

Studies on Adhesion of Allylic Resin. III. Rheological Treatment for the Adhesion of Diallyl Phthalate Resin

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Synopsis

Rheological treatment was carried out for the joining system of diallyl phthalate resin and dichromate-treated copper foil. Rotational and diffusional segmental motions in the diallyl phthalate molecule are required to obtain the necessary bonding strength, and this consideration was confirmed by Kanamaru's setting rate theory. Furthermore, the bonding strength was dependent on the setting temperature and time, and these results were investigated by the dynamic properties of diallyl phthalate resin.

INTRODUCTION

The authors recently reported an effective method for the surface treatment of copper foil for adhesive bonding to diallyl phthalate (DAP) resin.^{1,2} The technique is a simple one. The copper foil is merely dipped into a potassium dichromate acid-sulfuric acid mixture solution at 60°C for 5 min.

We have investigated the surface characteristics of the dichromate-treated copper foil and the chemical and physical properties of the interface of DAP resin. From the results, it is believed that the adhesive bonding is a result of the chemical affinity of chromium ion to the dichromate-treated copper surface and the allyl groups in DAP molecule.

In this communication, the authors are reporting on the rheological considerations of the adhesive bonding between the dichromate-treated copper foil and DAP resin.

In order to orient the allyl groups in DAP resin toward the attractive centers of the adherend, i.e., the chromium ion, internal molecular motion and segmental diffusional motion in DAP molecule are required. It is of interest to develop the relationships between the adhesive reaction at the interfaces and physicochemical properties of DAP resin.

EXPERIMENTAL

The copper foil used as the adherend was treated in a dichromate solution (potassium dichromate, 76 g/l.; sulfuric acid, 0.67*N*) at 60°C for 5 min.

Adhesive bonding was performed under pressure and heat, that is, the copper-clad laminates of DAP were prepared under a pressure of 38 kg/cm² using varied setting times and temperatures.

Adhesive strength of DAP to the treated copper foil was determined by measuring the peel strength (180°) to the adherend. The peeling test was carried out in a conditioning room at 20°C, 65% R.H., at a peel rate of 100 mm/min.

RESULTS AND DISCUSSION

Rate of Setting of Adhesive Joint and Activation Energy

The adhesional setting is the reaction by which secondary and primary bonds are formed on the adherend surface between the attractive centers of each of these two molecules. Viewing from a kinetic consideration of the reaction rate, the process of the adhesional setting is composed of the diffusional motion of the adhesive molecules to the surface of the adherend.

In order for diffusion in highly polymeric systems to be possible, the reactive groups and polar groups in the adhesive must first be arranged in a most favorable state of orientation toward the surface of adherend. From these considerations, the reaction of adhesional setting in viscous high polymers is governed by the molecular motion of the matrix containing the attractive groups.

Recently, Kanamaru³ considered the adhesional setting rate by rheological treatment and obtained the following equation:

$$F(t) = K(1 - e^{-t/\tau}) \quad (1)$$

where F is the adhesive strength; K is a constant independent of t , the setting time; and τ is the retardation time of the resin ($= \eta/E$, η being viscosity coefficient and E the dynamic modulus).

Thus, for change of joint strength with the setting time t , a similar sigmoidal curve for the F -versus- $\ln t$ plot should be expected. The time

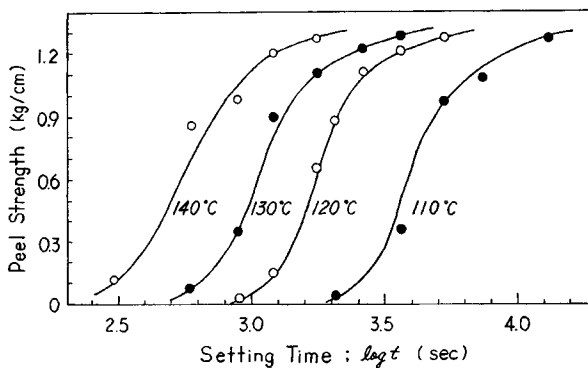


Fig. 1. Bonding strength vs. $\log t$ for the joining system of DAP and dichromate-treated copper foil.

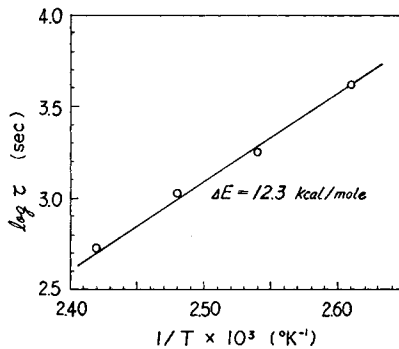


Fig. 2. Time parameter $\log \tau$ -vs.- $1/T$ plot.

parameter τ , characteristic of each of the reactions concerned, is obtained from the point of the inflection of the F -versus- $\ln t$ plot. If such experimental observations are undertaken at various temperatures T , the apparent activation energy ΔE [= $R d \ln \tau / d(1/T)$] is obtained from the approximately linear inclination of the $\log \tau$ -versus- $1/T$ plot.

From the above-mentioned theoretical considerations, the adhesional mechanism of DAP resin and the dichromate-treated copper foil was investigated experimentally, as shown in Figure 1. It shows the interrelation of adhesive strength and log of the setting time as a parameter of the setting temperatures.

It may be concluded that the F -versus- $\ln t$ plots are sigmoidal curves and that the adhesional reactions in DAP resin are governed by the rheological characteristics of the resin.

In Figure 1, the inflection points of t ($= \tau$) are the region of dispersion in the polymeric systems, and we can obtain the plot of $\log \tau$ versus $1/T$ (T = setting temp.). From the results shown in Figure 1, we are able to plot $\log \tau$ versus $1/T$, as shown in Figure 2, and thus calculate the activation energy of the adhesional reaction. The result is $\Delta E = 12.3$ kcal/mole, which is very reasonable compared to the general value of the segmental motion in the polymeric material.

From the above-mentioned discussions it is concluded that the adhesional setting reaction is governed by the diffusional theory of molecules and is represented by the relaxation mechanism of molecular motion having an activation energy ΔE , as follows:

$$\tau = A \exp (\Delta E / RT) \quad (2)$$

where τ is the retardation time.

Setting Temperature and Bonding Strength

As mentioned previously, diffusional motion of the polymeric molecule occurs in preference to the orientation of the polar groups to obtain the combining strength. This investigation suggests that the adhesional

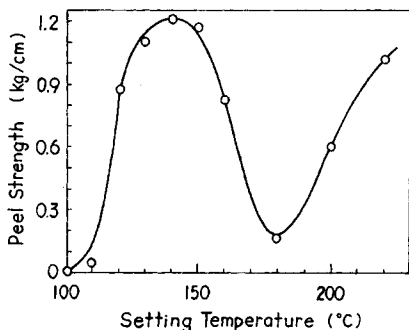


Fig. 3. Bonding strength at various setting temperatures. All setting times are 30 min.

strength depends on the setting temperatures because the molecular motion occurs at a particular temperature region.

Figure 3 shows the results of the temperature dependence of the adhesion strength between the dichromate-treated copper foil and DAP resin. The high values for the peel strength in the temperature region of 140°–150°C may be the result of the internal molecular motion in the DAP molecule which is occurring at the previous temperature region.

The dynamic properties of the DAP molecule was investigated by the Vibrating Reed Method,⁴ and the results are shown in Figure 4. This method yields the complex Young's modulus, E^* , given by

$$E^* = E' + iE'' \quad (3)$$

where $i = \sqrt{-1}$, and E' and E'' are, respectively, the real and imaginary components of the complex Young's modulus; the mechanical loss tangent $\tan \delta$ is obtained by E''/E' . In Figure 4, $\tan \delta$ of the DAP molecule has a

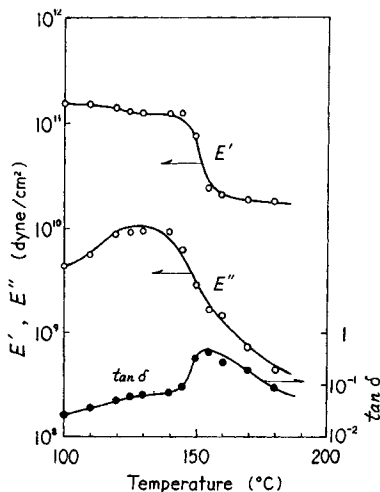


Fig. 4. Dynamic properties of DAP resin measured by the Vibrating Reed Method.

maximum value at a temperature of 150°C, and this result explains the relation of the setting temperature and the peeling strength, as was shown in Figure 3.

Setting Time and Bonding Strength

Equation (1) shows the setting time dependence of the bonding strength, and this is shown in the results in Figure 1.

However, we also observed the interesting result shown in Figure 5, namely, that bonding strength is decreased with excess setting time. Several possible reasons for this phenomenon are: (1) decomposition of the resin, (2) influence of the curing agent, (3) contraction in volume of the resin by the curing process, and (4) elastic coefficient of the resin.

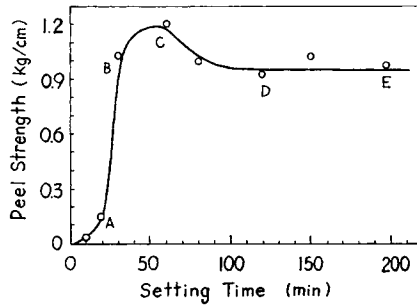


Fig. 5. Decrease in bonding strength by excess setting times. Setting temperatures are all 130°C.

The first reason should not result in a decrease in bonding strength because DAP resin has excellent thermal stability; and the second reason is not important since a very small amount of initiator was used in this experiment. Furthermore, DAP resin has excellent dimensional stability, and therefore the third reason should not contribute to the decrease in bonding strength. Accordingly, in this case, the most likely reason for this phenomenon is the elastic coefficient of the resin.

The modulus of elasticity of the resin was measured by the Vibrating Reed Method at points C and E in Figure 5, with the following results:

point C:

$$E' = 1.20 \times 10^{11} \text{ dynes/cm}^2$$

point E:

$$E' = 1.36 \times 10^{11} \text{ dynes/cm}^2$$

Such being the case, eq. (1) is represented as follows:

$$F(t) = (F_{\infty} - n\gamma E) (1 - e^{-t/\tau}) \quad (4)$$

and the apparent bonding strength is decreased by the increase in elasticity of the resin. Here, F_{∞} is the theoretical bonding strength (constant) and γ is the strain. That is to say, the increase in internal stress ($n\gamma E$) is the main cause for the decrease in bonding strength.

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