Effect of compound composition on fast reactions of polyurethane and unsaturated polyester in the bulk state

Yan-Jyi Huang, T. Jeffery Hsu and L. James Lee
Department of Chemical Engineering, The Ohio State University, Columbus, Ohio 43210, USA

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The effect of compound composition on fast polymerization of a reaction injection moulding (RIM) type polyurethane and a polyester sheet moulding compound (SMC) has been studied using a differential scanning calorimeter. It was found that both the reaction rate profile and the limiting conversion depended strongly on the resin composition and the type of additives.

(Keywords: polyurethane; polyester; polymerization; compound; composition; d.s.c.)

INTRODUCTION

Reaction injection moulding (RIM) and compression moulding of sheet moulding compound (SMC) are two of the most important plastics technologies used in the automobile industry. Due to the desirability of lightweight composite materials for structural parts, these processes kept a very fast growing rate in the automobile industry over recent years. Applications have also been extended to the housing and aerospace industries.

Since both processes include aspects of polymerization reactor analysis as well as polymer processing, the kinetic phenomenon is much more complicated than those in the conventional polymerization methods. For example, in order to compete with traditional injection and compression moulding processes, the cycle time (or the reaction time) of these processes has to be much shorter than that in a typical polymerization reaction (i.e., minutes or seconds vs. hours). The short cycle time and the bulk type of reaction can cause temperature control problems. On the other hand, since the polymerization step occurs simultaneously with the fabrication step, the reaction has to approach complete conversion because the residual reactants cannot be removed and will be defects in the moulded product.

Polyurethane reaction in the RIM process is a typical step growth polymerization. The materials are mainly composed of three parts, a diisocyanate, a low molecular weight chain extender (usually a diol but sometimes a diamine) and a low molecular weight prepolymer (typically 1000–3000 molecular weight), frequently a polyether or polyester. The interesting elastomeric properties are attributed to the formation of microdomains during reaction. The soft domain is composed of the rubber polymer, while the diisocyanate and the chain extender form the hard domain. Polyurethane block copolymers have been objects of considerable research interest over recent years. A detailed review has been given in a previous work[1]. For the reaction kinetics, in addition to the domain formation, gelation and crystallization also occurred in many polymerizations. It has been found that the degree of domain formation, the structure of crystallinity and the molecular weight of the copolymer are strongly dependent on the compound composition and moulding conditions[2]. Usually, if reaction temperature is higher than the glass transition temperature of the polymer, i.e., 110°C for polyurethane, and if the parts are properly post-cured, complete reaction and desirable morphology can be achieved. An RIM polyurethane reaction, however, involves fast exothermic polymerization in which a large amount of heat is generated in a short period of time and sharp temperature gradient exists inside the mould during the entire curing step[3]. Since the mould temperature is usually kept near 70°C, materials near the mould surface will be polymerized at a temperature much lower than that of the materials near the mould centre. An incomplete reaction and undesirable morphology may result for the surface materials, especially if the compound composition is complex.

The SMC reaction, on the other hand, is mainly a radical chain growth copolymerization between the styrene monomer and the unsaturated polyester molecule (usually a prepolymer with molecular weight in the range of 800–5000 and double bonds more than 10 per molecule[4]). The detailed recipes of SMC materials have been reviewed in the literature[4,5]. In addition to the resins, thickening agent, low profile additives, inert fillers and reinforcing fibres are added to the compound to improve the physical properties of the product. Initiator, catalyst, inhibitor and some other ingredients are also added to control the reaction course.

Several researchers have studied the reaction mechanism of the bulk copolymerization of unsaturated polyester–styrene system. Horie *et al.*[6] claimed that most of the reaction was diffusion controlled and final conversion was always incomplete. Kubota[7] studied the influence of reactive diluents, pressure, thermoplastic additives, fillers and the extent of thickening on the reaction rate profiles measured by d.s.c. He found that increasing the moulding pressure or the content of reactive diluent could reduce the cycle time of moulding.

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* To whom correspondence should be addressed.

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On the other hand, adding fillers and low profile additives usually prolonged the cycle time.

For the reaction kinetics, Stevenson[8], Lee[9], Kamal *et al.*[10] and others[11] developed a series of kinetic models based on either the usually accepted reaction mechanism or empirical equations. Most recently, Huang and Lee[12] proposed a more complete model which accounts for not only the kinetic effect of the free radical copolymerization, but also the diffusion effect and the glass transition of the SMC reaction.

Generally speaking, in the reactive polymer processing processes such as RIM and SMC, the reaction involves either a step growth polymerization or a radical chain growth polymerization in the bulk state. For many reactions, they are further complicated by the occurrence of multiple physical changes during the polymerization. These changes include domain formation (a change from a single phase to multiple phases because of the thermodynamic incompatibility of polymer segments or blocks), gelation (a change from a viscous fluid to a network gel with chemical or physical crosslinking), glass transition and crystallization (changes from the rubbery material to a glassy polymer or from an amorphous material to a semicrystalline polymer with increasing degree of polymerization and packing of polymer segments). These changes occur during the course of reaction and certainly interact with the ongoing chemical reaction. To date, the kinetics of these reactions are still poorly understood. How the physical changes develop during polymerization and how reactant composition influences the reaction kinetics are seldom considered.

In this work, a polycaprolactone based urethane and propylene–maleate polyester based sheet moulding compound were studied using a differential scanning calorimeter. The results permit a preliminary understanding of the structure variations and the reaction mechanisms of RIM and SMC processes.

EXPERIMENTAL

Polyurethane reaction

The polyurethane chosen for this study consists of a polyester soft segment based on a poly(ε-caprolactone diol) (PCP) (PCP-0240, Union Carbide) with a number average molecular weight of 2000, and a hard segment based on a liquid form of 4,4′-diphenylmethane diisocyanate (MDI) (143-L, Upjohn) chain-extended with 1,4-butanediol (BDO) (Aldrich Chemical Company). All materials were used as received. Before reaction, the diol was melted and degassed at 75°C with a vacuum pump for at least 1 h until no further bubbles were evolved. The BDO and the MDI were degassed at room temperature for 20 min. The catalyst dibutyltin dilaurate (DBTDL-T12, M and T Chemicals) was used at a concentration of 0.02 wt%. Filler used was $\frac{1}{16}$-inch milled glass fibres (739BB, Owens Corning Fiberglas (OCF)). All the reactions were carried out at equivalent stoichiometry.

Table 1 Polyurethane compounds used in this study

Mole ratio PCP/MDI/BDO	Hard segment (wt%)	Total* ΔH (cal/g)	Residual ΔH (cal/g)	Limiting conversion (%)
Without fibre				
0/6/6	100	78.8	17.70	~77.6
1/24/23	81.7	65.2	2.76	~95.8
1/6/5	45.1	48.7	1.79	~96.3
1/2/1	14.1	32.4	1.06	~96.7
With fibre				
1/6/5	36.7	37.5	0.90	~97.0

* Measured by the adiabatic temperature rise method.

The reaction kinetics and the crystallinity structure of all samples were measured by a differential scanning calorimeter (Perkin-Elmer DSC-2C). Isothermal reaction rate *versus* time profiles were measured at 70°C which is a typical mould temperature of RIM process. Polymerization runs were carried out with several mole ratios of PCP/MDI/BDO as shown in *Table 1*. Isothermal cures were ended when there was no further exotherm. Samples were reheated from room temperature to 230°C in the scanning mode with a heating rate of 10°C min^{-1} to determine the crystallinity and the residual reactivity left in the isothermally cured samples. Each sample was then annealed at 180°C for several minutes to ensure a complete reaction and reheated again in the scanning mode to determine the effect of high temperature treatment on the crystallinity structure of the reacted sample. Since the polyurethane reaction started during the sample preparation, d.s.c. experiment was not able to catch the entire reaction course; therefore, the total heat of reaction was measured by the adiabatic temperature rise method[2,13]. The catalyst concentration used in the adiabatic temperature rise measurement was 0.7 wt%.

For the 1/6/5 combination, which is a typical composition for automotive flexible fascia applications, a set of reactions were conducted in $\frac{1}{8}''$ thick aluminium moulds with mould surface temperature controlled at either 70°C or 110°C in order to elucidate the effect of reaction temperature on the product morphology. At 70°C, circulating water through the mould surfaces was used to control the temperature whereas circulating air was used at 110°C. Water temperature was controlled within ± 0.5°C, while air temperature could only be maintained within ± 5°C. Reactants were mixed and degassed at 60°C before being poured into the mould. For comparison, a similar set of reactions were also carried out for samples with a 1/3/2 composition.

All reactions were held 20 h at the given temperature. Since polymerization exotherm would raise the reaction temperature, especially near the mould centre[3], only materials near the mould surface were examined using d.s.c.

In order to understand the effect of post-cure on sample morphology, the mould-prepared 1/6/5 samples were post-cured in a vacuum oven for two hours at either 110°C—a temperature higher than all soft domain transition points, or 150°C—a temperature higher than the hard domain glass transition point. The samples were then characterized by d.s.c. as discussed before.

Styrene–polyester reaction

The SMC compounds used in this study were prepared from the following resins: a 1:1 propylene–maleate polyester combined with 35 wt% of styrene (P-340, OCF), an acrylic acid modified poly(methyl methacrylate) (PMMA) combined with 65 wt% of styrene (P-701, OCF), and styrene monomer. Resins were used as received without removing the inhibitor. The catalyst *t*-butyl perbenzoate (TBP, Lucidol) was used at a concentration of 1.3 wt%. Filler used was $CaCO_3$. To study the thickening effect, a 4 wt% of a thickening agent $Mg(OH)_2$ was also added to the compound. *Table 2* lists all recipes used in this work.

Table 2 Styrene–polyester compounds used in the study

Ingredient	Parts by weight						
Styrene	100	33	64	89	–	52	–
65% unsaturated polyester in styrene (P-340)	–	67	36	11	–	–	56.6
35% PMMA in styrene (P-701)	–	–	–	–	100*	–	43.4
Filler $CaCO_3$	–	–	–	–	–	48	143.0
Thickening agent $Mg(OH)_2$	–	–	–	–	–	–	9.8
Mole ratio of styrene:polyester	pure styrene	2:1	5:1	20:1	pure styrene	pure styrene	2:1
Limiting conversion at 100°C	~100	85	93	98	~100	~100	–

* Part of styrene was evaporated to make 48% PMMA in styrene

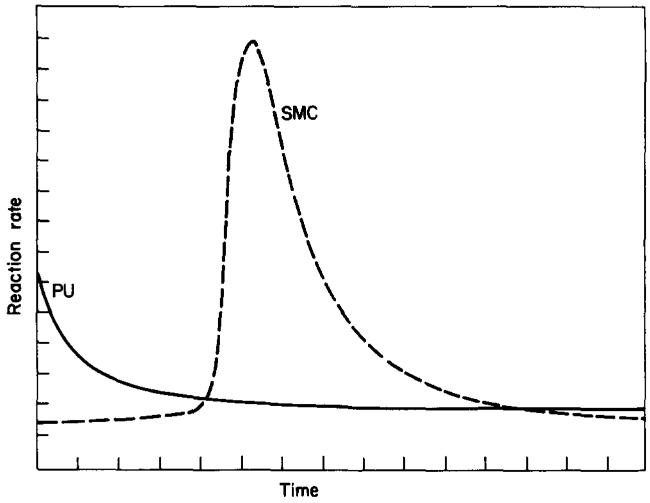

Figure 1 Typical isothermal reaction rate profiles for polyurethane and SMC reactions

Isothermal reaction rate *versus* time profiles were measured at 100°C using the d.s.c. The residual reactivity was determined in the scanning mode as described for the polyurethane reaction.

RESULTS AND DISCUSSION

Polyurethane reaction

Figure 1 shows typical isothermal reaction rate profiles for the polyurethane reaction and the SMC reaction. For an externally catalysed step growth polymerization such as polyurethane, the reaction started immediately after mixing. The maximum rate occurred at the beginning of the reaction and decayed fast when the functional groups were consumed. On the other hand, for a thermally initiated free radical polymerization such as SMC materials, the reaction started after an induction time and passed through a maximum. By controlling the temperature and the amount of inhibitor, the SMC materials can be premixed and stored for a period of time before moulding.

Figure 2 shows the crystallinity and the residual reactivity of the polyurethane compounds measured by the scanning d.s.c. curves. The amount of residual heat, the total heat of reaction, and the calculated limiting conversions are listed in *Table 1*. For the MDI–BDO compound (sample 0/6/6), a severe incomplete reaction was observed. The Figure shows that the residual reaction started when the scanning temperature reached 90°C and the residual reactivity was >20%. This large residual exotherm overwhelmed the melting peak of MDI–BDO crystallinity. When the soft segment was added to the compound, the residual reactivity decreased drastically and some of the melting peaks of crystallinity started to show up. When the mole ratio of PCP to BDO was increased to higher than 1:1, there was essentially very little residual reactivity.

Figure 3 shows the melting peaks, measured by d.s.c., of samples after the high temperature thermal treatment. The 0/6/6 sample showed the maximum crystallinity. Adding soft segment not only reduced the amount of crystallinity but also shift the melting peaks to the higher temperature. When the mole ratio of PCP to BDO was increased to 1:1, there were almost no observable melting peaks in the sample. Multiple melting transitions of the 1/6/5 sample shown in *Figure 3* might result from the interaction of phase separation and crystallization since both physical changes occurred during the polyurethane reaction.

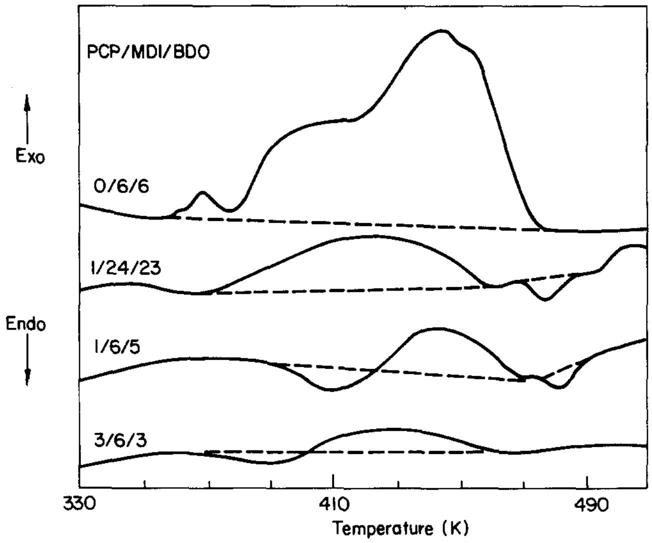

Figure 2 Scanning d.s.c. results of isothermally cured polyurethane samples

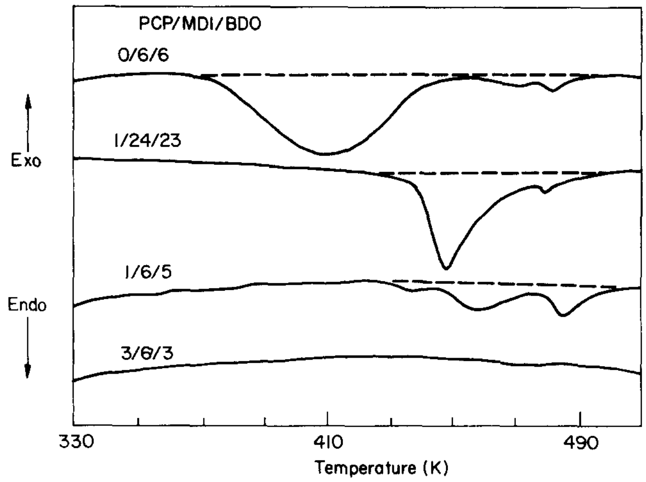

Figure 3 Scanning d.s.c. results of isothermally cured polyurethane samples after high temperature thermal treatment

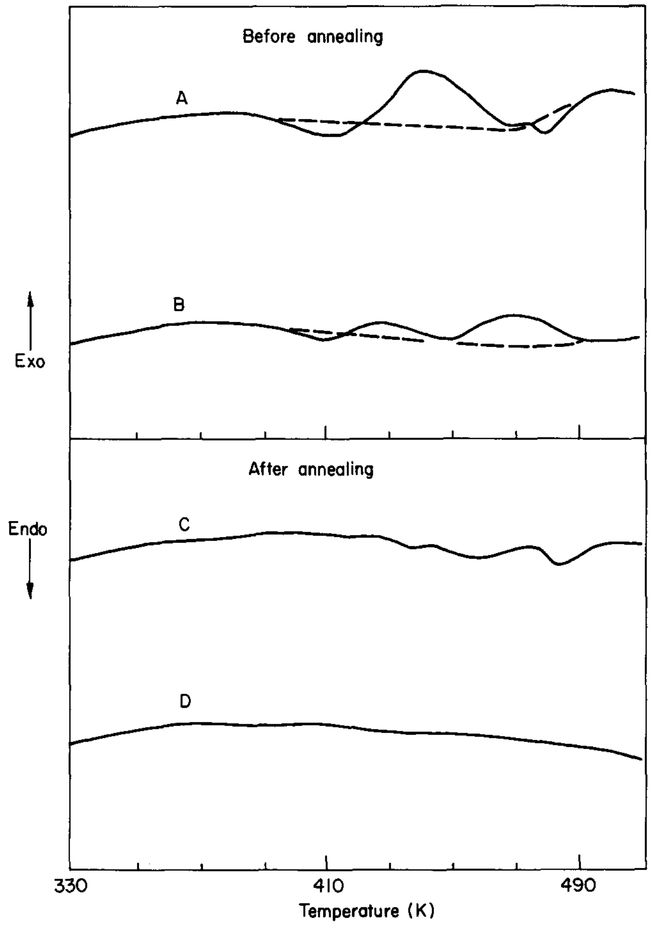

Figure 4 Scanning d.s.c. results showing the effect of filler on 1/6/5 polyurethane samples (a) before high temperature thermal treatment. (A) No filler added, (B) 30 wt% milled fibre added. (b) After high temperature thermal treatment. (C) No filler added, (D) 30 wt% milled fibre added

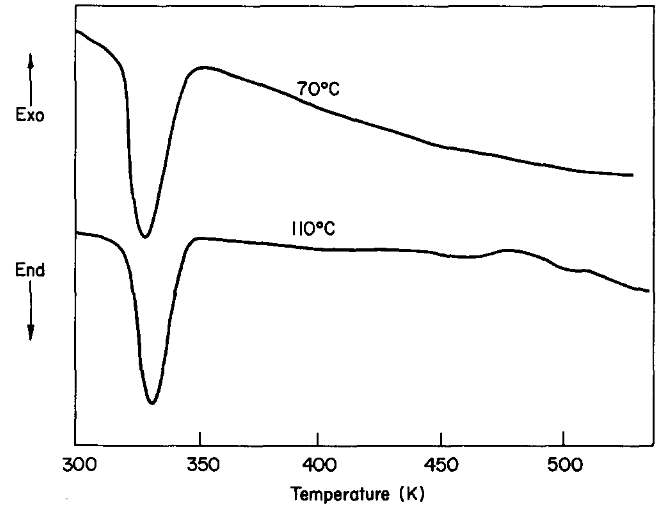

Figure 5 Scanning d.s.c. results of mould-prepared 1/3/2 polyurethane samples

Figure 4 shows the effect of adding glass fibre to the polyurethane compound. The melting peaks disappeared; the residual reactivity, however, was not affected as shown in *Table 1*.

The d.s.c. results for the mould-prepared samples are shown in *Figures 5* and *6*. For the 1/3/2 samples, d.s.c. scanning (*Figure 5*) showed only minor differences of thermal behaviour between polymers reacted at lower and higher temperatures. In looking at the 1/6/5 samples (*Figure 6*), four distinct transition temperatures were observed: a soft domain glass transition at ~ −50°C or −60°C (not shown in the Figure), a soft domain melting peak at ~45–50°C, a hard domain glass transition at ~90–120°C and a hard domain melting peak at ~200–215°C.

For the 70°C sample, d.s.c. scanning showed multiple hard domain melting peaks combined with some residual reaction exotherm at ~150–220°C. This represented further reaction for the previously unconverted material and possibly some rearrangement of the crystallinity structure, which was consistent with the result of d.s.c.-cured samples shown in *Figure 2*. At higher reaction temperature (110°C), multiple hard domain melting peaks merged to a single major peak; subsequently, the soft domain melting peak was significantly reduced. It was also shown that the temperature range between the two melting peaks was slightly wider for samples reacted at higher temperature. These phenomena can be explained as more uniform sequence length distribution of hard segments and better phase separation are obtained for polymers reacted at higher temperature.

Figures 5 and *6* clearly suggest that compound composition and the moulding temperature exert significant influence on the polyurethane morphology, especially when the hard domain content is high.

Post-cure at 110°C did not seem to change the morphological characteristics of any samples according to the d.s.c. results. For samples post-cured at 150°C, d.s.c. curves shown in *Figure 7* indicate that some morphology

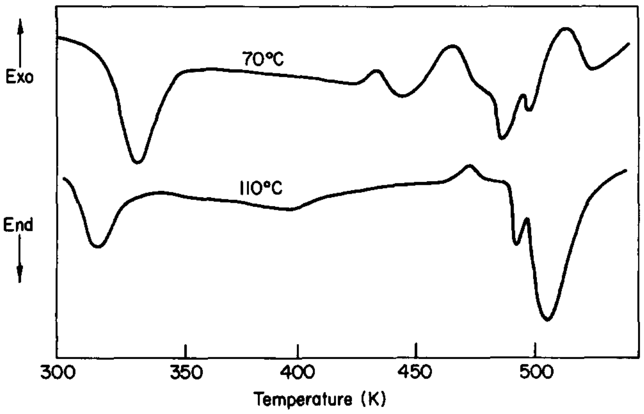

Figure 6 Scanning d.s.c. results of mould-prepared 1/6/5 polyurethane samples

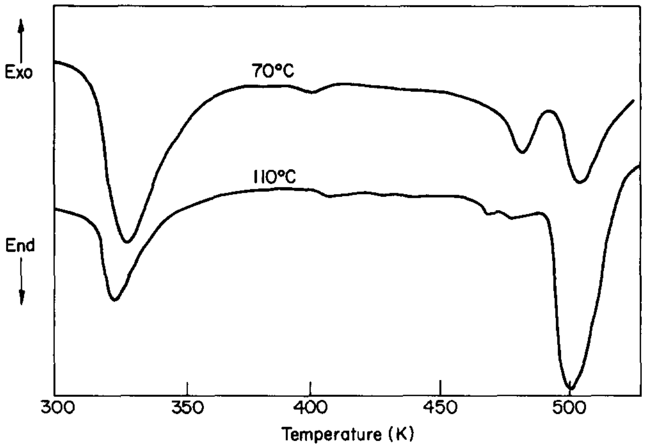

Figure 7 Scanning d.s.c. results showing the effect of post-cure at 150°C on the polyurethane morphology

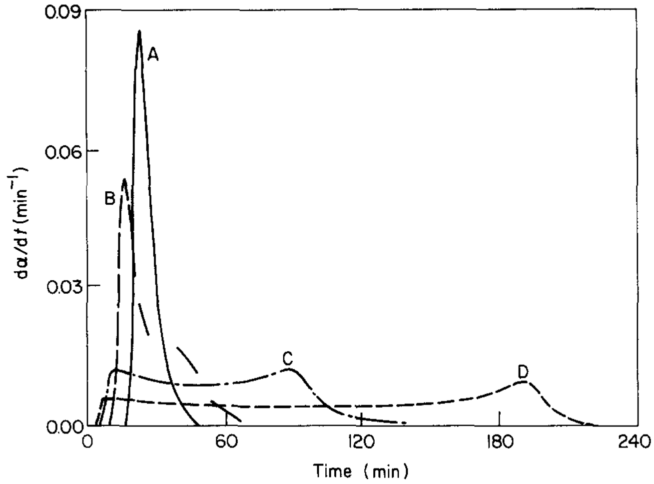

Figure 8 Isothermal reaction curves measured by d.s.c. for various styrene–polyester ratios. A = 2:1, B = 5:1, C = 20:1, D = styrene

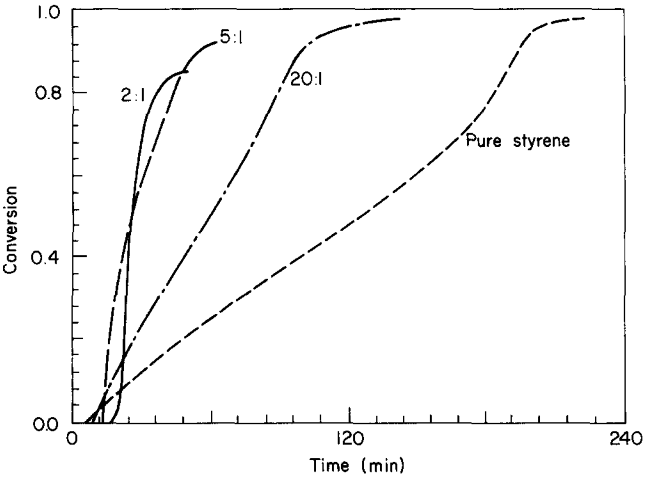

Figure 9 Conversion vs. time for styrene–polyester reactions of 2:1, 5:1, 20:1 and pure styrene reaction at 100°C

changes occurred at this stage. The many hard domain melting peaks of the 70°C sample shifted to a higher temperature and merged into two discernable peaks. The soft domain melting peak kept the same shape but shifted slightly to a lower temperature. This sample, however, was still quite different from the 110°C sample.

The 110°C sample seemed to have the same thermal behaviour before and after post-cure. This indicates that an appropriate reaction condition can produce a desirable polymer with stable properties in which the post-cure stage may not be necessary.

Styrene–polyester reaction

In this study, the mole ratio of styrene monomer to unsaturated polyester was varied from 2:1 to pure styrene. *Figure 8* shows the isothermal reaction rate profiles at 100°C. The 2:1 sample, curve A, has a typical composition of sheet moulding compounds. Curve D, however, represents the reaction rate profile of pure styrene. The styrene polymerization started after an induction time and the rate remained at a relatively constant plateau in the earlier part of the reaction during which the reaction was largely kinetic controlled since the diffusion effects on both polymer chains and monomers were insignificant[14]. The reaction rate decayed slightly primarily due to the consumption of monomers until a point where the influence of diffusion on the polymer radicals became significant. This point was usually called the on-set of the gel effect which could be identified as a rise of the reaction rate on the rate profile. Finally, at the later stage of the reaction, the rate decreased because of the decreasing of the monomer concentration and the increasing diffusion effects on both polymer chains and monomers. The reaction would terminate when the material changed from the rubbery state to the glassy state since the glass transition essentially froze the whole reacting system.

For SMC resin (i.e., the 2:1 sample), the reaction rate increased sharply after an induction time and dropped fast when it reached the maximum. This is because each unsaturated polyester molecule has ten or more double bonds[8]. A network structure was formed at the very beginning of the styrene–polyester copolymerization and most of the reaction proceeded after the gelation. Consequently, the reaction was affected by the diffusion effect, i.e., the gel effect, through almost the entire reaction course; therefore no plateau region was observed.

When the styrene to polyester ration was increased to 5:1 (curve B), a coexistence of the styrene homopolymerization and the styrene–polyester copolymerization was observed. When the ratio was further increased to 20:1 (curve C), the rate profile resembled the pure styrene reaction with a much shorter plateau region. This was due to the partial crosslinking of the polyester molecules which might cause an earlier on-set of the gel effect. Conversion profiles of these reactions are shown in *Figure*

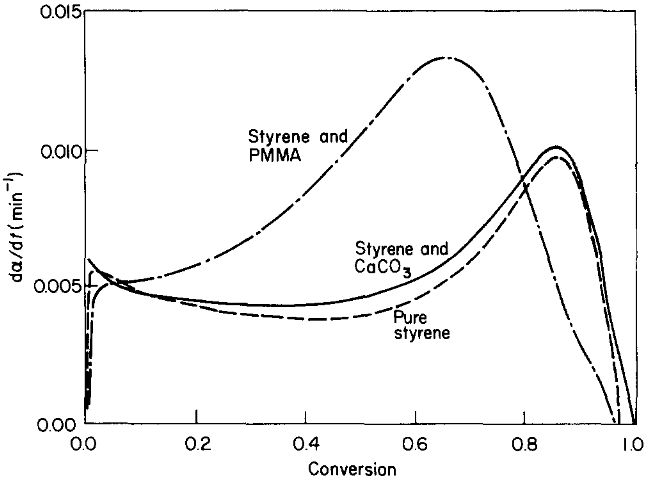

Figure 10 Rate vs. conversion for PMMA-in-styrene and $CaCO_3$-in-styrene reactions at 100°C

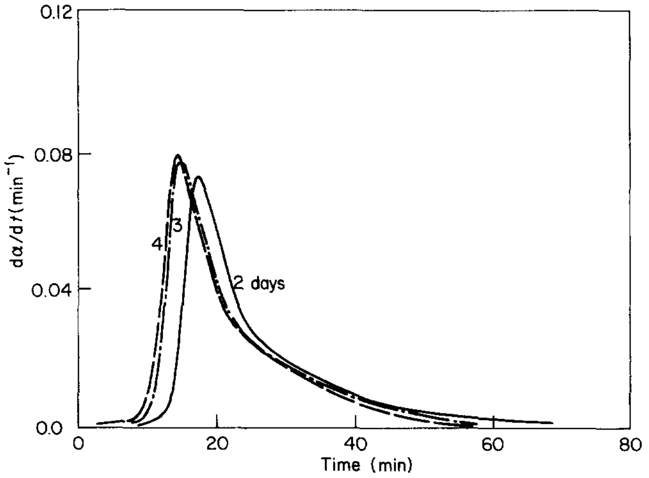

Figure 11 Effect of thickening on SMC reaction

9. Limiting conversion of each compound is listed in *Table 2*. As expected, the higher the degree of crosslinking, the higher the degree of residual reactivity.

Figure 10 compares the effect of low profile additive, PMMA, and filler, $CaCO_3$, on the rate profile of styrene reaction. It was found that adding PMMA caused an earlier on-set of the gel effect, but that the influence of adding fillers was very minor. Our explanation is that $CaCO_3$ does not dissolve in either the monomer or the polymer; therefore, even though the bulk viscosity of the compound increases (or the bulk diffusivity decreases) by adding the fillers, the styrene reaction is still relatively homogeneous on a local scale. On the other hand, PMMA dissolves in the styrene monomer and phases out during the polymerization[15], the close molecular contact between the styrene monomer and the PMMA causes a severe diffusion effect in the ongoing polymerization. The influence of adding low profile additives to the styrene reaction, however, is much less than adding the same amount of unsaturated polyester.

Figure 11 shows the effect of thickening on the rate profile of SMC reaction. Long maturation time slightly increased the reaction rate but the residual reactivity was found almost unchanged. Since the viscosity of SMC material increased several hundred times during the maturation period[16], this result was somewhat surprising. Our explanation is that the bonding between the thickening agent and the carboxyl group of the polyester molecule may be so weak that at the moulding temperature it is totally ineffective. Therefore, even though the compound viscosities before and after maturation are different at room temperature, there may be very little difference at elevated temperatures. This is supported by the rheological measurement done by Lee *et al.*[17]. They found that the shear viscosity of SMC compounds was much more temperature sensitive than that of typical polymer melts.

CONCLUSIONS

This work provides some experimental evidence of the influence of compound composition on bulk polymerizations of a segmented polyurethane and a polyester–styrene sheet moulding compound. It is clear that physical changes such as gelation, crystallization and phase separation are affected by the resin composition and the existence of various additives. These physical changes are superimposed on the chemical reaction, which usually results in a complex and heterogeneous copolymerization where not only the reaction rate profile but also the limiting conversion and the product morphology are strongly influenced by the moulding conditions. Post-mould treatment at higher temperature, such as post-curing a polyurethane sample polymerized at lower temperature, does not improve the morphological characteristics to the same level as those of a sample polymerized at higher temperature.

No theoretical modelling is presented in this work because it is obvious that more effort is needed in this area better to understand the mechanism and the interaction among the polymerizations, the physical changes and the product properties.

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