Effect of Imidization Temperature on Properties of Polyimide Films

KER-MING CHEN, TSUNG-HSIUNG WANG, and JINN-SHING KING

Industrial Technology Research Institute, Material Research Laborateries,
chutung, Hsinchu, Taiwan,
Republic of China

AINA HUNG*

Department of Chemical Engineering, Ming Hsin Engineering College,
Hsin-Feng, Hsinchu, Taiwan, Republic of China

SYNOPSIS

Some mechanical and electrical properties of the BPDA/ODA/PDA polyimide film prepared on mylar followed by various cure schedules have been studied. It has been found by FTIR that the imidization reaches its maximum after a 200°C cure schedule for this polyimide. However, the optimum condition of curing is a 350°C cure schedule. Following this cure schedule, one can obtained a polyimide film with good mechanical and electrical properties.
© 1993 John Wiley & Sons, Inc.

INTRODUCTION

The high performance packaging of high speed devices with greater package density requires multilevel technologies for interconnecting. Polyimide is well known for its high thermal stability, low dielectric constant, excellent mechanical properties, and good chemical resistance. Therefore, high-density interconnection technology based on a multilevel copper conductor and polyimide dielectric is a potential condidate for the multilevel multichip packaging applications.[1–3]

In the past few years, some of the topics investigated concerned the optimization of processing conditions for imidization reaction.[4–6] The chemical phenomena taking place during the imidization of polyamic acid films merit special attention. It has been found that the imidization mechanism is strongly influenced by the medium surrounding the amic acid molecule.[7,8] The solvent/polyamic acid interaction has been studied by many researchers since the solvent plays an important role in the imidization process and in the initial polyamic acid interaction with the substrate.[9–11] It has also been reported that the degree of imidization and molecular packing of the imidized polyimide film are functions of cure temperature and time.[12,13]

In the previous study we found that no matter curing in air or vacuum a high peel strength can be obtained when 2,2′,3,3′-tetracarboxybiphenyl dianhydride (BPDA)-based polyimide interface with copper foil.[14] In order to develop a base of understanding to evaluate the use of BPDA/ODA/PDA polyimide in the microelectronic devices and obtain the optimum condition of curing, some mechanical and electrical properties of this polyimide prepared on mylar or copper foil at various cure schedule have been measured.

The degree of imidization was studied by Fourier transform infrared transmission spectroscope (FTIR). The physical properties measured include thermogravimetric analysis (TGA), thermomechanical analysis (TMA), and tensile stress and strain. Some electrical properties, such as breakdown voltages, volume and surface resistance, and dielectric and dissipation factors were also studied.

EXPERIMENTAL

The polyamic acid investigated in this experiment was BPDA/ODA/PDA random copolymer in *N*-

* To whom correspondence should be addressed.
Journal of Applied Polymer Science, Vol. 48, 291–297 (1993)
© 1993 John Wiley & Sons, Inc. CCC 0021-8995/93/020291-07

Table I Polyamic Acid Cure Schedule[a]

Polyamic Acid	Atmosphere	Cure Schedules	Polyimide
BPDA/ODA/PDA = 0.98/0.70/0.30 (mole ratio) in NMP solvent, solid content: 13.4%	Air	1. RT $\xrightarrow[\Delta]{90\ min}$ 200°C (isothermal 1 hr) 2. RT $\xrightarrow[\Delta]{90\ min}$ 250°C (isothermal 1 hr) 3. RT $\xrightarrow[\Delta]{90\ min}$ 300°C (isothermal 1 hr) 4. RT $\xrightarrow[\Delta]{90\ min}$ 350°C (isothermal 1 hr)	PBDA/ODA/PDA film

[a] RT = room temperature; Δ = heating.

methylpyroledone (NMP). The mole ratio was BPDA : ODA : PDA = 0.98 : 0.70 : 0.30, the solid content was 13.4%, and the viscosity was 5400 cps.

The BPDA/ODA/PDA polyamic acid in NMP was spin-coated on clean mylar or pure copper foil. Then, the samples were cured in air by four different cure schedules as shown in Table I. The polyimide films obtained by lifting the films from mylar were investigated by FTIR from Nicolet 5-SX Fourier transform infrared spectroscopy. Thermogravimetric diagrams were obtained with a DuPont 951 thermogravimetric analyzer at a 10°C/min heating rate in N_2.

The polyimide film was cut into $\frac{3}{16} \times \frac{1}{2}$ in. strip (thickness: 25 μm) and tested with a Dupont 943 thermomechanical analyzer by heating from 30 to 400°C at a 10°C/min heating rate.

The stress and strain were measured by etching the polyimide film to 10 × 1 cm and tested with a Schimadzu AG-5000A autograph tensile test machine. The test speed was 10.0 mm/min, and the load cell was 10 kg. The breakdown voltage of each sample was measured by ramping the voltage at a rate of 1000 V/s until breakdown occurred with a AC dielectric test set Model 730-1. The electrode surface area was 0.8 cm. The surface resistance and volume resistance were measured at 1000 V after 3 min charging with Hewlett Packard 4329 A high resistance meter and 16008A resistivity cell. The dielectric constant and dissipation factor were measured at a frequency of 1 kHz by a Hewlett Packard 16047B/test fixture and 4275A/multifrequency LCR meter.

RESULTS AND DISCUSSION

The cure of polyamic acid to the corresponding polyimide involves several proceses as temperature increases: (1) solvent/polyamic acid decomplexation (there are two kinds of hydrogen bonding carboxyl-bonded or amide-bonded), (2) cycloimidization reaction, (3) water and solvent evaporation (bp of NMP is 202°C), and (4) molecular packing.

It has been reported that FTIR can be utilized to follow the formation of polyimide by studing the film of polyamic acid itself after lifting it from substrate by mechanical means.[4,5,15] The progress of the imidization reaction was followed by comparing spectra cured at various cure schedules and by measuring the increase or decrease of the polyimide characteristic transmission band. IR transmittance bands at 1775 cm and 740 cm^{-1} are attributed to the imide carbonyl group CO—NH. In the present experiment, by following the evolution of the imide transmission bands at 1775 and 740 cm^{-1}, the imidization level or cure advancement was evaluated qualitatively. IR spectra for the polyimide films prepared on mylar cured to various temperatures are shown in Figure 1. Imidization reaction has already started at the 100°C schedule because of the appearance of 1774 and 740 cm^{-1} bands. The intensity of these transmission bands increases with cure temperature. The imidization has reached its maximum after the 200°C cure schedule, because, cured at higher temperatures, 250°C, 300°C, or 350°C, the IR spectra do not change significantly.

The thermal stability curves assessed by TGA for the films prepared on mylar are shown in Figure 2. The TGA thermograms showed that all the films are stable to near 575°C except the film which was cured with the 200°C schedule. The film cured with the 200°C schedule starts to have a weight loss near 200°C, indicating incomplete solvent and water (released during imidization) removal during cure. The TGA diagrams of films cured at 250 and 300°C schedules show a small amount of retained solvent because only a small amount of weight loss was observed in the range of 200–575°C. When the cure temperatures were 250°C, almost no weight loss can be observed to about 575°C.

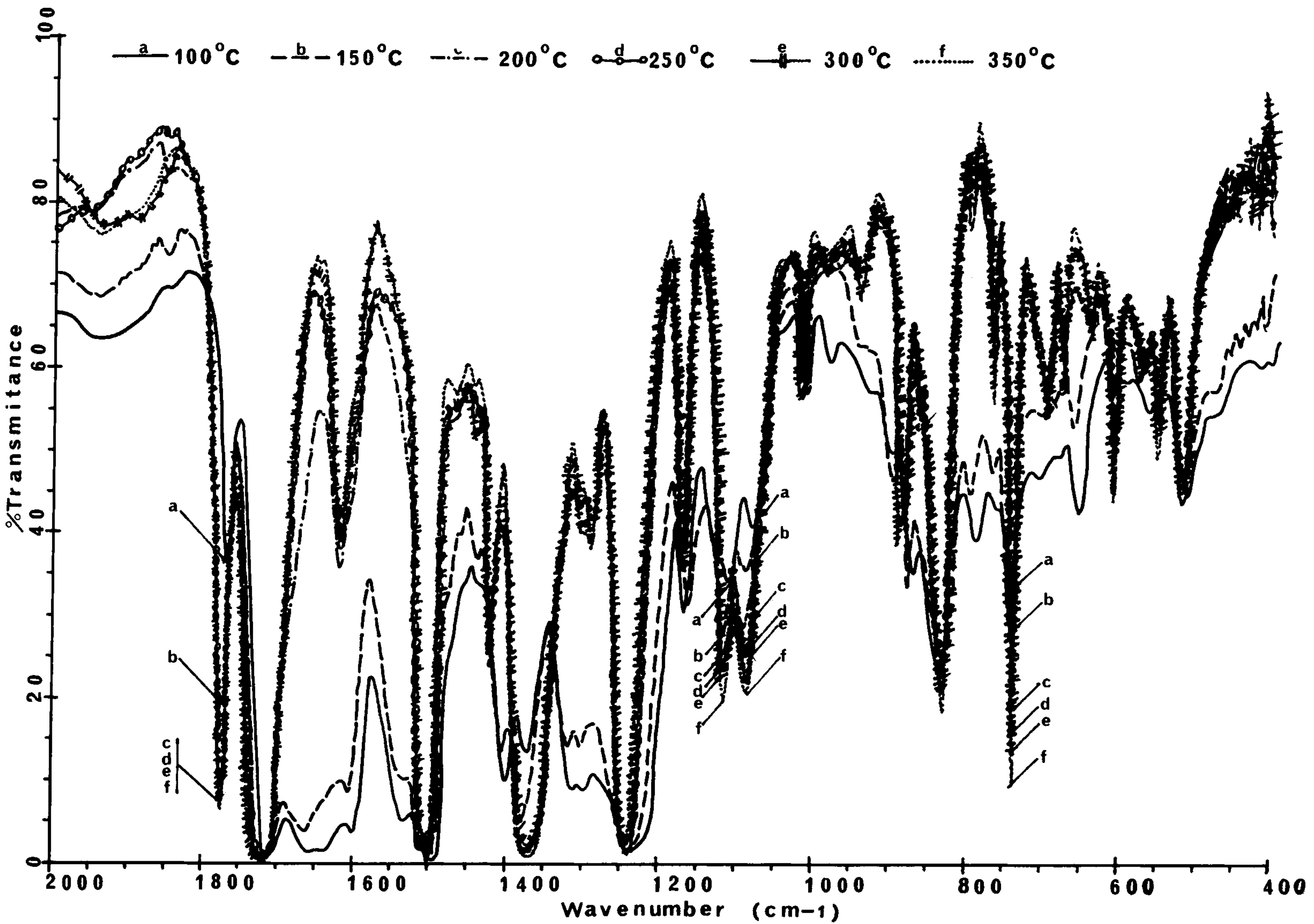

Figure 1 FT-IR spectra of the polyamic acid after curing at: (a) 100°C, 30 min; (b) 150°C, 30 min; (c) 200°C, 30 min; (d) 250°C, 30 min; (e) 300°C, 30 min; (f) 350°C, 30 min.

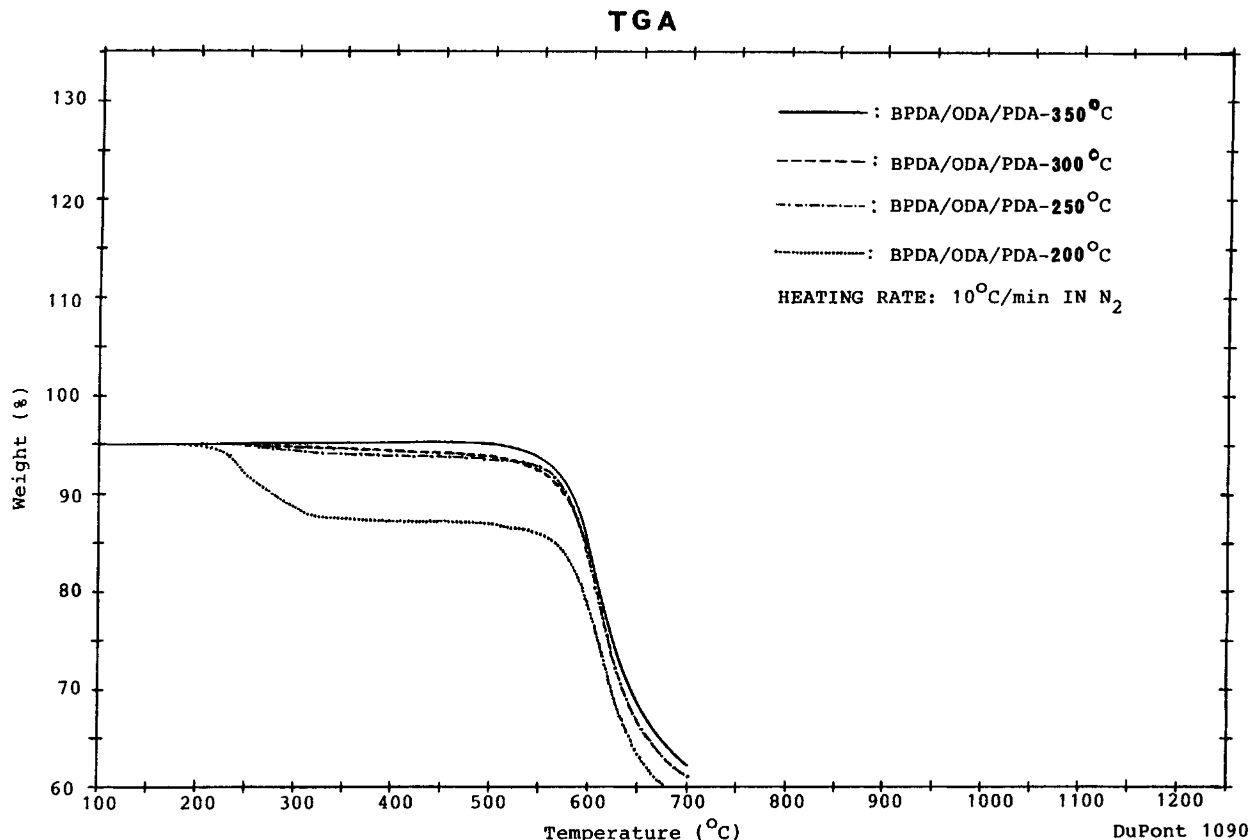

Figure 2 Thermogravimetric analysis of polyamic acid after curing at (a) 200°C, 1 h; (b) 250°C, 1 h; (c) 300°C, 1 h; (d) 350°C, 1 h (heating rate: 10°C/min).

The mechanical properties of a polymer is affected by a number of variables such as nature of the repeating unit and end groups, extent and method of imidization, processing atmosphere and temperature profile, and presence of absorbed moisture or retained solvent. All these effects can result in different configuration and conformation (geometrical arrangement of atoms in a polymer chain) of the polymer chain and hence different mechanical properties of polymer film. The mechanical properties of the films prepared on mylar studied by tensile test machine are listed in Table II. The stress and strain increase with increasing cure temperature up to 300°C; the stress levels off to about 26 kgf/mm, and strain levels off to about 49%. These results indicate that when the cure temperature is lower than 300°C, the chemical structure is weak at room temperature. It may be due to small amount of retained solvent and disordered molecular aggregation. When the cure temperature is 300°C or higher, the chemical structure is strong at room temperature, because, as the cure temperature increases, the retained solvent becomes less. Furthermore, high cure temperatures allow molecular packing (densification, ordering) to occur; therefore, intermolecular interaction is stronger, and high strength polyimide result.

The difference in glass transition temperature represents a difference in intermolecular interactions. The intermolecular interaction in polyimides can be looked at as polymeric chains with alternative donor and acceptor elements which can interact with

Table II The Mechanical Properties of Polyimide Films

Cure Schedule	Thickness (μm)	Tensile (KGF/mm^2)	Strain or Elongation (%)
a	26	15·0	11·6
b	22	16·5	19·7
c	22	26·0	49·1
d	22	26·8	50·0

[a] RT $\xrightarrow{90\text{ min}}$ 200°C (isothermal 1 hr).
[b] RT $\xrightarrow{90\text{ min}}$ 250°C (isothermal 1 hr).
[c] RT $\xrightarrow{90\text{ min}}$ 300°C (isothermal 1 hr).
[d] RT $\xrightarrow{90\text{ min}}$ 350°C (isothermal 1 hr).

each other to form interchain charge transfer complex.[16-18] The strength of the interaction is dependent on electron affinity of the dianhydride and ionization potential of the diamine. The stronger the charge transfer complex is, the closer the chain packing, and the greater the interchain interference with free rotation. This results in higher energy necessary for rotation, higher heat capacity, and higher T_g. Besides, the way of molecular packing can also affect the interchain interaction, and the cure schedule can influence the density of molecular packing. Therefore, as the cure temperature varies, the strength of interchain interaction changes, resulting in a different value of T_g, i.e., the thermoexpansion coefficient of polyimide film varies because of different curing temperatures. Since the higher the curing temperature is, the closer the molecular packing, therefore, the smaller the thermoexpansion coefficient (Fig. 3). The thermal properties of the films prepared on mylar detected by thermomechanical analyzer are shown in Figure 4. The apparent T_g's obtained from the dimensional change diagram shows that when the cure temperature is lower than 350°C, there is a thermodimensional change of films near 250°C. Since the polyimide film is completely imidized, measurement of an intermediate T_g is possibly due to incomplete solvent removal and low density molecular packing. The change of the ratio of the increase of free activity space and the rate of temperature increase is not much when the temperature is lower than 200°C. As the temperature increases, the activity (atomic rotation, bond vibration and molecular translation) of polyimide increases. When the temperature is close to 250°C, the activity space for polyimide reaches a maximum, i.e., T_g. Therefore, as the temperature increases to near 250°C, the drastic dimensional change of films starts. The film cured with the 350°C schedule shows thermodimensional change to some degree between 250 and 350°C, which may be due to some degree of crystal formation, observed by X-ray diffraction spectroscopy (XRD) in our laboratory. As the cure temperature is higher (350°C), the interchain interaction is stronger, and a regular molecular arrangement appears, i.e., forming crystal structure. The thermodimensional change between 250 and 350°C is limited because of the strong intermolecular interaction of the crystal structure. At 350°C the thermal energy overcomes the strong intermolecular interaction; hence, the free activity space expands rapidly. The temperature at which drastic dimensional change occurs is T_m for the crystal structure film.

Some electrical properties of the polyimide films prepared on mylar or copper cured at various cure schedule are summarized in Table III. The break-

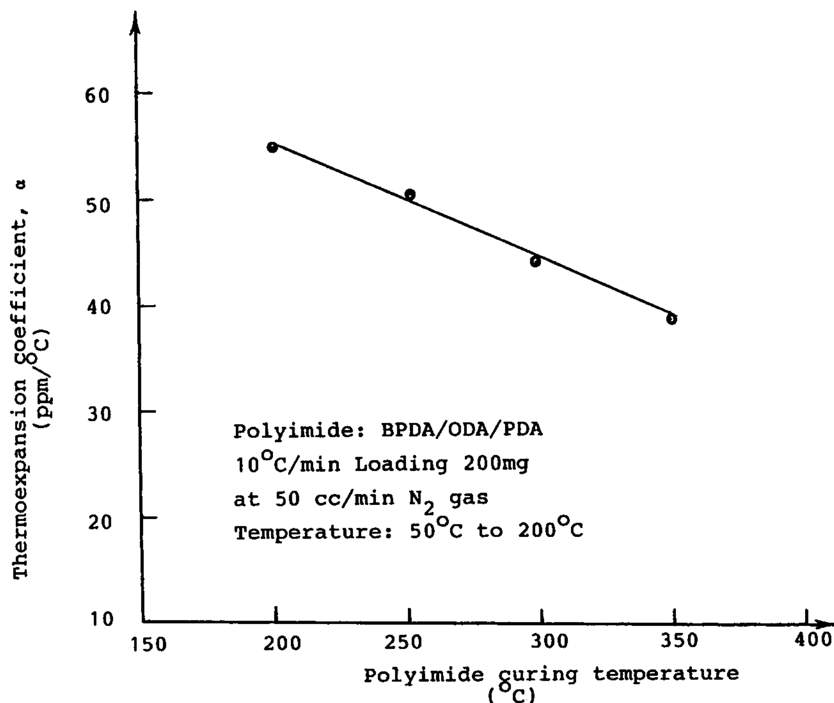

Figure 3 The effect of curing temperature for the thermoexpansion coefficient of polyimide film.

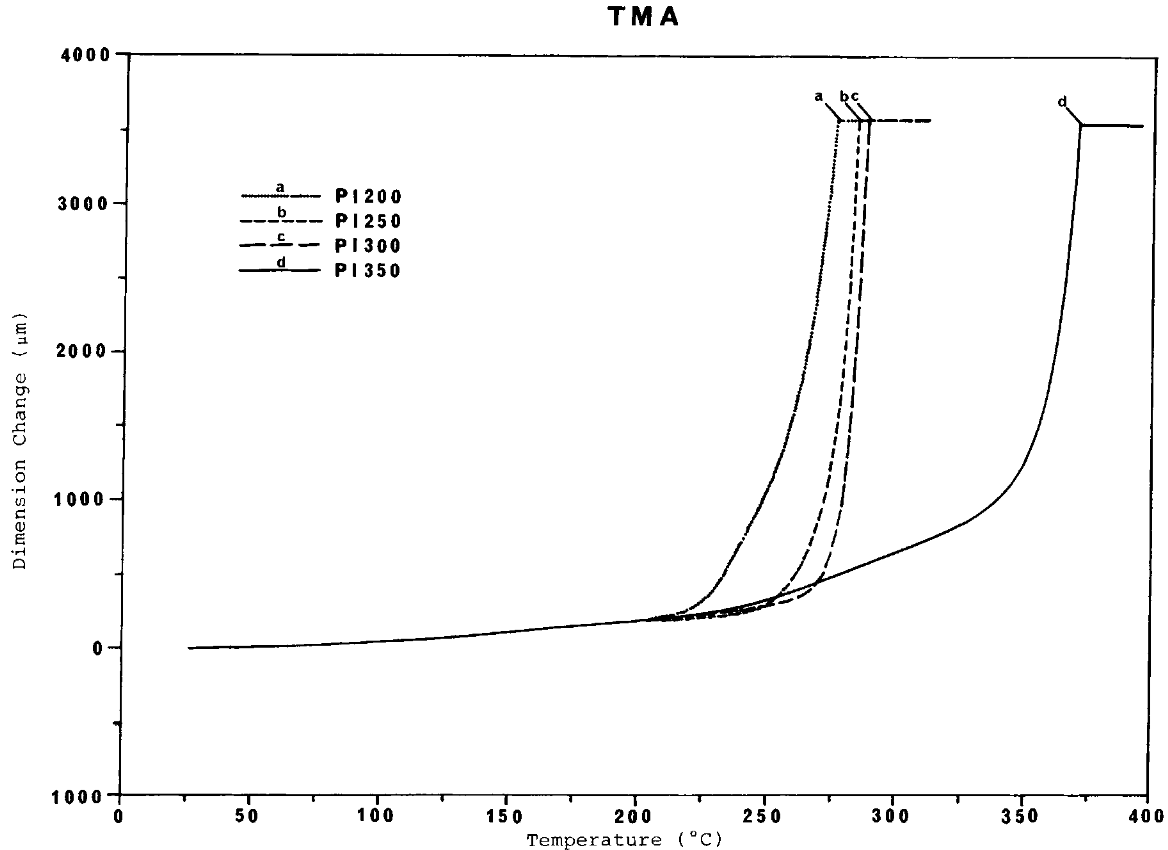

Figure 4 Thermomechanical analysis of polyamic acid after curing at (a) 200°C, 1 h; (b) 250°C, 1 h; (c) 300°C, 1 h; (d) 350°C, 1 h.

down voltages and volume and surface resistivity of the films cured at 300°C or higher are higher than those cured at lower temperature. For those films cured on copper, the breakdown voltages and volume and surface resistivity are all lower than those cured on mylar. The lowering of surface resistivity is much more significant than the lowering of volume resistivity. This is understandable because a small amount of copper is transferred or diffused into the polyimide film at the interface during cure, which lowers the surface resistivity and affects volume resistivity and breakdown voltage. The dielectric con-

Table III The Electrical Properties of Polyimide Films

Substrate	Cure Schedule	Thickness (μm)	Dielectric Constant	Discipation Factor	Surface Resistance (Ω)	Volume Resistance (Ω cm)	Breakdown Voltage (kV)
Mylar	a	26	4.4	0.023	$> 10^{16}$	1.0×10^{16}	5.5
	b	22	4.2	0.010	$> 10^{16}$	1.8×10^{16}	5.5
	c	22	3.5	0.009	$> 10^{16}$	3.1×10^{16}	5.8
	d	22	3.1	0.008	$> 10^{16}$	4.5×10^{16}	5.8
Copper Foil	a	45	4.5	0.014	$> 10^{16}$	3.0×10^{14}	5.8
	b	39	3.5	0.012	7.5×10^{12}	1.54×10^{16}	5.7
	c	37	3.5	0.011	1.1×10^{12}	7.9×10^{14}	5.6
	d	35	3.5	0.010	4.7×10^{11}	2.0×10^{14}	5.6

[a] RT $\xrightarrow{90\ \text{min}}$ 200°C (isothermal 1 hr).
[b] RT $\xrightarrow{90\ \text{min}}$ 250°C (isothermal 1 hr).
[c] RT $\xrightarrow{90\ \text{min}}$ 300°C (isothermal 1 hr).
[d] RT $\xrightarrow{90\ \text{min}}$ 350°C (isothermal 1 hr).

stant and dissipation factor of the films cured at 300°C or higher are lower than those cured at lower temperature. These phenomena may be due to retained solvent and low packing density when cured at low temperature[19] because the retained solvent NMP and the water released during imidization are polar compounds with strong polarization character, which will increase the dielectric and dissipation factor of the film. The fact is that the electrical properties of polyimide film like mechanical properties are also directly related to the chemical structure (polar group, molecular weight, molecular conformation, and crosslinking) and solid structure (crystallinity, internal defect, additives, molecular motion, and crystal interface) of the polyimide, although the impurity and moisture may also affect the electrical properties to some extent. For those films cured on copper, the dielectric constant and dissipation factor are higher as expected because of copper diffusion.

From the results of this experiment, we may speculate that, as the cure temperature increases, the various reactions proceed at different rate during cure. When the cure temperature is low, the decomplexation and imidization reactions are faster than the evaporation reaction. For the 200°C cure schedule, where the imidization was completed, there was still some amount of solvent retained. As the cure temperature increases, the rate of evaporation becomes faster comparatively. However, when the cure temperature is raised to 250 or 300°C, though the amount of retained solvent is small, it is not high enough for compact molecular packing. Therefore, the mechanical and electrical properties are not as good as when it is cured at 350°C schedule. The polyimide film cured according to 350°C schedule exhibited good mechanical and electrical properties, which are comparable to these cured at the longer time schedule reported previously.[20,21]

CONCLUSION

From the spectra obtained by FTIR spectroscopy we found that, for the BPDA/ODA/PDA polyimide film studied, imidization started near 100°C, and imidization reaches its maximum after the 200°C cure schedule. However, the TGA study showed incomplete solvent evaporation when it followed 200°C cure schedule. Tensile test study of the films at room temperature showed that cure temperature should be 300°C or higher to obtain a high mechanical strength film with strong interchain interaction at room temperature. Thermomechanical analysis indicated that, in order to obtain a high thermomechanical film with high packing density and strong interchain interaction or crystal formation, the cure temperature should even be higher or longer. For the film studied, 350°C with proposed cure schedule may be the optimum choice.

The authors would like to thank the Ministry of Economic Affairs of the Republic of China and Ming-Hsin Engineering College for their support.

REFERENCES

1. L. B. Rothman, *J. Electrochem. Soc.*, **130,** 1131 (1983).
2. A. Saiki, S. Harada, T. Okubo, K. Mukai, and T. Kimura, *J. Electrochem. Soc.*, **124,** 1619 (1977).
3. L. B. Zielinski, U.S. Pat. 3,985,597 (1975).
4. R. Ginsburg and J. R. Surko, in *Polyimides,* K. L. Mittal, Ed., Plenum, New York, 1984, Vol. 1, p. 237.
5. A. I. Baise, *J. Appl. Polym. Sci.*, **32,** 4043 (1986).
6. S. Numata, K. Fujisaki, and N. Kinjo, in *Polyimides,* K. L. Mittal, Ed., Plenum, New York, 1984, Vol. 1, p. 259.
7. L. A. Laius and M. I. Tsapovetsky, in *Polyimides,* K. L. Mittal, Ed., Plenum, New York, 1984, Vol. 1, p. 295.
8. L. Mimnemal and J. M. Van der Zande, in *Polyimides,* K. L. Mittal, Ed., Plenum, New York, 1984, Vol. 1, p. 589.
9. C. Feger, *Polym. Eng. Sci.*, **29,** 347 (1989).
10. M. J. Brekner and C. Feger, *J. Polym. Sci. Polym. Chem. Ed.*, **25,** 2005 (1987).
11. F. M. Fowkes and M. A. Mostafa, *Ind. Eng. Chem. Prod. Res. Dev.*, **17,** 3 (1978).
12. L. P. Buchwalter, *J. Vac. Sci. Technol.*, **A7**(3), 4772 (1989).
13. N. Takahashi, D. Y. Yoom, and W. Parrish, *Macromolecules,* **17,** 2583 (1984).
14. K. M. Chen, S. M. Ho, T. H. Wang, J. S. King, W. C. Chang, R. P. Cheng, and Aina Hung, to appear.
15. L. P. Buchwalter, *J. Vac. Sci. Technol.*, **A7**(3), 1772 (1989).
16. R. A. Dine-Hart and W. W. Wright, *Macromol. Chem.*, **143,** 189 (1971).
17. T. A. Gordina, B. V. Kotov, O. V. Kolnivov, and A. N. Pravednikow, *Vysokomol. Soed.*, **B15,** 378 (1973).
18. B. V. Kotov, T. A. Gordina, V. S. Vorschshev, O. V. Kolninov, and A. N. Pravednikow, *Vysokomol. Soed.*, **A19,** 614 (1977).
19. D.-Y. Shih, J. Catalodo, E. Galligan, W. Graham, R. MoGouey, S. Nunes, J. Paraszczar, and R. Serine, *J. Vac. Sci. Technol.*, **A8**(3), 1521 (1990).
20. L. B. Rothman, *J. Electrochem. Soc.*, **127,** 2216 (1980).
21. P. O. Hahn, G. W. Rubloff, and P. S. Ho, *J. Vac. Sci. Technol.*, **A2**(2), 756 (1984).

Received August 28, 1991
Accepted July 7, 1992