Journal of Hazardous Materials, 9 (1984) 31–39
Elsevier Science Publishers B.V., Amsterdam — Printed in The Netherlands

CHEMILUMINESCENCE OF POLYMERS: APPLICATIONS TO WEAPONS MATERIALS*

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ABSTRACT

We have designed and built an apparatus for the purpose of exposing samples of solid polymers to varying temperatures, atmospheres and stress levels while quantitatively recording the resulting chemiluminescence. We have acquired preliminary data with this apparatus that show a correlation between an enhanced chemiluminescence signal at a low level of applied stress and a decrease in tensile strength for the most commonly used epoxy resin in high performance fiber composites, TGMDA DDS. Our studies with cellular silicone cushions (which are used to accommodate thermal expansion and contraction) have defined the temperature regimes in which accelerated aging tests are valid for extrapolation to ambient temperature. Preliminary data on Kevlar fibers will also be discussed.

INTRODUCTION

Chemiluminescence is a highly sensitive technique for monitoring aging reactions of solid polymers via the very faint light they produce. It became apparant with the introduction of highly sensitive photomultiplier tubes and modern photon counting equipment that very faint chemiluminescence is a virtually universal property of oxidizable organic compounds. Chemiluminescence can be produced by several processes, we have studied that induced by either heating or applying tensile stress. In conventional thermally induced chemiluminescence the polymer oxidizes, presumably progresses through the formation of peroxide intermediates that have electronically excited states (e.g., ketones) which luminesce. This highly sensitive technique has been used to detect changes due to aging and temperature in various polymeric materials (resins, fibers, rubbers, food products) (1). Recently, polymeric materials have been studied by a novel chemiluminescence technique called stress chemiluminescence (SCL); in this technique the material is activated by bond scission caused by mechanical stress. Thereafter, the rest of the mechanism is assumed to be similar to

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*Work performed under the auspices of the U. S. Department of Energy by the Lawrence Livermore National Laboratory under contact number W-7405-ENG-48.

0304-3894/84/$03.00

conventional thermally induced chemiluminescence (2,3). It is the oxygen dependence that distinguishes SCL from triboluminescence, a technique in which the excited state is formed directly from mechanical stress (4).

Our work with thermally induced chemiluminescence has yielded information important to the realistic design of accelerated aging tests of weapons materials. All of the Arrhenius plots of chemiluminescence from cellular silicone cushions (a complicated filled polymer system) show a change in reaction mechanism, indicated by a break in the slope, at a temperature above 110°C. These data indicate that accelerated aging tests should not be done above the temperature of this change in mechanism. This result has been substantiated by traditional life testing.

We have demonstrated the correlation of SCL data with applied stress, temperature, atmosphere, mechanical damage, and accelerated aging for samples of the epoxy resin most commonly used in high performance fiber composites. Our results indicate a correlation of an enhanced chemiluminescence signal in a low stress environment with subsequent premature failure of the epoxy sample. Thus, while the generality of this result is not yet firmly established, the potential predictive capability of SCL would make this technique very valuable as a quality control test.

APPARATUS AND MATERIALS

The heart of the system, shown in Figure 1, is a light and vacuum tight sample chamber capable of holding two samples. Inside this controlled environmental chamber are a heater, various gripping mechanisms and a thermocouple for measuring the temperature of the sample. The chemiluminescence is directed onto the photocathodes of two RCA 8852 red biased photomultiplier tubes. The signals from the photomultiplier tubes are processed by a commercially available state-of-the-art dual channel photon counting system (PAR 1112/1121). We can use long pass or band-pass filters in a special holder in front of the photomultiplier tubes to determine the spectrum of the chemiluminescence, which provides information on the reaction mechanism(s) (5). Elevated temperatures are provided by a heater block extending across both samples and controlled by a unit separate from the computer.

For SCL experiments, tensile loads are applied by a stepping motor equipped with a gear reduction unit attached with a steel cable to one of the grips. Load cells of varying sizes can be mounted between a fixed framework and a second grip. The system is capable of applying loads up to 10,000 psi (for samples 0.025 in.^2) in a programmable sequence.

An LSI-11 microprocessor reads the load cell and runs the stepping motor until a desired stress level is reached. The computer also reads the thermocouple and photon counter and records load, temperature, extension and photon counts as a function of time to both a teletype and a floppy disk for storage and subsequent manipulation.

Epoxy samples were prepared from tetraglycidyl-4.4'-methylenedianaline (TGMDA) cured with 4,4'-diaminodiphenylsulfone (DDS) in a 100:23 ratio by weight. The resin was poured into sheets and cut into dogbone specimens. The cellular silicone cushions are a silica filled polysiloxane random terpolymer containing diphenyl, dimethyl, and methylvinyl siloxane subunits. The cellular structure is generated by removable fillers such as urea or blowing with hydrogen. A more detailed discription of both the experimental apparatus and materials is available elsewhere (6).

RESULTS AND DISCUSSION

Epoxy Resin

In Figure 2 the temperature and atmospheric dependence of SCL is illustrated. Experiments run at 80°C in nitrogen showed no SCL signal. This serves to underline that the phenomena involved is not triboluminescence since it is dependent on oxygen concentration. On the basis of these experiments we chose 80°C in oxygen as the standard conditions in which to explore the possibility of a predictive capability for SCL. We prepared a series of identical dogbone specimens and deliberately damaged some of them by scoring with a scalpel. The effects of heating in an oven at 70°C in air for one week were also investigated to see if SCL could detect the effects of mild accelerated aging. After recording the SCL of each of the samples under identical conditions, we loaded them to failure.

The results of this study are shown in Table 1 and the data indicate a clear correlation between an enhanced SCL signal and reduction in ultimate tensile strength. The four samples that failed at loads greater than 6900 psi (a) exhibited a 10 + 2% increase in SCL at 4000 psi. These samples were taken to be of high quality and their chemiluminescence under these conditions formed a basis for comparison with lower quality and deliberately damaged samples. An untreated sample that was inherently poor (d), due perhaps to unreacted crystals of epoxide or poor dogbone preparation, exhibited a 19% increase and broke at a low level of applied stress. The thermally aged (c) and scored samples (b,e) also broke at a low level of applied stress and showed a SCL signal higher than the five samples taken as a baseline. In our limited exploratory study, there is a clear correlation between enhanced SCL and premature mechanical failure. Also it is not necessary to take the sample to 4000 psi to measure SCL; there is a distinct enhancement in the chemiluminescence of the damaged samples that is not present with the good samples at 1200 psi. Therefore, SCL appears to be a test that can predict early failure well before the failure load is reached. We are currently in the process of repeating this study on a larger and more statistically valid scale. The new samples contain the BF_3 catalyst and are the formulation used for commercial graphite epoxy composites.

Chemiluminescence data can also be plotted in Arrhenius form with the slope of the least squares fit equaling -Ea/R, where Ea is the activation energy and R the molar gas constant. The Arrhenius plot for TGMDA DDS, shown in Figure 3, gives an activation energy of about 10 kcal/mole and is linear to room temperature.

Silicone cushions

While attempts to reproducibly measure the chemiluminescence of cellular silicone cushions as a function of stress have not been successful, we have been able to derive useful information from Arrhenius plots. The Arrhenius plots for the cushions we have studied all show a change in reaction mechanism, resulting in a break in the slope, at a temperature above 110°C (Figure 4). The temperature of this break is reproducible and varies from one type of cushion to another. Clearly, very different reactions (with activation energies of 20-30 kcal/mole) are taking place above 110°C as compared to those below (with an activation energy of less than 3 kcal/mol).

Traditional life testing done both at LLNL and Bendix, Kansas City consists in part of compression set testing performed at 70°C and 150°C. In a compression set test a cushion is compressed to a known thickness, exposed to the temperature of interest, and its relaxed thickness before and after compression are compared. In most types of cushions (including the sample represented by the dotted line in Figure 4), the data taken at the higher temperature does not extrapolate well to the lower temperatures that one might realistically expect the cushion to experience during its service life. High temperature data with the hydrogen-blown cushion (the solid line) shows a better correlation. The chemiluminescence data show that this is not at all surprising. At 150°C the chemiluminescence of the blown cushion is only slightly above that at 30°C and still within the regime of the lower temperature reactions. The urea filled cushion, however, shows an increase in chemiluminescence of two orders-of-magnitude and is in the regime where higher temperature reactions are dominant. These data also indicate that low temperature compression set could be done as high as 100°C with no loss in validity. As a direct result of this study compression-set testing was undertaken for the urea filled material at 50°, 85°, 110°, and 150°C. All of the cushions heated to temperatures below 150°C showed little or no change, but those heated to 150°C experienced a large degree of compression set as predicted by the chemiluminescence data. As a direct result of the chemiluminescene data the temperatures at which routine testing is done in both organizations has been changed. Currently samples of the hydrogen blown cushions are compressed and in ovens at 85°, 150°, 175°, and 200°C.

Kevlar

Figure 5 shows preliminary data from several strands of Kevlar fiber and is very encouraging. As with the epoxy, there is a reproducible increase in chemiluminescence with stress. The Kevlar shows a 15% increase over the baseline signal, compared to less than 10% for the epoxy at the same temperature and a comparable level of applied stress. The Arrhenius plot for Kevlar (Figure 6) yields an activation energy of 16 kcal/mole and shows a break similar to that seen with the cushions; however this break occurs at about 80°C rather than the >110°C seen with the cushions.

CONCLUSIONS

We believe that the future will see many applications of chemiluminescence and SCL. We plan to continue studying fibers, resins and eventually fiber composites (e.g., graphite-epoxy, Kevlar-epoxy). We also hope to do additional work to generalize our results to other polymeric materials.

We have demonstrated that chemiluminescence and SCL can reproducibly measure reactions in solid polymers and has the potential for prediction of premature mechanical failure non-destructively. We have used chemiluminescence and SCL to evaluate presently used accelerated aging tests and can use it to design future tests that are more relevant and realistic. Our results indicate that chemiluminescence, a dynamic microscopic process can be related to a macroscopic property of a solid polymer. The potential for SCL to make a valuable contribution, both empirically as a quality control test, and theoretically in understanding aging reaction mechanisms, is clearly present.

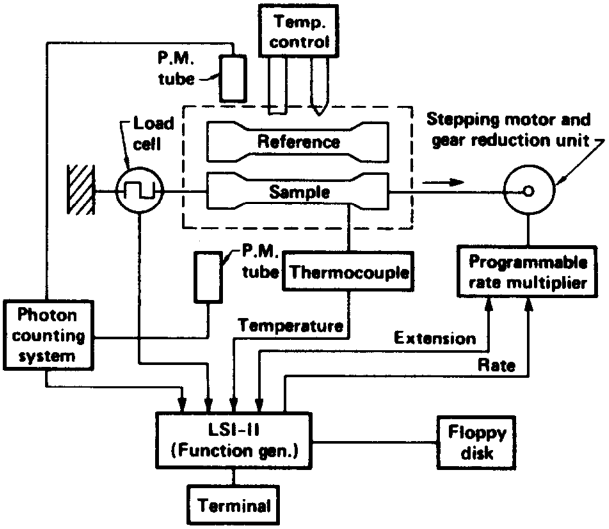

Figure 1. Diagram of stress chemiluminescence system.

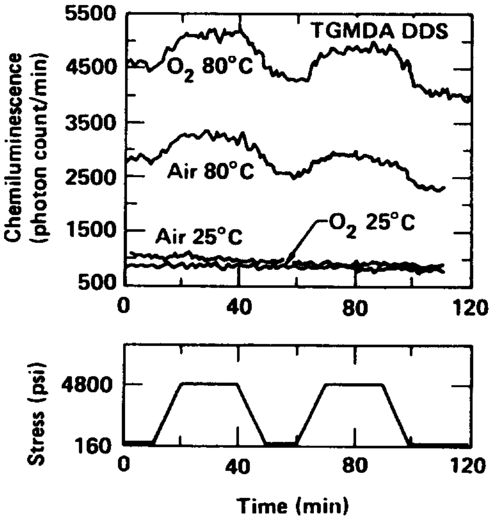

Figure 2. SCL of TGMDA DDS as a function of temperature and atmosphere

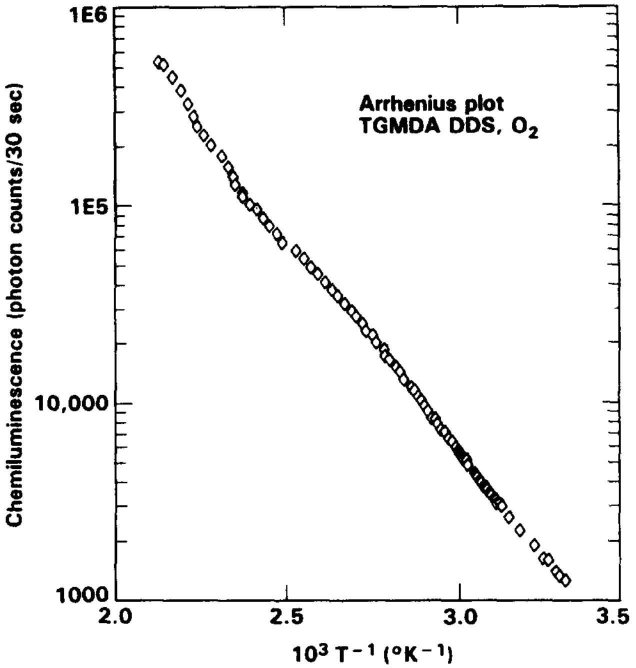

Figure 3. Arrhenius plot in oxygen for TGMDA DDS.

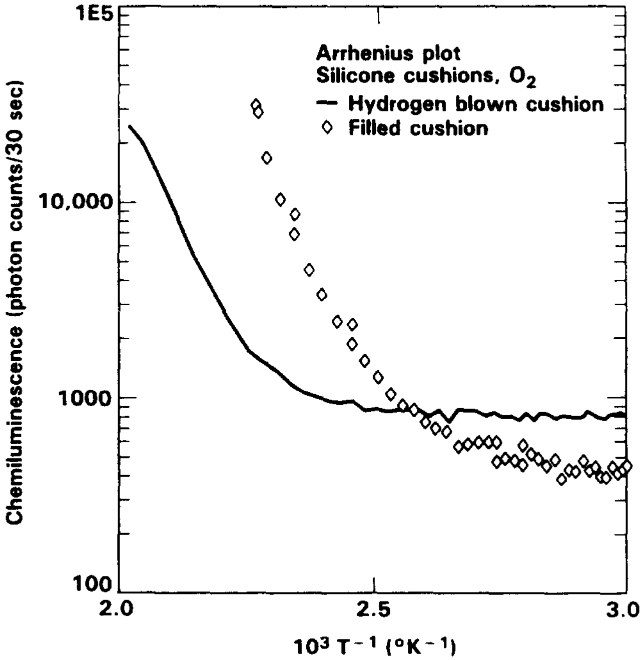

Figure 4. Arrhenius plot in oxygen for hydrogen blown cushion (-) and urea filled cushion (◇).

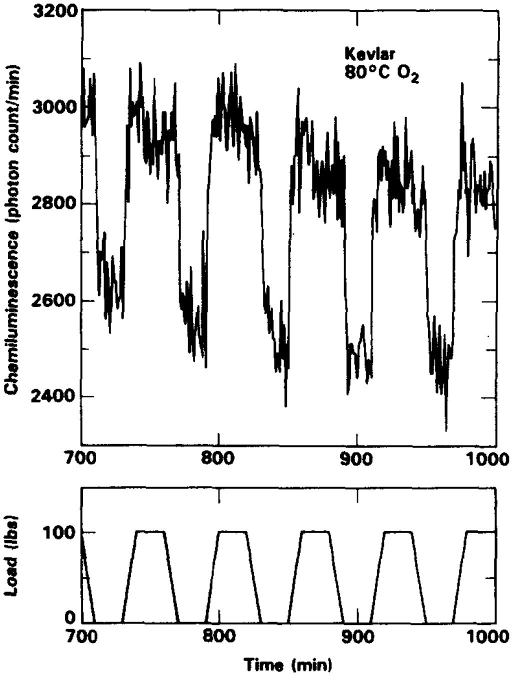

Figure 5. SCL of Kevlar fibers in oxygen at 80°C.

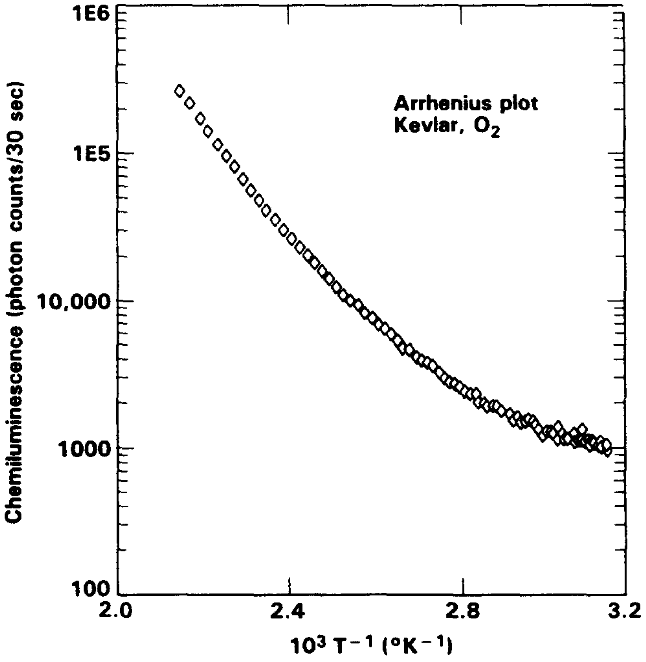

Figure 6. Arrhenius plot for Kevlar fibers in oxygen at 80°C.

TABLE 1. Enhancement in SCL vs tensile strength.

Sample	Characteristics	SCL%	Load at failure (psi)
(a)	Untreated	10 + 2	>6930
(b)	Scored	15	6360
(c)	Accelerated aged	21	6350
(d)	Untreated	19.5	6250
(e)	Scored	19.6	4600

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