Microdispersive Interfacial Mixing in Fast Polymerizations

Interfacial activity between liquid reaction injection molding (RIM) reactants was observed using light microscopy. Diisocyanates were brought into contact with various diols and diamines in a thin (250 μm) gap. A dynamic phenomenon, rapidly producing a well-mixed, intermaterial phase, was discovered. It was revealed that the rate of growth of this newly formed region was dependent on both the rate of reaction and the physical properties of the initially formed product species at the reaction interface. Spontaneous interfacial mixing also occurred without chemical reaction when a reaction product was dissolved in "capped" contacting reactant liquids. It is believed that strong interfacial intermolecular forces, inducing flow through the polymerization product layer formed immediately upon reactant contact, are responsible for the initial explosiveness of this microscopic process. The range of eventual thicknesses of the mixed, interfacial region (100-800 μm) for various typical RIM systems indicates that this microscopic subprocess may be significant to the fate of the overall process.

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Introduction

Since manufacturing economies favor solventless polymerization, the need to understand interfacial processes between liquid reactants intensifies. Any activity at the interface formed by reactant contact may have a significant effect on the overall process. Reaction injection molding (RIM) is an interfacial polymerization process in which two relatively low viscosity reactants are mixed and fed into a mold, with the ongoing reaction yielding a high molecular weight polyurethane or polyurea product in less than one minute. Despite the widespread use of this technology, there is little understanding of micron and millisecond scale physical events and actions involved in the overall chemical reaction.

In RIM, high-velocity impingement mixing is the macroscopic process by which sufficiently intimate contacting of reactants was once thought to occur. This mixing is critical, as insufficient reactant contact will result in unreacted species and thus poor final material properties (Bourne and Garcia-Rosas, 1985; Kolodziej et al., 1982; Lee et al., 1980; Nguyen, 1985; Tucker and Suh, 1980). Previous studies have concluded that the bulk fluid flow in the RIM mixhead is responsible for achieving mixing only to a reactant striation scale of 100 μm (Kolodziej et al., 1982; Pearson and Williams, 1985). There must be some process accountable for additional mixing to a scale of less than 1 μm to justify the high-quality product polymers formed in RIM.

Understanding such microscopic interfacial mixing phenomena should provide insight into the failure of previous polyurea RIM systems due to apparent mixing problems. Such chemical systems yield materials with excellent mechanical properties (Grigsby and Dominguez, 1985; Ewen, 1985; Vespoli et al., 1986), but rapid gelation, generally occurring in less than 1 s (Vespoli et al., 1986; Pannone and Macosko, 1987), results in large domains of unreacted species in the RIM product material. Since the extent and control of fluid mechanical mixing is limited by the rising viscosity, any microscopic interfacial mixing process must somehow be controlled and optimized for successful molding of such chemical systems.

It is of interest to investigate activity at a reactant-reactant interface using light microscopy. Low-magnification observations have revealed the presence of interfacial instabilities in the form of small-scale oscillations of the interface itself (Fields et al., 1987). Higher magnification studies have shown the formation of 1 mm scale droplets of one reactant on the other side of the interface (Wickert et al., 1987). These works, although pio-

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neering with regard to interfacial activity in these systems, have been concerned with microprocesses over longer times than those important for the fast RIM process. In this study, we strive for understanding of more rapid interfacial phenomena for small-scale, reaction-induced mixing. Through this knowledge, we wish to better explain the failure of some very fast RIM chemistries and aim to control such microprocesses in order to achieve success with these systems.

Experimental Procedure

Materials

Polyurethanes and polyureas are formed by reacting diisocyanates with polyols and polyamines respectively. The chemical systems studied here are components of those typically used, or with the potential to be used, to produce these polymers commercially via RIM; they are listed in Table 1. All reactant species are in the liquid state at room temperature.

Two types of diisocyanates were studied. Rubicon LF-168 (ICI) is a modified 4,4′ diphenylmethane diisocyanate (MDI), which has a functionality of 2.15 and is in the liquid state at room temperature. Desmodur W, supplied by Mobay Chemical, is a pure methylene bis(4-cyclohexyl isocyanate) (H12MDI).

In linear polyurethane formation, various diols were reacted with the diisocyanates. Texaco E2103, a polyether diol (α, ω) with a molecular weight of 2,300, and the chain extender 1,4 butanediol (BDO) (supplied by Aldrich) were used most frequently. The catalyst dibutyltin dilaurate (DBTDL), supplied by Morton Thiokol, was sometimes added to the polyol phase to enhance the chemical reaction rate. A monofunctional hydroxy-terminated poly(propylene oxide) of 2,000 molecular weight was made available by Dow Chemical.

In forming linear polyureas, Texaco Jeffamine D2000 poly(propylene oxide) (α, ω) diamine (molecular weight 2,000) and/or diethyl toluene diamine [combination of 2, 4 (80%) and 2, 6 (20%) isomers] (DETDA), supplied by Ethyl Corporation, were reacted with the diisocyanates. Texaco Jeffamines T403, T3000, and T5000 triamine-terminated polyethers (molecular weights 400, 3,000, and 5,000 respectively) were used in producing network polyureas.

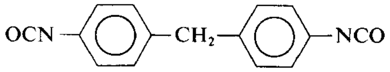
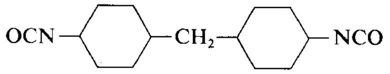
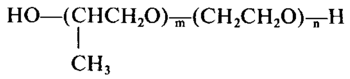
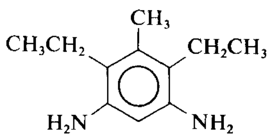
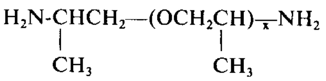
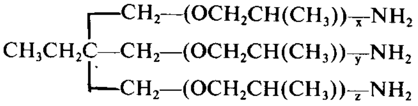
All hydroxy- and amine-terminated reactants were dried under vacuum at 45°C for at least 5 h to remove any water that would undesirably react readily with isocyanates to form carbon dioxide. Catalyzed reactants or reactant mixtures were mechanically stirred for 8 h at room temperature prior to use to insure adequate blending. If any impurities, such as dimer or trimer in the isocyanates, were visible under magnification, the reactant species was filtered through Eaton-Dikeman grade #54 filter paper.

Methods

Microscopic interfacial activity between contacted reactants was observed using Wild Heerbrugg M20 and Nikon Optiphot polarizing light microscopes with available magnifications of 40X, 100X, 200X, and 400X. The mechanical stage was fitted with a Cambion thermal microscope stage whose temperature was regulated by a Cambion Bipolar Controller (range of 0–50°C). A 35 mm camera, directly mounted on the Wild M20 microscope, and an MTI video camera (equipped with a Sony video recording system), mounted on the Nikon microscope, were used to record experimental observations.

The microscopic reaction interface was created between a 25 mm square coverslip and a 25 × 74 mm microslide (both previously flame dried) separated by two 250 μm dia. steel wire spacers, Figure 1a. Using a Gilmont microsyringe, a measured volume (typically 0.1 mL) of the diol or diamine was introduced to the gap between the slide and coverslip and allowed to move by capillary motion until it reached the center of the coverslip, Figure 1b. The assembly was then placed on the microscope stage

Table 1. Reaction Injection Molding Reactants

Reactant	Supplier Product Name	Structure	Molec. Wt.
4, 4′ Diphenylmethane diisocyanate (MDI)	ICI Rubicon LF-168		286
Methylene bis(4-cyclohexyl isocyanate) (H12MDI)	Mobay Desmodur W		294
Polyether diol	Texaco Thanol E2103	 $HO-(\underset{CH_3}{CH}CH_2O)_m-(CH_2CH_2O)_n-H$	2,300
1, 4 Butanediol (BDO)	Aldrich	$HO-(CH_2)_4-OH$	90
2,4 and 2,6 Diethyl toluene diamine (DETDA)	Ethyl Corporation		167
Polyether diamine (D2000)	Texaco Jeffamine D2000	 $H_2N\text{-}\underset{CH_3}{CH}CH_2-(OCH_2\underset{CH_3}{CH})_x-NH_2$	2,000
Polyether triamines			
(T403)	Texaco Jeffamine T403	 $CH_3CH_2C(-CH_2-(OCH_2CH(CH_3))_x-NH_2)(-CH_2-(OCH_2CH(CH_3))_y-NH_2)(-CH_2-(OCH_2CH(CH_3))_z-NH_2)$	400
(T3000)	Texaco Jeffamine T3000		3,000
(T5000)	Texaco Jeffamine T5000		5,000

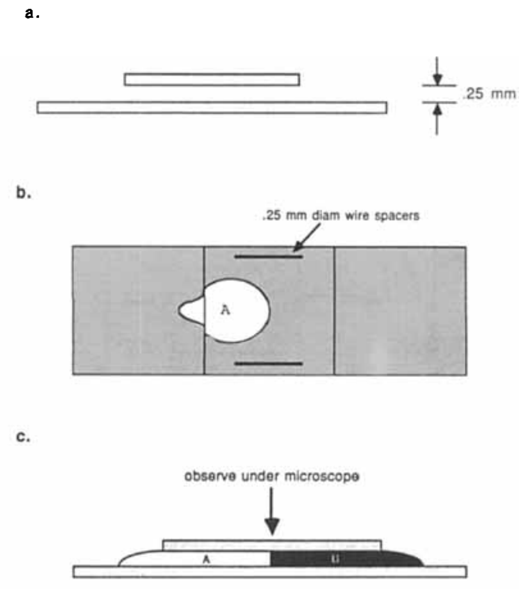


Figure 1. Creation of microscopic interface.
a. Gap set between coverslip and microslide
b. Reactant *A* introduced to gap by capillary action
c. Reactant *B* allowed to contact *A* by capillary action

and the leading edge of the reactant was brought into focus. An equivalent volume of the diisocyanate was then introduced in the same manner on the other side of the coverslip and the leading edge of this reactant was allowed to move slowly through the gap until it could just meet the other reactant, Figure 1c, squeezing out any intervening air. The velocity of reactant impact was measured to be at most 4 μm/s. This technique is similar to that of Wickert (1985), except that the contacting of the reacting species was much slower so that bulk fluid momentum effects could be minimized. The interfacial activity was then observed, with any measurements taken from a precalibrated, scaled eyepiece or from the viewing of prerecorded videotapes. In recording using the video camera, the film speed was 30 frames per second. We were thus able to obtain quantitative information regarding events on the time scale of 0.1 s from frame by frame observations.

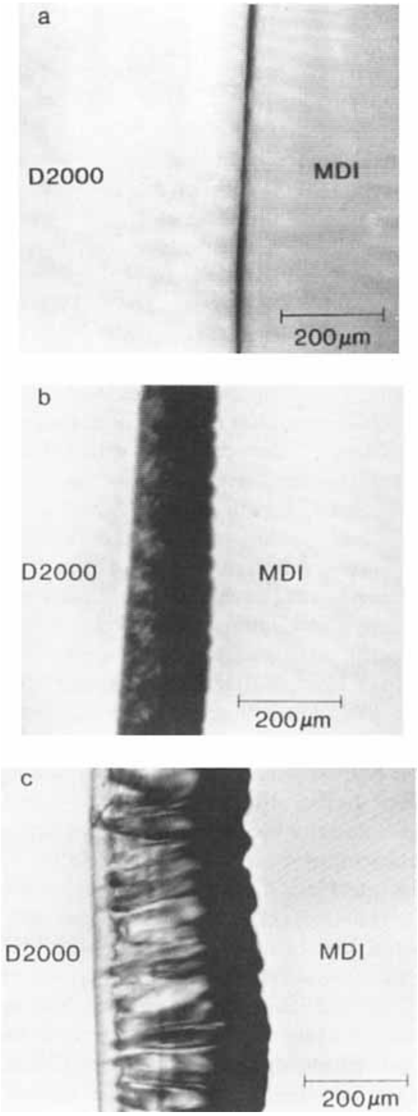


Figure 2. Interfacial mixing observed upon contacting a diamine (D2000) and MDI, 40X magnification.
a. Interface upon reactant contact
b. Interfacial region 0.2 s after contact
c. Interfacial region 0.8 s after contact

Results and Discussion

Microscopic interfacial activity between contacting polyurethane or polyurea reaction injection molding reagents was studied at 25°C. The basic interfacial activity observed was similar throughout the range of chemical systems employed. When observed edgewise from above at magnifications of 40X, 100X and 200X, the interface between the two reactants appeared to be a straight line at the moment of reactant contact, Figure 2a. In a fraction of a second after impact the interface seems to split rapidly, forming a third interfacial phase, with uniform boundaries, between the two reacting species, Figure 2b. This phase formation was observed to develop explosively as a fine dispersion of the polyol or polyamine, through the reaction product layer formed at the contact interface, into the diisocyanate. The mixed, interfacial region then continued to grow into the isocyanate phase as more of the dispersing reactant continued to move across the original interfacial contact plane, which remained stationary. As the dispersed interfacial region-diisocyanate front moved into the isocyanate phase, the interfacial mixed zone appeared to be a highly turbulent region, Figure 2c. Observations at 200X magnification indicated fine mixing of reactants on the micron level. The initial rapid rate of growth of this region (velocities averaged over the first 0.1 s after contact measured to be on the order of 300 μm/s) decreased at different rates depending on the species involved. Eventually (after 5 s to 20 min), the growth of the dispersed region ceased and high-viscosity product was present in the interfacial region of dispersion. Gel permeation chromatographic analysis of an isolated product layer (Machuga, 1988) formed at a D2000-MDI interface indicated a weight-average molecular weight of about 16,000 and a polydispersity of 4. These values, similar to those obtained in RIM samples (Willkomm et al., 1988), suggest a fairly high degree of conversion in the interfacial region and thus fine, small-scale mixing of reactant species.

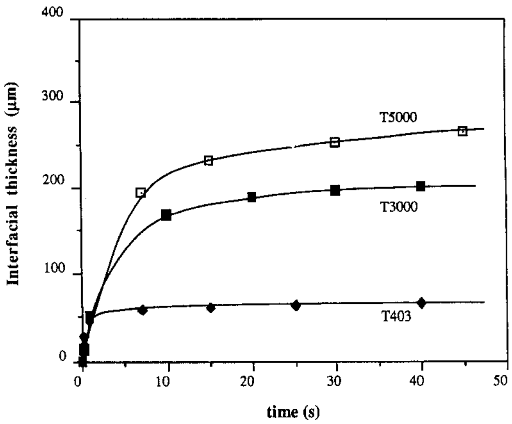


Figure 4. Growth of interfacial region for three polyamines contacted with MDI.

As previously noted, the typical phenomenon observed was similar for all polyurethane and polyurea systems studied. However, the characteristic events occurred in a wide range of time and size scales (in terms of longevity and magnitude of the growth of the interfacial region), which were different for the various chemical systems examined.

It was observed that the reaction rate of the chemical system, in terms of the rate of formation of urethane or urea linkages expected by reactant chemical structures, was a significant parameter in determining the extent of dispersive activity and thus microscopic interfacial mixing. The polyether diol was catalyzed with DBTDL at levels ranging from 0 to 1 wt. %. In typical RIM phase-separating polyurethane systems, mixed reactants would have characteristic gel times from approximately 25 min to 10 s over this catalyst concentration range. The interfacial activity observed, when contacted with MDI, was qualitatively similar to the phenomen previously described at all catalyst levels. The initial growth rate of the interfacial region was fairly constant over the range of catalyst concentrations, particularly at the lower levels. But, the rate of growth of the interfacial region was observed to decay more rapidly over time with increasing catalyst concentration, Figure 3.

Similar results were observed in experiments involving the addition of up to 30 wt. % BDO to the polyether diol (Machuga, 1988). Since BDO has a functionality concentration approximately 25 times higher than that of the polyether diol, its bulk reaction rate with isocyanates is significantly larger. The changing viscosity of the diol mixture, decreased with increasing BDO concentration, appeared to have a minimal effect compared to the elevated chemical reaction rate. This relation between reaction rate and interfacial dispersive activity was observed consistently over a variety of polyurethane RIM systems.

Initial contacting of various polyamines with MDI resulted in the observation of less interfacial activity at low magnification compared to the previous urethane systems. The extremely fast polyurea reaction system appears to conform to the reactivity-interfacial activity analogy. The sequence of T5000, T3000, and T403 aliphatic polyamines is increasing in chemical reactivity with diisocyanates, largely due to increasing concentration of functional groups. As expected from an extension of the observations made using urethane-producing systems, the rate of decay of interfacial region growth increased with increased reactivity, Figure 4. One could see that the phenomenon had indeed occurred, but the available resolution of the microscope made it difficult to compare, in qualitative detail, the activity within the interfacial region with that of the polyurethane systems.

When a less reactive diisocyanate (the aliphatic H12MDI has a half-life of about 0.05 s with aliphatic polyamines, compared to 0.002 for MDI (Pannone and Macosko, 1987; Charbonneaux, 1988) was used, the degree of interfacial activity was magnified and the occurring phenomenon was observed to be qualitatively identical to that of polyurethane systems. Quantifications of the growth of the interfacial region resulted in a reiteration of the tendency for the extent of interfacial dispersive mixing to decrease with increasing reaction rate, regardless of the nature of the particular chemical species present on either side of the reaction interface, Figure 5. The quantitative aspects (rate of decay and extent of mixing) of the phenomena appeared to be significantly less dependent on other conventional mixing parameters such as reactant viscosities, densities, or solubilities.

The interfacial growth velocities immediately after the initiation of the phenomenon were obtained for the various chemical systems studied. Reported values are quantities averaged over the first 0.1 s after reactant contact. It was observed that the initial growth velocity was essentially independent of chemical

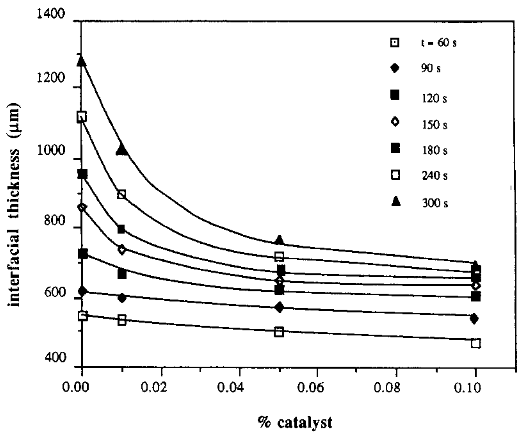


Figure 3. Growth of interfacial region over time for varying DBTDL catalyst concentration in polyether diol (E-2103)-MDI system.

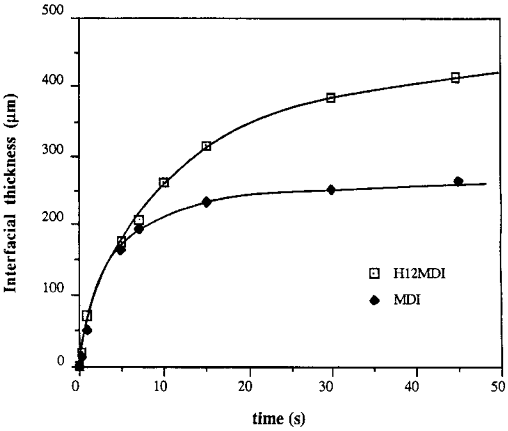


Figure 5. Growth of interfacial region formed upon contact of diisocyanates of different reactivity with D2000.

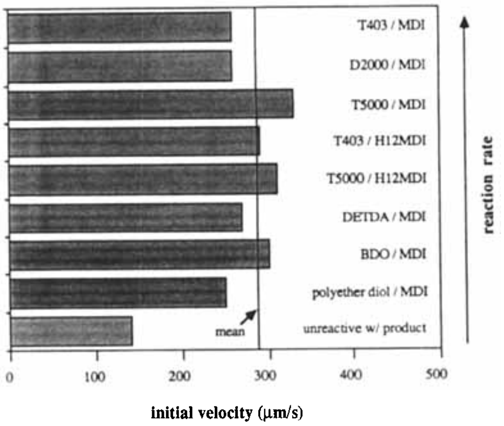


Figure 6. Initial interfacial growth velocities for various chemical systems.

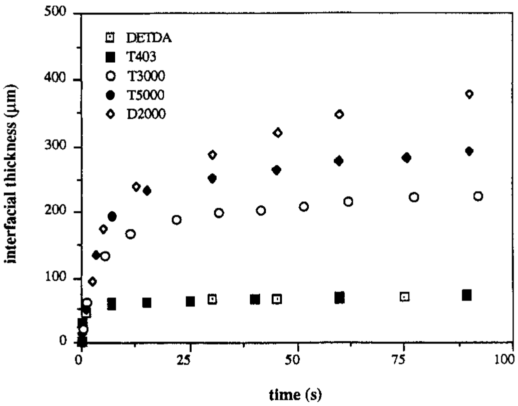


Figure 7. Apparent deviations from proposed reactivity-interfacial activity relationship.

Growth profiles for interfacial region formed between MDI and listed reactants

reaction rate for these systems within experimental error (±20 µm/s), Figure 6. The average initial velocity for reactive systems was found to be about 290 µm/s. It is only after the reactions proceed further that we see any differences in growth rate.

For these polyurethane and polyurea-producing systems, it appears that the chemical reaction rate is measurably significant only once the interfacial phenomenon has started to mix the two liquid phases. The absence of a noticeable trend in initial velocity over a wide range of reaction rates suggests that the initial explosiveness, or the associated driving force, of the interfacial mixing is not strongly dependent on this parameter. However, once the mixed phase begins to grow, reaction rate seems to be very important in determining the rate of decay of the growth of the interfacial region. The faster reacting polymerization systems generate viscous products rapidly. These prepolymers are critical in dissipating the dispersive flow momentum, induced by the apparently large initial driving force at the reactant contact interface. The rate of production of these products determines the magnitude of the resistance to flow over time and thus the extent of growth of the mixed phase between the two monomer species. Therefore, increased reaction rate results in a decrease in the intensity of interfacial mixing.

Two ambiguities arose from the proposed reactivity-dispersive activity relationship. DETDA is an aromatic diamine which, because of the electron-withdrawing nature of the aromatic ring, is much less attractive to isocyanate attack than the aliphatic polyamines T5000, T3000, and T403. Studies following the reaction kinetics in solution show a typical reactant half-life on the order of 1 s for DETDA and 0.002 s for the aliphatic polyamines (Pannone, 1985). Thus, DETDA is the least reactive polyamine in this study. Yet, it was observed that this species displayed the least amount of dispersive interfacial activity upon contact with the diisocyanates, Figure 7. One possible explanation is that the concentration of functional groups at the interface is higher than that of the other amines, due to the small molecular size of DETDA, thus increasing reaction rate. However, the equivalent weight of DETDA is similar to that of T403, so the aromaticity of DETDA should lower the reaction rate and allow for a further extent of interfacial mixing than in the case of T403. This was not observed experimentally.

Perhaps better reasoning is to consider the molecules produced with the formation of the first few urea linkages. In DETDA, steric hindrance caused by ethyl and methyl aromatic substituents inhibit free rotation and thus increase the rigidity of the formed urea linkage and the product molecule. A corresponding, relatively low molecular weight oligomer, produced by the formation of two urea linkages, is known to exhibit a high modulus in the bulk, due to a fairly high density of hydrogen bonds. Analogous oligomers formed with the other polyamines studied here tend to be only fairly viscous (Machuga, 1988). One can easily conceive of an increased resistance to the flow of a dispersing reactant into the high-viscosity interfacial region occupied by the oligomer, thus causing a faster decay in growth rate. The interfacial region formed in the DETDA-based system has, over time, a higher viscosity than in the triamine systems, even though the reaction products are generated at a much slower rate. The physical properties of the initial reaction products appear to be significant, in addition to their rate of formation.

Observations of activity at a D2000-MDI interface also appear to be inconsistent with the proposed relationship. Since D2000 is a primary aliphatic amine, the urea reaction rate constant will be essentially the same as for the triamines previously discussed. Since the equivalent weight of D2000 is equal to that of T3000, the reaction rates with MDI should be the same and one would expect to observe identical interfacial growth profiles for both systems. Experimentally, the interfacial activity is quantitatively similar at short times, Figure 7. However, at longer times (>4 s) the growth of the interfacial region between D2000 and MDI appears to decay at a slower rate than in the T3000 case, violating the proposed analogy.

The properties of the molecules initially formed immediately after reactant contact are again considered. With the addition of two MDI molecules, the produced urea oligomers of both D2000 and T3000 are fairly viscous (~0.2 Pa · s) liquids (Machuga, 1988). Thus, since the reaction rates of the species with MDI are comparable, one would expect the observed interfacial activities to be very similar at shorter times, when oligomers of this type are formed. However, T3000 (like T403, T5000) is a triamine, so its polyurea-producing system can easily form a crosslinked network at relatively longer times. Since D2000 is difunctional, only linear polyurea molecules are produced in reaction with MDI. The urea network formed in triamine-diisocyanate reaction systems acts as a higher resistance barrier to the dispersive flow of a reactant into the mixed interfacial region than the looser linear polyurea product structure. Therefore, the interfacial region formed between the diamine and MDI can grow to a larger thickness as viscous dissipation of the dispersive flow momentum is not as dominant.

Further Discussion

We have discovered a microdispersive interfacial mixing phenomenon that occurs when two reactive chemical species come together. It was demonstrated that the extent of dispersive interfacial activity was related to both the reactivity of the chemical species involved and the physical properties of the relatively low molecular weight oligomers formed immediately upon reactant contact. However, the initial growth velocity of the newly formed interfacial region did not appear to be related to the detailed chemistry of the reactant systems.

The observed interfacial phenomenon is initiated by an explosive dispersion of one reactant (polyol or polyamine), across the contact interface, into the other monomer phase (diisocyanate). Dispersive action through the initial contact plane continues and a mixed interfacial region forms and grows as reactants are continuously mixed on a micron scale by flow turbulence. It is possible that instabilities of the dispersive flow may produce breakup into the micron-size droplets of reactant observed in previous studies of similar interfaces (Wickert et al., 1987). Fine mixing yields high reactant-reactant contact area and the polyurethane or polyurea-producing reaction proceeds rapidly. Prepolymer formation results in a viscosity rise of the interfacial material, thus increasing the resistance to the dispersive flow across the interface. The physical characteristics of the prepolymer oligomers and their rate of formation dominate and determine the rate of dissipation of dispersive flow momentum. Microflow action eventually ceases and the microdispersive interfacial mixing is complete. Diffusion over longer times enables even higher reactant conversion in the dispersed region. The interfacial mixing activity is thus characterized by three stages:

1. Initial rapid dispersive flow across the formed reactant contact interface
2. Decay of flow momentum as the thickness of the intermaterial region and its viscosity increases
3. Molecular diffusion after dispersive flow ceases

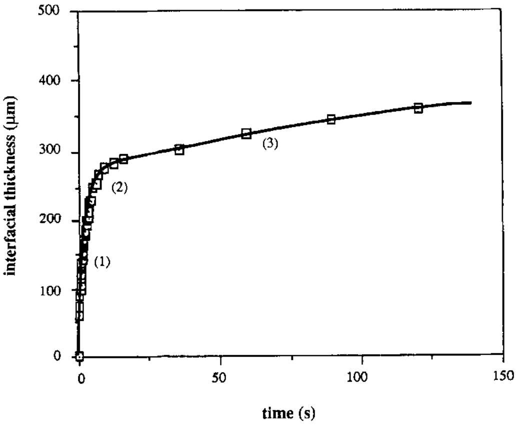


Figure 8. Three stages of interfacial mixing observed in D2000-MDI contact experiment.

(1) Explosive dispersive flow; (2) growth rate decays as flow momentum is dissipated; (3) diffusion at longer times

These stages are easily identifiable in the experimental interfacial thickness data, Figure 8.

It is of interest to understand the mechanism by which the transfer of the polyol or polyamine across the interface occurs. Under the low magnifications used here, details of any microstructures characteristic of this interfacial activity were not distinguishable. Although insufficient information is currently available to develop a viable mechanism for the overall micromixing process, we do wish to identify the origin of the apparently enormous driving force responsible for the high initial interfacial growth velocities associated with the dispersive flow.

Monomer physical properties, such as relative solubility, density, or concentration gradients, may play a role in the transfer of monomer across the interface, possibly similar to their importance in some emulsification processes. However, it is unlikely that these parameters alone could be capable of generating the dynamic, instantaneous dispersive activity observed upon reactant contact. This is particularly true for concentration gradients, which have been known to induce the formation of seemingly related emulsions in multicomponent oil-water systems only after diffusion processes have made the interfacial region chemically unstable over much longer times than those of concern here (Davies and Rideal, 1963; Benton et al., 1982).

The polymerization reaction may be a significant factor in promoting the occurrence of the observed phenomenon. The highly exothermic urethane or urea reaction may cause the interface to become unstable by initiating thermal gradients immediately upon contact of reacting species. Reaction products are generated rapidly as a third component at the liquid-liquid contact plane and may act as a surfactant, or "surf-product," which could induce interfacial instabilities.

To investigate the actual significance of these possibilities, the reactive nature of the system was eliminated in order to determine the microscopic fluid mechanical effects induced by the presence of the interfacial product alone. The monofunctional hydroxy-terminated polyether was methylated via a Williamson ether synthesis (Morrison and Boyd, 1973) in order to preserve the poly(propylene oxide) backbone, but to remove the reactivity with the isocyanate. The success of the methylation process was verified by the disappearance of the C-OH peaks near 65 ppm in ^{13}C NMR. To simulate the interfacial product oligomer, the functional polyether diol was reacted with a 3 mol % excess of phenylisocyanate to form two urethane linkages on the polyol molecule.

The unreactive polyether was contacted with MDI under the microscope at 25°C. As the liquids first contacted, the immediate, explosive growth of a forming interfacial phase, as observed in the reactive systems, did not occur. Instead, the liquids behaved as if they were merely immiscible. The interfacial contact plane remained intact and the species mixed slowly, at very small size scales, over time, Figure 9a. However, the dynamics of interfacial mixing were not even remotely representative of the explosiveness observed in the previous reactive systems. The small degree of mixing that did occur was probably due to diffusion, the slight miscibility of the two species, and any small momentum effects induced by the impinging fronts of the contacting species.

The phenylisocyanate-capped polyether diol was then blended into both the polyether and MDI at 10 wt. %. The obtained solutions were contacted under the video microscope and the activity at the liquid contact interface was observed. The

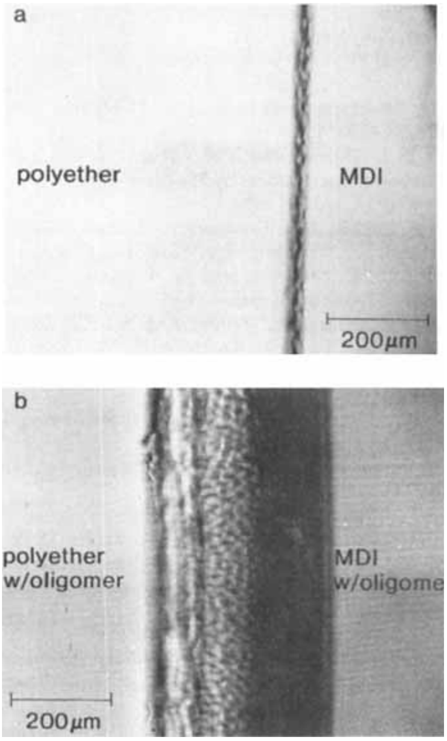


Figure 9. Effect of simulated interfacial product in unreactive system.

a. Interface between unreactive polyether and MDI 0.4 s after contact

b. Interface with 10 wt. % simulated urethane product dispersed in both phases, 0.4 s after contact

presence of the simulated interfacial urethane product had a significant effect on the events occurring upon liquid-liquid contact. Upon coalescence, the explosive growth of a third, mixed phase that was absent in the parent unreactive system, was indeed observed, Figure 9b. The original contact plane remained intact and the mixed interfacial phase grew only into the isocyanate-based phase as the polyether solution dispersed across the interface. Qualitatively, the observed activity appeared to resemble that of the previous polymerization systems. The growth of the interfacial region continued over a longer period of time, since no polymerization-induced viscosity rise was present to enhance the dissipation of dispersive flow momentum. The lack of polymerization allowed the mixed phase to be slightly soluble in both liquid phases, causing the boundaries of the interfacial zone to become less defined over time.

The apparent implications of this result are highly significant to the understanding of the operating mechanism. The experimental evidence implies that the interfacial mixing phenomena observed in the reactive RIM systems is not driven by the chemical reaction or by the bulk properties of the monomer species. However, it seems that the presence of molecular groups, characteristic of the chemical reaction products, at the liquid monomer-monomer interface strongly promotes the initiation of the microscopic mixing activity between the species.

We believe that a high local density of intermolecular attractions (namely, rapidly forming hydrogen bonds), between the urethane linkages present near the interface and isocyanate groups across the initial reactant contact plane, can induce mechanical interfacial instabilities. If the adhesive forces, generated by these interactions, between the two liquid phases become larger than the cohesive forces within the individual liquids themselves, the interfacial tension could become negative, resulting in compressive tangential stresses along the interface. The liquid contact plane would then "pucker" in the direction of the stronger molecular-scale forces, resulting in the transfer of the "molecularly inactive" monomer across the interface. In these experiments, it is highly probable that the adhesive forces could indeed exceed the cohesive interactions, as the intermolecular forces within the parent liquid phases are essentially only weak van der Waals attractions. This hypothesis is similar to those proposed in explaining some occurrences of spontaneous emulsification in multicomponent systems (Davies and Haydon, 1957).

It is interesting to note that the value of measured initial interfacial growth velocity for the nonreactive system, with product present, is about one-half of those obtained for the reactive systems, Figure 6. It seems logical to postulate that if the proposed intermolecular interactions are important, the intensity of mass transfer across the interface should increase with the concentration of these forces. This force density would increase with the local concentration of molecularly active groups at the interface, which is maximized in the reactive system. In this case, it is certain that the concentration of active urethane groups at the interface far exceeds the 10 wt. % dispersed throughout both liquid phases in the unreactive experiment. The result is a higher observed initial growth velocity of the forming mixed phase, experimentally supporting our suggested theory.

Conclusions

A dynamic, microdispersive interfacial mixing phenomenon was observed between contacting RIM reactant species. Immediately upon coalescence, a third, well-mixed phase forms explosively, as one monomer rapidly disperses across the interface into the other. The growth rate of this new phase decays as increasing polymerization product viscosity enhances the dissipation of dispersive flow momentum, and eventually mixing is purely a diffusion process. It was revealed that the extent of interfacial mixing was governed by the rate of formation and the physical properties of initial reaction products. However, the initial velocity of growth of the interfacial region was found to be independent of the chemistry of the reactive system within the reliability of our measurements.

In reaction injection molding systems, this interfacial phenomenon appears to be the significant mechanism responsible for mixing reactant species on the submicron scale. In order to optimize this mixing process, it appears necessary to employ a chemical system that initially produces low molecular weight, highly flexible oligomers at a relatively low reaction rate. Actual implementation of this concept may be difficult for polyurea systems, which have desirable final material properties but undergo extremely fast polymerizations in RIM. It seems probable that future endeavors are necessary to partially chemically inhibit the isocyanate-amine reaction, thus promoting more interfacial mixing while maintaining the rigid urea linkages necessary for final product properties.

An important result of unreactive experiments is the conclusion that the activity under investigation is not limited to special reactive cases, but is a more fundamental interfacial phenomenon that may be applicable to many liquid systems. Through these experiments, we believe that the primary criteria for the occurrence of rapid interfacial mixing between any two liquids are now established. The individual liquids must be fairly nonpolar, essentially with intermolecular forces no stronger than van der Waals interactions. It appears that a third species must be present near the interface. This component must be capable of rapidly developing strong interfacial, intermolecular forces with one of the liquid phases, while remaining relatively inactive with the other liquid. The directed net force normal to the interface represents a stress difference, which propels one liquid phase into the other.

The implications of these findings may be extended to systems beyond polyurethane and polyurea RIM. Similar phenomena could be valuable in any situation where mixing is desirable at an interface between dissimilar liquids. For example, a strong interest is currently devoted to the enhancement of oil recovery processes. In these systems, the formation of emulsions at oil-water interfaces aids in the entrapment and subsequent retrieval of petroleum. The application of the concepts presented in this study could assist in the development of new surfactants, which could be capable of promoting more dynamic, interfacial mixing of immiscible, unreactive liquid pairs. Such surfactants might be ionic, so that very strong molecular scale forces could be generated at these interfaces.

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