Viscoelastic Behavior of Flexible Slabstock Polyurethane Foams as a Function of Temperature and Relative Humidity. II. Compressive Creep Behavior

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SYNOPSIS

The compression creep behavior was monitored at constant temperature and/or relative humidity for two slabstock foams with different hard-segment content. The tests were performed by applying a constant load (free falling weight) and then monitoring the strain as a function of time over a 3-h time period. A near linear relationship is obtained for linear strain versus log time after a short induction period for both foams and at most conditions studied (except at temperatures near and above 125°C). The slope of this relationship or the initial creep rate is dependent on the initial strain level, especially in the range of 10–60% deformation. This dependence is believed to be related to the cellular struts buckling within this range of strain. At deformations greater than 60% and less than 10%, the solid portion of the foam is thought to control the compressive creep behavior in contrast to the cellular texture. Increasing relative humidity does cause a greater amount of creep to occur and is believed to be a result of water acting as a plasticizer. For low humidities increasing the temperature from 30 to 85°C, a decrease in the rate of creep is observed at a 65% initial deformation. At 125°C, an increase in the creep rate is seen and is believed to be related to chemical as well as additional structural changes taking place in the solid portion of the foams. The creep rate is higher for the higher hard-segment foam (34 wt %) than that of the lower (21 wt %) at all of the conditions studied and for the same initial deformation level. This difference is principally attributed to the greater amount of hydrogen bonds available for disruption in the higher hard-segment foam.

INTRODUCTION

The time dependence of the recoverability of a foam's shape and its load deformation behavior after it has been compressed or fatigued are two important properties of flexible slabstock foams. Both of these properties can be characterized by evaluating the viscoelastic behavior of the foam. In part I of our two-article series on the viscoelastic behavior, the time dependence of the stress relaxation behavior in tension and compression was presented for a series of variable hard-segment slabstock foams.[1] In continuing this understanding of the viscoelastic behavior, changes that occur in the foam's shape (creep) while the foam is under a constant load have been evaluated under controlled conditions of temperature and relative humidity. This change has been characterized by measuring the loss in thickness over time, that is, the compressive creep behavior on the same series of foams studied in the preceding article that evaluated the relaxation behavior in compression and tension.

Compressive creep measurements on flexible foams have been reported in the literature by Campbell as well as Terry.[2,3] Both of these authors reported observing near linear behavior in the form of strain versus log time while a given foam was under a constant load. Campbell also showed that

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the initial rate of creep was nonlinearly dependent on the initial level of compression (i.e., initial strain level). In addition, the creep rate was found to go through a maximum with initial strain at an initial displacement of 20–30% deformation. This change in the creep rate was attributed to the struts buckling and was confirmed through microscopy studies. The buckling effect appeared to begin after 10% initial strain and become less influential after 60% due to the fact that all struts displayed some buckling at this level of strain. Campbell measured the effects of some formulation variables on the creep behavior at the higher strain levels where creep was rather independent of the strain or the cellular texture of the foam. He reported that the density had little effect on the creep rate, but that the increasing water content (2.2–2.6 pph polyol) in a set of two foams resulted in an increase in the creep rate.[2]

In another related recent study, Huang and Gibson reported on the creep behavior for a set of rigid polyurethane foams under constant shear at stresses less than 50% of the yield strength.[4] The authors of this study developed model equations to predict the shear creep behavior for their foams. These models were based on a cubic cellular structure consisting of solid cellular walls containing linear viscoelastic material. Their experimental results did fit their models quite well for creep strain during loading as well as during unloading over rather long time periods. Huang and Gibson also reported that the creep behavior in shear was independent of density as well as constant stress at stress levels less than half the yield strength of the foam.[4]

In the report presented here, the effects of temperature and relative humidity on the compressive creep behavior of two flexible slabstock foams varying in hard-segment content will be presented. In addition, comparisons of these two variables on the creep behavior are made where possible to those of our previous work for the tensile stress relaxation and compression load relaxation behavior of these same foams.

Experimental

The foams used in this work were the lowest (21 wt %) and the highest (34 wt %) hard-segment content materials of the four slabstock foams described in earlier studies.[5–7] The formulation components used to produce these foams were an 80 : 20 mixture of TDI, 3000 MW polypropylene oxide-glycerine initiated polyol, water, silicone surfactant, as well as tin and amine catalysts. The two foams used in this work differ in that foam F1 was produced with 2 PPh polyol, whereas foam F4 was made with 5 PPh of water. The foams used in this study have been characterized by several morphological as well as structural techniques, and these results can be found in references 5–7 for the interested reader.

The experimental apparatus as well as the procedures for the compressive creep test were designed after a similar study by Campbell.[2] The experimental apparatus utilized for measuring the compression creep behavior under control conditions is shown in schematic form in Figure 1. The apparatus consists of a twin shaft web assembly with a moving carriage (see [1] in Fig. 1) that was manufactured by Thompson Inc. This piece served as the base for the compression creep device as well as to minimize friction. As shown schematically in Figure 1, the rest of the creep device was machined to fit with this assembly. Some of the other features are the environmental chamber (see [3] in Fig. 1) which was made by Russells Technical Products. This same chamber was also utilized for the compression load relaxation studies.[1] Also shown in Figure 1 is a linear voltage displacement transducer [LVDT (see [4] in Fig. 1)] and its capillary (see [5] in Fig. 1) which is attached to the moving carriage (the capillary slides freely inside the outer housing of the LVDT). The LVDT served to detect the movement

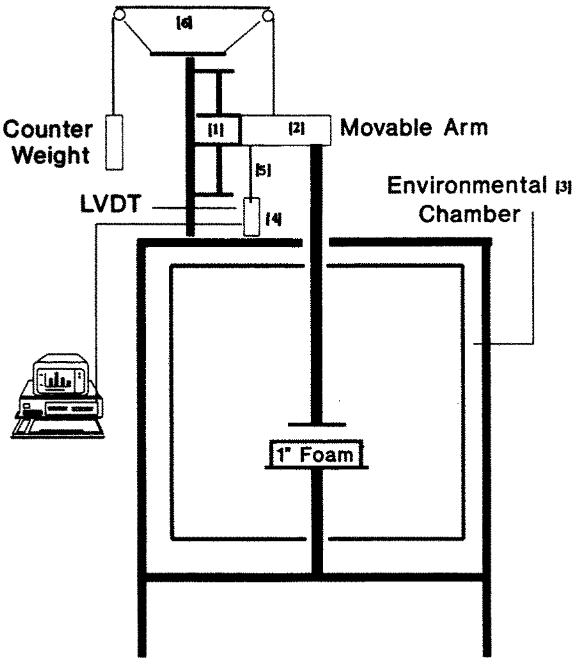

Figure 1 Schematic of compression creep device.

of the carriage and likewise the creep in the foam. In addition, the voltage signal from the LVDT was converted to a digital readout on the computer via an analog to digital (A/D) card in the computer. Through the use of a calibration curve, the digital signal was converted into compressive strain where it was then stored on computer disk. Finally, the constant load which was applied on the foam was controlled by the pulley system (see [6] in Fig. 1). The pulley system was incorporated into the design in order to be able to offset the weight of the carriage as well as the arm extension and thus enables one to apply loads as low as 100 g and as high as 5000 g.

A typical experiment involved placing a 4″ × 4″ foam sample of known thickness onto the 5″ × 5″ plate (see Fig. 1). The indenter was then lowered and held in place so that it was just touching the top of the foam. Meanwhile the desired testing conditions were approached and after maintaining the conditions for 30–45 min, a constant load was manually applied to the foam by releasing the extension arm into a freefalling motion. Upon releasing the arm, the compressive strain as a function of time was monitored via computer over a 3-h time period. The loads that were applied varied from 750 g to 3.5 kg. The testing conditions were carried out at low humidity (0–15%) at 30, 85, and 125°C and at high humidity (95–100%) at 30 and 85°C. In most cases, only one sample for a given foam, load, and testing condition was normally used, except in a few instances in order to obtain a percent error in the measurements. [This spread in the measured creep rates (defined below) varied no more than 5%.]

RESULTS AND DISCUSSION

Before discussing the above effects of specific variables on the creep behavior, a general introduction is given for the behavior of compressive strain with time and the approach utilized in evaluating this behavior. In Figure 2, the compressive creep behavior is given for F1 and F4 in the form of compressive strain versus log time after reaching the initial penetration level. This particular plotting scheme is also the same one used by Campbell as well as by Terry for their compressive creep studies on flexible foams.[2,3] As shown in Figure 2, the behavior is fairly linear for *linear* strain versus *log* time after a short induction period [up to −1.0 in log time (min)]. During this short induction period, there is very little change in the strain which has been observed for both foams F1 and F4 as well as at all testing conditions. Even though this period is greater for F1 than that of F4 in Figure 2, the length of the induction period does not appear to be dependent on hard segment content or the *conditions at which the test were conducted under*. In general, this period where very little change in the compressive strain is observed, is on the order of 6 s [ca. −1.0 in log time (min)] after reaching the initial penetration level. Terry has also reported observing a similar induction period for a noncrushed sample in his creep study, and, furthermore, an extension of this period upon crushing the foams before testing.[3] Though, Terry offered no explanation for this period and the extension of it, it appears at least for his results that this induction period may be a function of fatigue loss. It is also possible that the elastic response of the foam does provide some initial resistance to creep. Thus, to be consistent during this investigation, the foams were not preflexed before measuring the creep behavior.

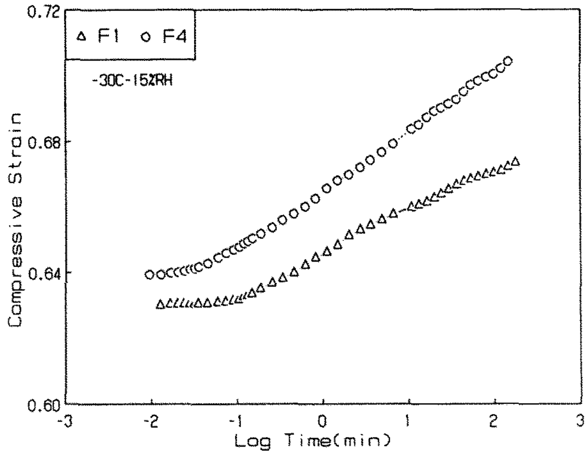

Figure 2 Compressive strain-log time creep behavior for foams F1(a) and F4(b) (load applied to F1 was 2.7 kg and that of F4 was 2.5 kg).

In evaluating the results given in Figure 2, the slope of the linear portion (data after the induction period) of the curve was measured by linear least squares. This slope represents the initial rate of creep at a given load. As discussed in the introduction, Campbell showed that the compressive creep behavior was dependent on the initial penetration level, that is, the initial compressive strain.[2] A similar dependency on the compressive creep behavior for foams F1 and F4 is discussed below.

Dependence on Initial Strain Level

In utilizing the above method of evaluation of the strain-log time creep behavior, the dependence of the initial creep rate (Δstrain/Δlog *t*) *on the initial* strain level was obtained and is shown in Figure 3 and 4 for F1 and F4, respectively, at 30°C–15% RH. For both F1 and F4, this behavior goes through a maximum near an initial compressive level of 40%. Campbell also showed a maximum at a slightly lower compressive strain level for flexible HR foams. In his investigation, Campbell attributed the dependence of the creep rate on the initial compressive strain to the buckling of the struts.[2] This phenomenon also appears to be governing the behavior shown in Figures 3 and 4 for the creep rate as a function of initial strain level (discussed in more detail shortly). As shown elsewhere for these foams, buckling of the struts is thought to occur at deformation levels beginning at 10% and on up to levels near 60–65%.[1,7] Indeed, the changes in the creep rate at initial deformations greater than 60% are comparable to the creep rate at much lower initial deformation levels (near 10–20%) as shown in Figures 3 and 4 for foams F1 and F4, respectively. Thus, as Campbell also suggested, it is thought that in these regions, the creep behavior of the solid material of the foams can be evaluated rather independently of the cellular structure.[2]

Before showing how the creep behavior is affected by the different variables at initial deformation levels near 65%, further discussion of the buckling effect and its relation to compressive creep in these materials is given. Campbell qualitatively described the buckling phenomena of the struts in flexible foams in terms of long-column buckling as shown schematically in Figure 5(A). In looking at Figure 5, as the column or likewise the struts are loaded from both ends and enough strain energy is built up, the column or similarly the strut will buckle spontaneously. In contrast, in the study mentioned earlier by Huang and Gibson, the strain levels utilized were much less than the region where the struts are believed to buckle, and thus the creep behavior was found to be independent of the load or stress applied.[4] The buckling phenomenon, however, is believed to take place after the force on the struts is greater than a critical value of force which is not only dependent on their length but clearly also on the solid wall material.[9] In addition, the localized strain on the buckled structure is much greater than before the column buckles. Thus, as Campbell sug-

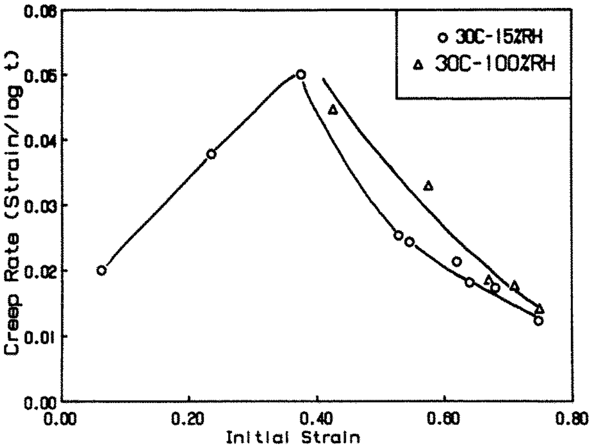

Figure 4 Effect of initial strain level on compressive creep behavior for foam F4 at 30°C (creep rates based on 3-h time period).

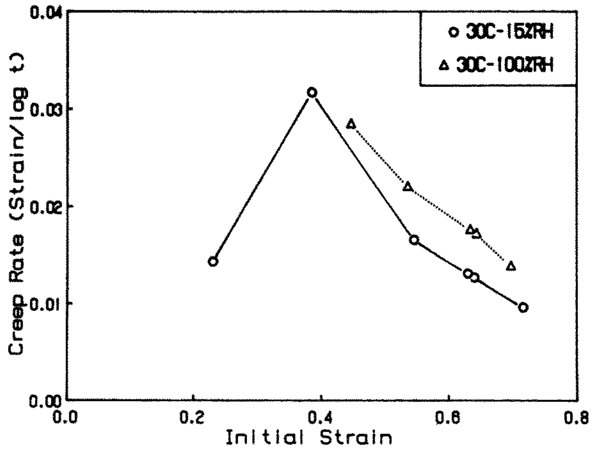

Figure 3 Effect of initial strain level on compressive creep behavior for foam F1 at 30°C (creep rates based on 3-h time period).

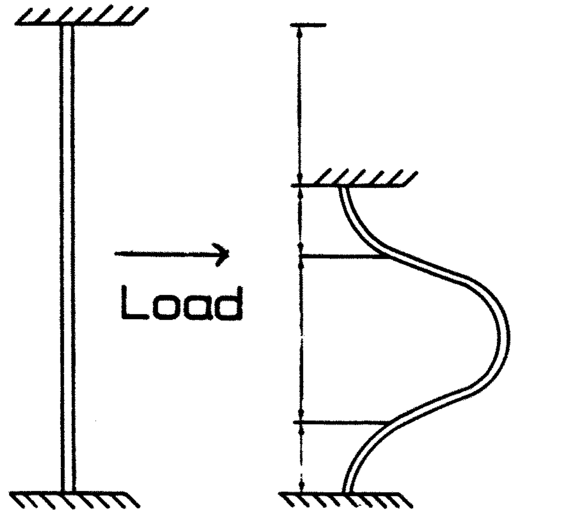

Figure 5 Schematic of long-column buckling undergoing vertical loading.

gested, this increase in *localized strain* brings about a sharp increase in the creep rate as shown earlier in Figures 3 and 4 beginning with initial deformation levels near 10–20%.[2] Thereafter, the rate of creep continues to increase due to an increase in the number of struts that undergo buckling. However, at initial deformation levels greater than 40%, the number of struts that undergo buckling during creep begins to decrease since the level of strain is approaching a point where densification begins to take place.

Effect of Relative Humidity on Foams F1 and F4

The effect of relative humidity at 30°C on the creep behavior for initial compression levels between ca. 40–75% is shown in Figures 3 and 4, for foams F1 and F4. Similar plots are given in Figures 6 and 7 but where the temperature was 85°C and the RH values were either 2% or 95%. At both temperatures and for both foams, increasing relative humidity does result in an increase in the creep rate. At 30°C and for a 65% initial compression level, the change in the creep rate due to increasing relative humidity is more significant for F1 than for F4 (note scale difference between the plots for F1 versus F4 in Figures 3 and 4). The values for the change in the creep rate with increasing humidity are 30% and 18% for foams F1 and F4, respectively. At 85°C, this change in the rate of creep, due to relative humidity in the rate of creep, however, appears to be similar and greater than at 30°C for both foams F1 (35%) and F4 (34%). Before, discussing the results further, it also important to note here that the loads applied at the higher relative humidities were lower (by ca. 15%) for a given initial strain. Although one is likely

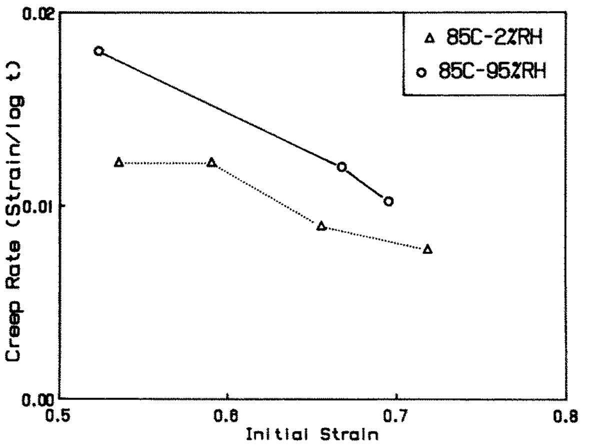

Figure 6 Effect of initial strain level on compressive creep behavior for foam F1 at 85°C (creep rates based on 3-h time period).

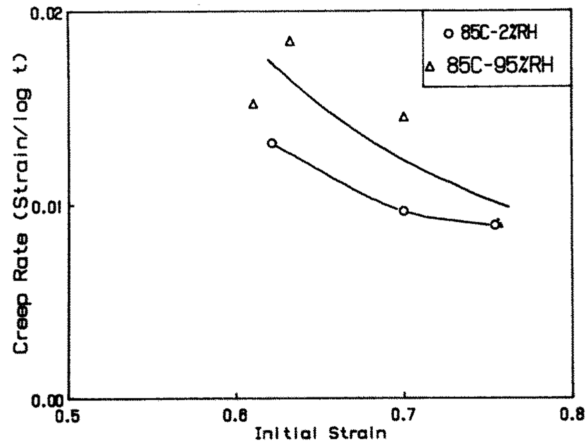

Figure 7 Effect of initial strain level on compressive creep behavior for foam F4 at 85°C (creep rates based on 3-h time period).

to predict that the creep rate will be less for a smaller load, it appears, however, that this difference in loads applied at low and high relative humidity is not influencing the creep rate significantly and that it is mostly dependent on the initial strain level. Thus, in the discussion to follow it will be assumed that the differences in the creep rates at a given temperature are principally due to relative humidity and are not affected to any great extent by the differences in the loads applied.

For both foams, it is expected that water will act as a plasticizer and thus allow for further chain slippage to occur which will lead to increased amounts of creep. In addition, the change in the rate of creep for foams F1 and F4 due to increasing relative humidity, indicates that the effect of water on the creep behavior for F1 is greater than that of F4 at 30°C, and, furthermore, that water apparently interacts more extensively with F1 than F4. Also, the increase that is observed in the change in the creep rate from 30 to 85°C demonstrates that the affinity of water increases with temperature for foam F4 and only changes slightly for that of F1. As suggested in the preceding publication for the load and tensile relaxation studies, this significant increase in the change of the creep rate for F4 is believed to be related to the greater ability of water to enter into the hard domains due to the weakening of the hydrogen bonds at the higher temperatures. Overall, the above trends are quite similar to the results obtained for the effects of humidity at 30 and 85°C for the load relaxation results presented in the previous paper. The one exception is that the change in the creep rate at 85°C is about the same for foams F1 and F4, whereas the change in the compression relaxation load decay rate was greater for F4.[1] This difference may be related to the higher scatter in the results obtained for the compressive creep behavior at 85–95% RH for F4 as shown in Figure 7.

Effects of Temperature on Creep Rate for Foams F1 and F4

The effects of temperature on the creep rate have been measured in the range of 30–125°C for foams F1 and F4. An example of the creep behavior for F1 and F4 at 125°C and dry conditions is shown in Figure 8. After the short induction period, the behavior exhibited in Figure 8 for both foams *is clearly much more nonlinear, unlike the behavior at 30 and 85°C,* and furthermore, similar nonlinear behavior has also been observed at other initial compression levels at the higher temperature. The nonlinearity observed in Figure 8 does indicate that additional causes for creep are occurring at the higher temperatures. These additional causes at 125°C are believed to take place for similar reasons discussed in the previous paper on the compression load relaxation and tensile relaxation studies of these same foams, that is, some chain scission will occur with time at the urea and urethane links promoting free NCO groups as noted by FTIR. More discussion on these causes will be given after considering the overall effect of temperature on the creep behavior for foams F1 and F4. The rate of creep as a function of initial compression strain level at the different temperatures is shown in Figures 9 and 10 for foams F1 and F4, respectively. In determining the creep rates at 125°C, the rate was *estimated by calculating the change in strain over the log time period (3 h)* in which this change took place. This simplified method was used *since the behavior for strain as a function log time is nonlinear at 125°C* as shown in Figure 8. Clearly, caution must be taken in applying such creep rate data to predicting longer or shorter time period creep behavior. From Figures 9 and 10, the effect of temperature on the creep behavior was determined at a 65% *initial* compression level and is displayed in Figure 11. As shown, the thermal dependence on the creep rate interestingly exhibits a decrease in the amount of creep from 30 to 85°C and increases from 85 to 125°C for both foams F1 and F4. The decrease in the rate of creep at 85°C is also thought to be related to similar decreases observed in the rate of load relaxation in compression

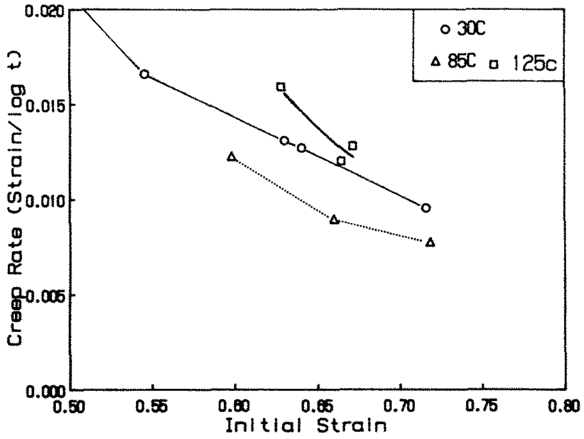

Figure 9 Effect of initial strain level on compressive creep behavior for foam F1 at temperatures ranging from 30 to 125°C.

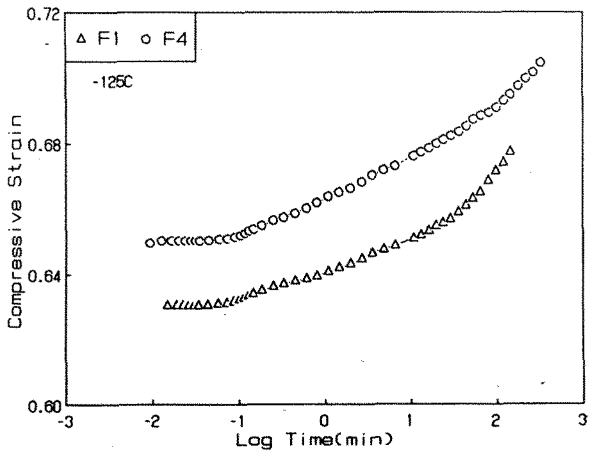

Figure 8 Creep behavior for foams F1 and F4 at 125°C (load applied to F1 was 3.5 kg and that of F4 was 2.1 kg).

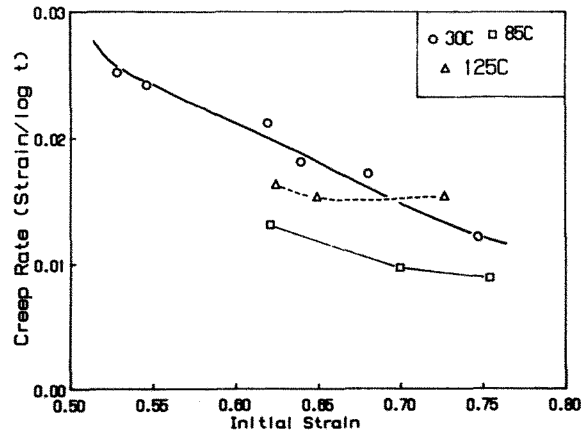

Figure 10 Effect of initial strain level on compressive creep behavior for foam F4 at temperatures ranging from 30 to 125°C.

as well as the stress relaxation in tension over a similar temperature range as discussed in our earlier paper.[1] That is, it is believed that the compressive creep behavior or the viscoelastic nature of these foams is being accelerated by increasing the temperature (up to 85°C). By accelerating the creep behavior, we mean that more creep is essentially taking place on a shorter time scale and can occur in the induction period up to 85°C. Therefore, it appears that as temperature is increased, more creep is taking place before the strain level is reached that is used to establish the beginning of the linear region. It is also important to note here that the loads applied to foam F4 at 30°C were slightly higher (ca. 7%) than at 85°C for a given initial strain level. On the other hand, the load applied to foam F1 at 30°C were approximately 7% lower than at 85°C. Although the smaller load applied to F4 at 85°C may contribute to its lower creep rate, this does not appear to be a factor for the observed creep rate at 85°C for F1. As suggested earlier, when considering the effects of relative humidity on the creep behavior, a small difference in the loads applied at two different conditions does not significantly affect the comparison of the creep rates at the two conditions. This suggestion also seems applicable to the variable temperature results.

At the higher temperature of 125°C, larger amounts of creep are expected to occur based on additional changes detected in the chemical nature of the network structure by the FTIR thermal studies as discussed in part I.[1] In the case of F1 at 125°C, the estimated creep rate or the amount of creep over 3 h at the 65% initial level is the highest of the three

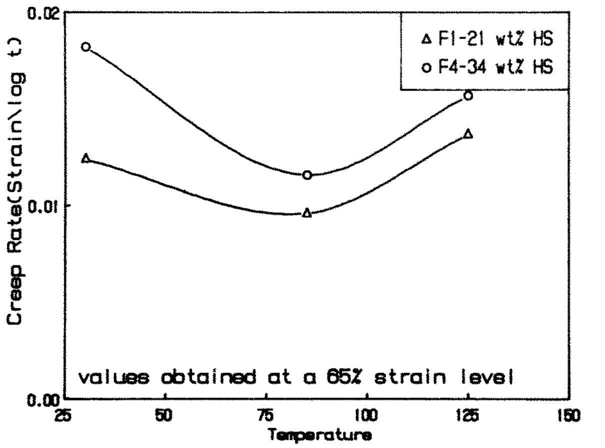

Figure 11 Effect of temperature on compressive creep behavior for foams F1 and F4. The relative humidities in all cases were low for 30 and 85°C and essentially at zero for the upper temperature of 125°C.

temperatures. This observation is consistent with the earlier load relaxation results reported for F1, and, furthermore, implies that the structural changes that have been indicated by the FTIR thermal studies are also affecting the compressive creep behavior for this foam. That is, further hydrogen bond disruption and possible chain scission in the urea and urethane linkages are responsible. On the other hand, the estimated creep rate for F4 at 125°C is higher than the creep rate 85°C, but, as somewhat unexpected, it is lower than the rate at 30°C (see Fig. 11). One possible contribution to this difference in creep rates at 30°C and 125°C for F4, is a 15% lower load is applied at 125°C to achieve the same initial deformation level. Again, this contribution is not believed to be a major factor, but it cannot be overlooked. It is also important to note that this difference in creep behavior at 30 and 125°C for Foam F4 is not observed at the higher strain levels as shown in Figure 10, that is, at initial strain levels greater than 70%.

Further insight can be gained by comparing the effect of temperature on the creep behavior for the two foams F1 and F4. First it is important to note here that over the full temperature range studied, the creep rate is greater for the higher hard-segment foam, F4. This behavior is principally attributed to the greater amount of hydrogen bonds available for disruption in F4 in comparison to the lower hard-segment foam, F1. By disrupting and reforming the hydrogen bond, local chain slippage is facilitated which will lead to a decrease in the amount of load that can be supported. However, since the load applied to the foam is constant, the foam creeps (compresses) to higher strain levels where the load can be supported. Second, the effect of temperature on creep is greater on F4 than on F1 from 30 to 85°C. This result is consistent with the earlier load decay values reported from the compression load relaxation studies for foams F1 and F4 in part I.[1] Finally, the amount of creep is higher at 125°C for F4 than for F1, but the increase in the effect of temperature from 85 to 125°C is greater for F1 than F4. As shown in the previous paper for the tensile and compression relaxation studies, temperature is believed to have a more significant effect on the viscoelastic behavior of F1 at temperatures above 100°C. This conclusion is supported by the FTIR-thermal studies on the plaques of these foams, that is, the FTIR-thermal studies indicated that the hydrogen bond disruption is most significant at the higher temperatures and there is believed to be some chain scission taking place within the urethane and urea linkages. Both of these structural changes are believed to have a more significant effect on the network structure of F1 than in the case of F4 due to lower structural order in foam F1 and its lower hydrogen bonding content thereby accenting its thermal response at higher temperatures.

CONCLUSIONS

After a short induction period (ca. 6 s), a near linear relationship between linear strain and log time is observed over a 3-h time period for the compressive creep behavior of flexible slabstock foams at most conditions. The slope of this relationship or the initial creep rate is dependent on the initial strain level, especially for initial compressions of 10–60%. Within this range, the buckling of the struts is believed to govern the compressive creep behavior of flexible slabstock foams. This belief is consistent with the results reported by Campbell on the compressive creep behavior for HR flexible foams as well as the microscopy work shown in his study. At initial compression levels greater than 60% and less than 10%, the solid portion of the foam is believed to control the compressive creep behavior in flexible foams. This conclusion is based on the fact that there is very little change in the level of buckling of the struts that is thought to occur outside of these strain regions for flexible polyurethane foams—at least for this short time period of 3 h.

At an initial compression of 65%, relative humidity and temperature affect the compressive creep behavior of foams F1 and F4 as expected. These effects are comparable to that on the compression and tensile relaxation behavior discussed in part I.[1] Increasing relative humidity does cause a greater amount of creep to take place and is believed to be a result of water acting as a plasticizer. Relative humidity also has a greater effect on the rate of creep at the higher temperature, especially in the higher hard-segment foam, F4. Within the range of 30–85°C, a decrease in the rate of creep is believed to take place possibly due to some increase in the amount of flow that actually occurs during the induction period. At 125°C, an increase in the creep rate is observed and is attributed to chemical as well as additional structural changes taking place in the solid portion of the foams. Such additional changes are believed to be due to chain scission in the urea and urethane linkages.

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