NOTE

The Significance and Error of Polymer Adhesion Measurements with the Ultracentrifuge

It has been proposed that the ultracentrifugal polymer adhesion measurement is not influenced by other film properties and is a "pure" measurement.[1,2] Yet, little has been published which substantiates this conclusion quantitatively. Because of great interest in the ultracentrifuge as an adhesion research tool[1-3] this note is offered to describe a statistical analysis of adhesion data. The analysis was initiated to increase measurement precision, find which factors are contributing to the error, and shed some light on the mechanism of failure when the polymer leaves the rotor.

The statistical analysis is for adhesion test data for an epoxy polymer cured with diethylenetriamine, details of which have been published.[2] Qualitatively it was observed that odd-shaped, thick test samples showed poorer precision and that measured stress values may be a function of sample shape. In addition, the adhesion was known to be a function of certain chemical factors.[2] In order to take into account possible and known variables, a multiple regression model was fitted and the significance of the results tested statistically. The initial model employed was:

$$F_i = \beta_1\eta_i + \beta_2\eta^2_i + \beta_3 \log t_i + \beta_4 \log a_i + \beta_5 \log b_i + \beta_6 r_i + \beta_7 W_i + \epsilon_i \quad (i = 1, 2, 3, \ldots, N)$$

where the β's are the population regression coefficients and the ϵ_i's are normally and independently distributed errors with mean zero and variance σ^2. Here, η is the viscosity, t the thickness of the sample, a and b the major and minor axes of the sample (regarding it as an ellipse), r the equivalence ratio of amine to epoxide, and W the epoxide analysis used to distinguish resin lots.[2] Physical dimensions of the polymer spot on the rotor were measured with an optical comparator and toolmaker's microscope. Spot diameters were approximately 0.0350 in. and thickness approximately 0.0040 in.

The mathematical model was justified as a first approximation after constructing plots of adhesion versus each of the variables; the adequacy of the model was later judged by fitting observed to predicted values. The logarithmic functions were used as a means of creating new variables, such as $t \times a$. In all, $N = 126$ observations were included in the analysis. Computation was facilitated by using the IBM 650 and Cohen's published regression program.[4] The analysis was repeated for six selected subset of variables, and the significance of each variable was tested by the appropriate F ratio. The results are summarized in Table I.

The physicochemical factors were found to be significant at a high level. Their significance persists, no matter what subset of variables is used in the regression model. The addition of the variable a or b does not add significant information not measured by t. The variable t does not add significant information not measured by a and/or by b. Despite the fact that the analysis was for six subsets, it was not repeated when t and either a or b was omitted. Hence, there is the vague possibility that, if t is excluded with either a or b from the model, the remaining variable, either b or a, may become significant.

In reporting previous results the effect of the adhesion of geometrical parameters a, b, and t was not taken into account. This model, therefore, is of particular interest. The error mean square of the adhesion measurement for the inclusion of all variables and the exclusion of the geometric variables may be compared as given in Table II. The error for the last case in Table II corresponds to a coefficient of variation of 10% for the observed mean adhesion of 1121 psi for the 126 observations.

TABLE I
Analysis of Variance

Source of variance	Degrees of freedom	Sum of squares, $(psi)^2 \times 10^{-6}$	Mean square, $(psi)^2 \times 10^{-6}$
Regression of all variables but t, a, and b	4	2.779	0.695[a]
Addition of t	1	0.120	0.120[a]
Further addition of a	1	0.011	0.011
Further addition of b	1	0.010	0.010
Error	118	1.421	0.012
Total	125	4.341	
Regression of all variables but a and b	5	2.899	0.580[a]
Addition of a and b	2	0.021	0.011
Error	118	1.421	0.012
Total	125	4.341	

[a] Significance at the 0.001 level.

TABLE II

	Error, $(psi)^2$
With all variables	12,000
With a and b omitted	12,000
With a, b and t omitted	12,900

The error of the adhesion measurement is unaffected by the exclusion of a and b from the calculation but not of t. The adhesion experimental error can be reduced by properly noting the effect of t judged from the values of the regression coefficients. For all independent variables included, $\beta_t = 0.259$. When a and b are omitted, $\beta_t = 0.230$. The approximate dependence of adhesion on $t^{1/4}$ is indicative of a mechanism of removal of the polymer spot from the rotor. It is noteworthy that regression coefficients for a and b indicate adhesion could depend on $\sqrt{(a/b)}$ in such a way that highest precision corresponds to $a = b$ (circular spots).

For thick spots, the adhesion becomes significantly dependent on thickness. Thicker spots have been observed to have a more conical shape and uneven thickness distribution. Thin spots are more even in their thickness distribution, almost flat rather than conical. After adhesive failure under the highest point, the centrifugal force will have an uneven distribution which will be a function of the thickness distribution. The applied force will be insufficient to overcome the adhesion at the edge of the thick sample, and only the major portion of the spot will fail and be removed. The periphery of the spot will be sheared through, which accounts for the portions of sample left on the rotor as a peripheral ring after the testing of thick, unevenly shaped spots. Under these conditions the assumptions made in the derivation of the equation for the calculation of the adhesive force[1] no longer hold. Consequently, the high test values observed for thick, uneven spots are in excess of the adhesive force and are rejected. In contrast, thin, almost flat, spots of even thickness distribution would be expected to fail evenly and completely, leaving no peripheral ring as has been observed.

The precision of the ultracentrifugal adhesion measurement can be improved by using uniformly shaped samples (preferably circular) of uniform but not necessarily constant thickness. The detailed statistical analysis indicates that within the 10% reported error the measurement of adhesion by ultracentrifugation is independent of sample geometry but very much dependent on chemical and polymer factors.

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POLYMER AND FIBER MICROSCOPY SOCIETY

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Needs of Microscopists and Needs of Management for Microscopy

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The microscopist as a specialist has certain needs as a professional which demand consideration by management. These must show an emphasis on opportunity to do interesting, worthwhile, and challenging work, an environment where scientific accomplishments are given full recognition, and opportunity to grow professionally through publications, study, and scientific work.

Management has a need of outstanding creative scientific work in basic and applied fields, a need which directly or indirectly is of economic value. The needs often bring pressures on the scientist and are misunderstood by him and thought to be in conflict with his own. Management and the scientist must work together if the needs of both are to be be satisfied.

Seeing Problems of Visual Microscopy

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Successful microscopy requires a correctly magnified image of a properly prepared specimen and adequate means of detecting and analyzing the information in the image. The human eye usually is the detector, viewing either the image directly or a record of the image, such as a photograph or cathode ray trace. Seeing requires that enough light of proper quality (intensity and color) be on the retina of the eye long enough to be coded into nerve impulses and for the impulses to be conducted to the brain and integrated into consciousness. Age, state of health, glare, and immediate adaptation modify vision. Seeing is a learned ability and training can improve it. Some of the basic factors of vision—size, contrast, color, acuity, radiation, etc.—are discussed as determiners of what can be seen with a microscope.