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95,073
BDX-613-534(Rev.)

**EVALUATION OF HIGH TEMPERATURE
DIELECTRIC MATERIAL**

Final Report

November 1973

Bendix Corporation
Kansas City, Missouri

MASTER

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EVALUATION OF HIGH TEMPERATURE
DIELECTRIC MATERIAL

Published November 1973

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PDO 6984375
Final Report

Contract Number AT(29-1)-613 USAEC

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EVALUATION OF HIGH TEMPERATURE DIELECTRIC MATERIAL

November 1973

Prepared by J. C. Daly

Laminated flat cables using Kapton film were fabricated; these cables withstood temperatures up to 1000°F (538°C) for 10 minutes and potentials as high as 20 to 30 kVdc. A superior polyimide adhesive, Thermostik-D', was originated in the Bendix Polymer Laboratory, and a moldable polyimide powder and a process for using it were developed. These materials exhibit electrical strengths up to 625 volts/mil (24 kV/mm) and temperature resistance as high as 850°F (454.4°C).

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SUMMARY

Existing and anticipated applications for high temperature plastic materials resulted in this investigation of high temperature dielectric materials. Evaluation indicated that films (analogous to duPont's Kapton film) made from pyromellitic dianhydride and 4, 4'-oxydianiline are superior to other polyimide films on the basis of physical, electrical, and visual characteristics.

Several different polyimide adhesive formulations were also developed and tested; it was found that lap shear tensile strengths as high as 2300 psi (15.9 MPa) can be obtained at room temperature and 800 psi (5.5 MPa) at 700°F (371°C). A polyimide adhesive (Thermostik-D') and an optimum cure for it was developed. A process for bonding polyimide films with Thermostik-D' to form polyimide flat cables resulted in cables that can withstand 20 to 30 kVdc while simultaneously being exposed (molten solder dip) to temperatures as high as 1000°F (538°C) for 10 minutes. A moldable polyimide powder and an optimized process which resulted in fabrication of void-free uniform parts was also developed; this material was used to terminate the cables.

A comprehensive study of the physical, electrical, spectral and chemical characteristics of polyimides and polyamic acid solutions was made by the Bendix Polymer Laboratory, Midwest Research Institute, and Kansas State College. It was found that equivalent weight, refractive index, viscosity, near-infrared spectra, visible spectra and lap shear tensile strength values could be used to characterize them.

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DISCUSSION

SCOPE AND PURPOSE

This project was initiated to meet new design requirements for flexible circuits in an electronic assembly and for flat cables connecting this assembly with other components. Advanced design concepts under development require high-temperature dielectric materials, and determinations of suitable materials and processes are needed. The materials involved in this investigation have processing characteristics quite different from epoxies, urethanes, and other more common materials. Commercial sources have little incentive to develop and transmit handling and processing information to the extent desired, so Bendix initiated investigations to establish empirical criteria.

The project had as its principal objective a comprehensive investigation of materials for insulating high voltage circuits (10,000 Vdc) while resisting temperatures over 600°F (316°C). The first phase was to evaluate high-temperature materials to identify processing characteristics critical to the manufacture of cables and flexible circuits. The second objective was to establish the relationships that existed between the physical, electrical and chemical nature of these materials and their processing characteristics--with the subsequent development of means for controlling the variables critical to processing.

PRIOR WORK

Bendix has been involved in one other endeavor in the area of high-temperature materials: an effort to establish a reproducible production process for laminating a flat cable that would withstand 4,500 Vdc at a temperature of 900°F (482°C) for 30 seconds. Conductors, films, adhesives (commercial), and equipment were investigated to learn the processes necessary to fabricate flat cables.

ACTIVITY

Polyimides

A literature search provided the basic information necessary to initiate laboratory work.

Basic Polyimide Chemistry

Polyimides are usually prepared in a two-step process. The first step, amidization, involves the reaction of a primary diamine and a tetrabasic acid dianhydride. The addition reaction is spontaneous and exothermic if the reactants are properly solvated.

The second step, imidization, is not spontaneous; it is proportional to the reaction temperature and reaches a maximum value between 120° and 140°C.

Problems of weight loss can be minimized by synchronizing the rate of volatile removal with imidization. Cure cycles can be developed for coatings, films, and adhesives in which these processes are synchronized so that blistering and associated problems are minimized. Aluminum foil can be placed over films while casting, so that the space immediately above the film's surface becomes saturated with dimethylacetamide (DMAc). This maintains a soft skin, enhancing the permeability of the film's surface, and abating the gas entrapment which creates blisters.

Heterogeneous Methods of Preparing Polyamic Acids

The following synthesis methods were evaluated to determine methods of preparing polyamic acids which might improve their processibility. The powdered diamine (A) or the dianhydride (B) are reacted stoichiometrically in the solvent (C). In the three methods evaluated, the solvent C is always in excess.

A + BC $\longrightarrow$ ABC (A is added to a solution of B in C)

B + AC $\longrightarrow$ ABC (B is added to a solution of A in C)

AB + C $\longrightarrow$ ABC (A and B are first blended dry, then slowly added to C)

The third method was found to be the most practical and to yield solutions of higher molecular weights, as indicated by viscosity measurements. Equipment similar to that shown in Figure 1 was used.

Figure 1. Basic Polyamic Fluid Synthesis Apparatus

Polyamic acid powders were prepared by precipitation from DMAc using a nonpolar solvent, such as benzene or diethyl ether, or by reacting the diamine and the dianhydride in anhydrous tetrahydrofuran (THF). The THF precipitation method was found to be the more efficient method of preparing unsolvated polyamic acids.

Polyimide Films

Polyamic acid solutions were prepared using the third heterogeneous method to prepare and evaluate polyimides as films.

Film evaluations used a 15 percent concentration level throughout the investigation for consistency. Shrinkage occurred in all cases and bubbling was a problem in the thicker films during cure. A fixture was constructed which held the film securely on all four edges and maintained tension on it while curing to minimize the shrinkage and control warp during cure. The optimum cure cycle was one allowing the solvent (DMAc) and the water liberated during imidization to escape as curing proceeded, synchronizing volatile liberation with imidization.

Studies revealed that films made from 4,4'-methylenedianiline and pyromellitic dianhydride (PMDA) and from 4,4'-oxydianiline and pyromellitic dianhydride exhibited appearances and mechanical qualities far superior to any others. The results of this evaluation are summarized in Table 1.

Kapton* film was evaluated for the effects of elevated temperature. Strips of film (1 by 8 by 0.005 inch)(25.4 by 203.2 by 0.127 mm) were heated to temperatures ranging from 450° to 800°F (232 to 427°C). Tensile strength tests were performed on these samples at room temperature and at 500°F (260°C). The results of these tests are shown in Figures 2 and 3. Samples tested at room temperature reached a maximum value when they had been exposed to 650°F (343°C), while those that were tested at 500°F (260°C) showed a steady increase in tensile strength as the exposure temperature was increased to 800°F (427°C).

Polyimide Adhesives

BKC-Developed Materials

Evaluation of polyamic acids as adhesives was directed to those prepared from diamines and dianhydrides.

*duPont trade name

Table 1. Summary of Evaluation of Polyamic Acids as Films

Amire to Synthesize the Polyamic Acid	Polyamic Acid Film Thickness, in Mils (μm)	Polyimide Film Thickness in Mils (μm)	Initial Film Thickness in Mils (μm)	Solvent
POP/PMDA*†	1.8 (45.7)	1.8 (45.7)	- - -	DMAc
p-ODA/PMDA*†	2.0 (50.8)	- - -	- - -	DMAc
PCH ₂ P/PMDA*††	1.0 (25.4)	1.0 (25.4)	15.0 (381)	DMF
PSO ₂ P/PMDA*†	- - -	- - -	15.0 (381)	DMAc
PCH ₂ P/PMDA**†††	- - -	- - -	35.0 (889)	NM2P
POP/PMDA**†††	3.1 (78.7)	2.7 (68.6)	35.0 (889)	DMAc/DMF
PCH ₂ P/PMDA††	2.6 (66.0)	2.1 (53.3)	35.0 (889)	DMAc
PCH ₂ P/PMDA††	1.0 (25.4)	1.0 (25.4)	15.0 (381)	DMAc
EDA/PMDA#	- - -	- - -	- - -	DMAc
PDA/PMDA#	- - -	- - -	- - -	DMAc
1,5 NDA/PMDA#	- - -	- - -	- - -	DMAc
<p> *Used in Cure Cycle I. **Used in Cure Cycle II. †Resultant film brittle, unusable. ††Resultant film brittle but usable. †††Resultant film of excellent quality. #Would not form a film. </p> <p> Explanations of abbreviations: POP = Bis (4-aminophenyl) ether PSO₂P = Bis (4-aminophenyl) sulfone PCH₂P = Bis (4-aminophenyl) methane p-ODA = p-phenylenediamine EDA = Ethylenediamine PDA = Propylenediamine 1,5 NDA = 1,5 diaminotriazole PMDA = Pyromellitic dianhydride DMAc = Dimethylacetamide DMF = Dimethylformamide NM2P = N-methyl-2-pyrrolidone </p>

Figure 2. Tensile Strength of Cured Kapton Film at Room Temperature

Systems that were of little use as adhesives were eliminated by analysis of limited reported properties of the various chemical combinations. Polyamic acid systems containing pyromellitic dianhydride were often brittle and in many cases would not bond the Kapton film at all. This eliminated half of the systems that were originally considered. Systems that incorporated diamines restricting the freedom of rotation of individual units of the polymer resulted in materials of crystalline nature. Systems employing aliphatic diamines such as ethylene diamine exhibited inferior thermal stability. Because of these observations, systems employing the following materials were eliminated: PMDA, 4,4'-azodianiline, 2,4-diamino-6-phenyl-triazine, 3,5-diaminotriazole, ethylene diamine, propylene diamine and hexamethylene diamine. Attention was focused on those systems employing 3,3',4,4'-benzophenonetetracarboxylic dianhydride (BTDA) and the following diamines: 4,4'-oxydianiline, n-phenylenediamine, 4,4'-sulfonedianiline and 4,4'-methylenedianiline.

Figure 3. Tensile Strength of Cured Kapton Film at 500°F (260°C)

Physical and Electrical Testing

An additional comparison was made of polyamic acid systems as adhesives. Pieces of stainless steel were bonded with them in the fixture shown in Figure 4. The specimens were prepared from machined pieces of 4.0 by 1.0 by 1.125 inch (101.60 by 25.4 by 28.4 mm) stainless steel (Alloy 316) that had been lightly sandblasted.

The seven systems chosen for further evaluations are shown in Table 2. Tensile specimens were prepared using the polyamic acids shown in Table 2 as 25 percent solutions. Data shown in Table 2 indicate that BTDA, in com-

Text continued on Page 24.

Table 2. Average Lap Shear Tensile Strengths of Various Polyamic Acids*

Notation**	Average Lap Shear Tensile Strength, psi (MPa)
PSO ₂ P/BTDA	1980 (13.7)
m-ØDA/BTDA	2100 (14.5)
POP/BTDA	1640 (11.3)
PCH ₂ P/BTDA	2108 (14.5)
DAØTA/BTDA	Would Not Bond
POP/PMDA	Would Not Bond
PCH ₂ P/PMDA	595 (4.10)

*Bonding stainless steel to stainless steel (ASTM 1002-64)	
**Equivalents of the abbreviations are:	
PSO ₂ P	Bis (4-aminophenyl) sulfone
m-ØDA	m-Phenylenediamine
POP	Bis (4-aminophenyl) ether
PCH ₂ P	Bis (4-aminophenyl) methane
DAØTA	2,4 Diamino-t-phenyl-s-triazine
PMDA***	Pyromellitic dianhydride
BTDA***	Benzophenonetetracarboxylic dianhydride

***Combinations of an amine and a dianhydride are referred to in this report as systems. System D was PCH₂P/PMDA while System D' was PCH₂P/BTDA.

Figure 4. Bonding Fixture Used to Prepare Lap Shear Tensile Specimens

Figure 5. Assembly Used to Prepare Electrical Specimens

Figure 6. Heating and Cooling Bench Used to Prepare Physical and Electrical Specimens

bination with either PSO_2P , $m\text{-ODA}$ or PCH_2P produces an adhesive of far superior physical capabilities than the other systems that were evaluated. Values of the order of 2,000 psi (13.79 MPa) were obtained for these systems.

Electrical testing was accomplished by preparing samples from two 5.75 by 3.0 by 0.005 inch pieces (146 by 76 by 0.127 mm) of Kapton film and one 6.50 by 0.25 by 0.005 inch (165 by 6 by 0.127 mm) soft aluminum conductor. The film and the conductor were degreased using trichloroethylene. A 3-mil (76 μm) coating of the adhesive was applied to one side of each piece of film. The coated film strips were placed in a forced air oven at 400°F (204°C) for 10 minutes, after which they were removed and the conductor placed between the two coated surfaces of the film. This electrical lay up was sandwiched between 22 plies of glass cloth and two 4.0 by 8.0 by 0.50 inch (101.60 by 203.20 by 12.7 mm) pieces of stainless steel. This assembly (Figure 5) was then placed in the Wabash press (Figure 6) at 720°F (382°C) and under 550 psi (3.79 MPa).

Dielectric breakdown voltage and current leakage (at 10.0 kV) test were determined in accordance with ASTM D149 and D150 with results shown in Table 3. Systems superior in the physical evaluations generally exhibited superiority in electrical evaluations.

The $\text{PCH}_2\text{P}/\text{BTDA}$ combination (System D') was selected and optimization of processing this polyimide adhesive system was continued throughout this program. Figures 7, 8, and 9 show test effects on samples of 316 stainless steel bonded with $\text{PCH}_2\text{P}/\text{BTDA}$ adhesive. Figure 7 is a plot of lap shear tensile strength as a function of cure temperature. This plot shows that as the cure temperature is increased from 500°F (260°C) to 900°F (482°C), with the cure time, pressure and adhesive thickness held constant, the lap shear tensile strength reaches a maximum value at approximately 700°F (371°C). Figure 8 is a plot of lap shear tensile strength as a function of applied cure pressure. Pressure was increased from 100 psi to 5000 psi (689.48 kPa to 34.47 MPa); maximum strength is obtained when a cure pressure of 630 psi (4.34 MPa) is used. Figure 9 is a plot of lap-shear tensile strength as a function of adhesive thickness.

The adhesive thickness between the bonded pieces of the specimen was maintained by using calibrated shims as shown in Figure 10. Figure 9 indicates that adhesive thicknesses greater than 1.5 mils (38 μm) do not bond very well at all. Plots of cure temperature, time and pressure show that the variation of curing conditions had little effect on the electrical strength of the sample cables. Negligible effects are shown for all variables of processing except cure time. Studies indicate that as the cure time is

Table 3. Electrical Strengths of Various Polyimide Adhesive Systems

Sample*	Leakage Current, (μ A at 10.0 kV)		Breakdown Voltage (kV)		
	Individual	Average	Individual	Average	Rating**
A-0	0.35	0.27	35.5	34.25	5
	0.15		37.5		
	0.33		21.0		
	0.25		43.0		
B-0	0.15	0.22	35.5	40.63	2
	0.23		42.5		
	0.28		42.0		
	0.23		42.5		
C-0	0.10	0.17	36.5	37.33	4
	0.27		29.0		
	- - -		- - -		
	0.15		46.5		
D-0	0.37	0.61	38.5	41.67	1
	1.20		37.5		
	0.27		49.0		
E-0	0.30	0.28	34.0	38.5	3
	0.15		50.0		
	0.38		36.0		
	- - -		34.0		

*A-0: BTDA - Bis (4-aminophenyl) sulfone
B-0: BTDA - m-phenylene diamine
C-0: BTDA - Bis (4-aminophenyl) ether
D-0: BTDA - Bis (4-aminophenyl) methane
E-0: BTDA - p-phenylene diamine
**Ratings based on dielectric strengths.

Figure 7. Lap Shear Tensile Strength Versus Cure Temperature, Thermostik D'

Figure 8. Lap Shear Tensile Strength Versus Cure Pressure, Thermostik D'

Figure 9. Lap Shear Tensile Strength Versus Adhesive Thickness, Thermostik D'

Figure 10. Spacer Positioning for Making Thickness Samples

lengthened past 14 minutes the current leakage increases significantly. It was concluded that the optimum curing conditions for bonding 5-mil (127 μm) Kapton film using System D' were as follows.

Temperature: 700°F (371°C)

Pressure: 630 psi (4.34 MPa)

Time: 10 minutes

Adhesive Thickness: 1 mil (25.4 μm) (3-mil (76 μm) application of 25 percent solution)

Commercial Polyimide Adhesives

The knowledge of composition and performance characteristics of commercial polyimide adhesives was desired as an aid in the fabrication of flat cables. The commercial materials studied were: duPont's RC-5077, Monsanto's Skybond 700 and 703, Narmco's Thermadite 17 and Quantum Chemical's Quantad 159. Infrared spectral analyses of these materials showed that all five were polyamic acids dissolved in N-methyl-2-pyrrolidone. This identification was accomplished by heating the adhesive mixture and obtaining the infrared spectra of the distillate.

Four commercial adhesives were converted to the imide form prior to submittal for elemental analyses (Table 4).

Table 4. Summary of Elemental Analyses of Four Commercial Adhesives, in Percentages

Adhesive	Carbon	Hydrogen	Nitrogen	Oxygen*
RC-5077	71.90	4.46	4.52	19.1
Skybond 700	67.52	4.02	4.52	23.9
Skybond 703	70.93	4.85	4.53	19.7
Quantad 159	69.73	3.63	3.72	22.9
*The percent oxygen is calculated as the difference of the sum of the percentages of C, H, and N from 100 percent.				

The thermograms of the differential thermal analysis (DTA) of each adhesive (as the imide) showed that from 25° to 500°C no thermal transitions were detected. This is indicative of good thermal stability.

Thermogravimetric analysis (TGA) was performed on each adhesive, analyzed as received from the manufacturers. The TGA plots of percent weight loss of the sample as a function of increasing temperature in air are shown in Figure 11 for all the adhesives except Thermadite 17. The type of information obtained from TGA may be seen by considering one of the curves as an example. In the case of RC-5077 the solvent begins to evaporate at about 50°C, as evidenced by the loss in weight. The TGA curves of the adhesive Thermadite 17, in both air and nitrogen, are shown in Figure 12. The major difference is the 20 percent residue, presumably carbon, which is still left at 1,000°C.

Pilot Production of Dual-Conductor Flat Cables

The Bendix Polymer Laboratory developed a polyimide adhesive (Thermostik System D¹) and process for bonding polyimide films. This adhesive and process was evaluated for making dual-conductor flat cables. The objective was to fabricate cables comparable to or superior to those cables fabricated using commercially available polyimide adhesives.

Equipment

The press used to prepare the test cables was a Bendix-fabricated press fitted with three P-10 Enerpac rams. The platens were Meehanite, heated by seventeen 800-watt cartridge heaters (Figure 13). Throughout the evaluation a Marksman recorder was used to monitor the temperature in each of the 16 zones of each platen. The temperature of each platen was maintained at 700° ± 10°F (366 to 377°C) throughout the evaluation. After the samples were fabricated, the mold was removed from the heating press and placed in a Bendix-fabricated cooling press. A drying fixture (Figure 14) was used to apply tension to the adhesive wet film, and a forced air oven maintained at 600°F (316°C) was used to remove the solvent from the adhesive (Figure 15) prior to the curing process. A Meehanite mold was used to fabricate the cables (Figure 16).

Procedures

Flat cables were fabricated as follows.

Three pieces of Kapton film (36.0 by 4.50 by 0.005 inch) (914 by 114 by 0.127 mm) were visually examined for pin holes and other imperfections.

Text continued on Page 35.

Figure 11. Thermogravimetric Analysis Curves of Commercial Polyimide Adhesives

Figure 12. Thermogravimetric Analysis Curves of Thermadite 17 in Air and in Nitrogen

Figure 13. Three-Pressure-Point Press

Figure 14. Drying Fixture

Figure 15. Forced Air Oven (Center) and Layup Hood (Right)

Holes 1, 2, 3, and 4 (Figure 17) were punched in each piece of film using a punch fixture (Figure 16). The film was cleaned both sides with methyl-ethyl ketone and a lint-free cotton pad; the film was then placed on a flat plate-glass working surface.

Three mils ($76\text{ }\mu\text{m}$) of Thermostik-D' was applied to each piece of film, using a Gardner knife (Figure 18). The film was placed on drying fixtures for solvent removal in the 600°F (316°C) oven over a ten-minute period.

One film from those previously coated was selected to be coated on the other side (to be the center laminate). This piece of film was placed, coated side down, on a clean glass surface. The side to be coated was cleaned as before and this film was taped to the glass surface. The micrometer settings were increased 0.5 mils to compensate for the previous coating to the other side and to allow a 3-mil ($76\text{ }\mu\text{m}$) application of Thermostik-D' to this surface.

The double-coated film was placed on the drying fixture and solvent was removed from the set side in the 600°F oven (316°C) for an additional ten minutes. Holes 5 through 16 were then simultaneously punched in all three pieces of adhesive-coated film. Six alignment pins were placed in the mold and five pieces of glass cloth (3 by 36 inches (76 by 914 mm)) were aligned over them.

A one-side-coated piece of film was placed, coated side up, in the mold. A cleaned conductor was placed on top of this film. The double-coated film, the remaining conductor and the outer single-coated film were then aligned in the mold. Five more pieces of glass cloth and the male portion of the mold were assembled, then the excess was trimmed from the mold and the alignment pins were removed.

The mold was centered in the press and subjected to $700^{\circ} \pm 10^{\circ}\text{F}$ (366 to 377°C) for ten minutes while under 100 to 700 psi (0.69 to 4.83 MPa). The mold was removed from the hot press and placed in a cooling press for 15 to 30 minutes. The molded cable was removed, trimmed and tested for a total cycle time of approximately 40 to 50 minutes. Figure 19 shows a finished cable (untrimmed) in comparison with one of the smaller samples.

Synopsis of Dual-Conductor Flat Cable Processes

Twenty-seven cables were made per specification to evaluate the Bendix polyimide adhesive (Thermostik-D'). The first ten cables (Set 1, Table 5) were made to establish the available facilities and optimize pressure because the wider-than-usual conductor altered the core pressure. The remaining seventeen samples (Set 2, Table 6) were prepared at the optimized cure pressure.

Figure 16. Punch Fixture and Mold for Cables

Figure 17. Hole Punch Pattern for Kapton Film Laminate

Of the 17 samples in Set 2, 94.1 percent exhibited dielectric breakdown voltages greater than 10 kVdc. These findings are summarized in Tables 5, 6 and 7.

Causes of Failures

Samples whose dielectric breakdown was less than 15 kVdc were analyzed for defects. Lack of cleanliness (glass fibers, dirt, etc) or atmospheric water absorption (Samples 6 and 19) was responsible in all cases. The samples of dual-conductor flat cables exhibited dielectric breakdown voltages of 18 to 20 kVdc, with individual values as high as 51 kVdc.

Conclusions to Dual-Conductor Flat Cable Development

Bendix adhesive Thermostik-D' is satisfactory for fabricating dual-conductor flat cables. The material produces a cable exceeding in properties other cables produced with other adhesives and processes. Cables whose dielectric breakdown voltages exceed 18 to 20 kVdc can be consistently produced, using the prescribed procedure and Thermostik-D'.

Coalescible Polyimide Moldings

The preparation of polyimides via the esters of tetrabasic acids such as 3, 3', 4, 4'-benzophenonetetracarboxylic dianhydride (BTDA) was found to be most convenient.

Figure 18. Gardner Knife, Kapton Film, and ThermoStik-D' Adhesive

Figure 19. Untrimmed Cable and Electrical Specimen

Table 6. Flat Cable Testing, Set 2*

			Force, (lb)(kN)								
	Pressure (psi)(MPa)		Necessary		Obtained						
			Individual	Total	Individual			Total			
Sample	Desired	Actual	F _{AN} **	F _{IN} ***	F _{AO} †	F _{BO} †	F _{CO} †	F _{IA} **	Δt, min†††	Potential Max (kVdc)	Observations
11	100 (0.689)	91 (0.627)	2770 (12.322)	11700 (52.04)	2600 (11.51)	2400 (10.68)	2600 (11.39)	10690.0 (47.55)	5	>20.0	
12	200 (1.379)	194 (1.338)	5550 (24.69)	23400 (104.09)	5400 (24.02)	5300 (23.4)	5400 (24.02)	22640.0 (100.71)	20	19.5	
13	300 (2.068)	295 (2.034)	8320 (37.0)	35100 (156.13)	8400 (37.36)	8300 (36.92)	7800 (34.70)	34460.0 (153.29)	20	>20.0	
14	400 (2.758)	399 (2.751)	11090 (49.33)	46800 (208.13)	11000 (48.93)	11200.0 (49.82)	11000 (48.93)	46690 (207.69)	45	20.0	Glass fibers caused short.
15	500 (3.447)	506 (3.489)	13870 (61.70)	58500 (260.22)	13800 (61.39)	13500 (60.05)	14000 (62.28)	59210 (263.38)	1,200	>20.0	Precure: 10 min at 600°F (315.6°C) followed by 20 hr at 500°F (260.0°C)
16	600 (4.137)	594 (4.096)	16640 (74.02)	70200 (312.26)	16500 (73.39)	16400 (72.95)	16500 (73.39)	69480 (309.06)	20	13.0	
17	700 (4.826)	697 (4.806)	19410 (86.34)	81900 (364.31)	19500 (86.74)	19300 (85.85)	19200 (25.41)	81580 (362.88)	20	16.0	
18	100	96 (0.662)	2770 (12.322)	11700 (52.04)	2600 (11.51)	2600 (11.51)	2800 (12.31)	11250 (50.04)	5	>20.0	Poor wetting; fingerprints.
19	200	202 (1.393)	5550 (24.69)	23400 (104.09)	5400 (24.02)	5600 (24.82)	5800 (25.80)	23630 (105.11)	5	50.0	Layup left out overnight.
20	300	257 (1.772)	8320 (37.0)	35100 (156.13)	8200 (36.52)	8200 (36.52)	7800 (34.70)	30040 (133.62)	20	>20.0	
21	400	409 (2.820)	11090 (49.33)	46800 (208.13)	11000 (48.93)	11200 (49.82)	11800 (52.49)	47820 (212.71)	30	16.0	Glass fibers caused short.
22	500	501 (3.454)	13870 (61.70)	58500 (260.22)	13900 (61.79)	13900 (61.79)	13900 (61.79)	58650 (260.89)	Weekend	19.5	Stored at 175°F; glass fibers caused short.

*All samples in Set 2 were prepared using 3-mil (76 μm) applications of Thermostick-D' at 700°F (371.1°C) and under the indicated pressures.

**F_{AN} - The necessary force on each individual ram

***F_{IN} - The necessary total ram force

†F_{AO}, F_{BO}, F_{CO} - The obtained individual force gage readings (averages)

††F_{IA} - The actual calculated total force

†††Δt - The time lapse between fabrication and testing

Table 6 Continued. Flat Cable Testing, Set 2*

			Force, (lb)(kN)								
			Necessary		Obtained						
Pressure (psi)(MPa)			Individual	Total	Individual			Total		Potential	
Sample	Desired	Actual	F _{AN} **	F _{1N} ***	F _{AO} †	F _{BO} †	F _{CO} †	F _{1A} ††	Δt, min†††	Max (kVdc)	Observations
23	600	589 (4.061)	16640 (74.02)	70200 (312.26)	16800 (74.59)	16000 (71.35)	16200 (72.15)	68920 (306.57)	Weekend	>20.0	Stored in desiccator.
24	700	706 (4.868)	19410 (86.34)	81900 (364.31)	19600 (87.14)	19100 (85.01)	20000 (88.74)	82560 (367.25)	60	>20.0	
25	700	706 (4.868)	19410 (86.34)	81900 (364.31)	19600 (87.14)	19100 (85.01)	20000 (88.74)	82560 (367.25)	20	18.5	
26	500	502 (3.461)	13870 (61.70)	58500 (260.22)	13800 (61.39)	14000 (62.28)	14000 (62.28)	58790 (261.51)	20	>20.0	
27	500	502 (3.461)	13870 (61.70)	58500 (260.22)	13800 (61.39)	14000 (62.28)	14000 (62.28)	58790 (261.51)	20	24.0	

*All samples in Set 2 were prepared using 3-mil (76 μm) applications of Thermostick-10, at 70°F (37.1°C) and under the indicated pressures.

**F_{AN} - The necessary force on each individual ram

***F_{1N} - The necessary total ram force

†F_{AO}, F_{BO}, F_{CO} - The obtained individual force gage readings (averages)

††F_{1A} - The actual calculated total force

†††Δt - The time lapse between fabrication and testing

Table 7. Statistical Evaluation of Samples
in Set 2

Criteria (kVdc)	Quantity*	Passed Test (Percent)
20.0	10/17	58.7
19.0	12/17	70.5
16.0	15/17	88.0
15.0	15/17	88.0
10.0	16/17	94.1
5.0	17/17	100.0
*Quantity = Number of Cables Passed/ Total Number of Cables Fabricated		

The presence of the ester group on the polyamic acid, in lieu of the carboxylic acid group, alters the rate of imidization. This alters the processing conditions necessary to initiate and maintain imidization. A thermogravimetric analysis (TGA) comparison of Curves A and B in Figure 20 shows this reaction.

Curves C and D of Figure 21 are differential thermal analysis curves (DTA) of a typical polyamic acid and the n-hexyl ester of PCH₂P/BTDA, respectively. Both DTA and TGA show that in the coalescible polyimide, which is actually a mixture of free polyamic acid, polyamic acid ester and polyimide, imidization takes place at an appreciable rate over a broader temperature range. This results in a steady and much slower evolution and diffusion of volatiles to the surface of a specimen, and the probability of splitting is diminished.

The coalescible polyimide powders have been used to fabricate molded discs which were as thick as 0.375 inch (9 mm) with a 4.0 inch diameter (101 mm), by cold pressing in a closed mold with subsequent curing at 650° to 700°F (340° to 366°C) for 1 to 2 hours. This results in a dark brown composite with a Shore D hardness of 75 or more; these discs have been subjected to temperatures as high as 750°F (399°C) for 1 to 2 hours with little or no degrading effects observed. Darkening of the surface and shrinkage of approximately 0.001 inch (0.025 mm) were the only noticeable effects.

Figure 20. Thermogravimetric Analysis of a CPI and a Polyamic Acid

Figure 21. Differential Thermal Analysis of a CPI and a Polyamic Acid

Processing

Vacuum Bag. It was found that CPI material could be successfully compression-molded or molded using vacuum-bag techniques. The setup used was made of 316 stainless steel, with an aluminum base and frame. The bag itself was formed from 3-mil (76 μm) Kapton film and a 0.1875 inch (5 mm) silicone rubber gasket (Figure 22).

Compression Molding. The compression-molding processing of coalescible polyimides was optimized on the Brabender Plasticord. This instrument plots the torque (in meter-grams) necessary to stir a material at a constant rate as a function of time at a constant temperature, or as a function of temperature at a constant speed (Figure 23). When the material being evaluated undergoes a change in morphology, phase, or state, the torque necessary to maintain the stirring rate constant is immediately changed.

Material. The material used throughout the Brabender Plasticord evaluations and in the cure cycle evaluations was CPI-8129, a coalescible polyimide (CPI). It was prepared by reacting the dihexyl ester of 3,3',4,4'-benzophenonetetracarboxylic dianhydride with bis (4-aminophenyl) methane in stoichiometric amounts. This particular lot (Lot 8129) is a pilot plant lot, in which 5,828 grams of material were obtained after purification. This amount constituted a 40 percent yield.

Based on rheological information, compression-molding was successful. The material was charged to a 4-inch-diameter (101 mm) compression mold

Figure 22. CPI Vacuum Bag Assembly

Figure 23. Torque Versus Time and Temperature of CPI Powder During Brabender Plasticord Experiment

and subjected to 800°F (427°C) under 1500 psi (10.3 MPa) for 10 to 15 minutes. This resulted in a mustard to dark brown or black material that was relatively hard and strong but with a semi-porous nature (Figure 24).

A 3-inch-diameter (76 mm) mold was fabricated; this allowed the necessary heat and pressure to be applied to the circular parts. The material when subjected to the 800°F (427°C) press temperature, while under pressures of approximately 2500 psi (17.2 MPa), became dark brown and in some instances was observed to be extruded through openings in the mold.

These 3-inch diameter (76 mm) discs were used to characterize the material electrically. The dielectric strength, dielectric constant and dissipation factors at 60 Hz, 1 kHz and 1 MHz were determined per ASTM's D149 and D150 for this material and are listed in Tables 8 and 9. These values are well in line with those reported for other commercial materials with glass fillers; our material used no fillers. Commercial materials have approximately 60 to 65 percent glass filler.

Termination of the Flat Cables

To evaluate the use of this moldable polyimide in a typical application, processing for construction of the dual conductor flat cables with this type of termination was initiated. A mold was designed with two insert plates that were removable and that would allow the cable to be carefully fitted between the halves of the mold.

This process yielded excellent terminators for the cables. Table 10 shows some of the variations in this process that were evaluated and their results. Figures 25 and 26 show views of a typical termination.

Coalescible Polyimide Synthesis Scale-Up

Laboratory preparation of CPI material produced only about 1,000 grams of material at a time. A larger batch of CPI material was made to determine that scale-up of the synthesis procedure was feasible.

Characterization of Polyamic Acids and Polyimides

The following processes and information were developed from an evaluation of the aging characteristics of polyimide adhesives.¹

Formulations prepared from methylenedianiline and benzophenonetetracarboxylic dianhydride were tested in terms of relative strengths at temperatures of 75°F (24°C), 550°F (288°C), and 700°F (371°C).

Figure 24. CPI Insulated Compression Mold and Cured Samples

Figure 25 Enlarged View of CFI Termination on a Flat Cable

Figure 26. CPI Terminated Flat Cable.

The viscosity and refractive index of nine formulations were monitored during a 256-day aging period.

Bond strength and other property measurements were made at age levels of 1, 2, 4, 8, 16, 32, 64, 128, 192, and 256 days following preparation of the adhesive solution.

Testing of adhesive-bonded stainless steel coupons revealed these strengths for the strongest adhesives: at 75°F (24°C), 2905 psi (20 MPa); at 550°F (288°C), 1837 psi (12.5 MPa); at 700°F (371°C), 772 psi (5.3 MPa).

Adhesive strengths for all samples became stable after 16 days aging and remained stable up to the 256-day test limit.

Temperature was the most important factor affecting bond strength. Adhesive bonds were four times stronger at 75°F (24°C) than at 700°F (371°C), and were 2.5 times stronger at 550°F (288°C) than at 700°F (371°C).

Studies of polyamic acids were conducted under differing conditions of temperature and concentration in the ultraviolet (UV), visible and near-infrared regions of the electromagnetic spectrum.²

In the UV region all systems showed a high-intensity band from 205 to 220 nm and broad low-intensity bands at 260 to 270 nm and 320 to 330 nm. In the visible region dimethylacetamide showed intense light scattering in the red end, which can be used as a measure of particle size. Thin films or sections give intense absorption in the blue and transmission minima from 695 to 715 nm.

Sample	60 Hz		1 kHz		1 MHz	
	Dielectric Constant	Dissipation Factor	Dielectric Constant	Dissipation Factor	Dielectric Constant	Dissipation Factor
1	3.58	0.00274	3.74	0.00546	3.49	0.01674
3	3.81	0.00406	3.99	0.00435	3.69	0.01381
4	3.78	0.00401	3.82	0.00464	3.67	0.01377
5	3.87	0.00404	3.86	0.00477	3.72	0.01411
6	3.80	0.00398	3.85	0.00520	3.69	0.01425
7	3.80	0.00398	3.84	0.00496	3.69	0.01430
8	3.82	0.00394	3.87	0.00578	3.71	0.01542
9	3.80	0.00398	3.88	0.00592	3.74	0.01561
10	3.88	0.00393	3.94	0.00636	3.76	0.01634

*A General Radio Model 1615-A capacitance bridge was used for measurements at 60 Hz and 1 kHz. A Boonton Electronics Model 75A-S8 bridge was used for the 1 MHz measurements. The samples were tested in a Balsbaugh Laboratories Model LD 3 test cell using the two-fluid system. A test potential of one volt RMS was applied for all measurements.

Table 9. Electrical Characterization of 3-Inch Diameter CPI Discs (ASTM D149)*

Sample	Thickness, Mil (mm)	Breakdown Voltage (kV)	Dielectric Strength Volts/Mil (kV/mm)
1	178 (4.5)	70.0	393.3 (15.6)
3	144 (3.7)	97.0	673.6 (26.2)
4	145 (3.7)	80.0	551.7 (21.6)
5	144 (3.7)	90.0	625.0 (24.3)
6	145 (3.7)	85.0	586.2 (23.0)
7	145 (3.7)	90.0	620.7 (24.3)
8	145 (3.7)	60.0	413.8 (16.2)
9	144 (3.7)	50.0	347.2 (12.5)
10	144 (3.7)	70.0	486.1 (18.9)
<p>*The short time test was used on Sample 3 using a rate-of-rise of 500 volts/second. The step-by-step test was used on all the other samples. The initially applied voltage for the step-by-step test was 50 kilovolts, the voltage was increased in 5 5 kilovolt increments, and the time period at each step was 1 minute.</p>			

The near-infrared region proved to be the most useful. A concentration of 20 percent, reaction temperatures below 40°F (4.4°C), and storage temperatures of 5°F or less (-15°C) give optimum results.

Table 10. Evaluation of Processing for CPI Cable Terminations

Sample	Preheat*	Cure**				Mtl Charge (g)	Results
	Mtl Time (hr)	First Stage		Second Stage			
		Time (min)	Pressure psi (MPa)	Time (min)	Pressure psi (MPa)		
1	***	5	2130 (14.7)	5	3200 (22.0)	***	Best yet.
1A	***	5	2130 (14.7)	10	3200 (22.0)	***	Both halves cured.
2	4	5	2130 (14.7)	5	3200 (22.0)	35	Outside good, powder poorly mixed, small voids.
2A	4	5	2130 (14.7)	10	3200 (22.0)	14	
3	7	5	2670 (18.4)	5	3730 (25.7)	25	Part broke during cure. Tremendous pressure drop, second stage.
3A	7	5	2670 (18.4)	10	3730 (25.7)	25	
4	24	5	2670 (18.4)	5	3730 (25.7)	21	Voids, poor mixing, poorly fused, but hard.
4A	24	5	2670 (18.4)	10	3730 (25.7)	21	
5	2	5	2670 (18.4)	5	3730 (25.7)	20	Hard; mold leakage.
5A†	2	5	2670 (18.4)	10	3730 (25.7)	20	
6	48	5	2670 (18.4)	5	3730 (25.7)	20	Porous and more brittle; twice as thick.
6A††	48	5	2670 (18.4)	10	3730 (25.7)	20	
7	2	5	2670 (18.4)	5	3730 (25.7)	20	Made without 1 center plate. Surface blisters and voids.
7A	2	5	2670 (18.4)	10	3730 (25.7)	20	
8†††	2'48	5	2670 (18.4)	15	3730 (25.7)	12.5/12.5	Spotted but good; small voids.

*Material temperature was 600°F (315.6°C), mold time one hour, mold temperature 600°F (315.6°C) on numbered samples and HOT on alphanumeric samples.

**Press temperature was 800°F (426.7°C).

***Data unavailable.

†Tremencous pressure loss during second stage of A when t = 6.5.

††Material used in Sample 6 lost 40 percent of its weight during the 48-hour precure at 600°F (315.6°C).

†††Made by blending equal amounts of the 2- and 48-hour-cured portions of Batch 2.

ACCOMPLISHMENTS

This project on high temperature dielectrics (polyimide materials) has resulted in the following accomplishments.

Sufficient high temperature polymer data and expertise has been accumulated to enable BKC to formulate and prepare a reproducible polyimide adhesive (serviceable up to 700°F (371°C) for 10 minutes) from known, commercially available ingredients.

The Bendix-developed polyimide adhesive has been characterized, and bonding process variables determined.

A polyimide molding compound, of known formula which can be adjusted for specific applications, has been developed. This compound, a natural extension of the basic work above, will provide a molding or encapsulating compound for 700° to 800°F (371 to 427°C) operation.

Although specific applications (configurations) do not exist at this time, this polyimide molding compound has been refined to the point of molding actual hardware of a developmental nature as well as standard test specimens. This material could replace Vespel in some present applications with possible local molding of parts.

Limited experiments with the same basic chemical compounds indicate a high probability of successful film manufacture. This could permit elimination of variable film from outside sources and may make possible multilayer construction without using adhesives.

The assembly of a prototype press bed-frame with pressure and construction innovations unique to compression press design has been completed. This construction, while too light for actual production work, will permit study of ideas believed essential to the application of linear and ladder polymers of the future.

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