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Study of the cure kinetics of structural adhesives by ultrasonic interface waves

S. I. ROKHLIN*
Department of Materials Engineering, Ben-Gurion University of the Negev, PO Box 653, Beer-Sheva 84105, Israel

E. SEGAL
Ha Galil 45, Haifa 32 686, Israel

An ultrasonic method for *in situ* study of the curing kinetics of structural adhesives is described. The measurements are performed by ultrasonic interface waves, which produce shear oscillations in the plane of the bond line. The shear resistance of the interface changes in the curing process: softening of the prepreg and its transition to the liquid phase, and the beginning and the termination of the polymerization reaction. Measurements performed at temperatures from 60 to 120° C for the FM–73 adhesive showed that the activation energy of the curing reaction is 38.9 kJ mol^{-1}.

1. Introduction

The prepreg of a structural-adhesive film consists of a mixture of an epoxy resin and a hardening agent which are at the initial stages of the reaction. In order to prevent the reaction, the prepreg is stored at low temperature, so that the mixture of epoxy resins and hardening agents would be in the glassy state. Upon heating the bond specimen, the adhesive becomes liquid and the crosslinking reaction starts. In the course of this reaction the adhesive first undergoes transition to the gel (rubbery region) and then, as the crosslinking reaction progresses, to the glassy state.

It was shown by Rokhlin *et al.* [1] that a thin polymer film, situated in a solid body, is capable of localizing the energy of elastic waves in the form of interface waves. When the film thickness is much smaller than the wavelength, the interface wave produces only shear strain in the interface film. In this case, the shear modulus of the film is rather simply related to the phase velocity of the interface wave. Using this equation, the shear modulus of the film can be calculated from the measured phase velocity of the interface wave. An example of such a measurement is given in [1].

The rate of the crosslinking reaction, as that of any chemical reaction, depends significantly on the temperature. It was recently shown [2] that the change in the velocity of the interface wave in the course of adhesive curing occur simultaneously with the changes in bond strength, and consequently corresponds to the change in percentage of crosslink. This means that changes in the velocity of the interface wave may provide information on the reaction kinetics.

2. Experimental procedure

A possible method for obtaining interface waves is shown schematically in Fig. 1. The surface wave, excited in the lower substrate, is transformed in the interface region into an interface wave. Due to the closeness of velocities of the surface and interface waves, only a small part of

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* On sabbatical leave at the Department of Welding Engineering, Ohio State University, 190 W, 19th Avenue, Columbus, Ohio 43210–1182, USA.

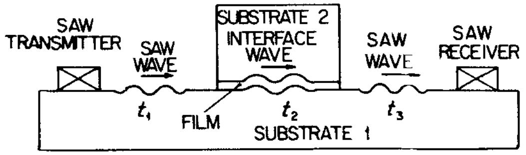

Figure 1 Illustration of the interface-wave method. t_1, t_2, t_3 are the times at which the wave train appears at the points indicated.

energy is transformed into bulk waves. The interface wave leaving the interface zone is retransformed into a surface wave, and is sensed by a receiver. In this work we are using a modified differential arrangement [3] (an ultrasonic bridge) for measuring the relative changes of the interface-wave velocity. This method makes it possible to eliminate the effect of the temperature dependence of the substrates and transducers on the measurement.

The duraluminum test specimen is placed between two heaters (Fig. 2) in order to enable attaining a minimum gradient over the thickness of the adhesive layer. The temperature is measured by three thermocouples, placed close to the adherent surfaces. The temperature gradient in the course of measurements did not exceed 0.5° C. Pressure, supplied by a press, is transmitted through a steel ball, which ensures rigorously normal application of force to the tested section. The lower adherent was 340 mm long, 90 wide and 50 mm thick. The upper adherent was of the same width and thickness, but 80 mm long.

Comb transducers [3] were used for excitation and reception of surface waves. The middle transducer (transmitter) radiates an ultrasonic surface wave symmetrically into two arms of the bridge. In the left arm, the surface wave incident on the boundary between the free surface of the lower substrate and the interface region is transformed into an interface wave. After leaving the interface region, the interface wave is transformed into a surface wave, and is sensed by a receiver. A surface wave propagates along the entire right arm. An offset block is placed in the right arm for equalization of the thermal masses of both arms in order to eliminate the temperature gradient along the specimen. The offset block does not affect the propagation of the surface waves, since there is no acoustic contact between the block and the substrate. If the dimensions of both arms of the bridge and of the transducers are the same, then the use of the differential arrangement eliminates the effect of the thermal expansion of the specimen. The pulse signal from the generator is fed to the middle ultrasonic transducer, which radiates surface waves symmetrically into two identical arms of the acoustic bridge. Both signals are sensed by receivers, and are fed through attenuators to the measuring system with precise overlap capability. The relative changes in the phase velocity during the adhesive curve were determined by measuring the phase shift of the r.f. signal filling the pulse. The phase shift in the working channel (arm with interface film) relative to the reference signal gives the relative change in the phase velocity of the interface wave, and depends only on changes in the elastic properties of the interface film.

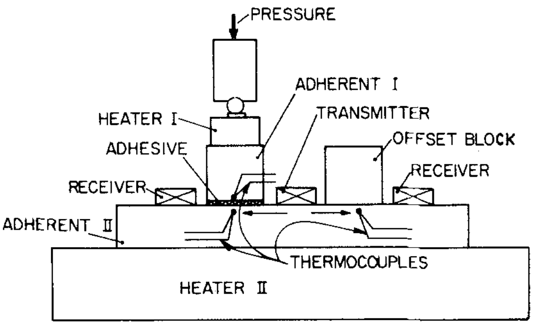

Figure 2 Schematic diagram of the specimen for the ultrasonic measurements.

The relative change in the phase velocity of the interface wave can be found from the expression

$$\frac{\Delta V}{V} = V_0 \frac{\Delta \tau}{L} \Big/ \left(1 - V_0 \frac{\Delta \tau}{L}\right) \qquad (1)$$

where $\Delta\tau$ is the time delay in the working channel relative to the reference channel [3]; L is the length of the interface segment where the phase shift occurs; V_0 is the starting phase velocity of the interface wave and ΔV is the change in the phase velocity of the interface wave induced by changes in the properties of the interface film.

The present study was performed with FM–73 structural adhesive, manufactured by American Cyanamid. This is a tape-form structural adhesive, based on a B-stage modified epoxy resin impregnated with Dacron fibres. The adherent surfaces were prepared prior to bonding by using MS–111 stripping agent, manufactured by the Miller-Stephenson Chemical Co., and this was followed by thorough washing with acetone. Such treatment of the adherent surfaces yields reproducible data on the bond strength under identical cure-cycle conditions.

We employed a cure cycle consisting of raising the temperature at a constant rate from room temperature to the curing temperature and of subsequently holding this temperature. The cure cycles were performed at a pressure of 40 psi (276 kPa). The heating rate was the same at all cure temperatures, i.e. the duration of heating was reduced with reduction in the curing temperature. The thickness of the adhesive film was determined after breaking the specimens and was usually from 90 to 100 μm.

3. Results and discussion

Fig. 3 shows the variations in the phase velocity of an interface wave during a typical cure cycle at 120° C for the FM–73 adhesive. The same figure shows, at the top, the temperature variation. The ultrasonic data are represented for the phase shift $\Delta\tau$, from which one can easily calculate the variations in the velocity of the interface wave from Equation 1. An increase in phase shift corresponds to increasing phase velocity and shear modulus.

Characteristic points of the cure cycle are noted on the phase-shift curve. The adhesive prepreg starts softening upon heating, and hence the velocity of the interface wave (shear modulus) starts dropping. Near Point A the prepreg becomes liquid (between 60 to 70° C). This figure also presents the relative change in the thickness of the cemented specimen due to thermal expansion. The measurements were performed by means of a mechanical indicator.

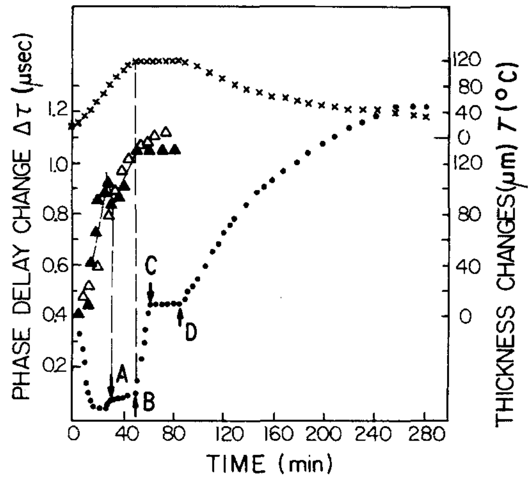

Figure 3 Ultrasonic data for a typical cure cycle of FM–73 structural adhesive. The cure temperature is 120° C. ● Phase shift, x temperature. Thickness changes: ▲ for specimen with adhesive, △ for specimen without adhesive.

When the adhesive becomes liquid due to heating, its thickness decreases. When this happens (with the mechanical properties remaining unchanged) the velocity of the interface wave should increase [1]. When a temperature of 120° C is attained, the velocity of the interface wave starts increasing steeply (Point B on the phase variation curve). This is due to the increase in the crosslinking reaction in the adhesive, and consequently to the increase in its shear modulus. The temperature in this region is maintained constant (at 120° C). After approximately 10 min of holding at this temperature the crosslinking reaction is completed (Point C on the velocity curve). Point D on the phase shift curve corresponds to the start of cooling of the specimen. The increase in the phase shift in this region corresponds to an increase in the shear modulus of FM–73 adhesive with cooling.

In order to establish that B–C in Fig. 3 corresponds to the high-rate cross-linking reaction, the ultrasonic data were compared [2] with measurements of the variation in the shear strength of the bond for different time points of the cure cycle. The strength values thus obtained are shown in Fig. 4 [2].

Fig. 5 shows the variation in the time delay of the interface wave, measured during curing of FM–73 at different temperatures. The curves represent the process starting with transition of the prepreg to the liquid state (Point A in Fig. 3). Reaching of the plateau at the end of the curves corresponds to cessation of the curing reaction.

Increasing the time delay corresponds to a rise in the shear modulus of the adhesive. In order to explain the behaviour of curves in Fig. 5, Fig. 6 shows schematically the change in the absolute value of complex shear modulus in the course of crosslinking reaction at a specified temperature. The adhesive undergoes a transition from the liquid phase to the rubbery region, which corresponds to completion of approximately 70% of the crosslinking reaction; this is followed by a plateau, where the elastic properties change little; and finally, as the modulus is increased

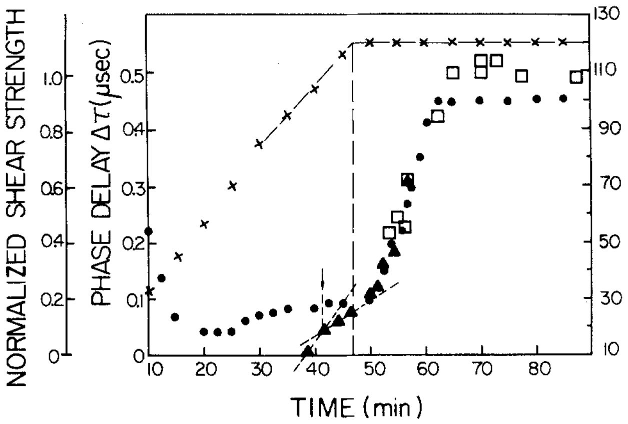

Figure 4 Comparison of the ultrasonic data with the variation in relative bond strength in the course of the cure. ● Phase shift, × temperature. Strength: ▲ rapid cooling, △ slow cooling (after shift).

further, the adhesive undergoes transition to the glassy region.

Transition to the rubbery state (gelation) is designated by arrows in Figs. 5 and 6. It is seen that the gelation region has corresponding to it a relatively slight change in the interface-wave velocity. However, the sensitivity of the method is sufficient for detecting this region. The gel point is seen also in Fig. 4, both on the velocity curve, as well as on the curve of variation of the bond strength.

Reducing the cure temperature decreases the rate of reaction and the gel point is shifted on the time axis. The percentage of crosslinked connections in the gel point is a material property and not affected by temperature. Therefore a shift of the gel point on the time axis characterizes quantitatively the variation in the reaction rate as a function of the temperature.

The curing data are summarized in Fig. 7 in the form of an Arrhenius plot. The points pertaining to the gel point are designated by crosses. They are presented only for lower temperature ranges of curing ($T \leqslant 100^\circ$ C). For higher temperatures the times to gelation are comparable with the time of heating, and therefore the curing reaction may not be considered as isothermal. The curing activation energy found in our experiments for the FM–73 adhesive, $E = 38.9\,\mathrm{kJ\,mol^{-1}}$, is in agreement with published data for different epoxy-resin systems [4].

The gelation process is followed by a plateau, with a subsequent explicitly-seen transition to the glass region. This transition yields significantly greater changes in the interface-wave velocity as compared with gelation. This fact is due to specific features of the method of interface waves. The changes of the film properties at very low values of shear modulus (as in the gel point) result in small changes of the interface wave velocity [1]. The glass transition region also shifts with the temperature. Unlike the gel point, the location of this region on the time axis is not associated with certain values of the

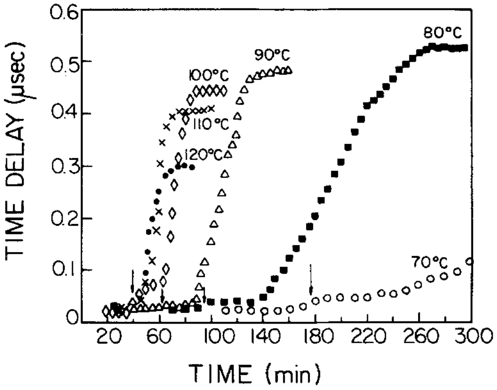

Figure 5 The variation of the time delay of the interface wave, measured during curing at different temperatures.

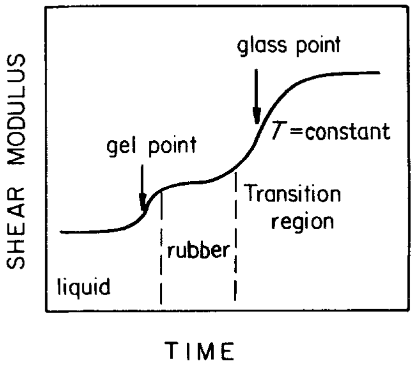

Figure 6 Schematic diagram showing the change of the shear modulus in the course of cure.

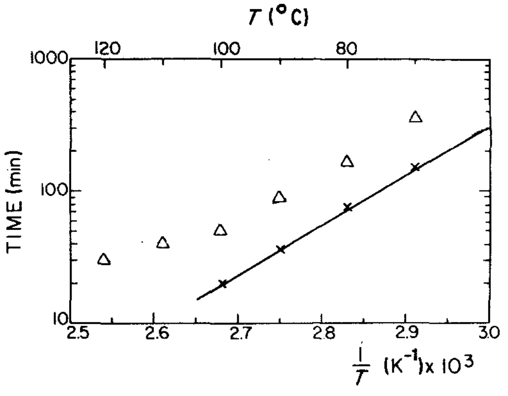

Figure 7 An Arrehenius plot of the cure data: x, time to gelation, Δ, time to vitrification.

crosslinking, and can correspond to different reaction stages.

It is seen from Fig. 5 that the range of curing-induced time delay increases with reduction in curing temperature (change from Point A to Point C in Fig. 3). This phenomenon is explained schematically in Fig. 8. The dashed curve shows the change in the interface-wave velocity due to rise in the shear modulus of the adhesive with reduction in temperature. The abscissa (temperature) for this curve is shown in the figure by a dashed line. The solid curves show the variation in the velocity of the interface wave in the course of curing as a function of time for fixed temperatures $T_1 > T_2 > T_3$. It is assumed here that for these temperatures an identical crosslinkage network is obtained toward the end of the crosslinking reaction. When the final crosslink structure for different polymerizations is the same, a higher shear modulus is attained at polymerization temperature T_3 than at temperature T_1. This explains the difference in the location of the end points in Fig. 5 along the ordinate.

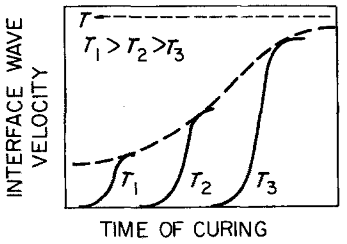

Figure 8 Schematic explanation of the increase of the curing-induced change in the interface wave velocity with reduction in curing temperature. The broken line corresponds to the interface wave velocity change with temperature. The temperature axis is shown by a dashed line in the top of the figure.

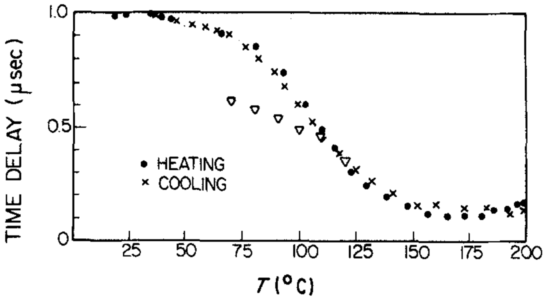

Figure 9 The change of the interface wave velocity due to temperature cycling for sample bonded at 120° C. The triangles correspond to the state after cure at the temperature read out from the abscissa.

Fig. 9 shows the change in the interface-wave velocity due to temperature cycling of a specimen bonded at 120° C. The triangles designate points taken from Fig. 5 and corresponding to termination of reaction at the given temperatures. It is seen that already at reaction temperatures below 100° C one obtains a lower velocity (shear modulus of adhesive) than for a specimen obtained at 120° C. This means that a less developed crosslinkage network is obtained when curing FM-73 below 100° C.

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