

Water Permeation of Polymer Films. III. High-Temperature Polyimides

E. SACHER and J. R. SUSKO, *Materials Analysis, IBM Corporation, Endicott, New York 13760*

Synopsis

Various freestanding, commercially available polyimides have been found to have virtually identical water permeation properties. However, conformally coating them prevents their relaxing their swelling stresses to accommodate the motions of permeating water molecules, manifesting this inability through changes in the diffusion coefficient.

INTRODUCTION

Polyimides and their variants constitute a commercially available class of high-temperature stable materials. They are generally available in both solid (film, sintered block) and solution (polyamic acid precursor) forms.

The high-temperature stability of these materials is due to the intrachain overlap of π orbital systems, permitting extensive electron delocalization.¹ Thus, the structure, through its ability to participate in π orbital overlap and its influence on the coplanarity of adjacent, overlapping systems, dictates to what temperature a polyimide may be raised and for how long.^{2,3}

"High-temperature stability" is a misleading phrase, since these materials are rarely, if ever, raised to near their decomposition temperatures (near 400°C for the least temperature stable²). Rather, what is required is the short-term high-temperature stability necessary to prevent degradation during the momentary temperature excursions experienced during manufacture. Because of an inherent exposure to chemicals during manufacture, chemical stability is also required.

Because of the general ability of polyimides, as a class, to endure the temperatures and chemical exposures of processing, these cannot be used as criteria in choosing one polyimide over another. One function performed by polyimides is to act as a thin film dielectric. Such materials, which contain ionic impurities, increase their conductivities in the presence of water⁴ because of the solvation of these ions, which then participate in the conduction process. Since it is entirely possible that ions may migrate to an electrode and cause electrolytic corrosion,⁵⁻⁷ a possible criterion for choosing a polyimide might be based on how quickly and to what extent water permeates into it.

A previous article in this series⁸ considered du Pont's Kapton polyimide, a commercially available film of poly(4,4'-oxydiphenylpyromellitimide). The present study considers several other polyimides, all of which were cast from their precursor solutions; both supported and freestanding films were studied in an effort to understand the sources of any differences.

EXPERIMENTAL

Two experimental techniques were used. The Dohrmann Envirotech Polymer Permeation Analyzer, model PPA-1, extensively modified as previously described,⁸ can only be used for freestanding films. Supported films, cast onto aluminum, were evaluated by following the uptake of water with time on a high-vacuum sorption apparatus incorporating a Perkin-Elmer Recording Microbalance model AR-2.

Sorption data were converted to the diffusion coefficient D through the method of Zhurkov and Ryskin.⁹ The maximum water uptake gave the concentration C of water in the polymer, from which the solubility coefficient S was calculated. The permeation coefficient P was calculated as $D \times S$. For aluminum-supported films, the value of the thickness used to calculate D was twice that of the sample.¹⁰

The various materials, their casting solvents, and cure conditions are shown in Table I. Amoco AI-10 is believed to be a condensation product of trimellitic anhydride and 4,4'-methylenedianiline, to give an amide-imide. In *N*-methylpyrrolidone (NMP) solvent, it wet both metal and quartz plates poorly. However, small uniform sheets could be made on a scrupulously cleaned and flamed quartz plate. After removing solvent at 100°C, the film was removed from the quartz and cured. The cure conditions were dictated by IR/TGA studies, which showed that the AI-10 cured at 180°C/1 hr, although solvent was retained to 300°C.

du Pont PI-2550 is believed to be a condensation product of 3,3'-4,4'-benzophenonetetracarboxylic dianhydride with 4,4'-methylenedianiline or 4,4'-oxydianiline. IR cannot distinguish between the two condensation products, and their T_g 's are identical.¹¹ An NMP solution readily coated both metals and quartz. As with the AI-10, a film was cast and dried on a quartz plate at 100°C, removed, and cured at 180°C/1 hr. Here, too, solvent was retained to 300°C.

The composition of Monsanto Skybond 703 is unknown, although company literature¹² indicates the cured material to be a crosslinked polyimide. IR showed that two polyimide peaks form during cure, at 1780 and 1857 cm^{-1} ; this indicates the material to be an unsymmetrical polyimide or a mixture of two. The peak at 1857 cm^{-1} grows more slowly than the other, and was the one used to follow total cure. Solvent was found to be retained to 500°C, where air degradation began. Cast films, dried but uncured, could not be removed from quartz or metal substrates. As a result, they were cast onto aluminum foil pretreated with a 1% (w/w) aqueous solution of Union Carbide A1100 silane adhesion promoter and dried. Such films were referred to as "mounted." Dilute HCl was used to slowly remove the aluminum backing; after washing in running deionized

TABLE I
Cure Conditions

Material	Casting solvent	Cure conditions
Amoco AI-10	<i>N</i> -methylpyrrolidone	180°C/1 hr
du Pont PI-2550	<i>N</i> -methylpyrrolidone	180°C/1 hr
Monsanto Skybond 703	<i>N</i> -methylpyrrolidone	300°C/½ hr
Gulf Thermid 600	<i>N</i> -methylpyrrolidone	300°C/½ hr
Hitachi PIQ	<i>N</i> -methylpyrrolidone/dimethylacetamide	300°C/½ hr

water for several hours, such films were referred to as "demounted." Optical microscopy indicated no obvious surface effects due to demounting.

Gulf Thermid 600 was originally formulated by scientists at the Hughes Aircraft Corp.¹³ It is an acetylene-terminated polyimide prepolymer which, when heated, is anticipated to undergo reactions typical of acetylene-vinylacetylene formation, followed by cyclization to benzene. While vinylacetylene formation was found by IR, cyclization, which involves the shift of bulky groups, was not found. Above 200°C, this material is well known to continue to react as temperature and/or annealing time increases,¹³⁻¹⁶ suggesting a complex series of reactions involving moieties other than terminal acetylene groups. After vinyl acetylene formation at 210°C, confirmed by IR, raising the temperature to 230°C and holding it constant at the new setting produced a DSC exotherm without noticeable changes in the IR. Such exotherms, with no obvious IR changes, were continually produced as the temperature was further raised to above 300°C. In this case, too, cast films, dried but uncured, could not be removed from quartz or metal and were cured on A1100-treated aluminum foil. Solvent removal appeared complete at 250°C.

A publication by Hitachi scientists¹⁷ indicated that PIQ is an acronym for a "polyimide isoindroquinazalinedione." However, as confirmed by *Chemical Abstracts*, the structure given is for a polyimide isoindoloquinazolinedione.* DSC indicated that cure began on melting of the precursor, above 150°C, with total solvent removal at about 320°C. Here, too, films were cured on A1100-treated aluminum.

All films were 15-50 μm thick and were uniform over the areas used. Several runs were made under each condition. Data were taken at 10-15°C intervals in the temperature range of 25-85°C and at 10-15% intervals in the relative humidity range of 10-100%.

RESULTS

All data fit Arrhenius plots, as in eq. (1):

$$X = X_0 \exp(-E_X/RT) \quad (1)$$

where X is an observable, X_0 is a constant, E_X is an energy, R is the gas constant, and T is the absolute temperature. Values of X_0 and E_X so obtained are found in Table II. The concentration of water sorbed into the various polymers is plotted in Figure 1 as a function of relative humidity. As with the Kapton,⁸ the C values were temperature independent in the range studied. From these data, one may compare freestanding films with mounted films, the Polymer Permeation Analyzer with the sorption balance, and the effect of demounting the mounted films.

The freestanding films (Kapton, PI-2550, and AI-10) are characterized by low, mostly negative values of E_P , which indicates a minimal variation with temperature. Since $E_P = E_D + E_S$, both E_D and E_S are found to be similar in magnitude and opposite in sign; E_S is expected to be negative in sign, since it is the molar heat of water adsorption.⁸ On the other hand, mounted films (Skybond 703 and Thermid 600) are characterized by large negative values of

* A referee has kindly indicated that it is more commonly referred to as a polybenzimidazoquinazoline.

TABLE II
Values of Permeation Constants at 50% RH

$P_0 \times 10^8$, std cc cm/cm ² sec torr	5.99	3.46	51 μ m Kapton ^b (PPA)	51 μ m PI-2550 (PPA)	51 μ m PI-2550 (SB ^d)	30 μ m AI-10 (PAA)	18 μ m Mounted Skybond 703 (SB)	18 μ m Demounted Skybond 703 (SB)	18 μ m Mounted Thermid 600 (SB)	18 μ m Demounted Thermid 600 (SB)	28 μ m Demounted PIQ (SB)
E_p , kJ/mole	1.0 ± 0.33	-1.28 ± 0.88		-3.12 ± 1.34	-7.35 ± 3.47	-1.23 ± 0.28	-19.0 ± 2.5	-1.03 ± 4.98	-18.5 ± 2.0	-18.2 ± 1.5	-21.3 ± 3.4
Statistical significance ^a	>0.9950	>0.9000		>0.9750	>0.9500	>0.9975	>0.9995	>0.4000	>0.9995	>0.9995	>0.9995
D_0 , cm ² /sec	0.137	0.0316		0.0286	0.101	0.0304	0.0000112	0.0213	0.0000343	0.000357	0.0000625
E_D , kJ/mol	46.4 ± 1.3	42.0 ± 1.8		40.5 ± 2.0	41.6 ± 5.2	40.6 ± 1.3	17.3 ± 3.6	41.5 ± 2.4	22.7 ± 1.6	29.5 ± 2.4	23.9 ± 3.4
ΔS_D^\ddagger at 40°C, J/mole K	18	5.7		15	16	6.3	-59	2.4	-51	-32	-46
Statistical significance ^a	>0.9995	>0.9995		>0.9995	>0.9995	>0.9995	>0.9995	>0.9995	>0.9995	>0.9995	>0.9995
$S_0 \times 10^7$, std cc/cc torr	4.34	11.0		9.86	2.74	0.173	52.4	18.9	15.8	2.50	3.73
E_s , kJ/mole	-45.4 ± 1.3	-43.2 ± 1.9		-43.6 ± 2.2	-46.3 ± 3.9	-41.8 ± 1.2	-37.4 ± 2.9	-42.3 ± 1.2	-41.0 ± 0.5	-46.1 ± 1.2	-45.2 ± 1.3
Statistical significance ^a	>0.9995	>0.9995		>0.9995	>0.9950	>0.9995	>0.9995	>0.9995	>0.9995	>0.9995	>0.9995

^a From both *t*-test and correlation coefficient.

^b From ref. 8, included for comparison.

^c Polymer Permeation Analyzer.

^d Sorption balance.

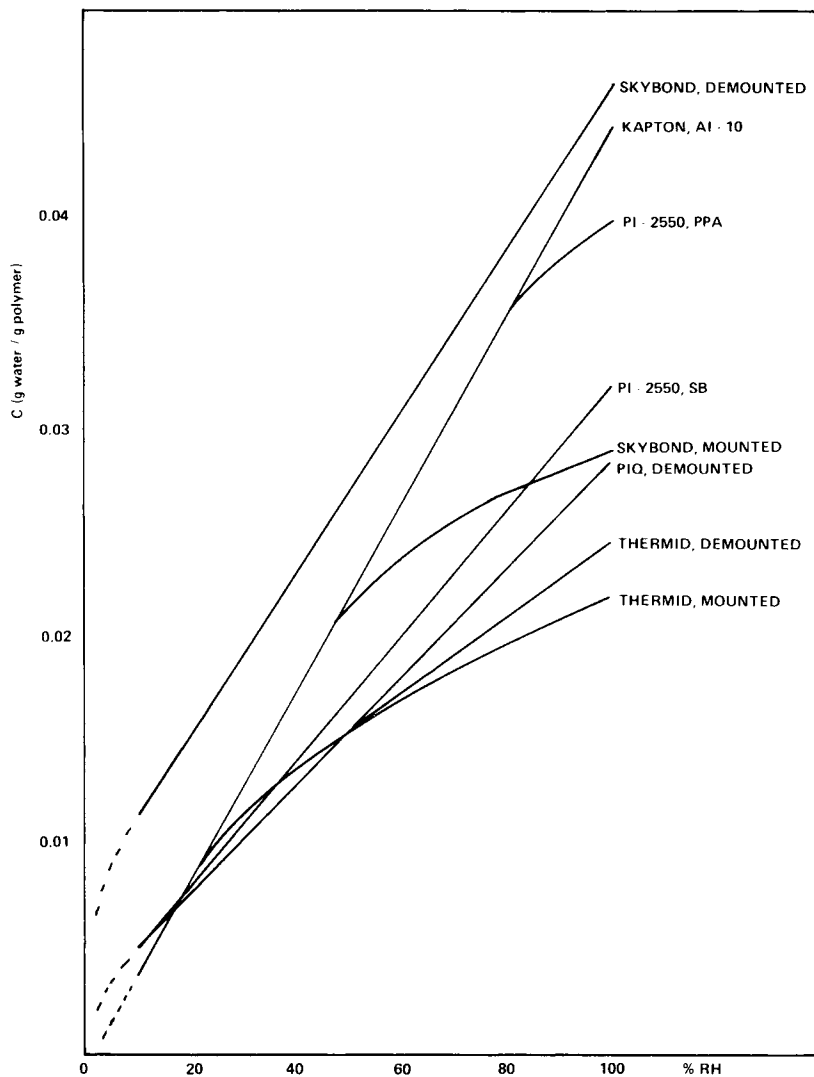


Fig. 1. Henry's law plots for the various polyimides.

E_P , compensating lower positive values of E_D , and little change in E_S . A significant decrease in D_0 , on mounting, is reflected in a negative value in ΔS^\ddagger_D , the entropy of activation for diffusion, rather than the expected positive value.⁸

Surprisingly, all the freestanding films measured on the Polymer Permeation Analyzer, as well as most others in Figure 1 (the standard errors of the estimates of the linear plots were all $< \pm 0.002$ g water/g polymer), fell along the same line as did the previous Kapton data⁸ and, as with the Kapton, were temperature independent. This similarity is difficult to understand, since relative humidity is independent of the material being studied. The Kapton study⁸ found that at 100% R.H., 1.03 mole water was absorbed per mole polymer repeat unit. In the present study, the C value for the freestanding AI-10 at 100% R.H. was found to be equivalent to 0.88 mole water per mole polymer repeat unit (MW = 334 g/mole); the PI-2550 measured on the Polymer Permeation Analyzer gave 0.94

TABLE III
 Estimated Molecular Weights

Material	Molecular weight, g/mole
Thermid 600	
Mounted	1198 ^a
Demounted	822
Skybond 703	
Mounted	620
Demounted	457
PIQ, demounted	692

^a The molecular weight of the prepolymer¹³⁻¹⁶ is 1098 g/mole.

mole water per mole polymer repeat unit (MW = 380–382 g/mole), while measured on the sorption balance this value was 0.86.

Assuming ~1 mole water per mole polymer repeat unit for Skybond 703, Thermid 600, and PIQ, as well, one may evaluate their molecular weights from the values of C at 100% RH. This was done, and is shown in Table III. The determinations for both Skybond 703 and Thermid 600 suggest that debonding in dilute HCl may have a deleterious effect on the molecular weight (partial hydrolysis?) or that the stresses influence the C values. While there is a paucity of data on chemical exposure of polyimides, both Kapton¹⁸ and Thermid¹⁹ suffer changes in mechanical properties after prolonged exposure even to water or water vapor at elevated temperatures. In any case, molecular weights have not decreased to the point at which they affect the diffusion process.^{20,21}

One may assume that a freestanding film, able to strain on swelling by the permeant, will respond as indicated earlier in this section. An inability to strain will cause changes²²⁻²⁴ in D but not in S . A comparison of the data for freestanding and mounted films (Table II) demonstrates this; further, the change in D_0 is reflected in the sign of ΔS^{\dagger}_D . However, removing the mounting does not necessarily mean that the demounted film is then free to relax. This may be seen by comparing demounted Skybond 703 with demounted Thermid 600: the demounted Skybond responds similarly to freestanding films, as described earlier in this section, even to having a positive ΔS^{\dagger}_D . This indicates that the interfacial stresses in the mounted sample were relaxed on demounting. On the other hand, the demounted Thermid responds in a manner almost identical to that of mounted Thermid, indicating the stresses were not relaxed on demounting. Clearly, this is understandable in light of the known propensity of Thermid to continue to react (crosslink) as the temperature is increased,¹³⁻¹⁶ indicating that the stresses exist in the bulk and not at the interface. While mounted PIQ was not available to us, we may judge from the similarity of the response of the demounted PIQ to demounted Thermid 600 that it also retains the stresses of the mounted film, suggesting a somewhat more complex cure than the simple condensation of polyamic acid to polyimide.¹⁷

The Polymer Permeation Analyzer (PPA) and sorption balance (SB) are fundamentally different in how they measure permeation. The PPA uses an He carrier gas to carry water vapor from one side of the sample to the other, while the SB follows sorption at all exposed surfaces. Each uses an appropriate approximation to calculate D as the equilibrium is approached, while at equilibrium

TABLE IV
Comparison of Permeation Data for PI-2550 Obtained by Polymer Permeation Analyzer and Sorption Balance at 50% R.H.

$T, ^\circ\text{C}$	$P \times 10^8$ ^a		$D \times 10^{-9}$ ^b		S ^c	
	PPA ^d	SB ^e	PPA ^d	SB ^d	PPA ^e	SB ^d
30	9.65	16.9	3.01	6.88	32.0	25.9 ₅
50	8.94	14.1	8.15	19.1	11.0	8.33
70	8.36	12.0	19.6	47.1	4.26	3.05

^a Units of std cc cm/cm² sec torr

^b Units of cm²/sec.

^c Units of std cc/cc torr.

^d Measured value.

^e Calculated value.

the PPA measures P and the SB measures S . Therefore, the PPA uses its measured properties D and P to calculate S , while the SB uses its measured properties to calculate P , the calculated property accumulating any errors in measurement. Thus, while both methods should give equivalent values of D , assuming that equally valid approximations were used in their calculations, the values of P obtained on the PPA are to be preferred, as are the S values obtained on the SB. These properties can be directly compared for the PI-2550 found in Table II, and are shown in Table IV. Surprisingly, the D values obtained by these two methods have the largest difference, between a factor of 2 and 2.5, with both P and S differing by less than a factor of 2. However, all differences in P , D , and S lie within the precision of the data, as seen by substituting maximum and minimum E_X values. Thus, within the precision of the experiments, the data obtained by both methods are equivalent.

DISCUSSION

Several important findings result from the data obtained. First, considering the freestanding films, which permeate through their ability to accommodate the motions of water molecules through straining, the permeation properties are virtually the same, even to the concentration of water sorbed at normal operating humidities and temperatures. Thus, a choice cannot be made among them based on water permeation.

Second, the diffusion coefficients of materials clearly depend on whether they are measured on freestanding or, more realistically, on conformal coatings. Since the latter use restricts relaxation, the actual diffusion coefficient will depend on the shape of the structure coated and on the coating thickness. As seen in Table II, differences may be spectacular.

Finally, demounting shows that stresses are not always relaxed and are, therefore, not totally due to interfacial bonding. Rather, as in the case of Thermid 600, and possibly PIQ, continued reaction causes crosslinking. One must be concerned that such reactions during processing may lead to embrittlement and, ultimately, to cracking during swelling.

The authors wish to thank the du Pont Company for supplying some of the samples and P. A. Lazarou for obtaining most of the data.

References

1. E. Sacher, *J. Macromol. Sci.*, **B12**, 603 (1976).
2. H. Lee, D. Stoffey, and K. Neville, *New Linear Polymers*, McGraw-Hill, New York, 1967, Chaps. 6 and 7.
3. N. A. Adrova, M. I. Bessonov, L. A. Laius, and A. P. Rudakov, *Polyimides*, Technomic, Stamford, CT, 1970.
4. E. Sacher, *IEEE Trans. Electr. Insul.*, **EI-14**, 85 (1979).
5. I. C. G. Ogle and G. W. Poling, *Can. Metal. Quart.*, **14**, 37 (1975).
6. D. A. Vermilyea, *Mater. Sci. Eng.*, **25**, 29 (1976).
7. J. C. Wood, *Corrosion-NACE*, **34**, 70 (1978).
8. E. Sacher and J. R. Susko, *J. Appl. Polym. Sci.*, **23**, 2355 (1979).
9. S. N. Zhurkov and G. Ya. Ryskin, *Zh. Techn. Fiz.*, **24**, 797 (1954).
10. C.-H. Shen and G. S. Springer, *J. Composite Mater.*, **10**, 2 (1976).
11. J. K. Gillham, K. D. Hallock, and S. J. Stadnicki, *J. Appl. Polym. Sci.*, **16**, 2595 (1972).
12. Monsanto Technical Bulletin No. 6236A, 1976.
13. A. Landis, N. Bilow, R. H. Boschan, R. E. Lawrence, and T. J. Aponyi, *Polym. Prepr. Am. Chem. Soc. Div. Polym. Chem.*, **15**(2), 537 (1974).
14. N. Bilow, L. B. Keller, A. L. Landis, R. H. Boschan, and A. A. Castillo, SAMPE Symposium Preprints, San Diego, Cal., Meeting, April 28-30, 1975, p. 791.
15. N. Bilow and A. L. Landis, *Polym. Prepr. Am. Chem. Soc. Div. Polym. Chem.*, **19**(2), 23 (1978).
16. P. A. Antonoplos and W. J. Heilman, *Am. Chem. Soc. Div. Org. Coat. Plast. Chem. Prepr.*, **38**, 584 (1978).
17. A. Saiki, H. Harada, T. Okuba, K. Mukai, and T. Kimura, *J. Electrochem. Soc.*, **124**, 1619 (1977).
18. du Pont Technical Information Bulletin H-1D, date unknown.
19. Gulf Specialty Chemicals Data Sheet, DLB/10/77.
20. H. Fujita, in *Diffusion in Polymers*, J. Crank and G. S. Park, Eds., Academic, New York, 1968, Chap. 3.
21. K. Ueberreiter, in *Diffusion in Polymers*, J. Crank and G. S. Park, Eds., Academic, New York, 1968, Chap. 7.
22. J. Crank, *J. Polym. Sci.*, **11**, 151 (1956).
23. G. Astarita and G. C. Sarti, *Polym. Eng. Sci.*, **18**, 388 (1978).
24. G. C. Sarti, *Polymer*, **20**, 827 (1979).

Received March 14, 1980

Accepted August 20, 1980