Viscoelastic recovery behavior and imperfection in reactive polymer network of viscoelastic polyurethane memory foams

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ABSTRACT

The relationship between polymer network parameters and speed of viscoelastic (VE) recovery was studied for viscoelastic polyurethane foams. Reactive network simulation method was developed which use relative reactivity parameters derived from literature and from experiment. Relative reactivity of butylene oxide (BO) based secondary hydroxyl groups were estimated by comparing simulation results with experimentally derived sol fraction. From the analysis, it is found that BO and propylene oxide (PO) hydroxyl end groups have relative reactivity to isocyanates that are not very different. We also find that the isocyanate conversion is lower only about 91–96%, even though the isocyanates are the limiting factor (i.e. molar ratio NCO:OH = 0.9). It is also found that a foam with faster VE recovery is predicted to have smaller elastically effective chain (EEC) mass fraction (i.e. more imperfect polymer network) and higher sol fraction. Surprisingly, the same foam after solvent extraction was found to have slower VE recovery. It is concluded for foam systems with T_g near ambient temperature, that while lower EEC fraction can lead to slower VE recovery, a large amount of sol fraction in the foam system can cause faster VE recovery via plasticization of the polyurethane matrix.

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1. Introduction

Various shape memory polymer schemes are possible, of which thermally induced recovery of shape is the most commonly used strategy [1,2]. One of the most commonly used shape memory materials is viscoelastic memory foams, which in part originates from the "temper foam" by NASA Ames research programs [3], and which have been made widely available in bedding mattress applications. Stress-strain behavior as a function of temperature has been modeled previously [4], which is important since it is desirable for the foam to soften at around or below skin temperature (about 33 °C at torso). Shape memory is important because of the compression packaging that is increasingly used [5], so that when a foam mattress is unpacked and brought to room temperature, the mattress shape is recovered in less than an hour. Much of the design criteria for polyurethane (PU) memory foam in mattress applications differs from the more elastic "conventional" flexible polyurethane foams, even though its morphology is phase separated into hard and soft domains, much like the "conventional"

flexible foams [6]. Unlike "conventional" foams where the urea hard segment length averages about 4–6 urea units long, viscoelastic memory foam formulations result in urea hard segment length of about 2 urea units or less on average [7]. A comprehensive recent literature on segmented polyurethanes is available by Yilgor et al. [8] This relatively short hard segment means that, despite the phase separated morphology, a large fraction of the hard segment chains (especially those of 1 urea unit in length) would be soluble in the polyether-rich soft domain [9], which can partly contribute to a higher T_g and thus a memory effect. The TDI Supersoft VE foam technology was discovered a few years previously by Obi et al. [10,11] In particular, porous strut morphology, i.e. struts that resemble Swiss-cheese-like structure, were discovered [10,12]. It was found by Aou et al. that these Swiss-cheese-like structures in the struts are only observed in systems where a combination of TDI, an EO-rich polyol, and BO-4000 BO monol or high molecular weight polybutadiene were used [12]. Cases where any of these were absent were not observed to yield the porous struts.

There are many advantages that are immediately noticed with the TDI Supersoft VE foam. Some of the advantages include enhanced foam softness, superior air flow, superior compression set properties, and lower density. Some of the shortcomings are higher ball rebound resiliency, lower tear strength, and faster

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viscoelastic (VE) recovery, as observed both visually by a hand-squeeze like method and the often used VE recovery time test (which is conducted after an ASTM CFD load test). The faster VE recovery meant that it was on the faster end of the range seen for memory foams.

There is already understanding on the directions of formulation adjustment for ball rebound resiliency and tear strength. Ball rebound resiliency is dependent on tan-delta @ RT and T_g [10], and therefore on polyol EW and % NCO [12,13]. Tear strength is dependent in part on isocyanate index (i.e. the stoichiometric ratio between NCO functional group and OH functional group, times 100; water is counted as two hydroxyls). However, prior understanding of T_g-based control of VE recovery speed, while valid for a given set of formulation, is not a complete enough description. A more complete description of factors that affect VE recovery is needed to remedy the VE recovery time shortcomings of the Supersoft VE foam. Therefore, focus was placed on understanding the physical and chemical parameters that affect VE recovery behavior, with the goal of achieving broader understanding on how to manipulate this property for any type of VE foam systems (TDI vs. MDI, low vs. high density, high vs. low air flow, etc.).

Viscoelastic (VE) recovery time is a phenomenon that is perhaps the most recognizable characteristic of a viscoelastic foam. That characteristic gives VE foams the more commonly known name of "shape memory foam," i.e. the foam has some finite memory of the applied compression that persists for seconds after the compression is removed. It is useful to list what is known as fact regarding polyurethane VE foams as pertains to VE recovery time. By foam manufacturing practitioners, squeezing VE foams by hand (i.e. observing the "strain recovery") is the primary way for them to verify the slowness of VE recovery, their specification for stress VE recovery time tests notwithstanding. This report describes and discusses this difference between stress and strain recovery times, and why one method of recovery time measurement is superior to the other.

Examining details of features of the VE recovery process shows that it is not a simple process. Longer dwell time in the compressed state tends to lead to longer recovery time. The extent of applied compression affects the speed of recovery from compression, once the compressive stress is removed. That is, if the foam is compressed only a small amount (say, 25–50% of original dimension), then the foam recovers its original dimension very rapidly without much of a memory effect. Also, at low compression, the foam appears to deform and recover in a continuous manner. When the foam is compressed a lot more (say, 80–90%), then the recovery behavior slows down considerably for shape memory foams. In addition, the foam appears to deform continuously, but recovers in a way that some struts/windows appear to be sticking to each other and snap apart at some point during recovery, in a very discontinuous manner. This is consistent with reports by Krebs and Hubel [14,15], that adhesion between struts upon compression plays a role in VE recovery behavior. The high compression regime of deformation is what we are observing when we pinch the edges of a memory foam to see slow recovery, or squeezing/crushing the foam by hand to watch the slow recovery of the foam. In light of this fact, it is conceivable that mechanical properties that reflect mainly low deformation regime (such as DMA tan-delta) may not be predictive of VE recovery time.

There are influences coming from varying formulation components as well. First, VE foams with a high fraction of dangling chains in the polymer network, which can be achieved with lower isocyanate index or use of monofunctional polyether alcohols [16], would lead to greater viscoelastic dissipation [17], and thus slower VE recovery. Second, it is also known that even conventional foams can be made to recover slowly via a "pneumatic effect," if the air

flow (or air permeability) of the foam is very low. Third, foams with higher T_g (such as PO-700 (i.e. glycerine/propylene oxide based polyether with molar mass of 700 g/mol) based foams) show slower VE recovery than those with lower T_g (such as PO-1000-based foams). Also, foams that use monofunctional polyethers or lower isocyanate index are known to lead to slower VE recovery. Finally, the conversion of isocyanate (NCO) functional groups were estimated on the basis of comparing experimental sol fraction against simulated sol fraction for various levels of NCO conversion. These elements are examined in detail.

2. Results and discussion

2.1. Strain recovery time and "hand-squeeze" test

To understand the foam VE recovery ("memory effect") phenomenon itself, it was necessary to quantify it. For this purpose, the height sensor on the RAPRA setup was used to monitor the foam dimensional recovery (or "strain recovery") after release of compression. Fig. 1 shows a typical result. The foam was 50 mm thick (with lateral dimensions of 100 × 100 mm) and compressed down to 10 mm consistently through use of a solid spacer. This resulted in an 80% foam compression. The foam was held at that compression level for 10 s, then the compressive stress released, which in the case of Fig. 1 is around 7.22 s (notice the brief sharp upshot in height value around ~7.4 s due to removal of the solid slab which interferes with the height measurement). Note that the top of the solid slab compressing the foam is around 16 mm thick, so that before release of compression, the height sensor reads a value of 26 mm for the "foam height." Dimensional recovery takes place following a sigmoidal-type curve, reaching a plateau value corresponding to the original dimension of the foam, which happens around 8.12 s in the case of Fig. 1. So for this particular foam, the strain recovery time would be around 0.9 s in total.

Despite the accuracy of the strain recovery time measurement, it was also recognized that squeezing/pressing the foam down by hand is a commonly used way of judging the degree of memory effect. VE recovery is in the end subjective property related to perception of 'shape memory,' as opposed to a foam mechanical property such as load bearing or tear resistance. For this reason, it
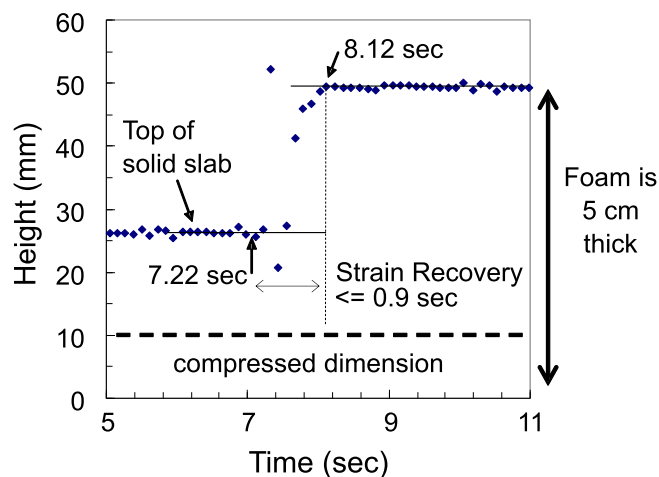

Fig. 1. Example of Strain Recovery Time Measurement starting @ 80% compression. "Time zero" in this example is 7.22 s. The up-peak at ~7.3 s represents the interference of the solid compression slab with the height sensor as it was moved away from the top of the foam (original foam dimension is 50 mm). The dashed line represents the compressed foam height, and "0 cm" represents the bottom base of the equipment on which the foam rests.