

Processing of Polyurethane–Polyester Interpenetrating Polymer Network (IPN)

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Synopsis

The kinetics and heat transfer during the curing of a polyurethane–polyester interpenetrating polymer network (IPN) were investigated experimentally and theoretically. A model based on the additivity rule of constituent ingredients was used to predict the IPNs reaction kinetics and heat transfer. Compared with the adiabatic temperature rise measured during reaction injection molding and the temperature profiles measured during a casting process, the model prediction is close to the experimental data. Deviations of model prediction from experimental results were found in the comparison of reaction rate profiles measured by differential scanning calorimetry. This suggests that reaction interactions may exist in the polymerization system.

INTRODUCTION

Polyurethanes are widely used in polymer industries. They are, however, considered inappropriate for structural applications because of their high thermal expansion coefficient and low rigidity at high temperatures. One approach to improve the material properties is by introducing a second reactive polymer into the polyurethane reaction to make up the deficiencies of the existing material. This approach is essentially an application of interpenetrating polymer network (IPN). The dual reactions in an IPN system also offer some advantages in processing. For example, the addition of a less viscous resin to the urethane material can reduce the resin viscosity and, consequently, facilitate the mold filling. Furthermore, a mixing-activated step growth polymerization, such as polyurethane, can be used as an internal heat source to initiate a thermally activated chain growth polymerization.

Most IPNs are developed for slow processes such as coating and casting. For fast processes like reaction injection molding (RIM), there are only a few commercially available IPN compounds. Ashland Chemical developed an acrylamate polymer^{1,2} that is basically a polyurethane with a high level of unsaturation on the polyol chain, which forms a second network with a crosslinking agent, acrylic monomer. Amoco Chemical developed a series of polyurethane-polyester hybrids which can be used in various reactive processes.³

Most research efforts on IPNs have been on synthesis method, morphology, and mechanical properties.^{4–9} The processing aspects have not been studied in detail. Nguyen and Suh,^{10,11} and Lee and coworkers^{12–15} studied poly-

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urethane-polyester IPNs. They found that processing conditions such as molding pressure, temperature, compound composition, and reaction rates can all affect the morphology and, subsequently, the physical properties of IPNs. The reason that IPN is more sensitive to processing conditions than the constituent polymers may be due to strong interaction between the two polymerizations.

In this study, experimental and theoretical investigations of kinetics and heat transfer of polyurethane-polyester IPNs were attempted. Experimentally, IPNs were molded by reaction injection molding (RIM) and casting processes. Theoretically, a model based on the linear combination of the constituent components of IPN was proposed to simulate the reaction kinetics and heat transfer. Comparisons between experimental data and theoretical modeling were made and the differences were discussed.

EXPERIMENTAL

Materials

The ingredients of the polyurethane-polyester IPN used in this study are listed in Table I. The recipe can be divided into two parts, namely, a polyurethane and a polyester. The polyurethane chosen for this study consists of a soft segment based on a poly(ϵ -caprolactone diol) (TONE-0240, Union Carbide) and a hard segment based on a liquid form of 4,4'-diphenyl methane diisocyanate (MDI) (143-L, Dow Chemical) chain extended with 1,4-butanediol (BDO, Aldrich Chemical). MDI was degassed and demoi-
sturized at room temperature for 20 min to remove water and air. The treated MDI solution was then filtered under vacuum. TONE-0240 is a long chain diol with a number-average molecular weight of 2000 and is a solid at room temperature. A heating plate was used to melt this material. BDO is a low molecular weight diol with a viscosity slightly higher than that of water. The mixture of the molten TONE-0240 and BDO was degassed for 40 min at 60°C under vacuum to remove water and air. The molar ratio of TONE-0240/MDI/BDO was set at 1/6/5 which is a typical recipe for RIM elastomers. The catalyst, dibutyl-

TABLE I
Materials Used in IPNs' Study

Ingredients	Percentage
<i>Polyurethane (50%) in IPN</i>	
MDI (Dow, 143L)	41
Polyol (Union Carbide, TONE-0240)	48
Butanediol (Aldrich, BDO)	11
Catalyst (M&T Chemical, T-12)	0.033 (casting) 9.1 (RIM)
<i>Polyester (50%) in IPN</i>	
65% unsaturated polyester in styrene (OCF, P-325)	67
Styrene	33
Initiator (Lucidol, PDO)	1.38

tin dilaurate (T-12, M & T Chemical), was used as received. The amount of T-12 was 0.033% by weight of resin for a reasonable reaction time so that the sample preparation for casting process was possible. In the RIM process, the amount of T-12 used for polyurethane reaction was increased to 0.1% by weight of polyurethane resin.

For the polyester part, styrene was used as a crosslinking agent for the unsaturated polyester resin (P-325, OCF) which is a 1:1 propylene-maleate polyester combined with 35% by weight of styrene. Styrene was not freed of inhibitor in all cases. Initiator PDO (Lucidol) was used as received. [PDO (*t*-butyl peroxy-2-ethyl hexanoate) is a diluted high temperature initiator.] The amount of PDO used was 1.38% by weight of polyester resin. The molar ratio of styrene to the double bonds of unsaturated polyester was adjusted to 2:1.

The ratio of polyurethane to polyester was fixed at 50/50 by weight for most IPNs prepared. To study the effect of compound composition on kinetics and heat transfer of IPN, the ratio of polyurethane to polyester was also varied from 100/0, 75/25, 50/50, 25/75, to 0/100.

Instrumentation and Experimental Procedure

Kinetic Measurements

For the polyester resin, a Perkin-Elmer differential scanning calorimeter (DSC-2C) was employed to follow the reaction course. Due to the volatile nature of styrene, all samples were prepared in volatile sample pans which are capable of withstanding at least 30 psia internal pressure after sealing. Ingredients of each sample were weighed in a balance (Mettler, Model-80) with a total weight in the range of 20–25 g. When the weighing was completed, all ingredients were mixed thoroughly to ensure a homogeneous solution. About 15 mg of the sample was then transferred to the sample pan. A dry nitrogen supply was employed to purge the oxygen and moisture that might exist inside the sample holder. An empty pan with the weight equivalent to that of the sample pan was put in the reference pan holder. The reaction exothermic rate versus time was measured in the isothermal mode. To check if residual activity existed after an isothermal run, a scanning run was performed from room temperature to 237°C, which is far above the glass transition temperature of both polyurethane and polyester. This scanning run ensured the completion of the polymerization. A second scanning run was conducted immediately after the first scanning to determine the base line.

The thermal data measured during reaction were converted to the fractional conversion results as a function of time. Several assumptions are made for the calculations. First, there is only one reaction taking place at a time and, second, the thermal properties of the system are assumed unchanged during reaction. For unsaturated polyester resins, kinetic parameters were determined from isothermal reactions at 90, 100, and 110°C.

For catalyzed urethane reaction, the conventional analytical tools are not able to measure the reaction rate because the reaction is too fast to follow. A very useful method to follow the reaction course is the measurement of adiabatic temperature rise.^{16–18} The kinetic parameters and the heat of

reaction of polyurethane reaction were determined using the adiabatic temperature rise method. An insulated paper cup was used as the reactor with a thermocouple inserted in the center and about 1 cm from the bottom of the paper cup to measure the temperature rise. A laboratory-scale RIM machine was used to provide thorough mixing of the reactants. The reaction was so fast that the error due to adiabatic assumption was negligible. After the center temperature reached maximum, it cooled down at a rate less than $0.2^{\circ}\text{C}/\text{min}$. The measured temperature rise, along with the density and heat capacity of resins, were used to calculate the heat of polyurethane reaction, assuming constant density and heat capacity.

Reaction Injection Molding

A laboratory-scale RIM machine was constructed to carry out the experimental work. This machine is capable of delivering up to 250 mL of liquid at rates up to 125 mL/s and a maximum pressure of 2000 psi in the material cylinder. Using a 0.635 cm (1/4 inch) diameter mixing chamber with 0.0794 cm (1/32 inch) diameter nozzles, these flow rates are able to produce nozzle Reynolds numbers (Re) in the order of 300 to 500 for the reaction systems explored in this work. More detailed description of this machine can be found elsewhere.¹⁹

To test the mixing and curing characteristics of the reaction systems, reactants were mixed by impingement mixing in the RIM machine and injected into an adiabatic reactor (i.e., an insulated paper cup). Adiabatic temperature rise versus time was recorded for mixtures produced. For IPN reactions, the initial material temperature was set at 55°C . The high exotherm released from polyurethane can be used to trigger the polymerization of polyester.

Casting

To simulate, slow processes in reactive polymer processing such as resin transfer molding (RTM), a casting set-up was designed to study the heat transfer of polyurethane-polyester IPNs. A glass tube with an inner diameter of 2.25 cm and an outer diameter of 2.45 cm was used for the casting experiment. IPN components were first mixed in a suction flask by a magnetic stirrer until no bubble was observed. This bubble-free mixture was then transported to the casting tube. A rubber stopper with two thermocouples passing through it was provided to tightly seal the casting tube to prevent any volatile loss of styrene monomer at high temperatures. Once the IPN mixture was in the tube, polymerization was allowed to proceed and the temperature profiles were recorded. One thermocouple was positioned near the center and the other near the wall to measure the temperature profiles across the tube. The reactor was set in a constant temperature bath using aqueous ethylene glycol solution as heating/cooling medium. A mechanical stirrer was inserted in the bath to maintain a homogeneous heating/cooling effect. Deviation of bath temperature from set point was within 1°C . Two casting temperatures of 80 and 120°C were used.

To check for residual activity in the cast IPN samples, a Fourier transform infrared spectroscope (FTIR) (Nicolet, Model 20-DX) with a resolution of 4 cm^{-1} was employed. The sample from casting experiment was ground into

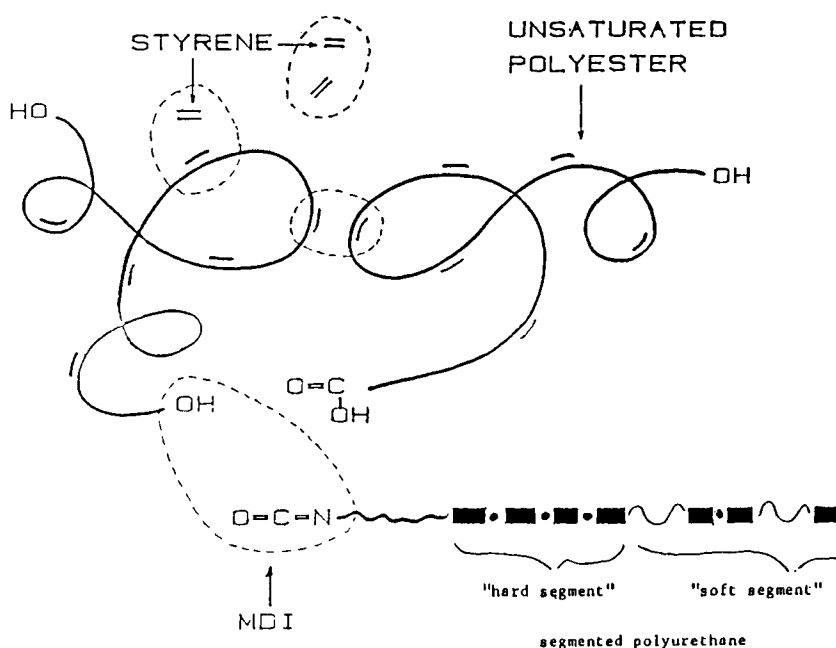


Fig. 1. Schematic diagram showing the reaction mechanism of PU/PES IPN.

powder using a grinder. The ground powder was then mixed and diluted with potassium bromide (KBr) powder which is infrared inactive and transparent. About 10 mg IPN sample was diluted with 400 mg KBr. The mixture was then put into a Perkin-Elmer pellet-making device under a press with pressure up to 1000 psi. A transparent thin KBr pellet (~ 0.05 cm) of 1.3 cm diameter was obtained and was analyzed by FTIR at room temperature. The spectrum was obtained with the average of 10 scans.

RESULTS AND DISCUSSIONS

The reaction mechanism of polyurethane–polyester IPN is schematically described in Figure 1. The long chains represent unsaturated polyester molecules that are prepolymers with molecular weight ranging from 500 to 3000 and C=C bonds ranging from 6 to 10 per molecule. Styrene monomer serves as a crosslinking agent to link C=C bonds on the adjacent polyester molecules. Isocyanates react with polyols and diols to form soft and hard segments in the urethane phase. Grafting between the two phases may occur through the reaction of isocyanate groups and hydroxyl or carboxyl groups at the end of polyester molecules. Such a multiphase system may be considered as a grafted IPN.

Kinetic Measurement of IPNs by DSC

Figure 2 shows rate profiles of typical polyurethane and polyester reactions measured by DSC in isothermal mode. In general, the reaction of polyurethane (a step-growth type) starts immediately after mixing. The maximum reaction rate happens at the very beginning of polymerization. On the other hand, the reaction of styrene–unsaturated polyester (a free radical type)

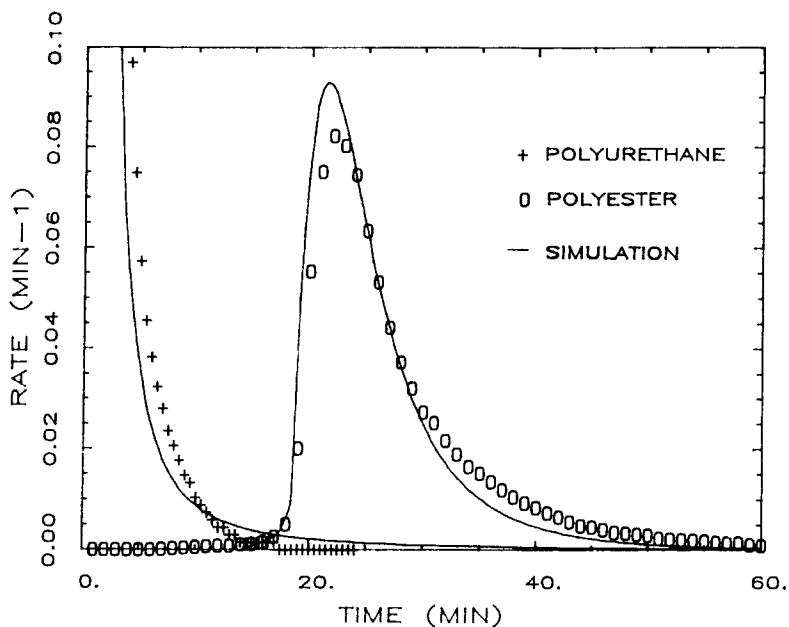


Fig. 2. Comparison of experimental data and model prediction of reaction rate vs. time for polyurethane (+) and polyester (O) at 353.5 K.

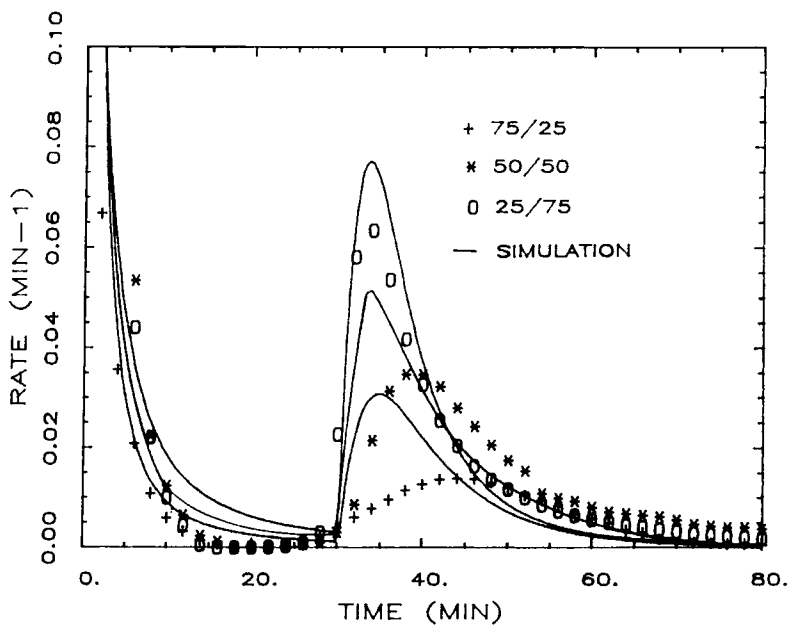


Fig. 3. Comparison of experimental data and model prediction of reaction rate vs. time for IPNs at three compositions (353.5 K). (+) 75/25; (*) 50/50; (O) 25/75.

starts after an induction period. The initial reaction is relatively slow and then reaches a maximum exothermic rate. The induction time and the time to reach the maximum exotherm are temperature dependent.

Figure 3 illustrates the compositional effect on the polyurethane–polyester IPN reaction measured by DSC. Due to different reaction mechanisms (i.e., polyurethane is activated by mixing, while styrene–unsaturated polyester is often thermally activated), urethane polymerization always occurs in a condition in which polyester phase is either unreacted or only partially reacted, which resembles a polyurethane solution polymerization with polyester resin serving as a solvent. On the hand, styrene–unsaturated polyester polymerization often occurs in a condition where the polyurethane phase is either totally or partially reacted, which means most polyester reaction occurs in the solid state.

Qualitatively speaking, while polyurethane reaction remained nearly the same, increasing polyurethane content had a great effect on styrene–unsaturated polyester reaction. When the polyurethane content was increased, not only did the polyester reaction peak move to the right, which indicates a longer induction time, but the peak also became broader, indicating a longer reaction time. This implies that the diffusion of polyester reactants in a high-polyurethane content IPN became more difficult.

Reaction Injection Molding

Shown in Figure 4 is the adiabatic temperature rise of polyurethane resin with a gel time less than 10 s and a maximum adiabatic temperature rise of

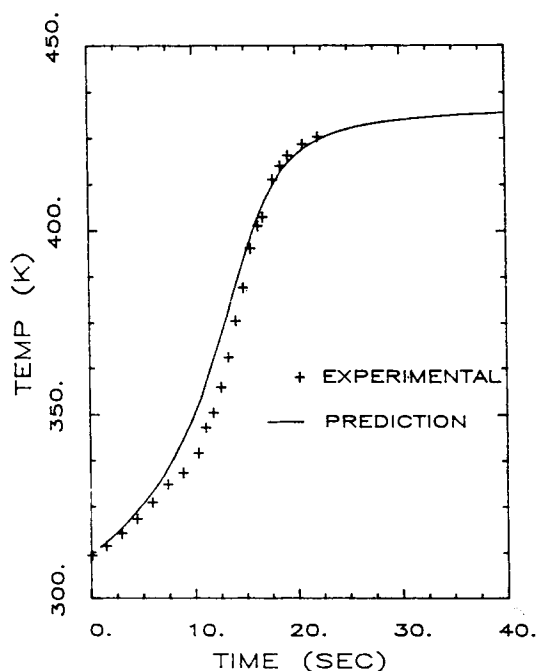


Fig. 4. Adiabatic temperature rise of polyurethane reaction in RIM. The solid line is curved fitted by multiple linear regression. (+) Experimental; (—) prediction.

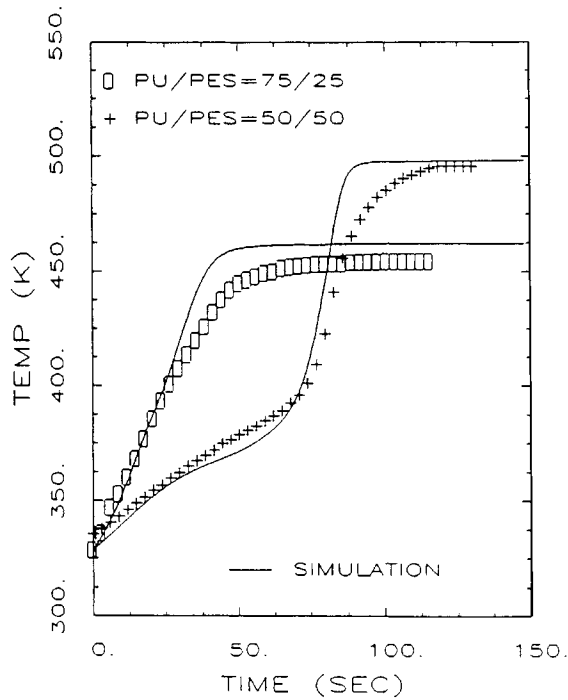


Fig. 5. Adiabatic temperature rises of IPN reactions in RIM for two compositions. (○) 75/25; (+) 50/50.

117.5°C. The kinetic parameters of polyurethane reaction was determined from this temperature rise curve, which will be discussed later.

For IPNs, Figure 5 shows that adding the polyester phase promotes the maximum adiabatic temperature rise up to 127.5°C for the 75/25 (PU/PES) IPN and 167°C for the 50/50 IPN. The initial temperature rise of the 50/50 IPN is slower than that of 75/25 IPN, mainly due to the lower polyurethane content. However, the temperature rise of PES is higher in the case of 50/50 IPN. Since the PDO-initiated polyester is a thermally activated reaction, the polymerization can only happen when sufficient heat is released from the polyurethane reaction. Therefore, the reaction of IPN in adiabatic condition is in a sequential order as indicated by the S-shaped temperature rise of the 50/50 IPN reaction shown in Figure 5. For the 75/25 IPN, the trend is not that obvious since the entire reaction is polyurethane dominated. These characteristics are indicative of possible uses of IPNs in applications where increased flow times are necessary but longer cycle times are not acceptable. One such application is in the area of structural RIM (i.e., mat-reinforced RIM), where glass fibers placed in the mold require longer flow time to fill the mold and to wet out the glass fibers, but fast cycles are critical in the economics of the application.

Casting

Temperature profiles of polyurethane and polyester reactions in casting at a mold temperature of 353.5 K are given in Figure 6. The difference of tempera-

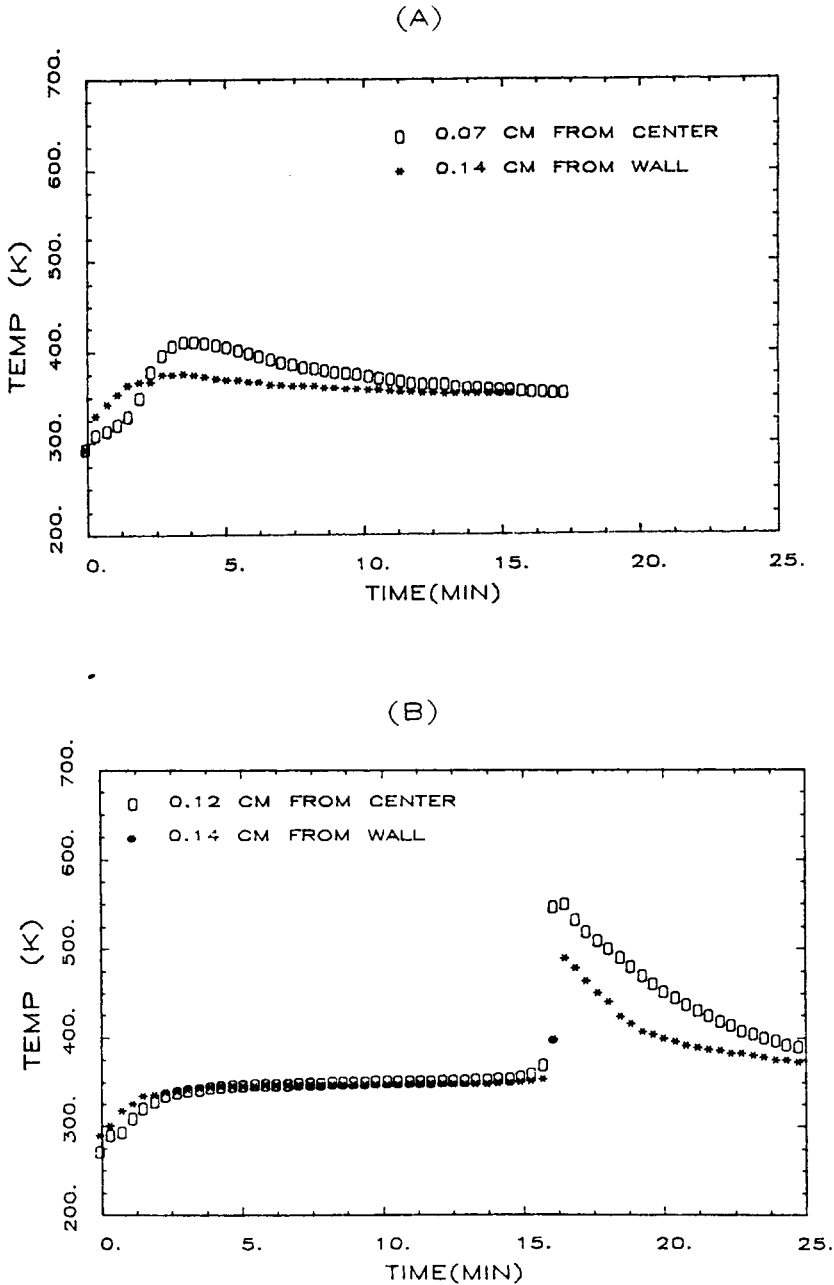


Fig. 6. Temperature profiles of cast polyurethane (A) and polyester (B) at 353.5 K.

ture profile at the center and the wall is obvious in both cases. For the material cured near the tube wall, the temperature change was moderated by heat exchange with the tube surface. For the mixing-activated polyurethane reaction, the reaction started upon heating, while for the thermally initiated polyester resin, the reaction started after an induction period.

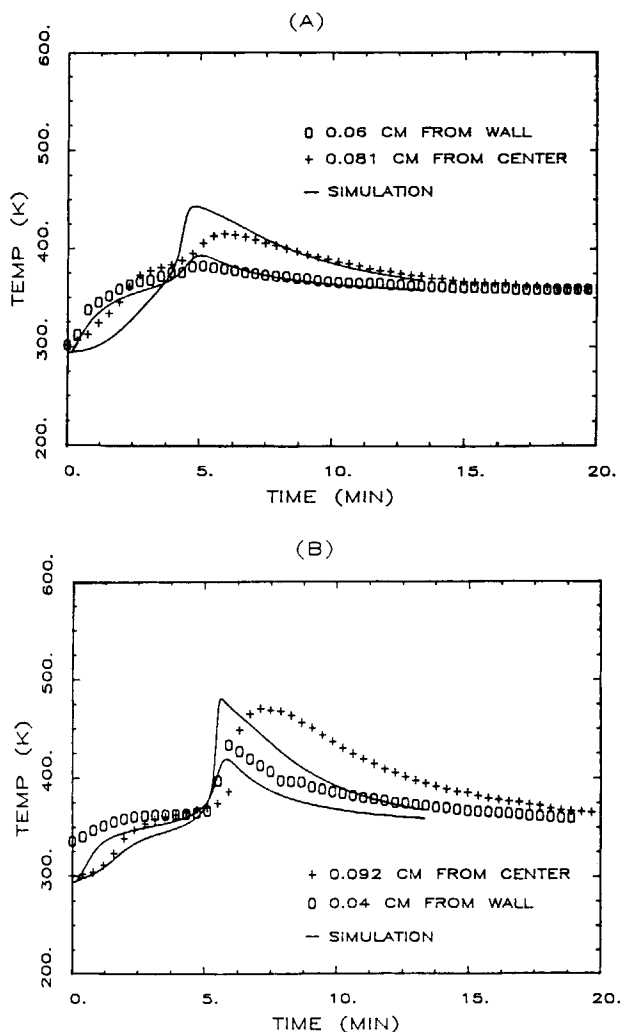


Fig. 7. Temperature profiles of cast 75/25 (A) and 50/50 (B) IPNs at 353.5 K.

To explore the effect of compound composition of curing of IPN, the composition ratio was varied. Casting results of IPNs at 353 K are given in Figure 7. The temperature profile, especially the maximum temperature rise, is composition dependent. Comparisons between IPNs show that increasing polyester content in IPNs causes a higher reaction exotherm. The maximum temperature of the 75/25 IPN is about 100°C less than that of pure polyester resin. The IPNs show a curing rate in between those of the constituent components. Figure 8 shows temperature profiles of the 50/50 IPN cast at 393 K. As expected, at a higher molding temperature, the reaction time is shorter and the maximum temperature is higher. Although it is not possible to monitor conversion profiles of polyurethane and polyester during casting, the final conversion of the case samples can be analyzed using infrared spectroscopy (IR) since the IR spectrum releases information about all the possible IR-active functional groups of polymers.

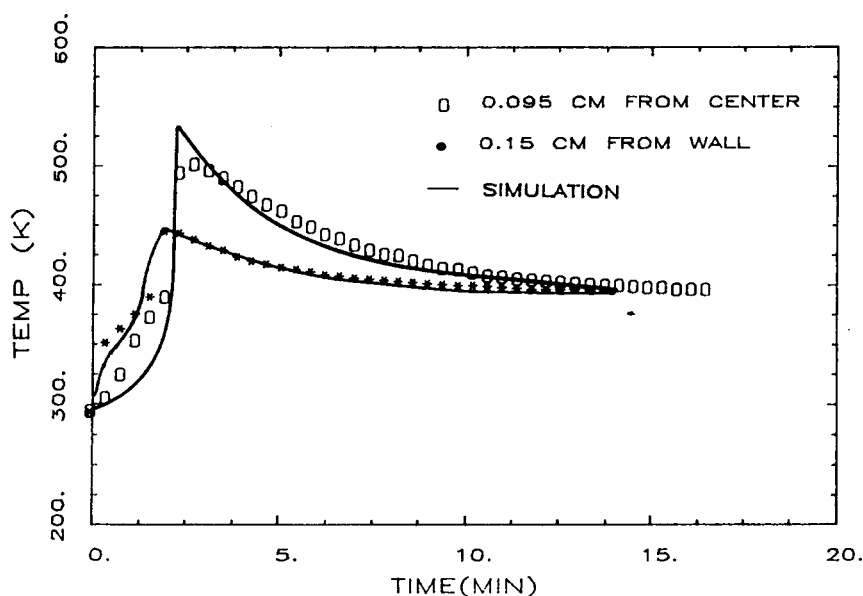


Fig. 8. Temperature profiles of cast 50/50 IPN at 393.5 K.

Infrared analysis is based upon the peak change of functional groups or characteristic linkages during reaction period. Therefore, there is more than one peak which may change when reactions take place. For example, Figure 9 shows the FTIR spectrum for a 50/50 IPN system before reaction. In principle, the isocyanate peak (2278 cm^{-1}), hydroxyl peak (3428 cm^{-1}), amine

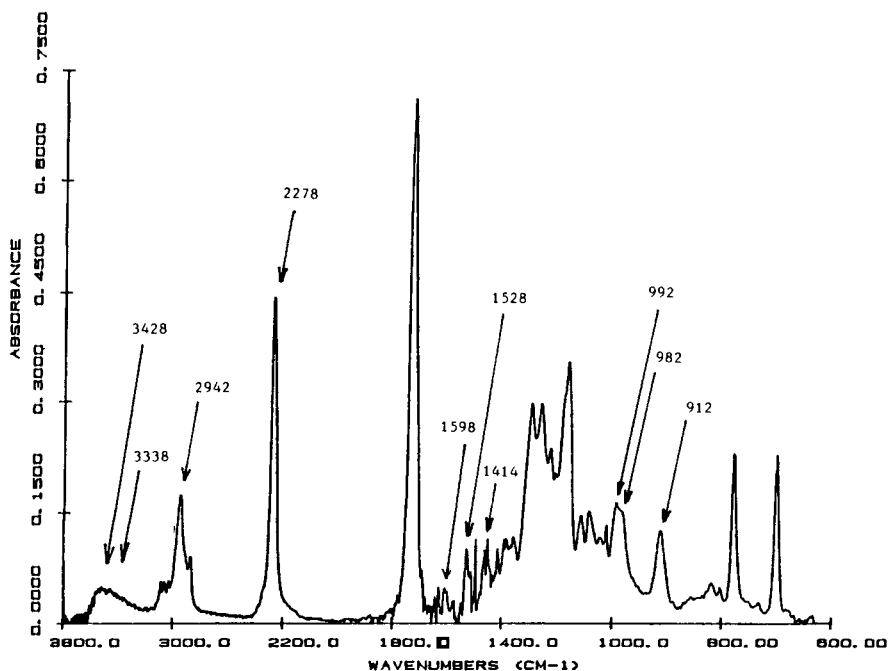


Fig. 9. FTIR spectrum of 50/50 IPN before reaction.

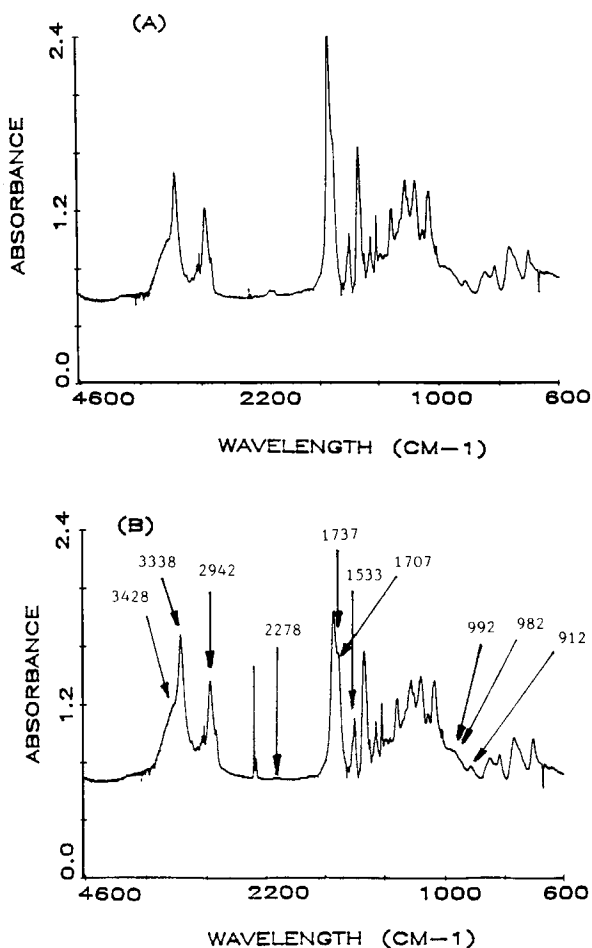


Fig. 10. FTIR spectra of 393.5 K-cast 50/50 IPN sampled (A) at wall and (B) at center of glass tube.

peak (3338 cm^{-1}), and urethane peak (trans at 1528 cm^{-1} , cis at 1414 cm^{-1}) can all be followed during urethane polymerization.

Polyester reaction can also be followed in spite of urethane reaction.²⁰ The peak at 1598 cm^{-1} indicates polystyrene formation, which is located in a region where too many peaks are overlapped with one another. Therefore, the reaction conversion of polyester is better determined from the consumption of styrene C=C bonds at peaks 992 and 912 cm^{-1} ($\text{CH}_2=\text{CH}$ deformation), and polyester C=C bonds at peak 982 cm^{-1} (trans $\text{CH}=\text{CH}$ deformation).

Figure 10 shows FTIR spectra of samples taken from the center and wall of a cast 50/50 IPN. The wall temperature during casting was 393.5 K. Both spectra were normalized according to an internal reference peak at 2942 cm^{-1} ($-\text{CH}$ stretching), which did not alter during polymerization. For polyester phase, peaks at 912 , 992 cm^{-1} (C=C for polystyrene), and 982 cm^{-1} (C=C for polyester) suggest that the reaction is nearly complete, with a small amount of residual activity. For polyurethane, the complete disappearance of $-\text{NCO}$ peak at 2278 cm^{-1} suggests that isocyanate reaction is complete in both

samples. However, peaks at 3428 cm^{-1} (—OH stretching), 3338 cm^{-1} (—NH stretching of amide), and $1737, 1707, 1533\text{ cm}^{-1}$ (amide I and II) all show different changes in peak height. The peak at 1737 cm^{-1} (amide I peak) of the IPN sample taken near the wall is higher than that of IPN sample taken near the center, while the peak at 3428 cm^{-1} (—OH stretching) of the IPN sample taken near the wall is lower than that taken near the center. Since the formation of urethane is the result of a reaction between isocyanate and hydroxyl groups, the consumption (change of peak height) of —OH peak should be equal to the consumption of —NCO peak and the appearance of amide I peaks if there are no side reactions. The results suggest that due to different thermal history along the radial direction in mold, samples at different locations experienced different polymerization mechanism. Some possible side reactions might take place for the cast sample, which include allophanate, biuret, urea, dimer, and trimer formations. Figure 10 implies that the sample at the wall has more urethane formation than the sample at the center. The formation of trimer (isocyanurate) at center is highly possible when reaction temperature exceeds 480 K .²¹ However, IR cannot distinguish the formation of urethane from isocyanurate.

KINETIC AND HEAT TRANSFER MODELING OF IPN REACTION

Kinetics

For externally catalyzed step-growth polymerizations such as polyurethane, a simple n -th order reaction model with Arrhenius temperature dependence is assumed, i.e.,

$$r_u = C_{uo} \frac{d\alpha}{dt} = A_u \exp\left(-\frac{E_u}{RT_u}\right) C_{uo}^n (1 - \alpha)^n \quad (1)$$

where r_u is the reaction rate of polyurethane, C_{uo} is the initial concentration of isocyanate functional groups, α is the extent of polyurethane reaction, E_u is the activation energy, R is the gas constant, T_u is the reaction temperature, and n is the reaction order. u stands for polyurethane phase. Kinetic parameters in Eq. (1) were determined by the adiabatic temperature rise measurement. The major assumptions made are as follows:

1. Homogeneous and well mixed system.
2. Reaction order n being the same throughout the entire reaction.

The energy equation for adiabatic condition is:

$$\rho_u C_{pu} \frac{dT_u}{dt} = -\Delta H_u r_u \quad (2)$$

where ρ_u is density, C_{pu} is heat capacity, ΔH_u is the heat of reaction of polyurethane. The extent of reaction is directly proportional to the amount of

heat generated if constant density and heat capacity are assumed. Thus,

$$\frac{C_u}{C_{u0}} = (1 - \alpha) = \frac{(T_{ad} - T_u)}{(T_{ad} - T_{u0})} \quad (3)$$

where C_u is the isocyanate concentration, T_{ad} is the measured maximum adiabatic temperature, and T_{u0} is the initial material temperature.

For free radical polymerizations such as styrene-unsaturated polyester, a kinetic model proposed by Stevenson²² and Lee²³ is used. The following assumptions are made:

1. Diffusion of monomer is neglected in propagation step up to high conversion.
2. Homopolymerization of unsaturated polyester is negligible.
3. Copolymerization of styrene monomer and C=C bonds on polyester chains can be described by a single average rate constant.
4. No monomer reacts until the number of initiator radicals created is equal to the effective number of inhibitor molecules initially present.
5. Free radical termination is significantly slower than that in the polymerization of low molecular weight species.

With these assumptions, the free radical reaction can be expressed as:

Initiation

$$\frac{dR\cdot}{dt} = 2K_d I \quad (4)$$

Inhibition

$$qZ_o = 2fI_o \left[1 - \exp\left(-\int_0^{t_z} K_d dt\right) \right] = 2f(I_o - \bar{I}_o) \quad (5)$$

Propagation

$$\frac{dM}{dt} = -K_p MR\cdot \quad (6)$$

or

$$r_e = C_{e0} \frac{d\beta}{dt} = 2f\bar{I}_o K_p \left\{ (1 - \beta) \left[1 - \exp\left(-\int_0^{t-t_z} K_d d[t - t_z]\right) \right] \right\} \quad (7)$$

where $R\cdot$ is the free radical concentration, I_o and Z_o are the initial concentrations of initiator and inhibitor. \bar{I}_o is the concentration of initiator after all the inhibitors having been consumed, f is the initiator efficiency, q is the inhibitor efficiency, t_z is the induction time before propagation, K_d and K_p are the rate constants of initiator decomposition and monomer propagation,

M is the monomer concentration, and β is the fractional conversion. The values of K_d and K_p are assumed to be Arrhenius temperature dependent throughout the entire cure period, and

$$K_d = A_d \exp\left(-\frac{E_d}{RT}\right) \quad (8)$$

$$K_p = A_p \exp\left(-\frac{E_p}{RT}\right) \quad (9)$$

For model prediction of polyurethane–polyester IPN, the individual kinetic models are combined in a simple additive manner. No component interactions are considered here.

Heat Transfer Model

The following assumptions are made for the casting process:

1. One-dimensional heat conduction.
2. Negligible molecular diffusion.
3. Homogeneous and well mixed reaction system at $t = 0$.
4. No flow.
5. Physical properties such as density ρ_I , heat capacity C_{pI} , heat of reactions ΔH_i 's, and thermal conductivities k_i 's being temperature independent.
6. Intimate contact between reacting polymer and tube surface.

With these assumptions, the heat transfer equations of the casting process can be described as follows:

IPN phase:

$$\rho_I C_{pI} \frac{\partial T_I}{\partial t} = k \left[\left(\frac{\partial^2 T_I}{\partial r^2} \right) + \left(\frac{1}{r} \frac{\partial T_I}{\partial r} \right) \right] - \Delta H_u r_u - \Delta H_e r_e \quad (10)$$

where I stands for the IPN and e stands for polyester phase.

$$\frac{1}{k_I} = \frac{W_u}{k_u} + \frac{W_e}{k_e} \quad (11)$$

$$\frac{1}{\rho_I} = \frac{W_u}{\rho_u} + \frac{W_e}{\rho_e} \quad (12)$$

$$C_{pI} = W_u C_{pu} + W_e C_{pe} \quad (13)$$

where W_u and W_e are the weight fractions of polyurethane and polyester, respectively. The initial conditions are:

$$T_I = T_{I_0}, \quad \text{at } t = 0, \quad \text{for all } 0 \leq r \leq d_1 \quad (14)$$

$$\alpha = 0, \quad \text{at } t = 0, \quad \text{for all } 0 \leq r \leq d_1 \quad (15)$$

$$\beta = 0, \quad \text{at } t = 0, \quad \text{for all } 0 \leq r \leq d_1 \quad (16)$$

and boundary conditions are:

$$\frac{dT_I}{dr} = 0, \quad \text{at } r = 0, \quad \text{for } t > 0 \quad (17)$$

$$T_I = T_g, \quad \text{at } r = d_1, \quad \text{for } t > 0 \quad (18)$$

or

$$-k_I \frac{dT_I}{dt} = -k_g \frac{dT_g}{dt}, \quad \text{at } r = d_1, \quad \text{for } t > 0 \quad (19)$$

where d_1 is the inner radius of the glass tube.

Glass phase:

$$\rho_g C_{pg} \frac{\partial T_g}{\partial t} = k_g \left[\frac{\partial^2 T_g}{\partial r^2} + \frac{1}{r} \frac{\partial T_g}{\partial r} \right] \quad (20)$$

with initial conditions:

$$T_g = T_o, \quad \text{at } t = 0, \quad \text{for } d_1 < r < d_2 \quad (21)$$

where T_o is the heating/cooling water temperature, and d_2 is the outer radius of the glass tube.

The boundary conditions are:

$$-k_g \frac{dT_g}{dr} = h_w (T_g - T_o), \quad \text{at } r = d_2, \quad \text{for } t > 0 \quad (22)$$

and Eqs. (18) or (19), where h_w is the overall heat transfer coefficient between water and glass tube. The reaction equations have the following constraints:

$$\frac{d\alpha}{dt} = r_u, \quad \text{for } t > 0 \quad (23)$$

$$\frac{d\beta}{dt} = 0, \quad \text{for } t < t_2 \quad (24)$$

$$\frac{d\beta}{dt} = r_e, \quad \text{for } t \geq t_2 \quad (25)$$

TABLE II
Parameters Used in Modeling of IPN

Parameters	PU	PES	IPN	Glass
ρ (g/cc)	1.14	1.10	1.12	2.375
C_p (cal/g/K)	0.4	0.4	0.4	0.18
λ (cm ² /s)	7.9×10^{-1}	8.2×10^{-1}	8.0×10^{-1}	8.42×10^{-4}
ΔH (cal/g)	139.2	95.95	—	—
A_d (app. unit)	—	2.8×10^{16}	—	—
E_d (kcal/g-mol)	—	31.0	—	—
A_p (app. unit)	2.0×10^7	4.6×10^5	—	—
E_p (kcal/g-mol)	10.6	10.0	—	—
n (reaction order)	2.0	—	—	—

The coupled Eqs. (10)–(25) are solved simultaneously using Advanced Continuous Simulation Language (ACSL).²⁴ The parameters used in computer simulation are listed in Table II.

The adiabatic reaction in the RIM process is a special case of the energy equation [Eq. (10)]. Assuming no heat exchange with surroundings, the energy equation becomes:

$$\rho_I C_{pI} \frac{dT_I}{dt} = -\Delta H_u r_u - \Delta H_e r_e \quad (26)$$

Parameter Estimation

Polyurethane

The kinetic parameters of polyurethane reaction are estimated from the adiabatic temperature rise method. Combining eqs. (1)–(3) gives

$$\ln \frac{dT_u}{dt} = \ln \left[\frac{\Delta H_u A_u}{\rho_u C_{pu}} \right] + \frac{E_u}{RT_u} + n \ln \left[\frac{T_{ad} - T_u}{T_{ad} - T_{uo}} \right] \quad (27)$$

The variables dT_u/dt , $1/T_u$, and $[(T_{ad} - T_u)/\Delta T_{ad}]$ can be evaluated from the temperature versus time curve of the adiabatic polymerization. By using a multiple linear regression procedure, one can obtain the order of reaction n , the activation energy E_u , and the frequency coefficient of reaction rate A_u . The parameters obtained are listed in Table II.

Styrene–Unsaturated Polyester

The kinetic parameters of polyester reaction are estimated following Lee's method.²³ Rearranging Eq. (5) in the following form:

$$\ln t_z = \ln \left\{ -\frac{1}{A_d} \ln \left(1 - \frac{qZ_0}{2fI_0} \right) \right\} + \frac{E_d}{R} \frac{1}{T} \quad (28)$$

By plotting $\ln t_z$ versus $1/T$ of isothermal DSC runs, a straight line is obtained. The slope gives the activation energy of initiator decomposition, $E_d = 31.0$ kcal/g-mol, and the intercept gives $A_d = 2.8 \times 10^{16}$. The exact amount of inhibitor in the resin is unknown. It is assumed that $qZ_0/2fI_0 = 0.01$. For isothermal DSC curves, the maximum rate of reaction occurs at a point, $t = t_m$, where

$$\frac{d^2\beta}{dt^2} = 0 \quad (29)$$

Combining eqs. (29), and (7), we have

$$(2f\bar{I}_0 A_p) \exp\left(-\frac{E_p}{RT}\right) = \frac{k_d \exp[-K_d(t_m - t_z)]}{1 - \exp[-K_d(t_m - t_z)]} \quad (30)$$

If we define $2f\bar{I}_0 A_p = \bar{A}_p$, the kinetic parameters \bar{A}_p and E_p can be calculated by the same way to calculate A_d and E_d . The results are $\bar{A}_p = 4.6 \times 10^5$ and $E_p = 10.0$ kcal/g-mol. Kinetic parameters of polyester reaction are also listed in Table II, along with other physical properties used in simulation.

Model Prediction

Comparison of model prediction and measured reaction rates of pure polyurethane and polyester by DSC in isothermal mode is shown in Figure 2. The prediction of each component is reasonably accurate. Figure 3 compares the model prediction and experimental data of IPNs measured by DSC in isothermal mode. The results show that for an IPN with lower polyurethane content (i.e., 25/75 IPN), the deviation of model prediction from experimental data is small. As the amount of polyurethane is increased to 50%, the prediction of polyurethane reaction remains satisfactory, a large deviation, however, exists in the prediction of polyester reaction. Compared to the predicted results, the experimental data show a delay of the onset of polyester exotherm and a lower and broader exothermic peak. In the prediction of reaction profile of IPNs with higher polyurethane content (e.g., 75/25 IPN), a much larger deviation is observed.

Since the IPN model used is a simple combination of two component models in an additive mode, the discrepancy between model prediction and DSC experimental results may be attributed to some possible component interactions. Since polymerizations of both components are diffusion controlled, especially in the high-conversion region, a strong diffusion effect may exist in the polyester phase because polyester polymerization takes place after polyurethane polymerization.

The predicted temperature rise versus time curves of IPN reactions in RIM are shown in Figure 5. The predictions follow the experimental data closely, which are much better compared to the predictions of isothermal reactions shown in Figure 3. This may be because the adiabatic reaction is so fast and exothermic that component interactions are totally or partially eliminated.

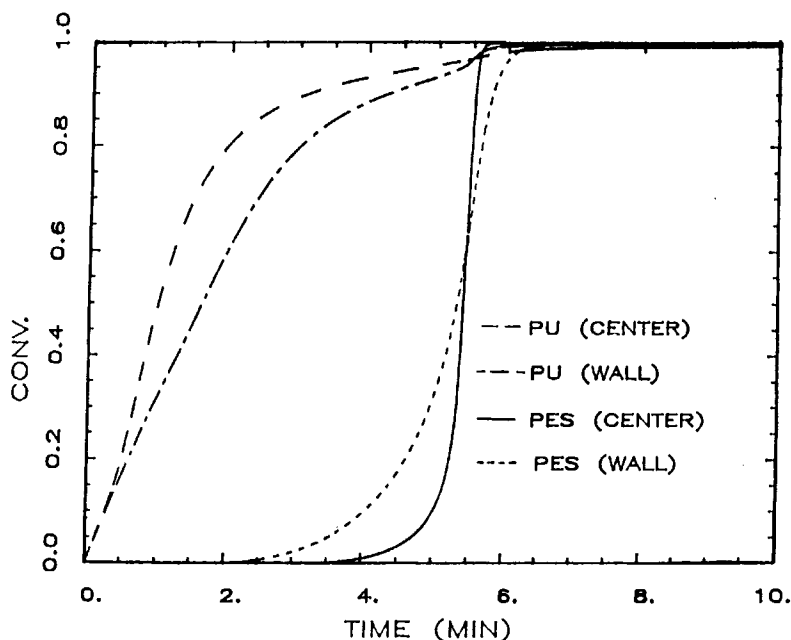


Fig. 11. Predicted conversion profiles of 50/50 IPN cast at 353.5 K.

Model predictions of temperature profiles in the casting of IPNs are shown in Figures 7 and 8. The prediction of 75/25 IPN [Fig. 7(A)] is reasonably good. For the 50/50 IPN [Fig. 7(B)], the prediction is good in terms of reaction exotherm, but it shows a much sharper temperature drop in the cooling region. For IPNs with low polyurethane content, the error in the cooling region is due to the lack of free radical termination in the modeling of polyester reaction. Figure 8 shows the comparison of predicted and measured temperature profiles of a 50/50 IPN cast at 393 K. The prediction is much better than that at lower molding temperature. Figure 11 shows the predicted conversion profiles of a 50/50 IPN sample cast at 353 K. The conversion at the center is higher than that at wall for polyurethane reaction. For polyester reaction, the material near the wall has a higher initial conversion than that at the center. But when the center temperature is greatly increased by reaction exotherm, the conversion at the center becomes higher than that at the wall.

Generally speaking, the model gives a reasonably good prediction of temperature profiles in casting and adiabatic temperature rises in RIM, but not for isothermal reactions. The discrepancies may result largely from component interaction since the model proposed is based on the additivity rule of constituent components and without any consideration of interaction. The interactions mainly come from the "cage effect" of polyurethane on polyester and the "solvent effect" of polyester on polyurethane.¹²

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