

Evaluation and Modelling of the Dynamics of Filled Flexible Polyurethane Foam

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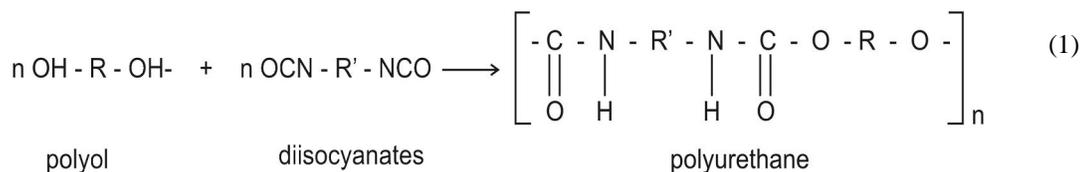
Abstract

Models for flexible polyurethane foaming process containing filler have been developed to predict the dynamics of the foam formation system. Kinetic parameters of the polymerization and blowing reaction for the co-generation of carbon dioxide were determined as necessary precursors for evaluation of the thermal model, assuming the foam reaction kinetics to be controlled by the rate of generation of carbon dioxide. The dynamics of the foam process evaluated in terms of the temperatures predicted agree well with the measured exotherm of the foam growth process during initial foam growth, but with reaction at gel point, the predicted temperatures were higher than experimentally determined. Mechanical properties of foam and hence its quality have been related to the dynamics of the foam formation system. High temperatures that favour formation of the chemical species – biuret and allophanate promotes foam of improved quality in hardness. [Nature and Science 2010;8(9):159-167]. (ISSN: 1545-0740).

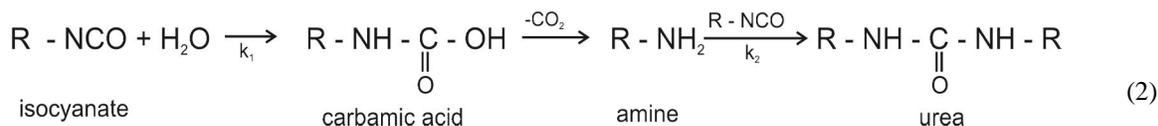
Keywords: flexible polyurethane foam, indentation hardness, temperatures, kinetics, calcium carbonate.

Introduction

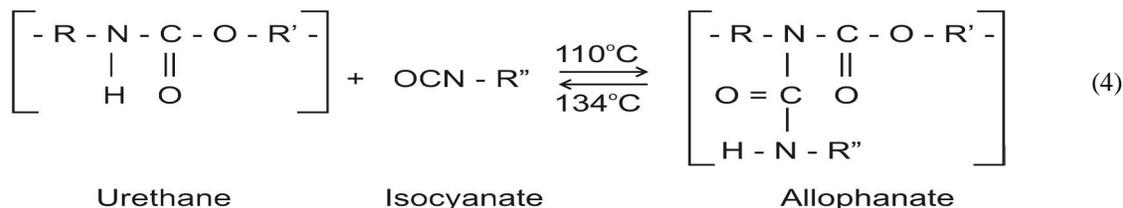
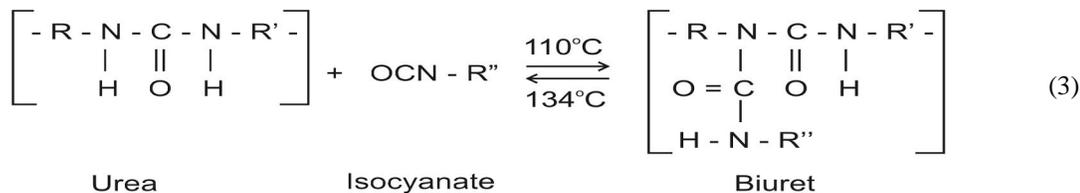
In applications that require materials with high and effective resistance to compression, fillers have been incorporated in flexible polyurethane foams. In many of these applications such as in mattresses, furniture, and upholstery, it is essential that the reaction of the polyisocyanate and polyol (poly (tetramethylene ether) glycol) in Equation 1 to form the polyurethane mass goes to completion so that mechanical strength is build up (Van Thuyne and Zeegers, 1978) in the foam for its effectiveness .



The polyurethane mass is blown by a gas produced in a reaction between isocyanate and water which occur simultaneously as that in equation 1.



The blowing and polymerization reactions are highly exothermic. In-situ evolution of the mechanical properties of the foam material have been linked with certain chemical species of the foam structural architecture formed during the sequence of foam development at certain temperature (Hauptman et al., 1980, have reported a temperature of 110 °C). It has been reported of these chemical species which are formed from the secondary reactions of isocyanate with urea (Equation 3) and urethane (Equation 4) of their influential roles in the improvement of mechanical properties such as hardness of the foam. The chemical species achieve this role by acting as polydisperse phase in the foam matrix structure.



By the incorporation of filler in flexible polyurethane foam, the biphasic medium created results in the filling of foam voids with the fillers at the polymer/filler interfaces. The liquid polymer contained in the cellular structure drains into the area joining three closely packed bubbles. On the other hand, fillers can encourage interactions with the polyether soft segment in the foam structure cell struts contributing to the thickness of the morphology. These two events are brought about depending on the granulometry, the surface state, and the filler type (Saint-Michel et al., 1980). From the interaction of the filler with the polyether soft segment will be an increase in the hardness of the foam as a result of the ability of the filler to create additional disperse phase in the foam medium. However, fillers are heat sinks (Elwell et al., 1996). They dissipate the heat of the foam reaction and may distort the formation of the chemical species biuret and allophanate if the exotherm of the foam medium is reduced below a certain level (Klempner and Sendjarevic, 2004 have reported a temperature of 134 °C). The volume fraction of filler that may then be used in foam to enhance its mechanical properties is thus limited. This makes a study of the dynamics of flexible polyurethane foam reinforced with filler important because the final foam morphology is determined by the kinetic competition between polymerization and poly disperse phase formation.

Theoretical modeling of the dynamics of polyurethane foaming process has been carried out before. These models derived their foundations from the studies reported in literature to understand the water-blown polyurethane foam formation process. For instance, infrared analyses of the reacting foams have been carried out by a number of investigators to determine the sequence of chemical reactions that occur during water-blown flexible polyurethane foam

formation (Edwards, 1981; Bailey and Critchfield, 1981). The study reported the detection of carbamic and arylamine carbamate during the initial period of foam rise, and subsequently detection of disubstituted urea when the rate of foam rise has reached a maximum (30 to 60 wt% of full rise height).

Van Gheluwe and Leroux (1983) have studied the sequence of reactions in polyurethane foams by measuring the temperature of the foam versus time and the change in temperature or first derivative with time to reveal that formation of urea predominates at the early stages of foam formation and maximum formation of urethane only occur at latter stages.

Hauptman et al. (1980) reported the presence of biuret and allophanate at temperature of 110 °C using the FTIR analysis of foam reaction.

Van Thuyne and Zeegers (1978) developed empirical correlation between the physical properties of the foam and basic measurements such as foam height, temperature, and pressure of the rising flexible polyurethane foam showing that the rate of each reaction directly affects the foam formation process and physical properties of foam.

In the FTIR study conducted by Elwell et al. (1996) to investigate the reaction kinetics and structure development in model flexible polyurethane foam systems, the decay of isocyanate has been correlated to the polymerization kinetics and evolution of hydrogen-bonded urea, the knowledge of which has provided determination of exotherm for the foam formation.

Theoretical model of physical blowing agent blown rigid polyurethane foam to predict the extent of cream time and rise period as well as the amount of blowing agent necessary to give desired foam density from a temperature vs. time data is available in the literature (Rojas et al., 1982). The study developed a diagram that contains all relevant information

theoretically built and used for selection of adequate parameters for any given formulation.

Theoretical models for water and physical blowing agent blown rigid polyurethane foam as well as prediction of heat and mass transfer controlled model for R-11 blown foaming dynamics are available in the literature (Baser and Khakhar, 1994a; Baser and Khakhar, 1994b). The model results agree well with the experimental observations.

However, no theoretical models are available for water-blown flexible polyurethane foam reinforced with filler. Thus, a good theoretical model of water blown foaming process would be helpful in development of new foam formulations containing filler.

Experimental Details

Materials

A typical formulation furnished by VITAFOAM Nigeria Plc for commercial flexible PU foam reinforced with filler was selected. The target density of this formulation was 25 kg/m³. The composition of the formulation was a toluene diisocyanate T-80 (80:20 Scuranate, Lyondell) with an average functionality of 2.7. It was reacted with a stoichiometric amount of a polyether polyol (Konix FA-717, Korea polyol Co.) with an OH value of 44 mg KOH/g polyol. The catalysts were dibutyltin dilaurate (D22, Union Carbide) and amine (DABCO, Air products). The surfactant was a silicone-polyol block copolymer. Calcium carbonate of particle sizes (PS) 0.06 and 841 μm and of volume fractions (VFF) 5 and 25 wt % were used as filler. The foam was prepared by substituting certain percentages of the polyol with the equivalent weight fractions of calcium carbonate so as to reduce the quantity of polyol for cost reduction without adversely affecting the mechanical properties.

Foaming Process

The components of the foam formulation were mixed in separate container with the aid of a Fisatom model 710 shaft stirring device (power 25 W, rotation 200 rpm). Once complete, homogenization of the mixture is achieved, the mixed reactants were then immediately transferred to a cubical box container (base: 36 cm, 43 cm; height: 27 cm) containing a thermocouple centered with respect to the base and protruding a few centimeter from the bottom. Its output was continuously monitored with a data logger (Jenway 220). The thermal losses by conductivity in this device are closer to that of an industrial foaming device with respect to a perfectly insulated apparatus that, on the other hand, is useful for collecting kinetic data. Due to the large number of reactant necessary to operate the foaming process, only 4 formulations were

tested (VFF = 5, PS = 0.06; VFF = 5, PS = 841; VFF = 25, PS = 0.06; VFF = 25, PS = 841 μm).

Mechanical Analysis

Indentation force deflection of the foams were measured according to ASTM D 3574-81 with the aid of a indentometer (Hampden EC30, V2.48/024, testing machine) at a loading rate of 30 mm/min. Indentation Force Deflection was quoted at 65 % indentations of the foam samples. The 65 % indentation gives the highest value and is usually comparable with the force exerted by a seated adult indicating the ability of the foam to support load.

Reaction Kinetics

The kinetic parameters for the reactions occurring in the foam system are as follows (1) polymerization reaction between polyol hydroxyl groups and isocyanate groups and (2) reaction between isocyanate groups and water to form the CO₂ gas that acts as a chemically generated blowing agent. The kinetic parameters for these reactions are precursors for developing a mathematical model for the description of the foam-growth process.

Methods of determining the kinetic parameters for the reactions of isocyanate with polyol have been described in references (Rojas et al., 1982; Baser and Khakhar, 1994a,b; Tesser et al., 1994). The method consist of a foaming process devoid of any blowing agent conducted in a well insulated container in which the temperature is continuously monitored by a thermocouple and collected with a data logger. Polyol and isocyanate are mixed and stirred for 10 s at 700 rpm with a stirrer. Temperature data were acquired with the use of a thermocouple inserted in the bulk of the mixture. The kinetic parameters were obtained as illustrated below:

Assuming that the heat capacity C_p is not a function of temperature, the energy balance is given by

$$\rho_p C_p \frac{dT}{dt} = (-\Delta H) \frac{dX}{dt} C_{Ao}$$

(5)

The ordinary differential equation can be integrated with respect to time to obtain

$$(-\Delta H)X = \frac{\rho_p C_p (T - T_o)}{C_{Ao}}$$

(6)

At completion of the reaction when X = 1, and being that the system is adiabatic, the heat evolved by the reaction result in increase in temperature till a maximum value T_{max} is reached.

Therefore expression 5 becomes

$$\ln \left[\frac{1}{(T_{max} - T)^n} \frac{dT}{dt} \right] = \ln A \left[\frac{C_{Ao}}{T_{max} - T_o} \right]^{n-1} - \frac{E_a}{RT}$$

(9)

Where n is the order of reaction, E_a is the activation energy, A is preexponential factor and R is gas constant. The preexponential factor E_a and activation energy were obtained by plotting

$\ln \left[\frac{1}{(T_{max} - T)^n} \frac{dT}{dt} \right]$ as a function of 1/T for

different values of order of reaction n. From the straight line graph obtained, the activation energy was calculated from the slope, and the preexponential factor is obtained from the intercept of the line. The procedure was repeated for reaction order varied from 0.5 to 2.0 with a step growth of 0.25. The best fit was obtained with reaction order n = 2. The heat of reaction (- H) was evaluated using equation 6. The experimental temperature profile is shown in Figure 1 and the linear fit of equation is shown in Figure 2. The kinetic parameters determined for this formulation are A_{OH} = 1.0797E4 m3/g-equiv/s, E_{OH} = 1.8879E4 J/gmol, (- H)_{OH} = 1.921E4 J/g-equiv.

$$(-\Delta H) = \frac{\rho_p C_p (T_{max} - T_o)}{C_{Ao}}$$

(7)

And $X = \frac{T - T_o}{T_{max} - T_o}$

(8)

If an n-order kinetic valid below gel point is assumed then equations 5 to 8 can be made to become

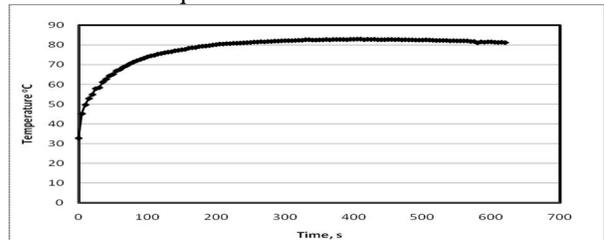


Figure 1: Adiabatic temperature rise curve used for determination of kinetic parameters

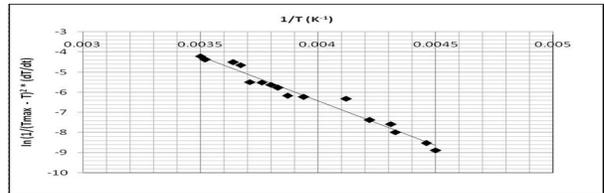


Figure 2: Plot of Left-hand side of Eq. 9 vs. 1/T for pure urethane mass.

Mathematical Modelling

As a consequence of the heat developed by the exothermic reactions, the temperature of the foaming process evolves with time. It is the main variable that controls the foam growth process in addition to the blowing agent concentration. The model is based on the assumption that the foam consists of a continuous polymeric phase and a gaseous phase homogeneously dispersed in the polymer. Other important assumptions of this model are the adiabatic conditions and the

presence of filler only as heat sink and reinforcement material. With the foaming process taken as a two-phase pseudohomogeneous system, the model is

developed by obtaining a thermal energy balance for the foaming system containing fillers.

$$\left[C_p + C_{CO_2} C_{P,CO_2} + \left(\frac{F_s d^3 C_{p,s}}{6} \right) \right] \frac{dT}{dt} = \left[\frac{(-H)_{OH} [OH]_0}{f} \right] \frac{dX_{OH}}{dt} + \left[\frac{(-H)_W [W]_0}{f} \right] \frac{dX_w}{dt} \quad (10)$$

The thermal energy balance gives the net rate of increase of temperature due to heat generated by the exothermic reactions of isocyanate with water and polyol, and the energy dissipated by the solid filler. The parameters C_p , C_{p,CO_2} , $C_{p,s}$ are the specific heats of respectively polymer, carbon dioxide and calcium carbonate. C_{CO_2} and F are respectively the amounts of carbon dioxide and calcium carbonate respectively in the liquid per mass of polymer. X_w and X_{OH} are the conversion of water and hydroxyl groups; H_{OH} and H_w are the heat of reactions of isocyanate with hydroxyl groups and water, respectively.

The rate of disappearance of the hydroxyl groups of polyol is given by

$$\frac{d[OH]}{dt} = -A_{OH} \exp\left(-\frac{E_{OH}}{RT}\right) [NCO][OH] \quad (11)$$

With water as the chemical blowing agent and a stoichiometric amount of isocyanate, concentration terms for isocyanate hydroxyl, and water are obtained

$$[NCO] = [NCO]_0 - 2([W]_0 - [W]) - ([OH]_0 - [OH]) \quad (12)$$

$$[OH] = [OH]_0(1 - X_{OH}) \quad (13)$$

$$[W] = [W]_0(1 - X_w) \quad (14)$$

With the assumption that the carbamic acid decomposes rapidly and the amine liberated reacts quickly with the isocyanate making k_2 far greater than k_1 in Eq. 1, then the rate of disappearance of water in the blowing reaction assuming first order kinetics with respect to concentration of water is given by

$$\frac{d[W]}{dt} = -A_w \exp\left(-\frac{E_w}{RT}\right) [W] \quad (15)$$

The conversion degree for the two reactions (1) isocyanate with hydroxyl group (2) isocyanate with water are expressed by the following relations, respectively

$$\frac{dX_{OH}}{dt} = A_{OH} \exp\left(-\frac{E_{OH}}{RT}\right) [OH][1 - g(x)] \times (r_{NCO} - 2r_w X_w - X_{OH}) \quad (16)$$

$$\frac{dX_w}{dt} = A_w \exp\left(-\frac{E_w}{RT}\right) (1 - X_w) \quad (17)$$

Equation 17 is rewritten to obtain

$$\ln \left[\frac{1}{(1 - X_w)} \frac{dX_w}{dt} \right] = \frac{-E_w}{RT} + \ln A_w \quad (18)$$

Temperature values obtained from adiabatic temperature measurements were used to calculate the kinetic parameters in Eq. 18. If the left hand side of the equation is plotted against $1/T$ for different values of T assuming a first order kinetics (Edwards, 1981), a straight line graph is obtained (see Figure 4). dX_w/dt was calculated by carrying out numerical differentiation of conversion vs. time data (see Figure 3). Experimental data up to only about 90% of foam full rise were used, as beyond this point the rate of foam rise decreases rapidly. The values of $A_w = 1.368E3 \text{ s}^{-1}$ was calculated from the intercept of the line and $E_w = 3.278E4 \text{ J/gmol}$ was obtained from the slope. The value of $(-H)_w = 7.81E4 \text{ J/gmol}$.

The descriptions of the terms in the equations are:

$$X_{OH} = ([OH]_o - [OH]) / [OH]_o$$

$$r_{NCO} = [NCO]_o / [OH]_o$$

$$r_w = [W]_o / [OH]_o$$

$$X_w = ([W]_o - [W]) / [W]_o$$

$$g(x) = 1 \quad \text{for } X_{OH} \leq 0.4$$

$$g(x) = 1.292 - 17.2(0.65 - X_{OH}) \quad \text{for } 0.4 \leq X_{OH} \leq 0.684$$

$$g(x) = 1.913 - 0.913 X_{OH} \quad \text{for } 0.684 \leq X_{OH} \leq 1$$

A_w and A_{OH} are the preexponential factors while E_{OH} and E_w are the activation energies for the reaction of isocyanate with hydroxyl groups and water, respectively.

The water-isocyanate reaction predominates at the early stage of foam process and is essentially completed before the formation of urethane from isocyanate-hydroxyl reaction. A significant excess of isocyanate is always present throughout the cause of the blowing reaction. Decay in isocyanate absorbance from FTIR study reported in literature (Saint-Michel et al., 2006) has been used to monitor conversion of isocyanate functional groups during foam reaction at this stage and at the latter stage when polymerization is prominent. The main source of heat during foaming reaction is that arising from consumption of isocyanate functional groups. It is assumed that the rate of water-isocyanate reaction is independent of the isocyanate concentration in the above Equation 2. Equations 10, 16, and 17 are solved simultaneously together to obtain profile for temperature of ordinary differential equation. The equations are non-linear and are integrated numerically with the aid of Adams-Bashforth-Moulton method. At each integration step in

time, the density of the foam, ρ_f , assumed homogeneous in each spatial location of the growing foam, can be evaluated by means of the relation

$$\rho_f = \frac{1}{\frac{C_{CO_2} 1000 RT}{PM_{CO_2}} + \frac{1}{\rho_p}} \quad (18)$$

where

$$C_{CO_2} = \frac{[W]_o X_w M_{CO_2}}{1000 \rho_p} - (CO_2)_D \quad (19)$$

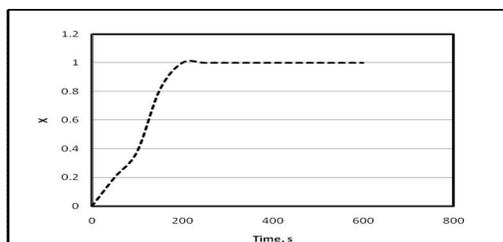


Figure 3: Reaction conversion vs time for the reaction of isocyanate with water.

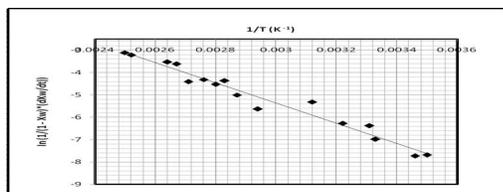


Figure 4: Plot of left hand side of Eq. 18 vs. 1/T for water-blown polyurethane foam without filler.

Results and Discussion

The temperature increase in the reaction processes that lead to formation of flexible polyurethane foam play a significant role in the build up of mechanical strength in the foam. The sequential development of exotherm facilitates the formation of chemical species (biuret and allophanate) which occur at temperature of 110 °C and which is the main constituent of foam structure responsible for stiffness exhibited by flexible polyurethane foam. In Figure 1, we have shown how the temperatures of a foaming process evolve with time for the case of the reaction of polyisocyanate with polyol in the absence of a blowing agent. When water and isocyanate reaction is contained, and when filler of composition 5 and 25 wt% of particle sizes 0.06 and 841 μm are incorporated in the foam reaction, the temperature profiles are depicted in Figure 3.

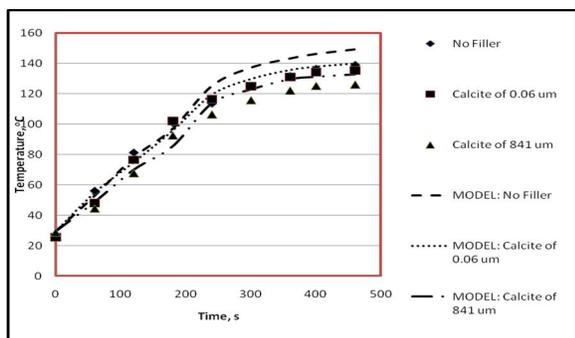


Figure 3: Temperature versus Time for Foam Reinforced with Calcite of 5 wt%

Table 1: Indentation hardness properties of the calcium carbonate reinforced flexible polyurethane foam.

Volume fraction (wt%) of filler in polyurethane foam	Indentation hardness (N) of foam reinforced with 0.06 μm sized filler	Indentation hardness (N) of foam reinforced with 841 μm sized filler
0	272.1	272.1
5	268.5	261.9
25	296.8	253.4

The maximum temperature for the isocyanate-polyol reaction is 82 °C while the maximum temperature of the reaction in which there is blowing is 140 °C. The formulation containing 5 wt% of filler of particle size 0.06 μm present a case in which the temperature of the filled foam process is less than the reaction for neat polyurethane with the maximum at 137 °C. Because of the high heat energy released by this reaction biuret and allophanate are decomposed (Klempner and Sendjarevic, 2004). Though the filler as heat sinks reduced the exotherm, it was not enough to stop the decomposition which hindered the stability of the chemical material to enhance the hardness of the foam material. In table 1, we have shown that hardness of foam is reduced compared to neat polyurethane when a composition of 5 wt% calcium carbonate is added in foam. On the other hand, exotherm for the foaming process reinforced with 5 wt% filler of 841 μm shows a substantial decrease in the foam temperature compared to both neat polyurethane and when reinforced with 5 wt% calcium carbonate of 0.06 μm. The maximum temperature with 5 wt% filler of 841 μm is 122 °C. In the foam reaction, biuret and allophanate are not formed. Moreover, the 841 μm filler has low surface area, its dispersion in the foam matrix influence excessive drainage of the polymeric content of the cell struts (Javni et al., 2002). This in addition to absence of biuret and allophanate created a foam morphology with depreciated mechanical properties.

Figure 4 presents the exotherm evolution of the foaming process containing 25 wt% filler of particle sizes 0.06 and 841 μm. The profile of the calculated exotherm approach a constant value at a temperature of 136 °C for the filler of particle size 0.06 μm, while the experimentally determined present a maximum temperature of 132 °C which is constant throughout the duration of the experiment. The theoretically

determined temperature is higher than that of the experiment because of the small adiabatic medium in which the experiment was carried out which the theoretical model does not take into consideration the significant heat losses experienced. For both cases, the observed temperatures are lower than when the formulation contained no filler and are between a temperature of 110 and 134 °C at a time the development of secondary reactions of isocyanate predominates. It has been reported in table 1 that mechanical properties of foam reinforced with filler of 25 wt% of 0.06 μm size is significantly improved compared to neat polyurethane. The hardness of foam with filler of 25 wt% of 841 μm size did not show any appreciable influence in the property. It can be deduced from the present work that mechanical properties of the foam can be theoretically determined through a correct estimation of the exotherm by the model developed in this study both for unfilled and filled polyurethane reaction processes. This can be done by using the model to select convenient operating parameters in order to obtain desired values of foam density, maximum temperature for formation of biuret and allophanate, and cream and rise times. The development of the models to achieve this objective is the focus for future investigation/research and publication. In addition, a good understanding of the foaming process is achieved through this study for foam formulations containing fillers.

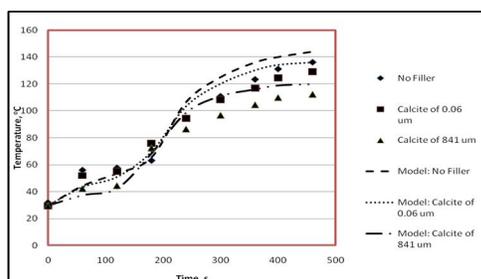


Figure 4: Temperature versus Time for Foam Reinforced with Calcite of 25 wt%

Another important result of the model is the density variation with time shown in Figure 5 for foam containing 5 wt% filler of particle sizes 0.06 and 841 μm . Although there is error in the foam density evaluation, the obtained agreement between the experimental data and the model can be considered satisfactory.

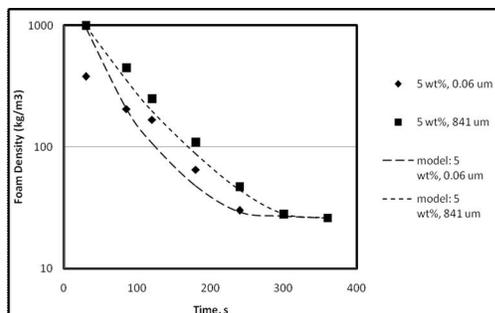


Figure 5: Experimental and theoretically predicted foam density profiles for foam reinforced with 5 wt% calcium carbonate of sizes 0.06 and 841 μm .

Conclusion

Different experimental runs have been conducted to study the kinetics of foam growth by using an industrial polyol-isocyanate-water formulation and filler as reinforcement agent. The experiment was interpreted by using a mathematical model in which all the phenomenon associated with filler as heat sinks have been considered. The model gives as results the evolution along the time of both the temperature profiles in the growing foam and its density. Kinetic parameters for the exothermic reactions of polyol with isocyanate and that for polyol-isocyanate-water reaction under adiabatic condition were evaluated. In all cases of the foam formulation considered, the model prediction is satisfactory compared to experimental observations. The model of the dynamics of water-blown polyurethane foam presented in this paper would thus be useful for the development of new foam formulation containing filler.

Nomenclature

A	Preexponential factor in kinetic expression.
C_p	Specific heat, J/kg K.
C	Mass of carbon dioxide per unit polymer mass.
d	Filler particle diameter, μm
E	Activation energy of reaction, J/g-mol.
$(-H)_w$	Heat of blowing reaction, J/g-mol.
$(-H)_{OH}$	Heat of gelling reaction, J/g-equiv.
M_{CO_2}	Molecular weight of carbon dioxide
[OH]	Concentration of OH end groups, g-equiv/ m^3
[NCO]	Concentration of NCO end groups, g-equiv/ m^3
[W]	Concentration of water, g-equiv/ m^3
W	Water added to polyol, g-mol.
P	Atmospheric pressure, N/m^2
R	Gas law constant, J/g-mol, K
r	Ratio

T	Temperature, K
t	Time, s
X	Fractional conversion
F	Filler volume fraction

Subscripts

o	Initial value
CO ₂	Carbon dioxide
f	Foam
OH	Polyol
NCO	Isocyanate
W	Water
P	Polymer
ad	Adiabatic
max	Maximum
Ao	Reactant
S	calcium carbonate

Superscripts

n	Apparent order of reaction
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Greek

	Density, kg/m ³
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References

- [1] Bailey Jr. F.E. and Critchfield F.E. Chemical Reaction Sequence in the Formation of Water-Blown Urethane Foam. *Journal of Cellular Plastics*. 1981; Nov/Dec: 333-339.
- [2] Baser S.A. and Khakhar D.V. Modeling of the Dynamics of R-11 Blown Polyurethane Foam

- Formation. *Polymer Engineering and Science*. 1994a; 34(8): 632-641.
- [3] Baser S.A. and Khakhar D.V. Modeling of the Dynamics of Water and R-11 Blown Polyurethane Foam Formation. *Polymer Engineering and Science*. 1994b; 34(8):642-649.
- [4] Edwards K.N. Urethane Chemistry and Applications. ACS Symposium Series 172, American Chemical Society. 1981; Washington D.C.
- [5] Elwell M., Ryan A.J., Grünbauer H.J.M., Van Lieshout H.C. An FT i.r Study of Reaction Kinetics and Structure development in Model Flexible Polyurethan Foam Systems. *Polymer*. 1996; 8: 1353 – 1361.
- [6] Hauptmann G., Dorner K.H., Hocker H., and Pfisterer G. Cellular and Non-cellular Polyurethanes. International Conference, Strassbourg, France, Urethane Division, SPI. 1980; 635.
- [7] Javni I., Zhang W. Karajkov V., and Petrovic Z.S. Effect of Nano-and Micro-Silica Fillers on Polyurethane Foam Properties. *Journal of Cellular Plastics*. 2002; 38: 229-239.
- [8] Klempner D. and Sendijarevic V. Handbook of Polymeric Foams and Foam Technology. 2004; 2nd Edition, Hanser Publishers, Munich.
- [9] Rojas A.J., Marciano J.H., and Williams R.J. Rigid Polyurethane Foams: A model of the Foaming Process. *Polymer Engineering and Science*. 1982; 22(13): 840-844.
- [10] Saint-Michel F., Chazeau L., and Cavallé J. Mechanical Properties of High Density Polyurethane Foams: II Effect of the Filler Size. *Composites Science and Technology*. 2006; 66: 2709 – 2718
- [11] Tesser R., Di Serio M., Sclafani A., and Santacesaria E. Modeling of Polyurethane Foam Formation. *Journal of Applied Polymer Science*. 2004; 92: 1875-1886.
- [12] Van Gheluwe P. and LeRoux J. Sequential Nature of the Formation of Flexible Polyurethane Foams. *Journal of Applied Polymer Science*. 1983; 28(6): 2053-2067.
- [13] Van Thuyne A. and Zeegers B. Kinetic Study of Flexible Polyurethane Foams Formation. *Journal of Cellular Plastics*. 1978; May/June: 150-160.

June 4, 2010.