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HIGH TEMPERATURE
NONPLANAR LAMINATES

PDO 6984970, Progress Report ✓

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HIGH TEMPERATURE NONPLANAR LAMINATES

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✓
Prepared by J. D. Stein, D/812, under PDO 6984970

Development of high temperature substrates was initiated to fabricate nonplanar laminates. Forming of readily available polyimide and fluorocarbon films was established, and the evaluation of thermal stability up to 500°F (260°C) initiated. The development of auxiliary materials suitable for high temperature system applications and specific adhesive evaluation is included.

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CONTENTS

Section	Page
SUMMARY.	5
DISCUSSION	6
ACTIVITY	6
<u>Forming of Individual Laminate Films</u>	6
<u>Bonding of Individual Formed Films</u>	7
<u>Forming Flat Laminates</u>	9
<u>Evaluation of Kapton Film and Laminates</u>	11
<u>Evaluation of Adhesives</u>	17
ACCOMPLISHMENTS.	19
FUTURE WORK.	19
REFERENCES	21
APPENDICES	
A. HIGH TEMPERATURE LAMINATE FABRICATION.	22
B. ADHESIVES FOR HIGH-TEMPERATURE NONPLANAR LAMINATES.	35

ILLUSTRATIONS

Figure		Page
1	Draw Ring Control Pressure Die.	7
2	Mechanical Forming.	8
3	Furnace Heated Laminating Fixture	9
4	Laminating Fixture Modified for Over- Pressure.	10
5	Mechanical Forming Fixture (P90650)	10
6	Pressure Forming Fixture (P88582)	11
7	Laminating Fixture Modified for Stabilization . . .	12
8	Kapton Shrinkage (As-Received).	13
9	Contour Change of Formed Kapton as a Result of Thermal Aging	16
10	FEP Bond Strength Versus Temperature	18

TABLES

Number		Page
1	Mechanical Properties of 0.005-Inch (127 μ m) Kapton Unaged and Aged at 500°F (260 C) for 34 Days	14
2	Contour Height Data for Formed 0.005-Inch (127 μ m) Kapton	15
3	Peel Strength Data Using Heat Sealable FEP.	18

SUMMARY

High temperature laminates are required for fabrication of nonplanar parts that use vapor deposition to deposit aluminum onto the laminate. Temperatures up to 400°F (204°C) may be encountered during the physical vapor deposition (PVD) of aluminum. Thermal stability is also required.

The feasibility of fabricating formed laminates of polyimide films fusion-bonded with fluorocarbon film was established, and the evaluation of thermal stability was initiated. This work was carried out between May and December 1974.

Methods have been developed to fabricate laminates from readily available Kapton and Teflon FEP by bonding individual, formed, and stable pieces, or by forming commercially available laminates. Thermal stability studies were initiated and laminates were plated by the PVD process without apparent bond degradation. Stability data for Kapton formed at 700°F (371°C) indicates adequate retention of contour after aging at 500°F (260°C) for 34 days. Data for Kapton was also obtained for "as-received" shrinkage, thermomechanical analysis (TMA), and mechanical properties after aging. The bond strength of the Teflon FEP has been found to decrease to a low value at 300°F (149°C).

From the present data, it is concluded that the Kapton formed and stabilized prior to bonding can provide functional laminates with the Teflon FEP fusion bond. Development will continue to form commercially available laminates.

Further development will require tests for part displacement resulting from process thermal cycles. Laminates fabricated from individually formed and bonded pieces and from commercially formed laminates will be tested. Auxiliary materials will be analyzed and specific adhesives will be evaluated.

DISCUSSION

ACTIVITY

Existing nonplanar laminates, exclusive of vapor deposited aluminum, consist of one layer of 0.004-inch-thick (102 μm) aluminum and two layers of 0.005-inch-thick (127 μm) Mylar insulation. Because the dielectric strength of polyimides (Kapton) and fluorocarbons (Teflon FEP) are high and films are readily available from Du Pont, it was established that the feasibility to construct laminates made from these materials would be developed.

Options to bond individually formed pieces and the forming of bonded flat laminates were evaluated as well as the options to use convex (male) or concave (female) single surface dies.

Forming of Individual Laminate Films

Forming studies conducted at LLL³ included forming of Kapton film up to 481°C maximum temperature and up to 2 hours at 371°C. Based on this information and the 570°C thermal degradation of Kapton, a forming temperature of 371°C for 30 minutes was selected for the feasibility study. The forming of single Kapton films coated with Teflon FEP, available from Du Pont as Kapton F, was not rigorously evaluated because the melting temperature of the Teflon FEP is approximately 260°C. The 0.002-inch-thick (51 μm) Teflon FEP and 0.004-inch-thick aluminum were formed by conventional techniques.

A draw ring control pressure die (Figure 1) was constructed to form 0.005-inch-thick Kapton film. The die consists of a single concave surface contoured to the desired radius. The flat work piece is located over the die cavity and held in place by a floating seal ring located inside the forming fixture lid. Nitrogen gas was used for the seal ring clamping pressure and the forming pressure to minimize discoloration of the Kapton. The technique developed was to heat the loaded fixture in a furnace preset to 765°F (407°C) with 10 psi (69 kPa) clamp ring pressure until the heated fixture reached 685°F (363°C). The clamp pressure was then increased to 45 psi (310 kPa) and a forming pressure of 35 psi (241 kPa) was applied. The forming pressure was maintained for 30 minutes at a maximum fixture temperature of 710°F (377°C). Forming and clamping pressures are retained until the part is cool. The total cycle time is approximately 4 hours. Parts fabricated

using this technique were found to conform well to existing precision etching fixtures, and over 90 parts were fabricated to support the PVD process development. Mechanical forming (Figure 2) was evaluated as a means of obtaining formed 0.005-inch-thick Kapton film with a 1 hour total cycle time. Special handling was required to obtain a satisfactory fit on the furnace heated laminating fixture and to prevent radial scratches from being exposed on the concave plating substrate surface. The special handling consisted of simultaneously forming two 0.005-inch-thick Kapton pieces, and using increasing pressure [14 to 75 psia (96.5 to 517 kPa)] to oppose the male die during the forming cycle. The positions of the pre-formed parts were then reversed relative to the male die for bonding. Some intermittent pits observed on the mating Kapton surfaces require investigation and additional development will be required for laminate fabrication.

Bonding of Individual Formed Films

A bonding fixture (Figure 3) consisting of a convex die surface was used to fusion bond laminates of the individually formed pieces. A Kapton blanket was clamped over the assembled laminate so that a vacuum could be applied to the assembly during the bonding cycle. It was established that a bonding cycle of 2 hours in a furnace preheated to 625°F (329°C) would affect a bond. Ten laminates were fabricated by the method and two were coated with aluminum by the PVD process without apparent degradation of the laminate bond. This method is considered satisfactory except for the process flow through time that requires three

Figure 1. Draw Ring Control Pressure Die

Figure 2. Mechanical Forming

Figure 3. Furnace Heated Laminating Fixture

furnace cycles per assembly. Modifications were required to bond mechanically formed films. The assembled laminating fixture was placed in the draw ring control pressure die (Figure 4) so that 40 psi (276 kPa) over pressure could be applied to the laminate. The loaded fixture was subjected to a furnace temperature of 700°F for 2 hours, and a thermocouple located within the fixture indicated a temperature of 640°F (338°C). Five laminates were fabricated by the technique, and the method can be developed if individually formed pieces are required for laminate fabrication.

Forming Flat Laminates

Flat laminates were bonded at Bendix using Kapton F (Kapton H coated with Teflon FEP). Forming of these laminates at 700°F resulted in blisters in the aluminum. Samples of the blisters were then heated to 700°F and the outgassed products analyzed using a mass spectrometer. There was no indication of FEP degradation products in the outgassed components of the blister area and it was concluded that these blisters resulted from entrapped air during initial lamination. A flat platen press and a roller laminator were explored as methods to bond laminates with FEP. It was concluded that existing equipment for these concepts will require development to laminate panels as large as 12 inches by 12 inches (305 mm by 305 mm).

Laminates of 0.005-inch-thick aluminum/0.005-inch-thick Kapton/0.005-inch-thick Kapton fusion bonded with Teflon FEP were purchased from the TME Corporation. Attempts to form this material with the female die (Figure 1) and the male forming fixture (Figure 5) resulted in loss of contour and bond at the aluminum FEP interface. Because this failure seemed related to shrinkage of the middle layer of 0.005-inch-thick Kapton, laminates of 0.005-inch-thick aluminum/0.002-inch-thick Kapton/0.005-inch-thick Kapton were purchased from TME. Laminates were formed at 350°F (177°C) using

Figure 4. Laminating Fixture Modified For Over-Pressure

Figure 5. Male Forming Fixture

a pressure form die (Figure 6). The formed laminates were stabilized for 2 hours at a furnace temperature of 700°F. The preformed laminates were assembled in the furnace heated laminating fixture with a preformed Kapton pressure blanket. The assembled laminating fixture was placed in the draw ring control pressure die so that vacuum and over pressure could be applied during the

Figure 6. Pressure Forming Fixture

thermal cycle (Figure 7). There was no indication of bond failure, and the feasibility to fabricate two parts per day was established. One laminate was aluminum plated by the PVD process without apparent bond degradation. Laminates of 0.005-inch-thick aluminum/0.005-inch-thick Kapton/0.005-inch-thick Kapton were preformed using the pressure form die. One of these laminates stabilized with the laminating fixture and a Kapton pressure blanket was satisfactory; however, the use of a new blanket resulted in bond failure at the aluminum to Kapton interface. The assembly was modified by evacuating the space between the laminate and a male formed pressure blanket. Laminates stabilized by the modified technique were improved, and development to form and stabilize thick laminates will be continued.

Evaluation of Kapton Film and Laminates

Laminates

The evaluation of thermal stability of laminates was initiated and one laminate subjected to simulated bonding cycles at temperatures up to 500°F was determined to be functionally stable when compared to fabrication tooling location holes.

Figure 7. Laminating Fixture Modified For Stabilization

A part was made with preformed 0.004-inch-thick aluminum, one layer of furnace formed 0.005-inch-thick Kapton, and one layer of furnace formed 0.005-inch-thick Kapton that was coated with aluminum by the PVD process. The components were bonded with preformed FEP using a furnace heated laminating fixture. The bond cycle was 2 hours at a furnace temperature of 625°F (329°C). The deposited aluminum was isolated from the male fixture by a 0.005-inch-thick Kapton cull sheet. There was no indication that the 625°F bonding cycle degraded the adhesion of the PVD aluminum to Kapton.

As-Received Kapton Film

Samples of 0.005-inch-thick Kapton H have been aged at 500°F for 34 days to evaluate shrinkage. One lot of material (mill roll No. 04528) was sectioned to produce both flat (12 inch by 12 inch) and formed samples selected from the beginning, middle, and end of the roll. Periodic measurements were made on the flat samples to provide shrinkage data (Figure 8). The maximum dimensional change was observed within six days at approximately 0.8 percent with a total change of 1.3 percent at the end of 34 days. DuPont XH-649 low shrink material was also evaluated and found to have decreased shrinkage in the transverse direction only. Tensile strength and elongation specimens cut from unaged and heat aged (260°C) Kapton H and XH-649 were tested (Table 1). The tensile strength of all unaged specimens was about 27,000 psi (186 MPa) and was about 23,000 psi (159 MPa) for the aged. The elongation for the unaged samples averaged about 55 percent and for the heat aged samples about 20 percent. This indicates that the Kapton was embrittled by long term heat aging.

Figure 8. Kapton Shrinkage (As Recieved)

Formed Kapton Film

Contour and thinning measurements were made on formed parts that were aged at 500°F for 34 days. Measurements were made for unaged (control) samples to evaluate changes resulting from 34 day exposure to 500°F. The contour measurements were made with an optical comparator by measuring the contour height at 0.5000-inch (12.70 mm) cord intervals. The deviation from the nominal radius was then calculated, and data for unaged and aged parts is presented in Table 2. The data indicates that the portion of the formed pieces required for product changes slightly as a result of thermal aging. This is shown schematically in Figure 9. Thinning data indicates that the thickness of the 0.005-inch-thick Kapton is decreased by approximately 0.001 inch for parts formed with the furnace-heated, draw-ring-control pressure die.

Table 1. Mechanical Properties of 0.005-Inch (127 μ m) Kapton, Unaged and Aged at 500°F (260°C) for 34 Days

Sample	Roll Direction	Tensile Strength		Elongation Percent
		psi	(MPa)	
Unaged Beginning of Roll	Machine	29,200	201	58
	Transverse	27,900	192	67
Unaged Middle of Roll	Machine	27,800	192	55
	Transverse	27,200	188	55
Unaged End of Roll	Machine	27,700	191	55
	Transverse	27,200	188	55
Aged Beginning of Roll	Machine	23,100	159	22
	Transverse	24,300	168	22
Aged Middle of Roll	Machine	22,100	152	22
	Transverse	24,700	170	22
Aged End of Roll	Machine	23,200	160	22
	Transverse	24,200	167	20
Oven Cycled H*	Machine	28,900	199	43
	Transverse	28,700	188	42
Unaged XH 649	Machine	27,600	190	57
	Transverse	28,500	196	57
Aged XH 649	Machine	22,000	152	18
	Transverse	25,200	174	15
*Simulated forming cycle: 700°F (371°C) for 30 minutes				

Table 2. Contour Height Data For Formed 0.005-Inch (127 μ m) Kapton

Cord Interval (mm)	Contour Height Deviation From Nominal Radius (μ m)									
	Unaged		Beginning of Roll Aged at 500°F 34 Days		Middle of Roll Aged at 500°F 34 Days		End of Roll Aged at 500°F 34 Days		Kapton XH-649 Aged at 500°F 34 Days	
	Machine Direction	Transverse Direction	Machine Direction	Transverse Direction	Machine Direction	Transverse Direction	Machine Direction	Transverse Direction	Machine Direction	Transverse Direction
+102	-2.54	+340	+1750	+1788	+2131	+2118	+2283		+1661	+1750
+88.9	-259	-17.8	+287	+490	+401	+452	+528	+897	-211	+325
+76.2	-208	-68.6	+96.5	+297	+122	+109	+71.1	+478	-107	+7.62
+63.5	-122	-229	+94.0	+208	+68.6	+68.6	+30.5	+361	-58.4	-7.62
+50.8	-48.3	-5.08	+83.8	+198	+71.1	+83.8	-5.08	+249	+45.7	-45.7
+38.1	+20.3	-7.62	+81.3	+183	+81.3	+43.2	+5.08	+183	+119	+81.3
+25.4	+2.54	-2.54	+112	+137	+73.7	+61.0	+48.3	+124	+124	+48.3
+12.7	0.00	-12.7	+50.1	+38.1	+25.4	+25.4	+76.2	+38.1	+63.5	+12.7
0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
(Midpoint)										
-12.7	0.00	-12.7	-38.1	-50.1	+102	+76.2	-63.5	+25.4	0.00	-38.1
-25.4	-53.3	-27.9	53.3	-142	+239	+264	+10.2	+35.6	+86.4	-35.6
-38.1	-109	-33.0	-71.1	-185	+272	+310	+43.2	+94.0	+107	-7.62
-50.8	-170	-81.3	-170	-246	+287	+338	+76.2	+135	+83.8	-43.2
-63.5	-224	-96.5	-211	-287	+284	+361	-45.7	+170	-274	-83.8
-76.2	-297	-107	-285	-208	+262	+312	-43.2	+300	-94.0	-145
-88.9	-373	-43.2	+7.62	+173	+554	+554	+338	+719	+249	+122
-102	+10.2	+353	+1724	+1699	+2106	+2106	+2245	+2512	+1674	+1763

CONTOUR OF KAPTON H (UNAGED)

CONTOUR OF KAPTON H AGED AT 500°F FOR 34 DAYS

Figure 9. Contour Change of Formed Kapton as a Result of Thermal Aging

Thermomechanical Analysis (TMA) of Kapton Film

Samples of formed Kapton parts and temperature cycled flat sheets were analyzed by TMA to characterize shrinkage as a function of temperature. Specimens were taken from each sample at different stress points, both perpendicular and parallel to the stock roll directions. A computer program was prepared to execute the mathematical computations, provide regression analysis, and plot the resulting data. Shrinkage was not detected with the normal TMA thermal cycle. Special experiments were conducted by holding the samples isothermally at a temperature near 300°C and measuring the displacement as a function of time. As-received material showed about 5 percent loss of normal extension in 2 hours. For the sample size used, this extension loss is equivalent to less than 1 percent total shrinkage. All samples tested from processed material that had been thermocycled showed no shrinkage in 2 hours. From these experiments, it is concluded that residual strain in 0.005-inch-thick Kapton formed at 700°F cannot be detected by normal TMA methods and that shrinkage is so time-dependent that shrinkage characterization by normal TMA methods is not practical.

Evaluation of Adhesives

Functional evaluation of the Teflon FEP adhesive has consisted of laminate and part fabrication. Laminates were fabricated by bonding 0.004-inch-thick aluminum/0.001-inch-thick FEP/0.002-inch-thick Kapton/0.001-inch-thick FEP/0.002-inch-thick Kapton. The bonds were made with a flat laminating fixture using vacuum and 30 psi over-pressure for 30 minutes at 600°F (316°C). Parts were formed from the laminates with forming pressure applied at 700°F, 450°F, and 150°F (371°C, 232°C, and 66°C) respectively. Bonds were similar for all parts, and it was concluded that gross thermal degradation of the FEP does not occur during a 700°F thermal cycle. Peel strength tests were made to obtain bond strength data before and after forming of laminates. Samples 0.5 inch wide (13 mm) and 9 inches long (229 mm) were pulled at a rate of 5 inches (127 mm) per minute. Data was obtained for flat laminates made and formed at Bendix and for flat laminates obtained from TME. The average bond strength in pounds per inch and the lowest bond strength in pounds per inch were measured for each sample; the data ranged from 0.15 lbs/in. (26 N/m) to 8.0 lbs/in. (1400 N/m) as shown in Table 3.

Bond strength tests at temperatures up to 500°F (260°C) were made for 0.005-inch-thick aluminum/0.005-inch-thick Kapton/0.005-inch-thick Kapton laminates received from TME. One-half-inch wide samples were pulled using a tensile machine without peel radius control. Bond strength decreased to a minimum of about 0.04 lbs/in. (7 N/m) at a temperature of approximately 300°F (149°C) (Figure 10). Samples subjected to 500°F were examined at room temperature and bond strength of the adhesive was high enough to cause the 0.005-

Table 3. Peel Strength Data Using Heat Sealable FEP

	Average Reading	N/M	Lowest	N/M
	lbs/in.		Per Sample	
BKC Flat Laminate (Kapton-Al)	2.10	368	1.88	329
Formed Laminate (Kapton-Kapton)	0.86	151	0.80	140
Formed Laminate (Kapton-Al)	1.56	273	0.94	165
Formed Laminate (Kapton-Kapton)	0.88	154	0.15	26
TME Laminate As Rec'd (Kapton-Al)	8	1400	5.6	981

Figure 10. FEP Bond Strength Versus Temperature

inch-thick Kapton to break before failure occurred at the adhesive/Kapton interface. Evaluation of this adhesive will continue and include stability of formed laminates as a function of temperature.

One laminate was fabricated using a condensation reaction polyimide adhesive. Material for the laminate was prepared by spray application of adhesive to flat panels and post curing at 400°F (204°C) to form a film. One layer of 0.004-inch-thick aluminum and two layers of 0.005-inch-thick Kapton were then laminated with the flat laminating fixture using vacuum and 30 psi (207 kPa) over-pressure for 30 minutes at 600°F. The resulting laminate was brittle, indicating degradation of the base Kapton. This laminate was formed at 700°F using the draw ring control pressure die and exhibited loss of bond and contour at the aluminum to Kapton interface. One laminate was fabricated by bonding individually formed 0.005-inch-thick Kapton to aluminum with a Du Pont modified acrylic adhesive reported to have a 4 to 5 lbs/in. (700 to 875 N/m) bond strength at 500°F. The adhesive supplied as a 0.002-inch thick film was preformed between FEP at 100°F (38°C) using a pressure form die. A bond cycle of 375°F (196°C) was used for 30 minutes with vacuum and 40 psi (276 kPa) over-pressure. The resulting laminate indicated lack of complete adhesive flow and higher pressure will be used to fabricate parts for adhesive evaluation.

ACCOMPLISHMENTS

Basic methods to fabricate functional laminates of Kapton film were established, and data obtained for individually formed 0.005-inch-thick pieces that indicate contour stability for 34 days at 500°F. Methods to apply Teflon FEP adhesive film were established and the evaluation indicates that although bond strength is low at temperatures above 300°F (149°C), the adhesive does not permanently degrade through processing cycles up to 700°F (371°C).

FUTURE WORK

Development to form and stabilize commercially available flat laminates will be continued to determine the requirements for reliable fabrication. Activity will include the examination of thermal cycles used during stabilization and fabrication variables associated with commercially available flat laminates.

Development of laminates fabricated from individually formed films will include the evaluation of commercially available film adhesives such as Pyralux WA/A (a modified acrylic supplied by DuPont). A thermoset adhesive provides the potential of lower temperature requirements for the bonding cycle and provides a better surface than Teflon FEP. Fabricated laminates will be subjected to a 300°F (149°C) aging study for 30 days to determine thermal stability. Measurements will be made to determine the change in contour, dielectric strength and bond strength caused by thermal aging.

Other probable future work will include the consideration of equivalent insulation materials such as polyimides, polyphenylenes and silicones. Initial activity will be to develop liquid adhesives for Kapton film with consideration of direct film fabrication. Commercially available polyimides and polyamide-imides will be tested.

REFERENCES

¹L. E. Peck and R. Kirzey, *Dielectric Materials Development*, Lawrence Livermore Laboratory, University of California, June 1974.

Appendix A

HIGH TEMPERATURE NONPLANAR LAMINATE FABRICATION

SUMMARY

Materials and lamination techniques have been selected to fabricate spherical substrates for the physical vapor deposition (PVD) of aluminum. The laminates are mechanically stable through subsequent fabrication operations that include oven drying at 150°C for 2 hours, PVD of aluminum at 200°C for 20 minutes within a vacuum, and bonding operations. Dimensions and dielectric strength are retained through unrestrained aging at 150°C for 35 days; however, the adhesive bond strength decreases by 50 percent.

Pyralux WA/A film adhesive (a modified acrylic supplied by Du Pont) is formed at 90°C and used to bond the laminate layers with a thermal cycle of 35 minutes at 190°C and 100 psi (689 kPa) pressure. The laminate layers consist of two pieces of 5-mil (127 μ m) Kapton formed at 370°C and one piece of 4-mil (102 μ m) aluminum formed at room temperature. The selected techniques are currently being applied to support orders.

Two adhesives were evaluated by laminate fabrication. Teflon FEP fusion bonds were made using a form die with a bonding cycle of 2 hours and a furnace temperature of 330°C. The Pyralux WA/A adhesive was selected because the Teflon FEP exhibited low (0.04 lb/in. [7 N/m]) bond strength above 150°C compared to 2 lb/in. (350 N/m) for Pyralux. No additional work is planned for these two adhesives; however, polyimide and polyamide-imide adhesives will be investigated to improve the laminate thermal resistance.

The feasibility of forming spherical substrates from pre-bonded flat laminates was investigated. Laminates fabricated with Teflon FEP, Pyralux, and modified epoxy adhesives were processed. The Pyralux and modified epoxy adhesives degraded at the 370°C required to stabilize Kapton. The Teflon FEP bond strength was not adequate to develop a reliable forming process. Flat laminate forming development will continue using adhesives that retain bond strength without degradation at 370°C. A polyimide material (Du Pont PZ-5077) is currently being investigated and preliminary forming experiments with laminates using this adhesive have been encouraging.

DISCUSSION

SCOPE AND PURPOSE

The purpose of this project is to develop stable, high temperature, nonplanar laminates suitable as substrates for metal deposition to fabricate spherical parts. The development includes the forming of readily available Kapton and film adhesives. Thermal stability of the bonded laminate is required for subsequent processing and certification. A 30-day aging test at 150°C is used to determine unrestrained thermal stability.

Fabrication development includes alternate approaches such as forming multilayered flat laminates and direct fabrication of shaped dielectric materials. The reported activities were accomplished between January and July 1975.

PRIOR WORK

Basic methods to form Kapton film and fabricate laminates were previously developed. Fabrication approaches that were explored included the evaluation of forming multilayered flat laminates and forming of individual laminate materials. Polyphenylene sulfide material properties² were evaluated for potential application. The prior development served as a basis for development activities to select present laminate fabrication techniques.

ACTIVITY

Background

Polyimide film (Kapton) is used to form 90-degree spherical segments. Two layers of formed Kapton film and one layer of formed aluminum are bonded using conventional laminating techniques.³ The film adhesives used are formed by conventional forming methods. The bonded laminate provides a substrate for a subsequent PVD process to obtain a second layer of conductive aluminum. Pressure forming of flat multilayer laminates is being developed to reduce the number of thermal cycles required for laminate fabrication.

Lamination of Formed Kapton

Six laminates of 4-mil aluminum/5-mil Kapton/5-mil Kapton (102 μm , 127 μm , 127 μm) that were fabricated with Teflon FEP, and six laminates that were fabricated with Pyralux WA/A adhesive were aged in the free state at 150°C for 35 days. The 5-mil Kapton film was formed at 370°C using a furnace heated pressure form die (Figure 1). The aluminum and adhesives were formed with conventional pressure-form dies. The laminates that were fusion bonded with FEP were made using a bonding-form die (Figure 2) with a bonding cycle of 2 hours and a furnace temperature of 330°C. The laminates bonded with Pyralux WA/A (a modified acrylic) were made using a conventional laminating fixture and a bond cycle of 190°C for 35 minutes. Two laminates from each adhesive group warped in the unrestrained configuration during thermal aging, however all laminates conformed well to the contour and location holes of existing fabrication tools.

Bond strength tests at temperatures up to 260°C were made for 4-mil aluminum/5-mil Kapton/5-mil Kapton laminates bonded with Pyralux WA/A. Samples 0.5 inch (12.7 mm) wide were evaluated using an Instron tensile machine without peel radius control. Bond strength decreased to a minimum of about 0.2 lb/in. (35 N/m) at 260°C for the Kapton to Kapton bond (Figure 3). The same samples after being subjected to 260°C were examined at room temperature and bond strength was high enough to fail the 5-mil Kapton although some exposed adhesive discoloration was noted. This data compared to previously obtained data for Teflon FEP¹ bonds that decreased to a minimum value of about 0.04 lb/in. (7 N/m) with some delamination after the 260°C exposure.

The Pyralux WA/A film adhesive is supplied with a polyester slip sheet and it was determined that the material could be formed at 90°C prior to removing the slip sheet. Because the adhesive has thermoset characteristics, an Audrey dielectric analysis was performed to determine the effect of forming temperatures. Samples were placed in an unheated press under 200 psi (1.38 MPa) pressure. The samples were heated at a constant rate to specific temperatures of 120, 150, 175, and 200°C and allowed to cure for 30 to 120 minutes. All samples exhibited essentially the same behavior, indicating that all four temperatures would provide a cure.

Several samples were tested at 90°C to determine whether any change could be induced. These samples appeared to be unaffected and cured as expected at 175 to 200°C. Dissipation was monitored during heat-up and cool-down to evaluate the adhesive cure. Unless degradation takes place, the heat-up and cool-down cycles are identical for a true thermoplastic or fully cured thermoset. It was determined that irreversible changes suggestive of a cure

Figure 1. Furnace Forming Fixture

Figure 2. Bonding Fixture

Figure 3. Adhesive Bond Strength Versus Temperature

occurred. However, the relationship between dissipation versus temperature at two frequencies (100 and 1000 Hz) is such that any changes may be related to molecular realignment rather than toward crosslinking.

There is also a lack of the intense variation in the dissipation which is common in thermosets and representative of catalyst interaction.⁶ The lack of change suggests that no crosslinking or chain extension has happened which would make the molecule less responsive to high frequencies and increase the power loss (dissipation) at 1000 Hz. As a result of the analysis it was concluded that the Pyralux WA/A does exhibit a structural change or realignment that can be called a cure and that this cure can occur over a wide temperature range (120 to 200°C).

The dielectric strength of laminates fabricated with both Teflon FEP and Pyralux was measured before and after thermal aging at 150°C for 35 days. The results (Table 1) indicate good dielectric strength retention.

It was concluded that laminates can be fabricated from individually formed materials, and, although the laminate thermal stability is

Table 1. Dielectric Strength of Laminates Before and After Thermal Aging at 150°C for 35 Days

Laminate Identification	Dielectric Strength (kVdc)	
	Before Aging	After Aging
H1001 (FEP)	65 to 58	53 to 52
H1004 (FEP)	63 to 52	58 to 58
HD001 (Pyralux)	57 to 54	61 to 58
HD004 (Pyralux)	74 to 46	47 to 44

limited by the adhesives, the developed process is satisfactory. The Pyralux adhesive provides a better surface than Teflon FEP for assembly bonding after the circuit pattern is etched in the formed aluminum and will be used until higher temperature adhesives have been selected.

Thermogravimetric analysis (TGA) verified that the solvent in Kerimid 501 polyamide-imide film is completely removed after 4 hours under vacuum at 150°C. Solvent has been removed from 12-inch (305 mm) square samples for forming evaluation. It is expected that the formed film can be evaluated as a higher temperature adhesive for bonding individually formed Kapton.

Forming Flat Laminates

Pressure forming of multilayered laminates provides an approach that will inherently reduce the number of thermal cycles required for laminate fabrication. Initial pressure forming experiments using aluminum/Kapton/Kapton laminates fusion bonded with Teflon FEP were unsuccessful; however, five laminates were satisfactorily pressure formed at 175°C and stabilized for 2 hours at a furnace temperature of 370°C using a restraining (stabilization) mandrel. Additional laminates were processed and visual evidence of laminate bond failure was encountered.

Flat laminates of 5-mil aluminum/2-mil Kapton/5-mil Kapton (127, 51, 121 μ m), and laminates of 5-mil aluminum/5-mil Kapton/ 5-mil Kapton obtained from the TME Corporation were processed with similar results. Process modifications to eliminate defects included the use of a wire bleeder ring and grit blasted Kapton pressure blanket to improve the mechanical restraint during stabilization (Figure 4). Delamination was minimized; however,

Figure 4. Stabilization of Preformed Laminates

small areas of bond failure were evident at the aluminum to Kapton interface.

Flat laminates were formed at 175°C with the pressure form die and furnace stabilized at different temperatures to examine the effect of the thermal cycle on residual stress observed in the FEP fusion bonded laminates. The residual stress was observed as warpage when the contoured portion of the part was removed from the flat brim. The warpage was greater for the 5-mil aluminum/2-mil Kapton/5-mil Kapton than for the 5-mil aluminum/5-mil Kapton/5-mil Kapton, indicating a compressive stress in the aluminum.

Furnace temperatures up to 400°C and times in the furnace up to 4 hours were examined. The residual stress was not reduced sufficiently to retain a good bond at the aluminum-to-Kapton interface. One laminate was furnace cooled overnight to cool the laminate uniformly with the stabilization mandrel. The residual stress was minimized and the bond integrity maintained. It was concluded that special equipment development is required to restrain laminate layers and control cooling rate for reliable fabrication.

Laminates were fabricated to examine the effect of a 260°C stabilization cycle. Flat laminates bonded with Pyralux WA/A were preformed at 175°C with a pressure-form die. The laminates were stabilized using a conventional laminating fixture with vacuum and 100 psi (689 kPa) over pressure, heated to 500°F in 25 minutes, maintained at temperature for 45 minutes, and then cooled to 40°C in 45 minutes. The stabilized laminates were destructively examined and found to be very brittle in the contoured area and flexible in the flat (brim) unformed area.

A flat laminate fusion bonded with Teflon FEP was preformed and stabilized by the same technique and found to exhibit similar

embrittlement. A laminate was fabricated with the 260°C thermal cycle using Kapton preformed at 370°C, Teflon FEP at the aluminum to Kapton interface, and Pyralux WA/A at the Kapton to Kapton interface (Figure 5). The resulting laminate was flexible in the contoured area and the flat unformed area. It was concluded from these experiments that stabilized Kapton is not embrittled by the 260°C thermal cycle, and additional investigation will be required to establish the effect on preformed flat laminates.

Flat laminate samples submitted by the Rexham Corporation were evaluated to determine compatibility with forming processes. Pressure forming at 370°C and 320°C caused adhesive degradation. One laminate was pressure formed at 175°C; however, delamination occurred prior to stabilization at 260 to 315°C. Laboratory characterization of the adhesive indicated an epoxy type with added plasticizer.

Flat laminates of aluminum/Kapton/Kapton were fabricated using DuPont Pyralin PZ-5077 polyimide adhesive. The flat samples were spray coated with the adhesive and press bonded using 500 psi (3.45 MPa) pressure and the following stepwise temperature cure cycle: 20-minute dwells at 120, 175, and 220°C, and a 90-minute dwell at 250°C. These laminates were well bonded, but the Kapton was very brittle.

Three of the flat laminates were formed at 370°F using a pressure form die. No delamination occurred during the thermal cycle and the parts were much less brittle; however, the Kapton and adhesive had turned black. One of the laminates subjected to the forming cycle fractured without forming. The fracture point was brittle and the remainder of the part was flexible. This laminate was also black.

Samples of the brittle laminate were reviewed with Du Pont. It is currently believed that the brittleness is caused by the by-product moisture from the curing of the PZ-5077 adhesive. The blackening is possibly caused by the residual N-methylpyrrolidone (NMP) in the adhesive. Work is continuing to remove more of the NMP and to further precure the adhesive to eliminate water, a by-product of the reaction.

Bismaleimide (BMI) type polyimides are being considered as adhesives for Kapton and potential Kapton replacement. Laboratory processes have been developed to produce BMI resins. Melt blends of BMI and methylenedianiline have been prepared to evaluate the ratio used in commercial products. The Hexcel Corporation has been contacted regarding a commercially available BMI type uncured film (F-178).

Figure 5. Laminate Assembly for 260°C Thermal Cycle

Stability of Materials

A study was initiated to determine the effects of temperature on the chemical stability of Kapton films. A literature search located many studies dealing with the effects of temperature and aging on Kapton films. Studies have included hydrazinolysis, infrared analysis, thermogravimetric analysis (TGA), and other techniques on films aged at 425°C. Reaction mechanisms have been reported for oxidative degradation.^{7,8,9} The mechanism involves initial oxidative attack on the amine derived oxyphenylene rings with subsequent free radical reactions forming crosslinked material, CO₂, and pendent carboxyl groups. The imide linkage, however, seems to remain relatively intact, as evidenced by the absence of reported amine detection. Aniline, amino phenol, and their oxidation products are formed upon chemical cleavage of the imide ring through hydrazinolysis, indicating phenyl ether bond fission occurs during oxidation. Aqueous potassium hydroxide reacts with Kapton fairly rapidly at room temperature and was investigated as a saponification media to determine the relative degree of oxidative degradation of Kapton during various processing conditions.

The visible depth of color (absorbance) of saponification reaction media and the water solubility of the saponified polymer were determined. Four types of samples were examined: unaged Kapton film; Kapton film aged for 34 days at 260°C; Kapton parts formed at 370°C; and laminate fabricated from individually formed Kapton. Essentially no degradation products are seen in saponification reaction media of unaged film as evidenced by very low absorbance (low color development). Aged or processed film, on the other hand, showed significant absorbance after 24 hours, and a sample which had been exposed to 370°C showed a greater degree of oxidative degradation than a sample which was aged for 34 days at 260°C. The absorbance observed from the laminate was approximately the same as that from unaged film; however, it is expected that saponification was hindered as a result of etch solution exposure and the FEP coating.

Samples of film, after soaking in 2N KOH for two weeks, were tested for solubility in water. Both unaged film and film aged for 34 days at 260°C were totally soluble in water after the KOH treatment. Samples formed at 370°C and treated with KOH were either insoluble or formed large bulky gels upon the addition of water, indicating substantial crosslinking had occurred during the forming process.

Kapton film (5 mil) was tested to determine the dielectric strength of as-received, 370°C formed, and 260°C aged material. Two locations were tested for each of three samples and the dielectric strength ranged from 28-40 kVdc (Table 2).

Peel strength test strips of aluminum/Kapton/Kapton bonded with Pyralux adhesive were aged from 1 to 35 days at 150°C and then peel-tested at room temperature. The film failed in all tests when the load was applied to the Kapton/Kapton bond. The Kapton to aluminum bond had an initial peel strength of 6 lb/in. (1051 N/m); however, after 10 days of aging the strength dropped to 4 lb/in. (701 N/m) and was 2.5 lb/in. (438 N/m) after 35 days at 150°C.

It is concluded that Kapton film provides adequate chemical, thermal, and dielectric stability and that the adhesive stability is marginal. The effect of humidity on dimensional change has been reported to be as high as 0.1 percent over a changing relative humidity of 11 percent to 72 percent. Equilibration of 3 hours has been recommended by Du Pont⁸ for precise dimensional measurements. The functional effect of humidity will be considered as new materials and techniques are developed.

ACCOMPLISHMENTS

Materials and processes have been selected to fabricate formed Kapton laminates suitable for metal deposition by physical vapor deposition. An adhesive has been selected to bond individually formed films and data obtained that indicates dimensional and dielectric stability for 35 days at 150°C; however, the thermal stability of Kapton laminates is limited because of adhesive bond strength.

FUTURE WORK

New thermally stable adhesives for lamination will be investigated. Du Pont has recommended specific silicone adhesives that will be evaluated in addition to the polyimide and polyamide-imide types. Methods to reduce fabrication cycle time will

Table 2. Dielectric Strength of 5-mil Kapton (Processed and Aged)

Sample Identification	Dielectric Strength (kVdc)
Formed at 370°C - A	34 to 38
Formed at 370°C - B	30 to 33
Formed at 370°C - C	28 to 31
As-Received - D	36 to 38
As-Received - E	30 to 40
As-Received - F	38 to 38
Aged 34 days at 260°C - G	34 to 37
Aged 34 days at 260°C - H	38 to 39
Aged 34 days at 260°C - I	31 to 32

include the continued evaluation of flat multilayered laminate processing with a single thermal cycle. New dielectric materials such as liquid or uncured film polyimides will be investigated to replace Kapton film and provide a potential direct method of PVD substrate fabrication.

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Appendix B

ADHESIVES FOR HIGH-TEMPERATURE NONPLANAR LAMINATES

SUMMARY

Nonplanar laminates were used as substrates for metal deposition. Adhesive is used to bond two layers of formed Kapton (polyimide film) and one layer of formed aluminum prior to physical vapor deposition (PVD) of a second layer of aluminum. The laminate adhesive must withstand the subsequent elevated temperatures of the PVD process, it must maintain its integrity during assembly bonding, and it must remain stable during long term aging.

Commercially available film adhesives were evaluated and found to be compatible with existing forming and bonding processes; however, the temperature resistance is marginal at 150°C and the adhesives cannot be considered for the forming of flat laminates at 370°C. Condensation reaction polyimide adhesives available as liquids were examined. The high boiling point (200°C) of the N-methylpyrrolidone (NMP) used to solvate these adhesives complicates processing. Solvent removal and elimination of water as a by-product of the condensation reaction is required prior to bonding. One adhesive of this type, Du Pont NR 150A, is thermoplastic and can be polymerized prior to fusion bonding. This adhesive was subjected to 370°C thermal cycles and will be considered for high temperature (300°C) lamination.

Bismaleimide (BMI) polymers were evaluated as adhesives for flat laminate fabrication and forming at 370°C. The solid resins were used in the powder form to establish thermal resistance and bond strength. Commercially available BMI with added methylenedianiline (MDA) was found to degrade during the 370°C forming cycle; however, BMI without MDA exhibited good thermal stability and Kapton adhesion. Laboratory formulation of BMI derivatives will be continued to improve adhesion to aluminum, and solvent systems will be investigated for application by commercial laminating firms.

SCOPE AND PURPOSE

High-temperature nonplanar laminates were used as substrates for metal deposition. The laminates consist of two 0.13-mm layers of Kapton and one 0.10-mm layer of aluminum bonded with adhesive. The laminate adhesive must be compatible with subsequent processing such as physical vapor deposition (PVD) and must remain stable after long term aging. The laminates are exposed to temperatures up to 200°C in a vacuum during the PVD process. Development includes the forming and application of film adhesives and the investigation of high temperature polymers that can be used to bond flat laminate layers prior to forming at 370°C. The reported activities were accomplished between August 1975 and February 1976, and the work is continuing.

PRIOR WORK

An adhesive was previously selected to fabricate laminates from individually formed Kapton and aluminum. The film adhesive is supplied by Du Pont and is characterized as a modified acrylic. The adhesive is satisfactory for subsequent processing; however, bond strength decreases by 50 percent after aging at 150°C for 30 days. The prior development served as a basis for development activities to evaluate adhesives with higher temperature capability and the consideration of forming prebonded flat laminates at 370°C.

ACTIVITY

Film Adhesives

Six film adhesives have been investigated (Table 1). Data for Teflon FEP and Du Pont Pyralux has been previously reported, and Pyralux WA/A was selected for laminate fabrication. Pyralux was examined by mass spectrographic and thermogravimetric (TGA) methods. The TGA indicates a 2-percent weight loss at 300°C and the beginning of thermal degradation. Laminates made with Pyralux were examined by mass spectrographic methods to determine outgassing characteristics of edge-exposed adhesive. Samples were subjected to an atmospheric bake at 150°C and 200°C prior to analysis. Additional samples were subjected to a vacuum bake at 150°C and 200°C prior to analysis. It was concluded that a vacuum bake at 200°C significantly reduces the outgassing for temperatures up to 180°C. A sample that had been baked and

Table 1. Film Adhesives Tested

Product Designation	Supplier	Material Type
Teflon FEP	Du Pont	Fluorocarbon
Pyrallux WA/A	Du Pont	Modified Acrylic
Skin Stick 400	Hexcel	Nylon Phenolic
Rexham 41B	Rexham	Modified Butyral Phenolic
Hexcel F-178	Hexcel	Bismaleimide
Kerimid 501	Rhodia	Polyamide-imide

then cut to expose a fresh edge gave results similar to those from a nonbaked sample.

Laminates fabricated with Pyralux adhesive have delaminated during the PVD aluminum deposition process. Destructive examination of the delaminated parts indicated a lack of adhesion at the Kapton/adhesive interface. Samples of Kapton and aluminum were analyzed by the Meseran³ technique to characterize surface polarity. Three different radioactive chemicals (tridecane, tetrabromoethane, and diethylsuccinate) were used for study. Radioactivity counts per 112 seconds were consistent (less than 100) with each of the chemicals for aluminum and as-received Kapton, indicating that the surfaces were free of polar contamination.

For aluminum or Kapton that was cleaned using an alkaline detergent (Metex) process, the radioactivity counts were greater than 100 with diethylsuccinate, indicating a polar residue. Samples of Kapton formed at 370°C were also evaluated and produced Meseran counts greater than 250 units for both sides of the formed material. The counts were consistent with each of the three chemicals and could not be reduced with trichloroethylene or methylene chloride solvents, indicating a change in surface activity as a result of the thermal cycle. Laminates fabricated with Kapton that had been cleaned using static eliminators to remove particulate matter were plated at a higher than normal plating rate to cause delamination. Examination indicated good adhesion to the Kapton and aluminum, with cohesive failure of the adhesive.

As-received Rhodia film adhesive, Kerimid 501, was used for flat laminate fabrication using a thermal cycle of 250°C for 15 minutes with vacuum and 700 kPa over-pressure. One laminate

formed at 370°C with a furnace-heated form die delaminated with adhesive degradation and indication of residual adhesive solvent. The polyamide-imide film adhesive with Mylar slip sheet was formed at 135°C using a conventional pressure form die. The material formed well; however, solvent bleeding was evident after the thermal cycle. It was concluded that N-methylpyrrolidone (NMP), which comprised approximately 25 percent by weight of the material, should be removed prior to bonding of individual formed Kapton with formed adhesive.

Additional 501 film adhesive was dried at 105°C for four hours to remove the NMP solvent. The dried film weight loss was about 25 percent and formed satisfactorily at 135°C using a conventional pressure form die. Formed Kapton laminates were bonded with the adhesive using a conventional laminating fixture with a 1-hour cure cycle at 250°C. Destructive examination of the laminates indicated, however, that the adhesive-to-Kapton bond was not acceptable.

A bismaleimide (BMI) type film (F-178) supplied by Hexcel, was evaluated for laminate fabrication. The unsupported film is difficult to handle and must be transferred to a flat bonding substrate. The adhesive was transferred to aluminum and formed well with the aluminum. Bonding to formed Kapton indicated that additional development is required to control excessive flow during a 190°C cure cycle. A flat laminate bonded with the adhesive was found to degrade during the 370°C forming cycle.

Hexcel's Skin Stick 400, a nylon-phenolic film adhesive was also evaluated. Thermogravimetric analysis indicates a 5-percent weight loss at 300°C, where thermal degradation begins; however, five laminates were fabricated with the film adhesive using existing fabrication techniques. The film was formed at 60°C using a conventional pressure form die. The laminates were bonded at 190°C for 1 hour. All laminates were vacuum baked at 200°C without degradation. Four laminates were coated with aluminum by the PVD process. One of the laminates was plated at 17.5 nm/s instead of the normal plating rate of 7.5 nm/s, and delaminated with cohesive failure of the adhesive.

A film adhesive from Rexham Corporation (Type 41B), a modified butyral-phenolic, was evaluated and found to have a bond strength similar to that of Pyralux (Figure 1); however, TGA indicates a lower temperature resistance. It was concluded from functional evaluation, TGA data (Table 2), and bond strength data (Figures 1 and 2) that Pyralux WA/A was the most suitable film adhesive tested.

Figure 1. Film Adhesive Bond Strength Versus Temperature (Kapton-to-Aluminum)

Figure 2. Film Adhesive Bond Strength Versus Temperature (Kapton-to-Kapton)

Table 2. Weight Loss by Thermogravimetric Analysis for Film Adhesives

Adhesive	Percent Weight Loss (at the beginning of thermal degradation)	Degradation Temperature (°C)
Pyralux	2	300
Skin Stick 400	5	300
Rexham 41B	6	260

Liquid Polyimide Adhesives

Three liquid polyimide adhesives, a condensation reaction thermoset (PZ 5077) and two condensation reaction thermoplastics (NR 150B and NR 150A), were evaluated. The solvent used for the three adhesives is NMP. Laboratory techniques were used to prepare samples for functional bonding and forming experiments.

Kapton and aluminum were spray coated with approximately 0.025 mm of PZ 5077. Kapton/Kapton/aluminum laminates were press bonded using 3.5 MPa pressure and a stepwise temperature cure cycle having 20 minute dwells at 120°, 175°, and 215°C and a 90 minute dwell at 250°C. These laminates were well bonded, but the Kapton was very brittle. Three flat laminates were formed at 370°C using a pressure form die. No delamination occurred during the thermal cycle and the parts were much less brittle; however, the Kapton and adhesive had turned black. One of the laminates subjected to the forming cycle fractured without forming. The fracture area was brittle and the remainder of the part was flexible.

Discussions with du Pont technical personnel regarding PZ5077 adhesive confirmed that moisture, a by-product of the condensation reaction polyimide, probably causes the embrittlement of the Kapton when laminated at 250°C, and residual NMP from the adhesive solution probably causes the blackening of the film at 370°C. Panels of PZ5077 coated Kapton and aluminum were then vacuum dried at 105°C for 16 hours prior to bonding. After lamination at 250°C, the laminates were flexible, and, after exposure to 370°C, the darkening due to adhesive degradation was minimized when compared to the previous brittle laminates.

Six additional flat laminates (aluminum/Kapton/Kapton) were fabricated by spraying six light coats of PZ 5077 adhesive and subjecting the panels to 125°C for 10 minutes between coats,

except for the third and sixth coats which were exposed to 260°C for approximately two minutes. The bonded laminates were flexible and light in color compared to previously fabricated laminates that were not exposed to the 260°C temperature prior to bonding. Forming experiments were conducted using a furnace-heated pressure form die. Two laminates formed at 370°C turned dark in color; however, flexibility was retained until the aluminum was removed. The Kapton/adhesive failed in a brittle manner when folded away from the adhesive/aluminum interface. One laminate was formed at 340°C with similar results. One laminate formed at 320°C was light in color and much less brittle after aluminum removal; however, aging studies at 150°C for 100 hours indicated a lack of dimensional stability.

A thermoplastic polyimide adhesive (Du Pont NR 150B) was evaluated for flat laminate forming. The adhesive requires a higher cure temperature (350 to 370°C) than is available with existing flat lamination equipment. A lower-temperature version of the adhesive, NR150A, was also evaluated. Flat laminates fabricated with NR 150A were bonded at 285°C; however, the bond was not uniform, indicating that high pressure (3.5 MPa) and temperature (300°C) may be required for good lamination. Two laminates were formed at 370°C without indication of thermal degradation and with bond strength retention at the aluminum/Kapton, and Kapton/Kapton interfaces.

Polyaminobismaleimide and Bismaleimide Resins

Laboratory activity was initiated to evaluate the use of a commercial polyaminobismaleimide resin system, Kerimid 601 from Rhodia, as an adhesive for Kapton. The use of the Kerimid 601 powder depends upon the development of a technique for depositing a uniform-thickness powder layer on a substrate. Exploratory attempts were made to determine if this powder could be deposited by electrostatic charge. The results were variable in that, with a given physical setup (Figure 3), static attraction between the Kapton and the powder was erratic.

Eight flat laminates (aluminum/Kapton/Kapton) were fabricated using room temperature vacuum dried Kerimid 601 powder adhesive. The laminates were prepared by applying powder to both sides of the unexposed (middle) layer of Kapton which had been dried and given a static charge. The bonds were made with a conventional laminating fixture and a 1-hour cure cycle at 190°C. The cured laminates were approximately 0.38 mm thick, indicating that 0.013 mm of adhesive had been applied to each side of the Kapton. All panels were vacuum dried for a minimum of 4 hours at 150°C prior to bonding.

Figure 3. Electrostatic Application of Powder Adhesive

Cure cycle evaluation included the examination of dwell time within the temperature range (110 to 155°C) at which the powder melts, residual methylenedianiline reacts with bismaleimide, and polymerization is initiated. A cure cycle was selected using a 5-minute dwell at 110, 130, and 155°C, followed by 1-hour at 190°C. Seven of the flat laminates were formed using a furnace-heated pressure form die. The laminates were formed using 240 kPa (35 psi) nitrogen applied at 325°C and maintained for 30 minutes. A maximum temperature of 330°C was noted for each laminate.

All laminates were well formed without evidence of delamination. Aluminum was deposited on three laminates by the PVD process. One laminate developed a blister during the preplating bake at 150°C. The plating reference temperature indicated that the laminates were exposed to 235°C during deposition. Dimensional change was detected (0.8 mm/165 mm) for two formed laminates aged at 150°C for 100 hours. Kapton formed with the same conditions used for the laminates was aged at 150°C for 100 hours. Dimensional change was detected (0.4 mm/165 mm) for the aged Kapton film.

The para methylenedianiline (MDA) based bismaleimide (BMI), a precursor to a polyaminobismaleimide resin system,⁴ was prepared for evaluation as a high temperature (370°C) adhesive. Laboratory samples of ether and sulfone based BMI were also synthesized. An ether based BMI without diamine addition produced an excellent Kapton-to-Kapton bond without discoloration after forming; however, bond failure occurred at the resin/aluminum interface. Two

laminates were processed with similar results. One additional laminate was prepared by precoating and curing the powder on aluminum prior to lamination. The formed laminate exhibited severe loss of adhesion.

The methylenedianiline based BMI was evaluated and found to be similar to the ether based BMI with good temperature resistance, excellent Kapton-to-Kapton bonding, and weak adhesion to aluminum. A laminate fabricated with a sulfone based BMI without diamine addition produced a formed laminate with good Kapton-to-Kapton bonding and without blisters at the aluminum/Kapton interface; however, the aluminum-to-Kapton bond was weak. All laminate materials including the sulfone BMI powder were vacuum dried at 100°C for four hours prior to lamination.

Laboratory samples of polyaminobismaleimide were prepared using both ether and sulfone based BMI. The materials were melt-blended with methylenedianiline and other aromatic diamines to provide a total of eight different combinations of resin powder. Two formulations were evaluated by flat laminate fabrication and forming at 370°C. One laminate, fabricated with a melt blend of six parts ether based BMI to one part methylenedianiline, degraded during the forming cycle. A melt blend of six parts ether based BMI, three-fourths part diaminophenyl ether, and one-fourth part methylenedianiline produced a formed laminate with good Kapton-to-Kapton bonding and a weak bond to aluminum.

Blisters were evident at the aluminum/Kapton interface, and water was the only material detected by mass spectrograph. It was concluded that the diamine addition to bismaleimide reduces thermal resistance (Table 3), and development will be required to provide satisfactory adhesion to aluminum. Peel strength test samples were prepared with BMI powder and tested at temperatures up to 260°C. The Kapton-to-Kapton bond exceeded the Kapton film strength at all temperatures. The Kapton-to-aluminum bond was approximately 35 N/m (0.2 lb/in.) throughout the temperature range; however, this value was increased to 350 N/m (2 lb/in.) by precoating the aluminum with NR 150A adhesive.

Additional formulations will be evaluated with structural modifications aimed at improved aluminum adhesion. It is concluded that bond strength up to 250°C can be attained by priming aluminum with a liquid thermoplastic adhesive (NR150A) and laminating with temperature-resistant BMI resins.

Table 3. Weight Loss by Thermogravimetric Analysis for BMI Resins

Resin	Percent Weight Loss (at beginning of thermal degradation)	Degradation Temperature (°C)
6 parts BMI + 1 part MDA	<1	350
BMI (without MDA)	<1	480
BMI (ether based)	<1	490

ACCOMPLISHMENTS

Film adhesives have been evaluated and found to be compatible with existing forming and bonding processes to construct Kapton-aluminum laminates from individually formed films. The film adhesives are not satisfactory for 370°C forming of prebonded flat laminates. A thermoplastic polyimide adhesive, du Pont NR150A, was selected for high temperature (300°C) flat lamination and has potential for forming thermally stable laminates. Polyaminobismaleimide and bismaleimide resins have been formulated and tested; both have good thermal stability and adhesion to Kapton, but bond strength to aluminum is poor.

FUTURE WORK

Solvents will be evaluated to allow the spray application of bismaleimide and polyaminobismaleimide resins. Flat laminates supplied by commercial laminators will be obtained for forming evaluation. Adhesives for the laminates will be specified by Bendix and will include Dupont NR 150A, bismaleimide type resins with and without solvents, and combinations of the adhesives to obtain satisfactory adhesion to aluminum.

Condensation reaction polyimides will be synthesized using low-molecular-weight ethers as the dispersing solvent rather than N-methylpyrrolidone (NMP). Recent literature^{5,6} indicates that the use of ethers instead of NMP as dispersing solvents in polyimide adhesives results in improved bond strength, greater thermal resistance, and fewer bondline voids. A specific resin system with potential is composed of benzophenonetetracarboxylic dianhydride (BTDA), meta,meta',diaminobenzophenone, and 2-methoxyethylether (diglyme). Meta derivatives of polyaminobismaleimides and bismaleimides will also be evaluated to determine if adhesion

to aluminum is better than that obtained with para derivatives. Specific candidates include: meta,meta',methylenedianiline, meta,meta',diaminodiphenylsulfone, and meta,meta',diaminobenzophenone.

REFERENCES

¹Deleted.

²Deleted.

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⁶D. J. Progar and T. St. Clair, "Solvent and Structure Studies of Novel Polyimide Adhesives," *Polymer Reprints*, Vol. 16, No. 1, April, 1975.