

Effect of Monomer Temperature on Foaming and Properties of Flexible Polyurethane Foams

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ABSTRACT: Polyurethane foam formation involves simultaneous polymerization and expansion. In an open cell foam, foam lamellae rupture at some stage of foam formation, resulting in a foam with continuous air channels. Experiments are carried out to study the effect of initial temperature of monomers on the open cell content of water-blown flexible polyurethane foams. The change in kinetics of the polymerization and blowing with initial monomer temperature is noted by measuring the gel and rise times during foaming. Both polymerization and blowing reactions are found to be faster with increasing monomer temperature. The cell size is found to increase with initial monomer temperature, and the height of the cured free rise foam is found to decrease. The open cell

content of the foam increased considerably with initial monomer temperature, leading finally to the collapse of the foam at the highest temperatures studied. The mechanical properties of the foam at different monomer temperatures are determined by making molded foams. The indentation load deflection decreased with increasing monomer temperature indicating the formation of softer foams, but showed a slight increase near the temperature of collapse. Other mechanical properties showed a small degradation with increase in initial monomer temperatures. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 105: 3439–3443, 2007

Key words: polyurethane foam; flexible; cell opening

INTRODUCTION

Flexible polyurethane foams have the largest production volume among various polyurethanes and are widely used as cushioning and packaging material.¹ During flexible polyurethane foam formation, isocyanate reacts with polyol to produce urethane. The reaction of isocyanate groups with water, which acts as a blowing agent, produces carbon dioxide that diffuses into the initially present bubbles to expand the foam. The process has several different stages, which include mixing and bubble dispersion, rising of the liquid foam, phase separation and cell opening, and formation of a foamed elastomer.^{2,3} Flexible polyurethane foam has a cellular structure in which a large fraction of the foam lamellae separating the cells are ruptured, making an interconnected “open cell” structure. In rigid foams, the lamellae generally remain intact, and the foam is referred to as “closed cell.” The performance of flexible foams depends to a significant extent on the fraction of open cells. For a soft, resilient foam, a high fraction of open cells is required.

The process of cell opening in polyurethane foams is a complex one, which is affected by many formulation parameters and physical factors. Several mechanisms of cell opening have been proposed. The onset of cell opening is attributed to the urea phase separation in some cases.⁴ Zhang et al.⁵ studied the effect of silicone surfactant on foam formation and found that the surface tension gradient generated by the added silicone surfactant stabilizes the cell window by reducing the liquid drainage rate, thus avoiding bubble coalescence and rupture. The surfactant, which controls the surface tension of the foaming solution, aids in the nucleation and stability of the bubbles during their early formation and growth.⁶ One mechanism of cell opening in polyurethane foams argues that, with increase in the temperature of the reacting mixture, owing to the exothermic polymerization and blowing reactions, the surfactant phase separates into insoluble liquid droplets at sufficiently higher temperatures, which act as a defoamer.^{7,8} Turner et al.⁶ argue that a majority of the cells open at gel point, because when a gel film is stretched by the expansion process, it ruptures easily because the viscosity is too high for flow and the molecular weight is too low for good strength. The effect of formulation on the open cell content has been studied.⁴ The conventional method of opening the cells in the foam is by using chemical cell openers, which alter the kinetic balance of the blowing reaction *vis a vis* the polymerization reac-

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tion.⁹ In these systems, the water forms hydrogen bonds with the hydroxyl rich cell opener at the initial stage of the process when the temperatures are low, initially retarding the blowing reaction. At later stages and higher temperatures, the water is released and the blowing is accelerated. The effect of the initial temperature of monomers on the fraction of open cell content, however, has not been previously reported.

The temperature at which the reaction starts determines the kinetics of both the polymerization and blowing reactions. Further, the initial viscosity of the reacting mixture and its variation with time is altered, resulting in a change in the rate of liquid drainage from the foam lamellae to the "plateau borders" formed at the intersection of three foam lamellae. In the present work, we investigate the effect of initial temperature of monomers on the open cell content and mechanical properties of flexible polyurethane foam. The kinetics of the foam formation at various initial temperatures is also studied. No chemical cell opener is used in the present study to avoid the competing effects of hydrogen bonding of water with the cell opener. Both free rise and molded foams are studied.

EXPERIMENTAL

Materials

The two main components of the formulation used were an MDI-based isocyanate (Huntsman Suprasec 6456) and a polyether-based polyol (Arcol 3553, Bayer Polyurethanes, India), having a hydroxyl value of 32 mg KOH/g of polyol and a molecular weight of 4900. The formulation comprising the surfactant, catalysts, crosslinker, and water is given in Table I. All the components are used as received.

Free rise foams

Both the polyol blend and isocyanate were heated separately in glass beakers from room temperature to the specified temperature in water baths. The weight ratio of polyol to isocyanate was 100:65 (isocyanate index = 100) in all the cases. The monomer

initial temperature range considered was 23–43°C, and the experiments were carried out at 2°C intervals. When both the monomers achieved the same temperature, they were added to a stainless steel mold and stirred at a speed of 2500 rpm for 7 s. The foam was allowed to rise freely. The adiabatic viscosity of the reacting mixture remains low until close to the gel point and then quickly shoots up to infinity.¹⁰ This phenomenon can be used to experimentally determine the gel point by moving a glass rod in the reacting liquid, until the movement is resisted because of a sudden rise in viscosity. This simple test for gel point gives reproducible results¹¹ and was used to measure the gel time. The time of end of foam rise (rise time) was also noted.

Molded foams

Molding experiments were conducted to find the variation in the mechanical properties of the foam with initial temperature of the monomers. The same formulation used for free rise foam was used in the molding experiments. The polyol blend and isocyanate were heated in an oven having a temperature controller and a digital temperature indicator. The heated reactants were quickly mixed and stirred with a multiblade stirrer at a speed of 2500 rpm for 7 s. The reacting mixture was poured into a stainless steel mold of size 40 × 40 × 10 cm³. The mold was quickly closed, and the foam was allowed to rise. The mold was opened after 5 min. The resultant foam was allowed to cure at room temperature for 48 h before doing mechanical tests.

Characterization of free rise foams

The foam height of the cured free rise foam, up to the shoulder of the foam, was measured in each case. Air flow through the free rise foam samples was measured according to ASTM D 3574. Foam specimens of base dimensions 50 × 50 mm² and height 25 mm were cut from the top and bottom part of the foam. The base was kept horizontal, that is, perpendicular to the blowing direction. The specimens were prepared, so that the upper surface of the top specimens was level with the shoulder of the bun and the lower surface of the bottom specimen was 10 mm distant from the bottom. Air flow rate was measured by a rotameter with a pressure drop of 12.7 mm water across the specimen thickness, which is 25 mm.

Open cell content was measured from scanning electron microscope images. A sample of size 1 × 1 × 0.5 cm³ was cut out from the samples used for the measurement of airflow. The cell window status was classified as open, partially open, closed, and pin holes⁵ as shown in Figure 1. The effective frac-

TABLE I
Formulation of Polyol Blend

Component	pphp ^a
1,4-Diazabicyclo[2.2.2]octane (Dabco 33LV)	0.30
Dimethyl aminopropyl alcohol (DMAPA)	0.25
Bis(2-(dimethylamino) ethyl) ether (Niax A1)	0.20
Tegostab B4113	0.60
Diethanolamine	0.10
Distilled water	3.95

^a pphp, parts per hundred parts of polyol.

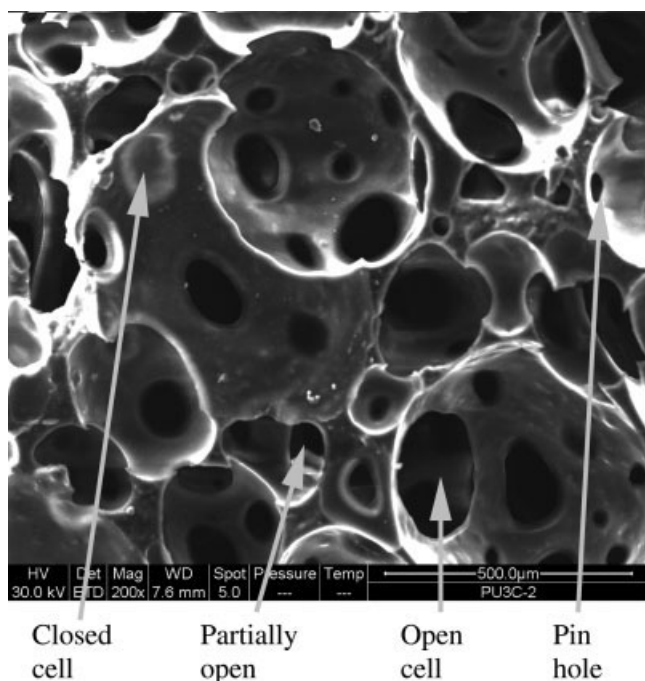


Figure 1 ESEM micrograph of flexible PU foam with cell window status marked.

tion of open cells was calculated by the following formula, proposed by Yasunaga et al.⁴

$$P_{\text{eff}} = \frac{N_{\text{open}} + 0.5 N_{\text{partial}}}{N_{\text{open}} + N_{\text{closed}} + N_{\text{pin}} + N_{\text{partial}}}$$

where, N_{open} is the number of open cell, N_{closed} is the number of closed cell, N_{partial} is the number of partially opened cell, N_{pin} is the number of pin holes. About 150 windows per sample were counted.

The cell window area of free rise foam was calculated by analyzing the SEM images using image

processing software (Image Pro Plus). The area of 20 windows per sample was measured, and the mean value and standard deviations are reported.

Characterization of molded foams

Mechanical testing of the molded foams was conducted after allowing the foam to cure for 2 days. The indentation load deflection (ILD) was measured by a Hampden machine (ISO 2439). A universal testing machine (Instron 3365) was used to measure tensile, elongation, and tear strengths (ISO 1798). A ball rebound machine was used to measure resilience.

RESULTS AND DISCUSSION

Free rise foams

Figure 2 shows the variation in gel and rise times with varying initial temperature of the monomers. There is a continuous decrease in the gel and rise times with increasing temperature of the monomers. Both polymerization and blowing reactions are thus faster at higher monomer temperatures. The foam collapses at 43°C and at higher temperatures. As shown in Figure 3, the final height of the foam decreases continuously with temperature, indicating a lower rise of the foam with increasing temperature. This implies a significant loss of the blowing gas with increase in the monomer temperature.

Figures 4 and 5 show the variation in the fraction of open cells and cell window areas with variation in initial monomer temperatures. The fraction of open cells increases with increase in initial temperature, and the fraction of open cells is greater at the top of the foam than that at the bottom (Fig. 4). This is due to the higher rate of cell window rupture in

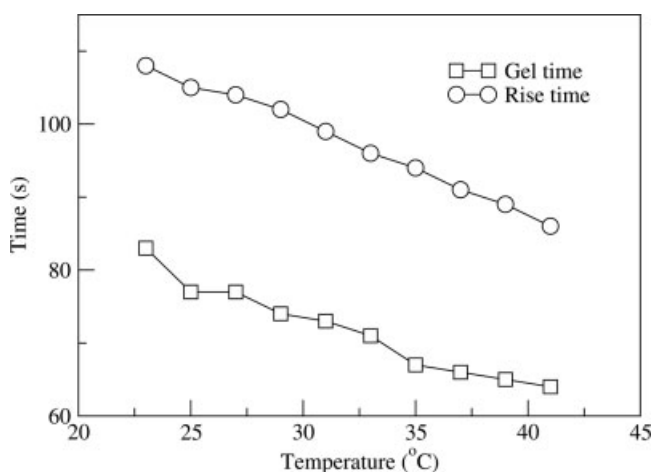


Figure 2 Variation of the gel time and the rise time with initial monomer temperature.

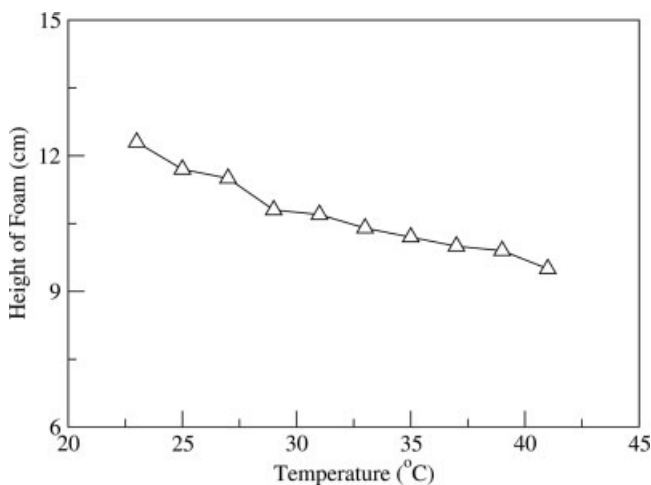


Figure 3 Variation of the final height of the foam with initial monomer temperature.

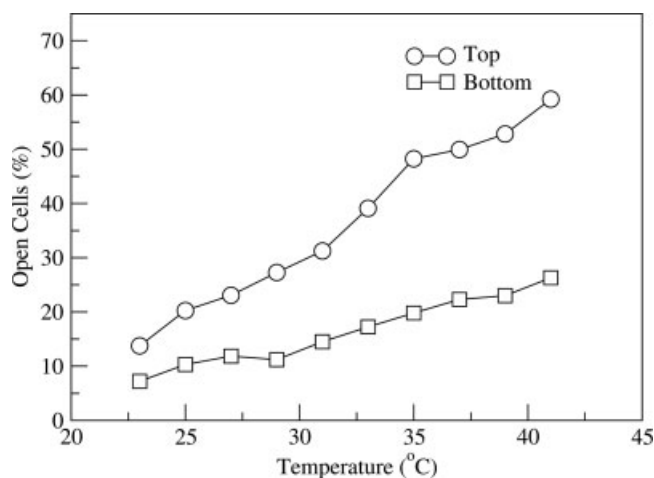


Figure 4 Variation of the percentage of open cells with initial monomer temperature.

the upper region due to gravity drainage of the reaction mixture. The cell window area increases slowly at lower initial monomer temperatures and rapidly at higher temperatures. This indicates an increasing rate of bubble coalescence with increasing initial monomer temperature. At temperatures near the collapse temperature of the foam, the cell window area becomes very high, indicating the presence of coarse cells. This is in accordance with the observation that the air flow increases substantially at temperatures close to the collapse of the foam, although the increase in open cell content is not very large (Fig. 6).

The results presented earlier show that higher initial temperatures result in a greater fraction of open cells and larger cells. We propose the following mechanism to explain the observed phenomena. Increase in temperature results in the reduction of viscosity of the reacting and foaming liquid. As a result, the rate of capillary drainage from the cell

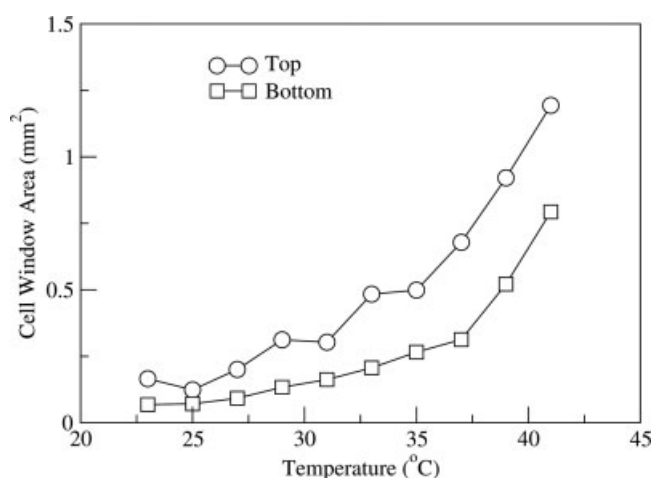


Figure 5 Variation of cell window areas of the foam with initial monomer temperature.

lamellae to the plateau borders is increased and the rate of decrease of lamellae thickness increases. Once the lamellae become sufficiently thin, they may rupture. In addition, the liquid drains through the plateau border network due to gravity flow. This accelerates lamellae thinning in the upper parts of the foam, resulting in a variation of the open cell fraction with height in the foam. The processes of lamellae thinning and gravity drainage are arrested when the polymer gels. The measurements indicate that the gel time decreases with increasing initial monomer temperature (Fig. 2). Thus, for the proposed mechanism to be valid, the reduction in the drainage time to achieve the critical thickness for rupture should be greater than the reduction in gel time. At sufficiently high temperatures, the surfactant, which consists of a polydimethyl siloxane backbone and polyethylene oxide-co-propylene oxide random copolymer grafts, may also phase separate and act as a defoamer.⁷ Both effects would cause the formation of coarse cells.

Molded foams

The mechanical properties of molded foams made at different initial monomer temperatures are shown in Table II. The ILD of the foam decreases with initial monomer temperatures, implying that the foam is softer at higher temperatures. A higher fraction of closed cells in the foam increases the hardness and thus the ILD of the foam, since the entrapped gas resists compression. Though the open cell content shows a continuous increase with increase in initial monomer temperature, the ILD, after decreasing initially, shows a slight upward trend at higher temperatures. This is because of a thicker outer skin formed at higher monomer temperatures. Mechanical properties other than ILD, such as tensile strength, elonga-

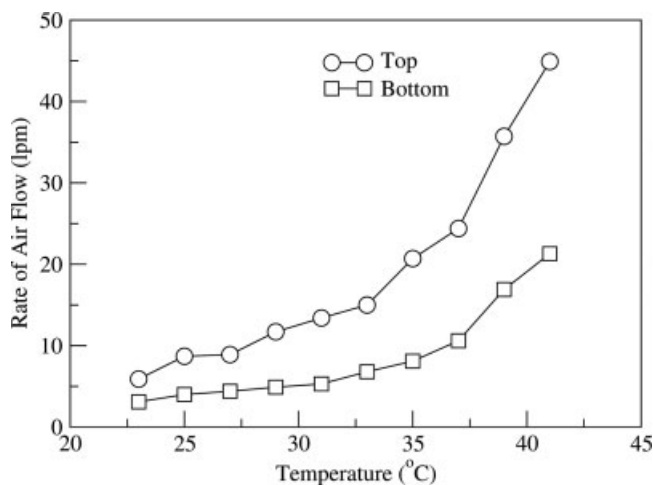


Figure 6 Variation of the rate of air flow with initial monomer temperature.

TABLE II
Mechanical Properties of Foam with Initial Monomer Temperatures

Temperature (°C)	Core density (kg/m ³)	ILD at 25% def. (kgf)	Tensile strength (kg/cm ²)	Elongation (%)	Tear strength (kg/cm)	Resilience (cm)
22	46.2	21.6	1.18	122	0.52	56
25	46.5	21	1.15	125	0.51	56
28	46.9	19.9	1.16	118	0.48	54
31	46.8	18.7	1.09	120	0.49	52
34	46	17.4	1.01	112	0.47	48
37	45.9	19.5	1.01	104	0.46	48
40	Under filled	–	–	–	–	–

tion, and tear strength, show a continuous decrease with higher initial temperature of monomers. Resilience of the foam becomes better with increasing initial monomer temperature. It has been found that, as the temperature of collapse approaches, there are many coarse cells in the foam due to excessive bubble coalescence and rupture, causing degradation especially in tear and tensile strengths.

CONCLUSIONS

The effect of initial temperature of monomers on the open cell content, kinetics, and mechanical properties of both free rise and molded flexible polyurethane foam has been studied. The gelling and blowing reaction were found to become faster with increased initial temperature of the monomers. In the free rise foam, the fraction of open cells and air flow were found to increase with increase in initial temperature of monomers. The increase in air flow rate was much greater than that of the fraction of open cells, because of the numerous coarse cells formed at higher temperatures. The foam collapsed at the highest temperature studied (43°C). The cell size was found to increase with increasing initial monomer temperatures, the increase being rapid at higher temperatures owing to bubble coalescence.

The variation in mechanical properties of the foam with varying initial temperature of monomers was

studied by making molded foams. The foam was found to become softer with increase in temperature. There was a small degradation in other mechanical properties of the foam with increase in initial temperature of reaction. The degradation became more significant near the temperature of collapse. The results of this work indicate that the initial temperature of monomers can be used as a processing parameter for controlling to an extent the fraction of open cells and thus softness in flexible polyurethane foams.

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