

Analysis of the Hardening Reaction of Furfuryl Alcohol Resin*

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Measurement of electric resistivity of thermosetting resins during their hardening stage along with the several other methods¹⁾ provides information on their curing degree. The methods, however, can be done only with difficulty with the common instruments readily at hand, because of the higher resistance value of resins.

In the earlier part of the resinification, mechanism of the accelerator's** action, unobtainable by chemical analysis²⁾, was easily pictured by this method³⁾, since the accelerator reduced the resistance of the reactant.

Addition of electro-conductive filler, which may similarly reduce the resistance, was considered to clarify almost the whole curing degree by employing common instruments. In this article, graphite powder was added to furfuryl alcohol (FA) resin—one of graphite-cement systems—and Kohlrausch bridge and drop-method were employed, which exhibited the activation energy of the final cure together with that of the apparent cure.

Experimental

Materials.—Resin—A neutralized initial condensate of FA. Viscosity—31.3 poise at 20°C. Mean Mol. Wt.—220 (Calculated from the freezing point depression of its dioxane solutions.)

Filler—Artificial graphite powder as shown in Table I.

Accelerator—*p*-Toluenesulfonyl chloride (I) and its sulfonic acid (II), reagents of G. R. Grade. **Solvent**—Dioxane (G. R. Grade) was used only when the filler was not added, in order to keep the reaction temperature constant.

Mixture of filler and accelerator—One hundred g. of I or 30.0 g. of II was mixed with 1000 g. of filler for more than 45 min. in a mixer at room temperature.

TABLE I
CHARACTERISTICS OF GRAPHITE POWDER

Moisture		0.25%	
Volatile Matter		0.84%	
Ash		0.09%	
Density ³⁰ ₄		2.073	
Distribution of Particle size	{	<80 meshes	0%
		80~120	1%
		120~160	19%
		160~200	22%
		200~250	3%
		>250	55%

Method.—1. *Determination of resistivity (ρ_d , ρ_a) and apparent resistance (R).* (1) In the case where copper electrode was employed: more than 20 of the similar electrodes $5\phi \times 100$ mm. copper, which were polished prior to use, held by the epoxy resin plate* at intervals of 14.0 mm. were set in equal depths of the cement. Seventy g. of the resin and the same amount of filler containing I or II were mixed in a tall beaker ($45\phi \times 85$ mm., for 100 cc.) for 5 min. A thermometer was inserted in the center of the reactant. The beaker was placed in a thermostat. The plate*, connecting electrodes, was sealed to the beaker with hard clay. Apparent resistance (R) was measured by Kohlrausch bridge from the beginning of resinification to the final cure.

When the filler was not used, solutions containing 1.0 g. of I or 0.2 g. of II as well as 7.0 g. of dioxane and 30.0 g. of resin were prepared, R of which was determined uniformly by Wheatstone bridge instead of Kohlrausch bridge.

Hereafter, experiments, where I is used, will be called A-series and those with II, B-series.

(2) After gel-time the resin (130 g.) and the same amount of the filler containing I or II were mixed and hardened in the beaker, exactly parallel with the above mentioned system. Samples immediately after gel-time were rapidly cut out in approximate sizes $10 \times 10 \times 20$ mm., which were closely held between copper films and their resistivity was measured by the drop method (D. C. employed), and further by Kohlrausch bridge. These will be called ρ_d and ρ_a , respectively.

2. *Measurement of adhesion power (F).* At the same time that the graphite cement was prepared as mentioned, above "impervious

* Presented at the 10th Annual Meeting of the Chemical Society of Japan held in Tokyo, April, 1957.

** *p*-Toluenesulfonyl chloride, which may react with the monomer or the initial condensate of the resin³⁾.

1) E. Barr, *Ind. Eng. Chem.*, **48**, 72 (1956).

2) S. Yamada and S. Hayashi, *J. Chem. Soc. Japan, Ind. Chem. Sec. (Kogyo Kagaku Zasshi)*, **61**, 342 (1958).

3) S. Yamada; This Bulletin, **27**, 479 (1954).

* Araldite D, cured with accelerator No. 951, resistance of which was infinitive between electrodes by 500 V. megger.

graphite** pieces, cut out as large as $10 \times 10 \times 20$ mm., were joined with the cement at the 10×10 plane under the same pressure. They were settled in the thermostat, being placed in a glass vessel with a stopper.

Adhesion power (F) was measured as the transverse strength at the joined plane, several values of which were averaged every time.

3. *Acetone extraction.* At the same time, when samples for measuring ρ_d and ρ_a were taken off, small cubes ($10 \times 10 \times 10$ mm. in size) were cut out at every curing temperature. Three pieces were held in the thermostat ($30 \pm 0.1^\circ\text{C}$) with 25.0 cc. of acetone and weighed after 16 hr.

4. *Other measurements.*—Shrinkage** of samples employed for the determination of resistivity, filler added, was measured with a micrometer, which gave an exactness of 0.2% to the completely cured cement pieces.

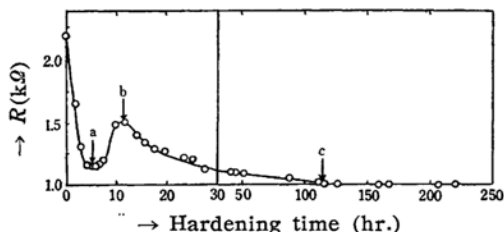


Fig. 1. An example of change in apparent resistance, filler employed.

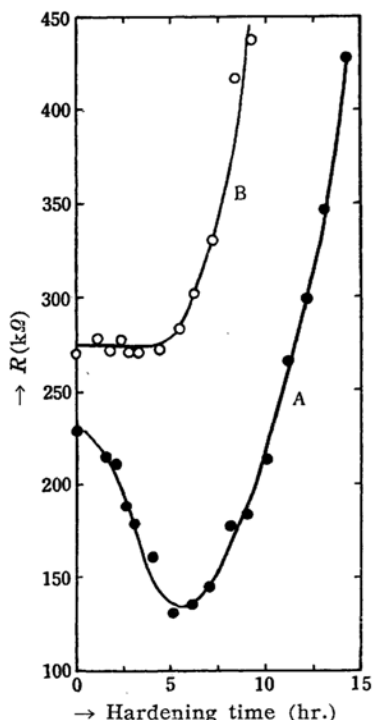


Fig. 2. An example of change in apparent resistance (R), without filler at the earlier stage.

Hardness** was measured with Shore tester complementally.

5. *Hardening temperature.* 20, 30, 40 and $50, \pm 1^\circ\text{C}$ were adopted.

Examples of data.—1. *Change in apparent resistance, R .* For instance, data in the case of B-series with filler at 20°C are given in Fig. 1. Reproducibility of the point a, b and c was excellent. Change in R of the reactants without filler at 40°C is shown as an example in Figs. 2 and 3.

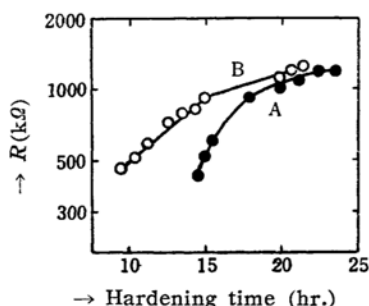


Fig. 3. An example of change in apparent resistance (R), without filler at the final stage.

2. *Change in adhesion power, F and hardness H .* Data at 30°C are given in Fig. 4 for example.

3. *Change in resistivity, ρ_d , ρ_a .* Data at 30°C are given in Fig. 5 for example.

4. *Change in acetone extract.* Data at 40°C are shown in Table II for example.

TABLE II
AN EXAMPLE OF CHANGE IN ACETONE
EXTRACT

Series	Reaction time (hr.)	Average (%)	Range (%)
A	51	7.60	0.55
	75	1.73	0.05
	99	2.50	0.35
	118	2.74	0.08
B	51	5.60	1.40
	75	3.30	1.70
	99	1.35	0.02
	118	1.85	0.10

5. *Change in shrinkage.* Data at 50°C are shown as an example in Table III.

Discussion

1. *Change in R , ρ_d and ρ_a .*—Elements of change in R may be assumed as R_h , R_w , R_a and R_g . For example; $-dR_h/dt = K_h \cdot V_h$, $-dR_w/dt = K_w \cdot V_w$ etc. Increasing and decreasing velocity of R_h , R_w etc. may be considered to be proportional to that of hardening and dehydrating process.

* "Impervious graphite" is made by impregnating a thermosetting resin.

** Samples were held in a glass vessel set in the thermostat, and at the stopper and the bottom of the vessel dry granules of calcium chloride were placed.

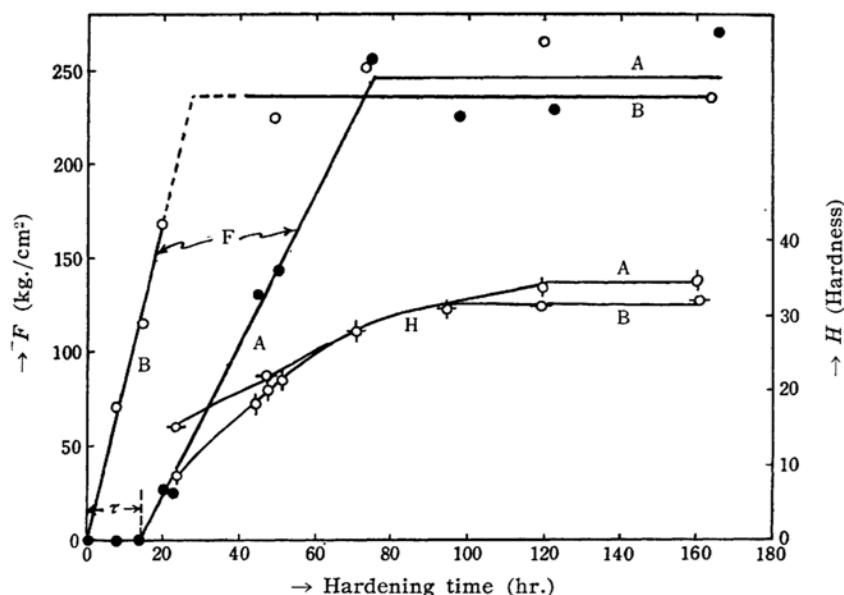
Fig. 4. An example of change in adhesion force (F) and hardness (H).

TABLE III

AN EXAMPLE OF CHANGE IN SHRINKAGE

Series	Reaction time (hr.)	10×10×20 mm.			10×10×10 mm.			10×10×10 mm.		
A	26	9.98	9.95	20.04	9.90	9.96	9.92	9.95	9.90	9.88
	50	-0.01	-0.03	-0.05	-0.01	-0.01	-0.03	-0.01	-0.01	-0.01
	74	"	"	"	"	-0.02	-0.02	-0.01	-0.02	-0.02
	94	0.00	-0.02	-0.04	0.00	"	-0.03	0.00	0.00	0.00
B	26	9.91	9.91	20.02	9.93	9.99	9.95	9.99	9.91	9.91
	50	0.00	0.00	-0.02	-0.02	-0.01	-0.02	0.00	-0.01	-0.02
	74	-0.01	-0.01	-0.03	-0.03	-0.02	-0.03	-0.01	"	-0.03
	94	"	"	-0.04	"	-0.01	-0.04	"	"	-0.04

TABLE IV

COMPLEMENTARY DATA TO EXPLAIN THE SETTLING DOWN TENDENCY OF RESISTANCE

Particle size of graphite powder (meshes)	Molding pressure (kg./cm. ²)	Comparison ^{a)} between ρ_1 , resistivity of sample immediately after molding and, ρ_2 , that after curing up to 200°C		Resin
24—32	40	$\rho_1 > \rho_2$ ($\alpha = 1\%$ ^{b)})		Initial condensate of FA ^{c)}
32—50	"	$\rho_1 = \rho_2$ (")		"
50—80	"	$\rho_1 < \rho_2$ (")		"
50	100, 200, 300, 400, 500, 600	$\rho_1 = \rho_2$ (")		Phenollic

a) Tested by analysis of variance in three-way layout.

b) Risk.

c) In the case where the ratios of the resin added to filler change, ρ_2 decreases to a ratio (12% to filler) and then increases starting from the ratio, as the amount of resin increases.

R_a and R_d correspond to the activation of $I^{(3)}$ and orientation of graphite filler respectively. Values of change in R , dR/dt may be plus, zero or minus depending on the value of each element. It is assumed that V_w and V_a contribute in

the early stage and V_h and V_g in the final stage. Change in R , ρ_d , and ρ_a indicated in Figs. 1 and 5, for example, are observed to be of a settling down tendency in the final stage.

On the contrary, the system without

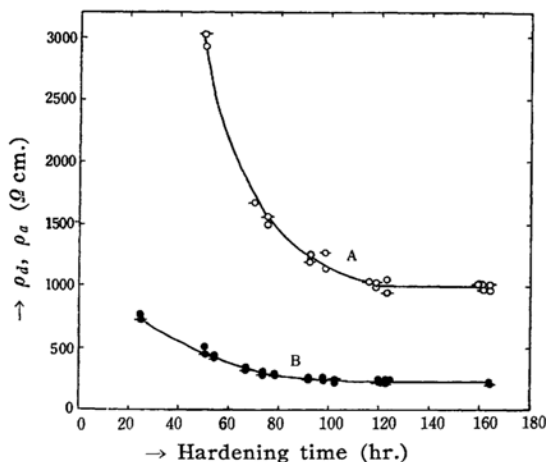


Fig. 5. An example of change in resistivity (ρ_d , ρ_a).

○●: ρ_d } These can be considered to
○●: ρ_a } be in an approximate agreement.

graphite filler indicates a reasonable increasing tendency as shown in Fig. 3 for example. This fact amply suggests that the effect of filler, $-dR_g/dt$, governs the hardening degree in final stage. Experimental facts from another view as shown in Table IV give a hint to the phenomenon, which may be derived from the following interpretation.

Data in Table IV indicate that the effect of graphite powder on the resistivity directly relates to its particle size and molding pressure. In this article, meshes smaller than 120 of graphite powder and the normal pressure were employed. The facts given in Table IV are summarized as follows.

(a) In the case where coarse particles were used, resistivity decreases with hardening and increase in resin content under a relatively low pressure.

(b) In the case where particle size is reduced, resistivity does not change or increase under the pressure.

(c) In the case of use of fine particles, resistivity does not change under pressure.

Accordingly, the phenomenon of the decreasing tendency even in the case of fine particles used under the normal pressure in these experiments may not be contradictory to this fact. Namely, it is understood that the orientation time of the filler in the resin depends on the hardening velocity, amount and particle size of added filler, and the operating pressure.

From b to c in Fig. 1, the effect of the

orientation is predominant, while the effect of hardening is observed from a to b.

Now that the settling time of resistivity can be assumed as the end point of hardening, its activation energy from this time, S_p , was calculated to 7 kcal./mol. in A-series*, 6 kcal./mol. in B-series as shown in Fig. 6. Such values can not be obtained from changes in acetone extract given in Table II. under similar conditions.

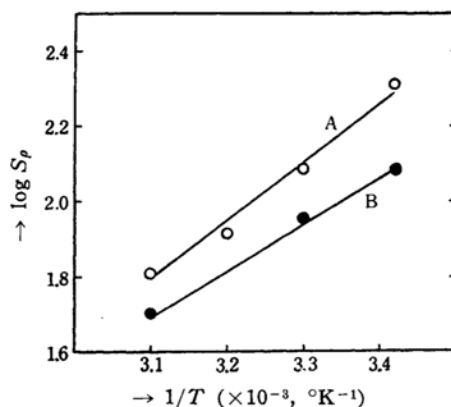


Fig. 6. Relation between $\log S_p$ and $1/T$.

Besides, the activation energy calculated from the time up to a certain R in Fig. 3 for example (no filler) was 12 kcal./mol.

Cell constant of the cell used, $K=9$ cm. was obtained by employing saturated aqueous solution of sodium chloride. The resistivity of the cut piece, ρ_a , was however found to be different from that calculated from R (with filler).

This proves that the mixing of resin and filler containing accelerator could not be uniformly processed even in such a small scale, which may be a point to take in consideration in applied use. Large variance in acetone extract as given in Table II may depend upon the same fact.

2. Change in adhesion power, F .—In A-series, the induction period τ for the increase of F was observed as shown for example in Fig. 4. This may be assumed to correspond with the activation velocity of I and gives activation energy of the process, 12 kcal./mol., as shown in Fig. 7.

Now further data in a previous paper³⁾ the relation between the decrease of the velocity of resistance in FA monomer and I, k_r ,—corresponds with the activation velocity of I—and the reaction temperature

* In A-series, accelerator concentration in the system is considered to increase because of formation of II and hydrochloric acid as I reacts with the resin³⁾. Accordingly the energy is only an apparent value differing from that in B-series.

was investigated as shown in Fig. 8. which gave the activation energy, 10 kcal./mol. It may be considered to be closely related to the above value, 12 kcal./mol., in the case

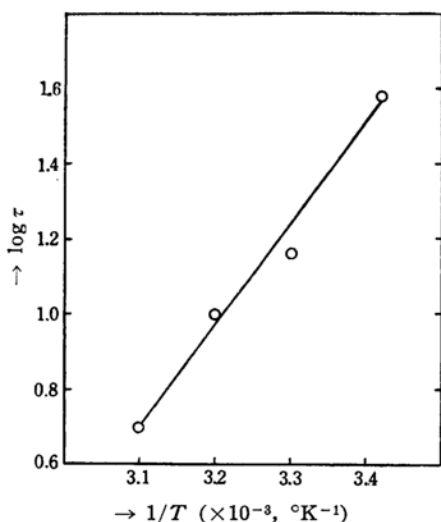


Fig. 7. Relation between $\log \tau$ and $1/T$.

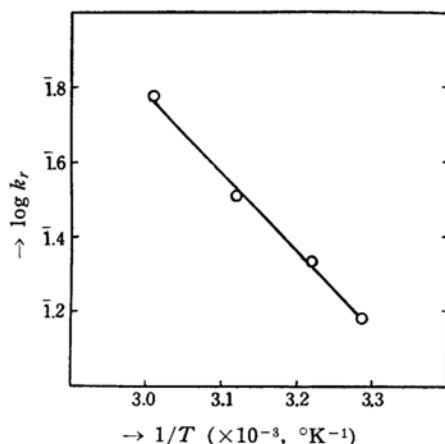


Fig. 8. Relation between $\log k_r$ and $1/T$.

where filler and initial condensate are employed. It is interesting that these values are relatively similar in spite of the difference both in the calculation method and of the reaction system.

Approximate saturation time of F , S_F , in B-series (catalyst concentration is constant), gave, as shown in Fig. 4, the activation energy, 16 kcal./mol., which may be

assumed as that for the apparent end point of the hardening process. In this determination, saturated value of F was obtained by averaging arithmetically, such a variance which was inevitable in such a case and similar variances are noted in many reference papers⁴⁾.

3. Other problems.—The saturation time of H was greater than that of F in each case as given for example in Fig. 4, which suggests that the saturation time of the F above mentioned gives only an apparent end point of the hardening process.

Change in shrinkage was in the limit of experimental error in almost all cases, which may explain that the settling down phenomenon of resistivity does not depend on the apparent shrinkage.

Summary

Decreasing tendency of resistance in the system consisting of furfuryl alcohol resin, graphite filler and accelerator was observed and analysed, and this observation gave an activation energy of the final cure, together with that of the apparent cure calculated from the saturation time of adhesion power. Besides, activation of sulfonylchloride accelerator was investigated taking account of the adhesion power increase and resistance decrease.

These considerations may be full of suggestions for the practical use of such a cement system.

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4) e. g., E. O. Hausman, A. E. Parkinson and G. H. Mains, *Modern Plastics*, 22, 151–154, 190–198 (1944).