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Modeling the Dynamics of Reactive Foaming and Film Thinning in Polyurethane Foams

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Flexible polyurethane foams are widely used in cushioning and packaging applications. A model for the dynamics of formation of polyurethane foams is presented, which includes thinning of foam lamellae. Experimental measurements for water blown flexible foam formulations at different water concentrations are presented to validate the model. Adiabatic temperature rise measurements during foaming are used to obtain the kinetic parameters of the reactions of isocyanate with polyol and water. The variation of foam density during foaming is studied by weight loss and video shooting methods and both are compared to estimate the amount of blowing gas lost during foaming. The average thickness of the foam lamellae of the solid foam is obtained by SEM measurements. The predictions of the model show good agreement with the experimental measurements of temperature and density with time and the final lamellar thickness. The results are important for understanding the cell opening process. © 2009 American Institute of Chemical Engineers *AIChE J,* 56: 522–530, 2010

Keywords: polyurethane foam, cell opening, film thinning, residual lamellar thickness

Introduction

Polyurethane foams are versatile class of polymeric materials with wide range of applications.[1] Polyurethane foams are prepared by the polymerization of a polyol with an isocyanate, in which the reacting mixture is foamed using one or more blowing agents. The foams may have open or closed cells. Open cells are those in which the foam lamellae separating adjacent cells are all ruptured during the foam formation process. In closed cells, the lamellae remain intact. Flexible, open cell polyurethane foams are used as cushioning material with applications in furniture, automobiles, and packaging.

The foam formation process consists of various steps; mixing of the monomers and bubble nucleation, rise of the liquid foam, phase separation, which leads to rapid modulus rise and cell opening, and formation of a foamed elastomer.[2,3] The phase separation and cell opening steps play a key role in the formation of flexible polyurethane foams and determine the fraction of open cells. If the cells are all closed, the volume of the gas entrapped in the cells reduces on cooling, causing shrinkage of the foam. Moreover, the gas entrapped in the closed cells also resists compression, hindering the cushioning quality of the foam. Ideally, 100% of cells should be open in flexible polyurethane foams.

During foaming, gas bubbles dispersed in the reacting mixture grow in size and eventually impinge on each other forming a foam comprising cells, which are bounded by nearly planar lamellae (liquid films). Foaming, film thinning, and cell opening in flexible open cell foam formation are complex processes. This reactive foaming process differs considerably from that of nonreactive foam systems. Although a few studies on the dynamics of foaming of closed cell rigid polyurethane have been previously carried out,[4–6] the dynamics of open cell polyurethane foam formation has not been studied. Modeling studies on the bubble size distribution in free rise polyurethane foam have been reported.[7] Theoretical studies of heat transfer and curing in polyurethane foam during reaction injection molding have also been carried out.[8] Experimental studies on the effect of formulation parameters on the open cell content of flexible polyurethane foam have also been carried out.[3] So far, no

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theoretical studies on film thinning during polyurethane foam formation have been reported. The rate of film thinning depends on several parameters and has important role in determining the fraction of open cells in the cured foam. The fraction of open cells has a strong influence on many mechanical properties of open cell foams. Thus, a good theoretical understanding of the dynamics of foaming and film thinning during polyurethane foam formation would be helpful in developing new foam formulations and also in controlling the fraction of open cells.

In this article, we have tried to model the dynamics of foaming process during open cell polyurethane foam formation. The region of interest lies from the nucleation of bubbles to the gelation of foam structure. Various physico–chemical aspects of foaming during this regime, such as kinetics of reactions, density variation, adiabatic temperature rise, and film thinning are modeled. Predictions on each of these processes have been compared with experimentally determined data. Additionally, the residual thickness of gelled foam lamella is predicted and compared with experimentally measured values. The studies focused on freely rising, water blown, open cell polyurethane foams with varying blowing agent concentrations.

Model Development

In polyurethane foaming, two reactions occur simultaneously. In polymerization reaction, the isocyanate reacts with polyol, giving a urethane linkage. In blowing reaction, the chemical blowing agent (water) reacts with isocyanate to produce carbon dioxide and urea. The gas bubbles dispersed during mixing grow due to the diffusion of blowing gas in to the bubble. At cream time, the reaction mixture becomes saturated with blowing gas (carbon dioxide) and the dispersed bubbles start growing. At sufficiently low foam densities, the bubbles are deformed into polyhedral cells, which may be idealized to be pentagonal dodecahedra. Three pentagonal lamellae of adjacent bubbles meet at 120° to form Plateau borders and four such borders meet at a tetrahedral angle of about 109°. Lamellae drain into the Plateau borders and these borders drain into the Plateau borders situated below. The rate of change of thickness of a foam lamella during foaming depends on viscosity of the polymerizing liquid and drainage from the film to the Plateau borders due to capillary forces. The capillary drainage of the liquid from the lamellae to the Plateau borders reduces the thickness of the film. Increase in viscosity due to polymerization reduces the drainage. In contrast, the increase in the temperature due to the exothermic reactions reduces the viscosity of the reacting mixture, accelerating the liquid drainage. The surfactant present in the reacting liquid limits the coalescence of bubbles.

The polyurethane foam is assumed to be a single pseudo-homogenous phase, and the energy and the mass balances are used along with kinetic and thermodynamic relations to obtain the density and temperature with time. The kinetic parameters of the reactions of isocyanate with polyol and water, respectively, are obtained separately and are assumed to be independent of each other.[4,5] The carbon dioxide generation is assumed to be water-isocyanate reaction controlled. Thus, all carbon dioxide generated after saturation is assumed to be in the bubble phase. For drainage from the films, the window lamellae are assumed to be plane parallel and tangentially immobile. For simplicity, the resistance to bubble expansion due to momentum transfer and bubble coalescence have been neglected.

Enthalpy balance

The thermal energy balance for free rising polyurethane foam with water as the chemical blowing agent under adiabatic conditions is given by

$$(C_\mathrm{P} + [\mathrm{CO_2}]C_{\mathrm{CO_2}})\frac{dT}{dt} = \left[\frac{(-\Delta H)_\mathrm{OH}[\mathrm{OH}]_0}{\rho_\mathrm{P}}\right]\frac{dX_\mathrm{OH}}{dt} + \left[\frac{(-\Delta H)_\mathrm{W}[\mathrm{W}]_0}{\rho_\mathrm{p}}\right]\frac{dX_\mathrm{W}}{dt} \qquad (1)$$

The thermal energy balance gives the net rate of increase of temperature due to the heat generated by the exothermic reactions of polymerization and blowing. The parameters C_P, $C_{\mathrm{CO_2}}$, $(-\Delta H_\mathrm{W})$, and $(-\Delta H_\mathrm{OH})$ are all assumed to be constant in the temperature range of interest.

Kinetics of polymerization and blowing

The polymerization of polyol and isocyanate to form urethane chain is assumed to follow second order reaction kinetics.[5] The rate of depletion of reactive end groups of polyol is given by

$$\frac{d[\mathrm{OH}]}{dt} = -A_\mathrm{OH}\exp(-E_\mathrm{OH}/RT)[\mathrm{NCO}][\mathrm{OH}] \qquad (2)$$

It is assumed that the above rate of reaction is unaffected by the reaction products of water isocyanate reaction. If the reaction mixture has water as chemical blowing agent and a stoichiometric amount of isocyanate, then

$$[\mathrm{NCO}] = [\mathrm{NCO}]_0 - 2([W]_0 - [\mathrm{W}]) - ([\mathrm{OH}]_0 - [\mathrm{OH}])$$
$$[\mathrm{OH}] = [\mathrm{OH}]_0(1 - X_\mathrm{OH})$$
$$[\mathrm{W}] = [\mathrm{W}]_0(1 - X_\mathrm{W})$$

The change in conversion with time is given by

$$\frac{dX_\mathrm{OH}}{dt} = A_\mathrm{OH}\exp(-E_\mathrm{OH}/RT)[\mathrm{OH}]_0[1 - X_\mathrm{OH}] \times (r_\mathrm{NCO} - 2r_\mathrm{W}X_\mathrm{W} - X_\mathrm{OH}) \qquad (3)$$

where

$$X_\mathrm{OH} = ([\mathrm{OH}]_0 - [\mathrm{OH}])/[\mathrm{OH}]_0$$
$$r_\mathrm{NCO} = [\mathrm{NCO}]_0/[\mathrm{OH}]_0$$
$$r_\mathrm{W} = [\mathrm{W}]_0/[\mathrm{OH}]_0$$

The isocyanate–water reaction occurs usually with many simultaneous side reactions. The reaction is chemically represented as

$$2\mathrm{R{-}NCO} + \mathrm{H_2O} \xrightarrow[k_1]{} \mathrm{R{-}NH{-}COOH} \longrightarrow \mathrm{R{-}NH_2} + \mathrm{CO_2} \xrightarrow[k_2]{} \mathrm{R{-}NH{-}CO{-}NH{-}R}$$

The electropositive substituents on the isocyanate (—CH_2— in the case of MDI) makes k_2 much larger than k_1 in the above blowing reaction because the carbamic acid formed is unstable.[9] It has been shown in literature that the reaction between water and isocyanate follows first order kinetics.[10] Assuming an Arrhenius temperature dependence of the rate constant and first order kinetics with respect to the concentration of water, the rate of blowing reaction is given by

$$\frac{d[\mathrm{W}]}{dt} = -A_{\mathrm{W}} \exp(-E_{\mathrm{w}}/RT)[\mathrm{W}] \tag{4}$$

The change in conversion with time is given by

$$\frac{dX_{\mathrm{W}}}{dt} = A_{\mathrm{W}} \exp(-E_{\mathrm{w}}/RT)(1 - X_{\mathrm{W}}) \tag{5}$$

where

$$X_{\mathrm{W}} = \frac{[\mathrm{W}]_0 - [\mathrm{W}]}{[\mathrm{W}]_0}$$

Viscosity rise during foaming

The viscosity of the reacting liquid in polyurethane foaming, as a function of temperature and conversion is given[11] by

$$\eta = \eta_0(T)\left[\frac{X_{\mathrm{NCO}}}{X_{\mathrm{NCO}(g)} - X_{\mathrm{NCO}}}\right]^{C_1 + C_2 X_{\mathrm{NCO}}} \tag{6}$$

where $X_{\mathrm{NCO(g)}}$ is the conversion at gel point. The initial viscosity is given by an Arrhenius relation of the form

$$\eta_0(T) = A_\eta \exp(E_\eta/RT). \tag{7}$$

Bubble size

The assumption that the foam expansion due to CO_2 is kinetically controlled is justified provided the rate of generation of CO_2 is slow relative to the rate of mass transfer to individual bubbles in the foam. The bubbles nucleated at cream time, grows by the mass transfer of the gas from the bulk liquid to the bubble. The rate of molar mass transfer to the bubble is given by

$$\frac{dn}{dt} = -k_{\mathrm{L}}([\mathrm{C}]_\infty - [\mathrm{C}]_i)4\pi R_{\mathrm{B}}{}^2$$

where $[\mathrm{C}]_\infty$ and $[\mathrm{C}]_i$ are the concentrations of gas at the bulk and at the interface. R_{B} is the radius of the bubble and n is the number of moles of gas.

Assuming ideal gas law, the volume of the bubble at any time $V_{\mathrm{B}}(t)$ is given by

$$V_{\mathrm{B}}(t) = \frac{n(t)RT(t)}{P}$$

The pressure inside the bubble is assumed to be atmospheric. Thus the radius of the bubble at any time t is given by

$$R_{\mathrm{B}}(t) = \left(\frac{3V_{\mathrm{B}}(t)}{4\pi}\right)^{1/3} \tag{8}$$

Thus the rate of molar mass transfer to the bubble from the bulk liquid is given by

$$\frac{dn(t)}{dt} = -4\pi D\left([\mathrm{W}_0]X_{\mathrm{W}} - [\mathrm{C}]_i\right)\left(\frac{3n(t)RT(t)}{4\pi P}\right). \tag{9}$$

Film drainage

The rate of lamellae thinning can be obtained from Reynolds equation.[12,13] Film thinning happens due to drainage as well as expansion of bubbles. The drainage equation is then

$$\frac{dh(t)}{dt} = -\frac{4\gamma h(t)^3}{3R_{\mathrm{p}}\eta(t)R_{\mathrm{B}}(t)^2} - \frac{2h}{R_{\mathrm{B}}}\frac{dR_{\mathrm{B}}}{dt} \tag{10}$$

where h is the film thickness, η is the dynamic viscosity, R_{P} is the radius of the Plateau border, and γ is the surface tension. The first term of right hand side is due to drainage, whereas the second term is due to bubble expansion. The surface tension is assumed to be constant in the temperature range of interest.

Experimental Details

Materials

The two main components of the formulation were a polyether polyol (Arcol 3553, Bayer Polyurethanes) with a hydroxyl value of 32 mg/g of KOH and a molecular weight ≈4900. The isocyanate used was polymeric MDI based (Suprasec 6456, Huntsman Polyurethanes). The polyol was kept under vacuum at 100°C for 2 h to remove traces of water. The polyol was mixed with catalysts (0.3 pphp Dabco 33LV, 0.25 pphp DMAPA, and 0.2 pphp Niax A1), surfactant (0.6 pphp Tegostab B4113), and crosslinker (0.1 pphp DEOA). Here, pphp denotes parts per hundred parts of polyol. Distilled water was used as blowing agent.

Dynamic measurements

The temperature rise and weight loss during foam formation was measured as a function of time using an experimental set up shown in Figure 1. A rigid circular disk of diameter 24 cm, made of epoxy, having level adjustment screws at the bottom was used as a platform. Three radial grooves, at an angle of 120° were cut in the disk and load cells of capacity 300 g having an accuracy of 0.01 g (Smart Sensors and Transducers, Mumbai) were inserted in to these grooves. A spirit level indicator was placed at the centre of the circular platform. These load cells were connected along with a K-type thermocouple to a data acquisition module (ADAM-4018, Advantech). The temperature and weight data were collected using data acquisition software (Adam View).

Foaming process

A transparent circular plate made of PMMA was placed over the assembly of load cells. A container made of expanded polystyrene having a diameter of 11 cm was placed over the experimental set up. The foaming was done in a cylindrical PVC container of diameter 9 cm. The volume of the container and the amount of reaction mixture was so chosen that the shoulder of the final foam was always

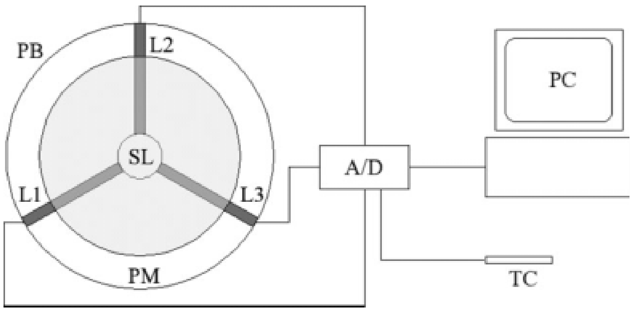

Figure 1. Schematic view of experimental apparatus used for weight loss and adiabatic temperature rise measurements.

L1, L2, L3 are load cells, SL is the spirit level indicator, PM is the support plate made of PMMA, for the support of the container in which foaming takes place and PB is the circular plate made of epoxy on which the load cells are mounted in the radial grooves. TC is a thermocouple and A/D is the analog to digital converter connected to a computer (PC).

below the neck of the container. The polyol was blended with all the foaming agents and was stirred at a speed of 2500 rpm. To this blend, isocyanate was added and stirred for 8 s at a speed of 3000 rpm. The weight ratio of polyol blend to isocyanate was 100:65 (isocyanate index = 100). Immediately after stirring, a K-type thermocouple was inserted in to the cylinder and the whole system was inserted in to the polystyrene cylinder. The thermal insulating nature of both PVC and polystyrene results in minimal heat losses from the container and the foam expansion is nearly adiabatic. Moreover, the air gap between the two containers adds to the heat transfer resistance.[6]

Experimental determination of kinetic parameters

Kinetic Parameters for Urethane Formation. The kinetics of the polyurethane reaction was obtained by analyzing the temperature rise measured during an adiabatic reaction of a nonfoaming system (with no blowing agent). The formulation of the polyol blend was kept exactly same as the case of foaming except that water was absent in this case. The polyol blend was mixed with the same amount of isocyanate in an expanded polystyrene container at a speed of 3000 rpm for 15 s. A K-type thermocouple was inserted at the centre of the well-mixed reactants. The data from the thermocouple was recorded using a PC as explained earlier. The kinetic parameters were obtained by a method developed by Lipshitz and Macosko.[14] The method is briefly given below.

Assuming that the heat capacity is independent of temperature, the energy balance is given by

$$\rho_P C_P \frac{dT}{dt} = (-\Delta H)\frac{dX}{dt}[\mathrm{C}]_0 \tag{11}$$

and the pregel reaction rate equation

$$\frac{dX}{dt} = A\exp(-E_a/RT)[\mathrm{C}]_0^{n-1}(1-X)^n \tag{12}$$

Integrating Eq. 11 with respect to time, we obtain

$$(-\Delta H)X = \frac{\rho_P C_P (T - T_0)}{[\mathrm{C}]_0} \tag{13}$$

At completion of the reaction (at $X = 1$) we have

$$(-\Delta H) = \frac{\rho_P C_P \Delta T_{ad}}{[\mathrm{C}]_0} \tag{14}$$

where

$$\Delta T_{ad} = (T_{max} - T_0)$$

Substituting Eq. 14 in Eq. 13 we get

$$X = \frac{(T - T_0)}{(T_{max} - T_0)} \tag{15}$$

Using Eq. 12 and Eq. 15, Eq. 11 becomes

$$\ln\left[\frac{1}{(T_{max} - T)^n}\frac{dT}{dt}\right] = -\frac{E_a}{RT} + \ln\left\{A\left(\frac{[\mathrm{C}]_0}{T_{max} - T_0}\right)^{n-1}\right\} \tag{16}$$

The above equation correlates the incremental change in temperature of the exothermic polymerization reaction to that of kinetic parameters. For the correct order, when the left hand side of this equation (designated as α) is plotted against $1/T$, the graph should yield a straight line. Thus this combined equation involving both kinetic and thermodynamic profile of the polymerization reaction could be used to get various parameters (A, E_a, and n) of reaction. The method is described as follows; T_0 and T_{max} were directly obtained from the experimental temperature vs. time data, and (ΔH) was obtained from Eq. 14. The experimental data was smoothed by using a first degree least square technique with a five point technique.[5] Numerical differentiation of the smoothed adiabatic temperature data was carried out using Mathematica 5.1 so as to calculate dT/dt. If the left hand side of Eq. 16 is plotted against $1/T$ for various values of T until the gel point, a straight line is obtained for the correct value of n. A least square technique was used with different values of n for which smallest mean square error was obtained with $n = 2$. The slope of the line gave the value of E_a, whereas the y-intercept gave the value of A. The viscosity of the adiabatic reacting mixture remains low, until close to gel point, and quickly shoots up to infinity.[14–16] This phenomenon is used to experimentally determine the gel point by moving a glass rod in the reacting liquid, until the movement is resisted by a sudden rise in viscosity.

Kinetic Parameters for the Blowing Reaction. The kinetics of the blowing reaction was obtained by analyzing the CO_2 generation with time. Because of the heat loss from the free surface, the temperature of the top skin is much lower than the inner core. This results in the formation of a dense skin, because the blowing near the top skin is slowed.[17] The dense skin prevents any significant loss of CO_2 throughout the foaming process, particularly after cell opening. The moles of CO_2 generated were calculated from the foam volume by assuming that the gas followed the ideal gas law and the internal pressure inside the foam was equal to the atmospheric pressure. The corresponding temperature of the gas (expanding foam) was obtained from the adiabatic temperature rise measurements. Rearranging Eq. 5 yields,

$$\ln\left[\frac{1}{(1-X_{\mathrm{W}})}\frac{dX_{\mathrm{W}}}{dt}\right]=\frac{-E_{\mathrm{W}}}{RT}+\ln A_{\mathrm{W}}. \tag{17}$$

The above equation correlates the incremental change in conversion of blowing reaction to that of its kinetic parameters. Numerical differentiation of the data of X_{w} with time was done to obtain dX_{w}/dt. The left hand side of Eq. 17, denoted as β, plotted against $1/T$ for different values of T, yields a straight line. The kinetic parameters are easily obtained from the slope and intercept of the fitted straight line. The data up to the end of visual foam rise was considered, because beyond this point the resistance provided by gelled polymer substantially reduces the rate of foam expansion.

Table 1. Material Parameters

Polyurethane	
ρ_{P}	1020 Kg/m^3
C_{P}	1134 J/Kg°K
Carbon dioxide	
$M_{\mathrm{CO_2}}$	44
$C_{\mathrm{CO_2}}$	836.6 J/Kg°K
Polyurethane kinetic parameters	
A_{OH}	12.553 m^3/g moles/s
E_{OH}	82.872×10^4 J/g mole
$-\Delta H_{\mathrm{OH}}$	5.036×10^3 J/g mole
Blowing reaction kinetic parameters	
A_{W}	39.2615×10^3 s^{-1}
E_{W}	39.667×10^3 J/g mole
$(-\Delta H_{\mathrm{W}})$	10.459×10^3 J/g mole
Viscosity parameters	
A_η	3.095 MPa s
E_η	2237 J/g mol
C_1	3.5
C_2	−2.0
Other parameters	
γ	0.03 N/m
R_{P}	10^{-6} m
h_i	20 μm

Density measurements

The density measurements were made by weight loss method and by direct video shooting of foam formation. The density of foam at any time t is given by

$$\rho(t)=V(t)/W_{\mathrm{cream}}$$

assuming that there is negligible loss of blowing gas from the foam. The density of foaming was also measured experimentally by conducting video shooting of the foam formation (Sony Handycam, DCR HC 32E PAL) of the foam rise, occurring inside a graduated glass container. The movie obtained was edited using software (Pinnacle Studio) to obtain the foam volume at different times.

The decrease in weight measured during the rise of foam is due to the increase in the buoyant force applied by the increasing volume of displaced air. No loss of weight is recorded until cream time as the CO_2 generated dissolves in the reacting liquid resulting in no foam rule. The force of buoyancy is given as

$$F_{\mathrm{buoyant}}(t)=\rho_{\mathrm{air}}V_{\mathrm{foam}}(t)g$$

The weight of the polymer at cream time is given by

$$W_{\mathrm{cream}}=m_{\mathrm{cream}}g$$

The loss of weight indicated during the rise of foam is due to the change in the buoyant force applied by air due to increase in the foam volume. The apparent weight any time t of foaming, after cream time is given by

$$W(t)=m_{\mathrm{cream}}g-\rho_{\mathrm{air}}V_{\mathrm{foam}}(t)g$$

From this, the volume of foam at any time t, after cream time is given as

$$V(t)=\frac{W_{\mathrm{cream}}-W(t)}{\rho_{\mathrm{air}}}$$

The fractional conversion based on the above assumption is given by

$$X_{\mathrm{W}}=\frac{P(V_{\mathrm{F}}(t)-V_{\mathrm{cream}})}{RTW_{\mathrm{cream}}}$$

Measurement of residual film thickness

The residual lamellar thickness was measured by a technique proposed by Yasunaga et al.[3] From the cured foam, a broken window was plucked out and was mounted normal to the platform of SEM (Philips, FEI Quanta) by embedding it inside synthetic clay. The scanning was done across the film thickness. This technique has been found to be very effective in determining the thickness of the cell windows and has been shown to give results similar to that obtained using Light Interferometry.[3] Around eight films plucked from various parts of the foam buns were analyzed.

Estimation of other parameters

The values of physical properties used in the calculations are listed in Table 1. The value of C_{P} was obtained by carrying out a DSC study of powdered polyurethane foam sample. The heating and cooling cycle was done from 5 to 170°C. The value of specific heat capacity, corresponding to room temperature (25°C) was taken. Molecular weights of MDI and polyol were measured by vapor phase osmometry after dissolving in THF. Values of the specific heat capacity of CO_2, ($C_{\mathrm{CO_2}}$) and the diffusion coefficient D were obtained from literature.[18] ΔH_{W} was calculated from the temperature rise data using energy balance equation. The solubility of carbon dioxide in the reacting polymer is shown to be very small,[5] and is hence neglected. The values of A_η,E_η,R_{p} and γ have been taken from the literature.[11,12,19]

Results and Discussions

Kinetics

The adiabatic temperature rise method is used to find the enthalpy of polymerization reaction and subsequently the

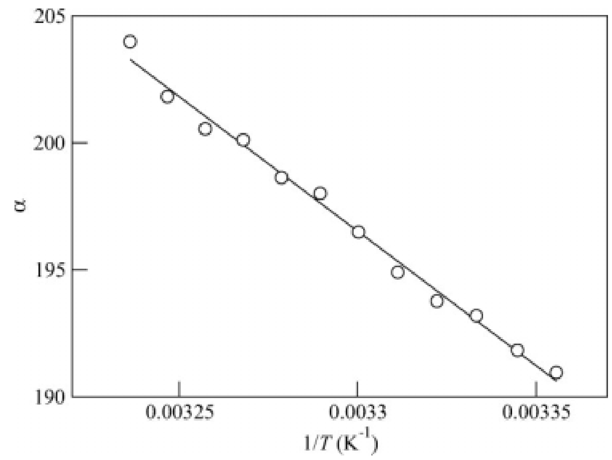

Figure 2. Kinetics of reaction between isocyanate and polyol in the absence of water.

The left hand side of Eq. 16 (α) is plotted vs. $1/T$ for polymerization reaction order $n = 2$.

kinetic parameters of the polymerization. The left hand side (designated as α in figure) of the combined equation (Eq. 16) plotted against $1/T$ for order of reaction $n = 2$ is shown in Figure 2. It can be seen that for order $n = 2$, a fitted straight line describes the data very well. By substituting $n = 2$ and from the resulting straight line, the pre-exponential factor A_{OH} and the activation energy E_{OH} are obtained from the slope and intercept of the fitted straight line. The values are given in Table 1. Consider next the kinetics of the blowing reaction. A graph of the left hand side of Eq. 17 (β) plotted vs. $1/T$ is shown in Figure 3 for different blowing agent concentrations. A single straight line fits the data for different blowing agent concentrations reasonably well. This indicates that the assumption of the reaction of isocyanate with water being first order in the water concentration is valid. The kinetic parameters of the reaction of water with isocyanate namely the pre-exponential factor A_W and the activation energy E_W is obtained from the intercept and slope of the fitted straight line, respectively. These values are indicated in Table 1.

Adiabatic temperature rise

The adiabatic temperature rise during the foam formation is shown in Figure 4. The estimation of enthalpy of polymerization reaction is done by analyzing the temperature rise during a nonblowing reaction. The values of enthalpy of both polymerization reaction ($-\Delta H_{OH}$) and foaming ($-\Delta H_W$) are shown in Table 1. It could be seen that the blowing reaction is more exothermic than the polymerization. Both theoretical and experimental values are shown. The theoretical predictions of adiabatic temperature show good agreement during the initial stages of foaming but are slightly higher than the theoretically predicted values in the post-gelation period. This is due to radiation heat losses from the foam, which is not accounted for in the model. Note that there is no film drainage in the post-gelation period so that this deviation does not affect the predictions of the variation of film thickness with time.

Density

Figure 5 shows the change in density of the foam with time during foaming, plotted from cream time onwards, and calculated from both weight loss data and video shooting techniques. The density shows no change until cream time because the CO_2 produced until cream time dissolves in the reacting liquid. Although there is an excellent agreement in the values of densities in the early stages of foam formation, in the later stages the actual densities are slightly higher than the ones predicted from weight loss technique. The difference is due to loss of carbon dioxide from the foam during foaming after cell lamellae have ruptured (i.e., after cell opening). The gas loss increases with increase in water concentration. Comparison of the densities measured by the two methods indicates a loss of CO_2 to be 5–10 wt %. The

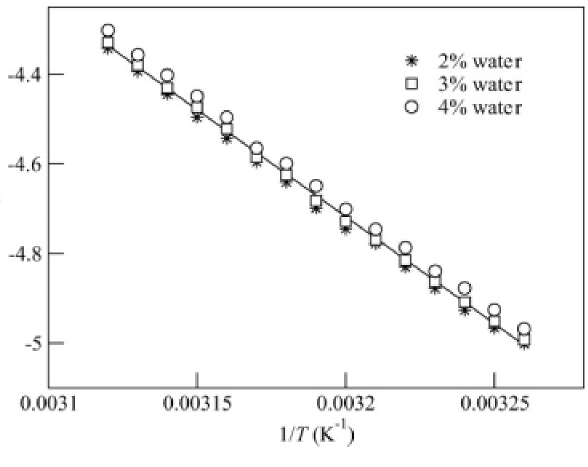

Figure 3. Kinetics of the reaction of isocyanate with water obtained from adiabatic temperature rise and foam density measurements.

The left hand side of Eq. 17 (β) is plotted vs. $1/T$ for reaction order $n = 1$ and different blowing agent concentrations.

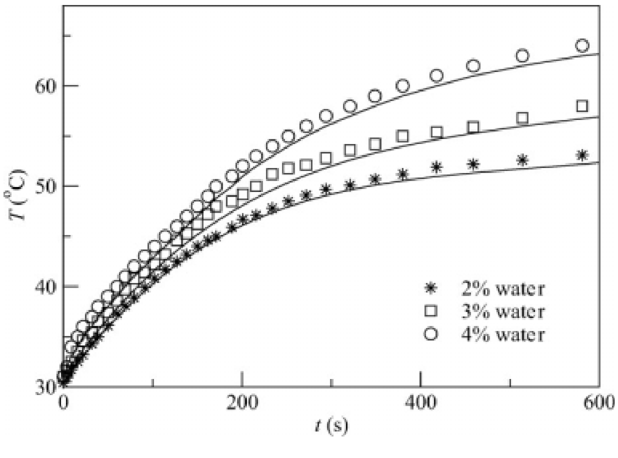

Figure 4. Variation of temperature with time during adiabatic foaming for different water concentrations as indicated in the legend.

Symbols show experimental data and the lines are the model predictions.

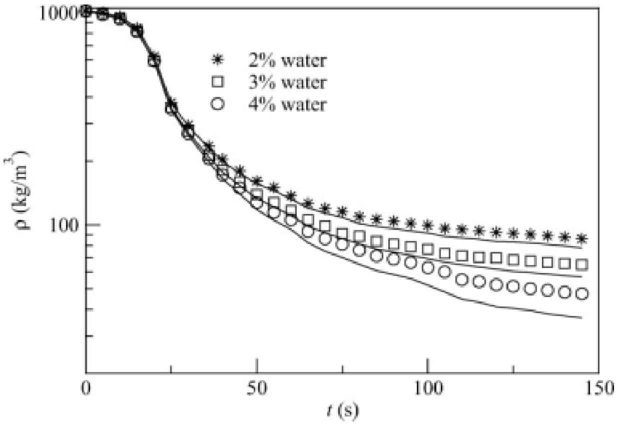

Figure 5. Variation of density (ρ) with time (*t*) during adiabatic foaming for different water concentrations as indicated in the legend.

Symbols show experimental data obtained from volume measured by video recording of the foaming and the lines are the values obtained from measurement of weight loss with time.

resistance provided by the thick top skin and that by the walls of the container limits the gas loss to such small quantities. The density measurements by both the methods were found to be the same throughout the foaming, in the case of closed cell foams, in which no gas loss is possible.[5]

Conversion

Figure 6 shows the conversions obtained by theoretical simulation for the blowing and polymerization reactions (up to gel time). The experimentally determined conversion values for the blowing reaction (obtained using weight loss method) are also shown. It can be clearly seen that the rate of blowing reaction is significantly higher than that of polymerization reaction. The higher relative rate of the blowing reaction ensures that the isocyanate concentration remains in excess through out the blowing reaction and thus the assumption of the rate of blowing reaction being independent of isocyanate concentration is justified. The rates of both, the polymerization and the blowing reactions, increase with increase in water concentration. There is excellent agreement between the conversions predicted theoretically and the experimentally determined values for blowing reaction.

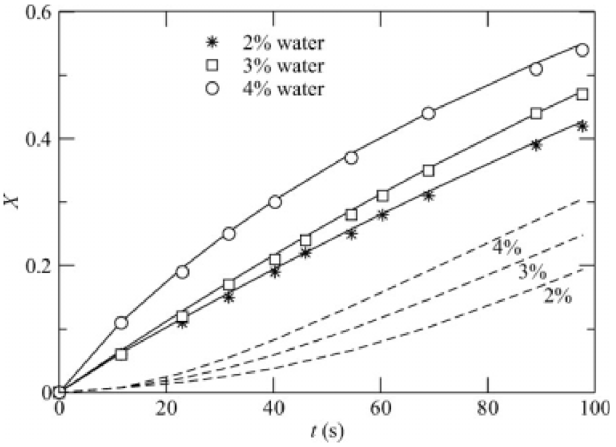

Figure 6. Variation of conversion (*X*) with time (*t*) for the polymerization reaction and the blowing reaction.

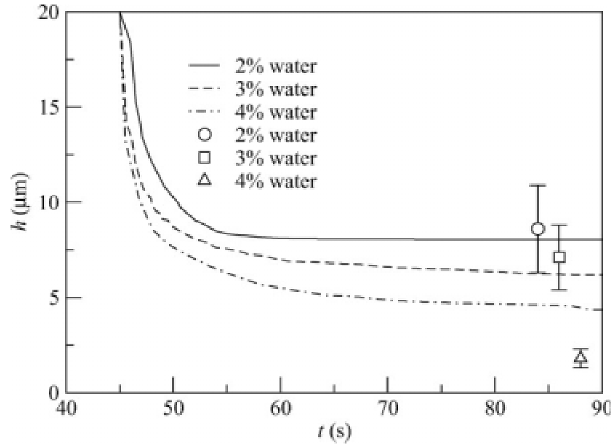

Figure 7. Variation of film thickness (*h*) with time (*t*) during foaming.

The lines show the predictions of the model for different water concentrations. The symbols give the measured values of the film thickness of the solid foams for the corresponding water concentrations.

Film thinning

Figure 7 shows the lamella thickness variation as a function of time. The integration of the equation is done from a time at which the foam volume is equal to about 65% of the cured foam volume at which the bubbles foam close packed spheres. At this time, the gas hold up in the foam would be sufficiently high to have bubbles to be close enough to form Plateau borders. The radius of Plateau border R_P is taken from the literature[12] and is assumed to remain constant. The initial film thickness is assumed to be $h_i = 20$ μm. The film thickness reduces rapidly with time initially and reaches a constant value near the gel time (Figure 7). The film thickness at gel time reduces with increasing water concentration. A sample SEM micrograph of a film plucked from a cured foam is shown in Figure 8. The measured values of the thin point thickness of the film are found to be 8.6 ± 2.3 μm for 2 pphp water, 7.1 ± 1.7 μm for 3 pphp water and 1.8 ± 0.5 μm for 4 pphp water. These data are also shown in Figure 7, and the predicted thicknesses are in reasonable agreement with the data. Earlier studies[3] using different formulations with 4% water found the film thicknesses to be 1.28 ± 0.40 μm and 0.82 ± 0.24 μm, which are in reasonable agreement with the current value.

Conclusions

The dynamics of various physico–chemical processes during open cell polyurethane foam formation has been theoretically described and compared with the experimental data. Apart from this, the residual film thickness of cell window

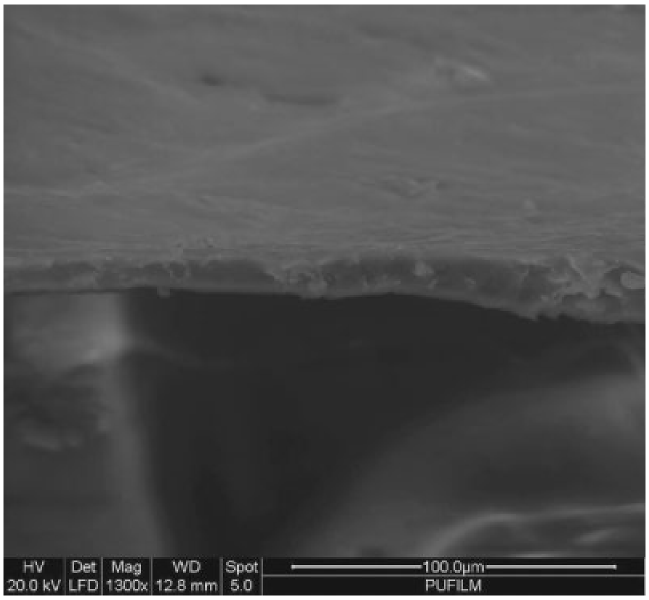

Figure 8. Sample SEM micrograph of a film plucked from a foam.

lamella is theoretically estimated and compared with the experimentally measured data. The results are validated for varying blowing agent concentrations.

The exothermic nature of both reactions has been theoretically described by estimating the adiabatic temperature rise during the entire process from enthalpy balance. The experimental measurement of the temperature rise is done by an automated system and compares well with theoretically predicted dynamics during the initial stages of foaming and slightly differs during the final stages of foaming probably due to the heat loss due to radiation.

The kinetics of foaming and polymerization are theoretically estimated assuming that they are independent of each other. The experimental results obtained show that this assumption is fairly true. Although the polymerization reaction has a second order rate dependence, the foaming reaction follows first order kinetics.

The variation in density of foam as a function of time from bubble nucleation (cream time) is estimated by weight loss and direct visualization methods, and the results are compared. By comparing these two techniques, the estimation of amount of blowing gas lost during foaming could be estimated. It is found that, although the cells are opened during foam formation, only a small amount of blowing gas is lost during foaming. This is due to the significant resistance offered by the thick top skin and the container walls. The small amount of blowing gas lost after the cell opens is manifested from the difference in the densities estimated from these two techniques during the final stage of foaming.

The change in thickness of film from the time at which the bubbles are adjacent enough to foam Plateau borders to that of gelation of polymer is theoretically estimated. The window lamella initially thins quickly to reach a constant thickness near gel point. The residual thickness of window lamella is measured by microscopy and compared with this constant value and is shown to be in agreement with theoretically predicted value. All these results are presented for varying water concentrations and are fairly reproducible at different blowing agent (water) concentrations.

The results presented are important for understanding the cell opening process in the manufacture of flexible polyurethane foams, because cell opening occurs only if the foam lamellae become sufficiently thin. To predict the fraction of open cells, the model presented here must be augmented with a model for film stability and rupture. Alternatively, the fraction of open cells may be correlated to the final lamellae thickness. These issues need further study.

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Notation

A = pre-exponential factor in kinetic expression, m^3/g-equiv s
$[C]_0$ = initial concentration, g-equiv/m^3
C_P = specific heat capacity of polymer, J/kg K
C_{CO_2} = specific heat capacity of CO_2, J/kg K
D = diffusion coefficient, m^2/s
E_a = activation energy, J/g mole
h = film thickness, μm
ΔH = heat of reaction, J/g-equiv
k_L = liquid phase mass transfer coefficient, m/s
n = order of reaction
[NCO] = concentration of isocyanate end groups, g-equiv/m^3
[OH] = concentration of hydroxyl end groups, g-equiv/m^3
P = atmospheric pressure, N/m^2
R = universal gas constant, J/mol K
r_{NCO} = ratio of initial concentration of isocyanate to hydroxyl end groups
r_{OH} = ratio of initial concentration of water to hydroxyl end groups
T = temperature, K
t = time, s
X = fractional conversion
V = volume, m^3
[W] = concentration of water, g-mole/m^3

Subscripts

o = Initial value
CO_2 = carbon dioxide
OH = polyol
NCO = isocyanate
P = polymer

Greek letters

γ = surface tension, N/m
η = viscosity, Pa s
ρ = density, kg/m^3

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