

The Effect of Paracrystal Formation on the Surface Tension of Annealed Polyimide

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INTRODUCTION

A previous paper¹ indicated thermomechanically, dielectrically, and with IR that physical rather than chemical changes occur on annealing du Pont Kapton 100H polyimide film at 240°C. Since nodules form on the polyimide surface under these conditions,² it was pointed out that the data, and particularly the dielectric data, were understandable if the nodules were paracrystalline, as had been shown for surface nodules on poly(ethylene terephthalate)³ and polycarbonate.⁴

Surface thermodynamics offers an ideal method of testing for paracrystal formation, using the method outlined by Kaelble.⁵ According to this method, one measures the contact angles made by various liquids on the substrate of concern, and the data are fit to the equation

$$\frac{W_a}{2\alpha_L} = \alpha_S + \beta_S \left(\frac{\beta_L}{\alpha_L} \right) \quad (1)$$

where W_a is the work of adhesion [$\equiv \gamma_L(1 + \cos \theta)$]; γ_L is the surface tension of the contacting liquid and θ is its contact angle; α_L and α_S are the square roots of the dispersive components of the liquid and substrate surface tensions, respectively; and β_L and β_S are those of the polar components. Since α_L and β_L are known for the contact liquids used and W_a is calculable, the surface tension of the substrate may be obtained through summing its components. The variations of these components with extent of annealing may be used to give an insight into surface rearrangements occurring during nodule formation.

A problem arises concerning the prior history of Kapton: its manufacture is proprietary, and one cannot be sure to what extent paracrystal formation has already occurred on receipt of the film. To obviate this, the polyamic acid precursor was obtained and its cure followed by thermogravimetric analysis, IR, and surface thermodynamics.

EXPERIMENTAL

Substrate surface tensions were calculated from contact angle data obtained on a Ramé-Hart NRL goniometer thermostatted to 20°C. The contacting liquids used were water, glycerol, formamide, ethylene glycol, tricresyl phosphate, and *n*-dodecane and were the purest obtainable. Several liquid surface tensions were evaluated on a Du Nouy tensiometer to assure they were within experimental error of those listed by Kaelble,⁵ and Kaelble's α_L and β_L values were used directly. Plots of $W_a/2\alpha_L$ versus β_L/α_L proved to be linear (with statistical significance to the 99th percentile), and α_S and β_S were obtained as the intercept and slope, respectively. An example is seen in Figure 1.

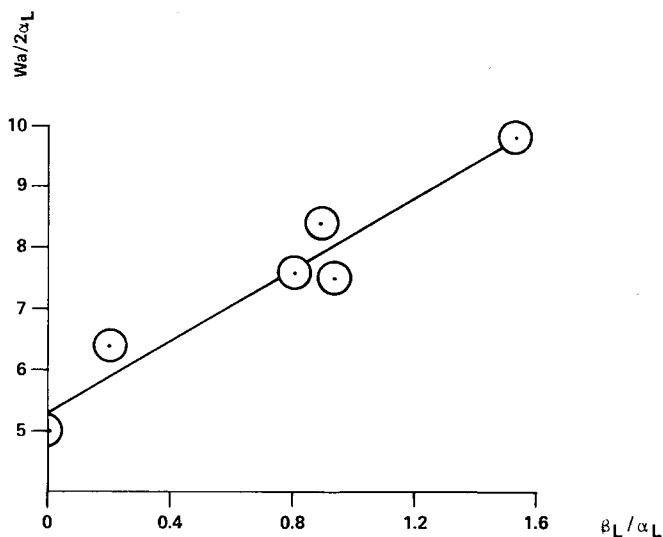


Fig. 1. A Kaelble plot of RC-5057 cured to 325°C. The T -test value of 7.736 and the correlation coefficient of 0.968 show, for a sample size of 6, α larger than 99% significance.

The polyamic acid precursor to Kapton was obtained as du Pont Pyre-ML wire enamel RC-5057, an N-methylpyrrolidone solution. A drop was smeared between salt flats to give a $\sim 1 \mu$ coating and was cured for successive 20-min intervals at 120°, 200°, 280°, and 325°C. Cure was followed with a Perkin-Elmer 621 grating infrared spectrophotometer and, on separate samples, with a du Pont 950 thermogravimetric analyzer.

RESULTS AND DISCUSSION

The cure data are found in Table I, where it is seen that the sample cured after a short time at 200°C. The continued small weight loss up to 325°C is probably

TABLE I
Physical Changes During Cure of RC5057

Condition	$\alpha_s^2 + \beta_s^2 = \gamma_s^a$			IR	TGA ^b
Solvent removal under vacuum	26.3	14.7	41.0	polyamic acid ^{6,7}	
Previous condition plus 120°C/20 min	24.9	15.9	40.8	partial conversion to polyimide	87.4 ± 1.1% weight loss
Previous conditions plus 200°C/20 min	25.9	11.8	37.7	almost complete conversion to polyimide	9.5 ± 0.8% quick initial weight loss, followed by slower 1.9 ± 0.9% weight loss
Previous conditions plus 280°C/20 min	27.2	9.8	36.8	polyimide ^{1,6,7}	0.8 ± 0.2% weight loss
Previous conditions plus 325°C/20 min	28.5	8.3	36.8	polyimide	0.4 ± 0.2% weight loss

^a In dynes/cm ± 0.5.

^b Percentage is that of total weight loss.

due to this thicker sample ($\sim 30 \mu$) retaining N-methylpyrrolidone, which is high boiling and tenacious. The IR data show complete cure prior to 280°C , so that any changes in surface tension which occur on further annealing to 325°C must be due to physical changes occurring on the surface, namely, nodule formation.

Since paracrystal formation occurs spontaneously ($\Delta F \leq 0$), it must involve reduction of the fields of the local dipoles rather than enforcement. Thus, in the absence of any competing (i.e., chemical) process, paracrystal formation should manifest itself through a decrease in the polar component of γ_S and a concomitant increase in the dispersive component (since polar component is being converted into dispersive component).

Table I shows that, while γ_S does not change on going from 280° to 325°C , the polar component β_S^2 decreases 1.3 dyne/cm and the dispersive component α_S^2 increases a like amount. This is what one would expect were the nodules that are being formed paracrystalline.

Qualitative support comes from the following. A proprietary topcoat known to bond to the carbonyl oxygen of the polyimides bonds better to the coating annealed at 280°C than to that annealed at 325°C . This is a clear indication that the carbonyls in the latter instance are less available for bonding, in direct support of paracrystal formation.

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