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Use of the Farol-Weissenberg Rheogoniometer to Follow the Early Stages of Cure of a Polyester Resin

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Synopsis

The Farol-Weissenberg rheogoniometer has been used to investigate the early stages of cure of a polyester resin. By using the oscillatory facility of the rheogoniometer it is possible to follow the response of the resin system to torsional shear from the time of gelation into the early region of the gel state. Measurements of torsional forces made possible the determination of a modulus of elasticity (γ_M) at intervals of time during the cure and this parameter is shown to increase with increasing degree of crosslinking.

INTRODUCTION

Many attempts have been made to develop techniques for following and assessing the curing of polyester resin systems. The need for the assessment of the state of final cure of a polyester resin is of obvious practical significance,[1] and a great deal of work has been carried out in this field. Most of the test methods that have been developed are based on an empirical examination of several physical properties of the crosslinked polymer, e.g., tensile, flexural, compressive, and impact properties.[2–4] However, the empirical nature of the test methods may lead to anomalies and may make comparisons difficult.

Dynamic mechanical testing can give quantitative results and recently the torsional pendulum has been successfully used in the study of the later stages of curing of novolacs, resoles, epoxy resins, and polyesters.[5–7] Unfortunately, extension of measurements to the early stages of cure has proved difficult. An interesting method of extending the range of dynamic mechanical testing is that devised by Lewis and Gillham.[8] According to these authors, a nylon braid impregnated with the polymer system to be studied is used as the supporting member for a free, torsionally oscillating mass. From the frequency of the oscillation an apparent rigidity modulus of the impregnated braid is calculated. The change in rigidity of the polymer system is thus followed during the full curing process. As a qualitative study this method is very useful but because of the compound nature of the braid, results obtained are not absolute.

The purpose of this work was to determine whether the Farol-Weissenberg rheogoniometer could be used with sufficient sensitivity and repro-

ducibility to extend the range of dynamic mechanical testing to the early stages of cure.

EXPERIMENTAL

Full details of the background, development and mode of operation of the Weissenberg rheogoniometer are given in the literature.[9–11] The instrument is, in essence, a highly instrumented cone-and-plate viscometer with facilities for oscillatory input and normal force measurements. Plates and cones are available in diameters of 2.5 and 7.5 cm., and the angle of the cone from the horizontal may be from 0.5° to 4°. A torsion bar controls the rigidity of the top platen (plate) and to cover a wide range of fluid viscosities, interchangeable torsion bars of different diameters are available. By experimental trial it was found that the platens of diameter 7.5 cm., (cone angle 1° 35′) used with a torsion bar of diameter 0.25 in., allowed satisfactory examination of the region of cure of interest.

In the work described, the effect of an oscillatory shear in the frequency range of 2.5×10^{-2} to 2.5 cps was investigated. The amplitude of the oscillatory shearing force applied at the lower platen (cone) was in the range 10^{-4}–10^{-3} radians.

Materials

The polyester resin used was Beetle 4116 (BIP Chemicals Ltd.). This is a general-purpose low-reactivity resin containing no thixotropic additives and dissolved in styrene to give a solids content of 61%.

The initiator system used was the methyl ethyl ketone peroxide–cobalt naphthenate combination. The methyl ethyl ketone peroxide was supplied as a 60% solution in dibutyl phthalate and the cobalt naphthenate as a 6% solution in white spirit which was further diluted to 0.3% in styrene before use. The following recipe, which was used throughout, gave a gel time of approximately 13 min.: resin (Beetle 4116), 100 g.; methyl ethyl ketone peroxide solution, 2 ml.; cobalt naphthenate solution, 10 ml.

Procedure

The rheogoniometer was set up and adjusted as described in the handbook.[9] The initiator system was well dispersed in the resin by stirring and the mix deaerated under vacuum at 25°C. for approximately 5 min. The liquid polyester was then spread uniformly over the lower platen in sufficient volume (4 cm.^{3}) to overfill the gap, and the cone and plate closed to the correct gap setting. Excess resin was trimmed from around the platens. Exactly 10 min. from the time of addition of the cobalt naphthenate solution the motor was started, the frequency and amplitude of the oscillation of the cone having been preset. After 13–14 min. the first recordings of the oscillatory input signal and the resultant output signal were made on a two-channel ultraviolet recorder.

Sticking of the resin to the platens appeared to be the major limitation of this technique, and it prevented examination beyond approximately 27 min. of cure. Up to this time it was found that the platens could be separated with relative ease and the adhering resin removed by acetone. Allowing the cure to proceed beyond 27 min. made separation increasingly difficult, and to prevent possible damage separation was always carried out immediately after the final set of measurements had been recorded.

The effect of varying frequency and amplitude of oscillation was investigated by using four amplitudes of oscillation at each of three frequencies. To establish reproducibility each run was repeated several times.

All experiments were carried out at a constant temperature of 25°C.

THEORY

In this work measurements were made only under conditions of oscillatory shear and consequently the discussion in this section will be limited to vibrational testing of the ground state. It is reasonable to assume that the material behaves linearly in the immediate neighborhood of this state.[10]

According to this assumption it is found for sufficiently small amplitudes of vibration that a simple harmonic input of shear strain with a certain frequency amplitude and phase, will produce a simple harmonic output of shear stress with the same frequency but with a different amplitude and phase.

Figures 1 and 2 show typical input and output traces for a linear viscoelastic material.

An elastic modulus referring to shear strains may be defined as follows:

$$\gamma_M = \Gamma_A(\omega) \cos \Gamma\phi(\omega) \tag{1}$$

where

$$\Gamma_A(\omega) = P_A/S_A$$

$$-\Gamma\phi(\omega) = P\phi - S\phi$$

S_A and $S\phi$ are the amplitude and phase of S_{12} (strain); P_A and $P\phi$ are the amplitude and phase of P_{12} (stress).

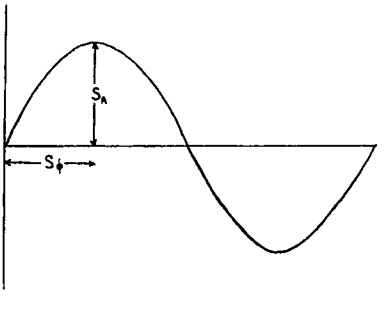

Fig. 1. Input trace for a linear viscoelastic material.

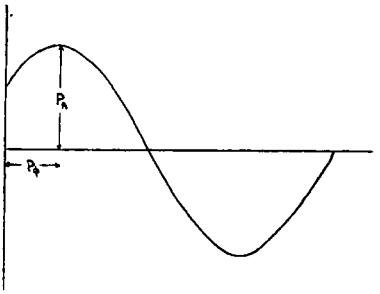

Fig. 2. Output trace for a linear viscoelastic material.

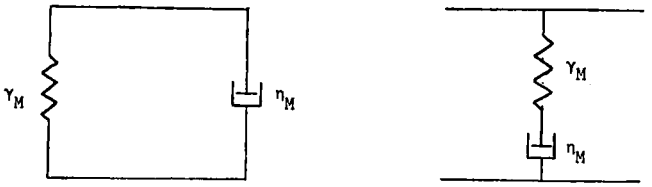

Fig. 3. Schematic representation of (*a*) spring and dashpot in parallel; (*b*) spring and dashpot in series.

A viscous shear modulus also referring to shear strains may be defined [eq. (2)]:

$$\eta_M = (1/\omega)\ \Gamma_A(\omega) \sin \Gamma_\phi(\omega) \tag{2}$$

The two shear moduli can also be defined with reference to shear stresses giving:

$$\gamma_F = \Gamma_A(\omega)/\cos \Gamma_\phi(\omega)$$

$$\eta_F = \Gamma_A(\omega)/\omega \sin \Gamma_\phi(\omega)$$

The physical significance of the two descriptions is shown by two models, each containing one frequency-dependent elastic spring and one frequency-dependent viscous dashpot, joined in parallel or in series (Fig. 3).

Although the two descriptions are mathematically equivalent for any given material, there is for most materials a distinct preference for one or other so that only the preferred one is in practical use. Solids are represented preferentially by the moduli with subscript M, and as the work described here has been concerned with measurements made on solid polyester, i.e., material after gelation, the modulus γ_M is used.

The expressions for γ_M and η_M may be converted into forms suitable for the direct insertion of experimentally measured quantities and become:

$$\gamma_M = (85{\cdot}3\alpha\Delta_T KC_3/\Delta_I d^3 C_1)[1 - (f/f_n)^2] \cos(\theta''_\phi - \theta'_\phi + C_4 - C_2) \tag{3}$$

$$\eta_M = (13{\cdot}6\alpha\Delta_T KC_3/f\Delta_I d^3 C_1)[1 - (f/f_n)^2] \times \sin(\theta''_\phi - \theta'_\phi + C_4 - C_2) \tag{4}$$

Here, α is cone angle in degrees (1.5833°); K is torsional constant for torsion bar ($K = 5.7464 \times 10^5$ dyne-cm./0.001 in deflection); d is diameter of platens (7.5 cm.); f is frequency of imposed oscillation (cps); f_n is natural frequency of torsion head (200 cps); $\theta'\phi$ is the phase of θ'; $\theta''\phi$ is the phase of θ''; Δ_T is the movement of the torsion head transducer (in thousandths of an inch). This movement is related to the actual angular movement of the top platen, θ'' (in radians) by:

$$\Delta_T = 10^4\theta''/2.54 = 3940\theta''$$

Δ_I is the movement of the wormshaft (in thousandths of an inch) as measured by the oscillation input transducer. The relation between this movement and the actual movement of the cone θ' (in radians) is:

$$\Delta_I = 1280\theta'$$

The quantities C_1 to C_4 represent correction terms which take into account the angular movement of the measuring system as well as its inertia and damping. For measurements on materials of constant elasticity it is possible to arrange conditions so that the angular movement of the flat plate is negligibly small compared with that of the cone and so that the rigidity of the torsion bar is so large that the effects of the viscous damping of the torsion bar and of the inertia of the flat plate are negligible by comparison. In this case $C_1 \simeq C_3 \simeq 1$ and $C_2 \simeq C_4 \simeq 0$. However, in this work measurements were made on a material of continually increasing elasticity, and conditions could not be so arranged. It was possible to minimize C_3 and C_4 by choosing the thickest possible torsion bar, but C_1 and C_2 had to be considered.

RESULTS

The oscillatory input signal from the cone and the resultant output signal from the plate were recorded by an ultraviolet recorder on the same coordinates. Δ_T (movement of torsion head transducer) was measured directly from the traces and plotted against time. Under each set of conditions (i.e., given frequency and amplitude of applied oscillatory shear) a number of runs were carried out. Figure 4 is a typical trace showing the good reproducibility obtained. Similar graphs were obtained for a range of experimental conditions (three different frequencies and four different amplitudes of the applied oscillatory shear were investigated). From each graph the ratio θ''/θ' was calculated corresponding to chosen cure times and the values so obtained plotted versus time for all results obtained at one given frequency but at different input amplitudes. Figure 5 shows the plot of all values of θ''/θ' obtained at a frequency of 2.5×10^{-2} cps. Figures 6 and 7 show similar plots of results obtained at different chosen frequencies. One curve can be drawn through all the experimental points obtained at different applied amplitudes (constant frequency) which indicates that the amplitude of the applied oscillation has no effect on the

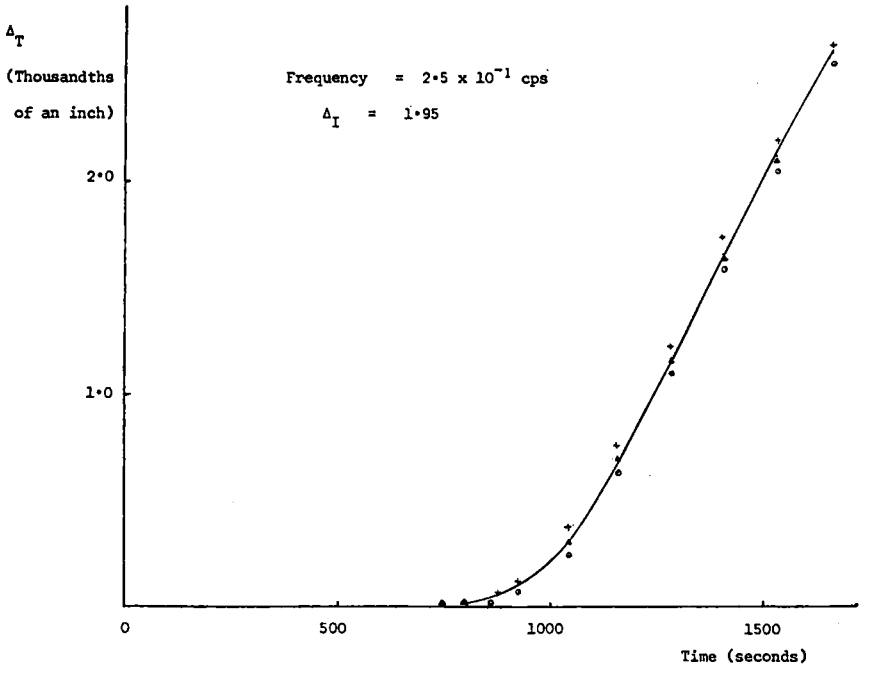

Fig. 4. Graph of Δ_T (movement of torsion head transducer) against time. Different runs are represented. Frequency $f = 2.5 \times 10^{-1}$ cps; $\Delta_I = 1.95$.

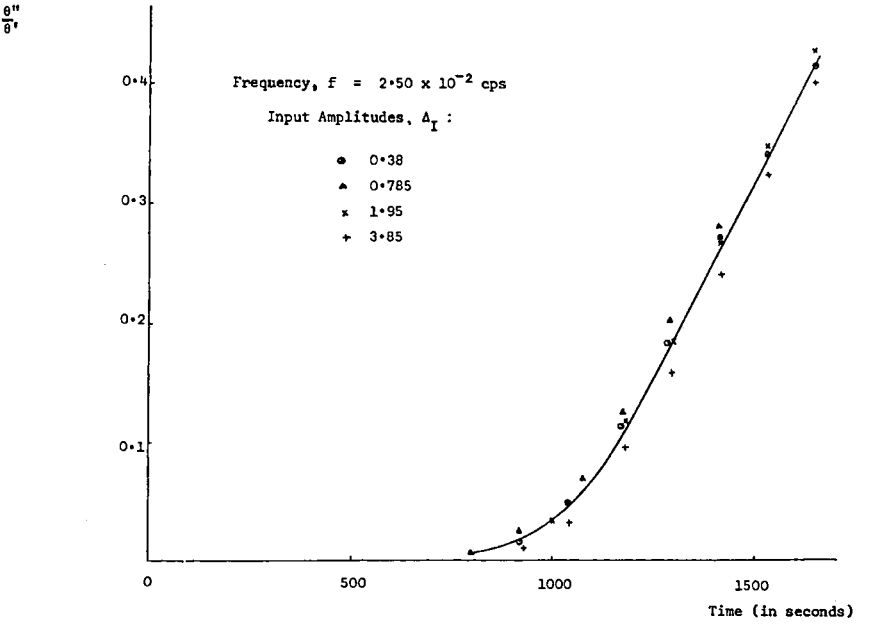

Fig. 5. Plot of θ''/θ' vs. time at various input amplitudes: (⊙) 0.38; (▲) 0.785; (×) 1.95; (+) 3.85. Frequency $f = 2.50 \times 10^{-2}$ cps.

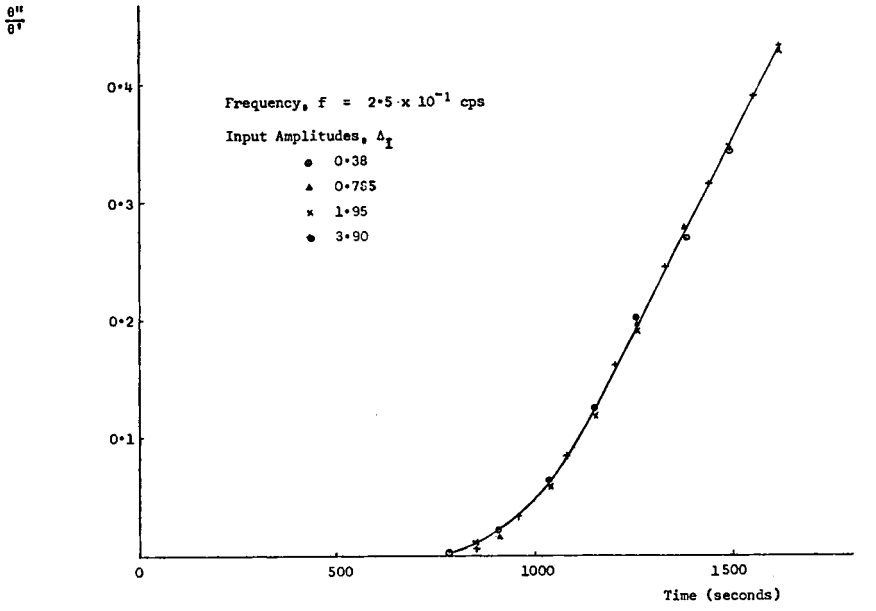

Fig. 6. Plot of θ''/θ' vs. time at various input amplitudes: (⊙) 0.38; (▲) 0.785; (×) 1.95; (+) 3.90. Frequency $f = 2.5 \times 10^{-1}$ cps.

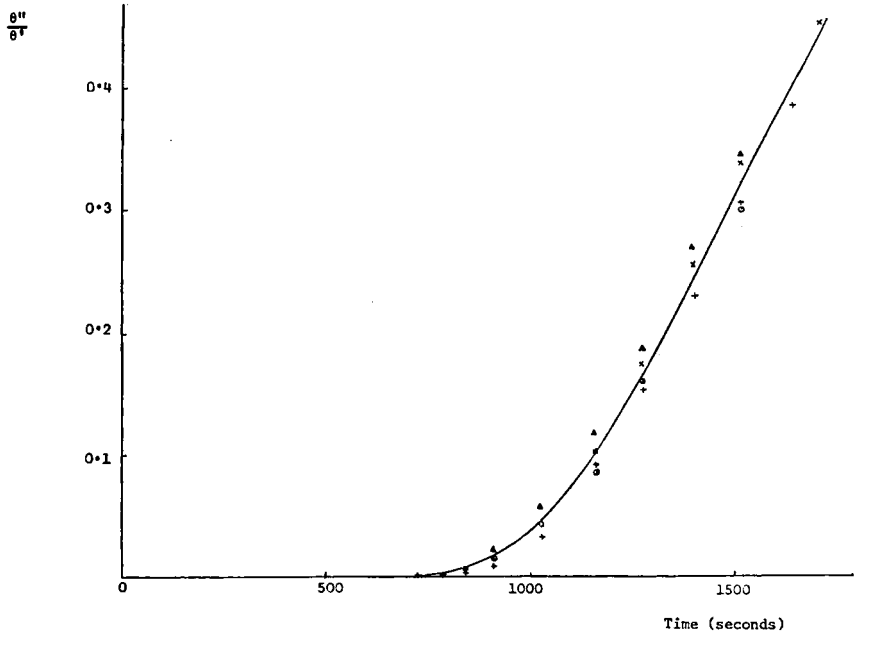

Fig. 7. Plot of θ''/θ' vs. time at various input amplitudes: (⊙) 0.385; (▲) 0.765; (×) 1.90; (+) 3.75. Frequency $f = 2.50$ cps.

material behavior over the amplitude range considered (approximately 3×10^{-4} to 3×10^{-3} radians).

From Figures 5–7 and by using eq. (3), ignoring C_3 and C_4 as previously mentioned, a modulus of elasticity (γ_M) corresponding to different cure times was calculated. It was found in all cases that after approximately 850 sec. cure, the phase differences between the traces became zero, and hence C_2 also became zero and could be neglected. The rapid disappearance of a measurable phase difference between the platens meant that η_M quickly fell to zero according to eq. (4). In some cases readings were taken before 850 sec. of cure; however, values of η_M were not calculated, as the small phase differences between the traces could not be measured accurately. This was inevitable as experimental conditions were deliberately adjusted in order that the region of particular interest, i.e., the region beyond the gel point, could be examined as fully as possible. Use of a thinner torsion bar (lower torsion bar constant) would have allowed closer examination of the liquid polyester prior to gelation. Since it was not possible to detect (after approximately 14 min.) any phase difference between the applied oscillatory trace and the output trace, it appears that the polyester system acts as an almost perfectly elastic solid in the early gel state.

In Table I, the calculated values of moduli corresponding to different frequencies of the applied oscillatory shear are compared.

The moduli obtained at various cure times are fairly constant and are independent of frequency. From these results it is concluded that the polyester in the gel state exhibits time-independent properties over the frequency range considered, i.e., the modulus of elasticity at a given cure time is independent of the rate of shear.

Figure 8, which is a plot of mean elasticity modulus versus time, clearly shows the increase in modulus with reaction time, i.e., degree of cross-linking. At the limit of the experimental measurements the value of the modulus is approximately 3.71×10^5 dyne/cm.^{2}, but the curve is still rising

TABLE I
Calculated Values of γ_M at Chosen Cure Times for Three Different Frequencies of the Applied Shear

Cure time, sec.	Modulus of elasticity γ_M, dyne/cm.^{2}			
	$f = 2.5 \times 10^{-2}$ cps	$f = 2.5 \times 10^{-1}$ cps	$f = 2.50$ cps	Mean
900	8.61×10^3	9.49×10^3	9.20×10^3	9.10×10^3
1000	2.20×10^4	2.67×10^4	2.36×10^4	2.41×10^4
1100	4.32×10^4	5.59×10^4	4.92×10^4	4.94×10^4
1200	8.16×10^4	1.04×10^5	8.83×10^4	9.13×10^4
1300	1.37×10^5	1.60×10^5	1.46×10^5	1.48×10^5
1400	1.99×10^5	2.25×10^5	2.07×10^5	2.10×10^5
1500	2.69×10^5	3.03×10^5	2.85×10^5	2.86×10^5
1600	3.48×10^5	3.95×10^5	3.71×10^5	3.71×10^5

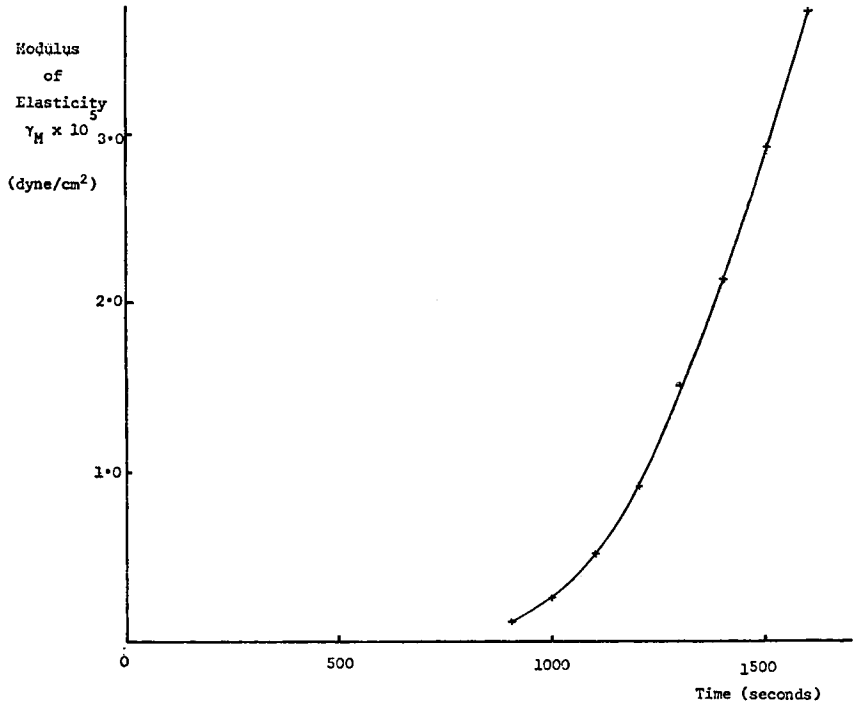

Fig. 8. Plot of mean modulus of elasticity vs. time.

sharply. No comparison of the dynamic-mechanical data with other results can be made, since no similar work appears to have been carried out in this region of cure; however, the relative rigidity results of Lewis and Gillham, plotted against time, give very similar curves to those of the modulus of elasticity.

CONCLUSIONS

The early stages of the crosslinking of an unsaturated polyester system can be followed with very good reproducibility by dynamic mechanical testing using the Weissenberg rheogoniometer. The instrument is very suitable for the accurate determination of dynamic mechanical properties during the early gel state of the curing polyester. A modulus of elasticity (γ_M) is calculated, and the change in this parameter with time during the cure is shown graphically (Fig. 8).

It is evident that dynamic mechanical analysis gives a new approach for investigating crosslinking mechanisms and it may prove to be invaluable in studying the complete polymerization characteristics and structures of polymers during crosslinking.

It may be possible to extend the range of testing by using the rheogoniometer to cover the later stages of cure, and further work is in progress. Work to assess the cure of the polyester prior to gelation is also necessary in

order that a complete characterization of the dynamic-mechanical properties of the material might be made over the whole range of cure of the resin.

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Résumé

On a utilisé le rhéogognomètre de Farol-Weissenberg en vue d'étudier les premières étapes du traitement de résines à base de polyester. En utilisant les facilités oscillatoires du rhéogognomètre, il est possible de suivre la réponse d'un système à base de résine au cisaillement de torsion à partir du temps de gélification jusqu'au début de l'état gel. Les mesures de forces de torsion rendent possible la détermination du module d'élasticité (γ_M) à des intervalles de temps au cours de ce traitement et ce paramètre croît avec un degré croissant de pontage.

Zusammenfassung

Das Farol-Weissenberg-Rheogoniometer wurde zur Untersuchung der Frühstadien der Härtung eines Polyesterharzes verwendet. Mit der Schwingungseinrichtung des Rheogoniometers ist eine Verfolgung des Verhaltens des Harzes unter Torsionsscherung vom Zeitpunkt der Gelbildung bis in das Frühstadium des Gelzustandes möglich. Durch Messung der Torsionskräfte konnte der Elastizitätsmodul (γ_M) in Zeitintervallen während der Härtung bestimmt werden und dieser Parameter zeigte eine Zunahme mit steigendem Vernetzungsgrad.

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