

The Mechano-Sorptive Behavior of Flexible Water-Blown Polyurethane Foams

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SYNOPSIS

Samples of flexible water-blown slabstock polyurethane foams were compressed under constant load to study the effects of cycling moisture content on creep behavior and compare this behavior with the creep response where either a constant high or low moisture environment existed at the same temperature. Three sets of foams were tested: (1) 4 pph water content slabstock foam; (2) 5 pph water content slabstock foam; and (3) 2 pph water content molded foam. As the moisture conditions were cycled from low to high humidity while maintaining constant temperature in an environmental chamber, the compressive strain increased in subsequent steps with larger increases observed during the desorption portion of the humidity cycling. All three sets of foams showed similar behavior at a given temperature. At a temperature of 40°C, the strain levels under cyclic moisture conditions surpassed those levels observed at the highest constant relative humidity. During the first absorption step, the creep level increased. During any subsequent absorption step, the creep level either increased very little or none at all. Finally, during any desorption step, the creep level increased. This overall phenomenon of enhanced creep under cyclic moisture levels is attributed to water interacting with the hydrogen bonded structure within the foam. These hydrophilic interactions, principally promoted within the hard segment regions due to high hydrogen bonding, are disrupted causing slippage and increases in strain. As the foam is rapidly dried, regions of free volume are induced by the loss of water thus causing further increases in strain prior to the reestablishment of well ordered hydrogen bonding. Further support to this proposition was given by the results obtained at a temperature of 90°C where it is well known that hydrogen bonds are much more mobile. Here, the strain levels under cyclic moisture conditions were nearly the same as those under constant high relative humidity. Weakening of the hydrogen bonds by means such as increased temperature resulted in similar strain levels to those under cyclic moisture levels.

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INTRODUCTION

The effect of moisture sorption on the mechanical properties of hygroscopic materials is termed mechano-sorptive behavior.¹ Transient moisture conditions can affect the performance and mechanical

properties of many materials and are of importance where materials are used for structural purposes. This phenomenon was noted and systematically studied nearly 30 years ago primarily on wood and wood-based products.^{2,3} More recently, studies have extended to paper, specific fabrics, natural, and synthetic fibers, all of which have a common characteristic of molecular hydrogen bonding.⁴ Cyclic moisture conditions have been found to greatly increase the creep level over the creep level at the highest constant moisture content in the same time

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period. Humphries and Schniewind⁵ observed this effect in Douglas fir columns where the creep level was two orders of magnitude higher under transient moisture conditions than that observed when in a high constant humidity environment. Hunt⁶ showed that in wood-based panels, creep levels were three orders of magnitude larger under cyclic moisture content than under a high constant moisture. Very recently, Wang and Dillard⁴ conducted similar tests on Kevlar® fibers and Kevlar® composites. They found that the level of creep was approximately 50% greater in cycling humidity and that the slope of a plot of creep versus log time, or the creep rate, increased dramatically when the moisture content was cycled either to lower or higher levels. Transient moisture conditions have also been noted to reduce the creep rupture life leading to failures in shorter times and lower loads. For example, Bryan and Schniewind^{7,8} found that the creep rupture life of Douglas fir beams was reduced by an order of magnitude when the moisture was cycled.

Many mechanisms have been proposed, yet one that fully explains such behavior has not been provided. However, the most widely accepted is that the entering and departing water molecules temporarily alter the localized hydrogen bonded structure, a common feature to all materials displaying the mechano-sorptive effect. Based on this mechanism, originally proposed by Gibson,⁹ absorption of moisture disrupts the original bonds. Hoffmeyer and Davidson have proposed a "slip plane" mechanism.¹⁰ After having observed failures at distinct planes through polarized microscopy, they proposed that the number of slip planes is affected and proportional to the amount of moisture change. In the case of Kevlar fibers, Wang and Dillard⁴ proposed a "crystallite rotation and slippage" mechanism. This mechanism proposes that during a sorption process, water molecules disrupt the hydrogen bonds which, in turn, allows for flow units (crystallites or molecular chains) to slip relative to each other and rotate toward the loading direction. Van de Put¹¹ proposed that the mechano-sorptive behavior is due to the onset of "holes" or flow units that allow an increase in molecular mobility.

Because water-blown flexible polyurethane foams are most widely used in load-bearing applications such as seating material etc., the mechano-sorptive phenomenon may be very important particularly in view of the high specific surface of these open-cell structures. In this study, compressive creep is monitored under cycling moisture conditions and constant temperature for three types of foams.

EXPERIMENTAL

Materials

The samples of flexible water-blown slabstock polyurethane foams were made at Dow Chemical in Freeport, TX. The formulation components and amounts used are given in Table I. There are three primary reactions in the production of flexible polyurethane foams. The first, known as the blowing reaction, is a reaction between the isocyanate group and water to give a primary amine and carbon dioxide with the intermediate being an unstable carbamic acid. The carbon dioxide serves as a blowing agent. The primary amine produced in the first reaction reacts with another isocyanate to give a disubstituted urea that is often classified as hard segment material. The third reaction is between an isocyanate group and a hydroxyl group to give a urethane that serves as a link between the polyol (poly-functional alcohol) chains, also known as the soft segment, and an aromatic diisocyanate. This reaction is referred to as the gelation reaction because it develops the network structure of the foams. The polyol used in the slabstock formulation is generally a polyether polyol and in this case was poly(propylene glycol). The polyol used in the molded-foam formulation is a polyol endcapped with ethylene oxide to promote

Table I Formulation Components and Amounts for Flexible Water-Blown Polyurethane Foams

Foam	F5	F8	F13
Isocyanate	T-80 (62.7)	T-80 (62.7)	TDI-80 (28.18)
Polyol	V-3100 (100)	V-3100 (100)	V4703/Cpp (64.7)/(35.3)
Water	DI (4)	DI (5)	DI (2)
Catalyst	T-9 DABCO 8264 (0.15)	T-9 DABCO 8264 (0.15)	DABCO 33LV NIAX A107 NIAX A4 (0.95)
Surfactant	BF-2370 (1.0)	BF-2370 (1.0)	Y-10515 DC-5244 (1.62)

The numbers in parentheses signify the formulation amounts. T-80: 80 : 20 mixture of 2,4- and 2,6-isomer of toluene diisocyanate; V3100: a 3000 M_w trifunctional propylene oxide glycerine; V4703, Cpp: 5000 M_w triol, and copolymer polyol, respectively; T-9: stannous octoate; DABCO 33LV, 8264: triethylenediamine in dipropylene glycol; NIAX A107, A4: tertiary amine; BF2370: silicone surfactant; Y10515; and DC5244: stabilizing and cell opening surfactants.

higher reactivity because of the fact that the end group will be a primary hydroxy. This molding process produces a less microphase-separated foam with less well-developed hydrogen bonds relative to propylene-oxide-based slabstock foams. Furthermore, these foams containing ethylene oxide are also more hygroscopic in nature, one of the reasons we chose to include a molded foam in this study.

The amount of water is related to the amount of hard segment because the TDI content increases as the water content increases. On a microscopic level, the polyurea (or TDI) and the polyol (or PPO) are not compatible, resulting in microphase separation. The polyurea repeat units aggregate together through hydrogen bonding and form physical "crosslinks," thus the term hard segment. This molecular model, along with each segment, is illustrated in Figure 1. The increased water content formulation containing a higher content of TDI typically leads to a stiffer foam, other factors being equal.

The cellular structure of a typical foam is represented in the SEM micrograph given in Figure 2. Figure 2(a) is a micrograph of a slabstock foam taken parallel to the blow direction and Figure 2(b) is a micrograph of a slabstock foam taken perpendicular to the blow direction. Figure 2(c) and (d) are micrographs taken along two orthogonal directions of a molded foam. Many observations can be made from these micrographs: First is the high sur-

face area for interaction with any penetrant, specifically water. Second, there is a very distinct directional geometric anisotropy observed in the slabstock foams. Parallel to the blow direction, the cell structures appear to be circular while perpendicular to the blow direction, the cells appear to be ellipsoidal in shape with the major axis aligned with the blow direction, hence this direction displays higher stiffness. In the molded foams, the cell structures, as expected, have little or no geometric anisotropy and promote much less mechanical anisotropy relative to a slabstock system. Also, the size of the cells appears to be smaller and have more residual window material.

Techniques

An instrument developed by Moreland¹² was used to monitor the compressive creep under constant load as a function of time for changing environmental conditions.¹² This instrument monitors the change in thickness of a foam in compression versus time. Figure 3 is a schematic representation of the instrument used to carry out the experimentation.

An environmental chamber (Fig. 3, part [3]) manufactured by Russels Technical Products was used to control the humidity and temperature. This chamber has the capability of controlling temperature in the range of -40 – 315°C and humidity in the range of 10–98%.

A linear voltage displacement transducer (LVDT) (Fig. 3, part [5]) is used to monitor the change in strain by the use of a freely moving capillary (Fig. 3, part [6]), within the LVDT housing. This capillary is attached to a moving carriage (Fig. 3, part [1]). An arm (Fig. 3, part [2]), which is also attached to the carriage, extends into the environmental chamber where a 2" indenter (Fig. 3, part [4]) on the end rests on the foam. The lower portion of the foam rests on a plate that has a fixed position inside the chamber. The load is controlled by a pulley system (Fig. 3, part [7]) that offsets the weight of the carriage and hence allows for precise control of the load within the range of 100–5000 g with an accuracy of ± 2 g.

The mechano-sorptive experiment involves first compressing the sample with a constant load, and then monitoring the change in strain with time while cycling humidity at a constant temperature. In this compression experiment, a $4 \times 4 \times 1$ " flexible polyurethane foam is first placed in the chamber set at a constant temperature and approximately 10% relative humidity (RH). After some period of time to

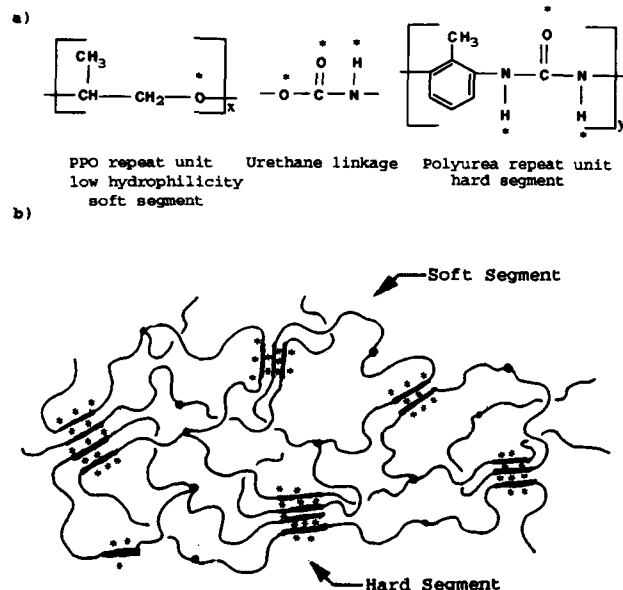


Figure 1 Simplified schematic illustrating potential sites for water to interact with the polyurethane foam in the (a) hard and soft segments and (b) the microphase separated model. *Potential sites for water interaction.

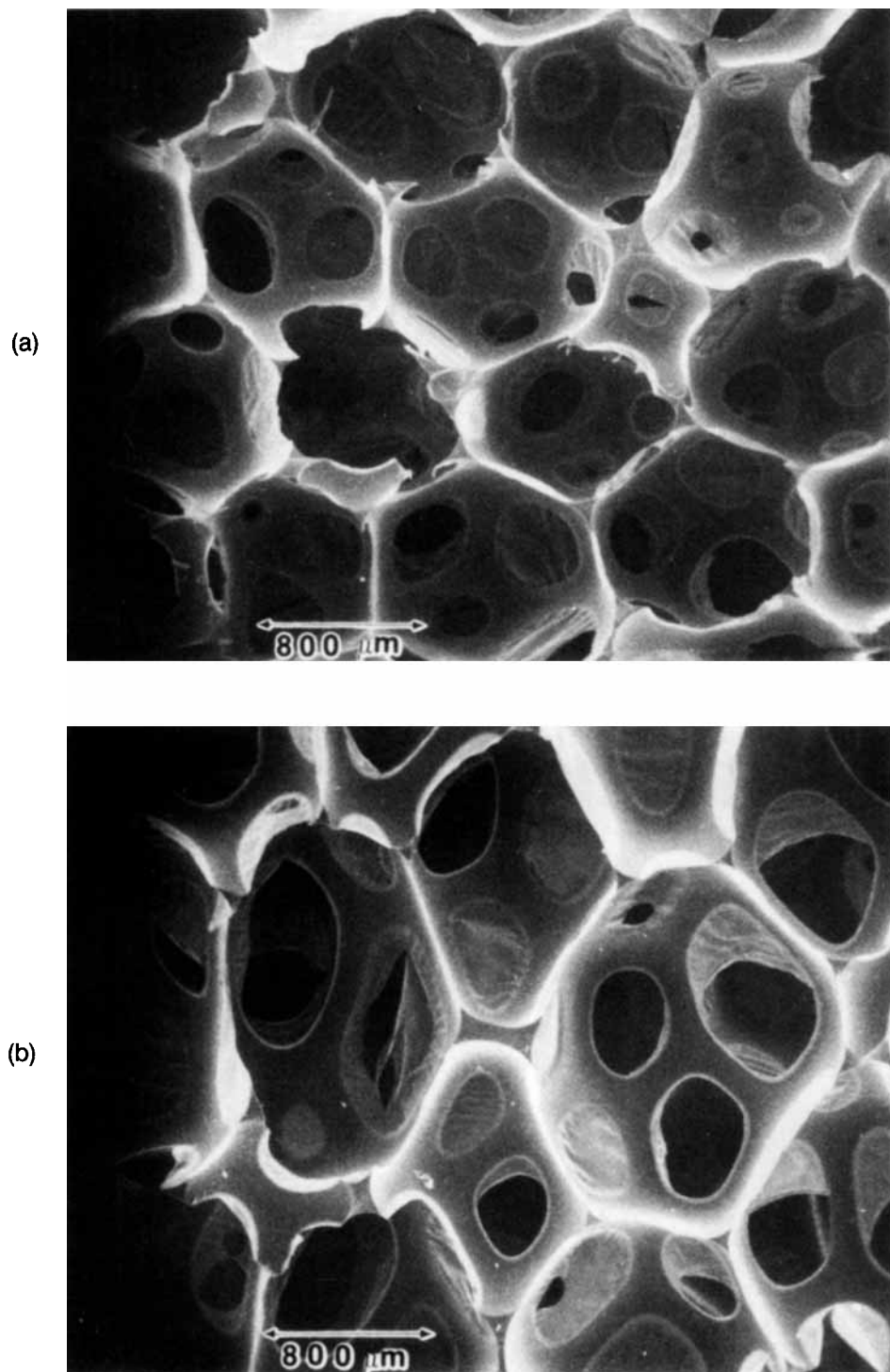


Figure 2 SEM micrographs of water-blown polyurethane foam: (a) (slabstock) view parallel to blow direction; (b) (slabstock) perpendicular to blow direction, blow axis is vertical; (c) (molded) parallel to rise direction; and (d) (molded) perpendicular to rise direction.

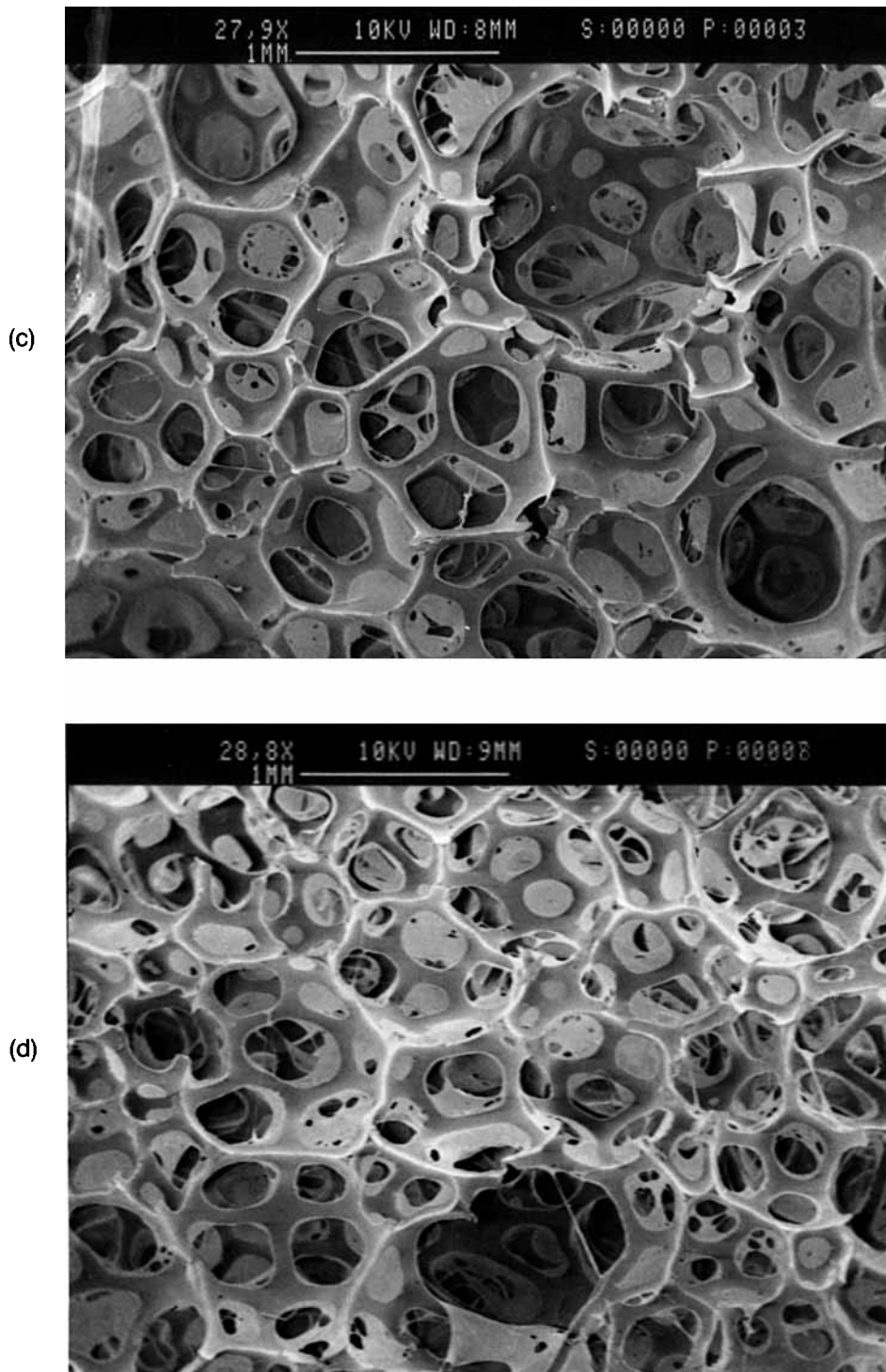


Figure 2 (Continued from the previous page)

allow the foam to reach the desired conditions in the chamber, the extension arm is released and allowed to drop onto the foam applying a constant load. A different load was used for each foam depending on the softness of the foam in order to

achieve similar initial strains and to keep the creep response within the range of the LVDT. The compressive strain is immediately monitored. After a period of about 60 min, the chamber humidity is rapidly increased to approximately 98% RH (oc-

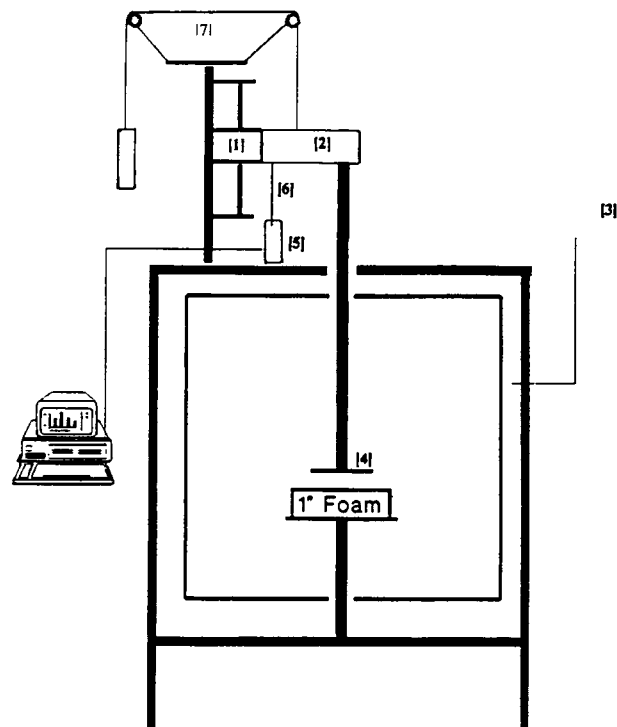


Figure 3 Schematic representation of instrument used for experimentation: [1] moving carriage that slides up and down; [2] arm extending into chamber; [3] environmental chamber; [4] 2" indenter that rests on foam; [5] linear voltage displacement transducer (LVDT); [6] moving capillary within LVDT; [7] pulley system to offset weight of carriage.

curing in a period of about 10 min) while the computer continues to monitor the strain. After the specified amount of time, the humidity is then decreased again to 10% RH. This completes one absorption-desorption cycle. Each experiment consists of four cycles excluding the initial loading cycle. The compressive strain is then plotted versus time over the entire period of these four cycles.

RESULTS AND DISCUSSION

The three foams studied show many similar features observed for wood and wood-based products under transient moisture conditions and a temperature of 40°C.^{1,4,5} Figure 4 shows the mechano-sorptive behavior for foam F5 (low hard segment) under a constant load of 1558 g. Curve (a) in Figure 4 corresponds to the creep response of F5 under constant 10% RH. The initial strain is approximately 17% and extends to approximately 22% after 550 min. Curve (b) corresponds to the creep response under constant 98% RH. The initial strain was 25% and

increased to about 33% after 550 min. Curve (c) corresponds to cyclic moisture conditions beginning at 10% RH. The strain initially at 18%, extends to 22% after 60 min at which point the humidity was increased to 98% RH. During this time the largest increase in strain was observed, that is, the strain increased to 32% followed by a decrease in the creep rate as noted by a near flat response. As the humidity was then decreased to 10%, the strain rapidly increased by 2% to 34%. The second cycle began with absorption and no increase in strain was observed until the onset of desorption when the strain increased by 2% again to 36%. Interestingly, subsequent absorption steps did not display increases in strain although subsequent desorption steps did and the strain level reached 38% after 550 min. This point will be addressed later.

The results of transient moisture conditions on the higher hard segment foam, F8, are illustrated in Figure 5. As can be observed, the compressive strain under a constant load of 1900 g, follows the same trend as foam F4. Curve (a) in Figure 5 is the creep response under constant 10% RH. The strain increased from an initial value of 20% after 600 min to 34%. Curve (b) represents the creep response under constant 98% RH. Here the strain level increased from 34%, initially, to 50%. Curve (c) represents the effect of transient moisture conditions on the creep response of F8. The response observed here was similar to that of foam F5, that is, the first absorption cycle displayed the biggest increase in strain as did each desorption step thereafter. The only exception here was that small increases in strain were observed during subsequent absorption steps. The strain here reached a final level of 58% after 600 min.

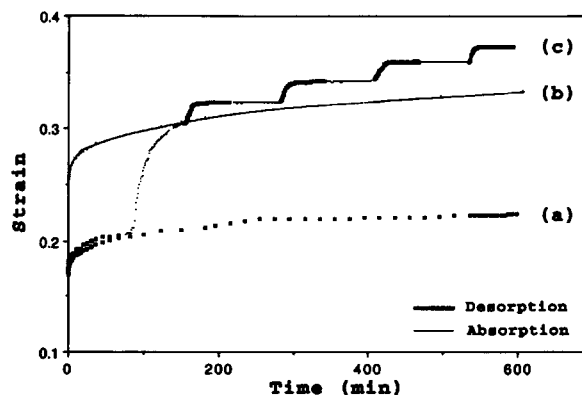


Figure 4 Mechano-sorptive behavior for flexible slabstock polyurethane foam F5 under constant load and temperature (40°C). (a) constant 20% RH; (b) constant 98% RH; and (c) cyclic moisture conditions.

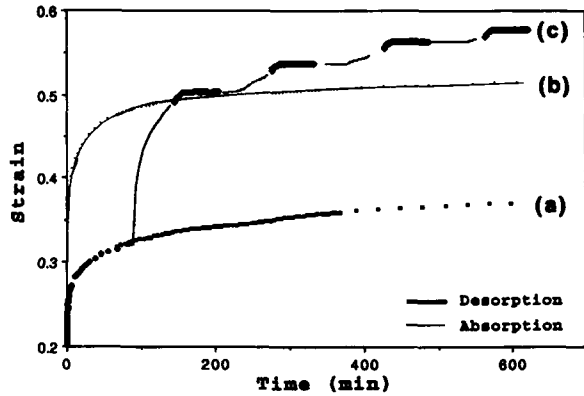


Figure 5 Mechano-sorptive behavior for flexible slabstock polyurethane foam F8 under constant load and temperature (40°C). (a) Constant 20% RH; (b) constant 98% RH; and (c) cyclic moisture conditions.

Figure 6 illustrates the mechano-sorptive behavior displayed by the molded foam, F13, under a constant load of 684 g. As in the previous cases, curve (c) representing the strain response under transient moisture conditions exceeds the strain in each case (low or high RH) where the humidity was held constant. Also, a much lower load gave approximately the same levels of strain indicating that the molded foam was much softer than the two slabstock systems. The increasing strain level would continue as the moisture cycling occurred until a point is reached where the covalent network of the foam accommodates the stress. In addition to this, further increases in strain leads to densification of the foam caused by the compression of the struts and remaining cell texture into a less porous solid.¹²

The mechano-sorptive phenomenon observed in

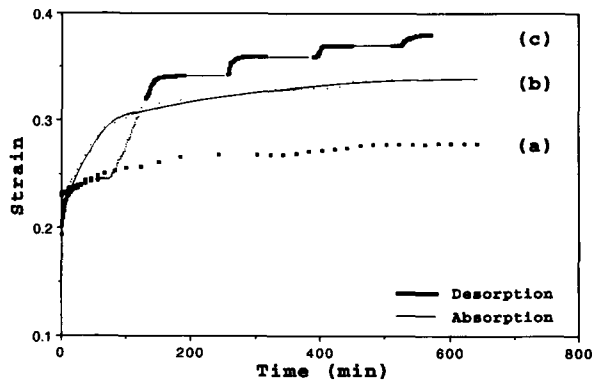


Figure 6 Mechano-sorptive behavior for flexible molded polyurethane foam F13 under constant load and temperature (40°C). (a) Constant 20% RH; (b) constant 98% RH; and (c) cyclic moisture conditions.

Figures 4–6 is caused by the polar water molecules interacting with the hydrogen bonds within the cellular structure of the foams, particularly the hard segment regions. As illustrated in the simplified morphological model given in Figure 7, this causes hydrogen bonds to be formed between the molecular structure of the foam and the water molecules thereby disrupting or loosening portions of the intermolecular forces within the foam and hence, causing slippage and creep. In desorption, these hydrogen-bonded regions with water are again disrupted or temporarily broken as the water diffuses from the system leaving increased regions of free volume thereby causing the foam to once again be less resistant to creep. The flux of water molecules into or out of the cellular structure, whether in absorption or desorption, disrupts the dynamic equilibrium of the hydrogen bonds causing bonds to be temporarily broken and reformed and, in turn, causing movement or creep within the foam.

The mechanism proposed here is basically in agreement with that proposed by previous authors

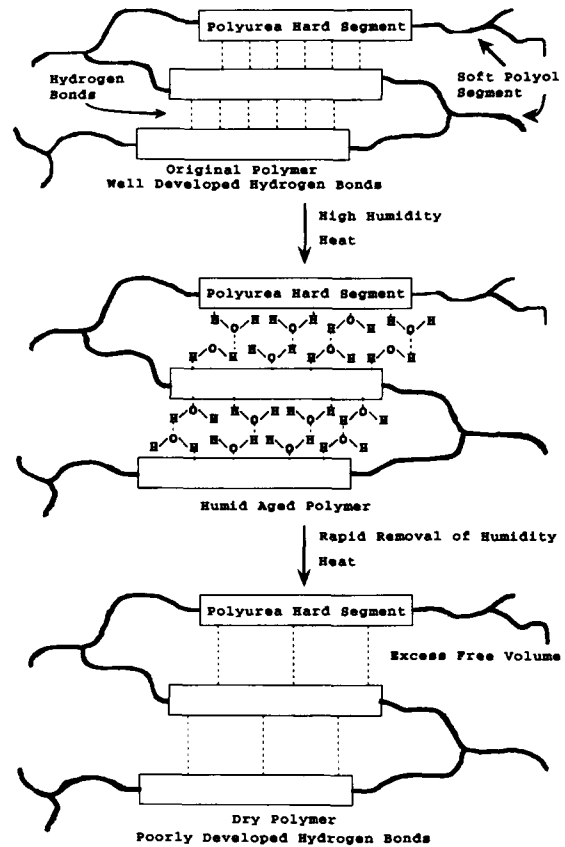


Figure 7 Tentative morphological model illustrating the effect that water absorption and desorption by the foam has on hydrogen bonds and structure.

with the exception that we emphasize that changes in the time-dependent free volume are also important, particularly as a result of desorption. Also, shrinking and swelling may have a small effect on the creep behavior as well particularly swelling at high humidity in the case of soft foam structures. In absorption, the foam may actually swell a small amount causing the strain to remain nearly unchanged; recall that during the latter absorption cycles, no significant creep occurred. The degree of this behavior is dependent, however, upon the load as well as the nature of the foam. Restated, the molecular interactions between the water and the foam that tend to promote creep may be somewhat balanced by the swelling of the foam during absorption. In desorption or shrinking, the swelling pressure will be reduced to zero.

In view of the proposed model, if one were to conduct the same experiment at a higher temperature where the hydrogen bonding is more mobile, the mechano-sorptive behavior would be expected to be less evident in the sense that the creep level under cyclic humidity does not exceed that at the highest constant humidity. Foam F13 was subjected to the same experiment conducted at 90°C. As can be observed from Figure 8, the creep response displayed at constant 98% RH was indeed very similar to that obtained under cyclic humidity conditions in the sense that the strain levels were nearly the same. At this temperature, the hydrogen bonds within the foam are much more labile than at the earlier lower temperature of 40°C. The weaker hydrogen bonded structure in this system at the high temperature, coupled with the high humidity further "plasticize"

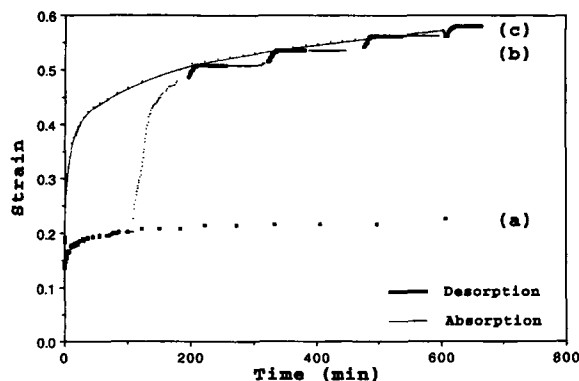


Figure 8 Mechano-sorptive behavior for flexible molded polyurethane foam F13 under constant load and temperature (90°C). (a) Constant 20% RH; (b) constant 98% RH; and (c) cyclic moisture conditions.

the foam causing strain levels to exceed those in Figure 6. In Figure 6, the strain levels for curves (b) and (c) reached 33% and 38%, respectively. However, in Figure 7, the strain levels for curves (b) and (c) reached 55% and 57%, respectively. The increased strain levels along with the similar response on curves (b) and (c) of Figure 7 further support the proposed mechanism.

CONCLUSIONS

Cyclic moisture conditions have a pronounced effect on the viscoelastic behavior of flexible water-blown polyurethane foams. Both slabstock and molded foams were compressed under a constant load and constant temperature in a changing moisture environment while the strain was monitored. The mechano-sorptive phenomenon was evident with all three foams following a similar trend where at 40°C the strain level surpassed those under constant relative humidity, either high or low. First, the creep level increased dramatically with the first absorption cycle. Then, in each subsequent absorption cycle, minute changes in strain, if any, were observed, but in each desorption cycle, increases in strain were evident. The effect of cyclic moisture content on creep is believed to be caused by the interaction of the water with the hydrogen-bonded structure within the foams causing them to be temporarily broken and reformed and hence, causing the foam to strain in correspondence to each change in moisture conditions. Of major significance is that during desorption, the increased free volume, along with the less ordered hydrogen bonds, allows for further increases in the strain in a step-like manner. Further support to this mechanism was given when the mobility of the hydrogen bonds was enhanced by increasing the temperature instead of cycling humidity. Here, the final strain level reached was almost identical to that where the humidity was cycled. Since polyurethane foam materials are inherently placed in changing environmental conditions, that is, changing weather conditions, it is clear that the mechano-sorptive phenomenon is very important because of the application of foams in load bearing and structural purposes.

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