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DIELECTRIC MATERIALS DEVELOPMENT

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ABSTRACT

Films and film forming were evaluated for application to the fabrication of dielectric components. Du Pont's Kapton H and Kapton XH649 were compared. Kapton H shrunk more in the machine direction and Kapton XB649 shrunk more in the transverse direction; the total shrinkage was less for Kapton XH649 than for Kapton H. Kapton H hats, made by vacuum/pressure forming, were inspected for change in contour at various temperatures and dwell times.

INTRODUCTION

A LLL physics/engineering group has asked the Chemistry and Materials Science Department to help select materials and develop processes for fabricating dielectric components. The effort reported here is directed toward the fabrication of the non-metallic components.

Dielectric components have been fabricated at both Bendix-Kansas City and LLL for several years. Recent studies indicate that the present polymeric materials [both dielectrics (Mylar)* and adhesives] are inadequate for dimensional stability. In addition, an elevated temperature requirement has been imposed on the dielectric materials development (indefinite exposure to 149°C or 30 d exposure to 260°C in a confined configuration).

We are currently evaluating three processing techniques for Laboratory application: (1) solution coating, (2) film forming, and (3) matched die molding with several polymeric molding compounds (polyimide, polyphenylene sulfide, polycarbonate, and polybenzimidazole).

The initial materials investigation has concentrated on films. Reasons for investigating films first include:

- Films are commercially available.
- Films offer the highest dielectric values.
- All previous developmental work at Bendix involved film fabrication.
- Films are available as both metal clad and non-metal clad laminates.
- Films have reasonable uniform thickness.
- Substitution of films would be least disruptive to Bendix fabrication procedures.

* Reference to a company or product name does not imply approval or recommendation of the product by the University of California or the U.S. Atomic Energy Commission to the exclusion of others that may be suitable.

DISCUSSION

Polyimide Films

The largest supplier of polyimide film in the U. S. is Du Pont, which markets their film under the trade name Kapton. The two grades of Kapton, "H" and "F," are probably manufactured by solution casting and a solvent extrusion process. The F grade has a coating of polytetrafluoroethylene (Teflon, TFE) on one or both surfaces. Film thickness varies between 12.7 and 127 μm , and the Teflon thickness ranges from 12.7 to 50.8 μm .

A third grade of Kapton polyimide film, available from Du Pont in limited quantity, is designated XH649. This experimental film is annealed after solvent extrusion to produce a product with more uniform shrinkage. Du Pont specifications call for the shrinkage of H and XH649 film to be 0.005 and 0.002 mils/in. (127 and 50.8 μm), respectively, after a thermal exposure of 250°C for 30 min. Experience at LLL has indicated a significant difference in shrinkage between the H and XH649 films. We have also noted that different lots of Kapton H and F film exhibit different shrinkage characteristics. This is possibly the reason that Du Pont developed its XH649 Kapton film.

Method for Measuring Film Shrinkage

Shrinkage of polyimide films has been measured both in the as-received rolled flat sheet stock and in pressure contoured geometries. Flat film is measured in the direction of extrusion (machine direction) and perpendicular to extrusion (transverse direction). The machine direction is always identifiable by very small continuous extrusion roll marks on Kapton film. To measure the film, holes about 0.158 mm in diameter are cut in 30.43-cm² and 25.4-cm² films. All film measured here was 127 μm thick. The holes are accurately aligned parallel and perpendicular to the roll marks in the film (machine and transverse directions). The spacing of the holes is either 25.4 cm or 20.32 cm depending upon the size of the film. For most of this work, the shrinkage measurements were made at 22°C and laboratory atmosphere (uncontrolled humidity). Recently, we stabilized all shrinkage measurements by exposing all films for 1 h at 22°C and 10% relative humidity. Shrinkage is defined as the change in distance between holes and is read on a dial gage.

Table 1 and Fig. 1 illustrate the variability of shrinkage in 127- μm -(0.005-in.) thick Kapton H film exposed to an air atmosphere for 150 min at various temperatures.

Table 2 and Fig. 2 show the continuing shrinkage of a single sheet of Kapton H film exposed 10 times to the same thermal cycle and twice to a lower thermal cycle. The exposure was in an air atmosphere with a heating rate of about 3°C/min and a cooling cycle of 4°C/min. The time for each cycle was 150 min. For cycles 1 to 10, the maximum temperature was 371°C. For cycles 11 and 12, lower temperatures were used but this did not result in additional shrinkage.

Table 1. Shrinkage of Kapton H film.^a

Temperature (°C)	Machine direction (mm/m)	Transverse direction (mm/m)
260	2.5	1.9
315	3.6	2.5
371	6.7	1.9
426	9.5	3.2
481	13.0	4.2

^aDu Pont thickness identification is 500H Electrical Grade.

Kapton H film was evaluated for short times by exposing identical flat sheets to elevated temperatures for 1, 2, 4, and 8 h. Four sheets of Kapton H film were cut into 30.48- by 30.48-cm pieces and placed in a preheated oven.

At the various time increments one piece was removed, stabilized, and measured for shrinkage. The results of these exposures, shown in Table 3, indicate that shrinkage in both directions varies with temperatures.

A sample of the experimental Kapton XH649 film was supplied by John Kreuz of Du Pont's Circleville, Ohio, plant. Our limited experience indicates that this film's shrinkage is more uniform between the machine direction and the transverse direction than that of Kapton H. Table 4 shows results of repeated thermal exposures. Unlike the standard Kapton H film, the XH649 material appears to shrink slightly more in the transverse direction.

Flat films of both Kapton H and XH649 were examined for additional shrinkage after a molding cycle and exposure to an elevated temperature of 260°C. The molding cycle was heating to 371°C in approximately 80 min, holding at 371°C for about 10 min, and cooling for about 60 min. The flat films were then exposed to a 260°C oven air atmosphere for about 23 h/d. Each film was equilibrated daily in a 10% relative humidity and 22°C atmosphere for 1 h before measuring for shrinkage. Table 5 tabulates the post-molding shrinkage. The data indicates a continued but much reduced shrinkage for both films at 260°C (111°C less than the molding temperature). Results indicate that the experimental film XH649 shrinks less than the standard Kapton H. Additionally, a reversal in the amount of shrinkage between the transverse and machine direction is noted. Kapton H always shrinks more in the machine direction, and Kapton XH649 always shrinks slightly more in the transverse direction.

Table 2. Repeated thermal exposure of Kapton H film.

Cycle No.	Peak temp. (°C)	Machine direction (mm/m)	Transverse direction (mm/m)
1	371	6.4	2.1
2	371	7.5	2.5
3	371	8.0	2.8
4	371	8.4	2.9
5	371	8.8	3.4
6	371	9.0	3.5
7	371	9.1	3.6
8	371	9.4	3.9
9	371	9.8	4.2
10	371	10.1	4.2
11	260	10.1	4.2
12	315	10.1	4.2

Fig. 1. Shrinkage of polyimide film at various temperatures.

Fig. 2. Shrinkage of polyimide film after repeated thermal exposures.

Table 3. Kapton H film shrinkage at various times and temperatures.

Exposure time (h)	Temperature (°C)	Machine direction (mm/m)	Transverse direction (mm/m)
1	260	3.6	1.3
2	260	3.8	1.5
4	260	4.2	1.6
8	260	4.5	1.6
1	315	4.8	1.8
2	315	5.5	2.3
4	315	6.5	2.8
8	315	7.3	3.0
1	371	10.0	2.6
2	371	10.4	3.4
4	371	13.1	5.8
8	371	16.2	8.5
1	426	18.3	10.4
2	426	23.3	13.3
4	426	27.0	21.0
8	426	46.8	40.8
1	481	56.6	37.8
2	481	62.3	56.0
4	481	Wrinkled	
8	481	Decomposed	

Table 4. Repeated thermal exposure of Kapton XH649 film. Each cycle is between room temperature and 371°C and lasts about 150 min.^a

Exposure No.	Machine direction (mm/m)	Transverse direction (mm/m)
1	3.1	3.8
2	4.4	5.3
3	5.5	6.7
4	5.7	7.6
5	5.8	8.1
6	6.3	8.6
7	6.8	9.2
8	7.0	9.5
9	7.4	10.0
10	8.4	11.4

^aNo lot or Du Pont number identification.

Our data on the shrinkage of Kapton film can be summarized as follows:

- As-received Kapton H (127 μ m thick) appears to vary between 1:1 to 3:1 in shrinkage between the machine direction and transverse direction.
- As-received Kapton H film has always shrunk more in the machine direction.
- Kapton XH649 (127 μ m thick) appears to shrink more in the transverse direction.
- The ratio of shrinkage for Kapton XH649 is approximately 1:1.2, machine direction to transverse direction.
- The total shrinkage for Kapton XH649 appears to be less than for Kapton H.
- Difference in shrinkage of Kapton XH649 and H materials, as suggested by Du Pont, has not been verified.

Contoured Film Vacuum Forming

More than three hundred parts have been fabricated by vacuum/pressure forming. Figure 3 illustrates three vacuum molds in starting, finished, and molding positions. Contoured Kapton H "hats" lose some of the molded contour if exposed to additional elevated temperatures. Figures 4 and 5 show the change in contour after reexposing hats molded at 371, 426, and 481°C to 481°C for 1 h.

Table 5. Post-molding shrinkage of Kapton H and XH649 films.

	Time exposure (d)	Kapton H		Kapton XH649	
		Machine direction (mm/m)	Transverse direction (mm/m)	Machine direction (mm/m)	Transverse direction (mm/m)
Shrinkage after molding (150 min at 371°C)	—	9.3	8.1	5.1	7.3
Additional shrinkage due to a constant exposure at a temperature of 260°C	1	9.7	8.3	5.4	7.5
	2	9.8	8.5	5.5	7.7
	4	10.0	8.8	5.8	8.0
	8	10.3	9.1	6.1	8.4
	10	10.5	9.2	6.4	8.9
	11	10.5	9.3	6.5	9.0
	13	11.1	9.7	6.6	9.3
	14	11.1	9.8	6.9	9.5

Contour (roundness and radius) has been measured on 12.7- μ m-thick Kapton H film with a knuckle gage. Figure 6 illustrates the probe of a knuckle gage in contact with the female surface. The single layer of 127- μ m-thick film is not sufficiently rigid to prevent the probe from disturbing the part during inspection. A method of metal spraying the male surface of the hat with a low-melting metal alloy (Carro-Tru) has been developed. Figure 7 illustrates the application of the low-melting alloy (melting point: 50°C) to the Kapton surface.

Knuckle gage inspection is used to determine the roundness of the formed Kapton hat. Figures 8 through 12 illustrate the difference in roundness of molded hats at 260, 315, 371, 426, and 481°C. The probe radius was held constant for these comparisons at 16.080 cm. Figures 13 through 15 illustrate the effect of molding or dwell time. The amount of time at temperature (371°C) was less than 5 min, 1 h, and 2 h. Both variables, dwell time and mold temperature, produced more spherical parts at maximum conditions.

Fig. 3. Three vacuum molds in starting, finished, and molding positions (1 to r).

Fig. 4. Change in pole light after exposure to 481°C.

Fig. 5. Change in geometry viewed from above after 481°C exposure.

Fig. 6. Knuckle gage inspection technique.

Fig. 7. Spray application of low-melting temperature metal alloy.

Fig. 8. Roundness of molded hat (Part No. C137) at 260°C as determined by a knuckle gage.

Fig. 9. Roundness of molded hat (Part No. C140) at 315°C as determined by a knuckle gage.

Fig. 10. Roundness of molded hat (Part No. C146) at 371°C as determined by a knuckle gage.

Fig. 11. Roundness of molded hat (Part No. C143) at 426°C as determined by a knuckle gage.

Fig. 12. Roundness of molded hat (Part No. C149) at 481°C as determined by a knuckle gage.

Fig. 13. Effect of the amount of time at temperature (371°C) on roundness of molded hat (Part No. D241) as determined by a knuckle gage. Time at temperature was less than 5 min.

Fig. 14. Effect of the amount of time at temperature (371°C) on roundness of molded hat (Part No. D244) as determined by a knuckle gage. Time was 1 h.

Fig. 15. Effect of amount of time at temperature (371°C) on roundness of molded hat (Part No. D254) as determined by a knuckle gage. Time was 2 h.

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