Small scale mixing phenomena during reaction injection moulding

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Small scale mixing and polymerization between reaction injection moulding (RIM) reactants which form polyurethanes or polyureas, were observed with microscopy. This provided resolution of phenomena which occur in the range of scales from about 0.1 μm to 100 μm, and times from second to minutes. Mixing of RIM reactants at such small scales may affect the rate and specificity of polymerization by establishing a short diffusional path length. When two drops of RIM reactant phases were contacted, it was observed that one phase often dispersed into the other, depending on the particular chemical system. Dispersion was also observed in material made using a small RIM machine. The scale of dispersion varied from ~0.1 μm in polyurea systems to ~3 μm in polyurethane systems. It is believed that interfacial chemistry and forces generated during mixing determine the scale of dispersion. The smaller the dispersion, the faster the rate of polymerization if diffusion is a limiting event. Thus, a change in dispersion size, caused by interfacial chemistry, is a mechanism which influences the rate of polymerization, and may affect ultimate product behaviour by altering a characteristic scale of segregation.

(Keywords: reaction injection moulding; polyurethane; polyurea; mixing; diffusion; polymerization)

INTRODUCTION

Reaction injection moulding (RIM) is a process in which two opposing liquid reactant streams are impinged in a T-mixer, the resultant mixture is fed into a mould, and a solid plastic part is produced. Mixing of reactants is critical to the process[1-4]. Insufficient mixing yields a product of low molecular weight and poor mechanical properties. It is noted that the RIM process requires reactions to be essentially complete in times less than 100 s.

Previous studies[2,5] have shown that mixing of reactants during RIM is achieved to a scale less than 100 μm, perhaps to ~5 μm. This scale of segregation provides a pathlength where inter-diffusion of opposing reactants takes place. During and after diffusion, polymerization can occur. Obviously, the smaller the scale of segregation, the faster the polymerization if diffusion of opposing reactants is the limiting process. Since this scale of segretation of reactants in RIM mixing is important, there is a motivation to explore how reactant phases mix at scales less than 100 μm.

One way in which such small scale mixing of reactants can be studied is to observe the interfacial zone between two reactant drops with light microscopy. Low magnification observations[6] revealed a tendency for interfacial instabilities. It is of interest to probe the interfacial zone with higher magnifications to observe small scale mixing phenomena for several chemical systems which yield polyurethanes and polyureas. It is also desired to relate such phenomena to the RIM process and ultimate product behaviour.

EXPERIMENTAL METHODS

Materials

The chemical systems studied were those capable of producing polyurethanes or polyureas via RIM. The diisocyanate which was used was 4,4′-diphenylmethane diisocyanate supplied by Rubicon in the pure form, or as liquid LF-168, which has a functionality of 2.15.

The diisocyanate was reacted with diols to yield a polyurethane. The diols studied include: Texaco E2103, a 2300 molecular weight polyether diol (α,ω), or a mixture of E2103 with the chain extender 1,4-butanediol (BDO) supplied by Aldrich. In some cases the catalyst dibutyltin dilaurate (DBTDL) supplied by M & T Chemicals was added to the diol phase.

To produce a polyurea, diisocyanate was reacted with diamine. The diamines studied include: Texaco D2000, a 2000 molecular weight polyether diamine (α,ω), the commercial chain extender diethyltoluene diamine (DETDA) supplied by Ethyl Corporation, and a mixture of the two previous materials.

All diols and diamines were stored over 4A molecular sieves to remove water, as the water/isocyanate reaction was not desired.

Light microscopy

Dynamic observations of the interfacial zone between two RIM reactants were made using a Wild model M20 light microscope. It offered nominal magnifications of 100, 200 and 400 times. Photography was accomplished with an attached 35 mm camera.

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Two drops of liquid RIM reactants were contacted at room temperature via capillary flow[7] between a microscope slide and a 22 × 30 mm glass coverslip. In this technique two 225 μm diameter steel wires, which served as spacers, were first placed on the slide, then the coverslip was added, see *Figure 1a*. With a 1 cc syringe one liquid reactant (A) was dispensed onto the slide near the edge of the coverslip so that the liquid was drawn between the slide and coverslip via capillary action, see *Figure 1b*. The assembly was transferred to the microscope and the stationary air interface of the first fluid was observed. While making microscope observations the second reactant (B) was drawn between the slide and coverslip from the opposite side until it slowly contacted the first fluid at a speed of about 20 μm/s, and in doing so forced the air out between the fluids, see *Figures 1c,d*. Upon contact a stopwatch was started and observations were made. Slow contact of the reactants was important so as not to form a contorted interface, which would make observations difficult to interpret.

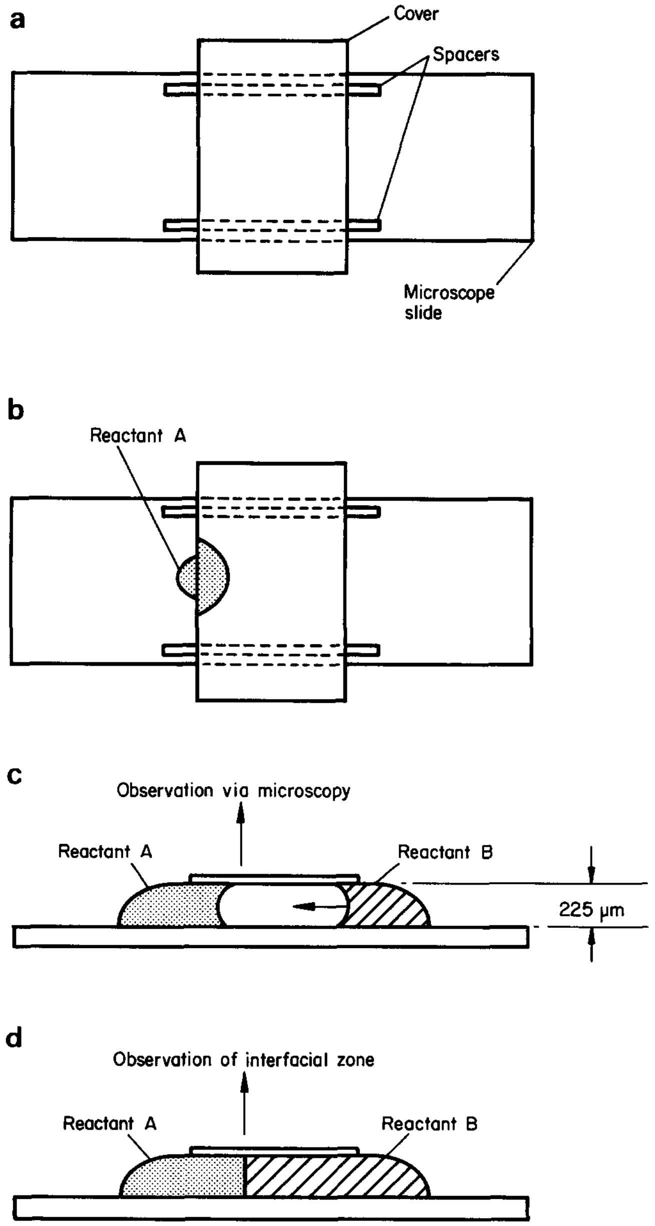

Figure 1 Technique used to contact two liquid reactants for microscope observation. (a) Top view of apparatus. (b) Addition of reactant A. (c) Side view of addition of reactant B. (d) Observation of interfacial zone between reactants

After the interface formed, the effect of shear on the interfacial zone could be qualitatively studied by perturbing (wiggling) the top coverslip relative to the bottom slide. Such perturbation represents the effect of external forces, as are experienced in fluid mechanical mixing, on interfacial stability.

Measurement of product molecular weight

The small quantity (a maximum of 0.1 g) of product which formed in the microscope experiments when stoichiometric equivalents of reactants were contacted was analysed via gel permeation chromatography (g.p.c.). Note that in this case one drop of reactant was contacted on top of the other in order to maximize the interfacial area. A Waters model 150C GPC, equipped with a refractive index detector and silanated silica columns, was used. Column temperature was 80°C, and the solvent was 1-methyl-2-pyrrolidinone (Aldrich). Relative molecular weight was determined with a polystyrene calibration. Samples were prepared by dissolving the reaction mixture between the slide and coverslip into 1-methyl-2-pyrrolidinone which contained enough di-n-butylamine to react with any remaining diisocyanate and inhibit further polymerization.

Reaction injection moulding

In addition ot the observation of the interfacial zone between two reactant drops, samples of polyurethane or polyurea were produced using a small RIM machine[8] which was equipped with an impingement mixer[9] (T-mixer) to contact the reactants. These samples were examined to determine how the previous type of microscope observations relate to phenomena observed in a process representative of commercial RIM.

For polyurethanes optical microscopy was used to look at the structure in the reacting mixture before and after solidification (gelation). A sample of reacting polyurethane was obtained just after it left the RIM machine, and while still in the liquid state. A drop of the sample was transferred to a microscope slide, a coverslip was added, and then the entire assembly was immersed in liquid nitrogen to preserve the sample for later viewing. Sample preparation, then freezing, took about 20 s. The slide assembly was then mounted in a microscope and observed over time as it equilibrated from −196°C to room temperature, and eventually solidified due to polymerization. A nitrogen purge was maintained over the glass slide assembly to prevent moisture condensation on the cold glass surfaces.

Scanning electron microscopy (SEM) was used to examine the fracture surfaces of RIM polyurea samples. Polyurea systems react too fast, with a gel time of the order of 1 s, for dynamic observations to be made using the preceding technique. Samples for SEM were fractured at room temperature, if brittle enough, or chilled using liquid nitrogen prior to fracture. Fractured surfaces were gold coated and examined in a JEOL model JSM-840 SEM at magnifications up to 50000 × . Note that SEM has previously been used[10] at magnifications up to 100000 × to examine biological specimens without the appearance of grain due to the gold coating.

RESULTS

Interfacial zone observed with light microscopy

When liquid MDI and E2103 polyether diol were contacted, and the zone between them observed with light microscopy, there was a tendency for the MDI to disperse into the polyether diol phase, see *Figure 2*. The size of the dispersion was about 3 μm in diameter on the average. The dispersion phenomena began upon contact as periodic erruptions of dispersion along the nearly planar interface between the two reactant phases. As time progressed more dispersion appeared, but at a steadily slower rate. By about 10 min after initial contact the tendency for dispersion had stopped. However, it was noted that if the coverslip over the slide was slightly perturbed, more dispersion could be generated. Evidently, the disturbance of initial contact, and those later, caused the dispersion to occur and reoccur.

When liquid MDI was contacted with a E2103 polyether diol phase which contained 0.1 weight per cent DBTDL catalyst, the tendency for MDI to disperse into the polyether diol phase was also observed, see *Figure 3*. One significant difference, as compared with the preceding observations, was that when catalyst was present the dispersion size was smaller. The dispersion diameter was 1.5 μm or less. Again, the rate of dispersion decreased, and stopped after several minutes. Additional dispersion would be generated if the slide assembly was perturbed.

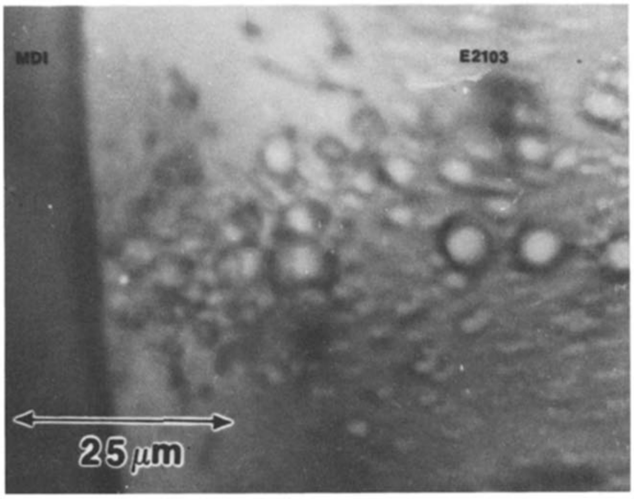

Figure 2 Dispersion of liquid MDI into E2103 polyether diol. The MDI is the slightly darker phase

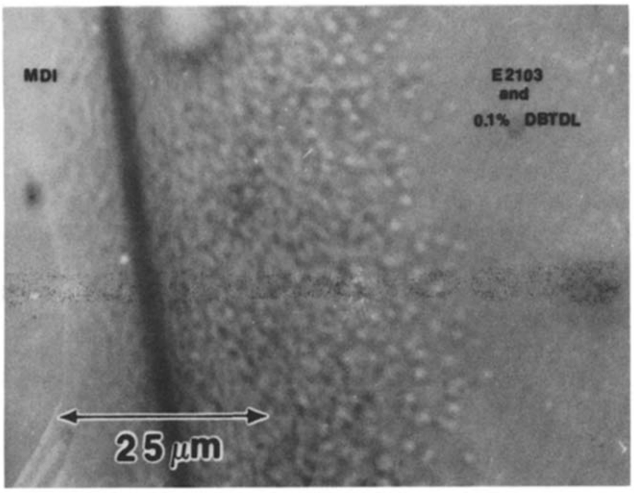

Figure 3 Dispersion of liquid MDI into a E2103 polyether diol phase which contained 0.1 wt% DBTDL as catalyst

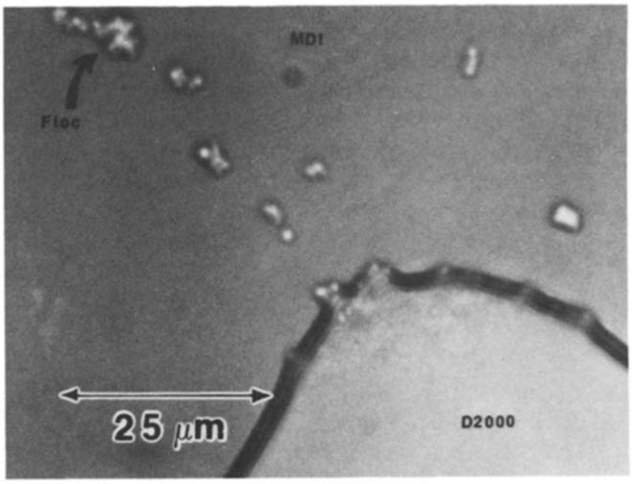

Figure 4 Dispersion of D2000 polyether diamine into liquid MDI. Dispersoids have flocculated in the MDI phase

A 4 to 1 mole ratio mixture of BDO and E2103 was contacted, and a 1 to 2 μm diameter dispersion of MDI formed in the diol phase. This dispersion did not continue for as long as in the preceding experiments; a tendency for the interface to be stable was noted.

The preceding chemical systems yield polyurethanes. In addition, observations of the interfacial zone between two reactants which yield polyureas were made. When liquid MDI was contacted with D2000 polyether diamine the interface between the two reactants was stable, no tendency for dispersion being observed. However, when a significant external perturbation was applied to the slide assembly, a dispersion of D2000 into the MDI phase was observed, see *Figure 4*. The dispersoids of D2000 appear floculated, and their size is 1 μm or less. It was difficult to focus on a dispersoid, which suggests a size for elemental structures to be of the order of 0.25 μm or less: the limit of resolution for a light microscope[11]. The tendency to disperse subsided shortly after the external perturbation.

When liquid MDI was contacted with DETDA, no tendency to disperse was observed. A stable interface was observed for at least 20 min. When the top coverslip of the contact apparatus was moved relative to the bottom slide, in order to apply an external perturbation, a lamellar structure formed as shown in *Figure 5*. No dispersion of one phase into the other was observed under optical microscopy.

The interfacial zone between liquid MDI, and a mixture of DETDA and D2000 polyether diamine, from which a 65 wt% hard segment polyurea (as based on MDI and chain extender) might be made, was observed. Again, a stable interface was noted between the two phases after contact. After a signficant external perturbation was applied to the slide assembly, a very small dispersion was noted. Its size was less than 1 μm, and it was similar to the dispersion that was observed when D2000 by itself was contacted with MDI.

Product molecular weight

After observation of the tendency for a stoichiometric equivalent quantity of MDI to disperse into E2103 polyether diol, the reaction mixture was analysed via g.p.c. Stoichiometric equivalents are needed to form a

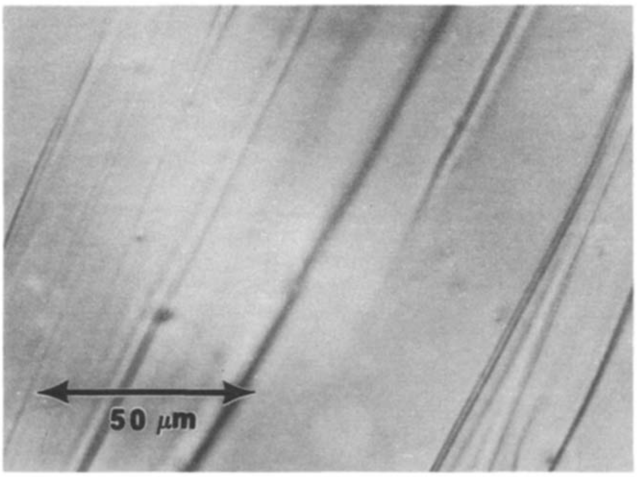

Figure 5 Lamellar structure between liquid MDI and DETDA after the top coverslip was moved relative to the side underneath

high polymer. At 69 min after contact, a product of 3300 number-average molecular weight was found to exist. Its polydispersity was 1.3. These data suggest that a product formed that consisted of one 2300 molecular weight polyether diol molecule, with one or two MDI molecules attached with urethane linkages. Evidently after such a 'surf-product' forms at the interface, reaction to form higher molecular weight species is inhibited for this chemical system. It is noted that linear polyurethanes of good properties, which are made from a MDI/B-DO/E2103 type system, typically have number-average molecular weights of about 20000[12].

Analysis of RIM samples

A 60 wt % hard segment polyurethane was analysed using light microscopy from the time just after it left the RIM impingement mixer. The polyurethane was made from pure MDI, and a mixture of E2103 polyether diol and BDO, which contained 0.005 wt % DBTDL. After leaving the impingement mixer the reaction mixture appeared cloudy to the naked eye, which suggested the existence of a dispersion. Microscopy confirmed the existence of a uniform dispersion, see *Figure 6*. Dispersoids of 5 μm diameter were observed, and in the gelled sample they were in contact with neighbours. Prior to gelation dispersoids moved free in the continuous phase, until they grew in size and bumped into each other. Evidently the dispersoids swelled in size as reactant from the continuous phase entered them to form a product. The dispersoids become difficult to resolve as adjacent dispersoids 'blend' into one another.

A 50 wt % hard segment polyurea was studied via microscopy. It was made from pure MDI, and a mixture of D2000 polyether diamine and DETDA. An initial analysis of a thin section of product via light microscopy revealed structures which appeared uniform throughout the sample and were approximately 1 μm in size, see *Figure 7*; however, the structures were apparently smaller than the resolution limit (0.25 μm) as sharp focus could not be achieved. Scanning electron microscopy on fractured samples showed features characteristic of a brittle fracture at 5000 ×, see *Figure 8*, with a hint of a very fine structure. A magnification of 50000 ×, see *Figure 9*, revealed a characteristic scale of about 0.1 μm in the sample.

DISCUSSION

The most important experimental observation was that there is a tendency for one reactant phase to disperse to some scale into the other, depending upon the particular chemical system. This was seen in all of the dynamic microscope observations of the interfacial zone between

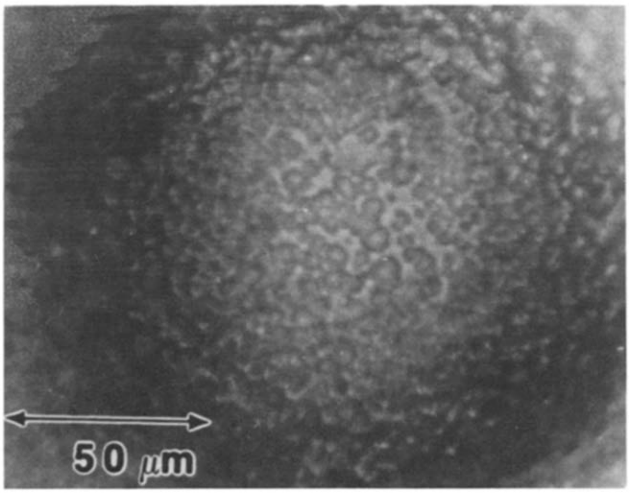

Figure 6 Dispersion produced, as seen after gelation, when a 60 wt % hard segment polyurethane was made via RIM

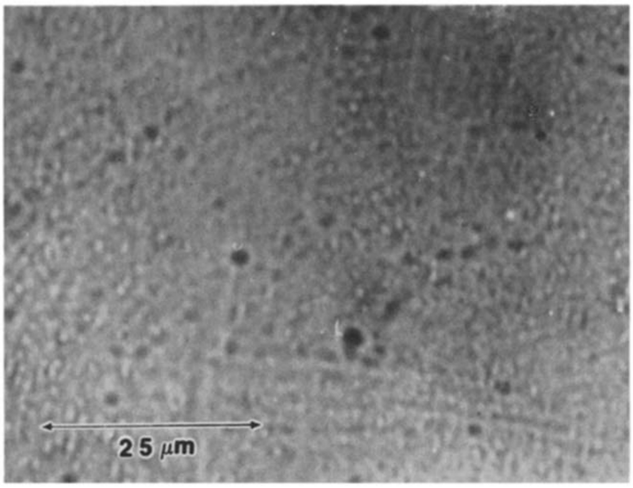

Figure 7 Optical micrograph of a 50 wt % hard segment polyurea RIM sample. Size of the uniform fine structure is believed smaller than can be resolved

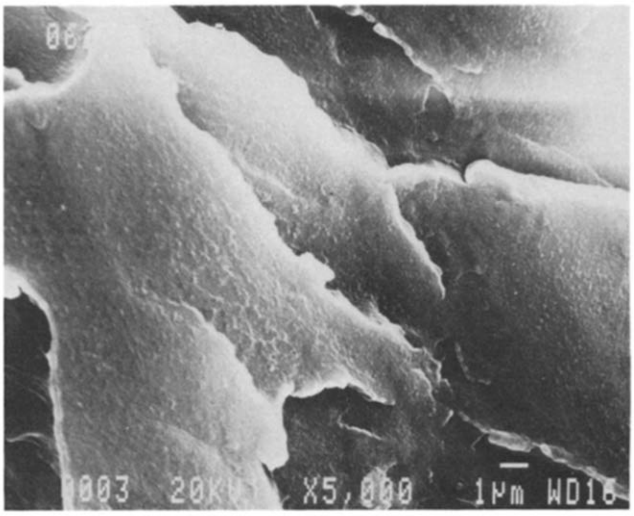

Figure 8 Scanning electron micrograph of a polyurea RIM sample

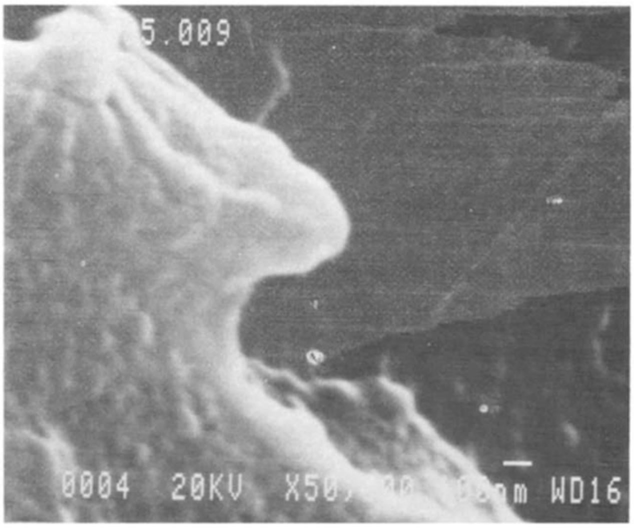

Figure 9 High magnification scanning electron micrograph of a polyurea RIM sample. A fracture dominates the centre

two reactants where a polyether diol or diamine was present. Analysis of product suggests that the high molecular weight reactant reacts with one or at most two MDI molecules, and it is speculated that this product forms a surface species which affects the stability of the dispersion.

The tendency for one phase to disperse uniformly into the other also exists during RIM, as shown by the microscope observations. The dispersion apparently is carried over into the final product structure. It is noted that micron scale heterogeneities have been observed[13] in polyurethanes.

The relatively low molecular weight product which forms at the interface between reactants may aid the dispersion process, which appears as one phase boiling into the other, see *Figure 2*. Imagine a large sheet of this product separating the two reactants. In fluid mechanical mixing there is a stretching tendency[14], as there is when the two drops on a microscope slide are perturbed. Such a stretch may cause the product layer to rupture, and via a capillary type of flow, one phase might disperse into the other, see *Figure 10a,b*. To analyse the flow at such a rupture, a balance between a capillary force and a viscous force can be made, see *Figure 10c*, assuming steady laminar flow through the rupture 'tube' and neglecting end effects:

$$2\pi R\sigma\cos\theta = 2\pi R\lambda\mu_A\left(\frac{v}{R/2}\right) \qquad (1)$$

where R is the tube radius, λ is the tube length, σ is the interfacial energy of mechanical importance between fluid phases A and B, θ is the contact angle, μ_A is the viscosity of phase A, and v is the volume average velocity of the flow. Rearranging equation (1) in terms of velocity gives:

$$v=\frac{\sigma\cos\theta}{2\mu_A}\left(\frac{R}{\lambda}\right) \qquad (2)$$

It is noted that a negative velocity results when phase A is non-wetting. This is simply flow in the opposite direction.

A typical velocity can be estimated by assuming an interfacial energy of 0.001 J/m^2 (low tension), a rupture tube diameter equal to the tube length ($2R=\lambda$), a viscosity of 0.05 Pa s, and a contact angle of zero. A velocity of 5000 μm/s is calculated, which would be the velocity of a dispersoid just as it leaves the interface. This rather large value may be accurate as the initial formation of a dispersoid was not observed; dispersoids suddenly appear and move away from the interface. As a dispersoid moves away from the interface, it is slowed in a short distance via viscous forces to a velocity that the eye can follow. This explains the dynamic dispersion phenomena observed via light microscopy.

The generation of a dispersion offers significant intermaterial area across which reactants can diffuse, then react. The smaller the dispersion size, the greater the intermaterial area per volume; hence, if diffusion of reactants through a growing product layer is the rate limiting event, then the dispersion size is critical in establishing the time it takes to form a product. Specifically, for such a diffusion controlled reaction the time to reach a particular conversion for various dispersion sizes is proportional to dispersoid size squared. It is noted that mould filling in RIM must be completed prior to the characteristic time for complete reaction.

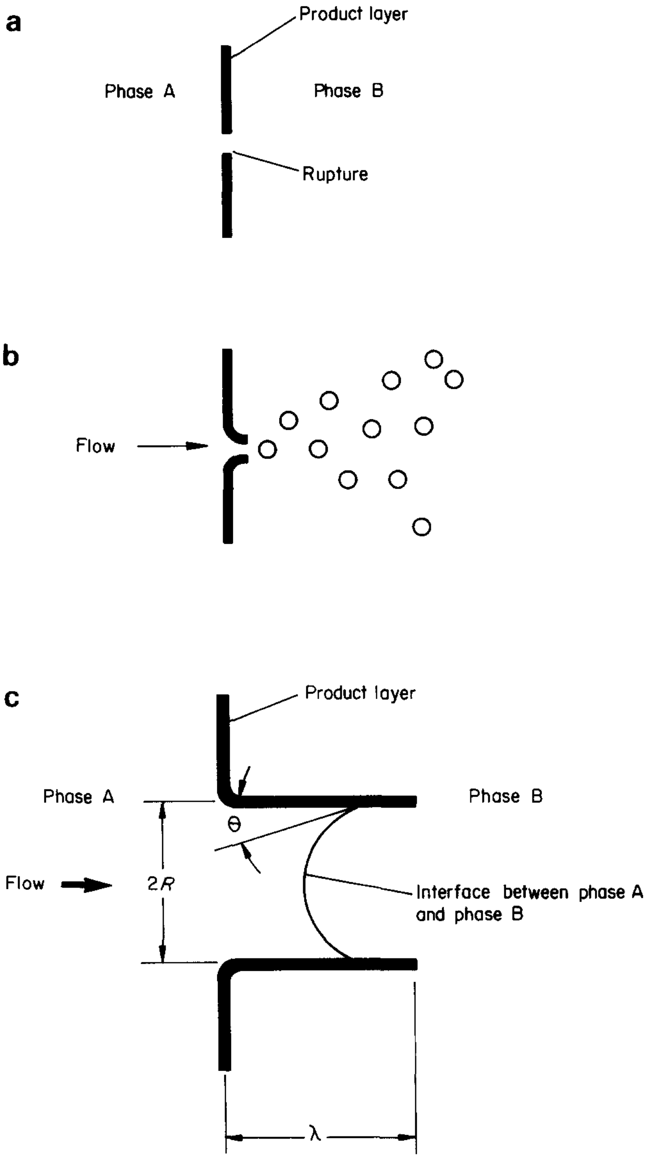

Figure 10 Generation of dispersion. (a) Rupture in the product layer between liquid phase A and phase B. (b) Dispersion occurs at a rupture. (c) A force balance can be made to analyse the flow at a rupture

Experimentally, the largest dispersion size was observed when E2103 and MDI were contacted. A smaller dispersion size was observed when a catalyst, DBTDL, was added to the diol phase. This suggests that DBTDL acts as a surface active species to reduce the dispersion size and increase the area per unit volume available for diffusion. Overall, increased rate of reaction is observed with the addition of DBTDL for polyurethane synthesis. This surfactant effect may complement DBTDL's behaviour as a coordination catalyst[15].

Additionally, the smallest dispersion size was observed in RIM type reactions that yield polyureas. This is consistent with their faster reaction rates as compared with RIM polyurethane reactions[16].

The dispersion of one reactant phase into the other, where diffusion at the dispersed space scale plays a role in establishing the observed reaction rate, offers an alternative mechanism for describing RIM reactions to prior chemical kinetic descriptions[16].

CONCLUSIONS

For the RIM systems studied, there was a tendency for one reactant phase to disperse into the other phase in impingement mixing. From the dispersion scale generated by such mixing, diffusion intimately contacts the opposing reactants so that they may polymerize. The scale of dispersion is influenced by the interfacial chemistry of the particular reactant phases, and any product that forms at the interface. Thus, by changing the reactants one may affect the scale to which they disperse, which changes the resultant intermaterial area per volume available for diffusion. If the polymerization is diffusion-controlled, the rate may be changed. In addition, a change in reactants not only produces a different polymer species, but a different dispersion may be created in mixing. Such a configuration carries over into the final product, and may have an effect on ultimate RIM product behaviour.

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