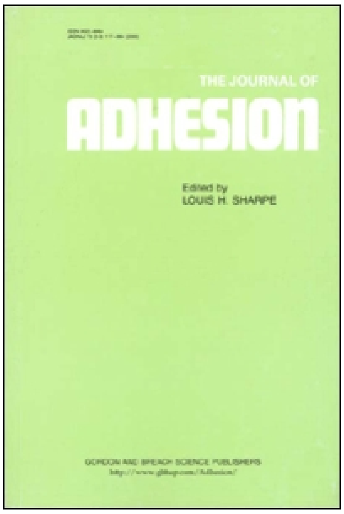

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The Effects of Cure Conditions on the Relaxation Behavior of Thermosetting Adhesives†

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The ability to dissipate mechanical energy by plastic (viscous) deformation is an important strength consideration for structural adhesives. The bulk solid viscosity parameter, μ, used in spring-dashpot mechanical-model characterization of polymeric materials, provides a convenient measure of this capability. The viscosity parameter, in turn, can be related to the relaxation time for the material with the use of the elastic modulus.

This paper presents a study of the effects of cure temperature and time on the stress relaxation behavior of Metlbond 1113 modified-epoxy adhesive with carrier cloth. Short term ($t = 1/2$ minute) relaxation data are successfully fitted with the modified Bingham mechanical model to obtain relaxation time and bulk solid viscosity parameter values corresponding to different cure conditions. Experimental results indicate that both the relaxation time and the bulk viscosity values behave in a bell-shaped increasing–decreasing manner with respect to the cure temperature for all cure time values. This behavior is similar to that of adhesive ultimate strength and elastic modulus as observed by us earlier.

KEY WORDS Adhesive relaxation; adhesive bulk solid viscosity; cure temperature and time; modified Bingham model; degree of crosslinking; mechanical model characterization.

INTRODUCTION

The strength characteristics of thermosetting structural adhesives may not directly be reflected in their bulk tensile strength but rather in their capability to dissipate mechanical (viscous) energy prior to catastrophic failure. The bulk solid viscosity parameter, μ, used in spring-dashpot mechanical-model characterization of polymeric materials, provides a convenient measure of this capability. The viscosity parameter, in turn, can be related to the relaxation time for the material with the use of the elastic modulus.

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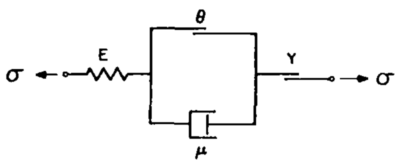
Bair *et al.*[1] state that, in practice, the strength of polymeric solids is derived not from maximum stress before yield but primarily from the ability to dissipate the mechanical strain energy during plastic deformation before failure.

The bulk solid viscosity and, consequently, the relaxation time for a thermosetting adhesive is expected to increase with increasing degree of crosslinking since the stress relaxation processes due to molecular chain movements are constrained due to the presence of crosslinks. Based on these considerations, a convenient way to assess the ability of a thermosetting adhesive to dissipate mechanical energy by plastic (viscous) deformation is to study its relaxation behavior.

The results of an investigation studying the effects of cure time and temperature on the bulk tensile relaxation behavior of Metlbond 1113 structural adhesive (Narmco Materials, Costa Mesa, CA, U.S.A.) will be presented in this paper. Metlbond 1113 is a commercially available, solid film, modified nitrile-epoxy resin supported with a synthetic fabric carrier cloth. The authors believe that the relaxation data to be presented give insight into the structural modifications of the model adhesive imposed by variation of thermal cure history.

The viscoelastic behavior of Metlbond 1113 has been previously investigated both in bulk tensile[2] and shear[3] modes. However, the effects of thermal cure history were not investigated. Renieri *et al.*[2] conducted both room temperature and elevated temperature relaxation tests on the bulk model adhesive. In their room temperature (*RT*) relaxation experiments, they varied the strain level and



MODIFIED BINGHAM MODEL

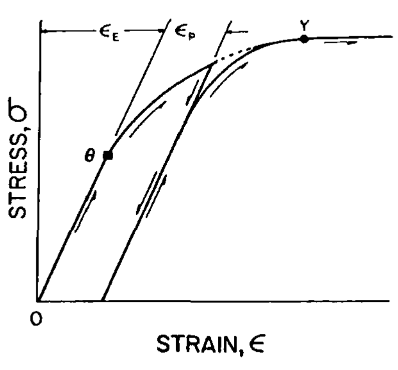


FIGURE 1 The modified Bingham mechanical model and the associated stress–strain diagram.

found that the relaxation response was nonlinear with respect to changes in the constant tensile strain level. In an attempt to predict *RT* relaxation response using the Modified Bingham Model (see Figure 1), they found that this model did not predict the relaxation behavior over the entire time span of their experiments (25 minutes). Sancaktar *et al.*[3] conducted *RT* shear relaxation experiments on Metlbond 1113 adhesive in the bonded form using the symmetric single-lap geometry. By varying the constant shear strain level in the adhesive, they also found that the relaxation response of the model adhesive was nonlinear with respect to changes in the constant strain level.

Metlbond 1113 is a thermosetting amorphous material and, when cured at temperatures well above room temperature, exhibits the behavior of glassy polymers at *RT*. Tobolsky[4] states that stress relaxation studies of amorphous polymers below their glass transition temperatures (*Tg*) give some insight into the nature of the glassy state such as the effects of cooling rate. For crosslinked materials, the stress relaxation processes due to molecular chain movements are strongly constrained by the crosslinks and relaxation mainly takes place due to the degree of free volume (inversely proportional to density) and its variation with cooling rates. Therefore, one may conclude that if the cooling rate is kept constant, the relaxation process, if any, at temperatures below *Tg* may take place mainly due to presence of uncrosslinked regions (resulting from undercure) or rupture of overstrained, degraded molecular chains.

ANALYTICAL CONSIDERATIONS

In a tensile relaxation experiment, the sample is extended up to a fixed elongation at a fairly fast rate and held at this constant elongation. Expressing the elongations in terms of strains, the total strain in the specimen ($\varepsilon_{\text{total}}$) is kept constant. For any relaxation process to take place, $\varepsilon_{\text{total}}$ should be composed of elastic (ε_e) and plastic (ε_p) strain components, *i.e.* the specimen should be loaded up to above its elastic limit. Therefore, we can write

$$\varepsilon_{\text{total}} = \varepsilon_e + \varepsilon_p = \text{constant} \tag{1}$$

Differentiating Eq. (1) with respect to time yields:

$$\dot{\varepsilon}_p = -\dot{\varepsilon}_e \tag{2}$$

Equation (2) indicates that any relaxation in the elastic stress must be matched by a corresponding plastic (irrecoverable) deformation at the same rate. Therefore, the elastic energy component initially stored in the specimen is consumed at a decaying rate to deform the specimen plastically. The force needed to hold the specimen at constant deformation is essentially a measure of the elasticity of the specimen. In the case of an ideal viscous material, this force (or stress) eventually (after long time) diminishes and equilibrium is achieved with some permanent deformation. For an ideal elastic material, however, this force remains constant and no relaxation occurs.

For lightly-crosslinked polymers, such as rubbers, the crosslinks keep the stress from diminishing, since the network structure prevents the stretched molecular segments from snapping back to their normally coiled equilibrium configuration unless the molecules are cut by degradation or because of the presence of imperfections orginally existing in the structure. Based on the kinetic theory of rubber elasticity[5] an estimate of the equilibrium stress relaxation modulus (E), which is basically equal to the asymptotic stress level divided by the constant strain level, is given as

$$E = 3RTd/M_c \tag{3}$$

where R is the universal gas constant; T is the absolute temperature of testing; d is the density and M_c is the molecular weight between the crosslinks. As a rough approximation to the highly crosslinked materials, such as the model adhesive, Eq. (3) implies that the equilibrium modulus, being proportional to the stress retained in the specimen when the relaxation rate is very small or almost zero, is directly related to the crosslinking density ($1/M_c$) or degree of cure.

As mentioned earlier, Renieri *et al.*[2] attempted to fit the Modified Bingham Model stress relaxation solution to the RT relaxation data of Metlbond 1113. The Modified Bingham Mechanical Model was originally proposed by Brinson.[6] The constitutive equations for this model are (see Figure 1).

$$\begin{aligned} \dot{\varepsilon} &= \dot{\sigma}/E & \sigma &\leq \theta \\ \dot{\varepsilon} &= \dot{\sigma}/E + (1/\mu)(\sigma - \theta) & \theta &\leq \sigma \leq Y \end{aligned} \tag{4}$$

where μ and E are the viscosity and the spring elastic coefficients respectively; θ and Y are the limiting (overstress) elastic and plastic (maximum) stress constants represented by sliding elements. The response of the Modified Bingham Model (MBM) to the relaxation loading is

$$\sigma(t) = \theta + (\sigma_0 - \theta)\exp(-t/\tau) \tag{5}$$

where σ_0 is the initial peak stress for a given deformation and $\tau = \mu/E$ is the relaxation time. Renieri *et al.*[2] found that Eq. (5) did not predict the RT relaxation behavior of Metlbond 1113 in the entire time span of their experiments (*i.e.* 25 minutes). However, they reported that application of Eq. (5) to short time relaxation data ($t < 2$ min) resulted in reasonable predictions.

EXPERIMENTAL PROCEDURES

To investigate the effects of cure time and temperature on the room temperature tensile relaxation behavior of Metlbond 1113, three different cure times of 20, 60 and 1000 minutes and fast cool-down conditions were used. The cure temperatures corresponding to these cure times ranged from 200°F (93°C) to 350°F (177°C) with 30°F (16°C) intervals. Additional information on curing procedure and specimen preparation can be found in Refs 7 and 8. The relaxation tests were performed on an Instron Testing machine (Model 1331) equipped with a function generator (Model 340A). At least two specimens were tested for each condition. Since the purpose of the relaxation experiments was to investigate the effects of cure conditions on the relaxation behavior, all the other parameters such as the test temperature and constant strain level had to be kept the same. Consideration of the elastic limit strains, as determined from bulk tensile tests,[2,7] resulted in the choice of input strain level in the range of 2.5–3.5 percent since the elastic limit changes with changing cure conditions. It was decided to choose a deformation of 0.052 in (1.32 mm) over a uniform gage length of ~1.6 in (4.06 cm) which would result in a total average strain of ~3.25%. Relaxation specimens were pin loaded up to the prescribed deformation in stroke control at 2.6 in/min (6.604 cm/min) head rate and kept at that extension. The load *versus* time data were recorded on a strip chart recorder. The time span for each experiment (relaxation period) was 50 minutes. It was observed that no stress-whitening occurred, corresponding to the extension imposed on the specimens, for all the conditions used. For a number of specimens, an Instron extensometer was used to check if the strain level over the 1 in (2.54 cm) gage length of the extensometer was constant. Corresponding to the 0.052 in (1.32 mm) extension used, the strain within the extensometer gage length remained constant. On doubling the amount of constant extension, however, the strain level did not remain constant and kept increasing, and the specimen completely stress-whitened between the grips. The relaxation experiments were performed in an environment of 72°F (22°C) and relative humidity of ~65 percent.

RESULTS AND DISCUSSION

The variations of engineering stress retained in the specimen, as normalized with respect to the corresponding peak stresses (σ_0), with time are shown in Figures 2, 3 and 4 for the cure time schedules of 20, 60 1000 minutes. Figure 2 shows that for the 230°F (110°C) cure temperature, the short term (50-minute) relaxation rate is drastically higher than for the other cure conditions. This indicates that the number of active load-bearing elements in the specimen (for the 110°C condition), which is proportional to the degree of crosslinking and/or degree of cure, was significantly less than those for the other three higher cure temperatures. It should also be noted that the 50-minute stress ratio is maximized for the 290°F (127°C) cure temperature condition and higher cure temperature reduces this ratio (Figure 2). An important point to be addressed here is the increasing-decreasing nature of the 50-minute stress ratio as the cure temperature is increased. The increase of the modulus may be attributed to the increasing degree of cure and/or crosslinking density whereas the decreasing part may be due to the degradation induced by high cure temperatures. Figure 3 shows the relaxation data for the 60-minute cure schedules. The variation of relaxation rate for short times may be easily observed. The 50-minute modulus again shows an increasing-decreasing type of behavior similar to that in Figure 2. Figure 4 reveals the relaxation results for the 1000-minute cure schedules. It can be observed that the

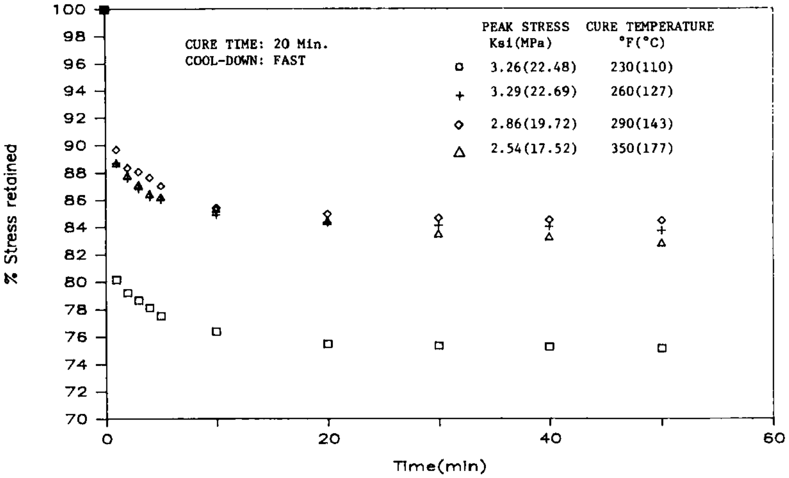


FIGURE 2 The effects of cure temperature on the room temperature tensile relaxation behavior of Metlbond 1113 for 20-minute cure time.

50-minute responses decrease as higher cure temperatures are used. The corresponding initial relaxation rates, however, increase at higher cure temperatures. The authors believe that in this case thermal degradation of the adhesive material caused by the higher cure temperatures results in a faster relaxation process.

An important remark should be made based on the *RT* relaxation results in Figures 2, 3 and 4. The cure conditions seem to affect the *RT* tensile relaxation behavior of the bulk Metlbond 1113 adhesive. Another point to be considered is that equilibrium modulus, if roughly estimated by the 50-minute stress ratio,

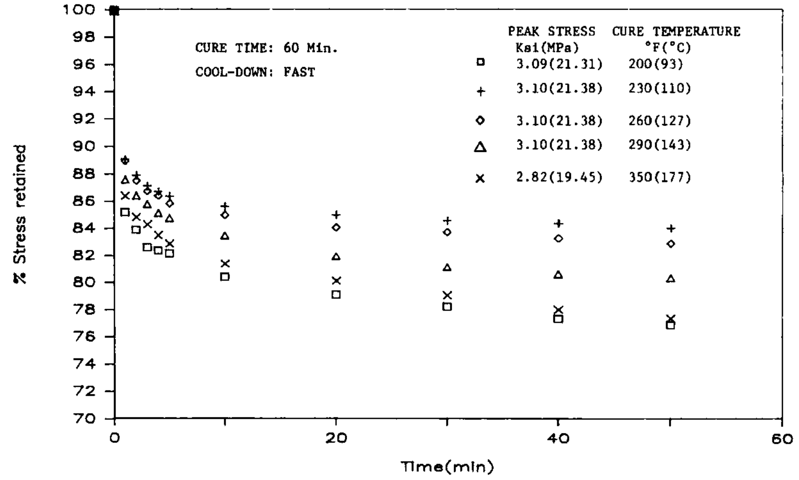


FIGURE 3 The effects of cure temperature on the room temperature tensile relaxation behavior of Metlbond 1113 for 60-minute cure time.

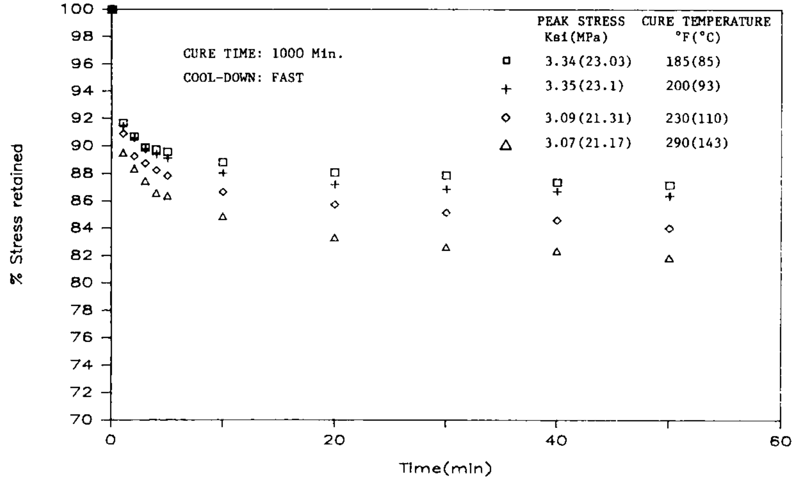


FIGURE 4 The effects of cure temperature on the room temperature tensile relaxation behavior of Metlbond 1113 for 1000-minute cure time.

reflects the increasing-decreasing variation with respect to cure temperature which is similar to that observed with bulk tensile strength values[7] (Figure 5).

In an effort to determine the effects of cure conditions on the level of energy-dissipating mechanisms, it was decided to apply the Modified Bingham Model to the relaxation results (Eq. 5) and to determine the viscosity parameter (μ) for different cure conditions. For this purpose, a nonlinear regression procedure (NLIN procedure available on SAS, Statistical Analysis System) was

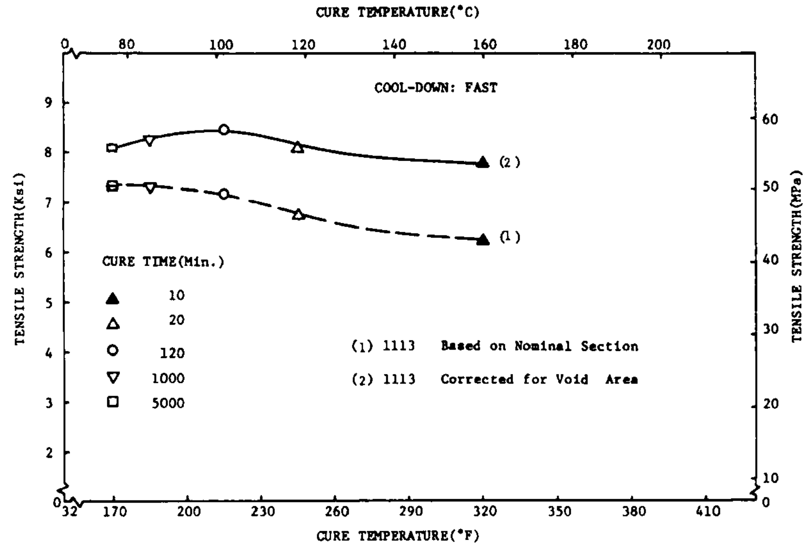


FIGURE 5 Metlbond 1113 optimum strength-cure behavior with and without void area correction.

used to fit the experimental data, *i.e.* the stress and time and peak stress values (σ_0), to Eq. (5) and determine the parameters θ and τ.

The initial attempts to obtain a good fit of Eq. (5) to the experimental results over the entire 50-minute time span were not successful. It was found that, for our data, the Modified Bingham Model did not predict the relaxation results over one minute of relaxation times. This observation is in agreement with that of Renieri *et al.*[2] on the same material. It was found, however, that the model could predict the short term relaxation results, *i.e.*[2] for $t \leq 1/2$ minute, very well. Figures 6 through 8 show some of the short term experimental relaxation results for the Metlbond 1113 with 20, 60 and 1000 minute cure schedules, respectively, and the corresponding theoretical predictions by the Modified Bingham Model, *i.e.* Eq. (5). For the purpose of clarity, some of the extreme cases of behavior are shown in these figures. Figure 6 shows that for the 20-minute cure temperature, the effect of increasing degree of cure is an increase in the $\frac{1}{2}$-minute modulus and a corresponding increase in the relaxation time. Figures 7 and 8 show the relaxation results and comparison with the Modified Bingham Model for the 60- and 1000-minute cure time schedules.

Figure 9 shows the cure temperature dependence of relaxation times (τ), as determined from the $\frac{1}{2}$-minute relaxation results and the Modified Bingham Model. This figure also reveals the increasing trends of the relaxation times as the cure temperature is increased, up to a point. Beyond this point, however, it may be observed that longer cure times tend to reduce the relaxation times more effectively as the degree of degradation increases with these longer cure times. This may be attributed to the fact that for a thermally-degraded material the

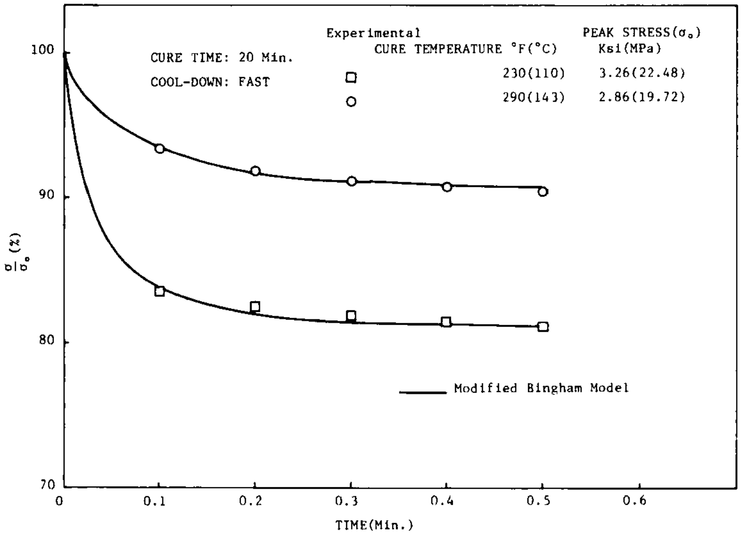


FIGURE 6 The effects of cure temperature on the short-term, room-temperature tensile relaxation behavior of Metlbond 1113 and comparison with the modified Bingham model for 20-minute cure time.

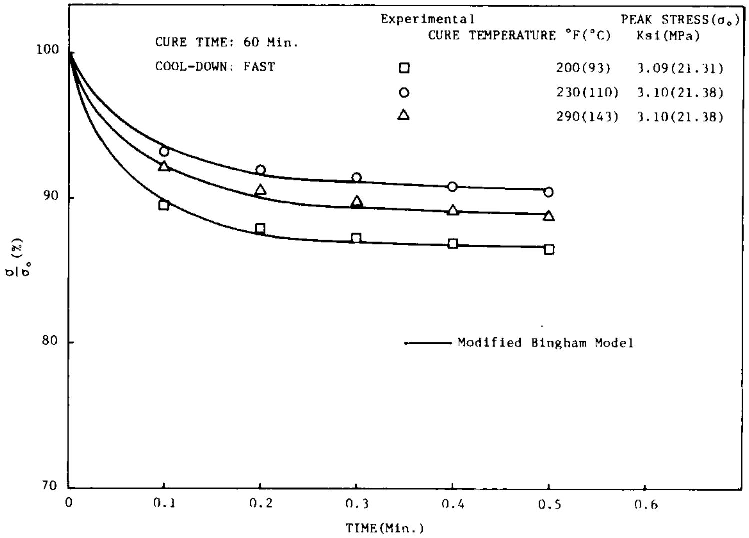


FIGURE 7 The effects of cure temperature on the short-term, room-temperature tensile relaxation behavior of Metlbond 1113 and comparison with the modified Bingham model for 60-minute cure time.

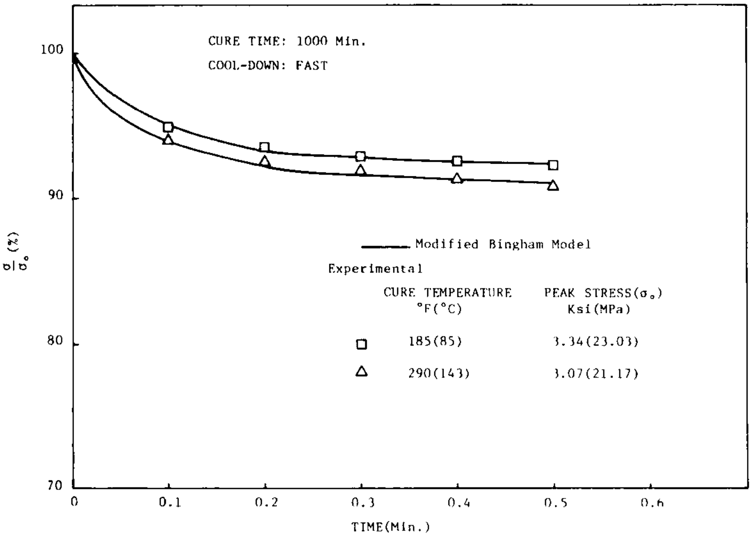


FIGURE 8 The effects of cure temperature on the short-term, room-temperature tensile relaxation behavior of Metlbond 1113 and comparison with the modified Bingham model for 1000-minute cure time.

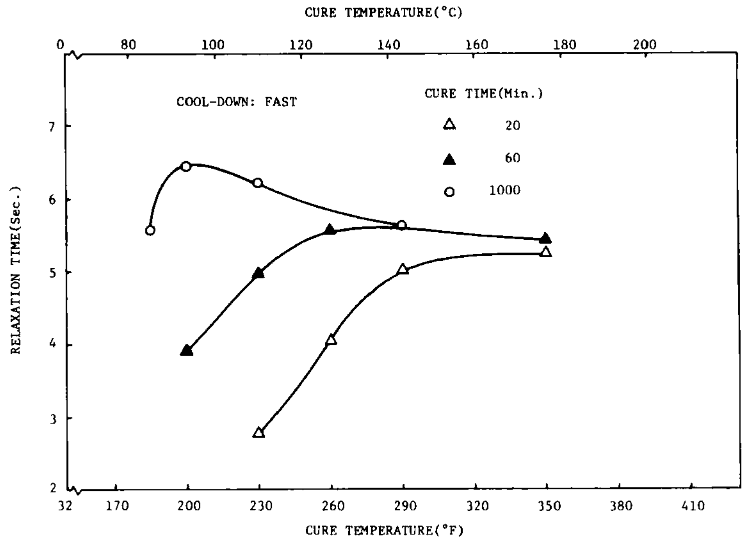


FIGURE 9 The effects of cure conditions on the predicted short-term, room-temperature relaxation time of Metlbond 1113 based on the modified Bingham model.

relaxation process is mainly due to the rupture of the already-weakened molecular chain segments.

As mentioned earlier, one of the goals of application of the Modified Bingham Model to the relaxation results was to determine the effects of cure conditions on the viscosity coefficient (μ) defined as $\mu = \tau \cdot E$; where τ is the relaxation time based on $\frac{1}{2}$-minute relaxation and E is Young's modulus. Since the viscosity parameter μ is dependent upon the values of τ and E, any calculated value for μ seems to depend on the time scale used in the evaluation of τ, which in this case is $\frac{1}{2}$-minute. Therefore, for the purpose of determining a viscosity parameter based on the Modified Bingham Model and $\frac{1}{2}$-minute fit to the experimental results, it is proposed to choose the $\frac{1}{2}$-minute modulus, *i.e.* the stress level $\sigma_{1/2}$ at $t = \frac{1}{2}$ minute divided by the total strain $\varepsilon_{\text{total}}$ as

$$\mu = \tau \cdot \sigma_{1/2}/\varepsilon_{\text{total}}. \tag{6}$$

It was found that, actually, the asymptotic stress level for $\frac{1}{2}$ minute of relaxation, according to the Modified Bingham Model, was very close to the measured θ value, for all cases. Since the total strain was the same for all of the specimens, a unit strain of $\varepsilon_0 = 1$ in/in was used to determine the viscosity parameters and their variations with repect to cure conditions. Consequently, the relation

$$\mu = \tau \cdot \theta, \tag{7}$$

was used when both the relaxation time τ (based on $\frac{1}{2}$-minute relaxations); and the elastic limit stress θ were found by fitting the Modifiied Bingham Model to

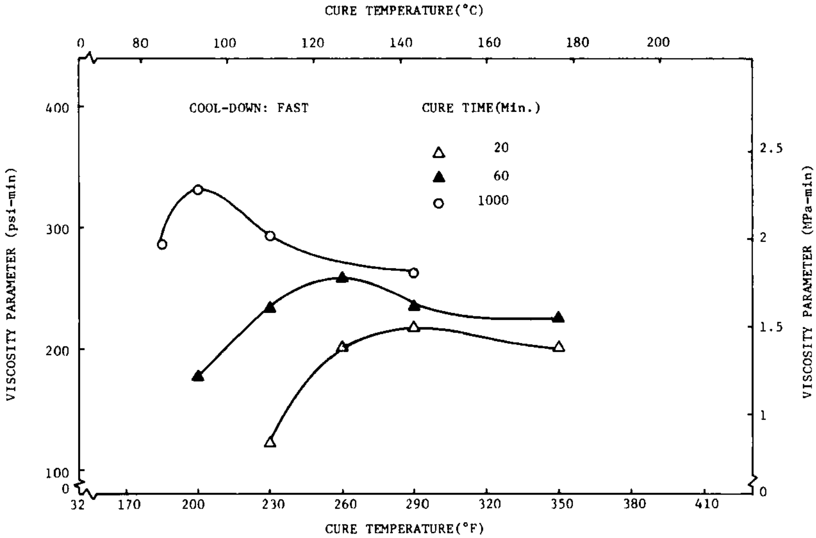


FIGURE 10 The effects of cure conditions on the viscosity parameter of Metlbond 1113 based on short-term, room-temperature relaxation data and the modified Bingham model.

the actual experimental data. This procedure alleviated the difficulty associated with determining the cure temperature and time-dependent Young's Moduli for each relaxation experiment.

Figure 10 shows the variation of the viscosity parameter, μ, as calculated by the above procedure, for different cure temperature and time values. It may be observed that the viscosity parameter, which is a measure of the model adhesive's resistance to flow and energy dissipation, exhibits an increasing-decreasing behavior for each cure time. The location of the peak viscosity parameters seems to shift towards lower cure temperatures as longer cure times are used. It may also be observed that the decrease of the viscosity parameter beyond the peak values is more drastic when longer cure times are used. This may be attributed to the stronger degradative effects of cure temperature for longer cure times.

A comparison of the viscosity-cure results (Figure 10) and tensile strength-cure results (Figure 5) for Metlbond 1113 for the 20- and 1000-minute cure times reveals an interesting observation. Based on the bulk tensile strength criterion, the optimum cure temperatures for the 20- and 1000-minute cure times and fast cool down condition were at 245°F (118°) and 185°F (85°C), respectively. Based on the viscosity parameter as another criterion, these optimum cure temperatures seem to shift towards higher values, *i.e.* 290°F (143°C) and 200°F (93°C) for 20- and 1000-minute cure times, respectively. Therefore, it seems that the optimum bulk tensile strength-cure conditions do not necessarily coincide with the optimum viscosity-cure conditions.

CONCLUSIONS

The authors believe that this investigation of the effects of cure time and temperature on the bulk tensile relaxation behavior of Metlbond 1113 has given insight into the structural modifications of the model adhesive imposed by variation of thermal cure history.

The results of the investigation also revealed that the Modified Bingham Model is suitable to predict the *RT* relaxation behavior of the model adhesive if it is used with short term ($t = \frac{1}{2}$ minute) data. It may be possible to predict successfully the relaxation behavior in the entire time span of the experiments if multiple Modified Bingham Models, with different spring and dashpot constants, are used in series. This would result in multiple relaxation times.

Our experimental results indicate that both the relaxation time and the bulk viscosity values for the model adhesive behave in a bell-shaped, increasing-decreasing manner with respect to the cure temperature for all cure time values. The viscosity parameter and, consequently, the relaxation time can be used as measures of the thermosetting adhesive's ability to dissipate mechanical energy by viscous deformation.

The observed bell-shaped behavior of the bulk viscosity parameter is similar to that of the model adhesive's ultimate strength and elastic modulus. On the other hand, the cure temperature-time conditions producing the maximum viscosity values do not coincide with those producing maximum tensile strengths but seem to shift to higher temperature conditions. This shift in cure temperatures to higher values is especially pronounced at short-time cure conditions. Obviously, the choice between the maximum tensile strength and maximum toughness will have to be confronted before optimum cure conditions are decided.

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