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Analysis of the resin transfer molding process using in-mold dielectric sensors

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Abstract

Interest in the potential use of resin matrix composites for structural automotive components has grown dramatically in the last five years. This has been evidenced by the formation of an Automotive Composites Consortium with the General Motors and Chrysler Corporations and the Ford Motor Company to investigate these materials. Efforts are under way within these member companies to study material properties, processing procedures, and energy management phenomena in order to allow the design of viable structural vehicle components, e.g. crossmembers, bumper beams, and front-end rails, utilizing resin transfer molding (RTM). While progress is being made in all these areas of investigation, it is extremely important that processing feasibility be adequately understood and demonstrated. It is particularly necessary to understand and control the curing process in the mold in order to project acceptable cycle times. In this investigation, a temperature, pressure, and cure (dielectric) sensor was mounted in the surface of an RTM mold. The cure behavior, mainly time to viscosity minimum and vitrification (determined from the dielectric data), was monitored as a function of various process parameters. These included mold temperature, resin pressure, resin chemistry, part thickness, and reinforcing fiber fraction. Results of cure sensitivity to the various controlled parameters and experiments with controlled press opening will be presented. Dielectric sensor output was shown to be an excellent indicator for controlling press opening based on the vitrification event.

INTRODUCTION

Resin transfer molding (RTM) offers a potential cost-effective means for producing strong, lightweight automotive composite parts. Interest in the use of resin matrix composites for structural automotive components, in particular, has grown dramatically in the last five years. As a result, the need to accelerate a research effort to investigate these materials and expand the knowledge base in this area has precipitated the formation of an Automotive Composites Consortium. Participating in the consortium are

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the Ford Motor Company and the General Motors and Chrysler Corporations. Efforts are under way within these member companies to study material properties, processing procedures, and energy management phenomena in order to allow the design of viable structural vehicle components, e.g. crossmembers, bumper beams, and front-end rails, utilizing RTM. While progress is being made in all these areas of investigation, it is important that processing feasibility be adequately understood and demonstrated. It is particularly necessary to understand and control the curing process in the mold in order to project acceptable cycle times for component production. However, relatively little is known about the reaction occurring within the mold and how that reaction can vary from run to run. Before RTM can be used in an automotive production line, the curing process must be well characterized so that minimum cure time can be used while still maintaining component integrity.

In this investigation, we have examined use of a commercially available mold-monitoring system to characterize a vinyl-ester RTM process. During this study, sensors for cure state (dielectric), pressure, and temperature were mounted flush in the molding surface. All three properties were monitored during the systematic variation of mold temperature, catalyst level, resin pump pressure, thickness, and composite composition. Statistically designed experiments were run in random order to supply information on the significant effects of these variables on the results or responses of the process. It was the goal of this experiment to determine the main effects of the five variables, as well as the two-factor and three-factor interactions of these variables, on the yields or responses of the experiment.

BACKGROUND

The dielectric technique has been increasingly finding its way into polymer processing environments during the past decade. The traditional parallel plate technique has been largely replaced with disposable single-surface comb electrodes (on flexible substrates) making it easily implemented into standard mold or tool resin processing applications. Most recently dielectric sensors are being used which are fabricated in high reliability ceramic with electrodes buried in the ceramic [1]. With this type of design, dielectric sensors can now be tool mounted and used repeatedly. In the work described here, a sensor was used with a 2.5 cm^2 sensing area which also included a temperature sensor. Smaller reusable ceramic sensors are currently being produced which are less obtrusive in the mold; however, these were not used in this investigation.

The dielectric technique measures the permittivity (dielectric constant) and loss factor of the polymeric system during reaction. The ionic resistivity is extracted from the loss factor values as shown in eqn. (1). Note that there is a very close relationship between the ionic resistivity and viscosity of the

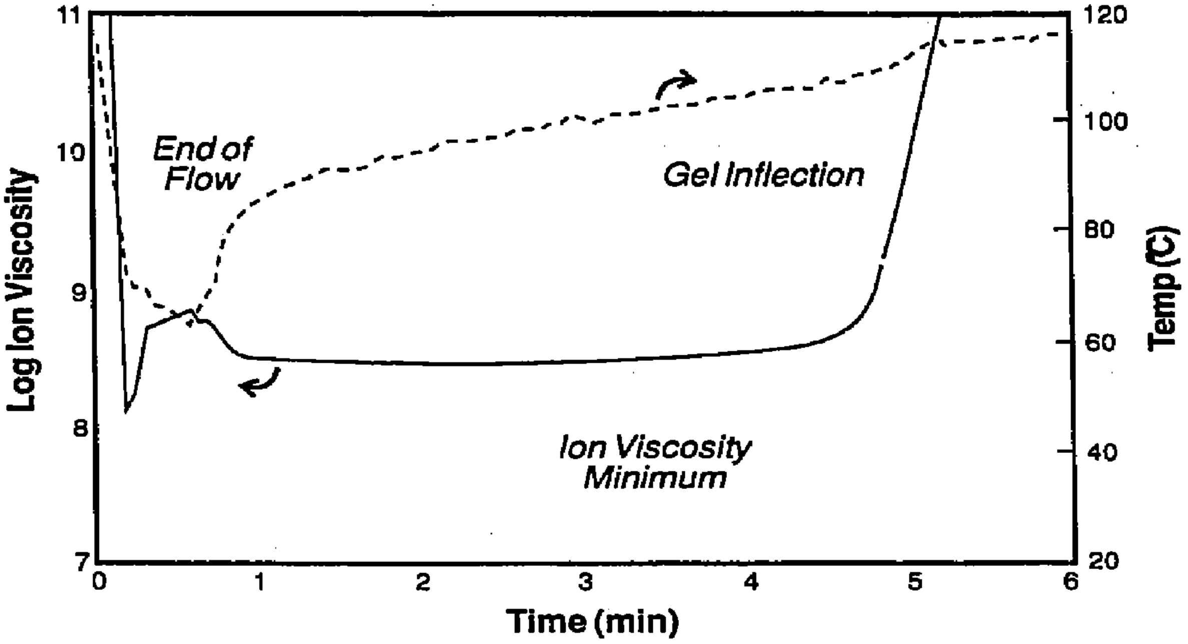

Fig. 1. Typical ion viscosity and temperature curve during vinyl-ester molding: solid line, IV; broken line, temperature (see corresponding pressure curve in Fig. 5).

material [2, 3] and thus the term ion viscosity (IV) is used

$$\text{Ionic resistivity} = \text{ion viscosity (IV)} = \frac{1}{\varepsilon'' e_0 \omega} \qquad (1)$$

where ε'' is the loss factor, e_0 the permittivity of free space (constant $= 8.85 \times 10^{-14}$ Farad cm^{-1}, and ω the angular frequency, is 2π(frequency). Equation (1) is only valid as long as the ionic contributions to the loss factor exceed that of the dipoles in the material. In order to ensure this condition, a low frequency (10 Hz) was applied during the course of this study.

During thermoset molding applications, a viscosity minimum (or ion viscosity minimum) for the resin is usually observed, owing to the initial heating of the resin which is then followed by reaction. In many systems, a reaction inhibitor is included, which results in the observation of a very broad viscosity minimum during the course of inhibitor consumption. Once the inhibitor is depleted, the viscosity is usually observed to increase rapidly. As the reaction starts to slow, the increasing viscosity begins to level out causing an inflection point. This general process was also observed for this RTM investigation (Fig. 1).

EXPERIMENTAL

The composite samples were prepared by placing the glass-mat reinforcing material in a 45.72 cm × 45.72 cm (18 inch × 18 inch) picture frame assembly. Frames of different thickness were utilized in order to produce

TABLE 1
Experimental conditions

	Minimum	Maximum
Mold temperature (°C)	77 (170°F)	140 (220°F)
Catalyst level (wt.%)	0.5	1.5
Resin pump pressure (kPa)	275.8 (40 psi)	551.6 (80 psi)
Plaque thickness (mm)	1.6 (0.0625 inch)	6.4 (0.252 inch)
Composition (wt.% glass)	24	48

plaques of 1.6 and 6.4 mm thickness. This assembly was gasketed securely and aligned precisely in a tool that had been pre-heated to the desired mold temperature. Vent and fill lines were connected to the tool which was then closed on the frame and clamped at 1200 psi during the molding operation. The pre-form was allowed to remain at temperature for 5 min minimum, prior to resin injection, to achieve thermal equilibrium. Dow 411-C-50 vinyl ester resin [1] catalyzed with USP 245 catalyst [2] (2,5-dimethyl-2,5-bis(2-ethyl hexoyl peroxy) hexane, was then introduced into the mold at a predetermined pump pressure until resin flowed from the vent lines. The vent lines were then clamped at a pre-selected injection pressure. The conditions, determined from experimental design, are summarized in Table 1.

A Micromet Instruments ICAM-1000 [3] mold-monitoring system was used to collect cure data (ion viscosity), pressure data, and temperature data from within the mold [1, 4]. To mount the sensors, a 2.5 inch hole was drilled in the bottom center of the mold so that the ceramic sensor could be inserted from the back of the mold and be flush with the surface (Fig. 2). The active dielectric sensing area of the sensor is 6.25 cm^2. The dielectric sensor, which also housed a thermocouple flush with the sensor surface, is 2.5 cm thick and was held in place using an adjustable steel strap. The pressure sensor was threaded and mounted in a drilled threaded hole in the center of the top mold half, directly above the dielectric sensor. The flush-mounted re-usable sensors were ideal for this study and elminated the need for disposable sensors which must be replaced after each run. Composite plaques did not bond to the sensor during de-molding and were thus removed with ease.

The resin was injected into the mold from an inlet tube in the center of the bottom platen (next to the dielectric sensor). A Graco model 962-008 pump was used to introduce the resin. Injection was terminated when resin

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[1] A trademark of Dow Chemical Company, Midland, MI, USA.

[2] A trademark of US Peroxygen Witco Chemical Corp., Richmond, CA, USA.

[3] A trademark of Micromet Instruments, Inc., Newton, MA, USA.

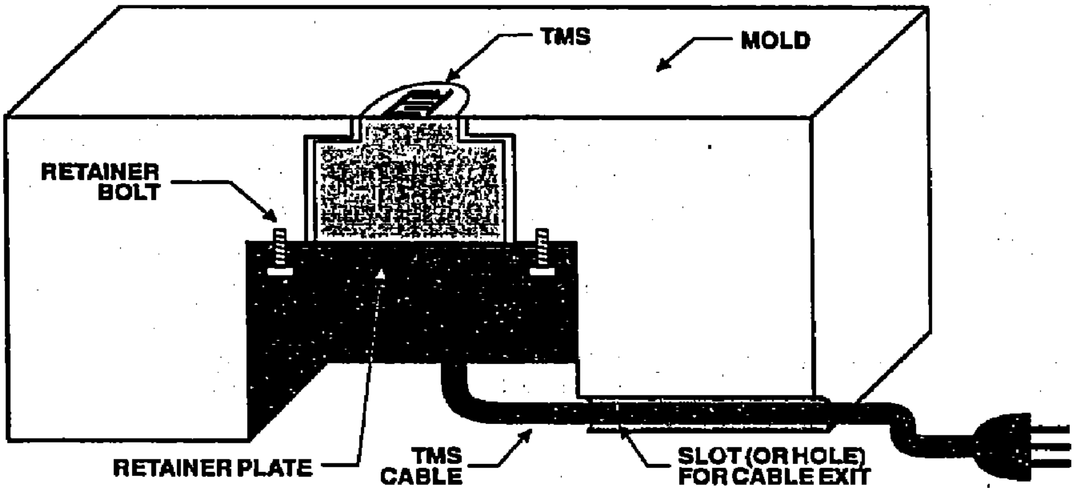

Fig. 2. Cross sectional schematic diagram of mounting method for the dielectric tool mount sensor (TMS).

was observed to exit from the vents around the edge of the mold. The temperature was controlled to ±3°C of the setpoint utilizing a Sterlco (F6026) oil heater[4].

The dielectric data were monitored at 10 Hz which was found to be optimum for the resin system utilized. In preliminary experiments, lower and higher frequencies were investigated. Data were recorded at regular intervals ranging from 2 to 5 s for a total experimental length ranging from 15 to 40 min. Micromet software routines were utilized to determine automatically the ion viscosity minima and ion viscosity gel-inflection points (near gelation).

The material and processing variables, at two levels each, were investigated in a statistically designed experiment. The purpose of the experiment was to determine the effects of these variables on two experimental responses. The two responses measured were viscosity minimum (s) and gel inflection (s). The design was a 2^5 factorial experiment with two replicates of each experimental point, which required 64 runs. This design provided the determination of all effects and effect interactions without confounding, and permitted a firm estimate of the standard error of the experiment. Several software packages were used to analyze the data statistically [5, 6].

RESULTS AND DISCUSSION

A typical cure curve for ion viscosity and temperature is shown in Fig. 1. Note that a large decrease in ion viscosity (IV) is observed as the resin first contacts the sensor. Because the cooler resin is still flowing in for the first

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[4] A trademark of Sterlco Inc., Milwaukee, WI, USA.

40 seconds, the temperature of the mold surface temperature detector decreases, causing an increase in IV. As flow stops at about 40 seconds, the temperature starts to rise back to near the setpoint. At the same time the ion viscosity again decreases further due to the temperature increase. After this point there is a long broad viscosity minimum caused by inhibitor consumption. As the inhibitor is consumed the reaction increases rapidly and is easily detected by the rapid rise in ion viscosity. Note that a small increase in temperature is detected at the mold surface during the rapid reaction. It was noted that data typically showed good reproducibility until the IV passed above a value of 10.5. Beyond this point the IV was sometimes observed to level out though in other cases it was observed to go off-scale. It is currently believed that this is due to rapid gelation, followed by vitrification of the material which may be accompanied by loss of contact between the sensor and the resin.

In carrrying out the statistical analysis, the standard error of the effect was calculated and then the *t*-ratio was obtained. The data generated for the effects and pertinent interactions are shown in Table 2: a *t*-ratio greater than 2.1 (or less than −2.1) is generally considered to be statistically significant. In other words, the larger the *t*-ratio, the larger the significance of that particular variable.

Utilizing statistical analysis, it was found that temperature and catalyst concentration have the largest influence on times to both the viscosity minimum (*t*-ratio −14.3 and −7.7 respectively) and the gel inflection (*t*-ratio −16.5 and −6.7 respectively). These effects are shown in the curves (Figs. 3 and 4) obtained from experimental dielectric data. The effect of temperature variation may be seen in Fig. 3. The process variables of catalyst concentration, pump pressure, and plaque composition were held constant at 1.5 wt%, 551.6 kPa (80 psi), and 48 wt.% respectively. At a temperature of 140°C (220°F), the times to viscosity minimum and gel inflection were 0.37 and 2.47 min respectively. At a lower mold temperature of 77°C (170°F), the respective values were considerably longer at 3.42 and 9.92 min. Curves for data taken at catalyst levels of 1.5 and 0.5 wt.% are shown in Fig. 4. The mold temperature, pump pressure, and plaque composition were held constant at 140°C (220°F), 551.6 kPa (80 psi), and 48 wt.%. Resulting times to viscosity minimum and gel inflection were 1.03 and 3.73 min, respectively, at the 1.5 wt.% catalyst level. When the catalyst concentration was 0.5 wt.%, the respective values were 2.37 and 4.97 min. It is apparent from this data that optimization of catalyst and temperature processing variables can have a profound effect on part turnaround time. It was also observed that when the upper limit values for mold temperature and catalyst concentration were utilized, panels of extremely good appearance were produced.

Intuitively, it might be expected that higher pump pressures would result in faster fill times and, therefore, less cooling of the mold in the vicinity of

TABLE 2

Effects and *t*-ratios of controlled variables on time to viscosity minimum and gel inflection

Variable	Viscosity min		Gel inflection	
	Effect[a] (s)	*t*-Ratio	Effect[a] (s)	*t*-Ratio
Catalyst Conc. *C*	−108.3	−7.7	−237.1	−6.7
Thickness *T*	37.2	2.6	74.8	2.1
Composition *tc*	−2.3	−0.2	−11.0	−0.3
Temperature *t*	−201.9	−14.3	−582.4	−16.5
Pressure *p*	−46.8	−3.3	−28.1	−0.8
CT	−0.2	0.0	−1.5	0.0
Cc	7.3	0.5	50.0	1.4
Ct	33.7	2.4	156.1	4.4
Cp	−15.8	−1.1	−10.7	−0.3
Tc	10.7	0.8	3.6	0.1
Tt	−41.1	−2.9	18.7	0.5
Tp	−13.9	−1.0	−50.0	−1.4
ct	26.5	1.9	40.7	1.2
cp	5.0	0.4	32.4	0.9
tp	−5.5	−0.4	−19.7	−0.6
CTc	−3.0	−0.2	−5.3	−0.1
CTt	0.6	0.0	3.3	0.1
CTp	17.3	1.2	22.7	0.6
Cct	−2.5	−0.2	−37.5	−1.1
Ccp	−0.9	−0.1	−29.0	−0.8
Ctp	9.2	0.6	−4.3	−0.1
Tct	−13.1	−0.9	−7.1	−0.2
Tcp	−8.2	−0.6	−26.7	−0.8
Ttp	2.0	0.1	29.5	0.8
ctp	−10.4	−0.7	−24.2	−0.7
CTct	−3.2	−0.2	14.5	0.4
CTcp	0.3	0.0	42.1	1.2
CTtp	−2.9	−0.2	−14.5	−0.4
Cctp	−9.7	−0.7	5.5	0.2
Tctp	10.3	0.7	42.2	1.2
CTctp	12.1	0.9	−16.3	−0.5
Average time (s)	(220.9)		(515.6)	
Standard error (s)	(14.1)		(35.4)	

[a] Note that effects are in seconds relative to the average times listed at the bottom.

the inlet port. Though it is expected that this influence would be small, less resin cooling would result in slightly faster reaction times. The statistical results show that though pressure had a significant influence on time to viscosity minimum (*t*-ratio −3.3), it had insignificant influence on gel inflection time (*t*-ratio −0.3). A typical pressure curve is shown in Fig. 5. Pressure data were useful in marking the point at which the mold was filled.

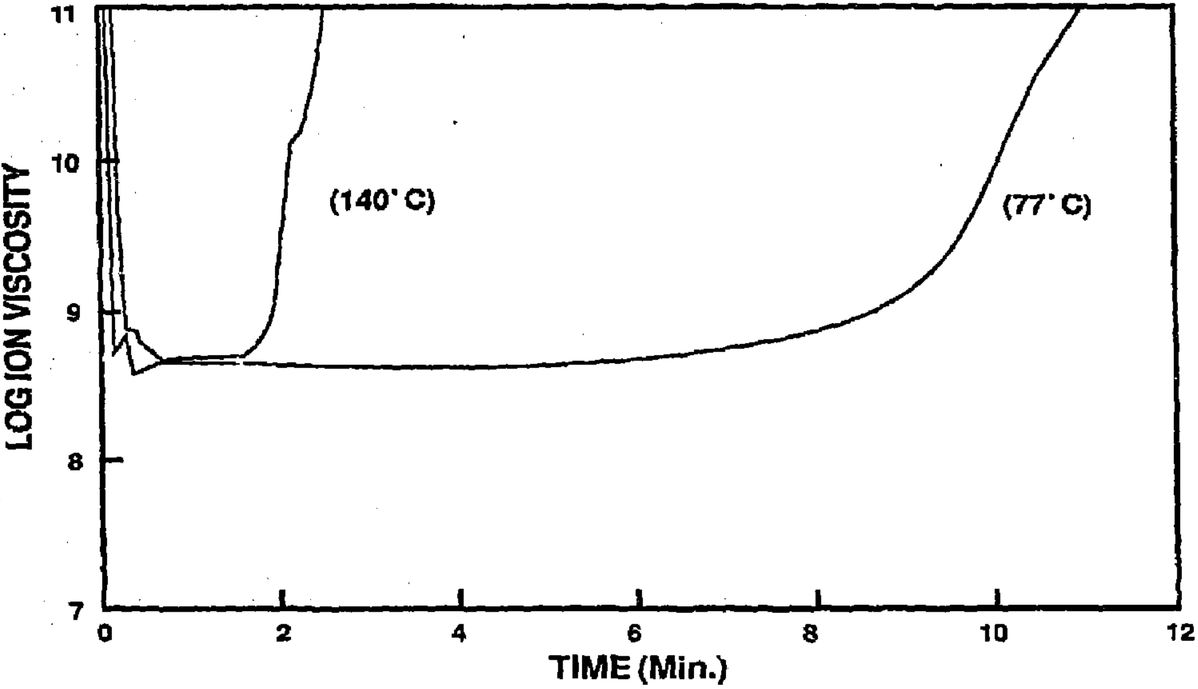

Fig. 3. Comparison of ion viscosity curves for mold temperatures of 77°C and 140°C: catalyst, 1.5 wt.%; pressure, 551.6 kPa; fiber, 48 wt.%; thickness, 6.4 mm.

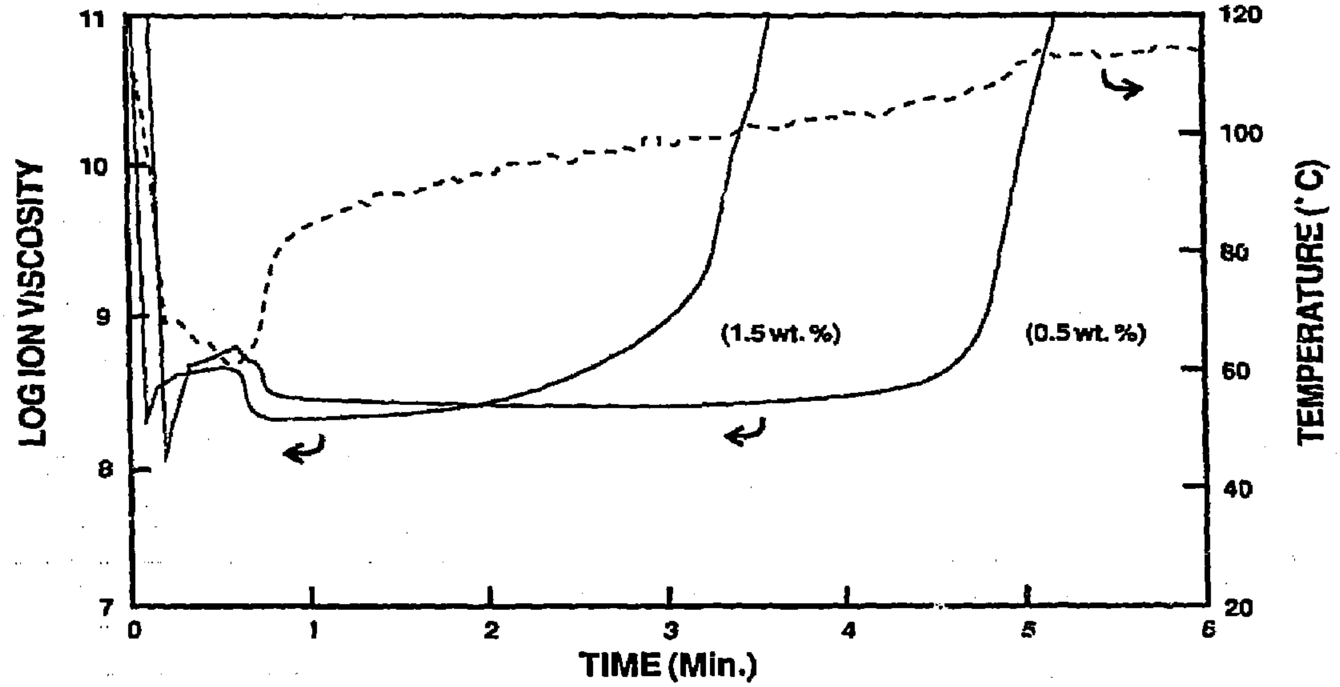

Fig. 4. Comparison of ion viscosity curves for catalyst levels of 0.5 and 1.5 wt%. Temperature curve corresponds to 0.5 wt.% plaque: temperature, 140°C; pressure, 551.6 kPa; fiber, 48 wt.%, thickness, 6.4 mm. Solid line, IV; broken line, temperature.

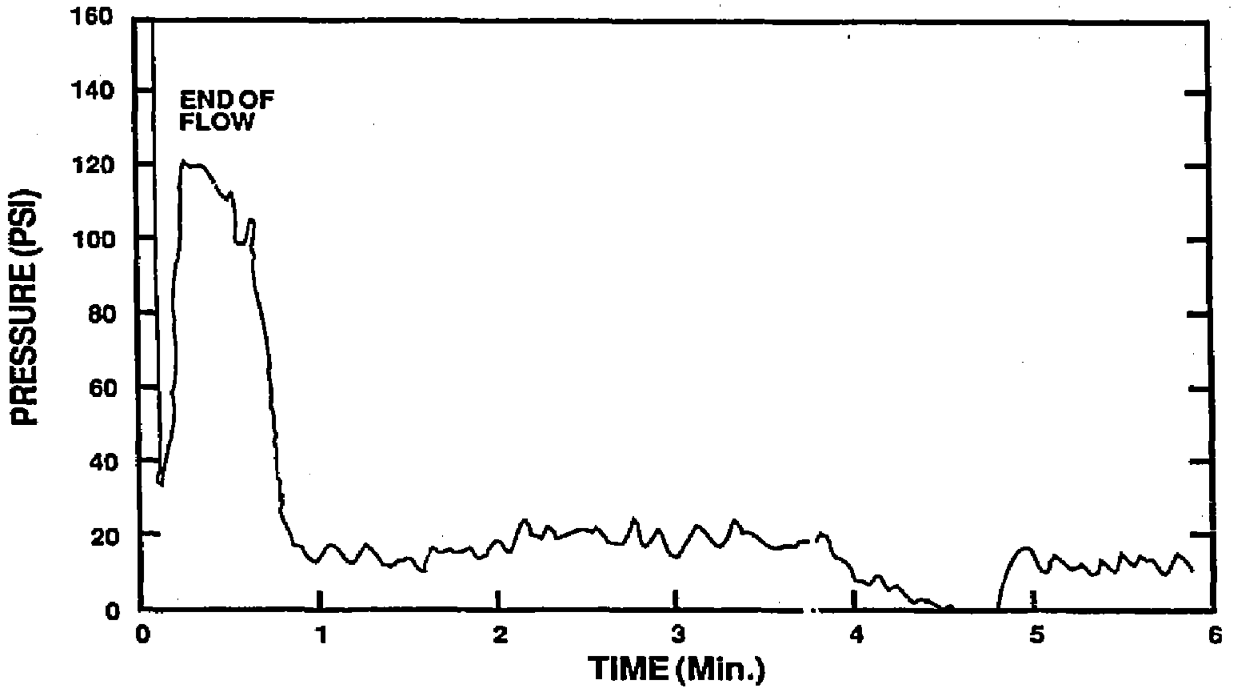

Fig. 5. Typical pressure curve during vinyl-ester RTM molding (see corresponding ion viscosity and temperature curve in Fig. 2).

As may be seen from the curve, the pressure is high during filling but then falls off as the external vent lines and then the injection line were clamped off.

Panel thickness had a significant influence on both time to viscosity minimum and time to gel inflection (t-ratio 2.6 and 2.1 respectively). The sign of the thickness t-ratio is in agreement with what is intuitively expected. As part thickness is increased, more thermal energy is required from the mold (and thus more time) for the reaction to be activated. This phenomena may be seen in Fig. 6.

Panel composition was found to have no significant effect on the time to viscosity minimum (t-ratio −0.2) and time to gel inflection (t-ratio −0.3).

It should be noted that there are significant two-factor effects on time to viscosity minimum (thickness/temperature, t-ratio 2.90) and on time to gel inflection (concentration/temperature, t-ratio 4.4). The two-factor concentration/temperature effect on time to gel inflection is shown graphically in Fig. 7. The non-parallel lines indicate the existence of a concentration–temperature two-factor interaction.

The statistical analysis, assuming linear dependences, revealed the parameter sensitivities for the measured resulting ion viscosity minimum and gel inflection point that are listed in Table 3. From this table, it can be observed that an increase in temperature of one degree would reduce the time to gelation by 17 s.

It is also important to note the size of the standard error, which was 14.1 s

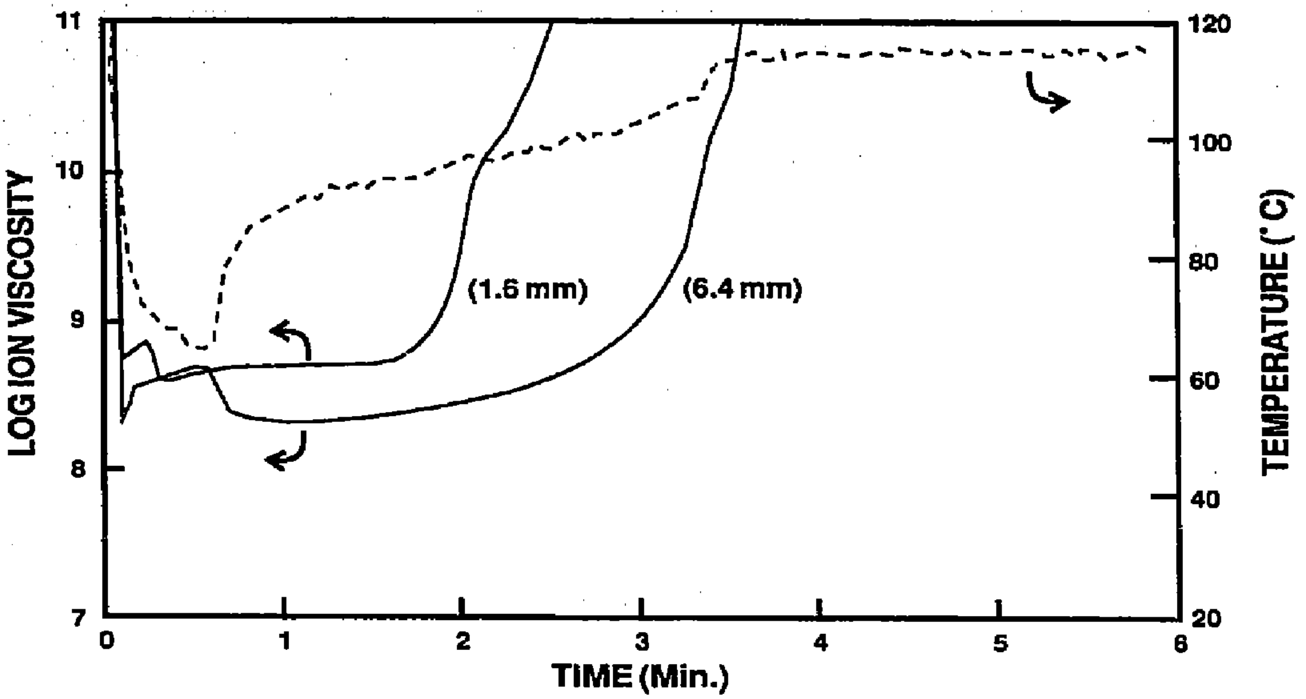

Fig. 6. Comparison of ion viscosity curves for thicknesses of 1.6 and 6.4 mm. Temperature curve corresponds to 6.4 mm plaque: catalyst, 1.5 wt.%; temperature, 140°C; pressure, 551.6 kPa; fiber, 48 wt.%. Solid line, IV; broken line, temperature.

for the time to viscosity minimum and 35.4 s for the time to gel inflection. This can be thought of as the variability due to other parameters (such as resin aging or humidity) not investigated in this study. This variability represents approximately 10% of the overall processing time suggesting that controlled mold opening using these mold monitoring techniques could translate into significant time/cost savings and more consistent part properties.

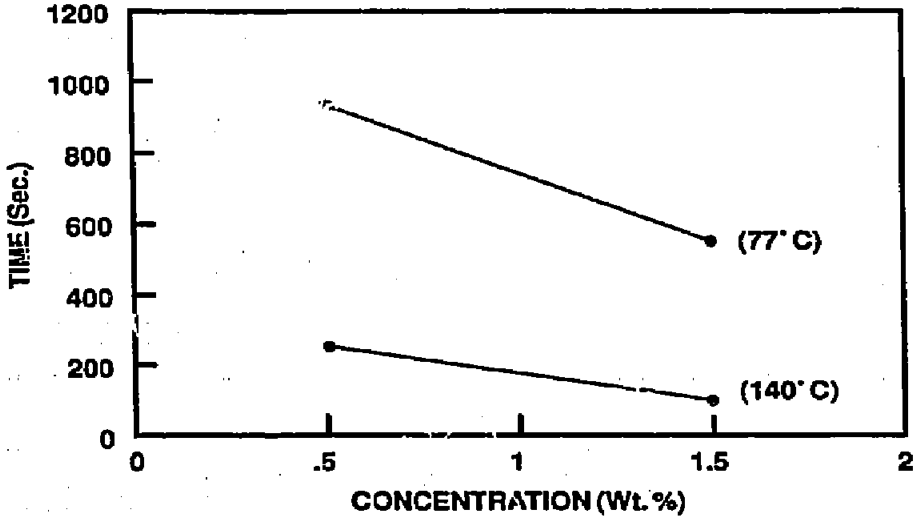

Fig. 7. Example of the statistically significant two-factor effect (non-parallel lines) of temperature and concentration.

TABLE 3

Effect sensitivities to variables[a]

Variable	Viscosity min.	Gel inflection	Units
Catalyst	−108	−237	$s\,(wt.\%)^{-1}$
Temperature	−6	−17	$s\,(°C)^{-1}$
Pressure	−1.2	−0.7	$s\,(psi)^{-1}$
Thickness	7.4	15	$s\,mm^{-1}$
Fiber volume	–	−0.5	$s\,(wt.\%)^{-1}$

[a] A negative sign indicates an inverse relation.

Controlled mold opening was investigated by opening the mold based on real time gel-inflection information. A series of plaques were fabricated opening the mold after the gel-inflection point with delay times of 0, 30, 60 and 90 s. The parts de-molded at 0 and 30 s were still flexible and stuck to the mold when the press was opened. The parts de-molded at 60 and 90 s after the gel inflection were rigid and easily removed. The results suggest that gel inflection time plus 60 s could be used for controlled mold opening for this particular part and resin system. The glass transition temperatures for all parts were measured by thermomechanical analysis (TMA) and found to be 99°C (±2°C) indicating cure continued in the parts after de-mold.

CONCLUSIONS

Significant influences were observed for catalyst, temperature, and thickness while resin pressure, and composition (fiber fraction) influences were minor. Increases in catalyst or temperature were shown to decrease reaction time. Increases in thickness increased the reaction time. This is due to the increase of heat required from the mold needed to bring the thicker parts to reaction temperature. In this system the catalyst levels proved to have a profound influence on reaction time. It is concluded from Table 3 that an error during weighing of catalyst in the order of 1000 ppm would influence the time to gel inflection by 24 s, a significant portion of the overall molding time. Similarly, a mold temperature deviation of 2°C would influence the time to gel inflection by 34 s.

Aside from the controlled variable influences, the statistical analysis shows that the process has variability in gel inflection time of about 10%. Controlled mold opening experiments using the gel inflection time plus 60 s produced rigid parts that were easily de-molded. This technique has potential for minimization of molding time through automated production cure control.

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