

Cure of Polyester Resins. I

G. S. LEARMONTH, F. M. TOMLINSON, and J. CZERSKI,
*Department of Chemistry, University of Aston in Birmingham,
Gosta Green, Birmingham, England*

Synopsis

The application of physical test methods to studying the crosslinking of unsaturated polyesters is reviewed. Experimental work on changes of hardness and electrical resistivity is described and it is shown that these are not mutually related, due to continual mobility of ionic conditions after the resin network is immobilized by gelation.

INTRODUCTION

Unsaturated polyesters contain alternate acid and glycol units and are arranged in relatively short linear chain molecules. These may be combined together by copolymerization with a monomolecular material (monomer), usually styrene. The process is interesting in itself, and also because it has an important effect upon the properties of plastics materials made from such polymers.

The process of copolymerization or crosslinking has been the subject of a long and elegant study, depending upon the methods of pure organic chemistry, by Hamann^{1,2} and co-workers. They conclude that crosslinking is initiated and propagated through the styrene and that neither the styrene nor the fumaric or maleic double bonds normally homopolymerize. The amount of crosslinking depends on the ratio of styrene to polyester.

The formation of an infinite network was considered in the classical papers of Carothers, Flory, and Stockmayer,³ and additional theoretical considerations affecting the conditions of formation of a polyester network have been stated by Gordon and Grievson.⁴

A good deal of empirical work has been recorded on the estimation of the "curing time" of polyester resins⁵ and a good knowledge has developed of the effect of conditions on the curing process. The effect of styrene content is well known and there is a report by Mikhailova and Sedov⁶ as well as the work by Hamann.¹

Chemical tests of degree of reaction are definitive to some degree, and bromine absorption⁷ and styrene and peroxide⁸ determination have been used. Acetone extract, i.e., gravimetric estimation of the amount of polymer not attached to the network, is useful.^{5,9} All these methods give variable results due to the immobilization of the system at an early stage and the necessity therefore of carrying out the estimations in a hetero-phase system.

It is possible, semiempirically, to use the normal methods of mechanical testing as an index of cure, at least in the later stages. These suffer from disadvantages, lack of reproducibility because of the empirical nature of test, effect of rate of strain, and lack of knowledge of the fracture mechanism. In addition it is not possible to obtain a quantitative relation between strength and the properties of the polymer molecules.

Differential thermal analysis¹⁰ has been used to measure the progress of crosslinking. Polymerization with the formation of unstressed single bonds is an exothermic process, and the amount of heat evolved, if it can be measured accurately, will serve as a measure of degree of reaction. There are several interesting phenomenological features about the curing of polyesters which have not been completely worked out, such as the effect of interrupting the (free radical) reaction and reinitiating it later by heating, also completion of the reaction by post curing. Until these phenomena are better understood it is difficult to rely on DTA as a quantitative method.

Lewis and Gilham¹¹ have an interesting technique in which a nylon braid is impregnated with resin and the changes in stiffness followed. There are some difficulties in interpretation of results, but this is a distinct improvement on the empirical methods.

The electrical properties of thermoset polymers are known to be sensitive to the degree of immobilization of the network.⁹ It is assumed that electrical conductivity in polymers of the type considered is for the most part an ionic diffusion process predominantly due to ionic trace impurities.¹² Capacity, on the other hand, depends on the polar properties of the dielectric, and may be expressed by a simple capacitance or in terms of recoverable (dielectric constant) and lost (loss factor) energy. It has been shown¹³ that, during isothermal polymerization of an epoxide resin, the logarithm of the resistivity is directly proportional to the rate of disappearance of the epoxide groups as determined by infrared analysis. If successive reactions are involved they may be followed by changes in the slope of the resistivity-time curve. In some cases resistivity is taken as an index of the rate of polymerization; an Arrhenius plot of log of rate of change of resistivity against reciprocal of absolute temperature will have a slope equal to the procedural activation energy of the polymerization.

We wished to study the effect of extent of network formation upon the properties of the massive polyester, and concluded that neat and effective methods may be found in the use of nondestructive techniques, in particular the application of dynamic testing techniques where a sinusoidal stress is applied to the test material and the response in strain is measured.

Gordon et al.¹⁴ reported the application of such a technique, where the sinusoidal stress was applied by a falling ball.¹³ This is virtually a single-pulse technique and was applied to measurement of glass transition point. The curing time at any given temperature is intimately connected with glass transition point in that curing must necessarily come to a halt when the T_g of the system reaches the curing temperature (owing to freezing of molecular relaxation processes at this temperature).

Barcol hardness has been widely used and recommended as a semi-empirical measure of the progress of curing.¹⁵

Tomkins¹⁶ studied curing of phenolic materials by indentation by a hot needle. This was a development of the Schmidt-Biesterfeld apparatus described in reports on wartime German technology.¹⁷

Our initial experiments were made to consider how far indentation methods, and in particular the hot needle method, were sensitive enough and reproducible enough to be used in fundamental work. In addition, we wished to study the preparation of samples of known degree of cure. As these methods will only work when the polymer is virtually an elastic solid, we also explored the use of resistivity as a suitable technique to follow the reaction from the liquid to the gelation state.

In future work we hope to apply dynamic techniques to study of resin systems similar to those described here.

EXPERIMENTAL

Hardness Measurements

The resin used was Beetle 4128 (B.I.P. Chemicals Ltd.). The styrene content varied from 30 to 40%.

The initiator was methyl ethyl ketone peroxide, 1.5% (Novadel Ltd., 5% in dibutylphthalate), and the accelerator was cobalt naphthenate, 1% (3.25% Co in white spirit).

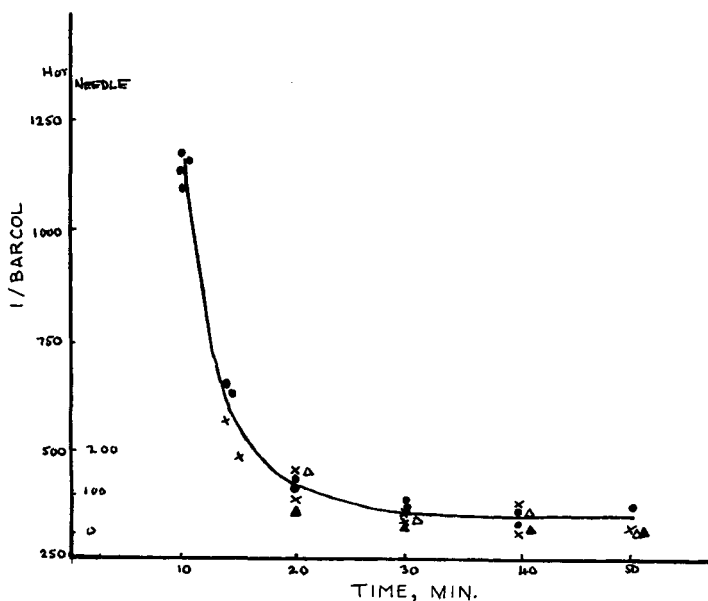


Fig. 1. Hardness vs. cure time: (●, Δ) Barcol, 35% styrene; (×, ▲) Barcol, 30% styrene; (●) needle, 35% styrene; (×) needle, 30% styrene.

Test specimens, $2\frac{1}{2}$ in. in diameter and $\frac{1}{4}$ in. thick, were cast in polyethylene molds. The resin was mixed carefully and poured into the molds at room temperature. After 2–3 min. for air bubbles to escape, excess resin was removed by sliding a glass cover over the resin surface on each mold. After 30 min. at 25°C . the gelled specimens were gently removed from the molds and placed in an oven at $40 \pm 1^{\circ}\text{C}$. After the required time at 40°C . two specimens were removed and the curing stopped by freezing in ice-water. After conditioning $1\frac{1}{4} \pm \frac{1}{2}$ hr. at room temperature (25°C .), the samples were tested. Barcol hardness was measured with the Barcol meter GXZJ 934-1, and 20 readings were made and averaged on each occasion.

Hot needle equipment was as described by Tomkins¹⁶ with the needle at $90 \pm 20^{\circ}\text{C}$. (This device was made available by J. Lucas & Co., Ltd.)

Results of hardness measurements are shown in Tables I and II and Figure 1.

TABLE I
Indentation Hardness

Styrene content, %	Indentation hardness at various times							
	10 min.	15 min.	20 min.	30 min.	40 min.	50 min.	100 min.	200 min.
40	1485	1206	892	605	504	498	417	396
	1466	1177	776	580	495	490	—	317
35	1158	649	440	363	330	333	342	335
	1134	647	425	365	358	358	332	337
30	1145	338	423	341	364	—	258	—
	1091	473	390	355	302	331	—	—

TABLE II
Barcol Hardness

Styrene content, %	Barcol hardness at various times						Part cured, %
	20 min.	30 min.	40 min.	50 min.	100 min.	200 min.	
30	7.4	19	20	20	—	22	50
	6.3	16	19	$20\frac{1}{2}$	21	—	59
35	1.7	28	$26\frac{1}{2}$	28	28	33	50
	21	27	29	28	—	34	50

Resistivity Measurements

In this method, which has been described by Delmonte,¹⁸ the resin was cured between plane glass plates separated by a rubber ring. To each plate, a foil electrode was attached by silicone grease.

Resistivity was measured between the electrode at 85 v. by using a sensitive ammeter (E.I.L. Model 29A, Electronics Institute Ltd., Rich-

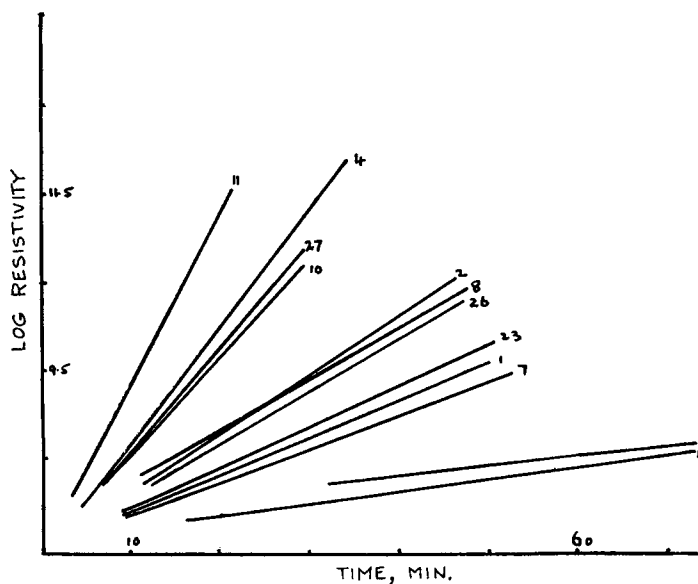


Fig. 2. Resistivity vs. cure time. Numbers on curves correspond to experiment numbers in Table III.

mond, Surrey, England), while the cell was immersed in a water thermostat held at 25°C.

Results are shown in Table III and Figure 2.

TABLE III
Resistivity^a

Time, min.	Expt. no.	Resistivity, ohm-cm.		
		12-28 ^b	1-4 ^c	5-11 ^d
25	1,5,12,13,14	0.259	0.707	0.041
35	2,15-19	0.439	0.826	
45	3,6,7,20,21,22	0.560	1.000	0.477
55	4,23,24,25	0.675	1.150	
65	8,9,26,27,28	0.875	—	0.767
75	10	1.114	—	1.041
85	11	—	—	1.301

^a Resin Beetle 836, Benzoyl peroxide catalyst, *N,N'*-dimethyl-*p*-toluidine accelerator.

^b Catalyst 1.5 phr, accelerator 0.05 phr.

^c Catalyst 1.5 phr, accelerator 0.10 phr.

^d Catalyst 1.0 phr, accelerator 0.10 phr.

DISCUSSION

The circumstances under which the two methods of assessment of degree of crosslinking are useful are very different. The indentation hardness methods will operate only when the specimen has acquired quite a high

degree of elasticity, i.e., in the later stages of curing. Both methods are relatively inexact and the results show quite clearly the difficulties which this causes. Figure 1 is a composite which shows both the effect of varying the method and varying the styrene content, but the points overlap almost completely and neither method can define the shape of the curve in the crucial area, where crosslinking is becoming a maximum. It is evident that the hot needle equipment is relatively sensitive and gives fairly reproducible results over quite a wide range, which would need to be covered by two or three Barcol instruments. The Barcol is a neat and handy empirical instrument, while the other is not portable. In the Barcol instrument error is introduced if the test surface is not flat, and this caused considerable difficulty at times.

After the initial experiments the catalytic system was changed from methyl ethyl ketone peroxide initiation with cobalt naphthenate accelerator to benzoyl peroxide accelerated by a tertiary amine. It was found that the original system was a little capricious, and it was not easy to obtain reproducible performance from it. We may be able to comment on this in later work.

We chose to measure resistivity to follow crosslinking, as, on the basis of previous work, we expected large changes in value. This was in fact found to be the case, but there is somewhat of an anomaly in the results. It is evident from Figure 2 that there is no sudden change in mobility of ions with viscosity, and in particular that no change takes place at gelation, which occurred between 6 and 25 min. under the conditions used. Warfield and Petree¹² and Judd agree that there is no change at the gelation point. It may be that the conduction measured is caused by mobile ionic particles, either monomer or impurities in the moldings, which are still mobile after gelation till a very high degree of crosslinking is achieved. More work is needed on this point.

The activation energy calculated from an Arrhenius plot of rate of change of resistivity against reciprocal of absolute temperature seems low (7.0, 7.9, 9.2 kcal./mole). This may be characteristic of the system used, though we have some empirical evidence to the contrary. We should prefer not to comment on this further at the moment. We do not yet have enough evidence to obtain an activation energy from the hardness measurements.

Neither method seems to be suitable for accurate measurement of the last stages of curing. While the hardness measurement appears to follow a curve with time (as we should anticipate), the resistivity in the case we have studied does not appear so related. The resistivity must, we suppose, reach a maximum value asymptotically, but has not done so in the time range covered in this study.

References

1. D. K. Hamann, *Angew. Chem.*, **71**, 596 (1959).
2. H. V. Boenig, *Unsaturated Polyesters*, Elsevier, Amsterdam, 1964.
3. G. M. Burnett, *Mechanism of Polymer Reactions*, Interscience, New York, 1954, p. 344.
4. M. Gordon and B. M. Grievson, *J. Polymer Sci.*, **17**, 107 (1955).
5. Sub-Committee of the Joint Services, W. W. Wright, Chmn., *Plastics*, **26**, 190 (1961).
6. Z. F. Mikhailova and L. N. Sedov, *Soviet Plastics*, **8**, 9 (1960).
7. A. C. Filson, *Plastics*, **27**, No. 293, 1 (1962).
8. B. Alt, *Kunststoffe*, **52**, 7, 394 (1962).
9. L. H. Vaughan, *Trans. Plastics Inst.*, **24**, 47 (1956).
10. G. B. Johnson, P. H. Hess, and R. R. Miron, *J. Appl. Polymer Sci.*, **6**, S19 (1962).
11. A. F. Lewis and J. K. Gilham, *S.P.E. Trans.*, **3**, 201 (1963).
12. R. W. Warfield and M. C. Petree, *Makromol. Chem.*, **58**, 139 (1962).
13. Magee and Rotarice.
14. M. Gordon, B. M. Grievson, and I. D. McMillan, *J. Polymer Sci.*, **29**, 9 (1958).
15. Robinson, *Brit. Plastics*, **35**, 80 (1962).
16. A. A. Tomkins, *Trans. Plastics Inst.*, **26**, 389 (1958).
17. British Intelligence Objective Survey, Reprint 433 (1951).
18. J. Delmonte, *J. Appl. Polymer Sci.*, **2**, 108 (1959).
19. N. Judd, in *Reinforced Plastics Conference*, British Plastic Federation, London, 1964.
20. T. Raphael and C. D. Armeniades, *SPE Trans.*, **4**, 83 (1964).

Received May 3, 1967