2,4-tolylene diisocyanate-based prepolymers were held at room temperature for mixing and the two prepolymers based on *m,m'*-DIBP and *m,m'*-MDI were heated to 100°C to obtain fluid materials.

Adhesive Application. The adhesive mixtures were applied to the aluminum substrates held in jigs. The lap shear specimens were prepared, using 1 in. x 3 in. x 0.064 in. aluminum specimens, in the jig shown in Figure 6. This jig permits a 0.5 in. overlap to be obtained automatically. All unboned areas were taped off using masking tape. The T-peel specimens were prepared, using 1 in. x 9 in. x 0.032 in. aluminum specimens, in the jig shown in Figure 7. The bonded area was 6 inches. Glass beads, 6-7 mils in diameter, were used as spacers. Pressure, 2 to 5 pounds, was applied by means of lead weights.

Physical Testing

The tensile shear strength determinations were carried out according to MIL-A-005090E testing procedure using an Instron tester. The T-peel strength determinations were done according to ASTM testing procedure D-1876.

Preparation of Diisocyanates

The diisocyanates that had to be synthesized were prepared using the same general procedure as given below.

$$HCl\cdot H_2N\text{-}Ar\text{-}NH_2\cdot HCl \xrightarrow{COCl_2} ClCONH\text{-}Ar\text{-}NHCOCl \xrightarrow[\Delta]{} OCN\text{-}Ar\text{-}NCO$$

A nitrogen swept four-necked flask equipped with a stirrer, condenser, dry nitrogen inlet, thermometer, heating mantle, and gas dispersion tube adjusted to reach below the liquid surface was charged with distilled-dried *o*-dichlorobenzene (500 ml/100 g dihydrochloride). A 20% sodium hydroxide solution was used to trap the off gases. The dried, finely divided diamine dihydrochloride was transferred into the reaction flask under nitrogen. Agitation was begun and chlorine-free dry phosgene (passed through mineral oil and sulfuric acid) was added rapidly with a slight dry N_2 carrier gas to prevent back-up of the various trap materials. The temperature rose to 40-46°C and then subsided. The flow of phosgene was reduced to maintain a slight positive pressure, and the temperature was increased to 120-125°C. The flow of phosgene was then increased to the maximum rate that the reaction mixture could adsorb. This condition was maintained until all the solid had entered solution. The flow of phosgene was again reduced to give a slight positive pressure and the reaction heated to 170-175°C and maintained for 2 hours. The addition of phosgene was then stopped and

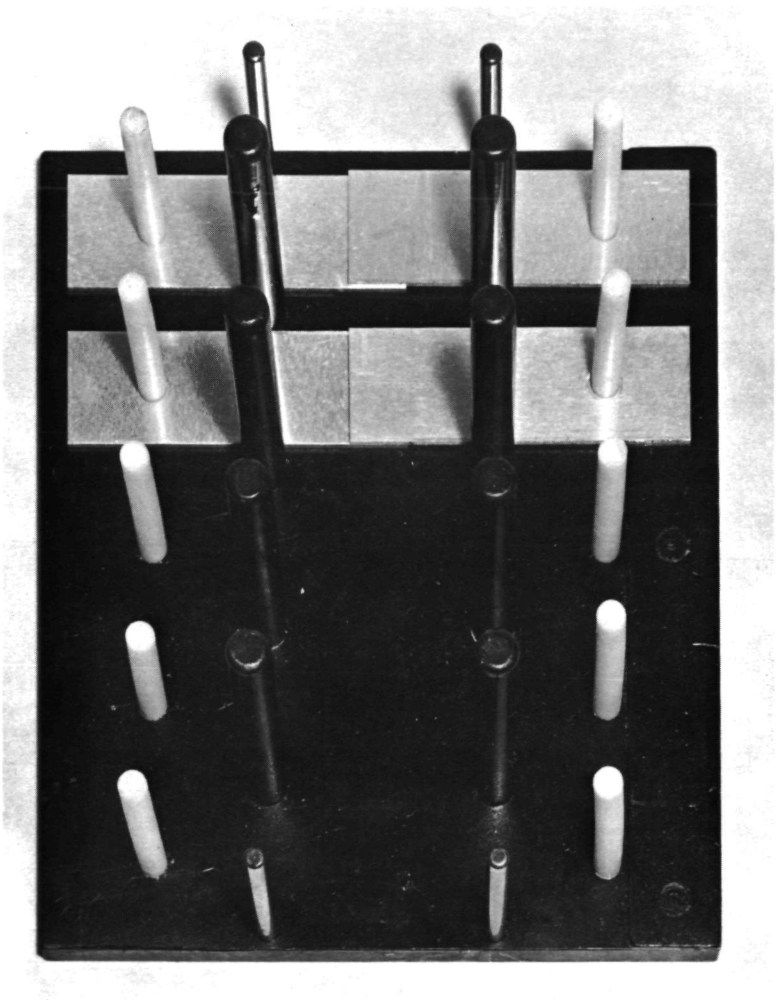


Figure 6. Lap shear specimen jig

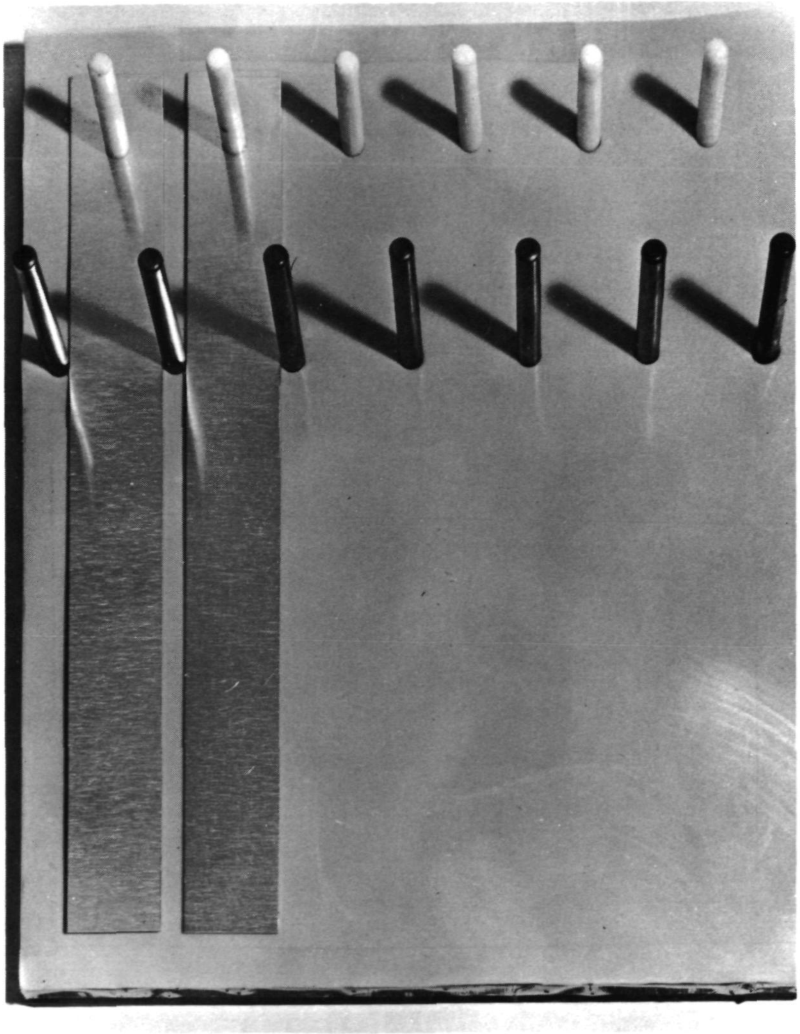


Figure 7. T-peel specimen jig

dry nitrogen passed through the solution which was held at 170-175°C for another one to one and one half hours. The reaction was then cooled to 120-130°C and filtered under vacuum and nitrogen through filter aid into a distillation flask. The majority of *o*-dichlorobenzene was removed on a rotary evaporator. The residue was fractionally distilled. The colorless distillate was analyzed for percent NCO as per ASTM D-1638.

Isocyanate Prepolymers

Given below is the procedure used for preparation of the isocyanate-terminated prepolymers used in this study. The percent isocyanate present in the prepolymers was determined using ASTM Method D-1638.

2,4'-Tolylene Diisocyanate and *m,m*'-Diisocyanatodiphenylmethane-Based Prepolymers. - The diisocyanate (two equivalents) was placed in a dried four-necked flask fitted with a mechanical stirrer, thermometer, dropping funnel, and dry nitrogen inlet. The polyol (one equivalent), which had been degassed and stripped of volatiles up to 95°C and 0.5 mm Hg, was added through the dropping funnel. The reaction temperature was held at 50±5°C by heating, cooling, and/or adjusting the rate of addition of the polyol. Heating was continued for two hours after any exotherm had ceased. During the last half hour the prepolymer was degassed at 1-5 mm Hg. The product was then stored under nitrogen in sealed bottles.

m,m'-Diisocyanatobenzophenone-Based Prepolymer. - The reaction set up described above was charged with 1.0 equivalent of diisocyanate and 0.25 equivalent of POLYMEG 2000. The mixture was heated to 100°C to form a fluid mixture, and after a small initial exotherm the remaining POLYMEG 2000 (0.25 equivalent) was added slowly. A temperature of 100°C was maintained for 3 hours after the addition was complete, and during the last 30 minutes the prepolymer was degassed at 5 mm Hg. The high temperatures employed here were necessary to get a fluid mixture.

Polyurethane Adhesives Pot Life Determination

The development of adhesives based on materials available in limited quantities required that a method for estimating pot life be devised which used small amounts of the adhesive formulation. The following method has been employed to obtain these estimates.

A 10 by 75 mm test tube was filled to within one-half inch of the top with the adhesive formulation. The test tube was placed in a holder and raised into position centered around a number seven spindle (no disk) attached to a Brookfield viscometer (model HAF). The viscometer was run at 10 rpm and readings were taken at regular intervals. Zero time was designated as the point when the curing agent was added to the resin. The readings were converted to viscosities using the appropriate factor. However, these viscosities can not be considered true viscosities due to the shape of the container.

CONCLUSIONS

Data obtained during this study indicate that the isomers of diaminobenzophenone and methylenedianiline other than the para isomers contribute to increased tensile shear strength of epoxy adhesives while affecting the toughness (i.e., T-peel strength) only slightly. These data support similar findings obtained in in-house NASA Langley studies on polyimide adhesives based on these diamines. Use of *m,m'*-MDA as an epoxy curing agent is particularly effective in increasing tensile shear strength relative to the state-of-the-art. It is likely that this adhesive would respond to optimization in a manner similar to the state-of-the-art adhesive based on *p,p'*-MDA.

It appears unlikely that a useful high strength polyurethane adhesive can be developed based on the three new curing agents studied in this project. The benzophenone-based diamines gave useful reaction rates but low strengths while *o,p'*-methylenedianiline reacted extremely rapidly.

The two new diisocyanates studied, *m,m'*-diisocyanatodiphenylmethane and *m,m'*-diisocyanatobenzophenone, did not show promise of giving any adhesive or processing property different enough from state-of-the-art materials to warrant further study.

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