

Polyurethane Foam Process Development. A Systems Engineering Approach

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Synopsis

A seven-step systems engineering approach is described and applied to the integral-skin foam system. Through the use of a hybrid computer simulation of a dynamic mathematical model, the two process variables with the greatest lever on the skin-forming process are determined. These data are then utilized to develop a new foam concept which makes it possible to control skin thickness and core foam density independently.

INTRODUCTION

Historically, polyurethane foam process development has been accomplished by the judicious use of established art as described by Saunders and Frisch.¹ Formulations were developed using paper cups and cake boxes, with the final product usually being produced on a slab machine or in well-vented molds. Thus, there was often a direct correlation between the free-rise cake box data and the production situation. When production scale-up difficulties arose, the information gained from the laboratory was sufficient to indicate what process variables must be adjusted to correct the process.

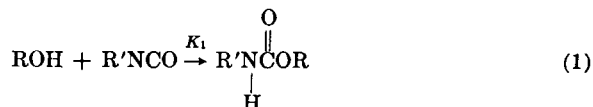
Over the last decade, the foam industry has tended toward molded systems including integral-skin foam, molded furniture, and molded automotive seats. In our laboratory, it has been found that cake box data do not always provide the needed information to carry these processes from the bench into production. Variables such as moldability, mold pressure, and molded foam temperature cannot be investigated using the cake box data because these variables are dependent on the mold size, shape, and temperature. It is the purpose of this paper to briefly examine two classes of polyurethane foam, water blown and fluorocarbon blown, as to their chemical variables. The paper will then discuss how the systems approach was applied to a specific freon-blown foam, the integral-skin foam process. This approach reduced the amount of time and effort needed for prototype work and provided a better understanding of the process variables.

From a chemical standpoint, it is convenient to divide polyurethane foam into two categories: freon-blown and water-blown foam.

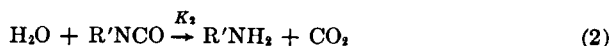
Water-Blown Foam

Water-blown foam generally has the following composition: water, polyol, isocyanate, catalyst, and surfactant.

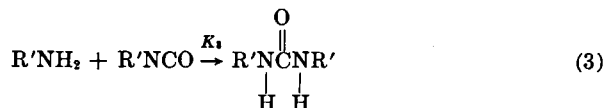
Since the surface chemical phenomena are very complex, the foam system will be analyzed as a process with the following variables: chemical reactions, gas evolution, and heat transfer. In the water-blown system, several chemical reactions are of potential importance.¹ The urethane reaction can be described as



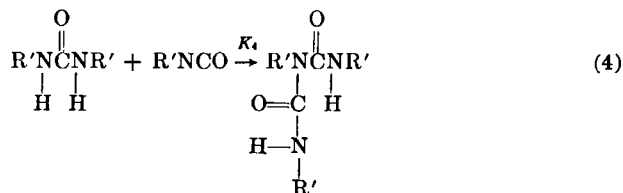
The reaction of water with isocyanate produces the gas which results in volume and pressure changes in the system. The urea formed as a result of the water reaction has been proposed¹ to account for part of the cross-linking in the water-blown foam systems. The sequence of reactions is as follows:



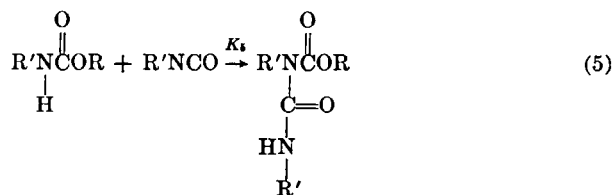
The amine now reacts with more isocyanate to form a symmetric urea:



The urea can further react to provide biuret crosslinks:



It is suggested that, to a lesser extent, crosslinks are provided by the further reaction of the urethane linkage as



which is the allophanate crosslink.

The water-blown foam system involves the solution to five chemical reaction equations plus the physical changes of heat transfer and pressure-volume dynamics. These physical changes are dependent on mold size

and shape. The influence of the physical changes on the chemical reactions will have considerable effect on foam properties, such as tear strength, tensile strength, and compression set, because these properties will vary in relation to the extent of the five reactions involved. The chemical rates are dependent on the temperature history at different parts of the mold which will vary with mold geometry. It can therefore be seen that the complete model for water-blown foam systems would be extremely complex, involving five simultaneous chemical reactions, pressure and volume changes, and heat transfer. To demonstrate the systems approach, it is more convenient to describe a somewhat less complex system, the solvent-blown system.

Solvent-Blown Foam

The solvent-blown foam system is much less complex chemically. The two reactions of importance are the urethane reaction, eq. (1), and the allophanate reaction, eq. (5). The pressure and volume changes are dependent on the vaporization of a solvent, usually a fluorocarbon. The freon-blown system thus needs only two chemical rate equations to describe it. In addition, from a simulation standpoint, the vaporization dynamics of the fluorocarbon must be described, as must the heat transfer transients, which will again be dependent on the mold geometry. The particular freon-blown system described in this paper is the integral-skin foam system.^{2,3,4}

Integral-Skin Foam

The integral-skin foam system falls into the solvent-blown category. The process is diagrammatically described in Figure 1 and is more completely discussed in a previous paper.⁵

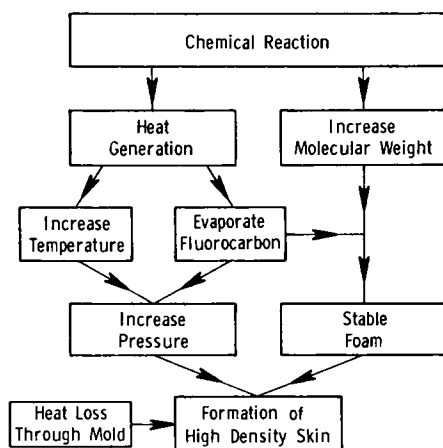


Fig. 1. Polyurethane foam process.

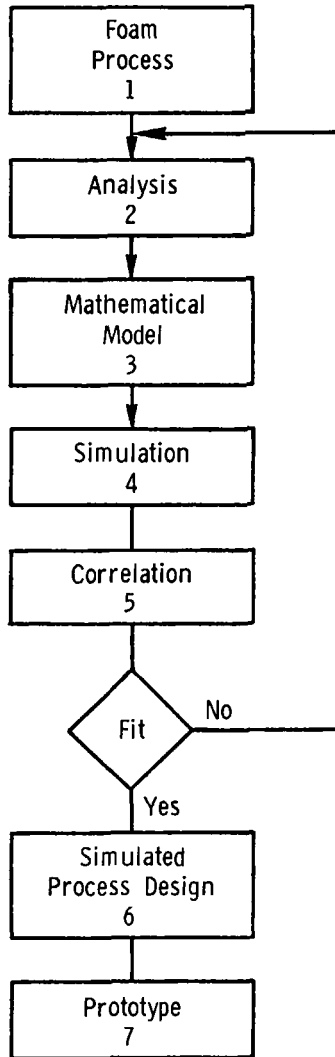


Fig. 2. Systems engineering method.

Application of the systems approach can be considered a seven-step exercise, as diagrammed in Figure 2, for the foam process. Steps 1 and 2 are described and discussed in a previous paper.⁵ Steps 3, 4, 5, 6, and 7 will be detailed in the subsequent sections of this paper.

MATHEMATICAL MODEL

The purpose of this analysis was to determine the process variables that provided greatest leverage in controlling the skin formation. The alphanate reaction is several orders of magnitude less important than the urethane reaction.¹ Therefore, the chemical model chosen dealt with only

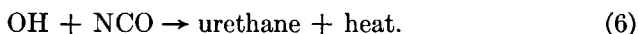
the urethane reaction, eq. (1). If the effect of crosslinking had been an important goal for the analysis, then the allophanate reaction would have been included.

The Model Assumption

1. Only one chemical reaction is important.
2. The chemical rate equation is elementary and irreversible.
3. The thermal diffusivities of liquid and solid are equal.
4. The thermal diffusivity of the foam is essentially that of the blowing agent vapor.
5. The blowing agent begins to vaporize at its normal boiling point.
6. Heat transfer is one-dimensional.
7. The blowing agent may be considered an ideal gas.
8. The skin is formed by the condensation of the blowing agent.
9. The heat is split between vaporization and bulk heating, while the blowing agent is vaporizing.

Chemical Rate Equation

Since only the urethane reaction is to be considered, the chemical model is



The rate equation may be written as

$$d[\text{OH}]/d\theta = -K_0(\exp(-\Delta E/RT))[\text{OH}][\text{NCO}]. \quad (7)$$

The activation energy and K_0 were found to depend on the catalyst concentrations by the following relations:

$$\Delta E = E_0 - EK_1[\text{amine}] - EK_2[\text{tin}] \quad (8)$$

$$\ln K_0 = AK_0 + AK_1[\text{amine}] + AK_2[\text{tin}]. \quad (9)$$

The six constants used in eqs. (8) and (9) were found to be dependent on the isocyanate used, the per cent of primary hydroxyl, and the type of tin and amine catalysts. To make the computer scaling more convenient, the following substitutions were made:

$$Y = ([\text{OH}]_I - [\text{OH}])/[\text{OH}]_I \quad (10)$$

$$[\text{OH}]_I = [\text{NCO}]_I. \quad (11)$$

Equation (10) is the definition of the per cent conversion of the polyol, and eq. (11) indicates that the simulation will be done only for an isocyanate index of 100. Substituting eqs. (10) and (11) into eq. (7) and rearranging yields

$$dY/d\theta = [\text{OH}]_I K_0 (\exp(-\Delta E/RT))(1 - Y)^2. \quad (12)$$

From eq. (12), it follows that the rate of heat generation is

$$Q = \Delta H [\text{OH}]_I (dY/d\theta). \quad (13)$$

Heat Transfer

It is well documented⁶ that the unsteady-state heat transfer equation may be written for Cartesian coordinates as

$$\partial T/\partial \theta = (K/\rho C_p)\nabla^2 T + Q/\rho C_p \quad (14)$$

For the one-dimensional case with the thermal diffusivity defined as $\alpha = K/\rho C_p$, eq. (14) reduces to

$$\partial T/\partial \theta = \alpha(\partial^2 T/\partial X^2) + Q/\rho C_p \quad (15)$$

In the simulation, the value of α is changed whenever there is a phase change. During vaporization, the heat generation Q is reduced by some fraction. That reduced fraction of heat is used to vaporize the blowing agent.

Pressure-Volume Changes

After the reacting mass reaches the normal boiling point of the blowing agent, the rate at which the fluorocarbon is vaporized will be

$$dM/d\theta = FQ/H_v \quad \begin{array}{l} T \geq T_B \\ M < M_0 \end{array} \quad (16)$$

The vaporizing blowing agent will produce either a volume or pressure change depending on the condition within the mold. Mathematically, until the mold is filled, a volume change will occur at 1 atm pressure. With a full mold, there will be a pressure increase due to the continued vaporization of fluorocarbon and the increased temperature within the mold. Experimentally, the blowing agent was found to vaporize over a range of temperatures higher than its normal boiling point. Therefore, the equations of change were written

For volume:

$$dV/d\theta = (R'/P_0)[T(dM/d\theta) + M(dT/d\theta)] \quad \begin{array}{l} T \geq T_B \\ M < M_0 \\ V < V_T \end{array} \quad (17)$$

For pressure:

$$dP/d\theta = (R'/P_0)[T(dM/d\theta) + M(dT/d\theta)] \quad \begin{array}{l} T \geq T_B \\ M < M_0 \\ V = V_T \end{array} \quad (18)$$

$$dP/d\theta = [R'(M_0)/(V_T - V_0)]dT/d\theta \quad \begin{array}{l} T > T_B \\ M = M_0 \\ V = V_T \end{array} \quad (19)$$

A fourth equation would be needed if the simulation was carried out to the point where the temperature in the mold went below the normal boiling point of the blowing agent. In integral-skin foam processes, the mold is generally 15° to 50°F above the normal boiling point^{2,3,4} of the blowing

agent. Therefore, the condensation dynamics for the bulk foam were not included in the model.

Skin Formation

The mechanism used for skin formation was the condensation of the blowing agent near the mold surface. This was considered to be a step function which occurred where the condensation temperature crossed the temperature gradient from the mold to the core foam. The condensation temperature was calculated as

$$T_C = T_B + 83.3 \ln (P/P_0). \quad (20)$$

Step 3 in the analysis is now complete. The next section describes the computer technique used for the simulation.

SIMULATION

The model developed involves the solution to several simultaneous differential equations which contain extremely nonlinear terms. There is a considerable amount of logical arithmetic to be done in determining the stage of the process, i.e., vaporization or not, mold filled, and changes in thermal diffusivity depending on the point of intersection between the temperature profile and the condensation temperature.

The goal of the analysis was to determine the effects on skin formation of the process variables such as part thickness, molecular weight, mold temperature, concentrations of catalysts, blowing agent, and packing. Therefore, the solution of the mathematics must be correlated with experimental data. This correlation is most easily accomplished for dynamic systems using an analog computer because it integrates continuously and provides

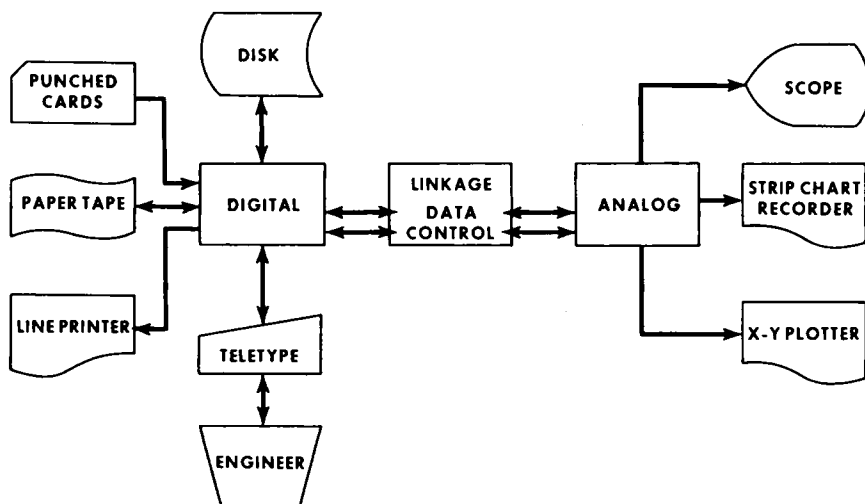


Fig. 3. Hybrid computing system.

for operator intervention. This intervention gives the added advantage of better problem understanding through man-machine interaction. Thus, the analog computer has been traditionally used as a model-building tool for systems involving complex transient responses.

The digital computer, on the other hand, is ideally suited for arithmetic computations, data reduction, and logical yes-no decision. It also is relatively easy to acquire the programming skills of the higher-level languages, such as Fortran, to the degree that complex problems can be solved.

The hybrid computer is a natural extension of these two basic types of computers. The hybrid computer consists of a digital computer and an analog computer connected by a high-speed data and logic transmitting linkage (Fig. 3). This arrangement provides the engineer with a number of advantages: (1) digital calculation of potentiometer setting from input data, (2) digital setup and checkout of potentiometers, (3) fast parameters updating, (4) simultaneous on-line analog-digital programming. These conditions provide fast setup and checkout of the analog program and the flexibility to do multivariable function generation with logical decision making during the course of the simulation.

Computer Solution

In this simulation, the computer solution was accomplished by solving the time-dependent variables continuously on the analog computer, with much of the nonlinear arithmetic and logical decision making relegated to the digital computer.

The solution involves the simultaneous solution to eqs. (12), (13), (15), (16), (17), (18), (19), and (20), with appropriate boundary and initial conditions to fit the process. Equation (15) is a partial differential equation with a heat source due to the chemical reaction. Because the temperature equation contains a source which is a function of both independent variables, the classical separation of variables technique does not apply. Therefore, a finite difference technique was developed as described by Rogers and Connolly.⁷ The difference scheme chosen is diagrammed in Figure 4. The simulated section was considered to be symmetric around the center line section 0. Eleven sections were used, with eight sections in the skin formation region within $1/4$ in. of the boundary. The three remaining seg-

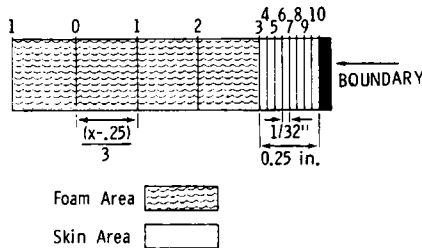


Fig. 4. Finite difference section.

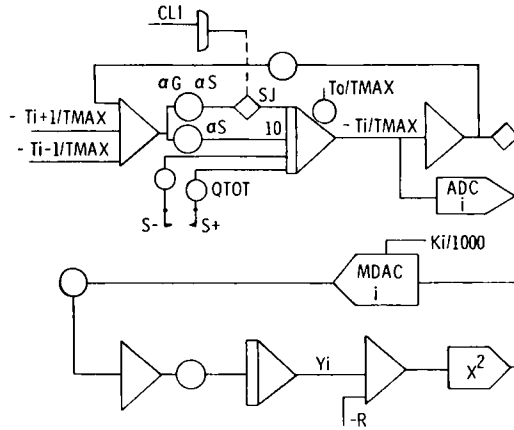


Fig. 5. Analog temperature diagram.

ments were divided equally from the center line to the skin-foam boundary. Using this scheme, eqs. (12), (13), and (15) are expanded to eqs. (22), (23), and (21), respectively:

$$\sum_{i=1}^{11} dT_i/d\theta = (\alpha/(\Delta X_i)^2)(T_{i-1} - 2T_i + T_{i+1}) + Q_i/(\rho C_p) \quad (21)$$

$$\sum_{i=1}^{11} dY_i/d\theta = [\text{OH}]_I(K_0(\exp(-\Delta E/RT_i))(1 - Y_i)^2 \quad (22)$$

$$\sum_{i=1}^{11} Q_i = \Delta H[\text{OH}]_I(dY_i/d\theta). \quad (23)$$

Thus, eqs. (12), (13), and (15) are now expanded into 22 linear differential equations and 11 algebraic equations. The unscaled analog computer diagram for a typical section is detailed in Figure 5. The two-line dependent derivatives are solved continuously on the analog computer. The temperature T is transmitted to the digital computer through the analog-to-digital converter, ADC. The "rate constant" K_i is then calculated and updated on the analog computer through the multiplying digital-to-analog converter, MDAC. During each transfer cycle, the digital computer compares the section temperature with the condensation temperature of the blowing agent. If the foam temperatures is greater than the condensation temperature, the digital switch is opened, thus increasing the thermal diffusivity. If the section temperature is below the condensation temperature, which is dependent on mold pressure as indicated by eq. (20), the thermal diffusivity is lowered, thus simulating the skin formation by a phase change back to the liquid state.

The volume and pressure relationships, eqs. (16) through (19), are solved as diagrammed in Figure 6. When the digital computer detects that the foamable mass has attained the normal boiling point of the blowing agent, a control line is reset which diverts a fraction of the heat gener-

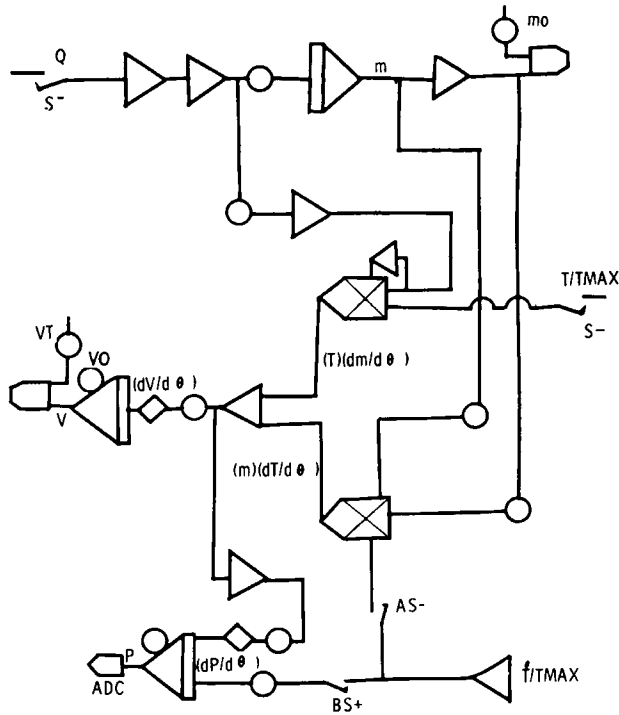


Fig. 6. Analog pressure-volume diagram.

ation away from mass heating to vaporization. The vaporization continues until all of the blowing agent is vaporized. The digital computer determines this by reading the state, logical yes or no, of a comparator. When the comparator changes state, the control line is set and all of the heat again goes to heating the foam mass. A complete computer program is available from the author upon request.

COMPUTER SIMULATION RESULTS

As was found in the laboratory,⁵ packing caused an increase in the skin formation (Fig. 7). The increase in per cent overfill caused an increase in pressure which is more than proportional to the per cent packing. This caused, in turn, an increase in the condensation temperature. The section in which the condensation temperature intersected the foam temperature was used to record skin thickness.

The effect of part thickness on skin formation at 100% overfill is found in Figure 8. It was determined that the model again showed good agreement with the laboratory data.⁵ The skin formation increased very rapidly as the part thickness was decreased. The pressure in the mold was observed to remain substantially constant. However, examination of Figure 9 indicates that the temperature profiles of the two systems are quite

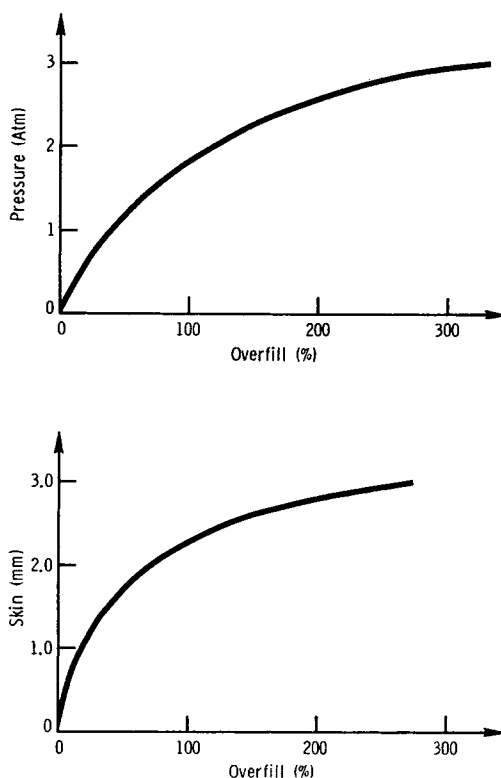


Fig. 7. Effect of packing.

different. The thermal gradient for the thicker mold is much steeper than it is for the $\frac{1}{2}$ -in. mold. The condensation temperature intersects the profiles at different distances from the wall, thus producing less skin in the thicker section.

The effect of wall temperature on skin formation is diagrammed in Figure 10. The skin thickness was found, in all cases, to increase as the wall temperature was decreased. The skin formation was most greatly affected by changes in wall temperature at the lower packing conditions.

Increased blowing agent caused large increases in the amount of skin formed, as is detailed in Figure 11. The increased blowing agent caused an increase in mold pressure which, in turn, caused significant changes in the condensation temperature. The point of intersection of foam temperature and condensation temperature was therefore moved further from the boundary, resulting in more skin formation.

Finally, the effect of reactant concentration in equivalents per cc on skin formation is diagrammed in Figure 12. The molecular weight of the polyol can be considered to be inversely proportional to the concentration of reactive OH groups. It is observed that as the concentration increases, there is a marked reduction in skin formation. This is due to the increase

in the rate of heat generation which increases the temperature gradient from the mold to the core foam.

After several thousand computer trials, the following trends were obtained to optimize the skin-forming process. The skin formation could be effectively controlled if the molded foam pressure and density could be independently controlled. Moreover, it was important to adjust the mold

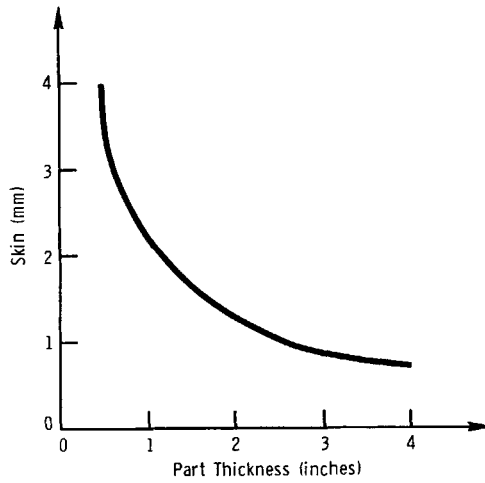


Fig. 8. Effect of part thickness on skin formation at 100% overfill.

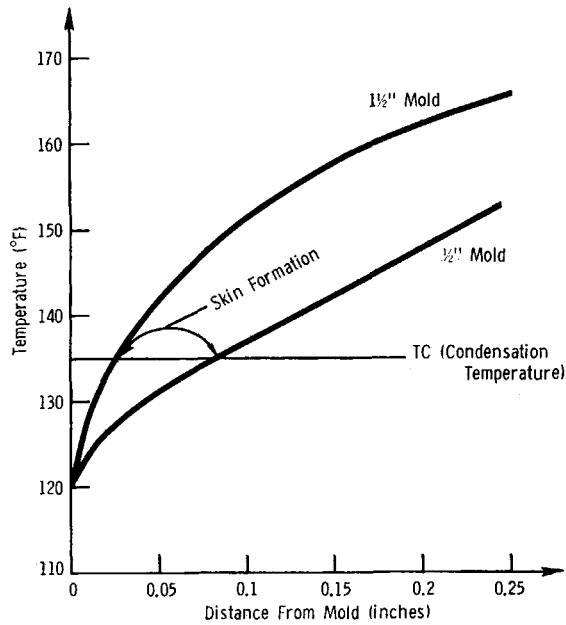


Fig. 9. Effect of part thickness on temperature profile and skin thickness.

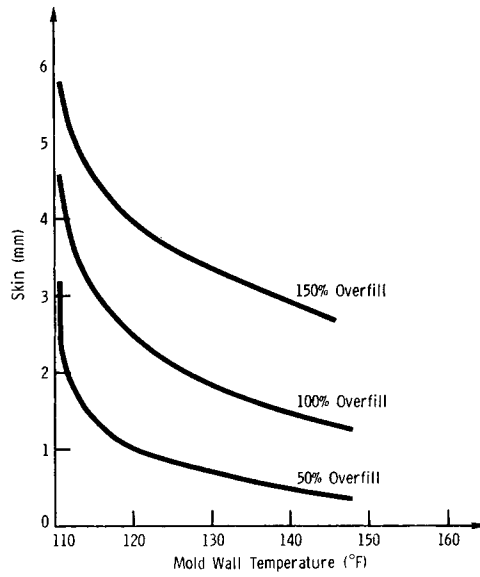


Fig. 10. Effect of mold wall temperature on skin formation with packing as parameter.

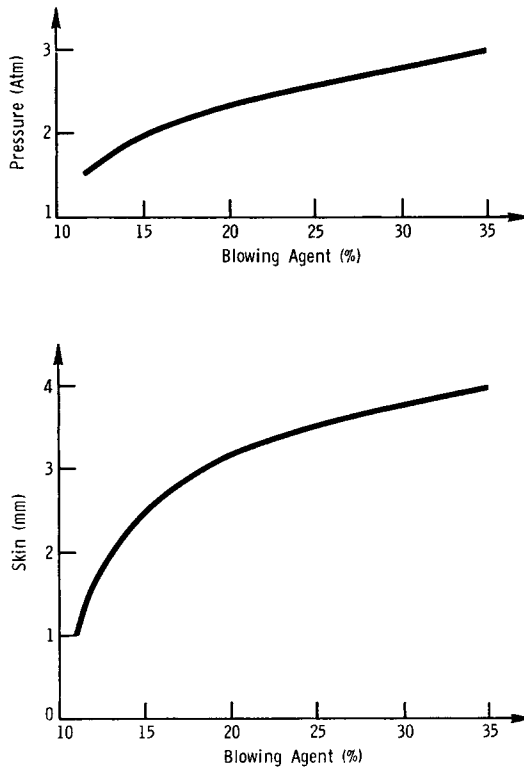


Fig. 11. Effect of blowing agent on pressure and skin formation.

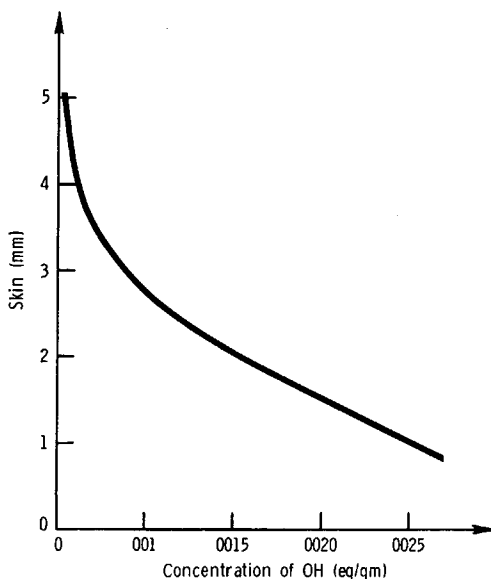


Fig. 12. Effect of reactant concentration on skin formation at 100% overfill.

temperature to be consistent with packing and percentage of blowing agent. It was also found that it is best to keep the molecular weight of the reactants as high as possible. Further analysis indicated that the most logical method to increase skin thickness while decreasing core density was to increase the percentage of blowing agent. In order to accomplish this, the computer simulation indicated that the mold temperature should be increased to compensate for the loss of heat due to greater vaporization. With these data available, prototype work was begun.

OVERBLOWN FOAM SYSTEM

The computer simulation indicated that the foam formulation should be changed in the direction of increased blowing agent. However, when the blowing agent concentration reached 16%, the foam collapsed when free-rise foams were attempted. The model indicated that this was the answer; so after some serious reflection, a formulation was prepared with 20% blowing agent and put in a sealed mold. The foam was demolded in 10 min, and a satisfactory part with an acceptable skin and a low core foam density was produced. Further prototype work was done which confirmed that to optimize the system the mold should be 15° to 20°F warmer than normally used, as was predicted by the model. This development enabled the production of test parts with satisfactory skin to be produced using 40% less foam materials.

APPLICATION TO WATER-BLOWN FOAM

The systems approach is now being applied to the water-blown foam system. This requires much more kinetic data because of the increased number of important reactions. Also, the goals have to be changed from that of understanding the skin formation to the understanding of the inter-relationship between mold shape and chemical reaction kinetics of cold-cure seat foam on its physical and chemical properties.

SUMMARY

Polyurethane foam systems were separated into freon-blown and water-blown types. A systems engineering approach was then defined and applied to integral-skin foam. A mathematical model was developed, and the hybrid computer simulation used for analysis was described. Computer data were presented which indicated that mold temperature and foam pressure were the two process-controlling parameters related to skin formation. A new foam concept was described which involves the addition of excess blowing agent to the foam system. This process provides the flexibility to independently controlled core foam density and skin formation for integral-skin foam parts.

Symbols

K_i	rate constant
OH	polyol
NCO	isocyanate
[OH]	hydroxyl concentration, equiv/cc
[NCO]	NCO group concentration, equiv/cc
ΔE	activation energy, cal/mole
R	gas law constant, cal/mole-°K
T	temperature (degrees Kelvin), °K
[amine]	amine catalyst concentration, g/g
[tin]	tin catalyst concentration, g/g
[OH] _I	initial concentration, equiv/cc
Q	heat generation rate, cal/sec
ΔH	heat of reaction, cal/mole
θ	time, sec
K	thermal conductivity, cal/cm-sec-°K
ρ	density, g/cc
C_p	specific heat, cal/g-°K
α	thermal diffusivity, cm ² /sec
M	moles of blowing agent, moles/cc
F	fraction of heat to vaporization
H_v	heat of vaporization, cal/mole
T_B	normal boiling point, °K
M_0	initial charge of blowing agent
V	volume, cc

R'	gas law constant, cc-atm/mole-°K
V_T	mold volume, cc
V_0	initial charge to mold, cc
T_C	condensation temperature, °K
P	pressure, atm

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