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RECENT DEVELOPMENTS IN POLYIMIDE AND BISMALEIMIDE ADHESIVES

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Research on high temperature resin systems has intensified during the past few years. In the Aerospace Industry, much of the motivation for this increased activity has been to replace heat resistant alloys of aluminum, stainless steel and titanium by lighter weight glass and carbon fiber reinforced composites. Applications for these structures include: (1) engine nacelles involving long time exposure (thousands of hours) to temperatures in the 150 to 300°C range, (2) supersonic military aircraft involving moderately long exposure (hundreds of hours) to temperatures of 150 to 200°C, and (3) missile applications involving only brief exposure (seconds or minutes) to temperatures up to 500°C and above.

Because of fatigue considerations, whenever possible, it is preferable to bond rather than mechanically fasten composite structures. For this reason, the increased usage of high temperature resin matrix systems for composites has necessitated the development of compatible and equally heat stable adhesive systems.

This paper briefly reviews the performance of high temperature epoxy, epoxy-phenolic and condensation polyimide adhesives. This review is followed by a discussion of three recently developed types of adhesives: (1) condensation reaction polyimides having improved processing characteristics, (2) addition reaction polyimides, and (3) bismaleimides.

All of the adhesives discussed in this paper are suitable for bonding honeycomb to skin sandwich structure. However, in the interest of brevity, with few exceptions I have chosen to use lap shear strength as the criteria for comparing performance of the various types of adhesive.

Epoxy Adhesives

Epoxy adhesives based on multifunctional resins are available which exhibit excellent strength retention at temperatures up to about 225°C. Where long term aging is required, epoxies are generally limited to applications requiring continuous service at temperatures no higher than 175°C. The adherends involved are most commonly aluminum alloys and epoxy matrix composite structures.

Epoxies are comparatively low in cost and are by far the simplest and most economical adhesives to process. Full cures may be accomplished at moderate temperatures (150 to 200°C). Furthermore, because curing is accomplished by addition reactions, no volatiles are evolved and dense, non-porous glue lines are easily obtained with low pressure bonding.

Figure 1 shows the lap shear strength of FM® 400 at various temperatures. This adhesive was designed for use on supersonic military aircraft and has excellent strength retention at temperatures up to 215°C. Strength then drops rather sharply to 6.9 MPa (1000 psi) at 260°C. The effect of heat aging on FM® 400 is shown in Figure 2. After 3000 hours aging at 215°C, the adhesive retains approximately 80% of its original lap shear strength. This is more than sufficient for most military aircraft.

Other multifunctional epoxy adhesives are available for use in applications such as engine nacelles, where resistance to heat aging for very long periods of time is required. Figure 3 shows the performance of an epoxy adhesive of this type when heat aged at 175°C.

It can be seen that there is no significant drop in lap shear strength after 20,000 hours at 175°C. It is interesting to note that the configuration of the bond line has a pronounced effect on the ability of the adhesive to withstand heat aging. In the lap shear configuration, the adhesive is protected from oxidation by solid metal skins. In the sandwich panel constructed of solid aluminum skins to aluminum honeycomb, there is a substantial quantity of air trapped in the panel which initiates oxidative degradation. As a result, this structure shows a 50% drop in flatwise tensile strength after 10,000 hours aging. Degradation is most rapid in the quiet nacelle type of sandwich panel constructed with perforated skins. In this configuration, the bond line is completely exposed to oxygen in the atmosphere and a 50% drop in lap shear strength occurs after about 5000 hours heat aging.

Epoxy-Phenolic Adhesives

Epoxy-phenolics rival the polyimide adhesives in their ability to withstand short time exposure to extremely high temperatures. For this reason, they are admirably suited for use on missiles, and are generally preferred to polyimides because of their lower cost and ease of processing. Bond pressures of .28 MPa (40 psi) and cure temperatures of 150°C are usually adequate for most applications.

Figure 4 shows the effect of temperature on the bond strength of an aluminum powder filled epoxy-phenolic adhesive. This adhesive (HT® 424) retains 6.9 MPa (1000 psi) lap shear strength at 540°C.

Figure 5 shows the effect that oxidation has on the life of the adhesive at 260°C. On a 17-7 PH steel substrate, the adhesive shows excellent strength retention after 500 hours when heat aged in a nitrogen atmosphere. On the same steel substrates, lap shear strength drops to zero after only 100 hours heat aging in air. It is interesting to note that degradation is much slower in an air atmosphere on an aluminum substrate. This illustrates the role of transition metals such as iron in catalytically promoting oxidative degradation of organic adhesives.

Condensation Reaction Polyimides

High temperature adhesives based on condensation reaction polyimide precursors have been marketed for over 15 years. Adhesives of this type are supplied in both liquid form and as solid films. In addition, they may be filled or unfilled. Aluminum powder filled adhesives have proved to be superior in strength to unfilled adhesives and are generally used for metal bonding applications. Unfilled adhesives are primarily used for radomes and other applications where radar transparency is required.

Condensation reaction polyimides require high cure temperatures; 260°C or even higher depending on the expected service temperature. Processing is further complicated by the high volatile content of these adhesives (about 12% for aluminum filled adhesives and 30% for unfilled adhesives). One processing advantage that they have over addition reaction polyimides is that they can be cured under pressure at 175°C and then post cured without pressure at higher temperatures. This permits the use of low temperature autoclaves and conventional bagging materials. Inexpensive ovens can be used for postcuring the bonded panels. A typical cure cycle for condensation reaction polyimides consists of heating the panel from room temperature to 175°C in 2 hours or less under full vacuum plus .28 MPa (40 psi) air pressure. Vacuum and air pressure are maintained while the panel is held at 175°C for 2 hours. Post curing of small panels may be carried out by placing them in a 175°C oven and raising the temperature to about 290°C and holding at 290°C for 2 hours. For large panels with impermiable skins, it may be necessary to very slowly raise the temperature to 290°C over a period of several hours to prevent blister formations in the glue line.

FM® 34 was perhaps the first polyimide adhesive developed that gained any significant commercial acceptance. Its performance at temperatures up to 540°C is depicted in Figure 6. It will be noted that its strength retention at 540°C does not significantly differ from that of the more easily processed epoxy phenolic adhesive (HT® 424). However, as can be seen from Figure 7, FM® 34 was far superior in thermal stability showing no significant drop in strength after 40,000 hours at 260°C.

FM® 34 contained an arsenic compound which inhibited catalytic decomposition by transition metal substrates such as titanium and steel. FM® 34 is no longer supplied and has been replaced with FM® 34B-18. FM® 34B-18 which is free of arsenic shows excellent strength retention after 1200 hours heat aging at 260°C, but degrades rapidly during the next 2000 hours. In applications where transition metals are not involved (for example, in bonding to polyimide composites) FM® 34B-18 is fully as resistant to long time heat aging as FM® 34.

Processing Condensation Polyimides to Minimize Volatile Problems

The volatiles released during the cure of condensation PI adhesives come from two sources: (1) volatilization of retained solvent and (2) water released during imidization of the precursor resin. The polyimide precursor resin is very high melting and very brittle and for this reason, solvent is left in the adhesive film as a plasticizer to impart drape and tack to the adhesive film as well as to insure flow during bonding.

As the temperature is raised during the bond cycle imidization occurs. Water is released as a result of this condensation reaction. If the retained solvent is not released soon enough in the bond cycle, sufficient imidization occurs to make the resin insoluble in the solvent and it precipitates. When the solvent is subsequently released later in the bond cycle, a weak porous bond results because the resin is inccapable of flow.

The solvent most commonly used in PI adhesives is N-methyl-2-pyrrolidone (NMP) which boils at about 200°C at atmospheric pressure. Since considerable imidization occurs long before the adhesive reaches even 175°C, precipitation of the resin would occur if processing were carried out at atmospheric pressure. For this reason, bonding is carried out under vacuum to insure release of the solvent earlier in the bond cycle. Figure 8 shows the boiling point of NMP at various degrees of vacuum. At about 13 psi vacuum, the boiling point is depressed to about 140°C. With a 13 psi or higher vacuum and a heat up rate of 1.5°C per minute or faster, volatile release occurs early enough in the bond cycle to minimize precipitation.

Improved Condensation Reaction Polyimides

The previous section has shown how good quality bonds can be obtained with the FM® 34 series of adhesives by carefully controlling processing conditions. However, this problem becomes particularily severe when wide area bonds with impermiable metal skins as adherends are involved. Under these conditions, volatile release is retarded and occurs later in the bond cycle resulting in excessive resin precipitation.

A new condensation reaction polyimide adhesive designated as FM® 36 was developed to overcome this problem. It is based on a more soluble precursor resin that remains soluble in the NMP solvent even after substantial imidization has occurred. FM® 36 is an unfilled adhesive designed for applications requiring radar transparency. Figure 9 compares its performance in a wide area lap shear panel to that of FXM 34B-32 (a radar transparent version of FM® 34). It can be seen that the lap shear strength of the two adhesives is comparable with a 2.5 cm width bond line. The lap shear strength of FM® 34B-32 drops to nearly zero with a 15 cm wide bond line, while the FM® 36 shows no drop in strength with a 22.5 cm wide bond line.

Figure 10 shows that FM® 36 has good strength retention up to 290°C. We have not as yet run lap shear tests at higher temperatures. Figure 11 shows that this adhesive retains about 60% of its original strength after 1000 hours aging at 290°C on a titanium substrate. We have previously noted that titanium accelerates the decomposition of adhesives. Therefore, we expect better strength retention after heat aging on composite substrates. Preliminary results substantiate this expectation, but we do not yet have a reliable data base because of sporadic interlaminar shear failures in the PI laminate substrates.

Addition Reaction Polyimides

Addition reaction polyimides make it possible to obtain bond lines with extremely low void contents. Adhesives of this type are generally supplied as supported film containing sufficient alcohol to impart tack and drape to the adhesive. A typical bond cycle is as follows:

1. RT to 205°C in 1 hour under 5 psi vacuum pressure.
2. Hold 15 minutes at 205°C maintaining 5 psi vacuum.
3. Apply full vacuum plus 100 psi air pressure for remainder of cycle.
4. Raise temperature to 290°C in about 40 minutes.
5. Hold 2 hours at 290°C.
6. Cool to 100°C before releasing pressure.

Unlike the condensation reaction type, addition reaction polyimides remain thermoplastic after imidization and solvent removal has occurred. Hence, when pressure is applied after solvent removal at 205°C, a dense non-porous glue line results. Upon heating to 290°C, further curing occurs via an addition reaction involving unsaturated end groups such as nadic anhydride.

Unlike the condensation reaction PI's which can be processed using the post cure concept, addition reaction PI's must be held under pressure throughout the cure cycle. Therefore, relatively costly high temperature presses or autoclaves are required to fabricate panels with addition PI adhesives.

FM® 35 is an addition PI adhesive containing an aluminum powder filler. As is shown in Figure 12, it is comparable in strength retention to the condensation PI's at temperatures up to 290°C. Figure 13 demonstrates that good quality large area bonds can be made with this adhesive.

Composites made from addition reaction PI's are generally fabricated using 200 psi pressure to insure low void content in the laminate. There is no significant difference in the lap shear strength of FM® 35 when bonding pressure is varried from .28 MPa (40 psi) to 1.38 MPa (200 psi). We have not, however, measured the void content of bond lines made at different pressures or the possible effect of variations in void content on strength retention after heat aging. This work is now in progress.

Bismaleimide Adhesives

Bismaleimide adhesives fill a niche between high temperature epoxy and PI adhesives. Unmodified BMI resins are hard, brittle solids. In order to impart drape to adhesive films based on these resins, they must be plasticized. However, unlike the PI resins, plasticization may be accomplished without resorting to the use of solvents. Volatile-free adhesive films having drape can be formulated through the use of reactive liquid monomers as plasticizers. Since cross linking occurs via an addition reaction, no volatiles are evolved during the cure of these adhesives.

Cure temperature requirements vary depending on the particular BMI resin employed and the specific monomeric plasticizers selected. In general, good results can be obtained using a cure of 2 hours at 175°C under .28 MPa (40 psi) pressure followed by a 2 to 4 hour post cure at 200 to 225°C .

Figure 14 shows the performance of an experimental BMI adhesive over a range of temperatures. Strength retention is surprisingly good up to about 300°C. However, in applications where long term exposure to high temperatures is involved, BMI adhesives are not expected to be durable beyond 200 to 225°C.

Almost limitless variations in formulation are possible with BMI adhesives. The experimental BMI on which data is presented in Figure 14 contains no toughener and as a result, has quite low lap shear strength. Considerable work is now in progress to formulate BMI's having optimum balance between toughness and heat resistance.

EFFECT OF TEMPERATURE ON EPOXY ADHESIVE (FM® 400)

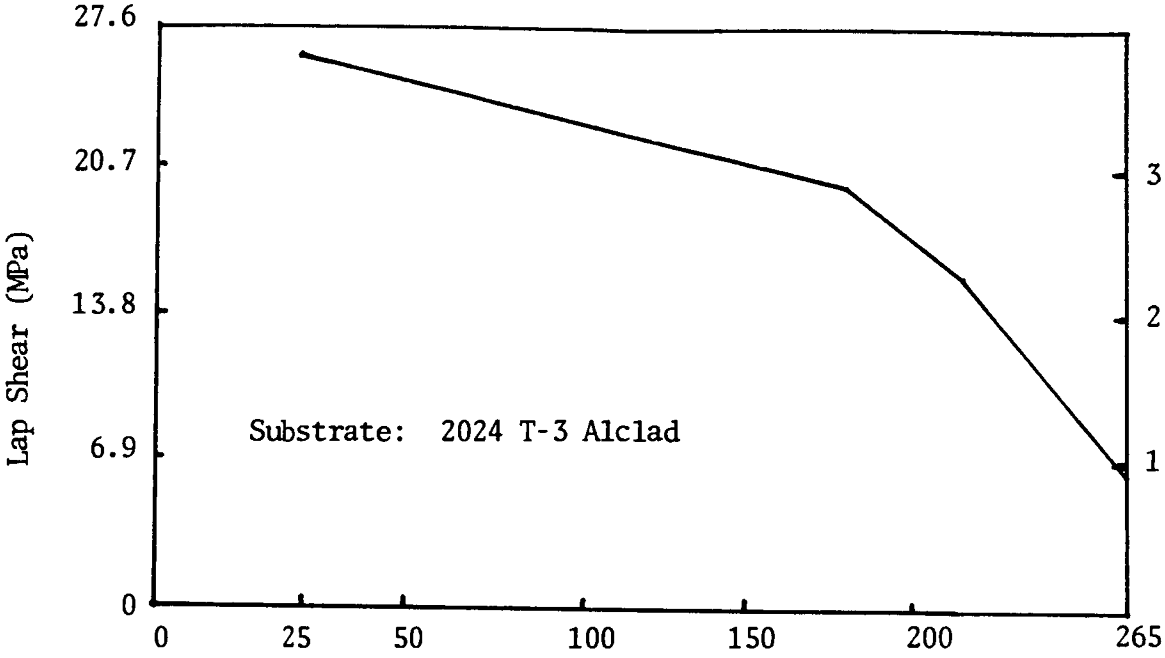


Figure 1

EFFECT OF HEAT AGING ON AN EPOXY ADHESIVE (FM® 400)

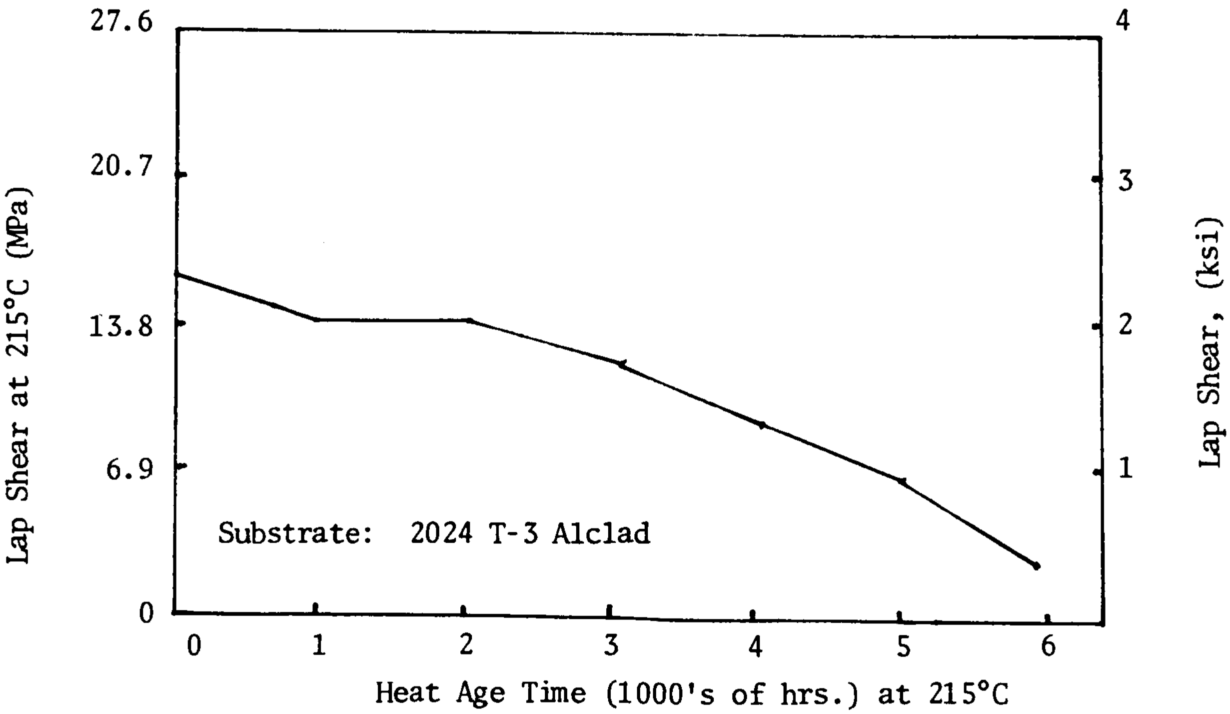
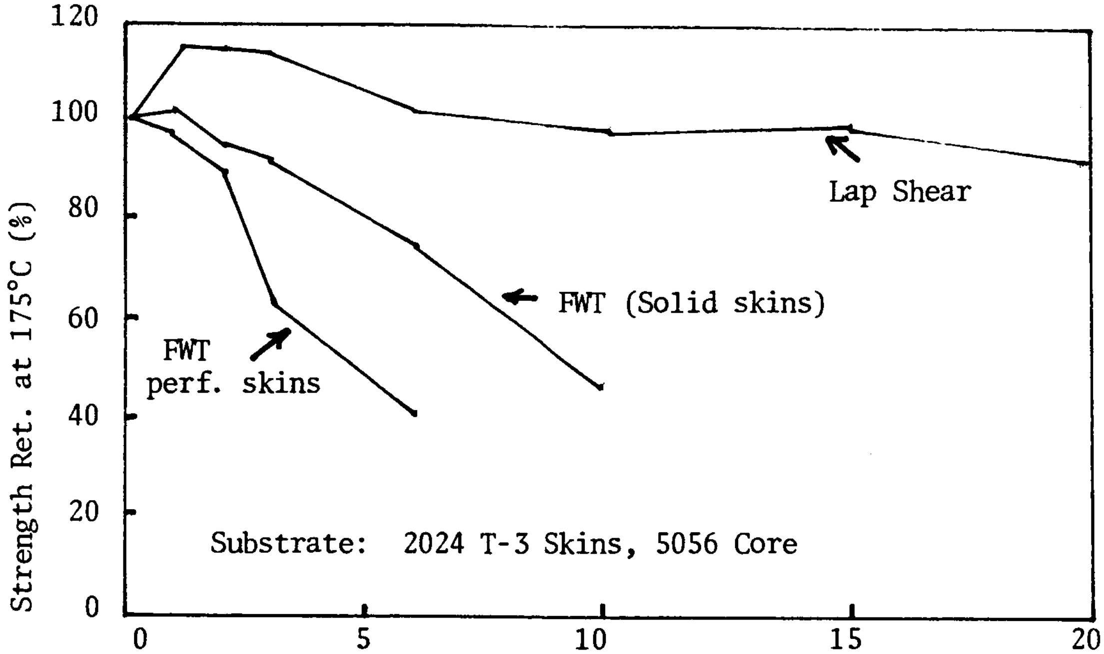


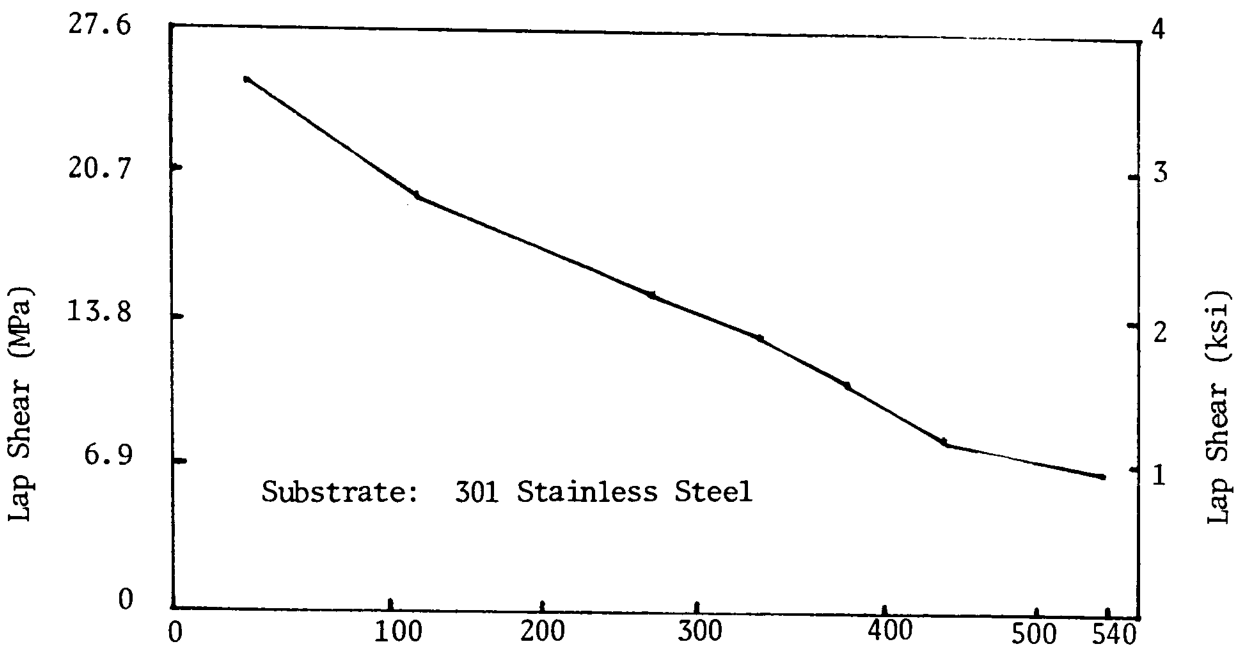
Figure 2

EFFECT OF BOND CONFIGURATION ON HEAT AGING



Aging Time at 175°C (1000 of hrs.)
Figure 3

EFFECT OF TEMPERATURE ON AN EPOXY-PHENOLIC ADHESIVE (HT® 424)



Test Temp. °C (1 min. exposure)
Figure 4

EFFECT OF HEAT AGING ON AN EPOXY-PHENOLIC ADHESIVE (HT® 424)

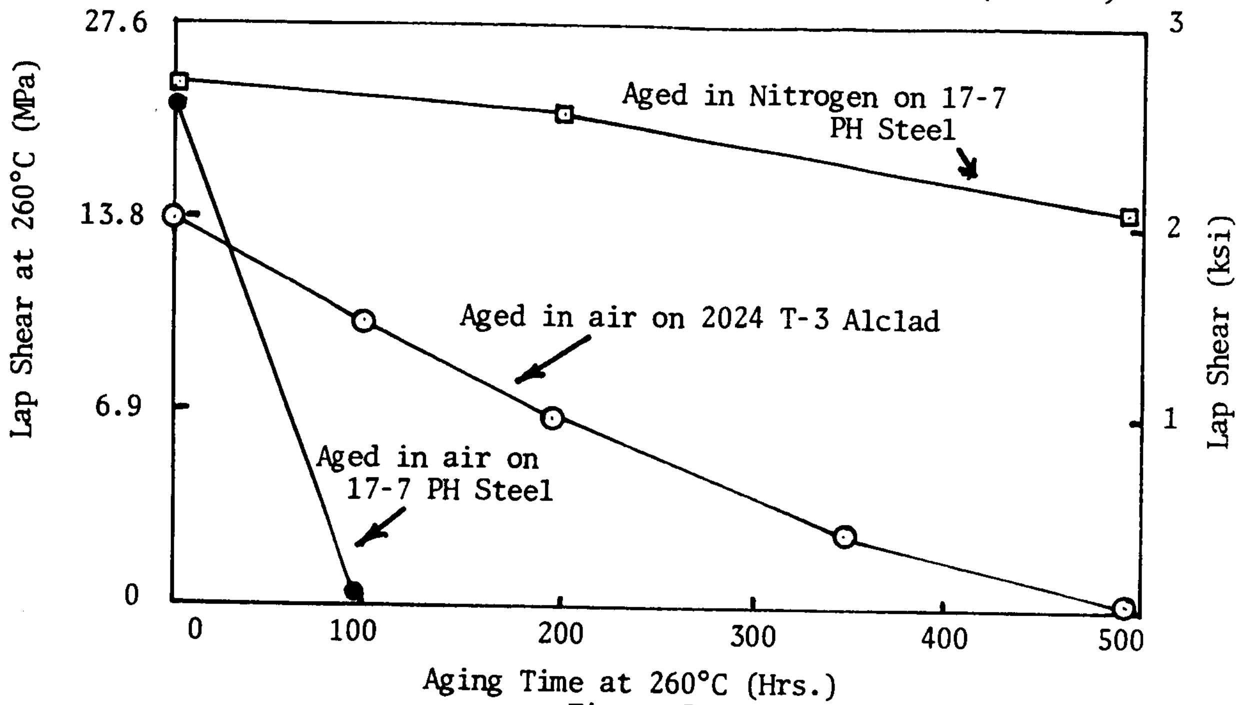


Figure 5

EFFECT OF TEMPERATURE ON FM® 34 (POLYIMIDE ADHESIVE)

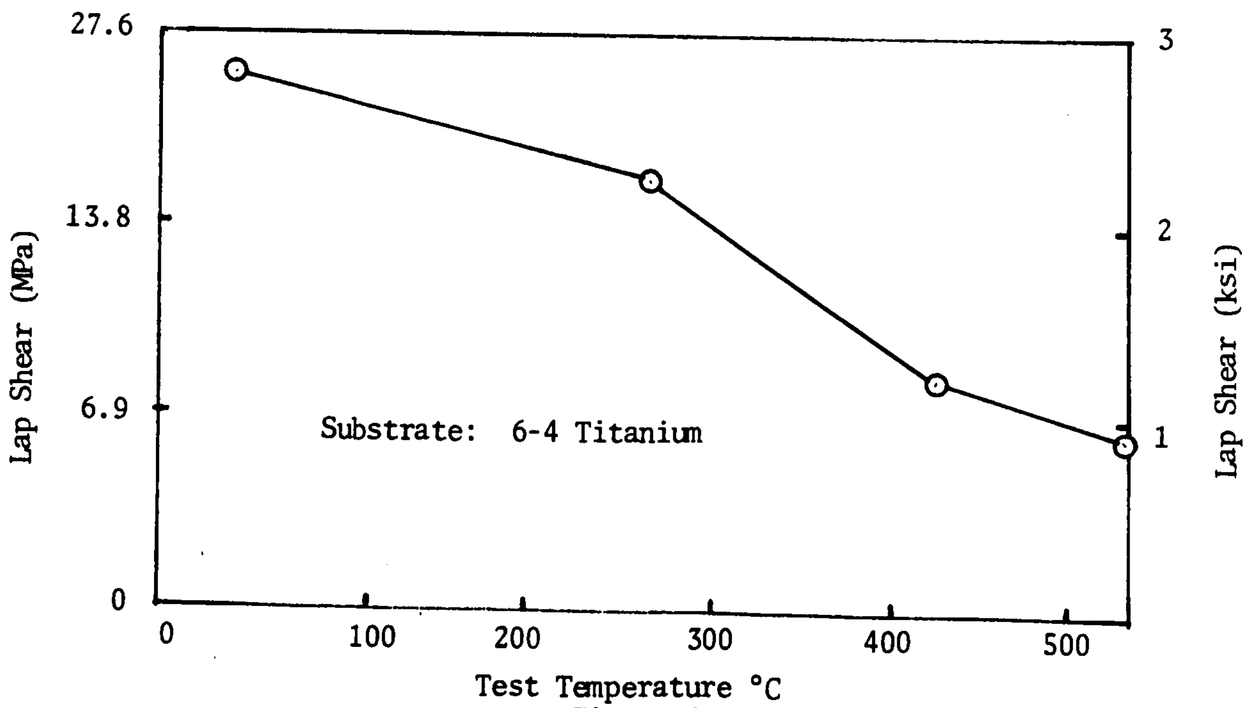


Figure 6

EFFECT OF ARSENIC COMPOUND ON THERMAL STABILITY

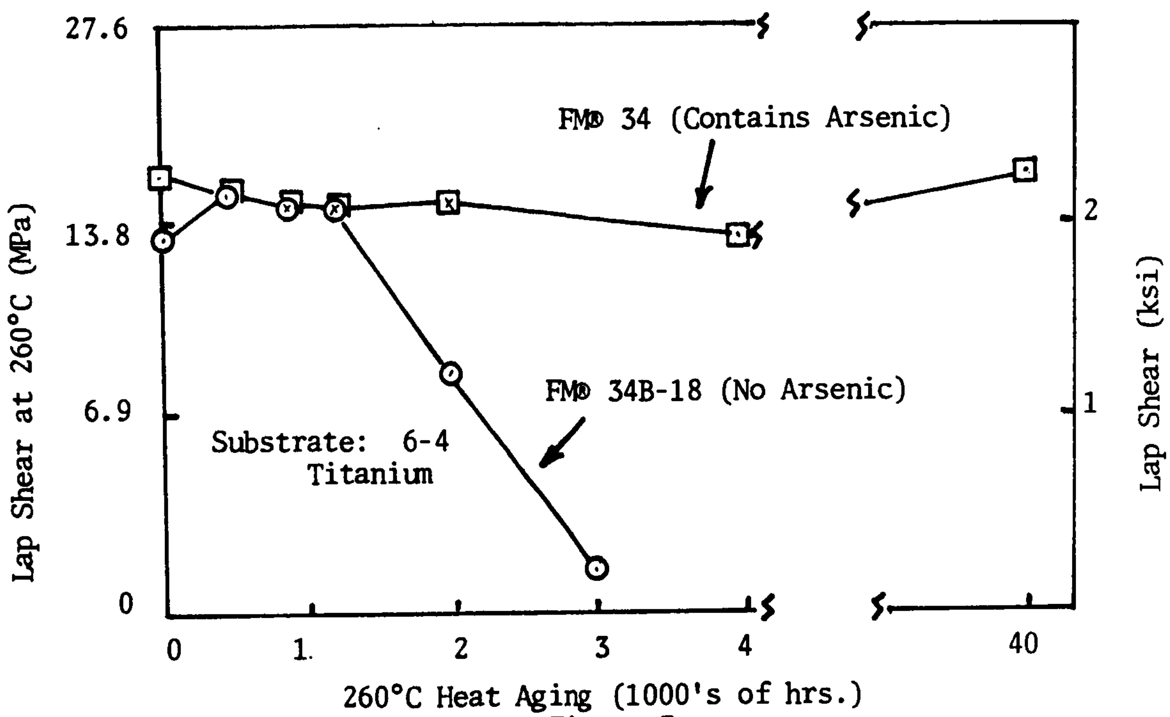


Figure 7

Boiling Point Curve of NMP

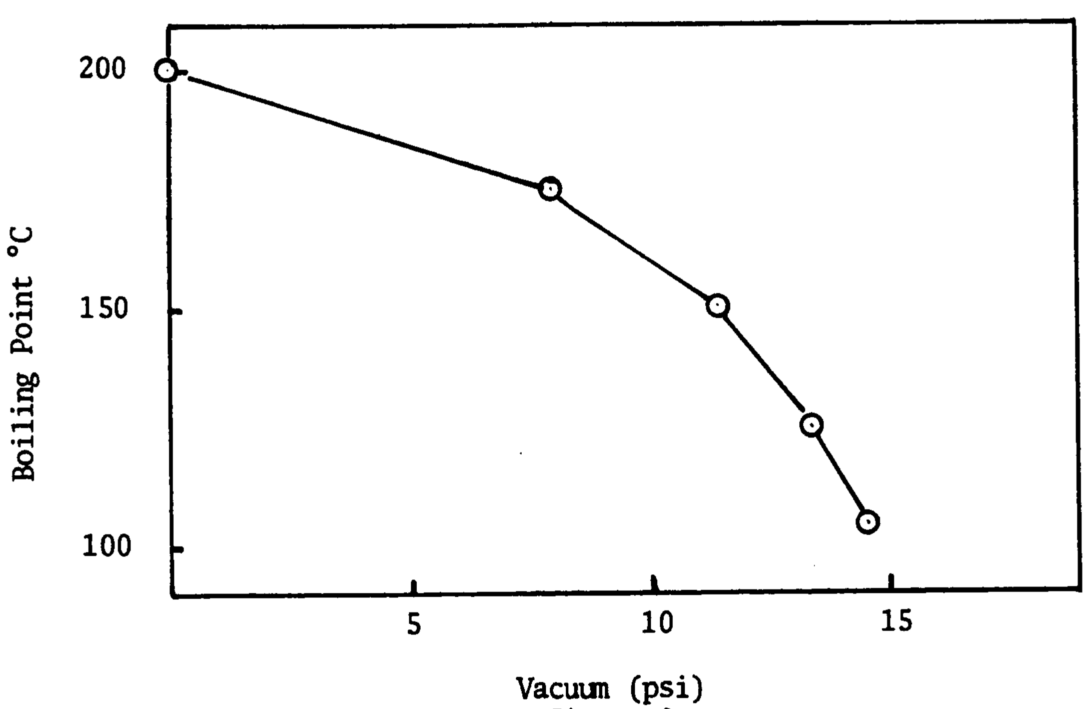


Figure 8

EFFECT OF PANEL WIDTH ON BOND STRENGTH

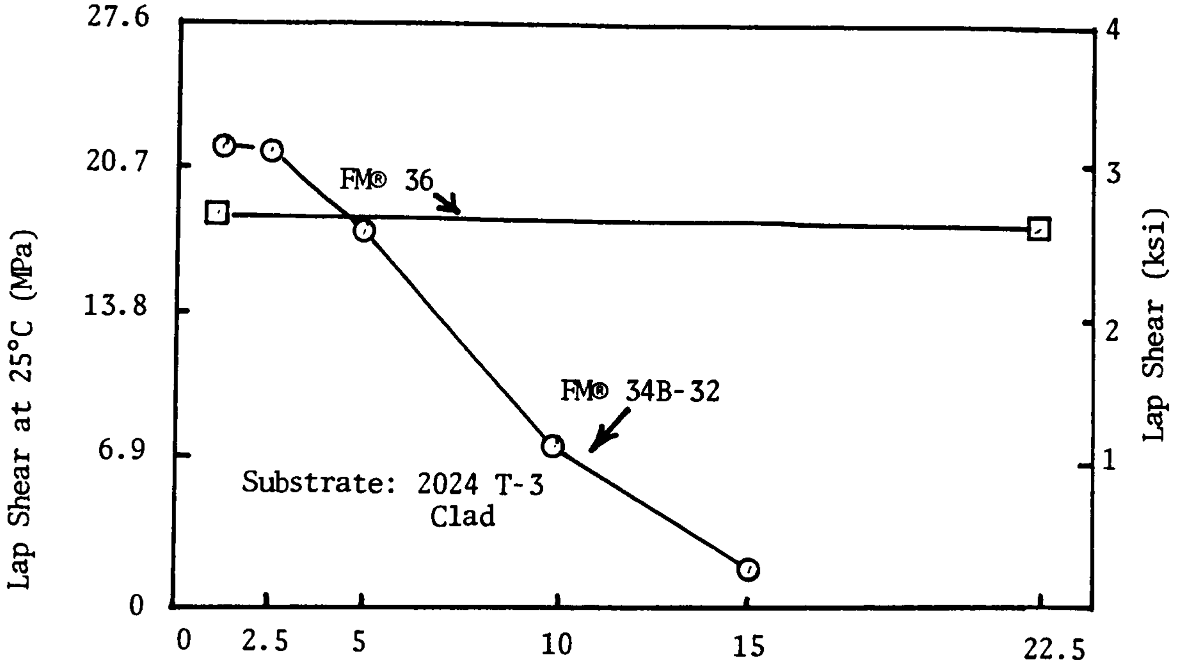


Figure 9

EFFECT OF TEMPERATURE ON FM® 36 (POLYIMIDE ADHESIVE)

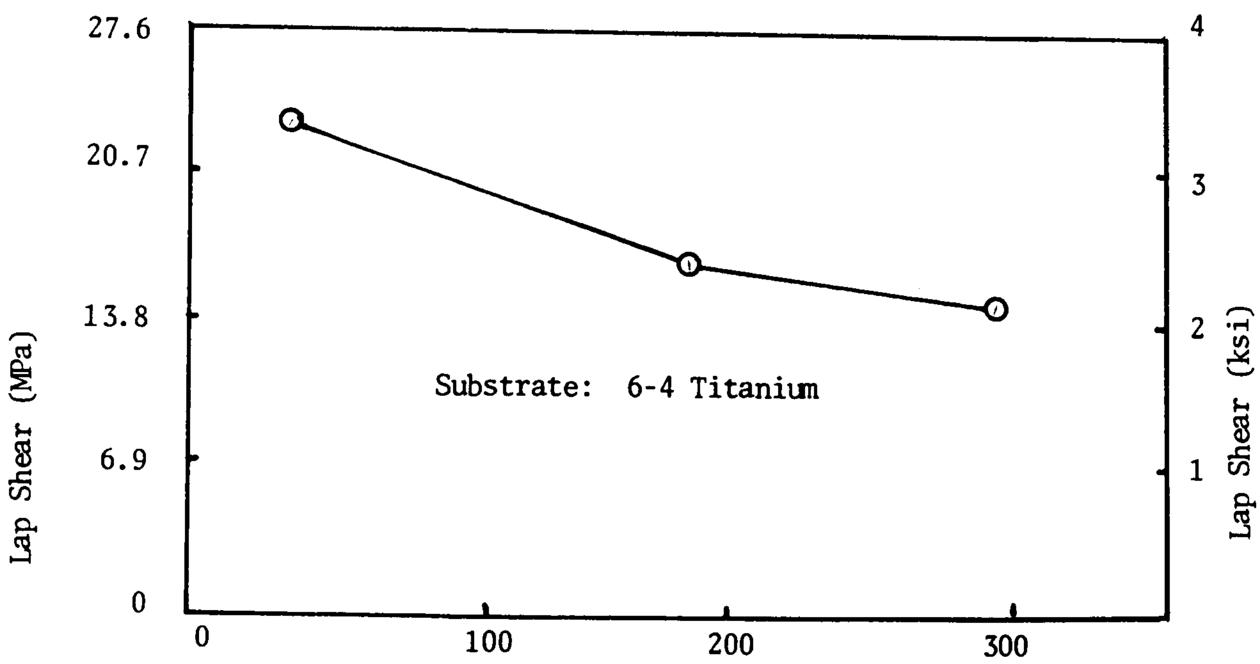


Figure 10

EFFECT OF HEAT AGING ON FM® 36 (PI ADHESIVE)

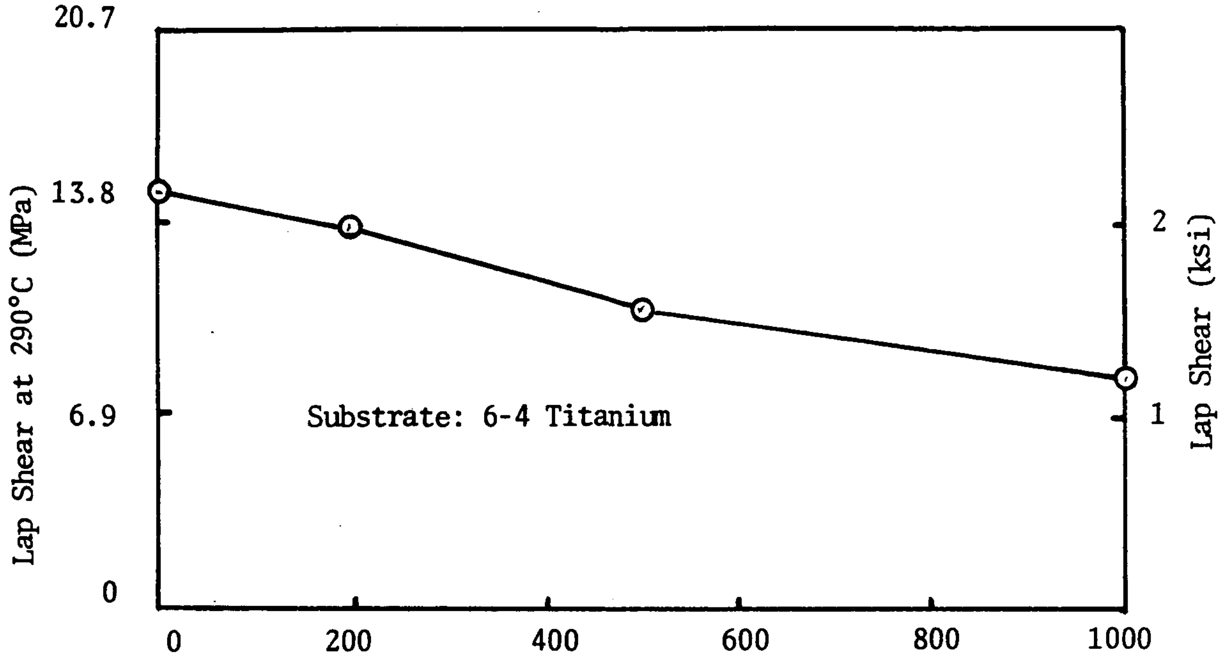


Figure 11

EFFECT OF TEMPERATURE ON AN
ADDITION REACTION PI ADHESIVE (FM® 35)

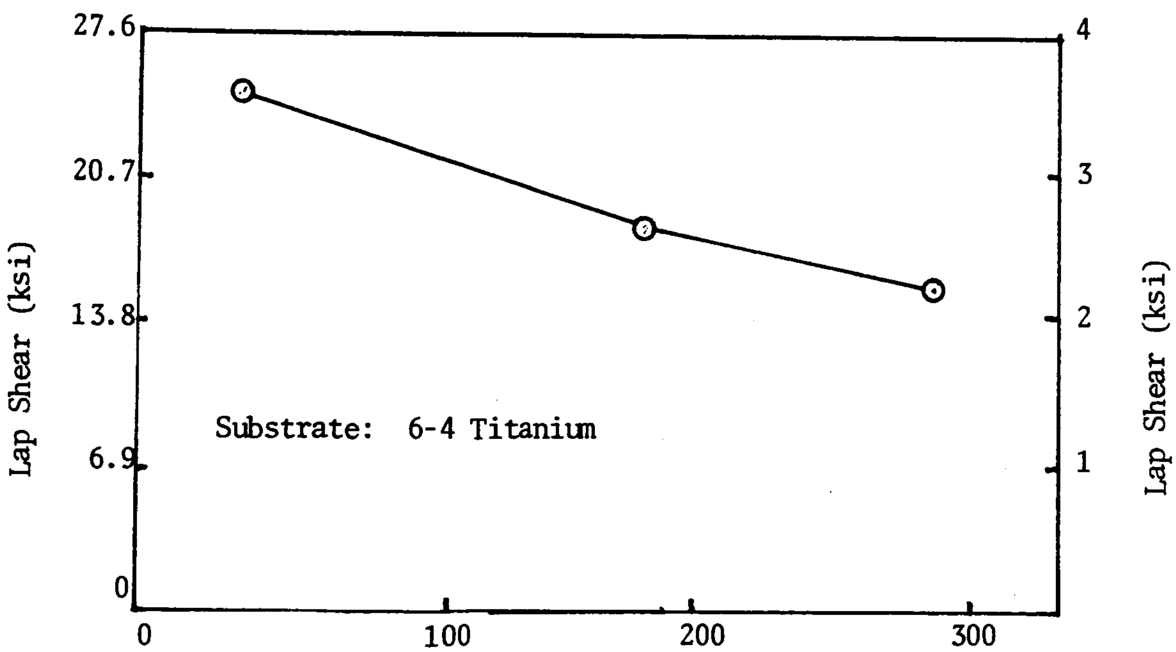


Figure 12

EFFECT OF PANEL WIDTH ON
BOND STRENGTH OF FM® 35

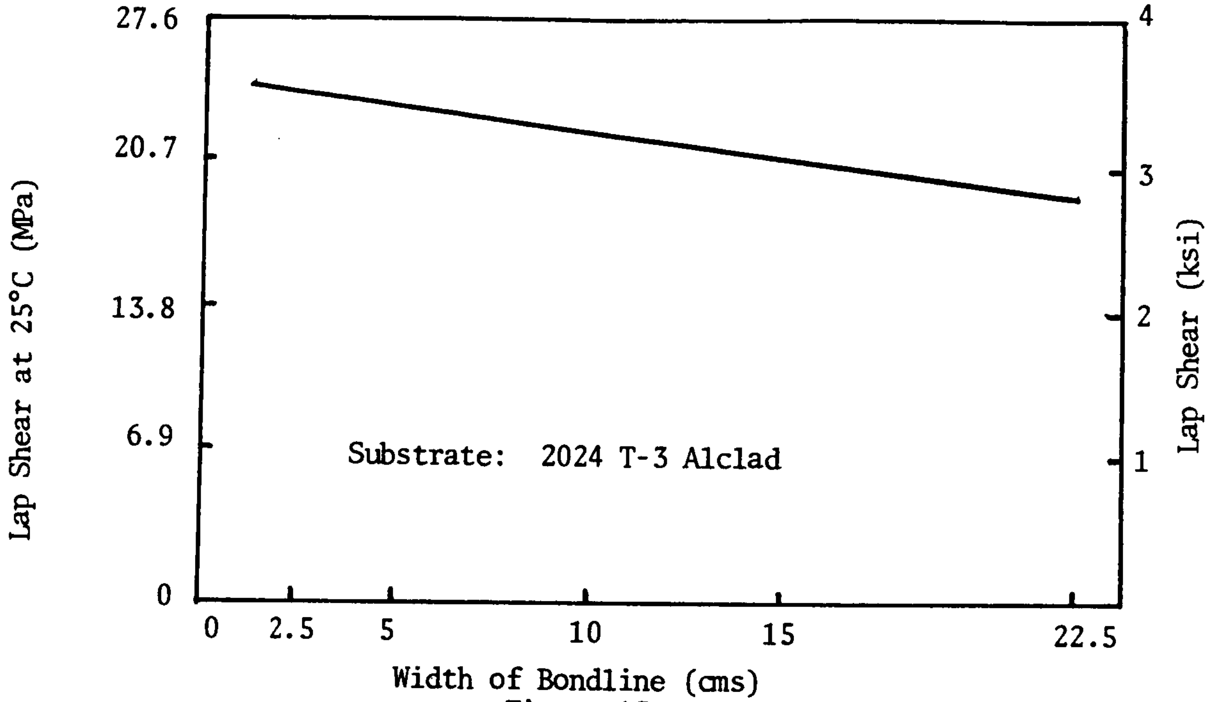


Figure 13

EFFECT OF TEMPERATURE ON A BMI ADHESIVE

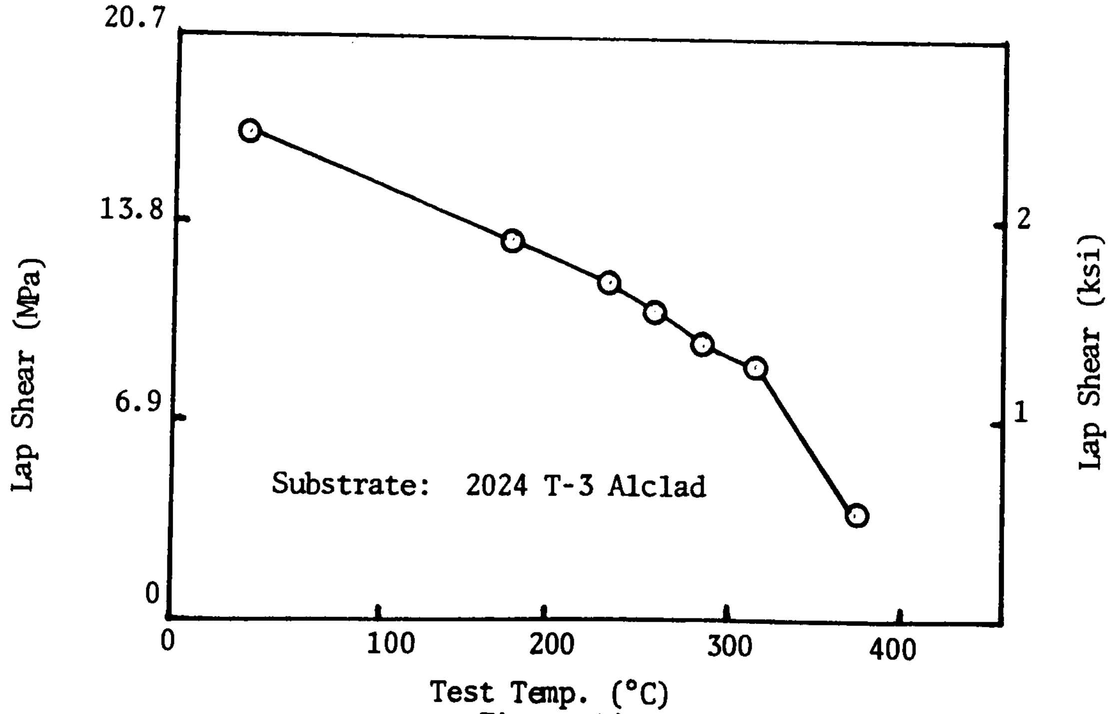


Figure 14