Effects of Temperature and Catalyst Level on the Cure Rate of Fiber-Reinforced Plastic (FRP)

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Synopsis

In order to allow manufacturers of fiber-reinforced plastic (FRP) products to determine an optimum catalyst level for their application, an investigation was made of the effects of ambient temperature and catalyst level on the gel time of polyester resins. Gel times were determined using standards set by the Society of the Plastics Industries, Inc.[5] The gel times thus obtained compared favorably with published gel times for general purpose polyester resins. It will be left to the individual manufacturer to determine the optimum catalyst level for his or her application, as very short gel times will cause the resin to harden too quickly to allow fabrication of large parts. In general, the optimum catalyst level is defined as that which produces the shortest usable gel time.

INTRODUCTION

The rate of production of fiber-reinforced plastic (FRP) products depends, to a large extent, on the conditions under which the parts are fabricated. Variables such as ambient temperature, part thickness, and catalyst level have profound effects on the cure rate of the resin used, thus having an effect on the rate of production of products. Humidity and sunlight also affect cure rate, but to a lesser degree.

In order for a manufacturer of FRP products to determine what amount of catalyst is best for the conditions under which he is working, an investigation of the gel times of two commonly-used resins was made at various temperatures and catalyst levels. The resin was catalysed and allowed to cure (harden) at constant ambient temperature. The temperature range was set at 65–95°F. The samples of resin were allowed to cure at 5°F increments within this range. Since the polyester resin used in FRP production undergoes an exothermic reaction when mixed with catalyst, the temperature of each resin sample was monitored to determine the gel time of the sample. Gel time is defined by the Society of the Plastics Industries (USA) as the time it takes the resin sample to reach 10°F above ambient temperature.[5]

The gel times thus determined for each resin–temperature–catalyst level combination were plotted to produce curves of gel time versus temperature for specific catalyst levels. The curves obtained will allow fabricators of FRP products to choose the catalyst level required to produce a set gel time at any temperature within the range.

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THEORY AND BACKGROUND

The production of FRP parts involves three basic components: polyester or epoxide resin, fiber reinforcement, and catalyst. These components, when correctly combined, form one of the most efficient building materials in use today. FRP laminates are lightweight, corrosion resistant, fairly inexpensive, and are, pound for pound, stronger than most metals.[1] Even though many different types of resins, catalysts, and reinforcements are used in the industry today, some are used so widely that they can be considered almost exclusively. Therefore, this investigation covers only those in most common use today.

Resins

Although there are several different classes of polyester resins,[2] the most widely used is classified as "general purpose." General purpose resin is a low viscosity, low reactivity, thixotropic polyester resin designed for open mold fabrication. The two general purpose resins used in this investigation were koppers 1061-5, manufactured by the Koppers Company, Inc., of Pittsburgh, PA, and Stypol 40-4074, manufactured by the Freeman Chemical Company of Port Washington, WI. Technical data on the Koppers resin are supplied.

The resins considered here, as with most polyester resins, are referred to as "unsaturated" (reactive) polyesters. These systems are mixtures of true esters dissolved in a polymerizable monomer (such as styrene) which provides crosslinking units. The two compounds (ester and monomer) coreact, or copolymerize, upon the introduction of a free radical donor catalyst (usually an organic peroxide) to form a rigid, infusible thermoset material.[2] Most resin manufacturers include some type of promoter to accelerate the curing process of the resin. The most common promoter is 0.4% of a 6% active cobalt naphthenate

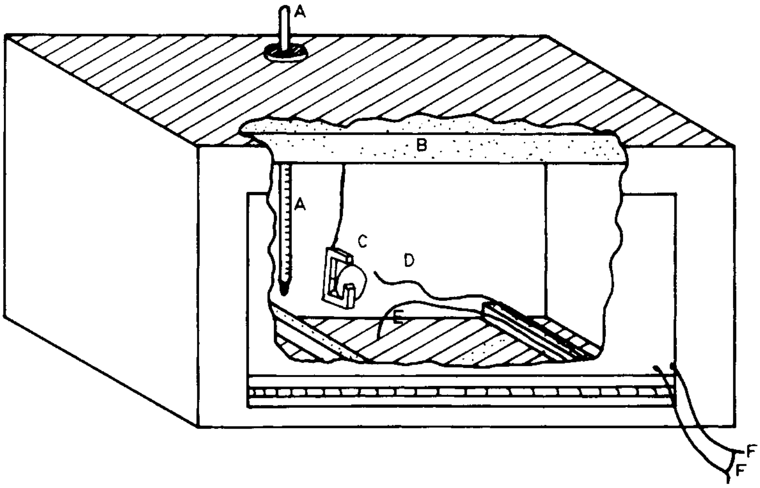

Fig. 1. Constant temperature environment: (A) thermometer; (B) electric heater; (C) thermostat (adjusting screw on back of box); (D) thermocouple reference junction; (E) thermocouple hot junction; (F) thermocouple leads (to voltmeter).

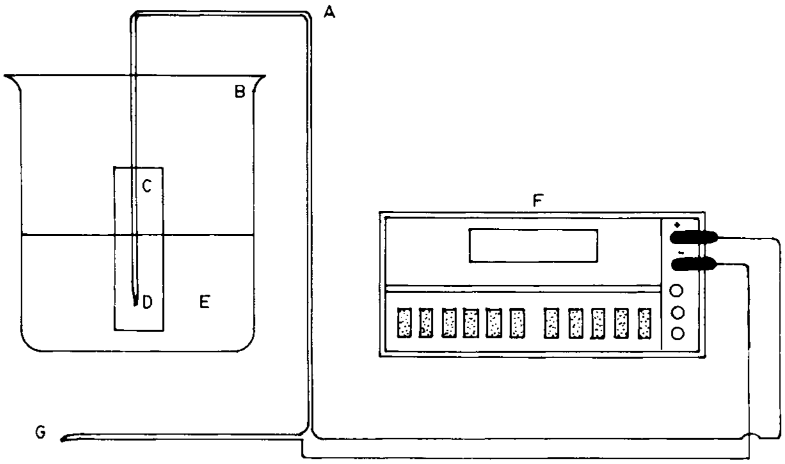

Fig. 2. Apparatus for monitoring resin temperature: (A) Copper constantan thermocouple wire; (B) 250 mL beaker; (C) waxed paper envelope; (D) thermocouple hot junction; (E) resin sample (100 mL); (F) digital voltmeter; (G) thermocouple reference junction.

solution. Dimethyl aniline and/or diethyl aniline are also added occasionally, but seldom in place of the cobalt solution.

Reinforcements

Of the many types of reinforcements used today, glass fibers, of one kind or another, are used almost exclusively. The three basic types of glass reinforcement are: woven cloth, made of uniformly woven strands of glass; chopped-strand mat, a cloth made of randomly-oriented short strands of glass; and continuous strand roving (gun roving), much like a large spool of twine. The gun roving is used exclusively for spray-up fabrication, in which the glass is fed to an air-powered gun which chops the glass into short strands and is sprayed onto a mold along with resin and catalyst.

When wetted with catalysed resin and then allowed to cure, the glass forms a rigid laminate, the laminate becoming much stronger as more layers of glass are used. The normal ratio of resin to glass is 3 : 1 (based on weight).[5]

Catalysts

Even though many different catalysts are currently in use, the most preferred is methylethylketone peroxide (MEKP), usually dissolved in benzyl phthalate or dimethyl phthalate. The catalyst used in this investigation was Thermacure 50, manufactured by the Freeman Chemical Co. Thermacure 50 provides gel times close to those found in literature, and it is 50% MEKP (by weight), which is generally considered average.

Fabrication Practices

Though there are many different methods for producing FRP parts, only open mold fabrication was considered in this investigation, as it is one of the most widely used methods. Open mold fabrication differs from other methods

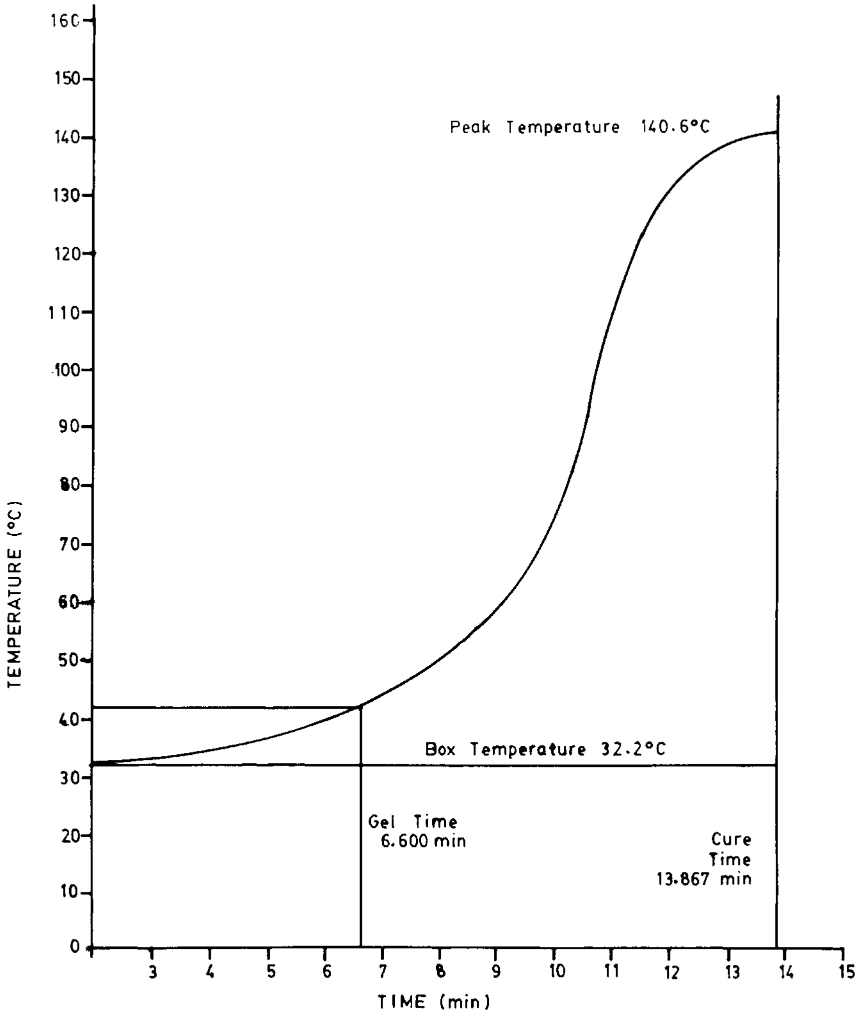

Fig. 3. Exotherm curve for Koppers 1061-5 resin, 2% catalyst, at 90°F.

in that it is carried out in open molds (as opposed to matched-die molds) at atmospheric pressure. In open mold fabrication, laminates are made by either (a) wetting layers of glass cloth and applying them to the surface of the mold until the desired thickness is obtained, or (b) spraying a mixture of resin, catalyst, and chopped glass fibers onto the mold. Molds can range in size from small molds less than one square foot to molds large enough to fabricate rocket engines.

DEVELOPMENT AND DESIGN

Since manufacturers of FRP products are in business to serve their customers efficiently and at the same time to make a profit for themselves, it is important for the manufacturer to make the most efficient use of time, materials, and

TABLE I
Table of Gel Times for Koppers 1061-5 Resin (Gel Time in Minutes)

	Weight percent MEKP			
Temperature (°F)	0.5%	1.0%	1.5%	2.0%
65	30.083	23.400	19.900	18.400
70	24.417	18.233	14.400	14.017
75	19.517	13.683	12.400	10.810
80	16.400	11.800	10.700	9.083
85	15.417	9.833	9.550	7.167
90	13.100	9.183	8.233	6.600
95	11.500	8.300	7.267	6.150

money. One of the best ways to increase efficiency in a large production operation is to have the shortest possible turn-around time of his molds. As a general rule, the sooner a part can be removed from a mold, the more parts can be built, and therefore the more cost-efficient the operation. The length of time a part remains in a mold depends almost exclusively on the cure rate of the resin used.

As mentioned earlier, the cure rate of polyester resin depends, to a large extent, on the ambient temperature, the part thickness, and the amount of catalyst used. As a general rule, an increase in temperature or catalyst level will cause a shorter gel time, as the cure process is exothermic and the cure rate increases as a function of temperature. Thicker parts will also cause a faster cure due to the amount of heat built up in the part during the curing process, while thinner parts cure more slowly due to a loss of heat to the environment.[1] It is partially for this reason that manufacturers often set $\frac{1}{8}$ in. as the lower limit for part thickness. Thus it becomes necessary for a manufacturer to know how much catalyst to use to obtain the best cure rate, based on the conditions under which he is working and the thickness of the part required. One factor which will tend to slow the cure is an increase in the weight percent of reinforcement used. Reinforcements, being inert, tend to lower the peak temperature of the resin mixture by absorbing heat from the reacting resin, thus lengthening the cure time.[5]

Although the fastest cure is generally considered the best, there is a limit to the amount of heat or catalyst that can be added to speed the cure rate. If too much heat or catalyst is added, or if too much thickness is built up, the part can develop severe internal stresses during the curing process. During the curing process, thermosetting polyester resins shrink in volume due to molecular crosslinking when passing from the liquid to the solid state. Also during curing the resin forms a bond with the reinforcing glass. Since the resin and the glass have different coefficients of thermal expansion, too much heat generated during the curing and cooling down cycle can create considerable internal stresses. These stresses can cause the part to "delaminate" during the cooling process.[2] Thus, when fabricating very thick parts ($\frac{1}{2}$ in. or more) it is usually advisable to build up layers slowly, allowing the laminate to cure and cool down before adding more thickness.

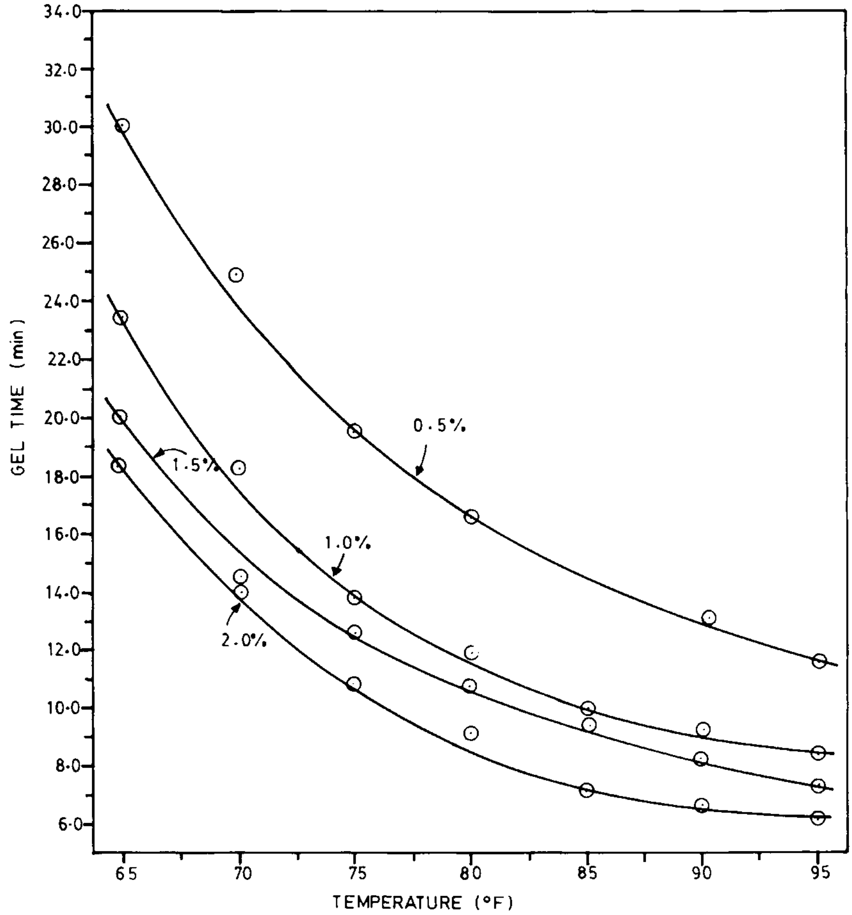

Fig. 4. Plot of gel time *vs.* temperature for Koppers 1061-5 resin at four concentrations of MEKP.

Once the principles for obtaining the shortest cure rate are understood it becomes necessary to develop a standard for determining the cure rate of a resin. One way is to determine the "gel time" of the resin at a particular temperature and catalyst level. The Society of the Plastics Industries (SPI) has devised a standard gel time test.[1] In the test, a 100 mL sample of resin is catalyzed with a precise amount of catalyst and allowed to cure at constant ambient temperature. The ambient temperature is kept constant using a constant temperature bath or a constant temperature box (Fig. 1). The constant temperature environment used in this investigation was constructed of insulated FRP, with an electric heater and thermostat to regulate temperature.

Since the SPI has set gel time as the time required for the resin to heat up 10°F above the reference temperature, it is necessary to devise a way to monitor the temperature of the resin as it cures. A copper-constantan thermocouple was fabricated and one end (hot junction) immersed in the resin during the gel time test. The other end (reference junction) was left in the constant temperature environment. The temperature difference between the resin and the

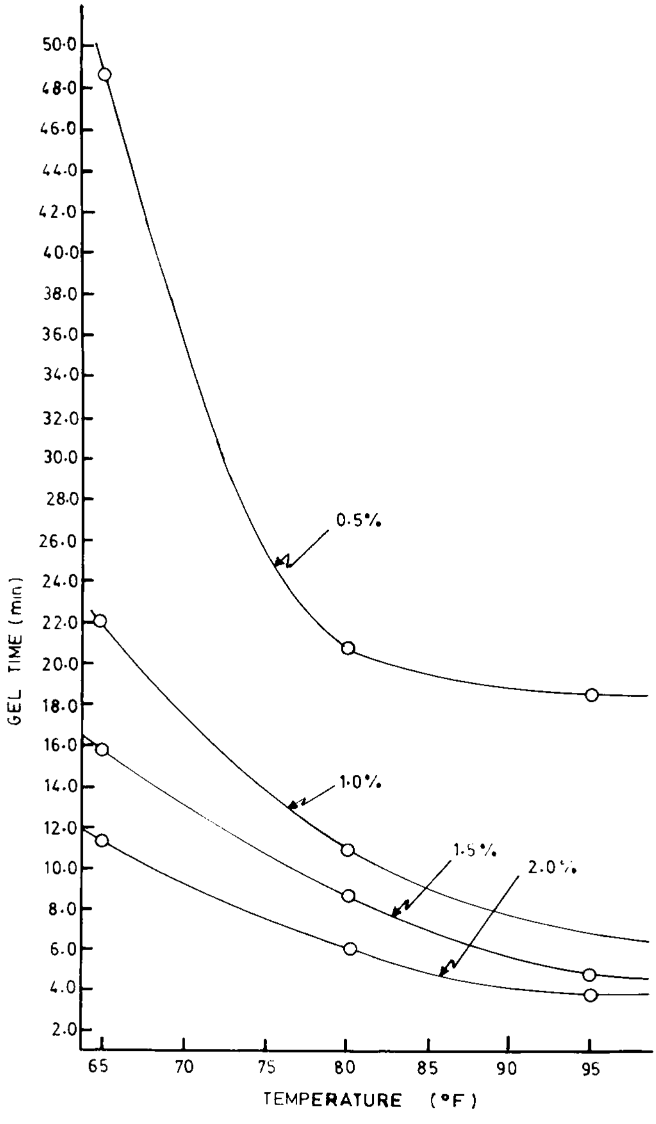

Fig. 5. Plot of gel time *vs.* temperature for Freeman Stypol 40-4074 resin at four concentrations of MEKP.

box temperature were measured using a digital voltmeter (Fig. 2). The curves thus obtained from plotting temperature *versus* time for each gel time test are referred to as exotherm curves and indicate the rate of reaction as a function of time (example curve, Fig. 3). The exotherm curve consists of three basic sections. The first section, ending at the gel time, indicates the point at which 35–40% of the unsaturated sites have reacted. The second section, from the inflection point (kick-off temperature) to the point at which the curve begins to level out, indicates the reaction progressing from 40% to approximately 80% complete. The third section, at the peak temperature, indicates the point at which the reaction is considered complete, with 92–95% of the unsaturated sites reacted.[5]

Gel time tests were run for 28 combinations of temperature and catalyst level for the Koppers resin, and for twelve combinations of temperature and catalyst level for the Freeman resin.

In addition to performing gel time tests on resin samples, several sample parts of FRP were fabricated in order to determine how much the addition of inert reinforcements lengthen the gel time by absorbing heat from the resin.

RESULTS

Once a gel time was determined for each combination of temperature and catalyst level for each resin, the gel times were tabulated for comparison (Table I). The gel times thus obtained and tabulated compared very well with general values found in the literature.[2,3] There are, of course, some differences in experimental values and published values due to differences in pressure and humidity and slight variations in composition of resin and catalyst.[3]

The gel times from Table I were plotted (Fig. 4) on a graph of gel time versus temperature for each catalyst level. From Figure 4, one can easily obtain an expected gel time based on the ambient temperature and amount of catalyst being used.

Table II contains values for the gel time of the Freeman resin, to be used in comparison with those for the Koppers resin in Table I. Notice that at low catalyst concentrations, the Stypol resin exhibits a much slower gel time, while at higher catalyst concentrations the Stypol is much faster. This is due to the confidential amount of 24% cobalt naphthenate promoter in the Stypol resin. The Koppers resin, however, has an overall cobalt concentration much closer to the averages considered in the literature.[3,4] It was also found, when plotting exotherm curves for the Stypol resin, that the Stypol reaches a somewhat lower peak temperature in a shorter time interval.

As for the effect of glass reinforcement on gel time, it was found that the thinner parts tend to cure more slowly, due to a loss of heat to the environment. On the other hand, the presence of glass had little effect on the gel time of the thicker parts, as the thickness caused a large build-up of heat in the part. Thicknesses were measured in terms of the number of layers of $\frac{3}{4}$ oz mat (chopped strand mat, $\frac{3}{4}$ oz per square foot) used.

TABLE II
Comparative Table of Gel Times for Freeman Stypol 40-4074 Resin

	Weight percent MEKP			
Temperature (°F)	0.5%	1.0%	1.5%	2.0%
65	48.683	22.067	15.767	11.333
80	20.733	10.933	8.450	6.017
95	18.617	6.883	4.767	3.883

APPLICATIONS

The curves of Figure 4 could be of great use to manufacturers of FRP products who want to increase production by having a faster mold turnaround. Once the manufacturer has determined the gel time he feels he can safely use, based on the size and thickness of the part required, the temperature, and the time required to fabricate the part, he can determine what catalyst level would be optimum. This can prevent long waits between parts and it can prevent losing parts due to a gel time too short to allow the resin to be used. One must remember, however, that very thin parts or parts with weight ratios of resin to glass of greater than 3 : 1 will produce a gel time 10–20% slower than those shown in Tables I and II. On the other hand, thicker parts tend to gel 5–10% faster due to a build-up of internal heat. These curves, when used to determine the catalyst level required to yield the fastest practical cure rate, can increase the profits of the manufacturer by allowing fabrication of more parts in one day.

The results obtained from comparison of the Freeman Stypol resin indicate that the Stypol would be easier to control in fabrication. One could decide whether to use Koppers or Freeman resin, based on the gel time required, since the Stypol is much slower at low catalyst concentrations and much faster at high catalyst concentrations. Also, the Stypol has a lower peak exotherm temperature than does the Koppers resin and therefore can be used where extreme heat is not desired.

References

1. de Dani, A., *Glass Fibre Reinforced Plastics,* Wiley-Interscience, New York, 1960.
2. Gaylord, M. W., *Reinforced Plastics—Theory and Practice,* Cahners, Boston, 1974.
3. Koppers Polyester Resin 1061-5 and 1061-5F, Koppers Co., Pittsburgh, PA, 1976.
4. Lubin, G., Ed., *Handbook of Fiberglass and Advanced Plastic Composites,* Van Nostrand Reinhold, New York, 1964.
5. Oleesky, S. S., and Mohr, J. G., *Handbook of Reinforced Plastics,* Reinhold, New York, 1964.
6. Walker, F. E., and Ward, D. S., Fiberglass products and Engineering Company, Memphis, TN.
7. Information from Fiberglass Products and Engineering Company, TN, 1983.

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