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## The Journal of Adhesion

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713453635>

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**To cite this Article** Clarke, J. A.(1972) 'Polymer Viscoelasticity: Relation to Peel Strength in Structural Adhesives', The Journal of Adhesion, 3: 4, 295 – 306

**To link to this Article:** DOI: 10.1080/00218467208072200

**URL:** <http://dx.doi.org/10.1080/00218467208072200>

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# Polymer Viscoelasticity: Relation to Peel Strength in Structural Adhesives<sup>†</sup>

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*(Received November 4, 1971)*

The two tests of most importance in evaluating structural adhesives for metals are (1) lap shear strength and (2) peel strength. Epoxies perform well in the first due to high tensile and shear strength. They are poor in the second unless modified to reduce brittleness. We have developed a urethane modified epoxy for this purpose. By taking climbing drum peel data in which both the temperature and the peel rate are varied, the time-temperature superposition principle can be tested. This principle is most generally applicable to thermoplastic materials between  $T_g$  and  $T_g + 100^\circ\text{C}$  ( $T_g$  = glass transition temperature), and serves as a measure of viscoelastic response in the polymer. First, good agreement was found for a thermoplastic adhesive (PE-AA film). This was done to verify that climbing drum peel data can be used in this manner. Next, data were taken for our urethane modified epoxy. Results showed adherence to the superposition principle only above the heat distortion temperature of the cured polymer. These results indicate, among other things, that our point of failure upon peeling is within the body of the adhesive rather than within a urethane-rich layer at the metal-adhesive interface.

## INTRODUCTION

Peel strength is an important but often poorly developed property in structural adhesives. Adequate peel strength calls for the presence of strongly developed viscoelastic properties. To achieve this, flexible modifiers or coreactants are incorporated into the polymer network. In some cases this will lead to formation of a second phase as the adhesive is cured; in other cases this does not occur. For either case, the important factor appears to

<sup>†</sup> This paper was presented at the *Symposium on Recent Advances in Adhesion* during the 162nd National American Chemical Society Meeting, September, 1971.

be the ability of the added viscoelastic elements to resist the applied peel forces. This effect may be measured by a technique analogous to one that applies to pressure-sensitive adhesives: Time-temperature reduction of the peel data by the WLF superpositioning procedure. This paper covers such a study for modified epoxy adhesives and shows that the WLF equation applies for data taken above the glass transition temperature of the cured epoxy.

## EXPERIMENTAL

Peel strength data were taken for several structural adhesives, varying both the peel rate and test temperature. The climbing drum test, ASTM D1781-62, was used. This was preferred to T-peel (ASTM D1876) or other methods because of the relatively constant angle of peel and the ability to duplicate results with reasonable accuracy. The test specimens were prepared from two 1" x 12" x 0.020" type stainless steel strips bonded with a 3 mil thickness of the adhesive under study. Each sample provided an eight-inch length of glue line that could be peeled, sufficient to vary the peel rate several times during a single test. The Instron Universal Tester allowed control of cross-head speed over a range of 0.05 to 10 inches per minute. This speed was used as the abscissa for the graphical analysis, in preference to calculating the actual strain rate for the adhesive at the point of failure. For the geometry of the experimental system, the rate of strain in tension is about 2.5 times the crosshead speed.

A Missimers Environmental Cabinet was used for test temperatures other than ambient. The data were worked up using methods applicable to viscoelastic materials as described in the next section. Tables I and II give typical data. A graphical method, illustrated in Figure 1, was used to determine if time-temperature superpositioning of the data is allowed. Where a reasonable fit was obtained, the WLF equation (below) was used to calculate a glass transition temperature ( $T_g$ ) for the adhesive and this was compared to the known  $T_g$  for the polymer. By comparing results for several adhesive types, some conclusions were drawn as to the basic requirements for peel strength.

## THEORY

For the outlined approach to be useful, two questions require a positive answer. These are:

1. Can a crosslinked polymer show a time-temperature dependency characteristic of viscoelastic behavior?

TABLE I  
Peel Strength  
Adhesive: XD-3599 (Urethane Modified D.E.R. 331)

Test Temp., °F	Instron Speed			Log $a_T$
	0.1"/min.	1.0"/min.	10.0"/min.	
-67°F	35 lb/in	32	26 brittle	
0	61	62	71	
R.T. (77°F)	85	107	104	
120	76	93	98	
150	66	79	85	
170	56	74	76	
190	62	79	82	
<sup>a</sup> 210	65	68	76	0 (ref. temp.)
230	37	55	61	-2.37
250	15	29	41	-4.18
270	4	13	30	-5.32

<sup>a</sup> At 210°F, a change from cohesive failure of the adhesive to what is termed "adhesive" failure occurs. That is, the point of failure is at or near the interface.

TABLE II  
Peel Strength  
Adhesive: Nitrile Rubber Modified D.E.R. 331

Test Temp., °F	Instron Speed			Log $a_T$
	0.05"/min.	0.5"/min.	5.0"/min.	
77°F	43 lb/in	82	91	
150	45	60	79	
180	46	50	74	
200	59	65	80	
220	56	63	77	
240	44	52	67	
260	26	38	55	0 (ref. temp.)
280	14	29	42	-.36
300	2	9	22	-2.215

The  $T_g$  value calculated from  $a_T$  is 258°F (126°C).

2. Can adhesive peel data show this effect? (It had been noted that this property depends strongly on method and rate of measurement.)

These questions have been answered separately by several observers<sup>1,2</sup>. The work of D. H. Kaelble is particularly relevant in first analyzing the stresses developed in an adhesive as a peel force is applied<sup>3</sup>, and also in the time-temperature reduction of peel data for pressure-sensitive adhesives<sup>4</sup>. Reference 5 gives a thorough treatment of this technique and of the WLF equation. This equation applies to the bracketed portion of the "master curve" shown in Figure 2, extending from the  $T_g$  value for the test polymer to about 100°C above this point. Extension into the glassy region, the normal service area for structural adhesives, is not allowed. However, the area that is covered is of prime interest, since it includes the upper useful service temperature for a given adhesive.

## WLF EQUATION

The WLF equation can be written as:

$$\text{Log } a_T = - \frac{17.4 (T - T_g)}{51.6 + T - T_g} \quad (1)$$

$T$  = Test temperature, °C

$T_g$  = Glass transition temperature for the polymer

$a_T$  = "Shift Factor", defined by Eq. (2) and measured graphically as the shift in the time or rate scale required to establish time-temperature equivalence.

$$\text{Log } a_T = \text{Log } \frac{\eta_T}{\eta_{T_g}} \quad (2)$$

where  $\eta$  is the "internal viscosity" of a polymer.

At  $T_g$ , the void fraction in the polymer increases to allow short segments of the polymer chain, perhaps 4 or 5 chain atoms, to move about freely and it is this motion that contributes to the reduction in the internal viscosity,  $\eta$ . The chemical composition of these segments is of minor importance, thus we can compare such diversified adhesives as epoxies, urethanes, acrylics, etc. by the WLF equation. Where it applies, the internal viscosity and the measured properties that are dependent on viscosity will vary strongly with temperature. Also, since we are dealing with viscoelastic polymers, this viscosity will vary with the rate of testing. Thus the abscissa for the master curve of Figure 2 could be temperature, time, or a combination of the two. Our objective is to confirm that peel strength is an adhesive property that follows this behavior.

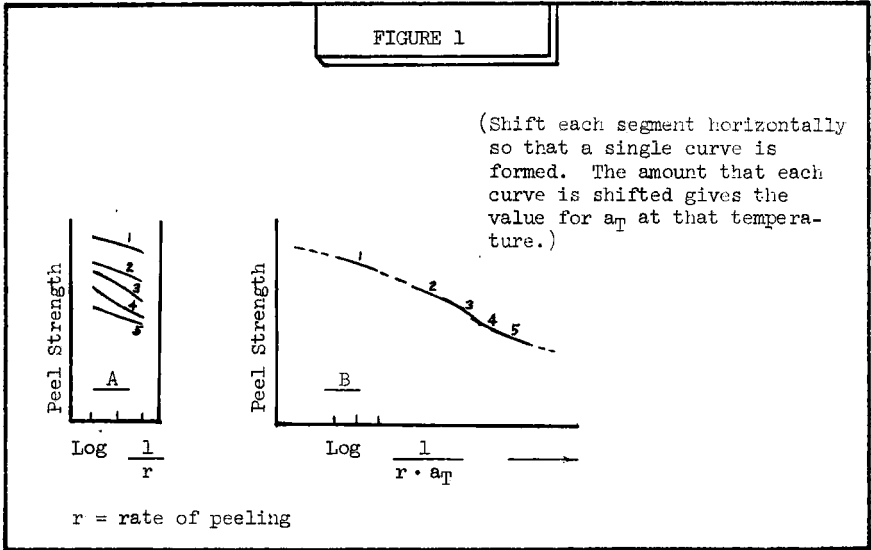


FIGURE 1 Illustration of time-temperature superpositioning technique

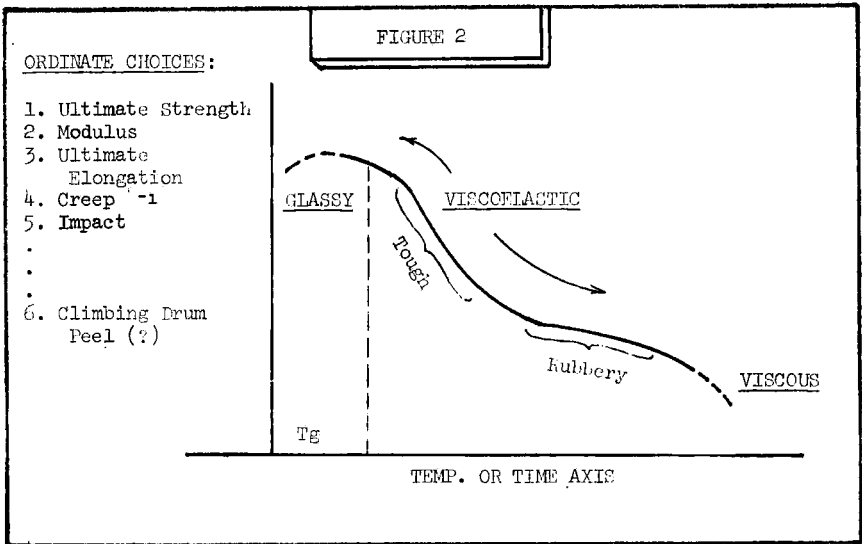


FIGURE 2 Polymer Master Curve, according to Reference 5, p. 145

## DATA

### I Verification of the WLF equation for climbing drum peel data

For a preliminary test, a film adhesive was used, composed of polyethylene-8% acrylic acid copolymer. This was chosen for two reasons—it is a thermoplastic above its  $T_g$  at room temperature and therefore should give data that fit the WLF equation; and it develops high peel strength as an adhesive for metals.

Type 304 stainless steel, 20 mil thickness, was bonded with this adhesive at 360°F under 30 psi pressure. The peel strength data are given below:

Test Temp., °F	Instron Speed			Log $a_T$
	0.1"/min.	1.0"/min.	10.0"/min.	
R.T. (77°F, reference temp.)	101 lb/inch	136	163	0
150	32	46	68	-3.1
170	28	35	54	-3.8
190	27	30	36	-4.5
210	13	15	22	?

These data are plotted on log-log paper, first as individual curves at a given test temperature as in *A* in Figure 1. These curves are then superimposed graphically to give a single "master curve" *B* as discussed in reference 5. The finished curve for the data above is shown in Figure 3. The horizontal distance that each curve is shifted gives the value for  $a_T$  at that temperature. A trial and error or preferably a graphical method can then be used to apply the  $a_T$  values to the WLF equation. This gives an experimental  $T_g$  for the polymer.

### Conclusions

The data obtained could be superposed, as shown in Figure 3. Reasonable  $a_T$  values were obtained and indicated that  $T_g = -6^\circ\text{C}^*$ . Using this in the WLF equation already given, points on the "master curve" were calculated and shown as  $\otimes$ 's in Figure 3.

These results showed that the climbing drum peel test can detect viscoelastic response in a polymer. The next step was to apply this to crosslinked adhesives.

### II Urethane modified epoxy adhesive, XD-3599.

This type of adhesive is described in U.S. Patent 3,525,779. It is a high peel strength structural epoxy, cured with 10 phr dicyandiamide. Samples were

† Torsion pendulum data indicate a  $T_g$  of about  $+2^\circ\text{C}$  for this type polymer.

prepared using the same metal substrates and cure conditions as for I. Data are given in Table I and the resultant plot is shown as Figure 4. The

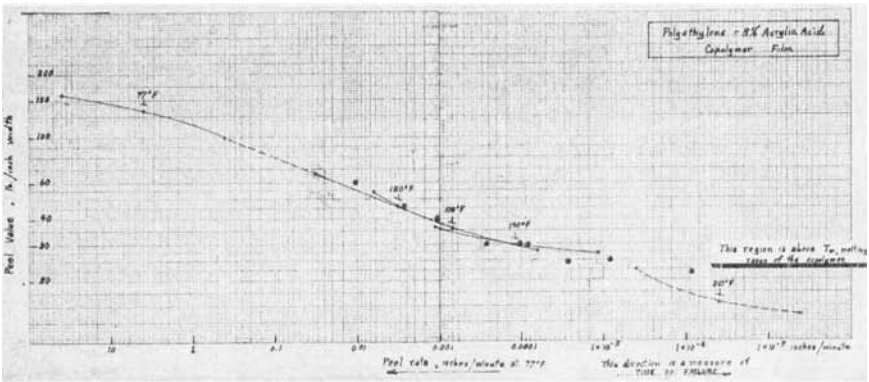


FIGURE 3 Peel Strength Master Curve, Polyethylene-Acrylic Acid Copolymer Film Adhesive.

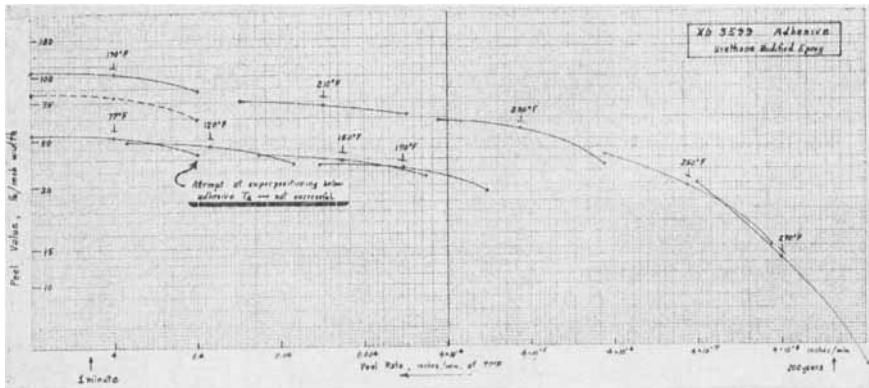


FIGURE 4 Peel Strength Master Curve, Urethane Modified Epoxy Adhesive.

plot indicates that superpositioning is allowed above  $T_g$ . The shift factors in turn give a value for  $T_g$  of 190°F (88°C). This is in close agreement with the 91°C value found by the torsion pendulum. Below  $T_g$  the shift factors were very erratic and the data for varying test rate at a single temperature gave too much curvature to justify superpositioning.

**Discussion**

The data include several points of interest.

1. For a crosslinked adhesive such as this example, there is sufficient internal mobility above the glass transition temperature to show the



viscoelastic response required by the WLF equation. The nonlinear response below  $T_g$  indicates presence of viscoelastic elements here also but their effect is suppressed by the crosslinked matrix.

2. The effect of temperature alone is of interest. There is a sharp rise in peel strength as the test temperature approaches  $T_g$ . This gives a hump in the peel-temperature profile, Figure 5, which indicates that the peel strength just above  $T_g$  is three times the predicted value by extrapolation from below this point. This could be viewed as the contribution by additional viscoelastic elements whose segmental motion is "freed up" at  $T_g$ .
- 2a. The tensile shear-temperature profile, Figure 6, does not show any inflection in this region to correspond to that for peel. However, such an effect may be obtained with certain adhesives. This is discussed by Malinskii *et al*<sup>6</sup>, who attribute the increase in tensile shear value as  $T_g$  is approached to "accelerated relaxation of unbalanced stress concentrations at this temperature."
3. Individual curves for each test rate, Figure 7, indicate that  $T_g$  may decrease with increasing test rate. This is contrary to the expected behavior for viscoelastic materials. We could speculate that here the lowest rates are giving test times longer than the relaxation time of some of the elements, so that the presence of the cross-linked network is more pronounced. As these additional viscoelastic elements enter at higher

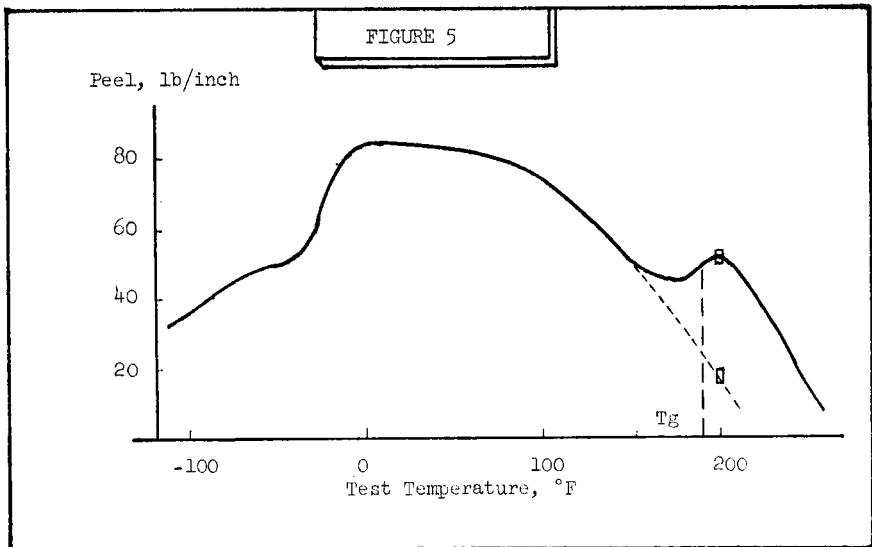


FIGURE 5 Temperature Profile for Peel Strength of Urethane Modified Epoxy Adhesive.

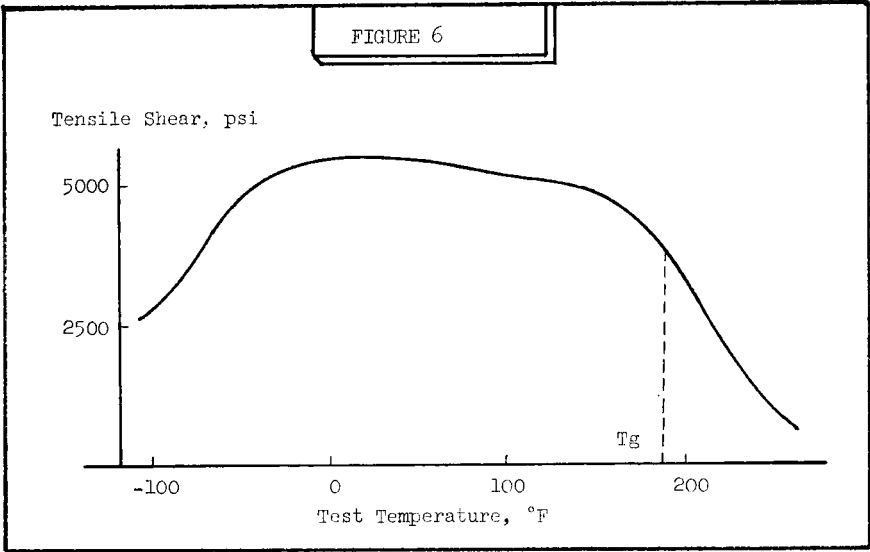


FIGURE 6 Temperature Profile for Tensile Shear Strength of Urethane Modified Epoxy Adhesive.

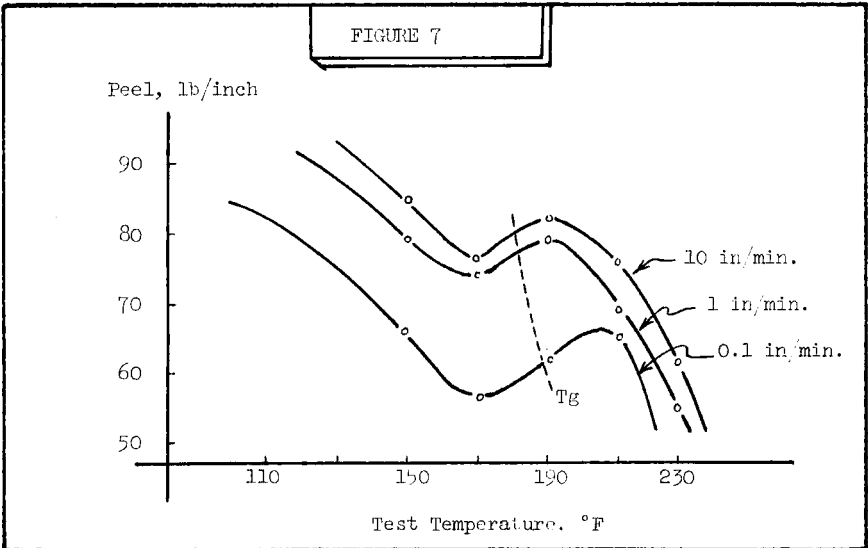


FIGURE 7 Examination of Temperature Profiles for Peel Strength of Urethane Modified Epoxy Near the Glass Transition Temperature.

test rates, the peel strength value will increase and its variation with temperature will lean towards a lower  $T_g$  more characteristic of the modifier alone. However, the accuracy of the data is not sufficient to dwell on this point.

4. The urethane modifier does not form a separate phase in this system, although electron micrographs (Figure 8A) indicate hazy inclusions in the cured polymer that may represent urethane-rich areas. This polymer mixture is probably typical of the borderline compatibility that is discussed in reference 5, page 81. It was thought possible before obtaining these data that selective migration of urethane to the metal interface was responsible for the high peel strength (typical of urethane adhesives). These tests indicate that the failure in peeling is within polymer representative of the bulk polymer alloy ( $T_g = 91^\circ\text{C}$ ) rather than within a urethane layer ( $T_g = -18^\circ\text{C}$ ) or unmodified epoxy ( $T_g = 126^\circ\text{C}$  with dicyandiamide cure). Note that the  $T_g$  value obtained through the use of the WLF equation is for that portion of the polymer which is actually being stressed to failure during the peel test. Thus if the point of failure were within urethane-rich or, more likely, within urethane-deficient regions, the  $T_g$  value measured in this way should deviate substantially from  $91^\circ\text{C}$ .

### III Commercial urethane adhesives

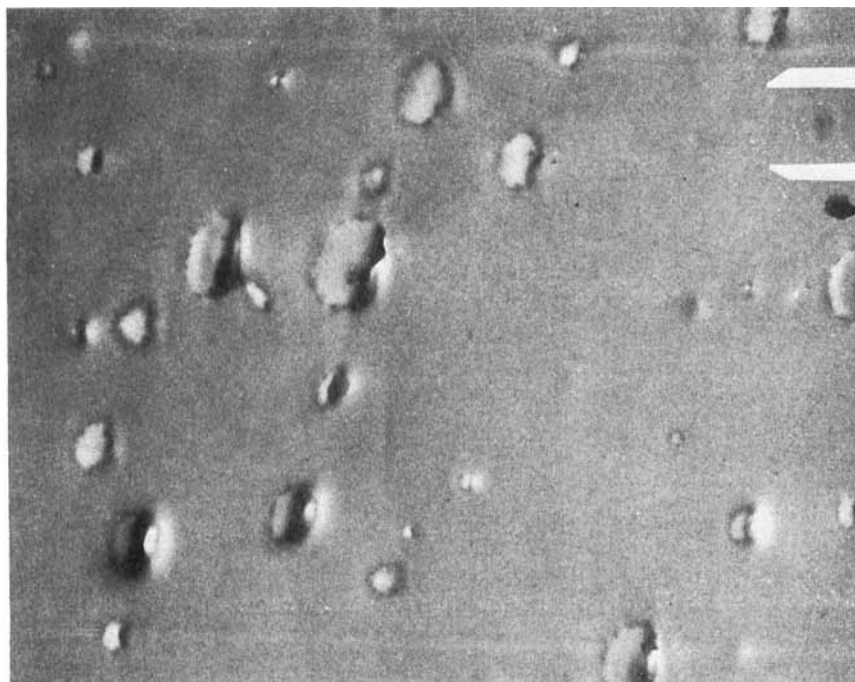
Samples were prepared as above for a two-part urethane, cured at  $200^\circ\text{F}$ . Usable data could not be obtained due to inability to control the point of failure as a given sample was peeled. Fluctuations here led to fluctuations in the recorded peel value.

### IV Nitrile rubber modified D.E.R. <sup>®</sup>331 (dicyandiamide hardener)

Table II gives the data for this system. Here again the data above  $T_g$  could be superpositioned, and an acceptable value for  $T_g$  was obtained through the WLF equation. A similarity to the urethane modified epoxy is shown by the sudden rise in peel strength as the test temperature approaches  $T_g$ . On the other hand, there are some marked differences between the two systems. Electron microscopy, Figure 8B, shows the rubber phase as discrete particles averaging 1 micron diameter. A minor amount of the rubber remains dispersed in the epoxy matrix, but the  $T_g$  is not lowered measurably from the  $126^\circ\text{C}$  value for unmodified D.E.R. 331.

The differences also include (1) adhesive, rather than cohesive, failure which prevails both above and below  $T_g$ , down to room temperature;

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B. Nitrile Modifier



A. Urethane Modifier

FIGURE 8 Electron Micrographs of Cured Modified Epoxies

2) a much stronger effect of test rate below  $T_g$ . This could be related to the broader molecular weight distribution for the nitrile modifier.

Peel Comparison in Glassy Region (Room Temp.)

	Test Rate = 0.1"/min.	1.0"/min.	10"/min.
A. Urethane-Epoxy	83	103	100 (relative
B. Nitrile-Epoxy	67	94	100 values)

Data below the glass transition temperature of course cannot be superposed with any meaning. If time and temperature were equivalent here, we would predict poorer elevated temperature performance for the rubber modifier. The low peel values at long test time would mean low values at higher temperature. But time and temperature are not equivalent here and the opposite is true; the nitrile gives the better high temperature properties since it does not reduce the glass transition temperature as strongly as the urethane.

### V Solid urethane modified epoxy resin.

XD-7127, a urethane modified D.E.R. 661 solid epoxy resin, was tested in a similar manner. The data did not superpose in any region. Here we have a mixture of two types of flexible chains; the urethane and the higher molecular weight components in the epoxy resin. The latter promote some degree of peel strength in unmodified D.E.R. 661. No attempt was made to separate the two contributory effects.

### CONCLUSIONS

Peel strength in a structural adhesive can be evaluated through the contributions of viscoelastic elements in the polymer network. Comparison of data taken above and below the glass transition temperature of the crosslinked polymer network are both important to this evaluation.

This method of analysis does not have great precision but it can be useful to gain an understanding of the mechanisms involved in developing peel strength in structural adhesives. This in turn gives us another opportunity to help close the gap between theory and practice in adhesion.

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