Chemiluminescence of Polysiloxane Cushions: Correlation with Physical Properties*

Cellular cushions are routinely used to maintain the shapes and relative positions of parts with widely different thermal expansion properties. At Lawrence Livermore National Laboratory (LLNL) and Bendix Corporation, Kansas City (BKC) cushions that are a silica-filled polysiloxane random terpolymer made from diphenyl, dimethyl, and methylvinyl siloxane subunits are primarily used. The cellular structure is formed by a leachable urea pore former. Cellular silicone cushions were selected for our purposes over other elastomers and foams because of their superior thermal properties, long term stability, and lower compression set (the ability to recover their original thickness when a load is released). At LLNL, temporarily filled rather than hydrogen-blown cushions are used because the porosity, and thus crucial mechanical properties, is more easily adjusted.

Until 1978, the molding compound and raw materials from which the cushions are made were purchased from an outside vendor and molded into parts at BKC. When these materials became unavailable, both BKC and LLNL were forced to find other suppliers and to develop the technology necessary to make the cushions. Since that time, a large effort has been made to replace and improve the original material and to optimize processing conditions.[1-4] LLNL is primarily responsible for the materials development including improving and predicting the long-term chemical and physical properties of different cushion materials.

Traditional life-testing consists, in part, of accelerated aging in the form of compression set testing.[5] In the past, cushion samples have been compressed to a known thickness, stored at 150°C for 24 h, allowed to recover, and their initial and final thicknesses compared. Historically, most of the data at 150°C from the cushions in which urea is used as a pore former correlated poorly with lower temperature data. Conversely, the high temperature data for hydrogen blown cushions did correlate well. Chemiluminescence was used to study this apparently anomalous behavior.

Chemiluminescence is a process in which a photon is released as the result of the decay of an excited state (e.g., a ketone) formed from an exothermic oxidation reaction. With the introduction of very sensitive photomultiplier tubes and modern photon counting equipment, it became apparent that very faint chemiluminescence is a virtually universal property of oxidizable organic substances. This very faint chemiluminescence is probably due to ongoing degradation reactions in the material, and because chemiluminescence can be detected so sensitively these reactions can be monitored tens to hundreds of years before their effect would become apparent on a macroscopic scale. Aging reactions in a myriad of substances have been studied using chemiluminescence.[6-8] We are reporting the correlation of chemiluminescence, a microscopic process, and compression set, a macroscopic physical property of cellular silicone cushions.
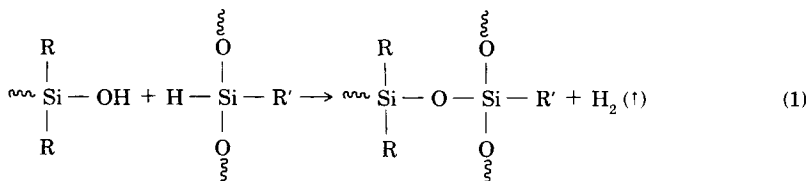
EXPERIMENTAL

Materials

Cellular silicone cushions are made from a raw gum (SE-54, General Electric) that is a formulation of methylvinylsiloxane, diphenylsiloxane, and dimethylsiloxane. This gum is mixed with an inert silica filler[9] and a processing aid that promotes favorable interactions

with the filler. This reinforced gum is milled, extruded, and aged for 1 week. A cure initiator (an organic peroxide)[10] and the temporary urea filler are added, and the resulting molding compound is shaped into test slabs in a high-pressure heated mold. The cushion is then washed to remove the urea and post-cured at an elevated temperature to complete the polymerization.

The hydrogen blown cushions are made from a raw gum (S5370 RTV, Dow Corning) that already contains the filler, a proprietary mixture of low and high molecular weight silanols, diphenylmethylsilanol, polymethylhydrogen siloxane, and tetrapropoxysilane. When stannous octate is added as a catalyst the siloxane reacts with the polysilanols liberating hydrogen which acts as a blowing agent as shown in eq. (1), where R represents either a phenyl or methyl group and R′ represents a methyl group[11]:

$$\underset{\underset{R}{|}}{\overset{\overset{R}{|}}{\sim\!\!\sim \text{Si}}} - \text{OH} + \text{H} - \underset{\underset{O}{|}}{\overset{\overset{O}{|}}{\text{Si}}} - \text{R}' \longrightarrow \underset{\underset{R}{|}}{\overset{\overset{R}{|}}{\sim\!\!\sim \text{Si}}} - \text{O} - \underset{\underset{O}{|}}{\overset{\overset{O}{|}}{\text{Si}}} - \text{R}' + \text{H}_2 (\uparrow) \qquad (1)$$

After the catalyst and gum are briefly mixed, the cushion is molded and cured at room temperature followed by an elevated temperature post-cure. The cushions used in this study were all of nominal 0.1 in. thickness and 45% porosity. A more detailed description of the formulations of both silicone cushions is available elsewhere.[12,13]

Apparatus

An apparatus that was designed and built at LLNL for chemiluminescence experiments was used in this study.[12] It consists basically of a light and vacuum tight sample chamber containing a heater and thermocouple. The chemiluminescence signal is detected by two photomultiplier tubes and processed by a state-of-the-art photon counting system. A computer system controls the experiment and records and manipulates the resulting data. The apparatus was originally designed for stress-induced chemiluminescence experiments of polymeric materials, but for these experiments was used only for thermally induced chemiluminescence. No stress was applied to the cushion samples. The samples were in the form of 2-in. square sheets so that the sample filled the entire field of view of the optical system.

Compression set testing was done at 40% compression in accordance with ASTM D 395, Method B, with the following modifications. The dial micrometer used for the thickness measurements had a presser foot 0.2 in.² in area and the total mass of the stem and foot was less than 13 g. The specimens were tested in their as molded thicknesses, were not piled up, and were sandwiched between stainless steel shims prior to loading into the compression set fixture.[5] These shims were used to allow measurement of the final thickness of the sample without pulling apart the sample during removal of the compression set fixture. Two separate test series were done: the first with two 2 mil stainless steel shims and one sample per fixture and the second with two larger 5 mil shims and three samples per fixture. The thickness of the shims was taken into account in the selection of the spacers. The first series consisted of 140 separate cushion samples in the form of 1-in. disks and the second of 114. The fixtures were exposed to temperatures ranging from 20°C to 200°C. Exposure times ranged from 0.5 to 60 days.

RESULTS AND DISCUSSION

Figure 1 is the chemiluminescence in oxygen of the cushions plotted as a function of temperature in Arrhenius form. The chemiluminescence of the hydrogen blown cushion is represented by the solid line and solid symbols and that of the cellular cushion by the solid line open symbols. Each plot is the average of three separate experiments with standard deviations ranging from 0.4 to 8%, and from 3 to 10%, respectively. Each plot shows a change in slope resulting from a change in reaction mechanism in the range from room temperature to 200°C. However, the hydrogen-blown cushion does not experience a significant change in reaction mechanism until the temperature is greater than 150°C, i.e., above the temperature used in
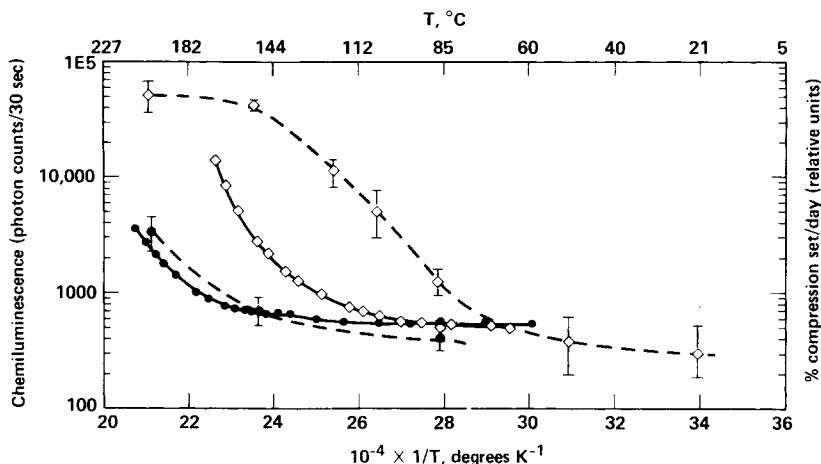
Fig. 1. Comparison of chemiluminescence (——) and compression set (- - -) data for polysiloxane cushions. The temporarily urea-filled cushion is represented by the open symbols and the hydrogen blown cushion by the solid symbols.

the compression set test. The cellular cushion during the compression set test is in the regime where the higher temperature reactions dominate since it experiences a change in reaction mechanism at a temperature near 110°C. This explains the inability to extrapolate high temperature testing data to lower temperatures for the cellular cushion. The short term testing done at 150°C promotes a chemical degradation reaction that does not occur at room temperature. Thus, chemiluminescence data can be used to define the valid temperature regimes in which to perform accelerated aging tests.

In order to draw a closer correlation between traditional testing and chemiluminescence data the % compression set results at each temperature were plotted as a function of exposure time. The data were linear least-squares fitted to a line and a slope extracted which corresponds to a rate, i.e., % compression set/day. This value, which represents as many as 25 separate test specimens for each temperature, is also plotted in Arrhenius form in Figure 1. The open symbols connected by a dotted line are the data from the cellular cushion and the solid symbols connected by the dotted line are from the hydrogen-blown cushion. The error bars represent one standard deviation of the slope of the line from the least squares fit. The curve for the cellular cushion appears to flatten out at the highest temperature. The reason for this is that at this temperature (200°C) even the shortest exposure times resulted in very large compression set values. Thus, the difference between the longest and shortest exposure times is slight resulting in a small value for the slope of the fit. In other words, the cushion has experienced nearly the maximum compression set possible at the shortest exposure time.

There is a remarkable correlation between the chemiluminescence data and the compression set behavior. It is clear that the cellular cushion undergoes a drastic change in its degradation mechanism above 100°C and the hydrogen-blown cushion does not experience a change until the temperature is above 150°C. It has been suggested that compression set is due in part to uncrosslinked dangling chain ends becoming temporarily entangled during the proximity enforced upon them by compression during the test conditions.[14] It is conceivable that these potentially reactive groups do react at elevated temperatures, producing the observed chemiluminescence. It also is possible that unreacted peroxide catalysts are responsible for the observed light which may result in further crosslinking and hence compression set.

It is clear that a correlation can be drawn between chemiluminescence data of a microscopic nature and compression set data, a macroscopic physical phenomena. In addition the chemiluminescence experiments presented here can be completed in their entirety in less than 2.5 h (i.e., six separate experiments). The compression set testing presented here, on the other hand, literally took months. As a direct result of these experiments quality assurance testing is now done both at LLNL and BKC at 70°C for 72 h.

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