

Curing of Highly Reactive Polyester Resin under Pressure: Kinetic Studies by Differential Scanning Calorimetry

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Synopsis

The curing characteristics of polyester under pressure affect the processing and molded properties of reinforced polyester molding compounds. In this paper, the kinetics of curing of polyester under pressure were investigated with differential scanning calorimetry (DSC). Based on the results thus obtained, the author discusses the effects of reactive diluent, pressure, low-profile agent, filler, and thickening on the curing of polyester.

INTRODUCTION

Recently, low-profile sheet and bulk molding compounds (SMC and BMC) have captured many applications in automotive and appliance components. Thus, the processing of SMC and BMC has become a significant part of plastics processing in these industries. Like processing of other plastics, the processing of SMC and BMC involves heat treatment under pressure. Their processing characteristics depend upon the thermal and rheological properties of the molding compound in a given mold. Of these two parameters, the thermal behavior of thermoset resins during processing is complicated by the highly exothermic nature of the reaction.

The curing of no-shrink polyester—so-called low-profile resins—is highly exothermic because the unsaturated polyester in the low-profile resin has a much higher concentration of reactive double bonds than conventional polyesters. In addition, the curing characteristics of low-profile polyester resin could be affected by the following factors in the SMC formulation and its processing: (1) a high concentration of reactive diluent in polyester,¹ (2) application of relatively high pressure during molding, (3) the presence of a thermoplastic as a low-profile agent, (4) the presence of a large amount of filler and fiber, and (5) thickening—viscosity build-up before molding.

Effective fabrication of these molding compounds requires basic information on the kinetics of curing under pressure in addition to the rheological properties of the molding compounds during molding. In particular, to attain the minimum cycle time in molding and the maximum mechanical properties of molded composites, in-depth knowledge of the curing characteristics is indispensable, and that is the purpose of this work.

Differential scanning calorimetry (DSC) provides a very useful technique to follow and analyze the kinetics of exothermic or endothermic reactions.²⁻⁵

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The heat generated or absorbed in the course of the reaction can be measured directly with DSC, and the rate of heat generation or absorption with respect to time or temperature can be obtained from the DSC curve. It is assumed here that exothermic heat of curing of polyester comes from the following reactions: (1) the propagation reaction in free-radical crosslinking of a reactive diluent with a reactive double bond of the unsaturated polyester; (2) The decomposition reaction of the peroxide initiator, the heat of which can be negligible to the heat from (1). It is also assumed that the crosslinking reaction results in very short chain lengths, because the styrene radical has a high propensity to react with unsaturated acid in the polyester. Given these assumptions, it is possible to follow the degree of curing with respect to time or temperature and to determine the final degree curing as well.

In this study, the high-pressure DSC was applied to the curing of highly reactive polyester. The data thus obtained will show the effects of reactive diluents, filler, thickening, and pressure on the curing kinetics.

EXPERIMENTAL

Unsaturated Polyester. Unsaturated polyester was prepared from dipropylene glycol, propylene glycol, and maleic anhydride. The ratio of dipropylene glycol to propylene glycol was 4 to 1. High-resolution NMR spectra of this unsaturated polyester showed that 93% of the maleic double bonds (cis form) were converted to the fumaric double bonds (trans form) during the polycondensation reaction. Therefore, this unsaturated polyester was mostly poly(dipropylene glycol fumarate) (DPGF). The acid number of this DPGF was 25, and the molecular weight, determined by gel permeation chromatography, was 2700.

Reactive Diluent. The styrene, vinyltoluene (60% meta, 40% para isomer), and *tert*-butylstyrene (95% para, 5% meta isomer) used contained 30 ppm of *tert*-butylcatechol, an inhibitor. The monochlorostyrene (40% para, 60% orthoisomer) contained 60 ppm of the same inhibitor. These reactive diluents were used to prepare polyester solution.

Initiator and Low-Profile Additive. The peroxide initiator was *tert*-butyl perbenzoate from Lucidol Chemical Co. with a purity of 98% and an active oxygen content of 8.07%.

The low-profile additive was cellulose acetate butyrate from Eastman Chemical Co. (EAB 450.01).

Filler and Thickening Agent. The filler was calcium carbonate, Camel White, from H. T. Campbell & Sons Co. This calcium carbonate has a specific gravity of 2.7 and an average particle diameter of 2.0 microns. The thickening agent was Multiflier M from the Marco Chemical Division, W. R. Grace & Co., which is a magnesium oxide suspension.

Differential Scanning Calorimetry. A du Pont 900 DTA equipped with a high-pressure DSC cell was used to measure the exothermic reaction of curing. A detailed description of this DSC cell is available from du Pont. High pressure was introduced to the DSC cell by means of dry nitrogen. The hermetically sealed pans, inside the DSC cell, were pressurized through a pinhole in the top of the pans.

The recorded ΔT in this instrument is given by^{6,7}

$$\Delta T = T_{rp} - T_{sp} = R_c(C_s - C_r) \frac{dT_r}{dt} + R_c \frac{dQ}{dt} - C_s(R_c + R_s) \frac{d(\Delta T)}{dt} \quad (1)$$

where T_{rp} , T_{sp} = reference and sample platform temperatures, respectively; C_s , C_r = sample and reference heat capacities, respectively; dT_r/dt = heating rate; R_c = thermal resistance of the constantan disc; R_s = thermal resistance between sample pan and sample platform; and dQ/dt = thermal event (endo or exothermic change) of sample.

It is assumed that the third term in eq. (1), the thermal lag inherent in the instrument, has no effect on the thermal curve. Then R_c is the proportionality constant to convert the ΔT output of the instrument to calorimetric units. The calibration constant, $1/R_c$, which is a function of temperature, was obtained through the heat capacity term, the first term in eq. (1). Aluminum oxide from the National Bureau of Standards was used for this purpose.

The continuous calibration curve thus obtained was again checked with $1/R_c$ obtained through the thermal event term (the heat of fusion), the second term of eq. (1), at the following temperatures: 122.4°C (melting point of benzoic acid), 156.6°C (melting point of indium), 232.0°C (melting point of tin), and 327.3°C (melting point of lead). Very good agreement in $1/R_c$ was obtained at the heating rate of 10° to 20°C/min. These calibration curves cover the temperature range from 90° to 330°C.

It was found that the calibration curve depends on the pressure applied to the cell, i.e., the lower the applied pressure, the smaller the calibration constant. Therefore, the calibration curve obtained at a specific applied pressure was used for the calculation in eq. (2), (3), and (4) at that specific pressure. It was also found that at high heating rates (25°C/min or higher) under high pressure (630 psi or higher), reproducibility of the calibration curve is poor. For this reason, a heating rate of 10°C/min was employed in this study.

For each set of DSC curves, a dQ/dt -versus-temperature T curve was obtained using the calibration curve discussed above. From the dQ/dt -versus- T curve, the heat of curing, Q , was calculated:

$$Q = \int_{T_i}^{T_f} \frac{dQ}{dt} dT \quad (2)$$

where T_i and T_f are the initial and final temperatures of curing, respectively. To calculate Q , numerical integration using the Simpson method was carried out by IBM 360.

The conversion at temperature T , α_T , was calculated by eq. (3):

$$\alpha_T = \frac{1}{Q_t} \int_{T_i}^T \frac{dQ}{dt} dT \quad (3)$$

where Q_t is the total heat of curing which could be obtained on the complete conversion of the reactive double bonds.

The rate of curing at temperature T , R_p , was calculated by Equation (4):

$$R_p = \frac{1}{Q_t} \left(\frac{dQ}{dt} \right)_T \quad (4)$$

Thermal gravimetric analysis on the cured resin indicated that the weight loss due to thermal degradation reached 1% of the total weight at 230°C. If the cured resin degrades and the resultant products start to evaporate, the analysis of the DSC thermogram, from a kinetic standpoint, becomes too complicated, if not impossible, to interpret. This is the reason that the DSC was, in most cases, run up to 210°C but never above 230°C.

RESULTS AND DISCUSSION

The curing of polyester is a process of free-radical copolymerization of an α,β -unsaturated acid in a polyester and a reactive diluent. Hence, the reactivity ratios and the mole ratio of the reactive diluent to the unsaturated acid affect the rate of curing as well as the composition of the cured resin.^{8,9} Although there is a possibility of homopolymer formation from reactive diluent, it was reported that even at high concentrations of styrene no polystyrene was formed during curing.^{10,11}

In this study, the mole ratio of a reactive diluent to unsaturated acid residue was kept at 1.98. For low-profile resins used in SMC or BMC, however, this high ratio is required for the following reasons: (1) to achieve the maximum conversion of reactive double bonds; and (2) to yield lower initial viscosity of the polyester resin. The ratio of reactive diluent to the unsaturated acid residue, in fact, determines the final degree of curing.⁸ In a solution of styrene and unsaturated polyester, a mole ratio of 1.6 to 2.0 yields the maximum combined conversion of styrene and unsaturated acid residue.⁸ Accordingly, the mole ratio of 1.98 will ensure a high final conversion and, consequently, a high crosslinking density in the three-dimensional structure. This high mole ratio also results in the low initial viscosity which makes it possible to incorporate a large amount of filler and yet easily impregnate glass fibers.

Even if the reactive diluents homopolymerize between unsaturated acid residues, the overall conversion (α_T) and rate of curing (R_p) can be calculated from eqs. (3) and (4), respectively. These calculations can be made because of the small difference between the heats of polymerization and copolymerization among styrene derivatives and polyesters.¹²⁻¹⁴ The rate of curing, unlike the reactivity ratios, depends upon, among other things, the temperature, pressure, matrix viscosity, and the nature of the reactive diluent. These effects will be discussed with the kinetic data obtained with the DSC.

Effects of Reactive Diluents

DPFG was dissolved in the following reactive diluents: styrene (ST) at 50 wt-% diluent concentration, vinyltoluene (VT) at 53.7 wt-%, monochlorostyrene (MCS) at 58.0 wt-%, and *tert*-butylstyrene (TBS) at 60.7 wt-%. In these four polyester solutions, the mole ratio of the reactive diluent to unsaturated acid residue of the polyester remains the same. All four polyester solutions contain 1.2 wt-% of *tert*-butyl perbenzoate.

As shown in Figures 1 and 2, the reactive diluents have large effects on the curing characteristics of the polyester solutions. The kinetic data calculated by eq. (2) are shown in Figures 3 and 4. Since the curing process of polyester

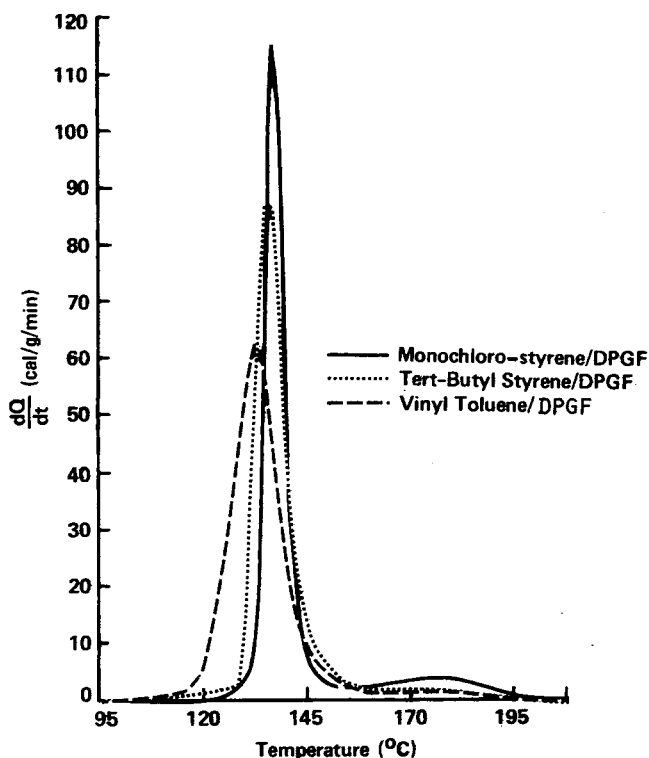


Fig. 1. Effect of reactive diluent on curing at 630 psi. Programmed heating rate: 10°C/min.

is a nonsteady-state polymerization, the rate of curing strongly depends upon the conversion (Table I). However, the initial rate of curing at 630 psi is of the following order: MCS solution (the fastest), TBS solution, ST solution, VT solution. The high initial rate of curing of MCS and TBS solution is mainly attributed to (1) the higher matrix viscosity of partially cured MCS and TBS solutions; the increase in the matrix viscosity reduces the rate of the termination reaction between the growing radicals and thus increases the rate of curing; (2) the higher temperature range of curing of MCS and TBS solution.

Common to the four thermograms in Figures 1 and 2 are the small exotherm in the temperature range of 160° to 190°C which depends upon the reac-

TABLE I
Rate of Curing at 630 psi (%/min)

Total conversion, %	MCS solution	TBS solution	ST solution	VT solution
10	29.6	26.2	17.7	13.4
20	47.3	41.5	30.0	21.6
30	62.7	50.0	36.3	26.8
40	68.0	51.2	38.5	31.0
50	62.1	47.4	39.0	32.5
60	53.4	37.0	34.1	28.6
70	37.7	26.2	26.4	22.6

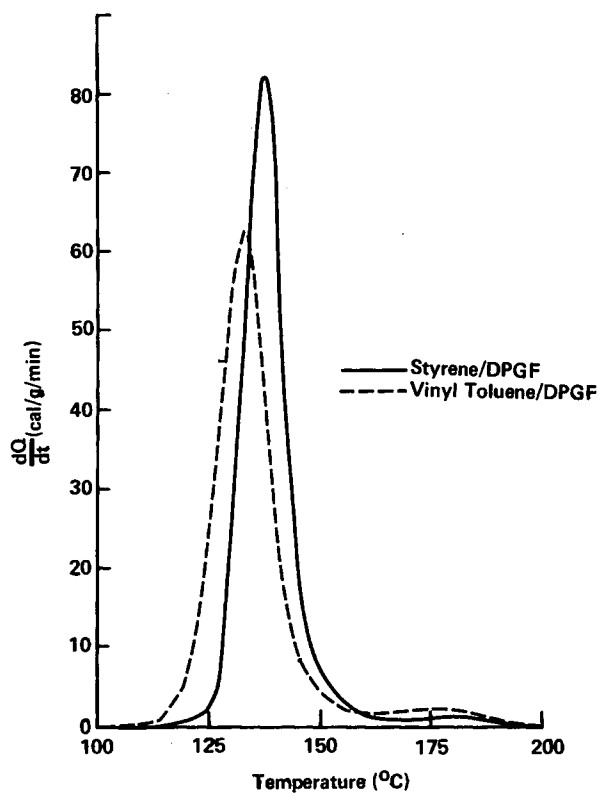


Fig. 2. Effect of reactive diluent on curing at 630 psi. Programmed heating rate: 10°C/min.

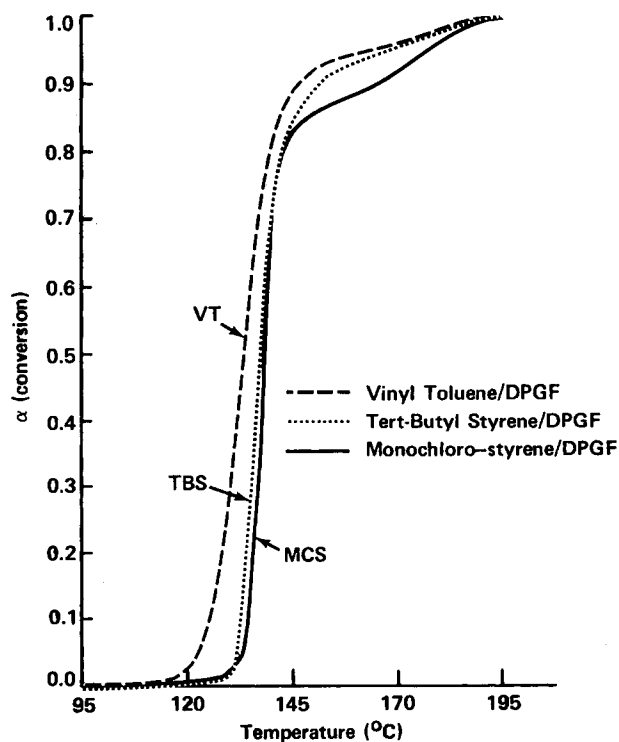


Fig. 3. Effect of reactive diluent on curing at 630 psi. Programmed heating rate: 10°C/min.

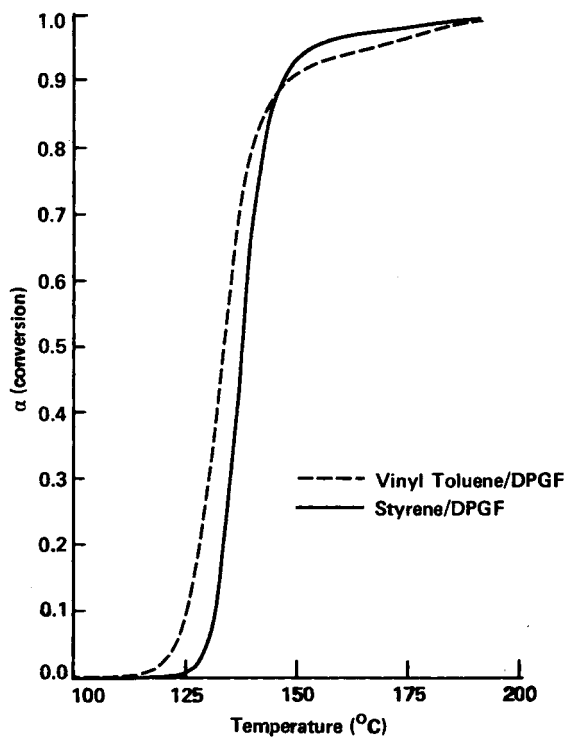


Fig. 4. Effect of reactive diluent on curing at 630 psi. Programmed heating rate: $10^{\circ}\text{C}/\text{min}$.

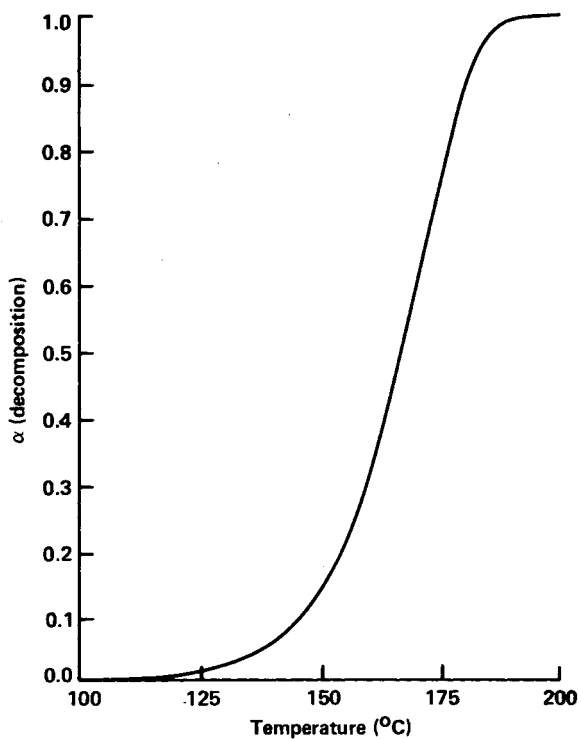


Fig. 5. Decomposition of *tert*-Butyl perbenzoate at 630 psi. Programmed heating rate: $10^{\circ}\text{C}/\text{min}$.

tive diluents (Figs. 3 and 4). The nature of this exothermic reaction has not yet been clarified in this study, but it is not due to the thermal curing of polyester because the decomposition curve of *tert*-butyl perbenzoate in Figure 5 clearly indicates the presence of the undecomposed peroxide in the range of 160° to 190°C. In fact, the thermal curing of these polyester solutions starts at higher temperature (175–180°C) under those conditions, resulting in the peak exotherm temperature at 200°C.¹⁵

It was calculated from Figures 1 and 2 that the heat of curing (Q) at 630 psi is 99.5 cal/g for the ST solution, 93 cal/g for the VT solution, 83 cal/g for the TBS solution, and 80.5 cal/g for the MCS solution. It was also calculated from the dQ/dt -versus-temperature curve of decomposition of *tert*-butyl perbenzoate that the heat of decomposition of this peroxide at 630 psi is 300 cal/g. The contribution of the heat of decomposition of *tert*-butyl perbenzoate was subtracted from the Q values calculated by eq. (2). Therefore, the heats of curing stated above are independent of the initiator.

Effects of Pressure

The formation of polymer molecules through addition polymerization almost always involves a decrease of volume per mole. Therefore, pressure is thermodynamically favorable to the radical polymerization. In fact, the rate of radical polymerization of styrene increases with pressure.¹⁶ In the curing of polyester, pressure affects both the rate and the total heat of curing. The rate of curing increases with increasing pressure (Figs. 6, 7, and 8). This increase in the rate of curing was observed in all polyester solutions.

The heat of curing (Q) also increases with increasing applied pressure (Table II). The Q values in Table II were calculated under the assumption that the initiator completely decomposes under those conditions. The increase in Q with increasing applied pressure indicates that a higher final degree of curing was attained with increasing pressure.

Effects of Thermoplastic Additive (Low-Profile Agent)

Cellulose acetate butyrate was used as a low-profile agent in styrene–polyester solution, because it makes the polyester system homogeneous. An inert thermoplastic additive does not participate in the curing of polyester but affects the course of the curing in two ways:

1. It increases the viscosity of the polyester solution. At room temperature, the viscosity of the styrene solution is 300 cp compared to 2000 cp for the styrene solution with 9.8% of cellulose acetate butyrate. The increase in

TABLE II
Heat of Curing (Q) at Different Pressures

Pressure, psi	Q of VT solution, cal/g	Q of ST solution, cal/g
15	86.5	93.5
110	87.5	—
320	93.0	98.0
630	93.0	99.5
940	94.0	100.5

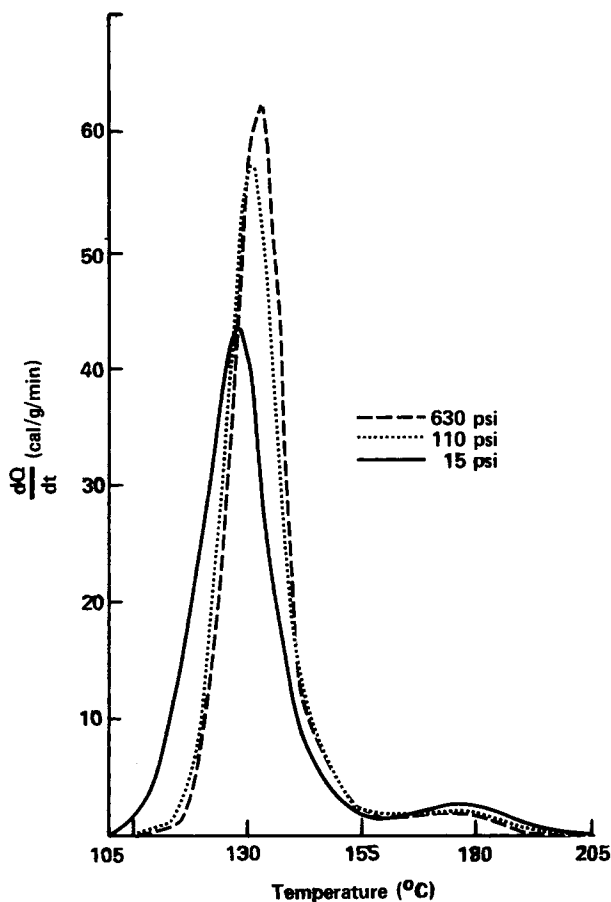


Fig. 6. Effect of pressure on curing of vinyltoluene/DPGF. Programmed heating rate: 10°C/min.

the viscosity reduces the rate of the termination reaction between the growing radicals and thus accelerates the rate of curing.

2. It causes a reduction in reactive double bond concentration and a phase separation between itself and the polyester at a certain earlier stage of the curing. When the thermoplastic precipitates from the polyester solution, styrene is possibly absorbed or occluded in the thermoplastic aggregate,¹⁷ causing the swelling of the thermoplastic. This absorption of styrene reduces the actual concentration of styrene available for copolymerization, thus resulting in a decrease in the rate of curing.

Figures 9 and 10 show the effects of low-profile additive on the curing. The presence of the low-profile additive at the 9.8% level slightly reduces both the rate and the final degree of curing. In this case, the retarding effect of the thermoplastic is more significant. With 6.7% of the low-profile additive, there appears to be no effect.

Effects of Filler

SMC and BMC usually contain 100 to 200 parts by weight (pbw) of filler in 100 pbw of polyester solution. The presence of a large amount of filler in the

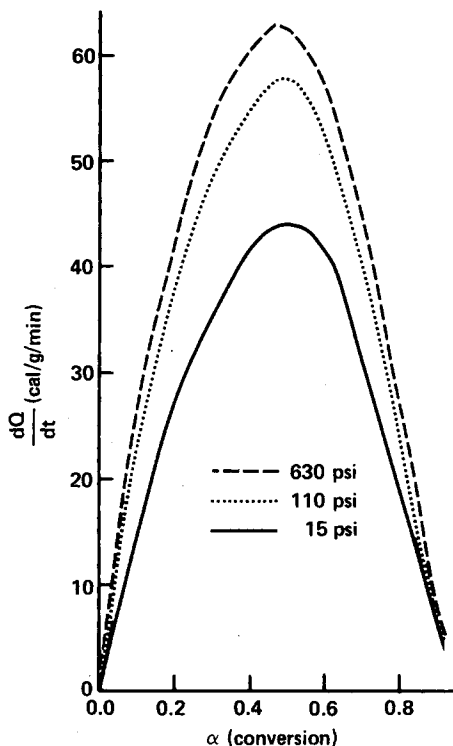


Fig. 7. Effect of pressure on curing of vinyltoluene/DPGF. Programmed heating rate: $10^{\circ}\text{C}/\text{min}$.

resin increases both the thermal conductivity and the viscosity of the resin system but reduces the number of the reactive double bonds per unit volume. The first two factors favorably affect the curing, while the last factor adversely affects the curing.

The one-phase low-profile resin was formulated from styrene, DPGF, and cellulose acetate butyrate. Figure 11 shows the effects of filler content on the curing at 940 psi. The calorimetric calculation on the filler resin was based on the resin component of the filler resin. With increasing filler content, the curing starts at a lower temperature. Up to 15% conversion, as shown in Figure 12, the rates of curing are almost the same. This indicates that the effect due to the increased viscosity is almost neutralized by the effect of the decreased double bond concentration.

However, the total heat of curing decreases with increasing amount of filler. This indicates that the final degrees of conversion decreases with the increase in filler content. Since the final degree of conversion and the volume ratio of filler affect the mechanical properties of SMC in the opposite manners, there should exist an optimum filler level for SMC with the maximum mechanical properties. In fact, the mechanical properties of SMC, such as impact and flexural strength, are functions of filler content with the maximum strength generally occurring at 150 to 200 pbw of filler in 100 pbw of resin.¹⁸ The optimum filler level for this low-profile resin is in the range of 150–180 pbw of filler in 100 pbw of resin.

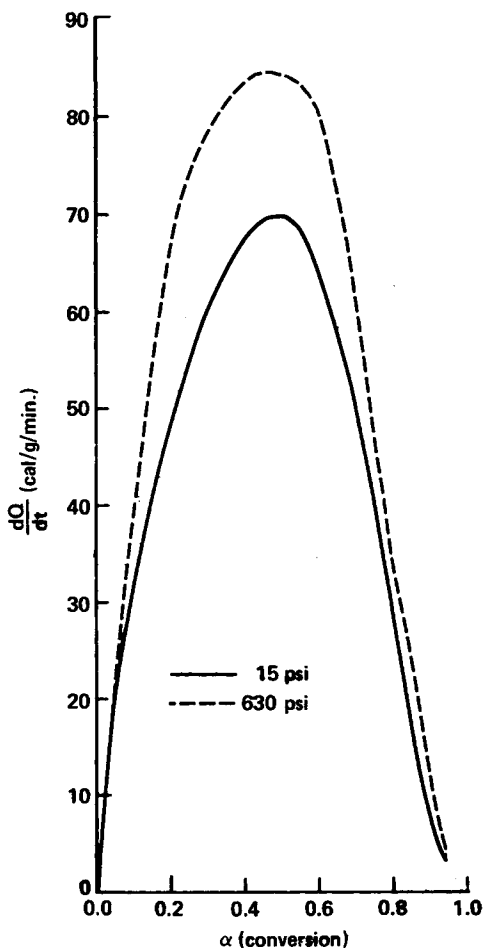


Fig. 8. Effect of pressure on curing of styrene/DPGF. Programmed heating rate: 10°C/min.

Effects of Thickening

In the processing of SMC and BMC, there is one step that precedes curing, namely, the thickening process. Thickening is a process whereby the viscosity increases by the ionic reaction of divalent metal oxide and terminal carboxylic acids group of the unsaturated polyester. This increase in viscosity enables the resin to transport the glass fiber uniformly during molding.

It was found that thickening in the absence of filler reduces the peak exotherm temperature (T_p) and the initial temperature of curing (T_i) as shown in Table III. With the progress of thickening, the initial rate of curing also increases. Yet, the heats of curing (Q) remain the same for the unfilled resins.

The thickening effects in the presence of filler are shown in Figures 13 and 14. Thickening in the presence of filler also reduces both T_i and T_p as shown in Table III.

The decrease in T_i and T_p caused by thickening, however, is larger in the presence of filler than in the absence of it. The Q of the filled resin always

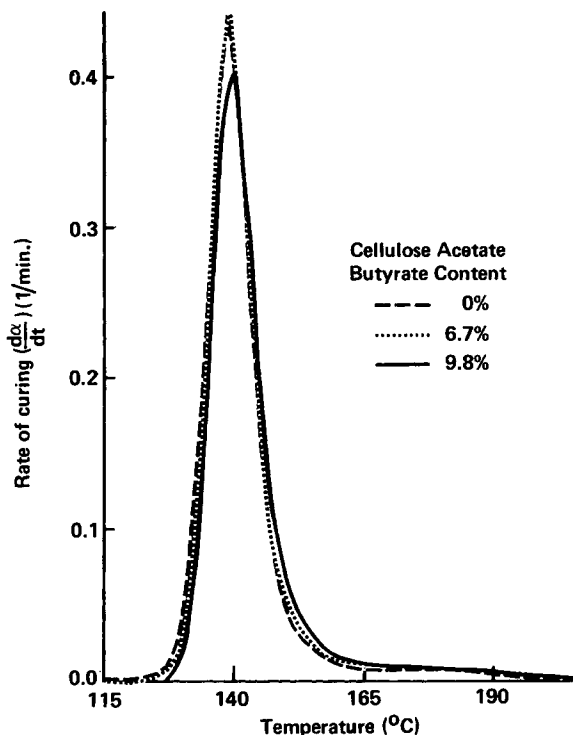


Fig. 9. Effect of low-profile additive on curing at 630 psi. Programmed heating rate: 10°C/min.

decreases with the progress of thickening. Therefore, the thickening effects are similar to the filler effects, that is, thickening depresses the T_i , T_p , and Q .

In the curing of filled resin thickened for a long period of time, we have observed a large decrease of Q . For example, a difference in Q of nearly 40 cal/g was observed for a filled resin thickened for 96 hr compared to uncompounded resin. To investigate further the effect of monomer loss as a possible source of the effects, two samples were thickened for 120 hr under the following conditions:

Sample A: Thickened at ambient pressure and at $20^\circ \pm 2^\circ\text{C}$ in a desiccator. The monomer loss was 8%, and the viscosity reached 110 million cp.

Sample B: Thickened at 300 psi of nitrogen and at $20^\circ \pm 2^\circ\text{C}$ in an autoclave. The monomer loss was 1.6% and the viscosity reached 60 million cp.

Figures 15 and 16 clearly show the differences in the curing pattern between sample A and sample B. Sample A not only exhibits a prominent sec-

TABLE III
Effects of Thickening on Initial and Peak Temperatures (T_i and T_p) of Curing at 940 psi (Programmed Heating rate: 10°C/min)

Thickening time, hr	Unfilled, °C		Filled, °C	
	T_i	T_p	T_i	T_p
Unthickened	117	139.5	112	135
48	114.5	137	106.5	131
96	108	131	—	—

^a 200 pbw of filler.

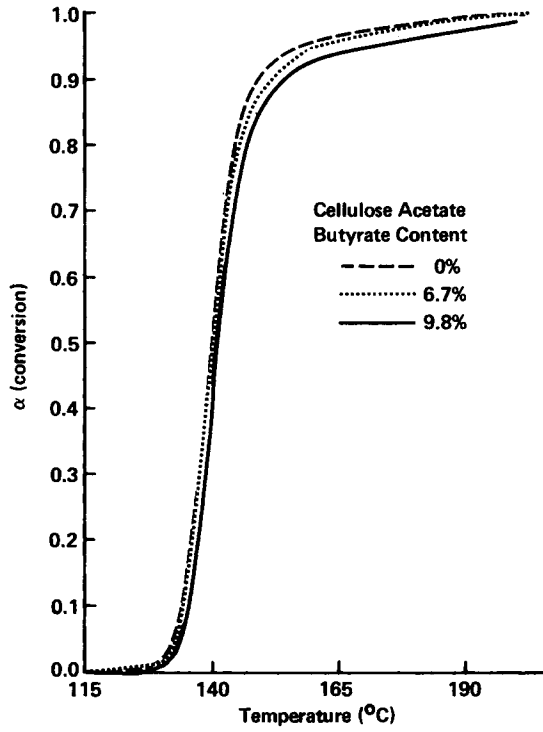


Fig. 10. Effect of low-profile additive on curing at 630 psi. Programmed heating rate: 10°C/min.

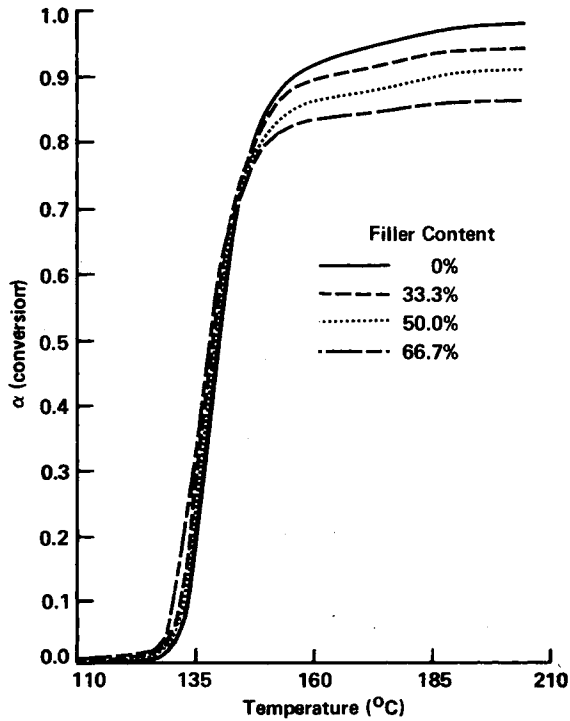


Fig. 11. Effect of filler on curing of low-profile polyester at 940 psi. Programmed heating rate: 10°C/min.

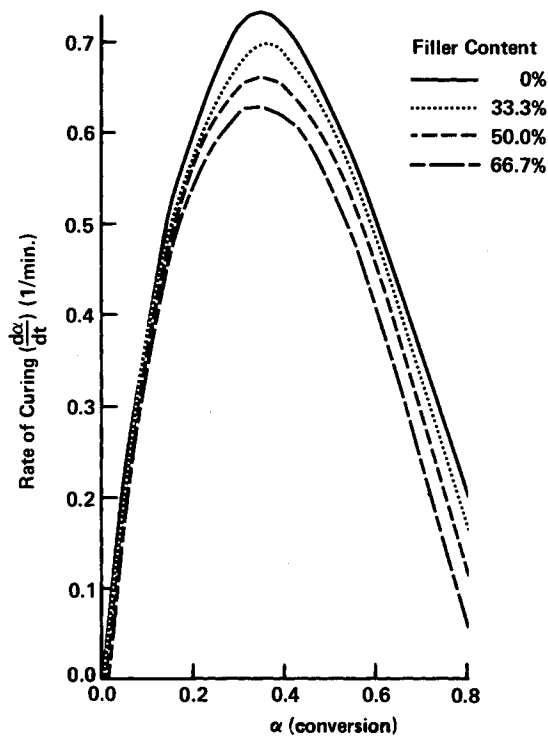


Fig. 12. Effect of filler on curing of low-profile polyester at 940 psi. Programmed heating rate: 10°C/min.

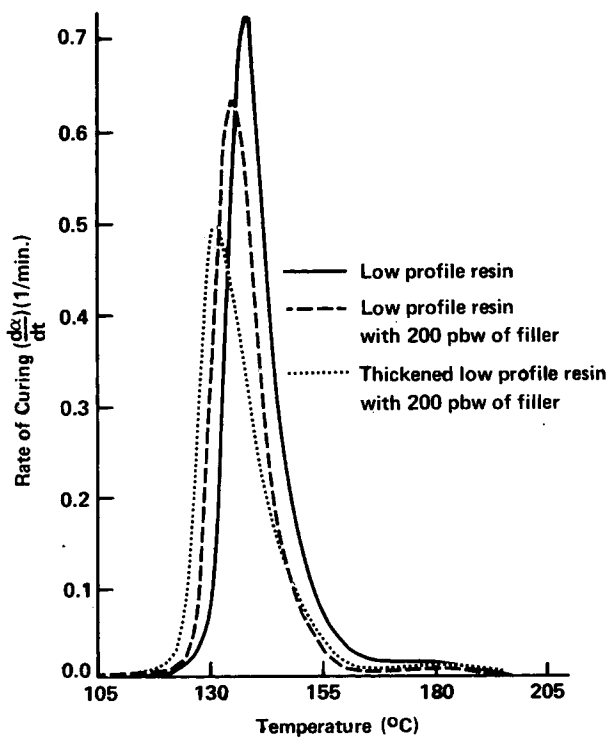


Fig. 13. Effect of thickening and filler loading on curing at 940 psi. Programmed heating rate: 10°C/min.

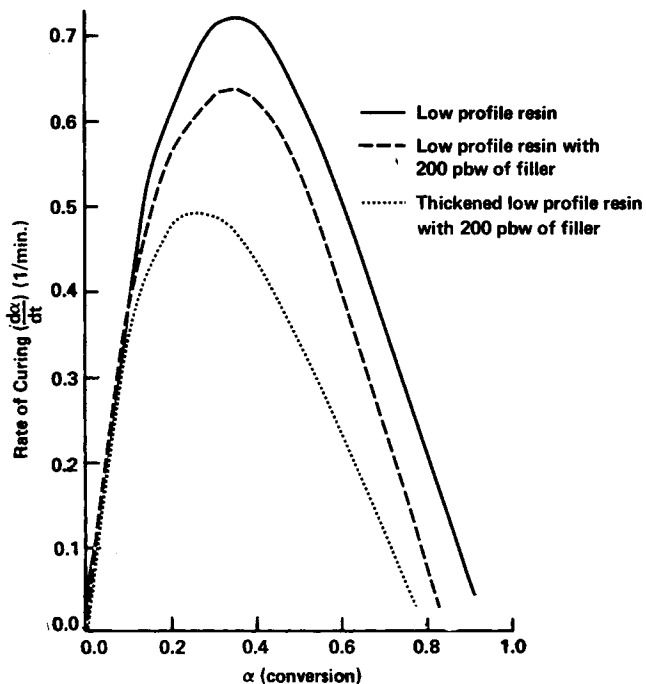


Fig. 14. Effect of thickening and filler loading on curing at 940 psi. Programmed heating rate: 10°C/min.

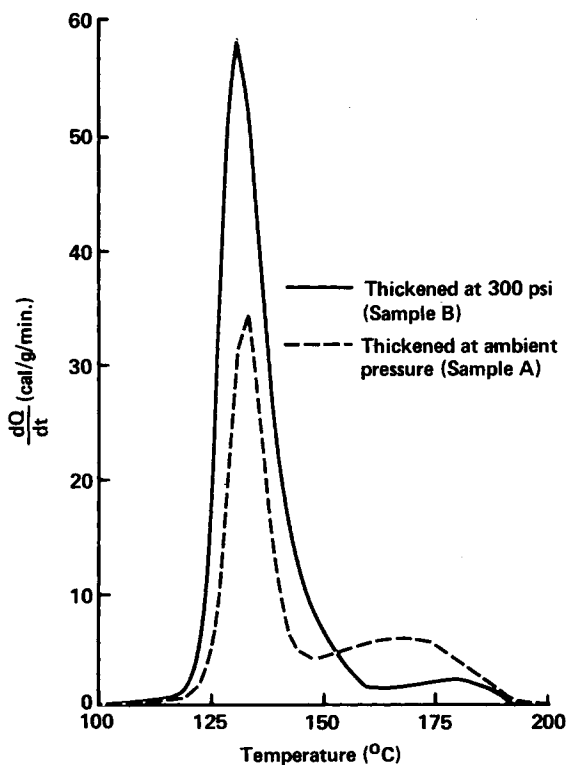


Fig. 15. Effect of thickening condition on curing at 940 psi. Programmed heating rate: 10°C/min.

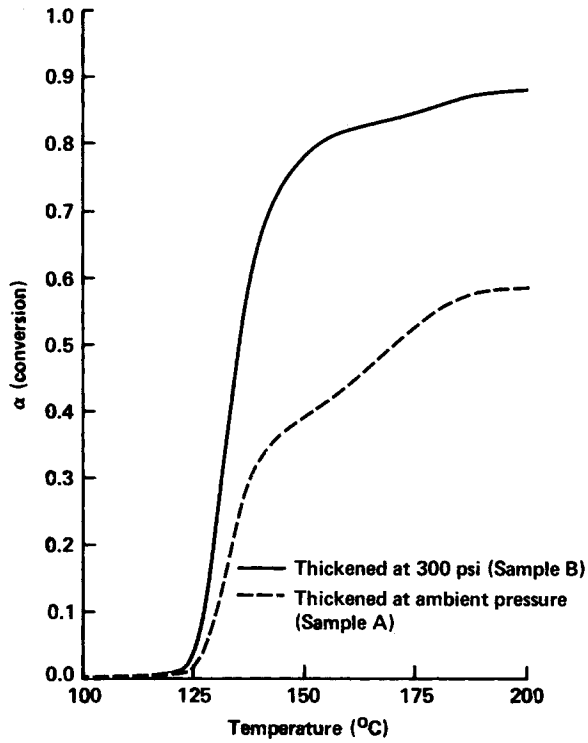


Fig. 16. Effect of thickening condition on curing at 940 psi. Programmed heating rate: $10^{\circ}\text{C}/\text{min}$.

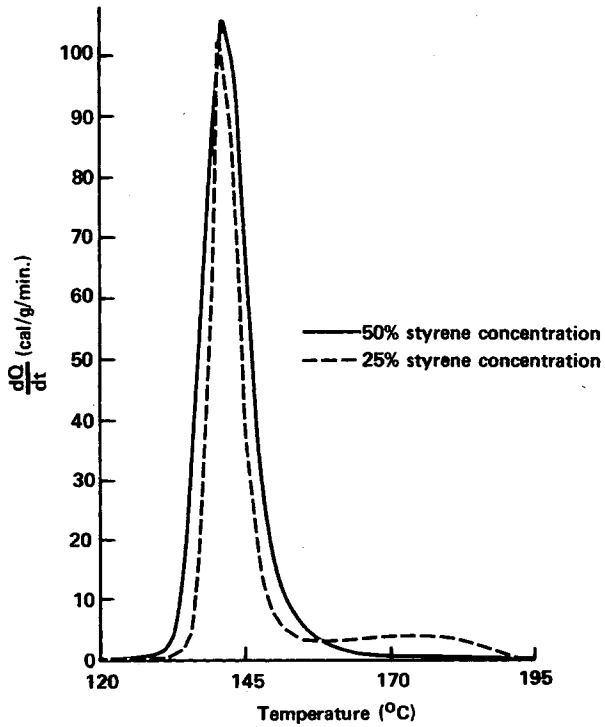


Fig. 17. Effect of styrene concentration on curing at 940 psi. Programmed heating rate: $10^{\circ}\text{C}/\text{min}$.

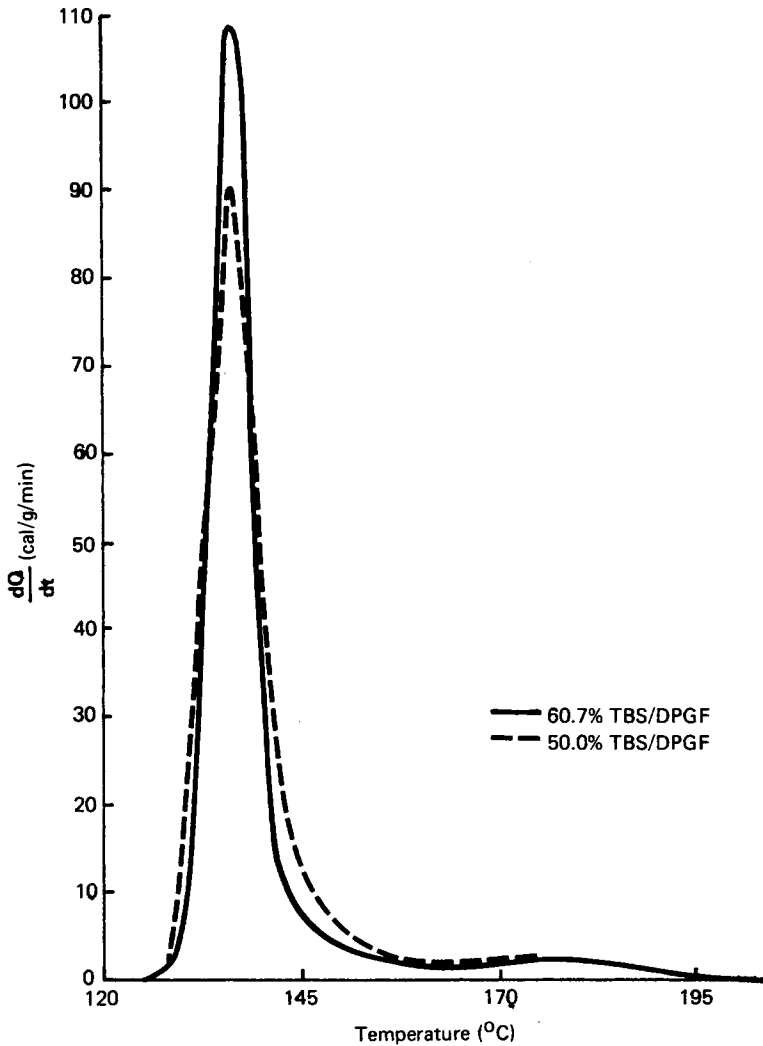


Fig. 18. Effect of *tert*-butylstyrene concentration on curing at 630 psi. Programmed heating rate: 10°C/min.

ond exotherm at the temperature range of 160° to 195°C, but also results in a much smaller Q (58 cal/g) compared to Q of sample B (90.8 cal/g). Before we draw the conclusion that these differences in the curing come from the monomer loss, however, it is necessary to isolate the effect of decreasing diluent concentration on the curing of polyester resin.

The second prominent exotherm seen in Figure 15 is undetectable in the curing thermograms of two polyester solutions of 25% and 50% concentrations (Fig. 17). The difference in Q of these two polyester solutions is only 20 cal/g. Figure 18 shows the curing thermograms of two TBS polyester solutions with 60.7% and 50.0% TBS concentration. Here, again, the difference in Q is very small (4.5 cal/g). It becomes now clear that the decrease in diluent concentration (monomer loss) does cause a decrease in Q but does not cause such a large decrease as detected for sample A in Figure 15. Also it is now clear that the monomer loss alone does not result in the second exotherm shown in

Figure 15. It is interesting to note that sample A has an extremely high viscosity. In addition to the monomer loss, this high viscosity may also be responsible for the unusual curing characteristics of sample A in Figure 15. A similar curing behavior may result when SMC or BMC is overthickened, i.e., thickened to an extremely high viscosity. Overthickening changes not only the flow characteristics of the molding compound but also its curing characteristics, which prolong the cure time and possibly create poor mechanical properties of molded compound.

Factors Affecting the Processing of SMC and BMC

On the basis of the results, we can now reason what factors affect the molding of low-profile polyester molding compounds:

1. Reactive diluent strongly affects the curing under pressure. Based on the effect of reactive diluent on the curing, MCS polyester solution provides a rapid curing resin, which could reduce the cycle time in the molding.

2. The presence of low-profile additive decreases both the rate of curing and the final degree of curing. Since its presence is indispensable for the formation of low-profile surfaces on the molded compounds, the minimum concentration of low-profile additive should be established to develop a balance between the molding characteristics and the properties of molded compounds.

3. Increase in filler content, while reducing material cost and increasing the modulus of molded compounds, results in a lower final degree of curing which adversely affect most of the mechanical properties of molded compounds.

4. The level of thickening affects not only the flow properties of molding compounds but also the curing characteristics. Overthickening results in an unusual curing pattern which might prolong the cycle time.

5. Application of higher pressure in the molding would contribute both to a shorter cycle time (faster rate of curing) and the superior mechanical properties (higher final degree of curing) of molded compounds. It is already known that the surface of the molded compounds is generally improved by increasing the molding pressure.¹⁹

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