

Characterization of Flexible Slabstock Foams Containing Lithium Chloride

J. C. MORELAND,¹ G. L. WILKES,^{1,*} R. B. TURNER,² and E. G. RIGHTOR²

¹Department of Chemical Engineering and Polymer Materials & Interfaces Laboratory, Virginia Polytechnic Institute and State University, Blacksburg, Virginia 24061-0211, Polyurethanes Products Research, Dow Chemical Company, Freeport, Texas 77541

SYNOPSIS

Characterization of a series of flexible polyurethane foams that contain LiCl in their formulation is discussed. These foams were developed in order to provide an alternative method to produce foams without physical blowing agents and still attempt to maintain specific important physical properties. Three high water content foams of varying LiCl content have been characterized by utilizing several morphological techniques as well as by their viscoelastic behavior. From a morphological standpoint, it appears that by adding LiCl to the formulation, there is less formation of urea-rich aggregates that occur when LiCl is absent. Also, the hard segments are more dispersed as single units within the network. The cellular texture of the LiCl-containing foams also shows a greater amount of cellular window material than the same foam without LiCl. Both of these changes due to LiCl addition are believed to bring about a significant increase in the amount of viscoelastic decay. This decay has been observed in tensile stress relaxation, compression load relaxation, and compressive creep studies. Temperature also has a more significant effect on the compression load relaxation behavior of foams with LiCl in their formulation than when absent. These differences in viscoelastic behavior between foams with and without LiCl in their formulation are attributed to the greater mobility of the hard segments in the presence of the LiCl additive serving as a localized "hard segment" plasticizer that also promotes more phase mixing in the foams. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

For the past several years there has been additional environmental concern over the use of chlorofluorocarbons (CFCs) for various applications and manufacture of several products. The blowing agent that is commonly used by itself or in a mixture with another low boiling inert solvent is CFC 11. This CFC is believed to have the greatest potential to deplete Earth's protective ozone layer—especially over Antarctica.¹⁻³ Because of this potential damage to the ozone layer, chemical companies who manufacture flexible polyurethane foams (as well as rigid foams) have begun to develop foams that involve

the use of alternative physical blowing agents or no physical blowing agents at all. Within this work, results will be presented on a "soft" flexible slabstock foam that contains no physical blowing agent.

The main objective for developing this foam was to manufacture a high water content foam that was "softer" but still retained important physical properties such as low compression set values. One means to meet this objective is to alter the solid morphology of the foam. From the initial morphological investigations on the solid structure of flexible slabstock foams reported by Armistead et al.,⁴ it was suggested that large diffuse urea-based structures (polyurea aggregates) on the order of 100–300 nm in size were present based on transmission electron microscopy (TEM) studies. In addition, these polyurea aggregates structures were also suggested to act like filler particles, therefore giving reinforcement to the foam's stiffness. With this in mind, there were efforts

* To whom correspondence should be addressed.

made to develop high water (hard segment) content foams and/or lower density foams with less of the urea aggregate structure in order to obtain a softer foam. One of these new systems involved adjusting the chemical formulation of a standard flexible slabstock foam by adding lithium chloride, which was dissolved in the formulation. Lithium chloride (LiCl) is very hygroscopic and thus will hydrogen bond to water readily. However, its function in the formation of the polyurethane foam is not well understood. In reviewing the literature, this particular salt as well as other lithium salts have also been previously used in facilitating formation of polymer solutions, including some polyurethanes. For example, Yoshikawa and Lyman⁵ showed that LiBr increased the solubility and decreased the solution viscosity of a copolyether urea-urethane dimethyl formamide solution. The authors of this study also gave evidence through solution nuclear magnetic resonance (NMR) that the LiBr ions associate with the urea groups of the hard segment, thus indicating that the LiBr disrupts the hydrogen bonding network of the hard domains. In other studies, lithium chloride has been added to aid in the solution formation of liquid crystal polyamide. It has also been shown to increase the solvating power of the solvent being used.^{6,7} The mechanism is not fully understood but is believed to be related to associations of the ions with the different chemical groups (carbonyl or N—H) on the backbone of the polymer chains or oligomers used in forming the liquid crystal polymer solutions.

Although there is not a complete understanding as to how LiCl effects the chemistry or formation of polyurethane foams, it will become evident in this study that some of the desired properties are obtained and some are not by the addition of LiCl to the formulation. In addition, from a morphological standpoint these new foams are quite interesting—especially the changes that occur in the solid portion of the foam, which are thought to be related to the larger urea aggregates whose structure is also still not fully understood. In adding to the understanding of the solid structure and the physical properties of these new flexible slabstock foams as well as slabstock foams in general, results from various morphological techniques and viscoelastic tests are presented on a set of foams with and without lithium chloride in their formulation.

EXPERIMENTAL

Specifics of the foams utilized for this study are given in Table I along with a few composition notes and

Table I Composition of Foams^a

Foam	LiCl Content (pphp)	LiCl Molar Content ^b	Density (lb/ft ³)
44-0	0	0	1.36
44-4	0.4	0.020	1.43
44-5	0.5	0.022	1.51

^a Comments: (a) All foams were made with 5 pphp H₂O and a 100 isocyanate index and (b) hard segment content is 34 wt % for all foams.

^b LiCl molar content is defined as the number of moles of LiCl molecules divided by the number of moles of urea and urethane molecules

density information. All three foams shown in Table I were made with 5 pphp water and an isocyanate index of 100 (not 110 as discussed in our earlier report on related foams⁴). The catalyst and surfactant levels are not made available due to proprietary reasons. However, the catalysts, surfactant, and polyol used to make these foams are typical of those used in manufacturing conventional slabstock polyurethane foams. As shown in Table I, foams 44-4 and 44-5 contain 0.4 and 0.5 pphp lithium chloride in their formulation, respectively, while the control foam, 44-0, does not contain any LiCl. The relative amount of LiCl in foam 44-5 on a molar basis corresponds to approximately 0.022 mol of LiCl to 1.00 mol of urea-urethane linkages. This ratio, of course, exemplifies the small amount of LiCl added to these foams but, at the same time, indicates there is 1 LiCl species for about every 45 urea-urethane linkages.

Several different techniques including scanning electron microscopy (SEM), TEM, differential scanning calorimetry (DSC), wide-angle X-ray scattering (WAXS), and small-angle X-ray scattering (SAXS) have been utilized to characterize the effect of adding LiCl to the formulation on the morphology of the solid portion of these foams. The TEM micrographs were obtained by using a JEOL 2000FX analytical TEM, which was operated at an accelerating voltage of 100 kV. The foam samples were prepared by first embedding small pieces of foam with D.E.R. 331 epoxy. Ultrathin sections (ca. 100 nm) were then cut at room temperature from these samples utilizing a diamond knife on a Riechert-Jung Ultracut E microtome and were mounted on a carbon-coated copper grid. The WAXS apparatus consists of a Phillips Table-Top X-Ray Generator PW 1720 with a standard vacuum-sealed Statton camera. The foam samples investigated by X-ray scattering were 10 mm in thickness and were compressed to approximately 3 mm. The exposure

times were in the range of 22–24 h. The sample to film distance was 7.8 cm. Small-angle X-ray scattering was also carried out with a Siemens Kratky camera system. The X-ray source was a Siemens Cu-W tube powered by a Siemens Model 1726 generator. A Braun position-sensitive detector was utilized to monitor the angular dependence of the scattering intensity. A computer program written in ASYST by Tyagi and modified by Huang of this same laboratory was used to convert and analyze the data. A Seiko thermal analysis system was utilized to determine the soft segment glass transition temperature of foams 44-0 and 44-5, the two extremes of the foam series. The samples were run from -150 to 150°C at a $10^{\circ}\text{C}/\text{min}$ heating rate. Scanning electron microscopy was also utilized to distinguish if there were any major differences in the bulk morphology of foams 44-0 and 44-5. A Cambridge Instruments Streoscan electron microscope was used to obtain the micrographs for these foams. Foam samples of approximately 2 mm in thickness were cut both parallel and perpendicular to the blow axis. The samples were placed on aluminum stubs that had been coated with silver conducting paint. This was followed by a gold coating of approximately 200 \AA with a Biorad Polaron sputter coater.

In addition to characterizing the morphology of these foams, the viscoelastic behavior was evaluated using tensile stress relaxation, compression load relaxation, and compression creep. All three of these viscoelastic techniques have been described in some detail in previous publications, and thus the interested reader is referred to Refs. 8 and 9 for specifics. The tensile stress relaxation tests were carried out at a 25% elongation and only at ambient conditions. Both the effects of temperature and relative humidity on the compression load relaxation behavior at a 65% strain level were evaluated for foams 44-0 and 44-5. Also, the effect of humidity on the compressive creep behavior of foams 44-0 and 44-5 was determined. The choice of tensile as well as compression deformation levels were based on our previous work.^{8,9} However, it is worth noting that the compression level is in line with the common identification load deflection (ILD) test used for characterizing foams.

RESULTS AND DISCUSSION

Transmission Electron Microscopy

As mentioned earlier, TEM has been useful for analyzing the presence of the large urea-rich based

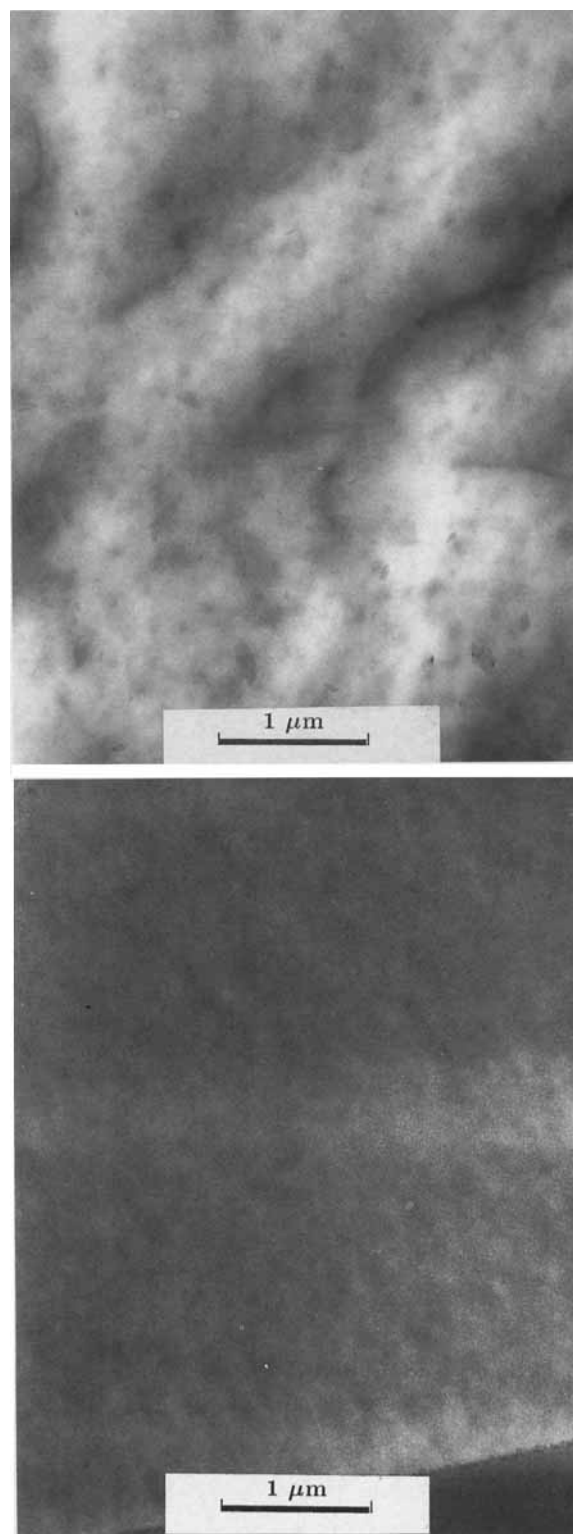


Figure 1 TEM micrographs for foams (a) 44-0 and (b) 44-5.

structures, i.e., the polyurea aggregates are believed to be the darker regions, some having dimensions as large as $0.3 \mu\text{m}$. In Figure 1, the effects of adding

0.5 pph LiCl to a standard flexible slabstock polyurethane foams formulation can be seen by comparing the TEM micrographs for foams 44-0 and 44-5. As shown by these micrographs, the differences in the phase segregation are rather significant upon addition of lithium chloride to the formulation. For foam 44-0, the phase segregation is pronounced and the polyurea aggregates are believed to be the darker phases in Figure 1 (a). On the other hand, the phase segregation for 44-5 is diffuse and the darker regions are not as noticeable. The TEM micrograph for foam 44-4, not shown here, is very similar to that of 44-5, but with slightly better phase segregation. Therefore, it does appear that by adding the LiCl to the formulation the "urea" segments of the urea aggregates have been more effectively dispersed within the chemical network structure of the solid portion of a high water content flexible slabstock foam. Although, the actual extent of this dispersion is not well understood, it is clear that the distinct polyurea aggregate structure has been reduced in size and/or has not formed at all in the LiCl-containing foams.

Thermal Analysis

Differential scanning calorimetry was also utilized to determine the effect of adding LiCl to the formulation on the soft segment glass transition and the phase separation of the hard and soft segments. The DSC traces are shown in Figure 2 for foams 44-

0 and 44-5. In comparing the two traces, the soft segment glass transition (near -50 to -45°C) is higher for foam 44-5 and is somewhat broader than that of 44-0. Both of these observations indicate more phase mixing is taking place in the lithium chloride foam. This behavior is consistent with the TEM results discussed above.

X-ray Analysis

Both WAXS and SAXS have been utilized to probe possible changes in the structural order of the foams due to the addition of LiCl to its formulation. The WAXS diffraction patterns are shown in Figure 3 for foams 44-0 and 44-5. In general, these patterns are similar to those reported by Armsitead et al.⁴ for a set of variable hard segment slabstock foams. However, the apparent diffraction peak at 0.45 nm is distinctly sharper for foam 44-0 than for 44-5. In addition, there is a sign of a weaker peak at 0.59 nm for foam 44-0 that is not observed at all in the case for foam 44-5. The differences in the WAXS patterns indicate that the local structural order of the hard domains is clearly reduced by adding the small amount of LiCl to the formulation. In view of the TEM results, this decrease in structural order in foam 44-5 is believed to be related to a significant reduction in the size of the polyurea aggregate and/or a removal of some of these structures. Another possibility is the order of both of the hard domains, aggregates and microdomains, altered in the lithium

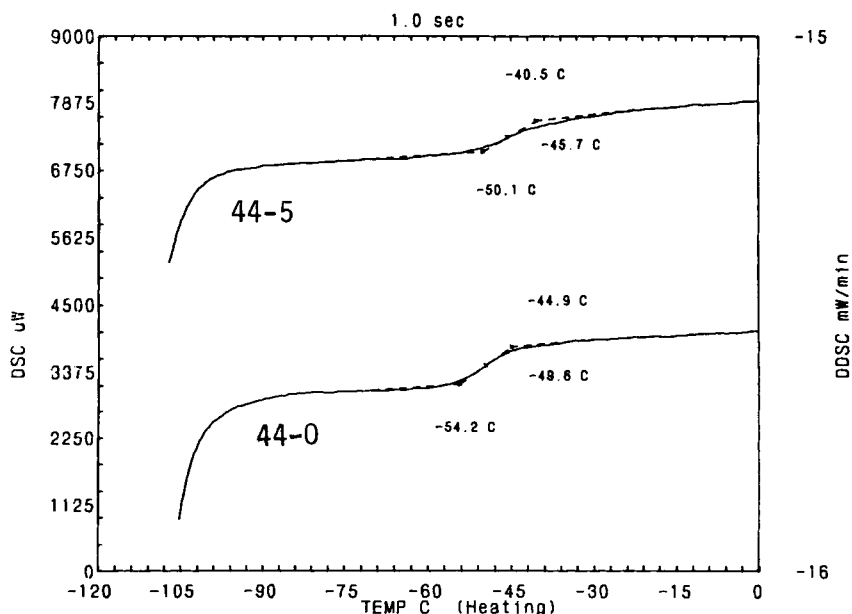


Figure 2 DSC traces for foams (a) 44-0 and (b) 44-5.

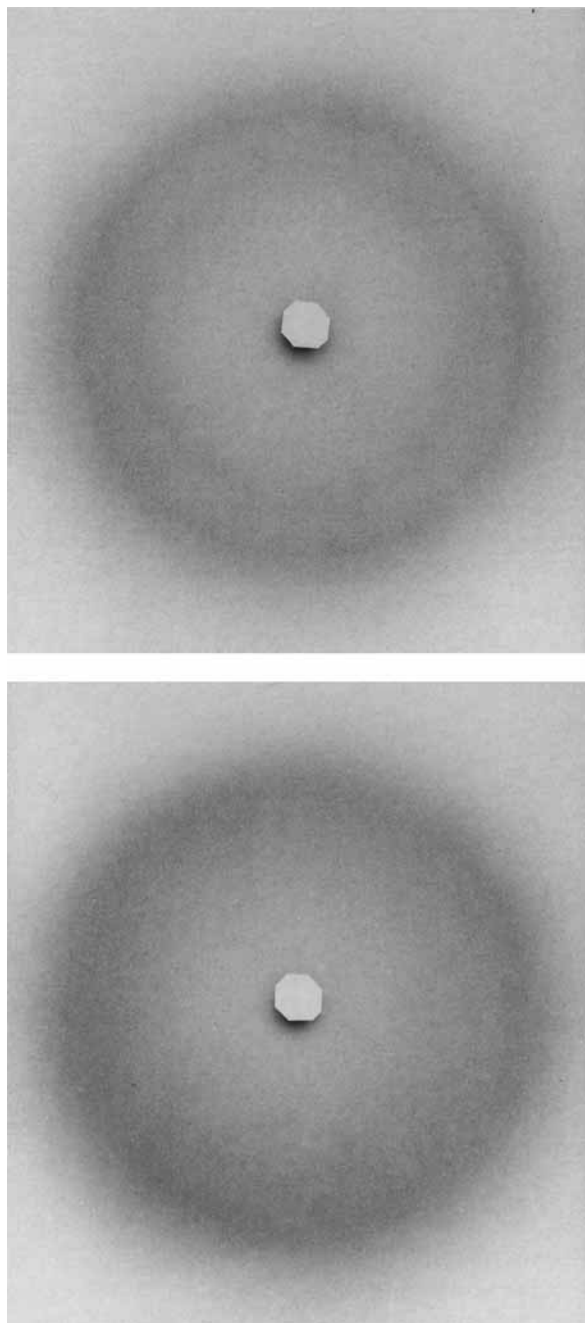


Figure 3 WAXS diffraction patterns for foams (a) 44-0 and (b) 44-5.

chloride foam. This may be a result of a reduction in the formation of segment–segment hydrogen bonds between the hard segments due to their association with the LiCl—recall that there exists, on the average, 1 LiCl for about every 45 urea–urethane groups.

The SAXS profiles are given in Figure 4 for foams 44-0 and 44-5 in the form of scattering intensity as

a function of scattering vector, s , where s is defined as $(2/\lambda)\sin(\theta/2)$ and λ is the wavelength of the X-ray source and θ is the radial scattering angle. Although neither of the profiles exhibit a sharp peak, both exhibit a shoulder similar to previous slabstock urethane foams analyzed in the same manner.⁴ The shoulders represent an interdomain interference peak that is the result of a partially periodic structure as has been discussed elsewhere.⁴ The shoulder is sharper for foam 44-5 in comparison to 44-0, but both shoulders appear to occur over about the same range of scattering vector, s . By applying Bragg's law to the shoulder region, a rough estimate for the center-to-center (interdomain) spacing between the scattering particles results in a value on the order of 8 nm for both foams. Also, the scattering intensity in the shoulder is about 18% higher at s equal to 0.081 for foam 44-0 than that of 44-5. In addition, the interfacial analysis on the SAXS behavior for these materials has led to an index of interfacial thickness of ca. 0.7 nm for both foams 44-0 and 44-5.

The above results from the SAXS scattering profiles do indicate that the spacing between the microhard domains is similar and indirectly signifies that these hard domains are comparable in size for foams 44-0 and 44-5 since the volume fraction of the soft phase is the same in both foams. The slightly higher scattering intensity for foam 44-0 in the shoulder region might suggest that there are more microdomains present in foam 44-0 than 44-5, although this speculation is difficult to further support since the interdomain distance appears to be nearly the same. In addition, the intensity difference might indicate that there is more phase mixing in foam 44-5 in comparison to 44-0. These speculations would imply that the LiCl addition is not necessarily promoting the formation of the smaller microdomains, but more single hard segment units. On the other hand the somewhat more distinct shoulder would tend to suggest that the hard domains in foam 44-5 are possibly more uniform in size in comparison to foam 44-0. Finally, the interfacial analysis indicates that a small, but similar, amount of phase mixing is taking place at the interface of the soft and hard segments in foams 44-0 and 44-5.

In short, the results from the above morphological techniques have definitely indicated that some structural changes in the solid portion of the foam have clearly taken place by adding LiCl to the formulation. These changes appear to be mostly related to the larger polyurea aggregates, suggesting that there is formation of smaller aggregates and/or that many of the urea hard segments are being dispersed

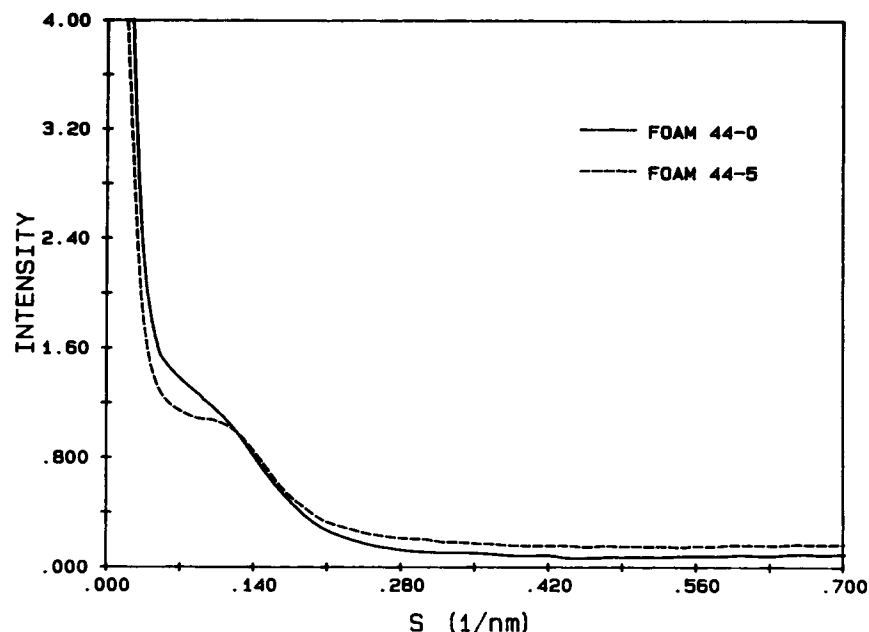


Figure 4 SAXS scattering profiles for foams 44-0 and 44-5.

more as single units in the network. In addition, based on the TEM micrographs and the DSC traces for foams 44-0 and 44-5, the phase mixing of the soft and hard units is believed to be greater for the LiCl foam. While the interpretation of all results is not complete, the suggested modifications in the solid textures due to the addition of LiCl to the formulation will aid in the discussion of the viscoelastic properties. Before discussing the effect that the LiCl addition has on the viscoelastic nature of flexible foams, the morphology of their cellular textures will also be presented.

Macroscopic Structure of the Foams

The SEM micrographs are shown in Figure 5 for foams 44-0 and 44-5 in both the parallel and perpendicular direction to the blow axis. At first glance the cellular textures for these two foams appear to be quite different due to a greater number of intact cell windows in foam 44-5 in comparison to 44-0. This is the main difference, but an important one, between these two foams with regard to their cellular textures. The size of the cells do appear to be similar and possibly slightly greater in size for foam 44-5. In addition, the regularity and the shape of the cells in the directions parallel and perpendicular to the blow direction of each foam are comparable for the two foams (see Fig. 5). The reader will note the distinct anisotropic features of the foams when

viewed in the two directions; this is typical of slabstock foams.

The difference in the amount of intact cell windows in foams 44-0 and 44-5 does appear to be related to the flow of the cellular membrane material into the struts. This step in the formation of an ideal foam is thought to occur after blow off or at the point where gellation takes place. The above process, of course, is dependent on the viscosity of the cell window material and, if the viscosity is high, it will prevent some of the flow of this material into the cell wall struts. Thus, it is speculated that the LiCl is possibly promoting gellation to occur more rapidly or earlier in the foam formation and thus bringing about a viscosity buildup in the cellular window material. The above difference in cellular textures also indicates that the LiCl could be acting like a surfactant by "solubilizing" the urea-based hard segments in the foaming solution and thus preventing their precipitation. Such precipitation of urea in non-LiCl-containing foams has been suggested by FTIR kinetic studies on the foaming mixture by other researchers.¹⁰⁻¹³ Also, it is generally accepted for flexible slabstock polyurethane foams that by adding too much surfactant, a foam with a large amount of closed cells is obtained.

The above differences in cellular texture are also believed to reduce the stiffness in foam 44-5 in comparison to 44-0. Basically, the stiffness in open cellular foams is known to be mostly dependent on the

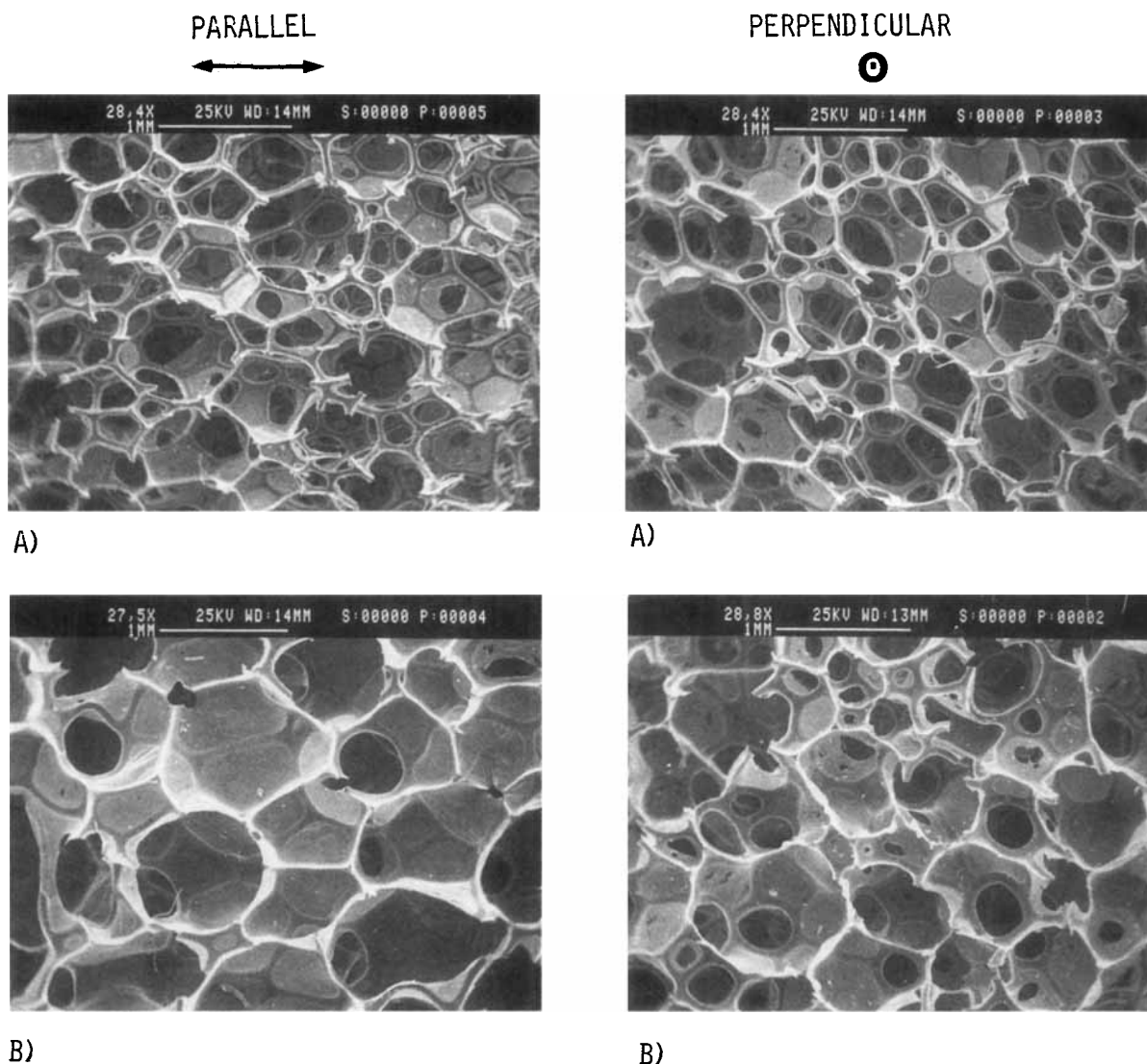


Figure 5 SEM micrographs of cellular textures for foams (a) 44-0 and (b) 44-5 (shown both parallel and perpendicular to blow axis).

struts.^{14,15} Therefore, the compressive load, as well as the tensile stress, in these two foams are expected to be higher in foam 44-0 in comparison to 44-5. In the next section, this point is addressed as well as the difference in the viscoelastic behavior of this foam series.

VISCOELASTIC BEHAVIOR

The viscoelastic behavior of other related slabstock foams has been evaluated by utilizing three tests: tensile stress relaxation, compression load relaxation, and compression creep—the details of each test have been discussed recently in two previous pub-

lications.^{8,9} In all cases, the loading direction was parallel to the blow axis—recall Figure 5. The reader is therefore referred to these two references for further details of the methods of analyzing the data from the three tests. In addition to evaluating the effect of the addition of LiCl to the formulation on the viscoelastic nature, the effects of temperature and relative humidity have also been measured for the compressive properties of foams 44-0 and 44-5.

As a point of clarification, when the phrase, the “effect of LiCl,” is used in the following discussion, it refers to the addition of LiCl to the formulation and the resulting changes in the solid morphology that are brought about by its addition. However, in a few instances, which are clearly stated, reference

is made to the LiCl *molecule* acting as a plasticizer in these materials. It is also speculated that the lithium chloride molecules are affecting the hydrogen bond behavior in the hard domains (both micro and aggregates) and thus LiCl will be referred to as a hydrogen bond (HB) plasticizer that when used in these foams would be expected to preferentially "plasticize" the hard segment regions. As discussed in the introduction, other authors have suggested a similar mechanism involving LiBr in a polyurea-urethane hydrogel.⁵

Tensile Stress Relaxation

The stress relaxation behavior $\log \sigma(t)$ versus \log (time) obtained at ambient conditions (25°C, 20% RH) is shown in Figure 6 for foams 44-0, 44-4, and 44-5. As exhibited in Figure 6, there is rather linear behavior for the initial 3-h period for all three foams, which is similar to the behavior reported in an earlier publication for a set of variable hard segment (differing water content) slabstock foams. Also, the initial stress level does decrease systematically with increasing LiCl content. This decrease in stress is believed to be a result of smaller and/or less of the urea aggregate structure present in the solid portion of the foams, which in turn is thought to reduce the reinforcement in the foam's struts. The difference

in cellular morphology for foams 44-0 and 44-5 is also believed to be another influential factor on the differences in viscoelastic response as alluded to in the discussion of the SEM micrographs for these foams (recall Fig. 5 for 44-0 and 44-5). That is, more material was contained in the cellular window material in foam 44-5 in contrast to 44-0. This observation suggests that a lower tensile stress in foam 44-5 versus foam 44-0 would be obtained since the struts give the foam the majority of its stiffness.^{14,15} Ashby,¹⁵ for example, has shown that the stiffness in open cellular foams is proportional to Et^3 where E is the modulus of the solid portion of the foam and t is the thickness of the struts. Thus, if thinner struts (44-5 vs. 44-0) are present, the stiffness and likewise the tensile strength will be reduced.

As displayed in Figure 6, there is also a noticeable difference in the rates of relaxation (the slopes) for the three foams. The stress decay rates as a function of LiCl content are given in Figure 7 along with the load decay rates from the compression studies. While the latter rates will be addressed later, we first will focus on the tensile relaxation studies. As shown in Figure 7, the stress decay rates do increase systematically with increasing LiCl content. This increase in the stress decay rates with LiCl content clearly appears to be related to the changes in the solid morphology discussed earlier. That is, the result of

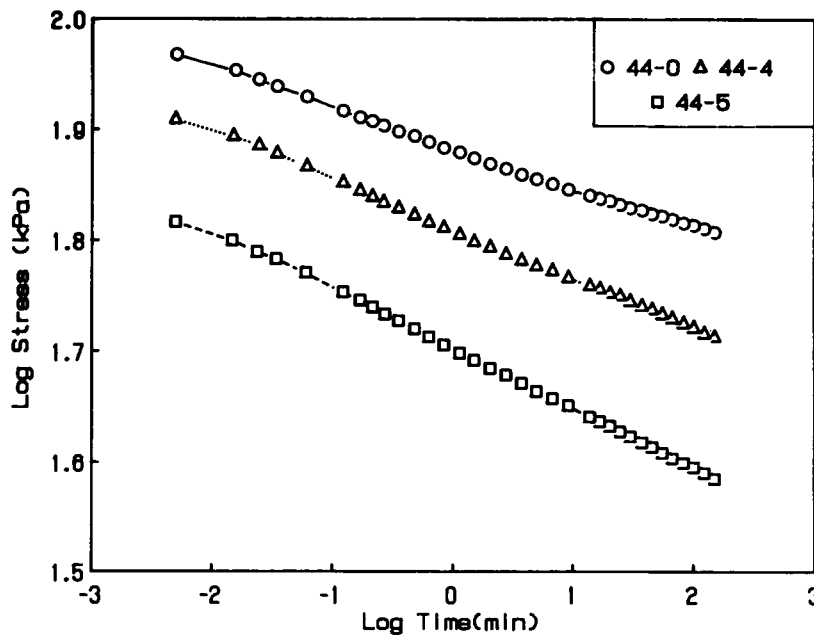


Figure 6 $\log \sigma(t) - \log t$ tensile stress relaxation behavior for foams 44-0, 44-4, and 44-5 (obtained at 25% elongation and at 25°C–20% RH).

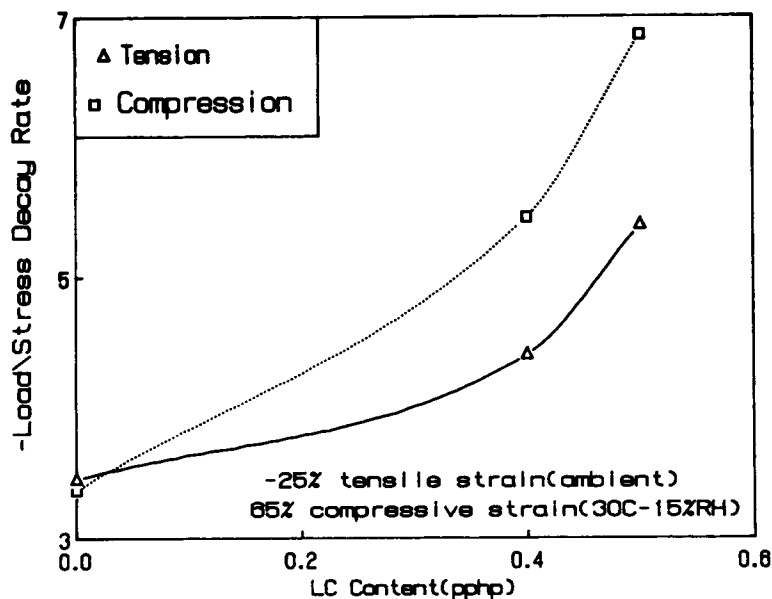


Figure 7 Effect of LiCl content on the relaxation behavior in tension and compression.

reducing and/or removing the urea aggregate structure in the LiCl foam is thought to allow for more mobility of the hard segments. Additional mobility is likely to cause more chain slippage, which will lead to further stress relaxation. This increase in the mobility of the hard segments may be a result of more phase mixing of the soft segments and hard segments. It could also easily be a result of a weaker hydrogen bonding network (recall the WAXS results), which is likely to allow for more disruption and reformation of hydrogen bonds. Another factor contributing to the increase in the stress relaxation for foams 44-4 and 44-5 is that LiCl could be acting as a "hydrogen bond (HB) plasticizer." By entering into the hard domains it would facilitate local chain slippage, which, of course, is known to cause additional stress relaxation. Indeed, this latter point is believed to be of considerable importance.

Compression Load Relaxation Behavior

The log load–log t relaxation behavior in compression is shown for foams 44-0, 44-4, and 44-5 in Figure 8 at a condition of 30°C and 15% RH. Although there appears to be only a small increase in the initial load levels with decreasing LiCl, it is important to point out that the density of these foams does increase by about 13% from foam 44-0 (0 pphp LiCl) to 44-5 (0.5 pphp LiCl)—see Table I. Thus, if one normalizes on the basis of density, this increase in the initial load level to obtain a 65% comparison is

considerably greater than it appears in Figure 8. Regardless, the decrease in the initial load levels due to the addition of LiCl to the formulation is consistent with expectations and is believed to take place for similar reasons discussed above when accounting for the decrease in the initial tensile stress levels.

A significant difference in the rate of relaxation is observed in Figure 8 for the three foams. Also note that the log load–log time behavior is not as near linear for the LiCl foams in comparison to the control foam—especially at short times. The load decay rates as a function of LiCl content that were given in Figure 7 and exhibit an increase with increasing LiCl content. This increase, like that observed in the tensile stress relaxation study, is thought to be related to the changes that occurred in the morphology. Some of the same factors, e.g., reduction and/or removal of the polyurea aggregate structures are also thought to lead to further relaxation in compression for the LiCl foams. In addition, LiCl is believed to be acting as a HB plasticizer by causing additional chain slippage, which will, of course, lead to further load decay.

In comparing the rates of relaxation for the two modes of deformation, there is more relaxation taking place over 3 h in compression versus tension for the LiCl foams whereas the rates are similar for the control foam. The latter result is consistent with our earlier data reported in a previous publication for a similar foam with the same hard segment content.⁸ Indeed this earlier result suggested the con-

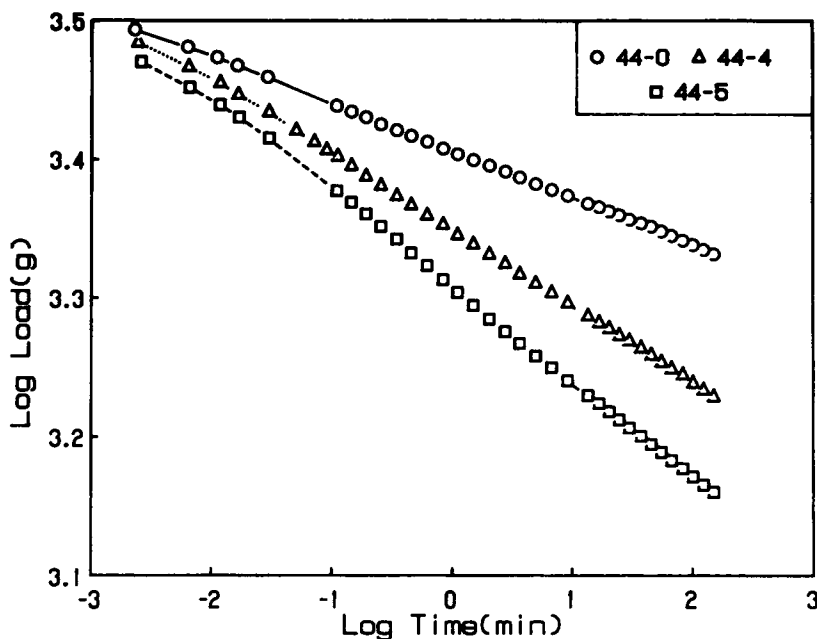


Figure 8 Log load(t)-log t compressive load relaxation behavior for foams 44-0, 44-4, and 44-5 (obtained at a 65% strain and 30°C-15% RH).

clusion that it is the solid portion of the foam in both tension and compression that is governing the relaxation behavior in contrast to the cellular texture. The rates of relaxation in compression and tension for the LiCl foams are also thought to be mostly governed by the solid material, but it is possible that the cellular morphology is influencing the viscoelastic decay in the materials addressed here. Recall, that the LiCl foams have a rather significant amount of intact window material whereas the foams without LiCl in their formulation do not (see micrographs for foams 44-0 and 44-5 in Fig. 5). Thus, it is possible that the viscoelastic decay of the intact windows are effected differently in the compression and tension modes whereas the material in the struts are not. While there is no proof for this speculation, there are some possible explanations. First, the level of deformation in compression (65%) is higher than in tension (25%), and this may provide a different dependence on the thinner cellular wall materials. It is also possible that in the compression of the LiCl foams, the material in the struts as well as in the intact windows is governing the relaxation. However, in tension, only the material in the struts is contributing to the relaxation behavior since many of the cell windows are disconnected enough that they may not bear much of the tensile load.

In short, there are some differences in the relax-

ation behavior in tension and compression for the LiCl foams that are not fully understood. However, it is believed that the changes that occur in the solid morphology by adding LiCl to the formulation are leading to the majority of the increase in the rate of relaxation in foams 44-4 and 44-5. In the paragraphs to follow, the effect of temperature and relative humidity on the load (compression) relaxation behavior are discussed by comparing the results obtained for foams 44-0 and 44-5.

The log load-log t variable temperature relaxation behavior is shown in Figures 9 and 10 for foams 44-0 and 44-5, respectively. Both exhibit a decrease in the initial load level with increasing temperature, and this decrease appears to be greater for the LiCl foam (see Table II). For example, a 26% decrease in the initial compression load is observed from 30 to 125°C for foam 44-5 and a 23% decrease for foam 44-0. In comparing the two surfaces in Figures 9 and 10, one may notice in the temperature range of 25-100°C that the log compression load-log time behavior is not as linear in the case of foam 44-5, especially at short times. At temperatures greater than 100°C, there is negative deviation from the earlier linear log load versus log t behavior for both foams (see Figs. 9 and 10). This negative deviation is believed to be promoted by the same mechanisms mentioned in our previous work;⁸ that is, further

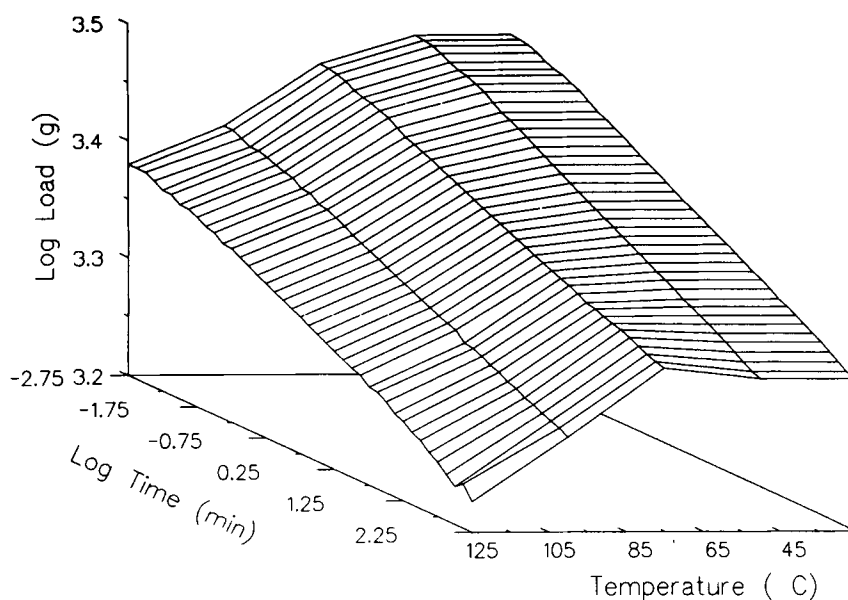


Figure 9 Variable temperature load relaxation behavior for foam 44-0 (obtained at a 65% strain level).

hydrogen bond disruption as well as possible chain scission in the urea and urethane linkages that occur at temperatures greater than 100°C, as has been noted by FTIR analysis.

In contrast, the behavior of the percent load decay and load decay rates differ with increasing temper-

ature for foams 44-0 and 44-5, as shown in Table II. This difference can also be observed in Figure 11 for the plot of the percent load decay values as a function of temperature. As shown, the behavior does appear to be more scattered and not that systematic for foam 44-5 in comparison to the non-

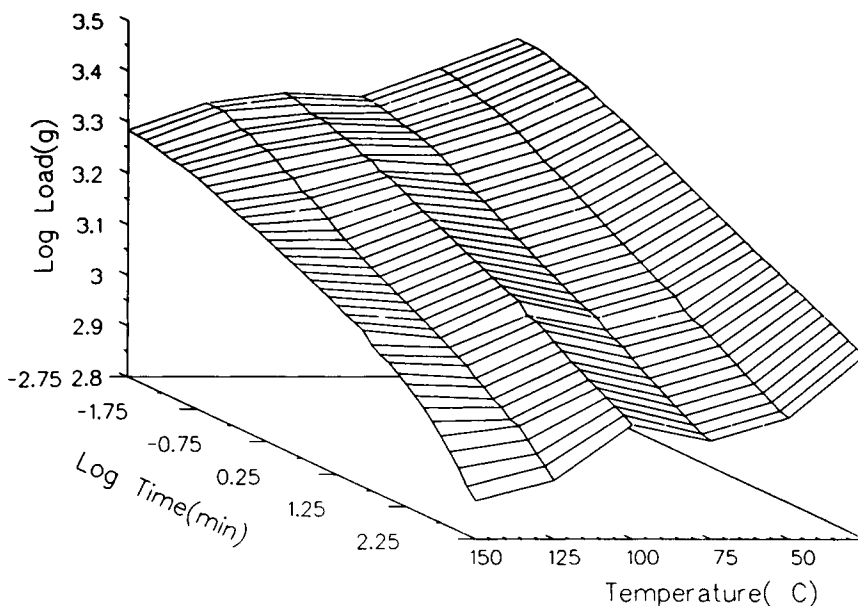


Figure 10 Variable temperature load relaxation behavior for foam 44-5 (obtained at a 65% strain level).

Table II Summary of Results for Variable Temperature Compression Load Relaxation for Foams 44-0 and 44-5^a

Temperature (°C)	L_0 (kg)		% Load Decay ^b		Slope ($\times 10^2$) ^c	
	44-0	44-5	44-0	44-5	44-0	44-5
30	3.1	2.9	32	52	-3.4	-6.8
60	—	2.6	—	59	—	-8.2
85	2.9	2.3	27	57	-2.7	-8.0
100	2.6	2.3	28	57	-2.8	-7.5
125	2.4	2.2	32	62	—	—
140	—	2.0	—	63	—	—

^a Based on two data sets at 85°C for 44-5, the range of error for the slope is on the order of ± 0.2 and that of the load decay is ± 2.5 .

^b Time frame is from 0 to 180 min.

^c Correlation coefficient is within 0.995 and 0.999 except at 125 and 140°C.

LiCl-containing foam 44-0 as well as results reported in the previous work (for other non-LiCl foams).⁸ However, this irregular behavior in Figure 11 for foam 44-5 is believed to fall outside of experimental error based on additional tests performed at 85°C, which indicated an error range on the order of $\pm 2.5\%$. In comparing the behavior in Figure 11 for the LiCl foam and its control, it does appear that

Table III Load Decay Values for Foams 44-0 and 44-5 at Different Temperature/Relative Humidity Conditions^a

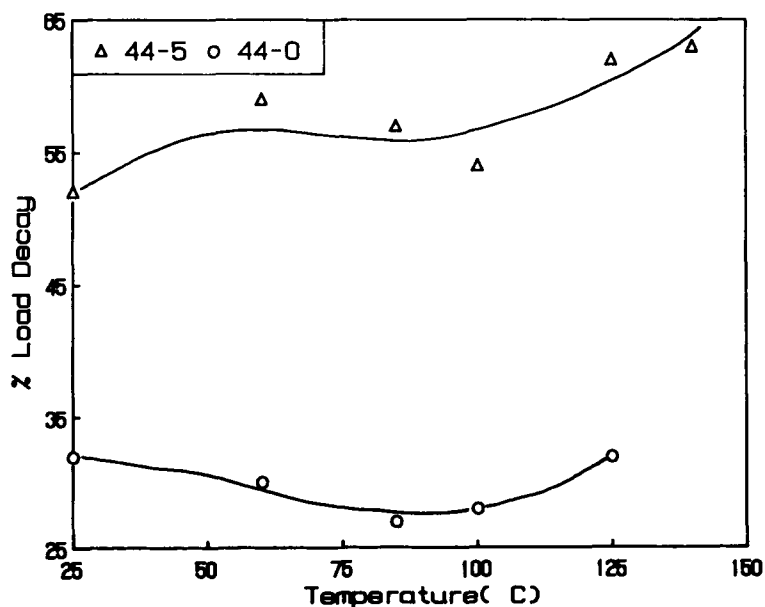
Condition	% Load Decay (Load Decay Rate $\times 10^{-2}$)	
	Foam = 44-0	44-5
30°C-15% RH	32 (3.4)	52 (6.8)
30°C-100% RH	36 (3.9)	62 (8.7) ^b

^a Behavior obtained over a 3-h time period.

^b Correlation coefficient not within 0.995 to 0.999.

temperature has a greater effect on the LiCl foam, 44-5. This effect is most pronounced by comparing the results at 30 and 125°C for the two foams (see Table III). The increase that is observed from 30 to 125°C is possibly a result of more hydrogen bond disruption taking place with increasing temperature in foam 44-5 in comparison to 44-0. This suggestion is likely to cause additional load decay by increasing the mobility of the hard segments.

The effect of LiCl on the compression load relaxation behavior at *low and high relative humidities* at 30°C is shown for foams 44-0 and 44-5 in Figures 12 and 13, respectively, and summarized in Table III. As shown there is a decrease in the load level with increasing relative humidity for both foams at

**Figure 11 Thermal dependence on load decay in foams 44-0 and 44-5.**

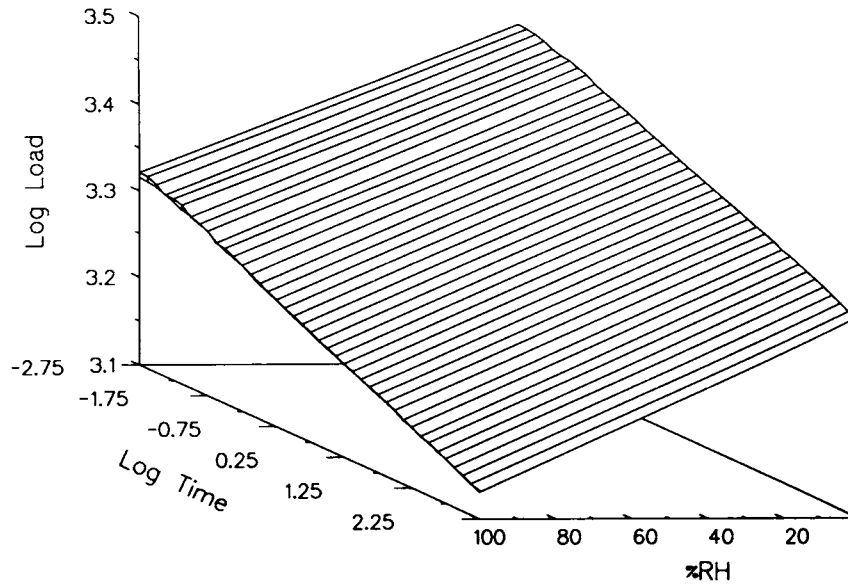


Figure 12 Effect of relative humidity on foam 44-0 at 30°C (obtained at a 65% strain level and at 15% RH and 100% RH).

30°C. As reported for a similar study on another set of slabstock foams, water is believed to act as a plasticizer in these materials and thus cause a decrease in the load level.⁸ As might be expected, however, the effect of moisture on the initial load level is greater for the LiCl foam.

At 30°C, the effect of LiCl in higher relative hu-

midity environments (15% RH vs. 100% RH) also results in nonlinear behavior for the log compression load-log t as shown for 44-0 in Figure 12 and foam 44-5 in Figure 13. In addition, a greater change in the rate of decay for foam 44-5 is observed with increasing relative humidity in comparison to foam 44-0 (see Table III and compare Figs. 12 and 13).

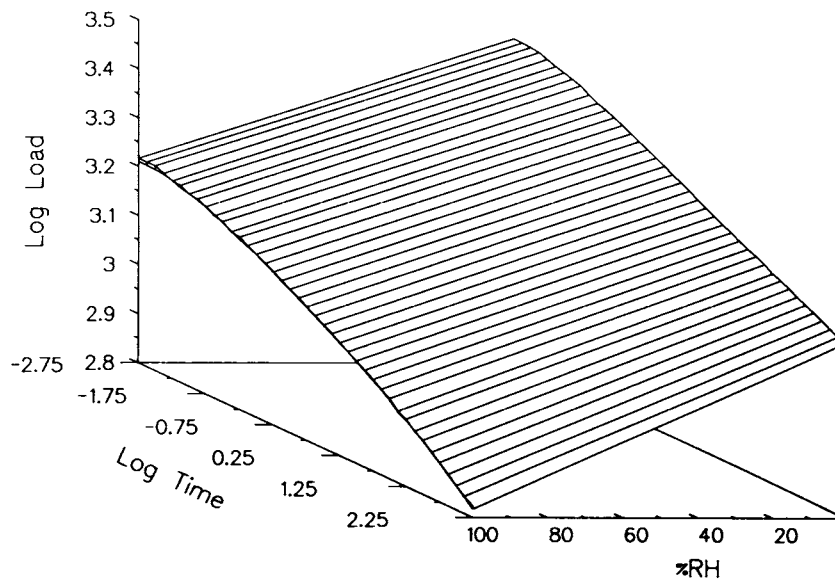


Figure 13 Effect of relative humidity on foam 44-5 at 30°C (obtained at a 65% strain level and at 15% RH and 100% RH).

This difference is believed to result from water being able to more prominently influence the chain slippage of the hard segments of the LiCl foam, since the majority of its hard segments are not believed to be a part of the polyurea aggregate structures as in the case of foam 44-0. In other words, the hard segments of foam 44-5 are thought to be more accessible by water in comparison to foam 44-0. Another factor is that water may absorb faster and to

a greater extent within foam 44-5, due to the presence of the hygroscopic LiCl. While the ratio of the LiCl molecules to the other key potential sites, i.e., urea-urethane links is about 1 to 45, it is still feasible that the presence of LiCl greatly increase the local water adsorption. In addition, since the LiCl molecules are thought to serve as an HB plasticizer, the additional absorption of water molecules will likely cause further relaxation.

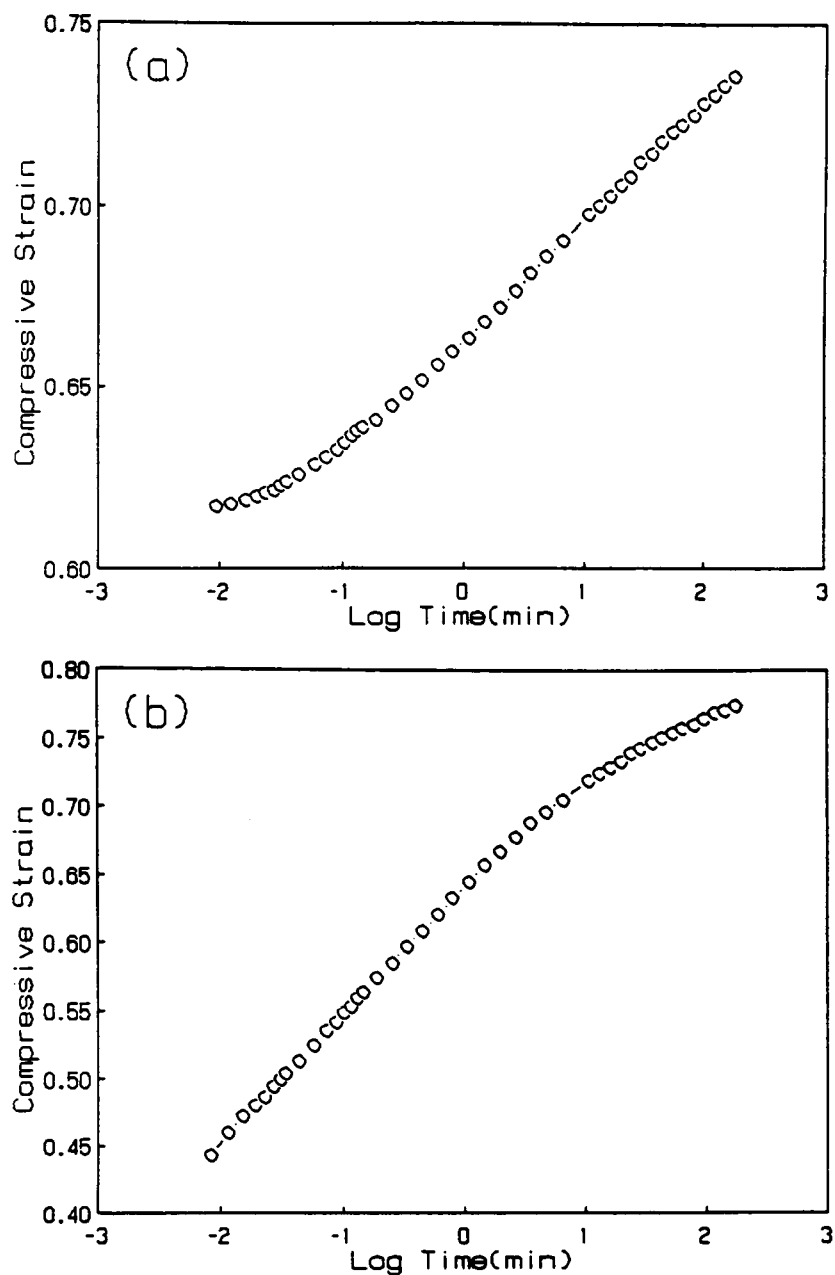


Figure 14 Compressive creep behavior for foams (a) 44-0 and (b) 44-5 (load applied to both foams was 2750 g).

Before discussing the compressive creep behavior, it is important to point out that the effects of temperature and relative humidity on the load relaxation behavior for foam 44-0 are comparable to that of a previously studied foam of the same hard segment content.⁸ However, the load decay rate and percent load decay values are slightly higher in the case of foam 44-0. This slight increase was somewhat expected since foam 44-0 has an isocyanate index of 100 and that of the other foam has a 110 index. This difference in isocyanate index would suggest a more complete network is formed in the higher index foam and indeed the viscoelastic results support this.

Effect of LiCl on Compression Creep Behavior

The compressive creep behavior is shown in Figures 14 (a) and (b) in the form of compressive strain versus $\log t$ for foams 44-0 and 44-5. As shown, the LiCl foam creeps immediately upon reaching an initial strain level whereas the control foam, 44-0, shows a brief induction period and then begins to creep like the behavior displayed for the set of slabstock foams whose behavior we recently reported.⁹ In addition, the behavior for foam 44-0 is rather linear for linear strain versus $\log t$ after the short induction period. On the other hand, foam 44-5 exhibits linear behavior for approximately the first 10 min [$\log \text{time (min)} = 1$] and then begins to creep at a slower rate.

This difference in behavior is believed to be related to the higher content of intact window material in foam 44-5 in comparison to 44-0. In the case of 44-5, this additional intact window material is thought to promote creep to take place immediately. That is, this immediate response could be a result of windows continuing to rupture and/or be deformed after applying the constant load and reaching the initial strain level.

From the compressive creep behavior given in Figure 14 (a), the creep rate was determined for foam 44-0 in a similar manner reported in a previous publication by taking the slope of the *linear portion* of the curve. In the case of foam 44-5, an *estimate* for the creep rate was obtained by calculating the *change* in the strain over the change in $\log t$, for nearly the 3-h period, since *linear behavior is not observed over the 3-h testing period*. The creep rates were obtained for both foams at the conditions of 30°C–15% RH for similar constant loads and at 30°C–100% RH for slightly higher constant loads for foam 44-0.

At 30°C–15% RH, the effect of LiCl on the compressive creep behavior is shown in Figure 15 by comparing the plots of creep rate as a function of initial strain level for foams 44-0 to 44-5. As one would predict, the creep rate is higher at a given initial strain level for equal constant loads applied to the foams for the LiCl foam, 44-5. This behavior is, of course, consistent with those results presented

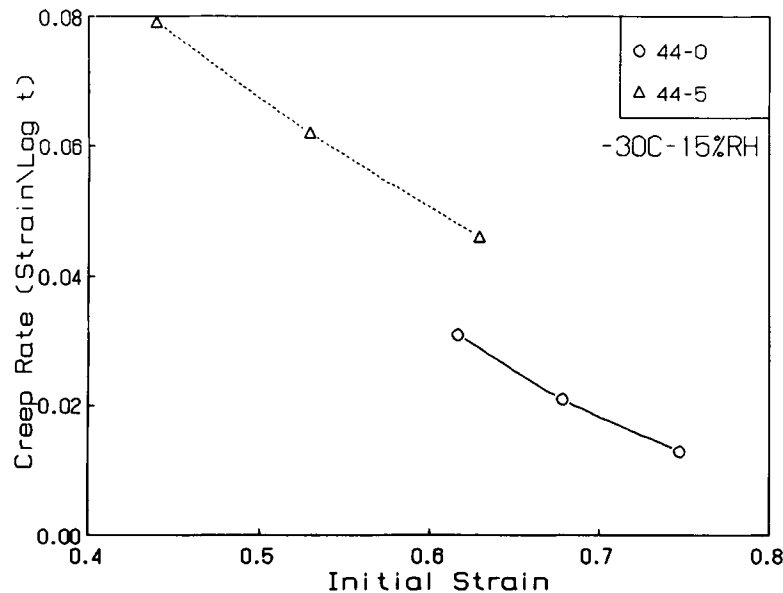


Figure 15 Effect of lithium chloride on compression creep behavior at 30°C–15% RH (similar loads applied to both foams).

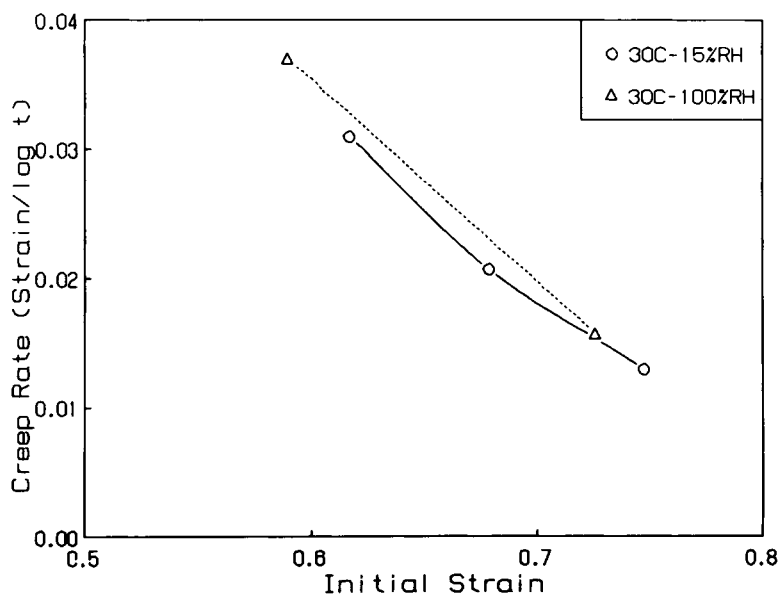


Figure 16 Compressive creep behavior for foam 44-0 at 30°C.

earlier for the tensile stress relaxation and compression load relaxation studies. The higher creep rates for foam 44-5 are thought to be mostly due to the differences in the solid morphology caused by the addition of LiCl to the formulation of foam 44-5. Again these differences in the solid structure are believed to be related to the presence of smaller and/or less of the urea aggregates structures in LiCl foam.

By reducing the size or amount of these structures, greater mobility of the hard segments is expected, which will allow for further creep in the solid portion of the foams. Another factor that is possibly effecting the creep in the solid portion of the foam are the LiCl moieties acting as a HB plasticizer. As mentioned earlier, such plasticization would cause additional local chain slippage within the hard do-

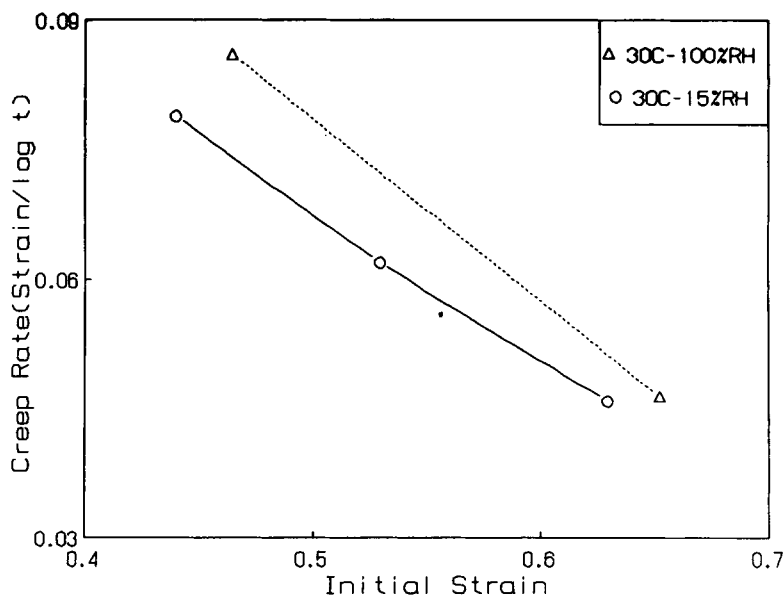


Figure 17 Compressive creep behavior for foam 44-5 at 30°C.

mains, which, of course, will lead to more creep. One other factor that may contribute to the difference in the creep rates for these foams is the greater amount of intact window material in the LiCl foam versus that of its control. As discussed above, this factor is thought to have a greater influence on the creep rate during the early stages of compressive creep in foam 44-5.

The effect of LiCl on increasing relative humidity at 30°C can be seen by comparing the compression creep behavior for foams 44-0 and 44-5 in Figures 16 and 17 respectively. This comparison demonstrates that foam 44-5 is affected more significantly by increasing relative humidity than that of foam 44-0. Again, this result is consistent with the results presented earlier for the compression load relaxation behavior at 30°C. It also indicates that water is influencing the creep behavior at 30°C more in the LiCl foam likely due to the greater accessibility to the hard segments.

CONCLUDING REMARKS

In conclusion, the addition of LiCl to the formulation does result in interesting changes in the solid morphology of flexible slabstock polyurethane foam. Most of these changes are believed to be related to the dispersion of the urea aggregate hard domains, which are believed to be present in the control foam, 44-0. Based on the different morphological techniques utilized for this study, it appears that for the LiCl containing foams, there is formation of smaller aggregates and/or the hard segments are being more dispersed as single or smaller units within the network. In addition, these results indicate that there is an increase in phase mixing of the hard and soft units due to the addition of LiCl.

Changes are not only detected in the solid morphology, but also in the cellular textures upon addition of LiCl to the formulation of foam 44-5. The key observation from SEM is that there is more intact window material in the LiCl foam (44-5) in comparison to its control (44-0). Also, the greater amount of intact window material in 44-5 is thought to be due to promotion of the gelling reaction by adding LiCl to the formulation and/or LiCl is acting like a surfactant by solubilizing the urea-based hard segments.

The above changes in the solid morphology as well as the cellular textures do have a rather significant effect on the viscoelastic properties. A significant increase in the viscoelastic decay is observed

for the stress relaxation in both tension and compression load relaxation. Furthermore, the compressive creep rate for the LiCl foams is greater than the control foam. This increase is attributed to the greater mobility or plasticization of the hard segments. In addition, it appears that the LiCl molecules are acting as a HB plasticizer and thus causing additional local chain slippage. In some instances, the intact window material is also thought to contribute to this increase—mainly for the properties measured in compression. Temperature has a more significant effect on the load relaxation behavior of the LiCl foam, 44-5, in comparison to its control. This greater effect is believed to be related to more phase mixing as well as more hydrogen bond disruption in foam 44-5. Relative humidity at 30°C also has a greater effect on the relaxation and creep behavior in the compression mode for foam 44-5 in comparison to foam 44-0. This behavior is attributed to the hard segments of foam 44-5 being more accessible to moisture than that of foam 44-0. In addition, it is speculated that the HB plasticizer, i.e., LiCl, is allowing for additional absorption of water molecules.

Overall, the addition of the LiCl to the formulation does result in altering the solid morphology rather significantly and likewise the viscoelastic behavior. These apparent changes in the solid morphology are unique but do result in generally undesirable viscoelastic properties. However, the structural changes caused by the addition of LiCl are a step in the right direction to making softer flexible polyurethane foams without having to use physical blowing agents, which are believed to be harmful to our environment.

Two of us (G.L.W. and JCM) would like to thank Dow Chemical for financial support of this research. We would also like to thank Gene Parks of Dow Chemical for supplying the well-defined samples and Gene Young for the TEM sample preparation.

REFERENCES

1. S. C. Stinson, *Chemical and Engineering News*, Oct. 24, 1988, p. 23.
2. *Proceedings (Abstracts) of the SPI Polyurethane Division Conference* (1990).
3. *Rubber and Plastics News*, October, 15, 1990.
4. J. P. Armistead, G. L. Wilkes, and R. B. Turner, *J. Appl. Polym. Sci.*, **35**, 601 (1988).

5. S. Yoshikawa and D. J. Lyman, *J. Polym. Sci. Polym. Lett. Ed.*, **18**, 411 (1980).
6. M. Planar and L. F. Beste, *Macromolecules*, **10**, 1401 (1977).
7. W. R. Krigbaum, F. Salaris, and A. Ciferri, *J. Polym. Sci. Polym. Lett. Ed.*, **17**, 601 (1979).
8. J. C. Moreland, G. L. Wilkes, and R. B. Turner, *J. Appl. Polym. Sci.*, to appear.
9. J. C. Moreland, G. L. Wilkes, and R. B. Turner, *J. App. Polym. Sci.*, to appear.
10. G. Rossmly, H. J. Kollmeier, W. Lidy, H. Schator, and M. Wiemann, *J. Cell. Plastics*, **17**(6), 319 (1981).
11. G. Rossmly, W. Lidy, H. Schator, M. Wiemann, and H. J. Kollmeier, *J. Cell. Plastics*, **13**(1), 26 (1977).
12. F. E. Bailey and F. E. Critchfield, *J. Cell Plastics*, **17**, 333 (1981).
13. G. Hauptman, K. H. Dorner, J. Hocker, and G. Pfister, *Proceedings of the 5th International SPI Conference*, 1980.
14. N. C. Hilyard, *Mechanics of Cellular Solids*, Applied Sci. Publishers, New Jersey, 1980.
15. M. F. Ashby, *Mettalurgical Trans*, **14A**, 1755 (1983).

Received January 12, 1993

Accepted October 18, 1993