# Re-examination of the relationship between packing coefficient and thermal expansion coefficient for aromatic polyimides

**Shunichi Numata, Koji Fujisaki and Noriyuki Kinjo**
*Hitachi Research Laboratory, Hitachi Ltd, 4026 Kuji-cho, Hitachi-shi, Ibaraki 319-12, Japan*

*(Received 31 October 1986; revised 9 April 1987; accepted 16 April 1987)*

The existence of a possible relationship between molecular packing coefficient and thermal expansion coefficient for various aromatic polyimides was investigated. Rod-like low-thermal-expansion polyimides without side groups were seen to have very high packing coefficients, pointing to free volume as a factor in lowering their thermal expansion coefficients. But the small packing coefficients for low-thermal-expansion polyimides with side groups indicated that this was not so. Also, even if the large packing coefficients tended to increase the Young's moduli for these polyimides without side groups, the rod-like polyimides with side groups have small packing coefficients and large Young's moduli. The polyimides with low packing coefficients were found to have very small diffusion coefficients for water vapour.

**(Keywords: polyimide; thermal expansion; low thermal expansion coefficient; rod-like structure; packing coefficient; density)**

## INTRODUCTION

Polyimides are extensively used in electronics[1,2], aerospace and large electric device applications, because of their excellent mechanical and electrical properties and thermal stability[3-11]. Particularly in microelectronics, polyimides have become indispensable for high-quality insulating films.

Previous studies[12-18] on the relationship between polyimide chemical structure and their properties showed that some aromatic polyimides with rod-like shapes have very low thermal expansion coefficients, and suggested that the high molecular packing coefficient or the small free volume would be related to the low thermal expansion. In the present study, however, we will show that such a relationship is not general and that rod-like polyimides with side groups provide small thermal expansion coefficients in spite of their small packing coefficients, though the thermal expansion coefficients for those without side groups decrease with increasing packing coefficient. Also, relationships between packing coefficient and Young's modulus and between packing coefficient and diffusion coefficient of water vapour for polyimide films will be presented.

## EXPERIMENTAL

### *Materials*

A polyamic acid varnish was prepared by reacting an aromatic diamine with a stoichiometric amount of aromatic dianhydride in *N*-methyl-2-pyrrolidone at room temperature. Monomers used in this study were as follows:

*Diamines.* (A) *p*-Phenylene diamine (*p*-PDA); (B) *m*-phenylene diamine (*m*-PDA); (C) 2,4-diaminotoluene (24DATO); (D) 2,5-diaminotoluene (25DATO); (E) 2,6-diaminotoluene (26DATO); (F) diaminodurene (DADU); (G) benzidine (BNZD); (H) *o*-tolidine (*o*-TLD); (I) 3,3′-dimethoxybenzidine (DMBZ); (J) 4,4″-diaminoterphenyl (DATP); (K) 1,5-diaminonaphthalene (DANP); (L) 2,7-diaminofluorene (DAFL); (M) 4,4′-diaminodiphenyl ether (DDE); (N) 4,4′-diaminodiphenyl sulphide (DDS); (O) 4,4′-diaminodiphenylmethane (DDM); (P) 3,3′-dimethyl-4,4′-diaminodiphenylmethane (DMDDM); (Q) 2,5-diaminopyridine (DAPY); (R) 4,4′-bis(*p*-aminophenoxy)-biphenyl (BAPB); (S) 2,2-bis[4-(*p*-aminophenoxy)phenyl]-propane (DAPP); and (T) 2,2-bis[4-(*p*-aminophenoxy)-phenyl]hexafluoropropane (DAPFP).

*Tetracarboxylic dianhydrides.* (1) Pyromellitic dianhydride (PMDA); (2) 3,3′,4,4′-benzophenone tetracarboxylic dianhydride (BTDA); (3) 3,3′,4,4′-biphenyl tetracarboxylic dianhydride (s-BPDA).

The sample number of a polyimide is expressed by a letter for the diamine and a number for the dianhydride. For example, No. A1 indicates the polyimide obtained from *p*-PDA and PMDA.

The varnish was coated on a glass plate and dried at 100°C for 1 h. Then, the resulting film was stripped off and heated at 200°C for 1 h and at 400°C for 1 h in nitrogen gas. This gave a polyimide film. In the case of the polyimides with methyl or methylene groups, their final heating was at 350°C for 1 h, instead of at 400°C. When the polyamic acid film was heated after stripping it from the glass plate, the film was tightly fixed on an iron frame to prevent shrinkage due to solvent evaporation and imidization (bifix cure) or it was held by springs so as not to hinder the curing shrinkage (free cure).

0032-3861/87/132282-07$03.00

*Thermal expansion coefficient*

A film 5 mm wide, 65 mm long (between chucks) and 20–60 $\mu$m thick was used as a sample. The sample was placed in a thermal mechanical analyser (TMA 1500, Shinku-Riko Co. Ltd). Then it was heated at the final heating temperature (350 or 400°C) in order to remove absorbed water, to complete the imidization and to get rid of any residual stress. After cooling to room temperature, the change in length of the polyimide film was measured at a heating rate of 5°C min$^{-1}$ in air. Since the thermal expansion coefficient was temperature-dependent, the average value between 50 and 250°C was used as the representative value.

*Density and packing coefficient*

First, a liquid mixture of xylene and carbon tetrachloride, which could suspend the polyimide film sample, was prepared at 30°C. The film density was determined by measuring the density of the liquid mixture at 30°C, using a tuning-fork type density meter (DMA 02C, Anton Paar).

The packing coefficients were estimated from the densities using the equation proposed by Slonimskii *et al.*[19] The packing coefficient $K$ is expressed as follows:

$$K=\frac{V_{\mathrm{int}}}{V_{\mathrm{true}}}=\frac{N_{\mathrm{A}}\sum_i \Delta V_i}{M/d} \qquad (1)$$

where $V_{\mathrm{int}}$ represents the intrinsic volume of the atomic groups forming the repeating unit, $V_{\mathrm{true}}$ represents the molar volume from experimental measurements of density, $\Delta V_i$ are the volume increments of the atoms, $M$ is the molecular weight of the repeating unit, $d$ is the density of the polymer, and $N_{\mathrm{A}}$ is Avogadro's number.

*Young's modulus*

A film 5 mm wide, 25 mm long (between chucks) and 20–60 $\mu$m thick was used as a sample. After the film was dried at 120°C for 10 min in the measurement oven, the Young's modulus was measured at 30°C using a Rheopexy Analyzer RPX-706 (Iwamato Co. Ltd). A dynamic measurement was carried out at 10 Hz, under 15 $\mu$m displacement and 200 g load.

*Moisture permeability* ($K$)

A moisture permeation cup containing desiccant was sealed with a polyimide film using solid paraffin. The moisture permeability $K$ was evaluated from its weight change, measured at regular time intervals, at 25°C and 75%, relative humidity (r.h.).

*Saturated absorbed moisture content* ($C$)

Saturated absorbed moisture content $C$ was measured from the weight changes of the polyimide film. The film was weighed after drying at 200°C for 1 h and after leaving it for 50 h under controlled conditions at 25°C, 75% r.h.

*Diffusion coefficient of water vapour* ($D$)

The diffusion coefficient of water vapour $D$ was evaluated from the moisture permeability and saturated absorbed moisture content using the equations:

$$D=P/S \qquad (2)$$

$$P=K/\Delta p \qquad (3)$$

$$S=Cd/p \qquad (4)$$

where $P$ represents the moisture permeation coefficient, $S$ is the moisture solubility coefficient, $\Delta p$ is the difference in water vapour pressures, $d$ is the density, and $p$ is the water vapour pressure.

## RESULTS AND DISCUSSION

*Thermal expansion coefficients of various aromatic polyimides and their chemical structures*

The thermal expansion coefficients of various aromatic polyimides and their chemical structures have already been reported[17,18]. These data are summarized in *Table 1*. The values enclosed in the boxes indicate that they are lower than $2\times10^{-5}$ K$^{-1}$. Blanks indicate that the data could not be obtained due to film brittleness. Most of the values are as high as those of ordinary polymers. There are, however, some polyimides that have low thermal expansion coefficients. The smallest value is $4\times10^{-7}$ K$^{-1}$ for the polyimide obtained from 25DATO and PMDA. This value almost equals that of quartz glass.

In comparing bifix and free cured films, most of the coefficients for the former are smaller than those of the latter. Secondly, polyimides with smaller coefficients have a larger difference in values between bifix and free cured films. As has been reported elsewhere[17], these results seem to be due to molecular orientation generated by prevention of curing shrinkage.

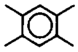
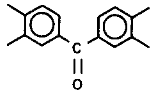
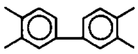
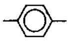
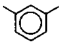
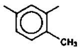
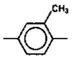
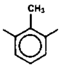
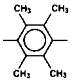
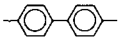
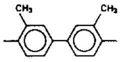
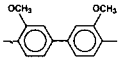
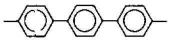
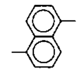
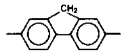
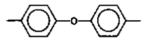
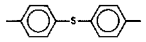
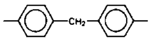
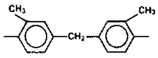
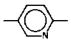
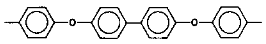
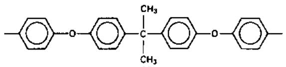
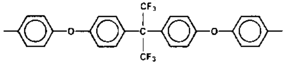
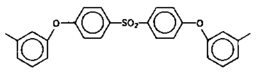
*Table 2* shows conformations of diamines and bis-imide skeletons of the low-thermal-expansion polyimides and other polyimides[20–22]. As we reported previously[18], all of the diamine skeletons of the low-thermal-expansion polyimides are composed of only benzene or pyridine rings fused at the *para* position. Also they include no bent structures such as a benzene ring fused at the *meta* positions, ether, methylene linkages, etc. Similarly, the pyromellite bis-imide skeleton is perfectly straight, and biphenyl bis-imide seems to be almost linear. Therefore, the conformations of these polyimides composed of linear diamines and bis-imides are almost linear[23]. By contrast, the high-thermal-expansion polyimides necessarily have bent structures, such as a benzene ring fused at *meta* positions, or ether, methylene, thioether, or ketone linkages. These results suggested that the thermal expansion coefficients of polyimides should be closely related to the linearity of the molecular structure.

A possible mechanism to explain the lowering of the thermal expansion coefficient is as follows. The low-thermal-expansion polyimides with rod-like structures have dense molecular packing, because they have very little steric hindrance. Therefore, their free volumes appear to be small. Since thermal expansion is an expansion of the free volume, it is reasonable that low thermal expansion coefficients result because of this small free volume. Examination of thermal expansion and molecular packing coefficients for various aromatic polyimides, as given next, shows that free volume is not the primary cause.

*Densities of polyimides*

Densities of various polyimides are shown in *Table 3*. Most are in the range 1.27 to 1.54, which are comparatively high values for polymers. In particular, it seems that those of the low-thermal-expansion polyimides are higher. Even if there are significant differences in thermal expansion coefficients between bifix

**Table 1** Thermal expansion coefficients ($10^{-5}$ x units $K^{-1}$) of aromatic polyimides

| | |  | |  | |  | |
|---|---|---|---|---|---|---|---|
| | | Bifix | Free | Bifix | Free | Bifix | Free |
| A |  | — | — | 2.10 | 4.34 | $\boxed{0.26}$ | $\boxed{1.90}$ |
| B |  | 3.20 | 3.70 | 2.94 | 3.67 | 4.00 | 4.22 |
| C |  | — | — | 3.95 | 4.70 | 3.19 | 4.67 |
| D |  | $\boxed{0.04}$ | $\boxed{1.65}$ | 2.59 | 4.06 | $\boxed{0.58}$ | 2.45 |
| E |  | 3.48 | — | 3.95 | — | 4.00 | 4.24 |
| F |  | $\boxed{1.61}$ | — | — | 3.89 | — | — |
| G |  | $\boxed{0.59}$ | $\boxed{1.83}$ | 2.17 | 4.37 | $\boxed{0.54}$ | $\boxed{0.92}$ |
| H |  | $\boxed{0.20}$ | $\boxed{0.64}$ | $\boxed{1.54}$ | 4.44 | $\boxed{0.56}$ | 2.77 |
| I |  | $\boxed{1.37}$ | 2.29 | 4.91 | 6.37 | 4.64 | 5.28 |
| J |  | $\boxed{0.56}$ | $\boxed{0.94}$ | $\boxed{1.83}$ | 3.10 | $\boxed{0.59}$ | $\boxed{1.38}$ |
| K |  | — | — | — | — | $\boxed{1.72}$ | — |
| L |  | $\boxed{1.58}$ | 2.71 | $\boxed{1.60}$ | 2.97 | $\boxed{1.13}$ | $\boxed{1.92}$ |
| M |  | 2.16 | 4.78 | 4.28 | 5.52 | 4.56 | 5.20 |
| N |  | 4.15 | 5.89 | 5.24 | 5.78 | 4.61 | 5.43 |
| O |  | 4.57 | 4.66 | 4.50 | 4.99 | 4.18 | 5.03 |
| P |  | 5.76 | 5.87 | 5.36 | 5.67 | 4.85 | 5.54 |
| Q |  | — | — | 2.61 | — | $\boxed{1.00}$ | — |
| R |  | 5.33 | 6.32 | 5.43 | 5.58 | 5.32 | 6.17 |
| S |  | 5.01 | 6.17 | 5.39 | 5.59 | 5.69 | 5.80 |
| T |  | 4.57 | 6.37 | 5.47 | 5.59 | 5.61 | 5.74 |
| U |  | 5.14 | 5.22 | — | — | 4.90 | 4.98 |

and free cured films, the densities of bifix and free cured films are almost the same.

This result suggests that very little change occurs in the intermolecular interactions by restraining the curing shrinkage, in sharp contrast with the significant change in molecular orientation. Therefore, the density data for bifix cured films are adopted for discussion below.

*Packing coefficient*

Molecular packing of the polyimides cannot be discussed simply by using their densities. The densities of their atoms must be considered in making any comparisons. In order to compare molecular packing, a 'packing coefficient' parameter has been proposed by Slonimskii *et al.*[19] Their investigation showed that most

**Table 2** Conformation of diamine and tetracarboxylic acid components

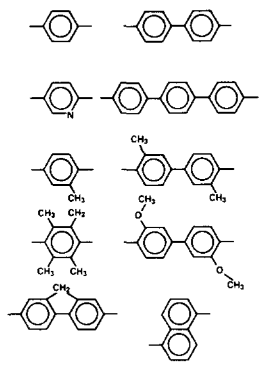
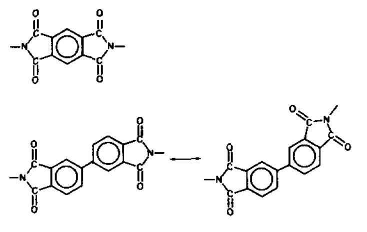
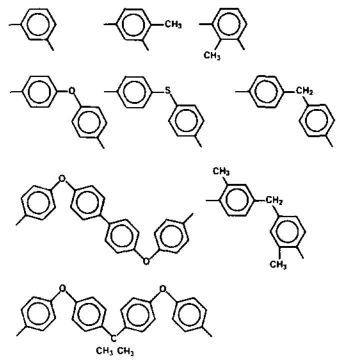
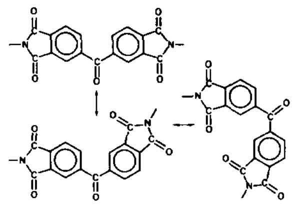
| TEC | $-R_1$-(diamine) | $R_2$ (tetracarboyxlic acid) |
|---|---|---|
| Low |  |  |
| High |  |  |

**Table 3** Densities of aromatic polyimides

| | Dianhydride | | | | | |
|---|---|---|---|---|---|---|
| | PMDA | | BTDA | | s-BPDA | |
| Diamine | Bifix | Free | Bifix | Free | Bifix | Free |
| (A) *p*-PDA | 1.54114 | 1.53954 | 1.45494 | 1.45542 | 1.46096 | 1.47543 |
| (B) *m*-PDA | 1.44836 | 1.44434 | 1.40844 | 1.41039 | 1.39164 | 1.39085 |
| (C) 24DATO | — | 1.39777 | — | 1.36705 | — | 1.34689 |
| (D) 25DATO | 1.43927 | 1.43192 | 1.39160 | 1.39635 | 1.39083 | 1.38374 |
| (E) 26DATO | — | — | — | — | — | — |
| (F) DADU | — | 1.38190 | — | — | — | — |
| (G) BNZD | 1.47041 | 1.46772 | 1.42469 | 1.42205 | 1.41981 | 1.41893 |
| (H) *o*-TLD | 1.34395 | 1.34680 | 1.32895 | 1.33052 | 1.33283 | 1.32848 |
| (I) DMBD | — | — | — | — | — | — |
| (J) DATP | 1.42819 | 1.42602 | 1.40715 | 1.40379 | 1.39930 | 1.39557 |
| (K) 15DANP | — | — | — | — | — | — |
| (L) 27DAFL | 1.46481 | 1.46373 | 1.42721 | 1.42636 | 1.42388 | 1.42332 |
| (M) DDE | 1.41725 | 1.41604 | 1.37277 | 1.37336 | 1.39198 | 1.39228 |
| (N) DDS | 1.40963 | 1.40920 | 1.37713 | 1.37755 | 1.36928 | 1.36821 |
| (O) DDM | 1.36533 | 1.36533 | 1.36991 | 1.36904 | 1.35901 | 1.34757 |
| (P) DMDDM | 1.32017 | 1.32124 | 1.30521 | 1.29699 | 1.29956 | 1.29704 |
| (Q) 25DAPY | — | — | — | — | — | — |
| (R) BAPB | 1.37155 | 1.37205 | 1.38010 | 1.38022 | 1.36182 | 1.36032 |
| (S) DAPP | 1.30481 | 1.30472 | 1.27930 | 1.27999 | 1.27112 | 1.26748 |
| (T) DAPFP | 1.42578 | 1.42364 | 1.39278 | 1.39045 | 1.38139 | 1.38319 |
| (U) *m*-APPS | 1.38726 | 1.38709 | — | — | 1.36583 | 1.36742 |

packing coefficients of ordinary polymers range from 0.665 to 0.695, but some unusual polymers have very high values. For example, the packing coefficient of polytetrafluoroethylene is 0.723.

Packing coefficients of various polyimides are shown in *Figure 1*. Even though their densities are considerably larger than those of ordinary polymers, most of the packing coefficients are in the same range. There are, however, some polyimides having high values. They are obtained from *p*-PDA, BNZD, DATP and DAFL, and their thermal expansion coefficients are very small. As expected, the rod-like low-thermal-expansion polyimides seem to be able to pack more compactly. This suggests that these low-thermal-expansion polyimides have molecular chains with very little steric hindrance.

Next, a relationship between molecular packing coefficient and thermal expansion coefficient is shown in *Figure 2*. As seen with only the data for polyimides without side groups, most have packing coefficients as low as ordinary polymers, and when the packing coefficients become higher, the thermal expansion coefficients become lower. However, in the case of rod-like polyimides with side groups on their molecular chains, their packing coefficients become smaller on introduction of the side groups. Dense packing should be hindered by a steric effect of pendant groups, which act as spacers for the polymer molecules. In spite of the low packing coefficient, their thermal expansion coefficients are almost the same.

These results suggest that molecular packing, i.e. free volume, is not the main factor in lowering the thermal expansion coefficient of polyimides. That is, although the rod-like low-thermal-expansion polyimides are easier to pack densely, there is no correlation between their packing and the thermal expansion coefficients. This conclusion is further supported by the observation that the densities of free and bifix cured films are almost the same in spite of significant changes in thermal expansion coefficients.

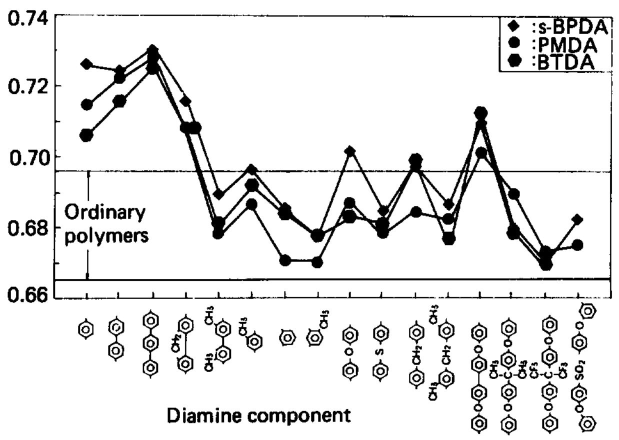


**Figure 1** Packing coefficients of various polyimides

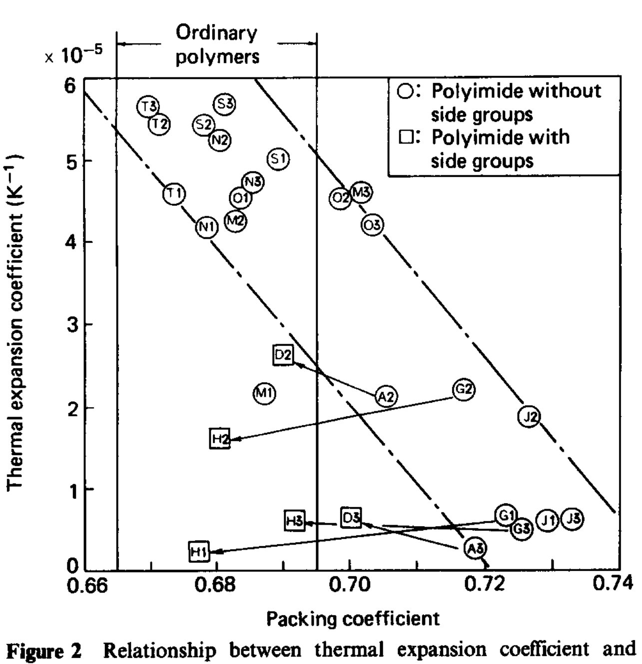


**Figure 2** Relationship between thermal expansion coefficient and packing coefficient for various polyimides

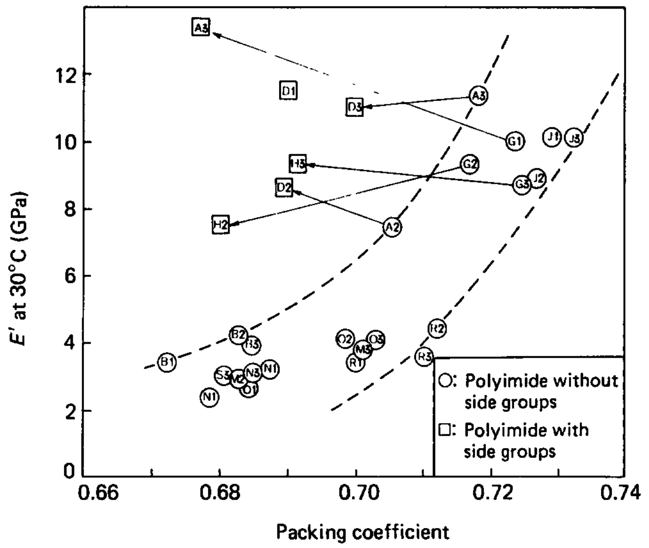


**Figure 3** Relationship between Young's modulus and packing coefficient for various polyimides

### *Relationship between packing coefficient and Young's modulus for various polyimides*

It has been reported by Yamada *et al.*[24] that Young's moduli are closely related to the molecular packing coefficient for molecular composites of flexible polymer molecules and rigid rod-like polymer molecules. Therefore, the relationship between the Young's modulus and the packing coefficient for various polyimides was also investigated here. As seen in *Figure 3*, for polyimides without side groups, those having a higher packing coefficient have a higher Young's modulus. However, for polyimides with side groups, even if their packing coefficient becomes lower, the Young's modulus hardly changes at all. This indicates that there is no correlation between Young's modulus and molecular packing coefficient. This conclusion is very similar to that reached for packing coefficient and thermal expansion coefficient. Higher Young's moduli appear because of molecular rigidity, just as for glass fibres in fibre-reinforced plastics (FRP).

### *Relationship between packing coefficient of polyimide and diffusion coefficient of water*

One of the most significant properties of highly packed polymers is their diffusion coefficient, because distances between polymer molecules are too small to allow small molecules to pass through them. Accordingly, the water permeabilities and absorbed moisture contents of various aromatic polyimides were measured and diffusion coefficients of water vapour were evaluated from these data. These results are shown in *Table 4*. *Figure 4* shows the relationship between molecular packing coefficient and diffusion coefficient of water for polyimides. Polyimides having higher packing coefficients have lower diffusion coefficients, as expected.

## CONCLUSIONS

The packing state of molecular chains has been studied for various aromatic polyimides in order to elucidate a mechanism describing lowering of their thermal expansion coefficients.

**Table 4** Moisture permeabilities, solubilities and diffusion coefficients for various polyimides

| Sample No. | Permeability constant $\times 10^{12}$ (g cm$^{-1}$ s$^{-1}$ cm Hg$^{-1}$) | Absorbed moisture content (wt%) | Solubility coefficient $\times 10^2$ (g cm$^{-3}$ cm Hg$^{-1}$) | Diffusion coefficient of water $\times 10^{10}$ (cm$^2$ s$^{-1}$) |
|---|---|---|---|---|
| A2 | 17.6 | 3.40 | 2.78 | 6.34 |
| A3 | 0.561 | 1.37 | 1.13 | 0.495 |
| B2 | 38.5 | 3.15 | 2.49 | 15.4 |
| B3 | 72.8 | 3.44 | 2.69 | 27.1 |
| D3 | 1.79 | 1.75 | 1.36 | 1.32 |
| G1 | 6.25 | 2.57 | 2.12 | 2.95 |
| G2 | 8.02 | 2.37 | 1.89 | 4.24 |
| G3 | 1.79 | 1.36 | 1.08 | 1.66 |
| H1 | 22.9 | 3.25 | 2.46 | 9.33 |
| H2 | 22.9 | 2.18 | 1.63 | 14.1 |
| H3 | 3.18 | 1.38 | 1.03 | 3.09 |
| J1 | 2.03 | 1.75 | 1.40 | 1.45 |
| J2 | 1.56 | 1.57 | 1.24 | 1.26 |
| J3 | 0.452 | 0.74 | 5.80 | 0.78 |
| M1 | 51.6 | 2.50 | 1.99 | 26.0 |
| M2 | 41.2 | 2.35 | 1.81 | 22.7 |
| M3 | 11.3 | 1.27 | 0.992 | 11.4 |
| O1 | 118 | 3.13 | 2.40 | 49.4 |
| O2 | 96.6 | 3.25 | 2.50 | 38.7 |
| R1 | 59.2 | 2.10 | 1.62 | 36.6 |
| R2 | 22.0 | 1.95 | 1.51 | 14.6 |
| R3 | 51.4 | 1.77 | 1.35 | 10.1 |
| S1 | 51.4 | 1.23 | 0.901 | 57.1 |
| S2 | 59.2 | 1.59 | 1.14 | 51.9 |
| S3 | 62.0 | 1.52 | 1.08 | 57.4 |
| T1 | 92.4 | 1.27 | 0.986 | 93.8 |

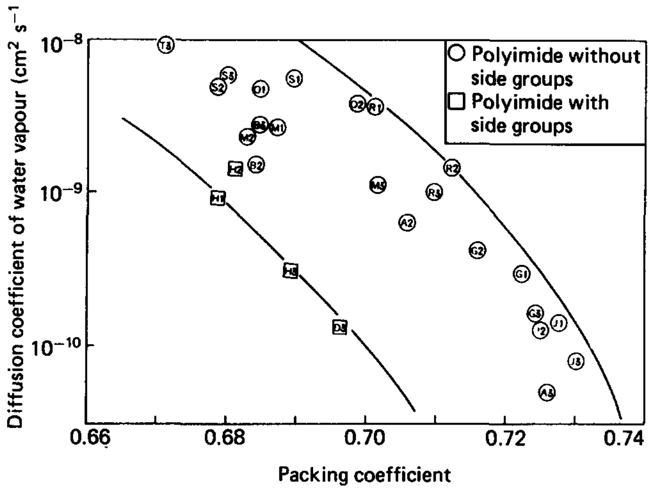


**Figure 4** Relationship between diffusion coefficient of water vapour and packing coefficient for various polyimides

There was very little difference between densities, i.e. packing coefficients of bifix and free cured films, in spite of significant changes in thermal expansion coefficients.

Low-thermal-expansion polyimides that had rod-like structures and no side groups had higher packing coefficients than ordinary polymers.

Even though molecular packing of the rod-like polyimides with side groups was loose, their thermal expansion coefficients were very small.

These results indicated that low thermal expansion did not appear because of their small free-volume fractions.

Rod-like polyimides having higher packing coefficients had very high Young's moduli, if there were no side groups. However, similar to the observations for thermal expansion coefficients, rod-like, low-packing-coefficient polyimides with side groups had high Young's moduli.

Rod-like polyimides with large packing coefficients had very small moisture diffusion coefficients.

## REFERENCES

1 Sato, K., Harada, S., Saiki, A., Kimura, T., Okubo, T. and Mukai, K. *IEEE Trans. Parts, Hybrid Packag.* 1973, **PHP-9**, 176, Sept.

2 Harasawa, K. and Oosawa, I. *Eng. Mater., Japan* 1982, **30**, 27

3 Sroog, C. E. *J. Polym. Sci., Macromol. Rev.* 1976, **11**, 161

4 Bower, G. M. and Frost, L. W. *J. Polym. Sci. A* 1963, **1**, 313

5 Sroog, C. E. *J. Polym. Sci. C* 1967, **16**, 1191

6 Koton, M. M. *Polym. Sci. USSR* 1971, **13**, 1513

7 Gillham, J. K., Hallock, K. D. and Standnicki, S. J. *J. Appl. Polym. Sci.* 1972, **16**, 2595

8 Koton, M. M. and Sazanov, Yu. N. *J. Thermal Anal.* 1975, **7**, 165

9 Johnson, R. O. and Burlhis, H. S. *J. Polym. Sci., Polym. Symp.* 1983, **70**, 129

10 Kochi, M. and Kambe, H. *Polym. Eng. Rev.* 1983, **3**, 355

11 Russell, T. P., Gugger, H. and Swalen, J. D. *J. Polym. Sci., Polym. Phys. Edn.* 1983, **21**, 1745

12 Numata, S., Fujisaki, K. and Kinjo, N. 'Polyimides; Synthesis, Characterization, and Applications', (Ed. K. L. Mittal), Plenum Press, New York, 1984, Vol. 1, pp. 259–71

13 Numata, S., Fujisaki, K., Kinjo, N. and Mukai, J. Papers of Technical Meeting on Electrical Insulating Materials, EMI-81-78, 1981

14 Numata, S. and Kinjo, N. *Kobunshi Ronbunshu* 1985, **42**, 443

15 Numata, S., Oohara, S., Imaizumi, J. and Kinjo, N. *Polym. Prepr., Japan* 1984, **34**, No. 4, 888

16 Numata, S., Oohara, S., Imaizumi, J. and Kinjo, N. *Polym. J.* 1985, **17**, 981

17 Numata, S., Oohara, S., Fujisaki, K., Imaizumi, J. and Kinjo, N. *J. Appl. Polym. Sci.* 1986, **31**, 101

18 Numata, S., Fujisaki, K., Makino, D. and Kinjo, N. Proc. 2nd Int. Conf. on Polyimides, pp. 492–510 SPE, New York, Nov. 1985; Numata, S., Makino, D. and Kinjo, N. *Polym. Eng. Sci.* in press

19 Slonimskii, G. L., Askadskii, A. A. and Kitaigorodskii, A. I. *Vysokomol. Soyed.* 1970, **A12**, 494

20 Bessonov, M. I., Kuznetsov, N. P., Adrova, N. A. and Florinskii, F. S. *Polym. Sci. USSR* 1974, **16**, 2425

21 Wellinghoff, S. T., Ishida, H., Koenig, J. L. and Baer, E. *Macromolecules* 1980, **13**, 834

22 Dien-Hart, R. A. and Wright, W. W. *Makromol. Chem.* 1971, **143**, 189

23 Kaneda, T., Katsura, T., Nakagawa, K. and Makino, H. *J. Appl. Polym. Sci.* 1986, **32**, 3151

24 Yamada, K., Mitsutake, T., Hiroshima, K. and Kajiyama, T. Proc. 2nd SPSJ Int. Polym. Conf., Tokyo, Aug. 20, 1986, p. 51