

Gel Time and Temperature for Two Thermosetting Resins

Steven D. Gordin, Akbar M. Eslami, Howard L. Price

Department of Technology
Elizabeth City State University
Elizabeth City NC 27909

Abstract

The results of an investigation of gel time and temperature of two thermosetting resins have been used to design a laboratory experiment for an undergraduate materials science course. The experiment is part of a larger effort to establish an undergraduate program in polymer composites. The experiment enabled each student to bring about the conversion of liquid resin to the solid state and to experience the attendant heat release.

Introduction

Polymer composite materials often are a combination of small fibers (glass, carbon, aramid) and a thermosetting resin such as unsaturated polyester, epoxy, phenolic, polyimide, polyurethane and others being used for specialty composites. All thermosetting resins must undergo a "cure". Cure is a time-dependent, exothermic, irreversible chemical reaction in which the low molecular weight liquid converts to a high molecular weight, cross linked solid that serves as a matrix for the fibers.

An important change during cure is gelation, when the reaction has proceeded sufficiently so that the resin has achieved a flexible but non-flowing three dimensional molecular structure. Gelation is accompanied by a release of heat resulting in a temperature rise. Gelation marks the end of the "working time" of the resin and fiber. Resin is no longer liquid and attempts to "work" it and the fiber -- shape and smooth them -- are ineffective and may compromise the properties of the composite. Thus, gel time is an important factor in the manufacture of all composites and gel temperature is important for thick or large cross section composites.

As part of an effort to establish an instructional program in polymer composites, an investigation has been made of the gel times and temperature rise of two thermosetting resins. These quantities are especially important in large cross section composites intended to support large external forces. The resins were a vinyl ester and a difunctional epoxy that would be used to make composites as part of the instructional program. The results of the investigation were used to design a laboratory experiment for an undergraduate materials science course. The experiment provided an effective way for each student to experience the conversion of liquid resin to the solid state with the attendant heat release. Both the investigation and the experiment are reported.

Experimental Procedure

The approach taken in this investigation was to track the quasi-adiabatic temperature rise of a known volume of activated resin as a function of time. The resins were activated by adding a measured amount of initiator (for the vinyl ester) or hardener (for the epoxy) to a measured amount of resin. At this time the reaction timer was started. The mixtures were stirred manually for approximately 60 seconds and then decanted into a 30 ml polypropylene cup. The cup was placed into a well in plastic insulating foam and covered with a foam lid. Penetrating the lid was a shielded iron-constantan (Type J) thermocouple that reached into the center of the activated resin. The thermocouple output was tracked with a strip chart recorder. Figure 1 is a schematic of the arrangement.

The surroundings of the activated resin were thermally passive, not active. Thus the resulting resin temperature rise is considered quasi-adiabatic, not truly adiabatic. The resulting temperature-time curves obtained with the strip chart recorder provided the gel time (to the nearest 0.5 minute) and associated temperature (to the nearest 1 C), as well as the time and temperature of the inflection in those curves. A typical time-temperature curve obtained in this investigation is shown in Figure 2. Typically, the temperature rose very slowly as the exothermic reaction proceeded. Upon approaching gel time, however, the temperature rose rapidly to an inflection point and then to a peak that was taken as gel time and temperature. In this condition the resin was a hot, soft, rubbery solid that cured to a hard solid in a matter of hours at room temperature. The gel time and temperature were determined by a point-to-point first derivative of the temperature-time curve, the inflection by the second derivative.

This experimental technique differed from ASTM D 2471 in several respects¹. For example, the components of the reaction were not heated separately in a temperature controlled bath as directed by that standard. The resin systems used in this investigation had been formulated to react in the room temperature range. ASTM D 2471 specifies volumes of 15, 45, 120 or 415 ml, depending on the intended application while a single 30 ml volume was used in this investigation. Moreover, ASTM D 2471 provides for the heated and activated resin to be placed in a metal container that is set on a thermally non-conducting surface at room temperature. Thus the reacting resin experiences some cooling around the sides and over the top surface. In this investigation, the activated resin was surrounded by thermal insulation thereby simulating a somewhat larger volume and providing a conservative estimate of gel time. Gel time of a given resin is longer in small volumes, shorter in large ones; gel temperature is lower in small volumes, higher in large ones.

Two resins were used, a vinyl ester and a difunctional epoxy, both of which undergo chain extension through end linking; that is, the reactive sites are located on the ends of the chains. Both resins are commercially available. The ester was Corez VE 8117 that was activated with methylethylketone (MEK) peroxide as an initiator. The recommended initiator concentration was 1.25%. The epoxy was West System 105 that was activated with West System 206 as an amine hardener. The recommended hardener concentration was 25%. Both resins can react to a hardened state within a few hours at room temperature. Room temperature rather than elevated temperature cure was chosen to emphasize that the temperature associated with gel is a function of the resin, not the surroundings. Both resins have been used in another investigation in our

laboratory to make glass fiber and carbon fiber laminates.

Results and Discussion

The results for both resins are listed in Tables 1 and 2 and shown graphically in Figures 3 and 4.

Table 1 and Figure 3 present the results for the vinyl ester. Figure 3(a) shows how the gel and inflection times decrease with increasing initiator concentration. The greatest decrease took place in roughly the 0-2% range, dropping from over an hour to approximately one-half hour. At concentrations above that range the times continued to decrease but at a much lesser rate. Gel temperature (Figure 3(b)) showed a similar pattern of little change at the higher concentrations, reaching a plateau around 185 C. The inflection temperature pattern was not as clear.

The gel time and temperature behavior reflect the molecular make up of the vinyl ester. As originally made, the resin is much too viscous to be used for composite materials. Consequently, it is diluted with styrene monomer. (It is the styrene monomer that gives polyester resins the characteristic odor that many people associate with “fiberglass” composites².) Fortunately, the styrene monomer enters into the gel and cure reactions and thus is a reactive diluent. As part of the final structure it need not be removed once the reactions have taken place. The function of the MEK peroxide is to break a carbon-carbon double bond on an ester monomer, bonding with one carbon and leaving a highly reactive free radical at the other carbon. Then another ester monomer or styrene monomer can bond at the free radical site. Initially, as initiator concentration increases, the bond breaking-free radical process accelerates leading to rapid chain extension. But longer chains cannot move as easily as the original short chains so the overall process slows. Additionally, the ester-peroxide link does not grow so while more ester monomers are activated more are removed from the chain extension process.

This acceleration-deceleration pattern is reflected in Figure 3 where the gel time decreases and the gel temperature increases sharply for low initiator concentrations. But above ~2% relatively little change is seen. An unseen change, not measured in this investigation, is a reduction of cross link density at higher initiator concentrations. One study³ suggests that cross linking in end linking resins such as those used here may not be as dense as has been thought. As cross linking is advantageous for most composites applications, an upper limit on initiator concentration should be determined for any polyester resin to be used for composites.

Table 2 and Figure 4 present the results for the epoxy resin. Figure 4(a) shows gel times starting around one half those of the vinyl ester. The times decreased with increasing hardener concentration as expected but exceeded 20 minutes even at the highest concentration. Gel temperature rose sharply (Figure 4(b)) and showed no sign of reaching a plateau. These results differ from those of the vinyl ester because the epoxy has a different reaction path. The epoxy has no reactive diluent and each chain end is an epoxide group represented as a triangle with carbon atoms at two apexes and an oxygen atom at the third apex. These chains are very stable and have an indefinitely long shelf life. Any of the numerous hardeners will have end groups that will react with the epoxide groups to bring about chain extension and cross linking. An initiator is not needed. Consequently the two are kept separate until a reaction is needed. For example, epoxy adhesives sold in home centers often have two tubes marked “A” and “B,” one containing

the epoxy, the other the hardener. The gel time decreased and the gel temperature increased as hardener concentration approached the stoichiometric concentration of 25%. Exceeding that concentration would mean that hardener was in excess as the epoxy was at hardener concentrations below the ratio. Consequently, the time would be expected to increase, the temperature to decrease. In broad terms, the vinyl ester has all the molecules needed to gel and form a polymer but the epoxy must have significant molecular structure added in order to gel and polymerize.

Application to Undergraduate Laboratory

The procedure of this investigation was used as a laboratory experiment in a sophomore materials science course. Information provided in class prior to the experiment focused on aspects that the students could easily experience and is summarized below.

The thermosetting resins used in this experiment begin as viscous liquids at room temperature. In this state the resins are small, short molecular chains of one or just a few repeat units of the molecular structure. These short chains are monomers (for one repeat unit) or oligomers (for a few units). In order to form a solid matrix for composite materials the monomers/oligomers must react with each other to form long molecular chains. In addition, the chains of thermosetting resins react from one chain to another forming cross links so that the resin becomes one massive, three dimensional molecule. In this state the solid polymer has greater mechanical stiffness and resistance to solvents than it would have otherwise. These reactions are exothermic and, generally, irreversible. Thus, unlike a thermoplastic, a reacted thermosetting resin will not soften and flow on subsequent heating.

Because the reactions are exothermic, tracking temperature changes as a function of time (Figure 2) is a long-used method of following organic reactions. These temperature changes reflect the motions and bonding of the oligomers in starting the three dimensional, cross linked structure. The structure building process generally is as follows. Due to the initiator or hardener a few of the oligomers react with each other with each reaction releasing a small quantity of heat. As the resin is a thermal insulator the heat is largely contained creating an adiabatic condition. The contained heat results in a small but continuing temperature rise. Typically, reactions of this type are very temperature sensitive with the rate rising exponentially with temperature. Thus begins an upward spiral with the reaction releasing heat that raises the temperature which leads to an increase in the rate of reaction that releases heat and so on. This upward spiral continues until the temperature rise accelerates rapidly upward finally reaching a peak value.

Each student, with guidance from the instructor, repeated the temperature tracking experiment for the vinyl ester using an initiator concentration in the 4-5% range. This range was used to obtain gel in less than half an hour and keep each exercise to one hour. The experiment began with the student donning a laboratory apron, safety goggles and rubber gloves. The student decanted some 50-60 grams of liquid resin into a 250 ml plastic mixing cup and determined the weight to the nearest 0.0001 gram. The next step was calculating the weight of 4.5% initiator and attempting to obtain that weight in a 30 ml cup. The exact amount was difficult to achieve so the student had to calculate the actual percentage (which had to be between 4 and 5%). The initiator was combined with the resin, the reaction timer was started and the student manually mixed the

two for 1-2 minutes. Then the student decanted the mixture into a 30 ml cup, placed the cup in the insulating foam, set the foam lid and shielded thermocouple into place and started a strip chart recorder to track the thermocouple output.

For the next 20 minutes the temperature rose very slowly, providing time for the instructor to emphasize important points of the classroom lecture. Once it began to rise the temperature excursion reached a peak in 2-3 minutes, tracking across most of the strip chart in the process. The cover and specimen was quickly removed and the thermocouple extracted to prevent its being molded into the specimen. Handling, gingerly in most cases, the hot, gelled resin at the end of the experiment emphasized for the student the exothermic nature of the reaction. The final step was to read the milliVolt output of the thermocouple and, using a conversion table, find the peak temperature (~180 C). The procedure for finding temperature constituted a final examination question.

The value of this experiment is that the student converted liquid resin into a solid without the application of external heat. The student made all the measurements and calculations and brought about a change that s/he could see. Subsequent experiments have involved making laminates with Style 181 glass fabric. Each student made a 15-ply, 100 mm square laminate from which a sample was cut for density determination and burn-out to obtain resin-fabric ratio. In another experiment, one team of students made a 50x500 mm laminate with the longitudinal direction of the fabric in the long (500 mm) direction of the laminate. The other team made a laminate with the longitudinal direction in the short (50 mm) direction. The two laminates were loaded in the cantilever configuration to show the effect of fabric direction on deflection under constant load. Experiments will become more advanced as we better learn what is possible and most effective.

Summary

Measurements have been made of the gel time and temperature of two thermosetting resins, a vinyl ester and a difunctional epoxy. Gel time is especially important as it determines how long the resin can be worked in making polymer composites. Measurements were made by tracking the quasi-adiabatic temperature rise of the resins as the exothermic reactions changed the resins from a workable liquid to a stable but unworkable gel. For the vinyl ester activated by MEK peroxide at reasonable concentrations at least one-half hour working time was available with a gel temperature of ~170 C. For the epoxy resin activated with stoichiometric concentration of amine hardener at least 20 minutes of working time was available with a gel temperature of ~200 C. The procedure of this investigation has been used as a laboratory experiment for a materials science course. The experiment is one in which the student, under the guidance of the instructor, makes all the measurements and calculations. As a result, the student brings about the conversion of liquid resin to a solid without the application of external heat.

Acknowledgment

Lee Vickery, a student in the Department of Technology, digitized the temperature-time curves and performed the point-to-point differentiation. The authors thank him for his help.

Bibliographic Information

1. Anon., Standard Test Method for Gel Time and Peak Exothermic Temperature of Reacting Thermosetting Resins, Amer Soc Test Materials D 2471.
2. Strong, A. Brent: Fundamentals of Polymer Resins for Composites Manufacturing, Composites Fabricators Association 1995.
3. Hinckley, Jeffrey A. and Young, Jennifer A.: Monte Carlo Simulation of Endlinking Oligomers. NASA TM-1998-207649, Apr 1998.

Biographical Information

STEVEN D. GORDIN is a student in the Department of Technology and a 2002 McNair Scholar. He helped develop the experimental technique used in this this investigation. He is a student member of the National Association of Industrial Technology (NAIT). He expects to graduate with a BS degree in 2005.

AKBAR M. ESLAMI, PhD is Associate Professor and has been Chair of the Department since 2000. He has specialized in finite element analysis and automation. He is a member of ASEE, ASME and NAIT. He served as a 2002 mentor to the first author. His address is aeslami@mail.ecsu.edu.

HOWARD L. PRICE, PE, PhD is Visiting Associate Professor in the Department. He specializes in the processing and properties of polymer composites and has helped establish a polymer composites program in the Department. He is a member of ASME and was a 2002 mentor to the first author. He is the author to whom inquiries on this paper should be sent. His address is hlprice@mindspring.com.

Table 1. - Characteristic Times and Temperatures as a Function of MEK Peroxide Initiator Concentration for a Vinyl Ester Resin

MEK PEROXIDE INITIATOR, percent	INFLECTION TIME, min	INFLECTION TEMPERATURE, C	GEL TIME, min	GEL TEMPERATURE, C
0.87	79.0	141	82.5	158
1.32	51.0	130	56.0	172
2.26	24.0	156	26.0	171
3.23	18.5	148	21.0	184
4.30	14.0	165	15.5	185
5.62	11.0	152	12.0	183

Table 2. - Characteristic Times and Temperatures as a Function of Amine Hardener Concentration for an Epoxy Resin

AMINE HARDENER, percent	INFLECTION TIME, min	INFLECTION TEMPERATURE, C	GEL TIME, min	GEL TEMPERATURE, C
11.7	30.5	114	34.0	124
16.1	25.0	123	28.5	161
19.6	21.5	146	23.5	174
24.5	20.5	176	22.0	203

Figure 1. - Plastic cup containing activated resin with thermocouple in the center surrounded by insulating foam.

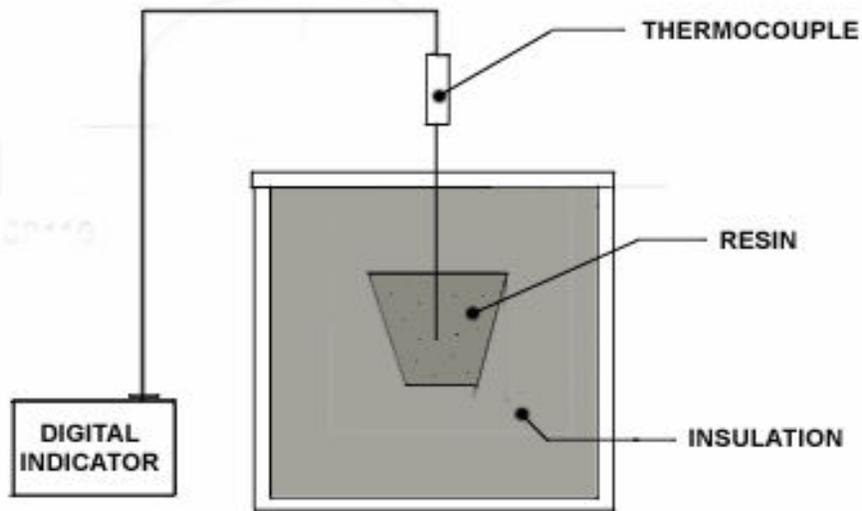


Figure 2. - Representative quasi-adiabatic temperature history of a reacting thermosetting resin showing the rapid temperature excursion that provides a measure of the gel time and temperature and the preceding inflection point.

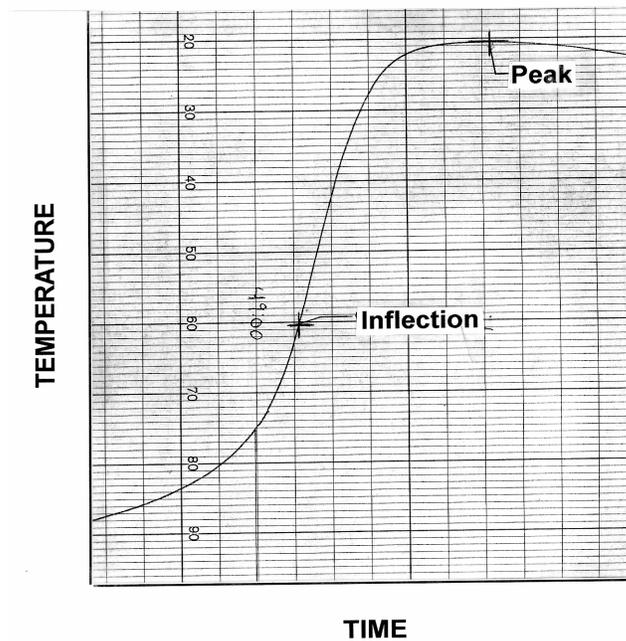


Figure 3. - Gel time and temperature as a function of MEK peroxide concentration for Corez VE 8117 vinyl ester resin (○ Inflection, □ Gel).

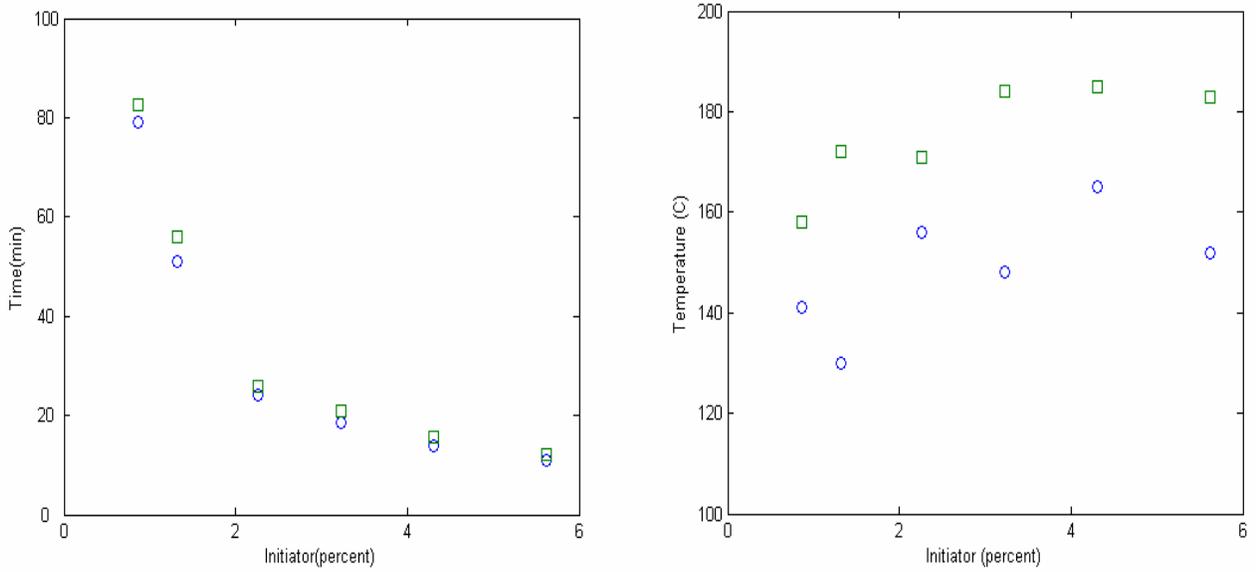


Figure 4. - Gel time and temperature as a function of West System 206 amine hardener for West System 105 epoxy resin (○ Inflection, □ Gel).

