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Cure of Polyester Resins. II

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Synopsis

The copolymerization reaction between unsaturated polyesters and styrene has been studied by a torsional pendulum. The accuracy of the dynamic-mechanical measurements obtained is discussed briefly, and the results are compared with those of previous work on the change of hardness during cure.

INTRODUCTION

The crosslinking of unsaturated polyesters by a copolymerization reaction between the double bonds from maleic or fumaric acids and styrene has previously been followed by various means. In a previous paper[1] methods were reviewed and hardness was measured during cure by Barcol and hot needle indentation methods. The study of this process of crosslinking has been continued by using dynamic-mechanical methods.

It is to be expected that dynamic-mechanical measurements of shear modulus and mechanical loss factor will show significant and characteristic changes during copolymerization. The modulus of elasticity has been shown to be directly proportional to the number of crosslinks at a given temperature and frequency.[2] Mechanical damping probably depends on the number of free reactive chain ends in the system[3] and should decrease during crosslinking.

Dynamic-mechanical tests involve the measurement of the deformation of a specimen in response to a sinusoidally varying stress. Such methods have been used extensively in studying polymeric materials[4,5] and indeed in studying fully crosslinked polyesters.[6,7] Special techniques of this type have been used to study the cure of resins other than polyesters.[8,9]

In order to cover the spectrum of applied frequencies and the range of viscoelastic behavior expected from a polyester resin, it is necessary to use a variety of instrumental techniques.

In this paper we describe the study of the crosslinking of a commercial, general-purpose, low-viscosity resin, B.I.P. Beetle 4116, by the use of a torsion pendulum. Some experiments were also carried out on a rather different resin from Scott Bader & Co. Ltd.

The torsion pendulum was used only from 0.5 to 5 cps.

Torsion Pendulum

The oscillations of a horizontal torsion bar suspended by a fine wire are damped by a test specimen which is clamped in a vertical position, fixed rigidly at its lower end to the base of the instrument. The natural oscillations of the pendulum are thus damped to an extent which depends on the modulus and mechanical damping of the polymer used. Many different recording systems have been used to record the oscillations; in this case the instrument, (Nonius, Delft, Holland) used an induction coil and a spark track through conducting recording paper.

The shear modulus G (in psi) is obtained from the period of oscillation p (in seconds) and the damping from the ratio of two successive amplitudes, as follows for samples of rectangular section:

$$G = 5.588 \times 10^{-4} LI/WD^3 \mu p^2$$

where the logarithmic decrement is given by:

$$\Delta = \ln (A_1/A_2) = \ln (A_2/A_3) = \ln (A_n/A_{n+1})$$

and where L, W, and D are the length, width, and thickness, respectively, of the specimen (in inches), I is the polar moment of inertia of the system (in grams-square centimeter), μ is a shape factor depending on the ratio of the dimensions, and A_n is the amplitude of the nth peak.

Alternately, for cylindrical specimens of radius r'',

$$G = 2.22 \times 10^{-5} LI/r^4 p^2$$

Since G depends on the frequency, which varies with the cure of the resin, it is necessary to make alterations to I by attaching weights to the torsion bar. This gives a plot of G against $1/p$, from which G at a single fixed frequency (say, 1 cps) may be interpolated.

Reproducibility

There are few errors inherent in the method of measurement. Apart from occasional slippage in the clamps or nonaxial alignment of the specimen, the main source of error is in the measurement of the dimensions of the specimen. Air damping can effect the results appreciably where internal friction is low. Care is required in reading the graphical records obtained, especially at high frequency. T.N.O., Delft,[10] who devised the instrument, claim an accuracy under favorable circumstances of $\pm 2\%$ for the modulus and $\pm 5\%$ for the damping factor.

The specimens of rectangular cross section used initially underwent shrinkage during cure, in such a way as to give faces with stress concentrations at the edges. Cylindrical ones were therefore adopted for preference in later work.

In addition to these general factors, the errors peculiar to the polymerizing system used are: (*a*) the error due to any nonuniformity of destruction of free radicals in the mass; (*b*) variation of the temperature of the sample

with time during curing. The reaction is strongly exothermic and so the temperature rises to an extent dependent on the sample size and type of mold.

A major objective of the work described here was to test the reproducibility of the results in these respects. Hence several castings were made under identical conditions.

EXPERIMENTAL

Formulations Used

The formulations used are given in Table I.

TABLE I

	Parts (by weight)		
	A	B	C
Beetle resin 4116	100	100	—
Scott Bader resin (isophthalic acid–fumaric acid–propylene glycol)	—	—	100
Benzoyl peroxide	1	1.25	1
N,*N*-Dimethyl *p*-toluidine	0.05	0.035	0.035
Curing temperature, °C.	35	70	70

Casting Procedure

A steel mold was used to cast eight specimens simultaneously. This mold could be used to give specimens of rectangular cross-section having dimension 6.0 ± 0.4 in. × 2.75 ± 0.010 in. × 0.140 ± 0.010 in. or alternatively cylindrical specimens, 6.0 ± 0.4 in. × 0.230 ± 0.010 in. diameter.

The composition was mixed very thoroughly and deaerated briefly under a moderate vacuum. It was then poured carefully into the mold and heated in an air oven. After a certain time the mold was opened, and the specimens replaced loose in the oven to be removed at regular intervals.

All measurements were made on specimens conditioned to a temperature of 25 ± 1°C.

The pendulum was calibrated, in order to calculate the moments of inertia used, by using a steel specimen which was assumed to have a modulus independent of the frequency changes involved.

RESULTS

Figure 1 shows how the changes in the shear modulus with time of cure for formulation A compare with the changes in Barcol hardness and hot needle indentation.

Figure 2 shows the changes in modulus and damping (logarithmic decrement) of another resin (formulation C) cured at 70°C.

In addition to the data shown in these figures, castings were prepared at the same cure time, in order to assess the reproducibility both of the method

TABLE II
Reproducibility for Shear Modulus G' for Formulation B, 24 hr. Cure at 45°C.

Specimen no.	$G' \times 10^{-9}$, dyne/cm.^{2}							Standard mean deviation between casting operations, %[a]
	Casting 1	Casting 2	Casting 3	Casting 4	Casting 5	Casting 6	Casting 7	
1	11.75	11.48	11.75	10.96	12.05	11.90	11.60	2.62
2	11.00	11.22	11.50	11.45	11.05	11.10	11.50	1.69
3	12.02	11.00	11.01	11.55	11.80	11.16	11.10	3.09
4	12.02	11.02	10.97	10.84	11.00	11.94	10.94	3.73
5	11.08	11.52	10.98	10.69	10.45	11.23	11.12	2.61
6	11.20	11.02	11.08	11.01	11.13	11.27	10.92	0.85
7	11.45	11.25	10.80	11.15	11.13	11.45	11.20	1.25
Standard mean deviation between specimens in the same casting, %[b]	3.34	1.52	2.43	2.26	3.56	2.45	1.79	

[a] Average mean deviation for different casting operations = 2.26%.
[b] Average mean deviation for different specimens in the same casting: 2.48%.

TABLE III
Logarithmic Decrements for Formulation B, 24 hr. Cure

Specimen no.	Logarithmic decrement Δ							Standard mean deviation between casting operations, %[a]
	Casting 1	Casting 2	Casting 3	Casting 4	Casting 5	Casting 6	Casting 7	
1	0.196	0.217	0.200	0.228	0.210	0.199	0.220	4.76
2	0.212	0.237	0.218	0.225	0.234	0.215	0.213	3.84
3	0.207	0.220	0.204	0.258	0.199	0.215	0.218	5.78
4	0.192	0.246	0.209	0.239	0.221	0.236	0.200	7.72
5	0.208	0.228	0.213	0.257	0.220	0.220	0.234	5.30
6	0.190	0.236	0.221	0.211	0.236	0.210	0.224	5.04
7	0.222	0.232	0.216	0.256	0.214	0.215	0.216	4.97
Standard mean deviation between specimens in the same casting, %[b]	4.56	3.46	3.01	6.28	4.56	3.24	3.21	

[a] Average mean deviation for different casting operations: 5.34%.
[b] Average mean deviation for specimens in the came casting: 4.05%.

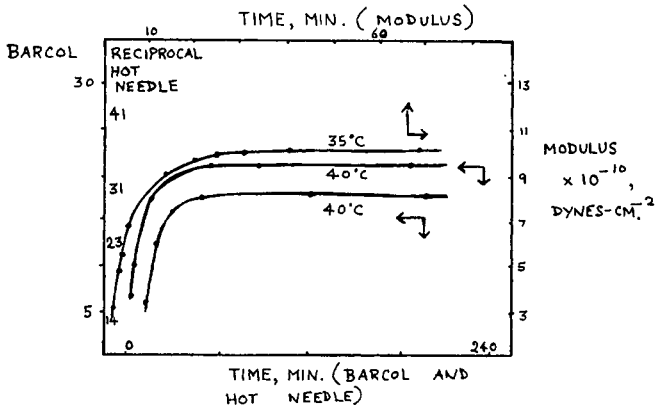

Fig. 1. Changes in shear modulus, Barcol hardness, and hot needle indentation (Formulation A).

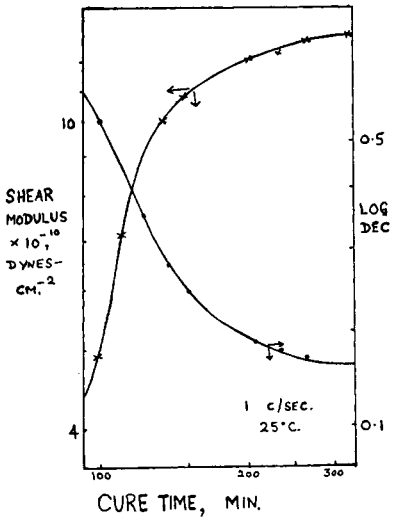

Fig. 2. Changes in modulus and damping during cure at 70°C. (Formulation C).

and of the reaction path. Seven specimens were prepared at a time, in one operation, and seven different casting operations were performed, making 49 specimens in all.

Moduli and logarithmic decrements are tabulated in such a way that the variation from specimen to specimen in the same casting, and also the variation between casting operations can be seen (Tables II and III).

It appears that there is little difference between the standard deviations obtained for the moduli in a given operation and the same deviation between several casting operations. In fact the latter appears slightly lower; although this would not be expected, the difference is too small to be significant. Damping terms are obtained which are predictably less con-

sistent between castings than between specimens in the same casting, and the magnitude of the standard deviation in all cases agrees with the figures given by T.N.O. for torsional pendulum used.[10] The implication here seems to be that for a given mold shape and size, there is no great difference between the state of reaction at a given time in one run and that in another.

CONCLUSIONS

The progress of crosslinking, as defined by measurements with the torsional pendulum, is closely related to that given previously by hardness tests (Fig. 1).

None of these methods can be used until well after gelation, though Lewis has used torsional braid techniques, which are basically similar, to give some indication of the earlier stages of reaction.

Figures 1 and 2 show that rapid changes are occurring in both modulus and damping at the point where measurements start. Hence other methods are required to supplement this technique by covering the earlier stages of cure.

Clearly we have defined the second part of a sigmoid curve, which shows the decrease in rate of curing. This fall-off in rate is associated with a decrease in the number of double bonds sufficiently mobile to take part in crosslinking, with a decrease in the concentration of free radicals, and with a decrease in the mobility of the system due to increasing crosslink density.

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