

The Density and Composition of Polyimide Surface Layers

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Synopsis

Density measurements as a function of polyimide film thickness have revealed that the surface layers, each 1.5 μm in thickness, have a density lower than that of the bulk by a statistically significant 1%. Infrared measurements have confirmed that this is due to the presence of isoimide in these surface layers: because of its nonlinear nature, this impurity structure causes a decrease in the measured density.

INTRODUCTION

Water permeation studies on a range of thicknesses of polyimide film have shown¹ that the boundary layers exhibit a substantially greater resistance to permeation than the bulk. This was subsequently found² to be due to the fact that, when polyimide is formed from cast polyamic acid films, the surfaces of such films possess an additional free energy per unit area, the surface tension, which causes the surface to react farther and faster than the bulk.

These surface layers have a cumulative thickness of $\sim 3 \mu\text{m}$ ¹ and are mechanically more brittle than the bulk. However, at least at the elevated temperatures at which ionic conduction predominates, there is no obvious contribution of these surface layers to the electrical conduction³ or other electrical properties.

Polyimide surfaces were recently investigated by ESCA.^{4,5} The first study⁴ found that, while the surface regions were structurally homogeneous, they did not represent stoichiometric polyimide. This was shown⁵ to be due to both faulty peak assignments and the presence of 8% isoimide. Because ESCA probes only the first few Angstroms of surface thickness, it is impossible to tell by this technique whether this apparent lack of stoichiometry persists into the bulk.

In a recent study in our laboratory,⁶ polyimide films were profiled by nuclear scattering techniques and found to have a composition independent of depth. The natural units of nuclear scattering ($\mu\text{g}/\text{cm}^2$) were converted to units of depth by dividing by an assumed depth-invariant polyimide density. The purpose of this note is to explore whether the isoimide structure, which has the same elemental composition as the imide structure, is perhaps confined to the outer layer. Its presence would be manifested in several ways, among them a lower density and a different IR spectrum.^{7,8}

Commercial DuPont Kapton type H polyimide film was used in the density study in nominal thicknesses of 7.6, 12.7, 25.4, 76.2, and 127 μm . Densities were determined at room temperature by submerging a sample in a small quantity of water in a test tube and then "titrating" with potassium iodide solution until the sample remained suspended in the liquid.⁹ These sets of determinations were repeated twice more over several days, using fresh potassium iodide solutions and distilled, deionized water. No attempt was made to compensate for the day-to-day temperature differences of $\sim 2^\circ\text{C}$, the batch-to-batch concentration differences of the potassium iodide solutions or the thickness variations of $< 4\%$ in samples randomly cut from rolls. It was consistently found that the density increased slightly but noticeably on going from 7.6 to 76.2 μm but decreased at 127 μm . Thus, for the purposes of the following correlation, the 127 μm data were not used.

The density of a polyimide sample, ρ , may be considered to be equal to the sum of bulk and surface densities, each multiplied by its volume fraction:

$$\rho = \rho_S v_S + \rho_B v_B \quad (1)$$

where the subscripts *S* and *B* refer to surface and bulk, respectively. Because these volumes differ only in thickness *l*, they are replaced by their respective values of l_i ; ρ_S may be assumed to be some fraction *x* of ρ_B :

$$\rho = \frac{x\rho_B l_S}{l} + \frac{\rho_B(l - l_S)}{l} \quad (2)$$

where $l = l_S + l_B$; this may be rearranged to

$$\rho = \rho_B + \frac{\rho_B l_S (x - 1)}{l} \quad (4)$$

Thus, a plot of ρ vs. $1/l$ should give a straight line, whose intercept is ρ_B and whose slope is $\rho_B l_S (x - 1)$. Knowing ρ_B and l_S (3 μm ; that is, 1.5 μm on each surface, as shown in Ref. 1) permits the evaluation of *x*.

The results are found in Table I where, to a statistical significance of > 0.9995 , eq. (4) is followed for all three sets of data. While these three sets of data appear to differ substantially, the values calculated from them are, in fact, remarkably similar; for example, the averaged density at $l = 25.4$ μm is 1.431 ± 0.002 g/cm^3 . Calculation gives $\rho_B = 1.433 \pm 0.001$ and $x = 0.988 \pm 0.006$. That is, ρ_S is found to be a mathematically statistically significant 1% lower than ρ_B . As care was taken to completely wet the samples and as measurements each required 1–2 min, these results cannot be attributed to entrapped air, permeation,¹ or other extraneous artifacts. The differences between sets of data may be attributed to the factors cited above, none of which would give rise to the negative slopes presented in Table I; rather, extraneous artifacts would affect the reproducibility of slope

TABLE I
 Linear Regression Analysis

Set	Intercept (g/cm ³)	Slope (g/μm cm ³)	Statistical significance ^a	$x (= \rho_S / \rho_B)$
1	1.435 ± 0.006	- 0.0147 ± 0.0038	> 99.95%	0.997 ± 0.001
2	1.433 ± 0.001	- 0.0497 ± 0.0106	> 99.95%	0.988 ± 0.003
3	1.431 ± 0.001	- 0.0959 ± 0.0162	> 99.95%	0.978 ± 0.008

^a Based on correlation coefficient values.

and intercept in a random fashion. We note, in passing, that because ρ_S and ρ_B differ by only 1%, ρ may be treated as thickness invariant in many circumstances, such as was done in the nuclear scattering profiles of Ref. 6.

It is interesting to speculate on whether isoimide formation may be the reason behind a surface which is more brittle, yet less dense than the bulk. The decrease in density at the surface suggests that surface crosslinking arguments may be excluded. It is possible that the same surface tension which causes the surface to react farther and faster than the bulk² also causes some surface structural modification, as has been found with ESCA.^{4,5} The depth of this structural modification is not known, although it must be greater than the escape depth of the ESCA-released electron (~ 20 Å for C1s). Further, nuclear scattering profiles⁶ showed no abrupt elemental changes though the thickness of the surface layer, suggesting a difference in structure without a change in atomic concentration.

The isoimide structure certainly meets this condition. It is known to be present in polyimide^{7,8,10,11} and has the same elemental composition as the imide structure. Further, because of its nonlinear chain structure, its density would be lower than of the linear imide.

In order to ascertain whether the surface layers were richer in isoimide structure, infrared spectra were obtained from all sample thicknesses with a Nicolet series 6000 FTIR. It had previously been shown¹¹ that the percent isoimide in polyimide films follows the equation

$$\% \text{ isoimide} = 11.4 \times A_{920} / A_{1010} \quad (5)$$

where A is the absorbance and the subscripts refer to the positions, in wavenumbers, of peak maxima. The percentage of isoimide as a function of film thickness is presented in Table II and plotted in Figure 1, along with the surface value of 8%, obtained from ESCA.⁵ Clearly, there is an increase in isoimide content with decreasing thickness.

Assuming that the isoimide is found exclusively in the surface layers, one may write, for $l > l_S$,

$$\% \text{ isoimide} = \frac{\% \text{ isoimide}_S l_S + \% \text{ isoimide}_B l_B}{l} \quad (6)$$

TABLE II
 Percent Isoimide

$l(\mu\text{m})$	% isoimide
0	8 ^a
7.6	4.10
12.7	4.01
25.4	2.95
76	2.91

^a From Ref. 5.

Rearrangement gives

$$\% \text{ isoimide} = \frac{(\% \text{ isoimide}_S - \% \text{ isoimide}_B) l_S}{l} + \% \text{ isoimide}_B \quad (7)$$

from which a plot of IR-determined % isoimide vs. $1/l$ has an intercept of % isoimide_B and a slope of $(\% \text{ isoimide}_S - \% \text{ isoimide}_B) l_S$. Such a plot of IR data is presented as the solid line in Figure 2. An analysis gives % isoimide_B = 2.74 and % isoimide_S = 6.57. The latter value is less than the 8% obtained for the outer 20 Å by ESCA. Assuming a value of 8% isoimide_S, one may calculate the expected slope. It is shown as the dashed line in Figure 2 and is only slightly different from that calculated. We take this as confirmation that isoimide does, indeed, exist exclusively in the outer layers of polyimide and is probably reasonably uniformly distributed throughout l_S .

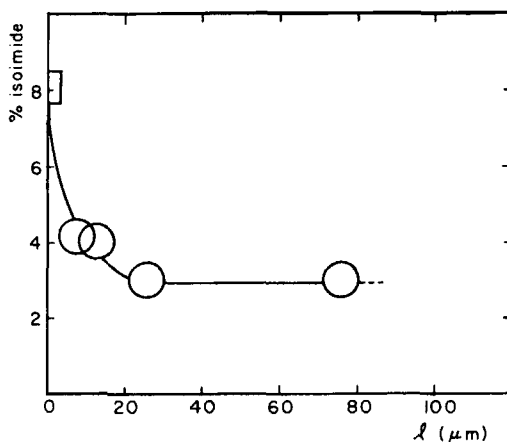


Fig. 1. A plot of the IR-determined % isoimide as a function of sample thickness. The point at zero thickness was taken from data cited in Ref. 5.

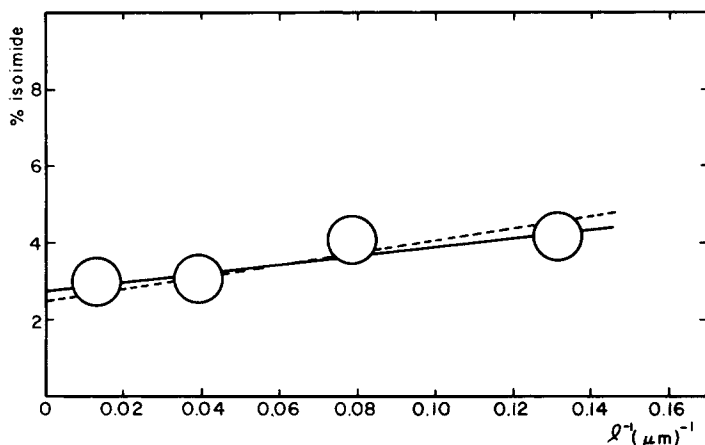


Fig. 2. A plot of the IR-determined % isoimide as a function of reciprocal sample thickness. The solid line is the slope corresponding to the points. The dashed line is that corresponding to an assumed 8% isoimide at the surface.

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