

ON THE USE OF DSC AND DMA TO CHARACTERIZE THE DEGREE OF MIXING OF IPNs PROCESSED BY RIM *

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ABSTRACT

In Reaction Injection Molding (RIM), the degree of mixing is governed by the Reynolds number (Re) of the streams. Dimensional analysis predicts the mix quality to vary as $(Re)^{-9/4}$. Past experiments at MIT showed that mixing did follow this relationship. The mixing theory is based on the hypothesis that the large scale mixing of the fluid components always occurs at high Reynolds numbers. On the other hand, the small scale of segregation of the mixture depends on the relative size of the turbulent eddies once the Reynolds number exceeds the critical value for the laminar/turbulent transition ($Re \approx 50$). There were, however, no experimental values to predict these small scale features.

Recent experiments have indicated that in the processing of Interpenetrating Polymer Networks (IPN) by RIM, the physical properties of the resulting alloys are highly dependent on the reaction kinetics and the degree of mixing. At high Reynolds numbers, thermal and dynamic mechanical measurements provide evidence of interphase mixing by shifts in the transition temperatures of the individual components.

INTRODUCTION

The sequential or simultaneous polymerization of a second monomer in urethane casting formulations to form interpenetrating polymer networks (IPNs) has been known for some time [1,2]. It is only recently, however, that this class of materials has been applied to reaction injection molding (RIM). The interest arises from the synergistic behavior obtained by reinforcing a rubbery matrix (polyurethane) with a dispersed polymeric organic glass (vinyl monomers, cyclic monomers, polyesters, or epoxies). Tailoring the compositions and controlling the corresponding reaction kinetics can provide two-phase polymers with a large range of morphologies.

The attraction of IPN systems is provided by the possibility of reinforcing a polymer matrix without the equipment problems associated with the use of

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inorganic fillers. These drawbacks include — to name a few — high viscosity slurries, rapid settling of fibers and particulates, and progressive erosion and wear of machine components (ball valves, delivery pipelines, cylinder liners in the metering pumps, and orifices at the impingement head).

Another attractive feature is derived from the choice of the second polymeric phase. Practice requires transferring the heat generated by the polyurethane reactants in the mold. A poorly controlled exotherm can shift the reaction from urethane to allophanate or urea to biuret, and consuming in the process excess isocyanate. It might also lead to partial degradation. With a polyurethane/vinyl polymer IPN system, however, the heat can be put to a more effective use. In this case, the large exotherm will thermally trigger the catalyzed vinyl monomer in the reaction mixture.

Precise stoichiometric metering and thorough mixing are essential to the success of RIM. The basic process consists of two or more streams of reactants emerging at high pressure from nozzles and impinging upon one another in a small chamber. The resulting turbulent motion rapidly reduces the scale of segregation of the mixture allowing diffusion to take place for complete reaction. A scale of mixing on the molecular level is ideally needed in the impingement mixing of IPN systems. This is rather difficult to achieve in practice. The strategy calls, therefore, for the creation by turbulence of a micromixing scale as small as possible. By adjusting the gel time of the reacting mixture, some control on the rate of phase separation can be achieved.

Basic work at MIT with low viscosity systems [3–5] showed that the small scale features of the mixing process vary according to the relation

$$l_m/D \sim \text{Re}^{-3/4}$$

where l_m = characteristic length scale of the mixture; D = impingement nozzle diameter; Re = stream Reynolds number based on the nozzle diameter. The correlation observed, however, was obtained with water/glycerine and liquid metals. This paper presents some preliminary results on the extent of mixing obtained with a polyurethane/polyester IPN processed by RIM.

EXPERIMENTAL

The materials used and their descriptions are listed in Table 1. Both polyol and polyester were dried at 70°C under vacuum (2 mm Hg) for 12 h. The monomeric styrene added to the polyester as a diluent was distilled under vacuum (10 mm Hg) at 50°C. The isocyanate, catalysts, and promoter were used without further purification.

The reactants were mixed in a specially designed high pressure RIM system which is described in more detail elsewhere [6]. Briefly, reactants were metered at adjustable pressures and velocities into a three stream impinge-

ment head. The polyol, T-12 and MEKP catalysts, and cobalt promoter were blended in one stream; polyester and isocyanate formed the second and third, respectively. Mixing occurs within a small chamber capable of handling impingement pressures up to 100 000 psi. The temperature of the mold was set concurrently at a predetermined temperature which controls the gel time of the IPN mixture.

Upon gelation, the specimens were postcured at 120°C for 1 h to allow the polymerization reaction to complete. Calorimetric studies were carried out on a Perkin-Elmer differential scanning calorimeter (model DSC-2). Specimens weighing around 20 mg were used. Measurements were done from -100 to 150°C under nitrogen and at a heating rate of 10°C min⁻¹.

Dynamic mechanical analysis was obtained with a Rheovibron Model DDV II direct-reading dynamic viscoelastometer. Sinusoidal deformation at 110 Hz was applied to samples 1.0 × 0.064 × 0.029 in (25.4 mm × 1.63 mm × 0.74 mm). The temperature range scanned and the heating rate were similar to the DSC case.

RESULTS AND DISCUSSION

Figure 1 shows the DSC scans of a 50/50 polyurethane/polyester IPN composition formed at different stream Reynolds numbers. In this paper, the glass transition temperature, T_g is defined as the temperature at which the change in heat capacity is half its maximum value. In a typical run, the

TABLE I
Material compositions and suppliers

Material	Composition	Supplier
Niax D-337	Polyoxypropylene triol, ethylene oxide capped and grafted with 10% acrylonitrile by weight	Union Carbide
Isonate 191	Modified diphenyl methane diisocyanate with 30% NCO by weight	Upjohn Co.
Laminac 4123	Orthophthalic polyester with about 20% styrene monomer	USS Chemicals
T-12	Dibutyltin dilaurate	M&T Chemicals
Lupersol Delta X-9	Methyl ethyl ketone peroxide in plasticizer	Penwalt Co.
Cobalt promoter	Cobalt naphthenate 12%	USS Chemicals
Styrene		Polysciences

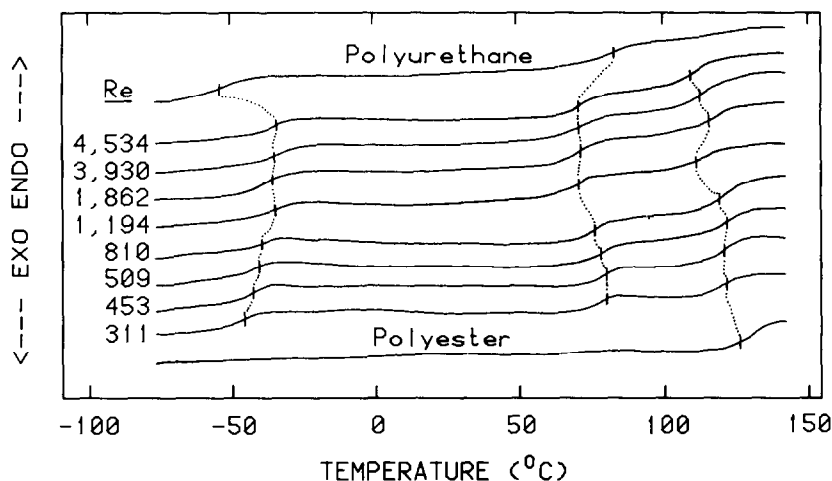


Fig. 1. DSC scans of a 50/50 polyurethane/polyester IPN composition formed at different stream Reynolds numbers. Mold temperature 248°F (120°C); gel time 125 s.

Reynolds number of the polyol line [Re_{polyol}] is approximately 10% higher than that of polyester [$Re_{\text{polyester}}$]. Although the lowest Reynolds number controls the scale of mixing and the resulting IPN morphology, Re_{polyol} rather than $Re_{\text{polyester}}$ was given to provide a basis for comparison with current commercial RIM machinery. For the IPNs formed at varying Reynolds numbers, the mold was set at 248°F (120°C) to maintain a constant gel time of 125 s.

Listed in Table 2 are T_g values obtained with the DSC and Rheovibron. The soft and hard segments of the polyurethane exhibit relaxation behaviors

TABLE 2

Glass transition temperatures^a of a 50/50 polyurethane/polyester IPN as a function of stream Reynolds numbers (mold temperature 248°F (120°C); gel time 125 s)

Polyol stream Reynolds No.	T_{g1} (°C)		T_{g2} (°C)		T_{g3} (°C)	
	DSC	Rheovibron	DSC	Rheovibron	DSC	Rheovibron
311	-47	-45	+79	+80	+125	+122
453	-45	-43	+79	+80	+123	+120
509	-43	-42	+78	+78	+122	+121
810	-40	-41	+77	+76	+120	+118
1194	-38	-36	+73	+70	+117	+110
1862	-37	-37	+72	+71	+115	+116
3930	-35	-36	+70	+70	+112	+113
4534	-35	-35	+70	+70	+110	+109

^a Polyurethane T_g : T_{g1} (soft segments) and T_{g2} (hard segments). Polyester T_g : T_{g3} .

at T_{g1} and T_{g2} , respectively. T_{g3} is the glass transition temperature of the polyester component. Good correlation between DSC and Rheovibron data was observed. At a fixed gel time, the dramatic evidence of the creation of a smaller mixing scale with higher stream Reynolds numbers can be seen by the inward shift of the glass transition temperatures—higher values for T_{g1} and lower values for both T_{g2} and T_{g3} . The relatively sharp transitions observed suggest the possibility of chain entanglement and interpenetration at the domain boundaries leading to increased interphase mixing. Chemical topology seems to be preserved since infrared analysis indicated no reaction between the two networks.

It was also found that the smaller scale obtained with better mixing led to improvements in thermal dimensional stability and stress-strain properties [7]. For instance, with the 50/50 polyurethane/polyester composition molded at 248°F (120°C), an order of magnitude increase in the stream Reynolds number can lead to improvements of 20 and 16% in heat sag resistance and tensile strength, respectively.

The IPN morphology is similarly affected by the reaction kinetics of the blend. DSC measurements of 50/50 polyurethane/polyester IPNs synthesized at varying gel times are depicted in Fig. 2. The corresponding glass transition temperatures are listed in Table 3. The stream Reynolds numbers were kept constant for these impingement runs. Adjustments were made, however, in the catalyst concentration and the mold temperature to result in different induction times to reach the gel point.

At constant Reynolds numbers, as the gel time was decreased, an inward shift in the T_g s was observed. The trend was analogous to the previous case where the gel time was held constant and synthesis was carried out as a

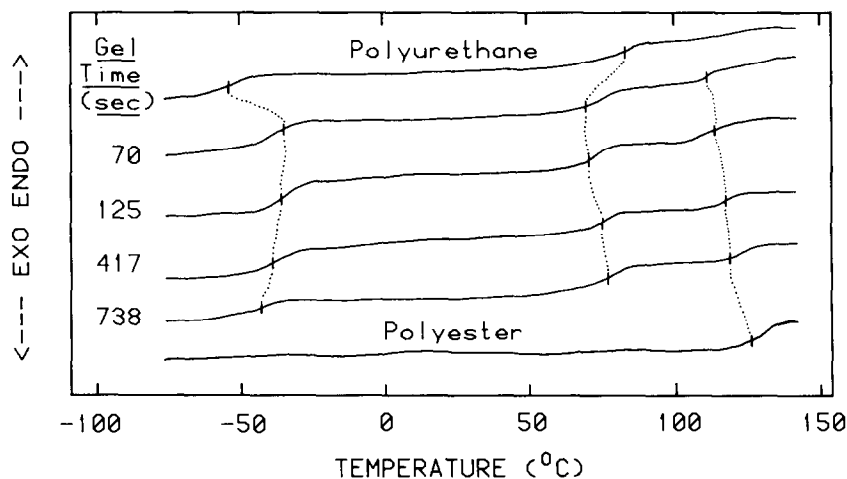


Fig. 2. DSC scans of a 50/50 polyurethane/polyester IPN composition formed at different gel times. Stream Reynolds numbers: polyester, 1677; polyol, 1862; isocyanate, 19980.

TABLE 3

Glass transition temperatures of a 50/50 polyurethane/polyester IPN as a function of gel times (stream Reynolds numbers: polyester, 1677; polyol, 1862; isocyanate, 19980)

Gel time (s)	T_{g1} (°C)	T_{g2} (°C)	T_{g3} (°C)
70	-36	+70	+111
125	-37	+72	+115
417	-39	+74	+117
738	-43	+77	+119

function of stream Reynolds numbers. Once the critical laminar/turbulent transition regime was passed, the mix quality obtained depended not only on the Reynolds number but also on the reaction rate of the mixture. Fast kinetics can lead to rapid network formation and trap in the process the turbulent microstructure obtained upon impingement. Phase separation due to coagulescence and thermodynamic incompatibility will also be limited. Work on finding a relationship between the IPN morphology and the RIM processing conditions is under progress [8].

CONCLUSION

The coupled nature of a turbulent reacting mixture encountered in RIM is reflected in the morphology of the final part. Impinging the reactants at high Reynolds numbers leads to a fine scale of mixing. Calorimetric and dynamic mechanical measurements show the extent of mixing as evidenced by an inward shift of the transition temperatures of the components. The curing kinetics have a similar effect on the phase relations. Fast rates seem to trap the fine scale generated before phase separation can occur.

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