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Mechanoluminescence of Anhydride and Imidazole Cured Epoxies under the Combined Effect of Thermal and Cyclic Mechanical Stresses

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Abstract—The luminescence of two crosslinked BA/FDGE epoxy resins under cyclic mechanical and thermal stresses has been studied. Spectra under thermal or combined thermal and mechanical stresses show the same patterns with a maximum around 550 nm indicating that the same molecular groups are responsible for the luminescence under both stresses. The luminescence also shows a delay with the applied stress decreasing with temperature. This study could help elucidate the mechanisms at the origin of mechanoluminescence and thermo-mechanical degradation in epoxy polymers.

Keywords—*mechanoluminescence, chemiluminescence, epoxy, cyclic loading, mechanical degradation, free radical formation, oxidation, thermal degradation*

I. INTRODUCTION

Thermal and mechanical stresses can be responsible for premature failure of dielectric materials used in electrical insulation. A better understanding of the degradation mechanisms under one or both stresses could prove helpful to provide a better insight into the endurance of dielectrics and in term design more durable materials.

Studying ageing phenomena through luminescence can help improve the understanding of mechanisms governing dielectrics lifetimes under various stresses. Spectral acquisitions can be particularly interesting as they are essentially a fingerprint of the degradation mechanisms. Spectral measurements in epoxy resins have for instance shown similarities between electro-, cathodo- and spontaneous (chemi-) luminescence [1].

Mechanoluminescence refers to the emission of light under mechanical stress, notably attributed to radiative de-excitation following bond rupture in a polymer network. Studying this phenomenon in dielectrics under tensile stress could help unravel the degradation mechanisms under mechanical loading and their similarities and differences with other stresses.

The objective of our work is to try to elucidate the mechanisms at the origin of mechanoluminescence under tensile cyclic loading and thermal stress of two anhydride and imidazole cured epoxies typically used in electrical insulation through both temporal and spectral acquisitions.

II. EXPERIMENTAL

A. Experimental set-up

An experimental set-up was developed to study the mechanoluminescence under tensile stress (Fig. 1). Samples can be stretched using a 5 kN Microtest dual leadscrew tensile

machine from Deben installed in a light-tight vacuum chamber.

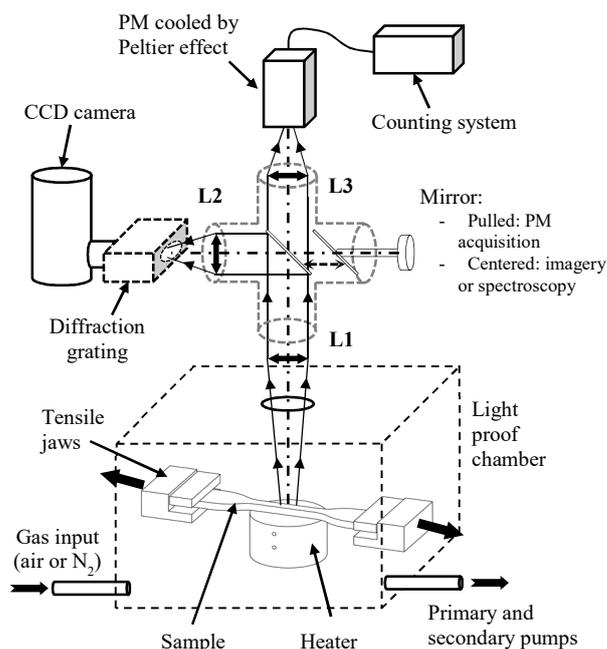


Fig. 1 Representation of the experimental set-up for mechanoluminescence detection with PM or spectra acquisitions.

Image acquisitions, spectral analyses and temporal light detection by photon counting can be performed with this setup. Light detection is made with a photomultiplier in counting mode (R943-02, Hamamatsu) cooled to $-30\text{ }^{\circ}\text{C}$ to reduce the thermal background noise to less than 1 count per second (cps) in average. The integration time was always set to 1 s. Images and spectra can be acquired with a CCD camera (Spectrum one D-91, Jobin-Yvon) cooled to $-130\text{ }^{\circ}\text{C}$. For spectra acquisitions, a diffraction grating is placed before the CCD camera. The entrance slit chosen has a width of 2 mm to balance between spectral resolution and admitted light flux. A resolution of 15 nm is achieved with this slit. A mirror angled at 45 ° is used to switch between counting mode and imagery/spectroscopy by deviating the light towards the CCD sensor. A set of lenses is used along the optical axis to focalize the light emitted by the samples on either the CCD sensor or the photocathode of the photomultiplier. The chamber can be evacuated to a primary or secondary vacuum and the atmosphere can be either air or nitrogen.

Samples can be stretched at 0.1 to 1 mm/min between 50 and 70 mm. Temperature is controlled by heat conduction

with a brass heater on which the samples rest. Textured jaws are used to prevent slipping during mechanical tests. Tensile testing and luminescence acquisition are synchronized using a MATLAB program.

B. Materials

The mechanoluminescence of two commercial epoxy resins was investigated. The first one (Epoxy 1) is an imidazole cured Bisphenol F diglycidyl ether epoxy (BFDGE) from Polytec (Polytec EP 630). It has a relatively high T_g of $T_{g1} = 120$ °C. The second resin (Epoxy 2) is an anhydride cured Bisphenol A diglycidyl ether epoxy (BADGE) from Huntsmann (CY225-HY227-DY062) with a tertiary amine used as a catalyst, whose mechanoluminescent properties in tensile rupture tests had already been characterized [2]. It has a moderate glass transition temperature (T_g) of $T_{g2} = 65$ °C due to a flexibilizer added in the network. The chemical compositions of Epoxy 1 and 2 are respectively given in Fig. 2.a and 2.b.

Dumbbell shaped 300- μ m-thick Epoxy 1 samples were prepared by molding. 67x10 mm² rectangular shaped 1-mm-thick Epoxy 2 samples were prepared by laser cutting vacuum molded discs.

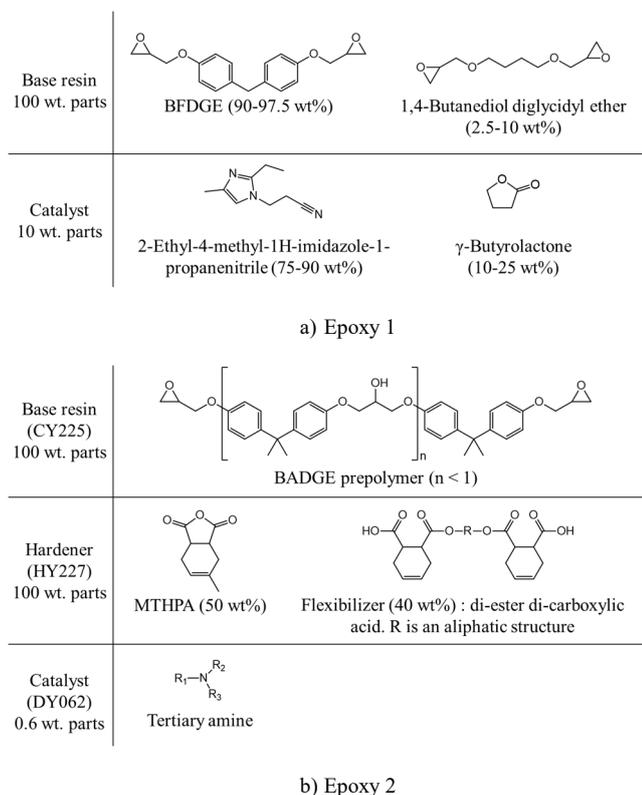


Fig. 3 Chemical compositions of the compounds used in epoxies 1 and 2.

C. Cyclic test procedure

Cyclic tests were done at a stretching speed of 1 mm/min. Temperature was controlled to be below T_g to study the materials in the glassy state. Preliminary rupture tests were performed to determine the linear regime of the materials at each temperature to ensure repeatability of the stress curves in each cycle.

The influence of the atmosphere was also studied, with cyclic tests done in air or in nitrogen atmosphere.

III. RESULTS

A. Time delay of light emission under cyclic load

The detection of luminescence with a photomultiplier allows for the temporal resolution of the measurement.

Fig. 3 shows a typical plot of the applied stress and the recorded luminescence as a function of time at 104 °C for Epoxy 1.

Almost as soon as stress is applied on the sample, the luminescence increases from the spontaneous level and exhibits a cyclic behavior similar to that of the stress. The luminescence level under stress does not return to its initial spontaneous level prior to the mechanical test, even at almost zero stress at the end of each cycle.

A clear time delay (indicated by dotted lines in Fig. 3) between stress and luminescence of the order of several seconds can be seen. Due to an important noise, it can be relatively difficult to estimate precisely its value. To do so, a sawtooth function fit has been applied to the luminescence data using the MATLAB curve fitting app. This method provides an easy and comparable way of determining the stress-luminescence delay.

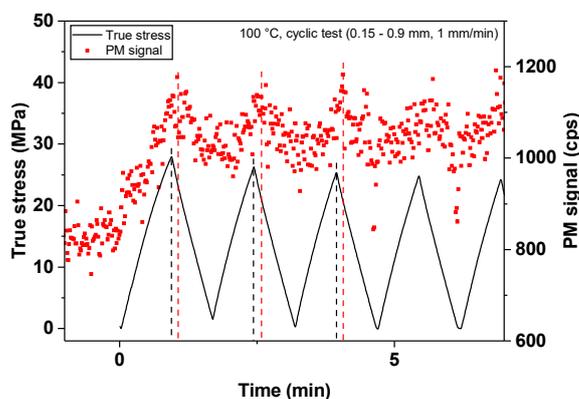


Fig. 2 Typical luminescence (red dots) under cyclic mechanical stress (black line) plot as a function of time at 104 °C for Epoxy 1. Only the first cycles are represented here for clarity. The dotted black and red vertical lines indicate respectively the maximum of stress and luminescence to represent the time delay between the two.

For Epoxy 1, it is found that the delay decreases with temperature, being about 10.5 s at 75 °C and 100 °C and 2.5 s at 115 °C. Time delays were of the same order of magnitude for Epoxy 2 with about 5.5 s and 4 s at respectively 55 and 60 °C. This delay and the mechanoluminescence intensity were also constant for each experiment, meaning that they did not change with the number of cycles.

B. Luminescence spectra

The luminescence could also be measured using a CCD camera and a diffraction grating to produce spectra resolved in wavelength. Studying mechanoluminescence spectra is of fundamental importance as it gives information about the energy of the emitted photons, which are the signature of excited molecular groups. Thus, comparing the spectra with or without mechanical stress could provide clues on the mechanisms at the origin of luminescence.

Typical spectra acquired at 90, 115 or 130 °C under thermal stress only or both thermal and cyclic mechanical stress for Epoxy 1 are given in Fig. 4.

All spectra are very similar in shape and exhibit a maximum at the same wavelength of about 555 nm. Signal intensity increases with temperature, which is consistent with PM acquisition luminescence levels.

Spectra under mechanical and thermal stresses systematically show a higher intensity than pure thermal spectra for all temperatures, even at 90 °C though it is barely visible. It makes sense since the levels of luminescence are higher when mechanical stress is applied. Integrating the curves gives that the application of mechanical stress at 90, 115 and 130 °C increases the signal respectively by 6 %, 40 % and 49 %.

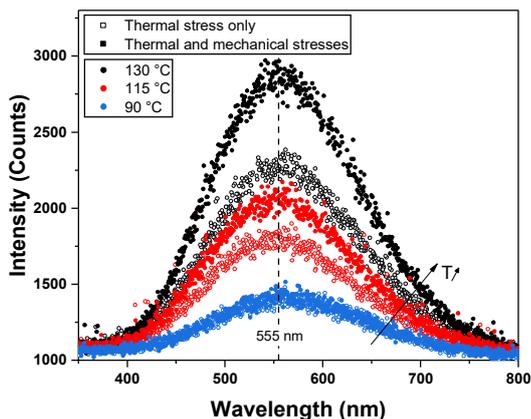


Fig. 4 Typical spectra under thermal or both thermal and mechanical stresses at different temperatures for Epoxy 1 in air. Integration time was 20 min.

Spectra of Epoxy 2 are also very similar, showing a maximum around 545-560 nm (Fig. 5). The intensity is much lower because luminescence levels were quite low at the temperatures investigated in this study. The shape of the spectra at low wavelengths (< 500 nm) is due to the noise of the CCD sensor. Integration time was set at 30 min to balance between intensity and noise. Spectra of Epoxy 2 are less clear than those of Epoxy 1 but still give valuable information on the overall spectral distribution.

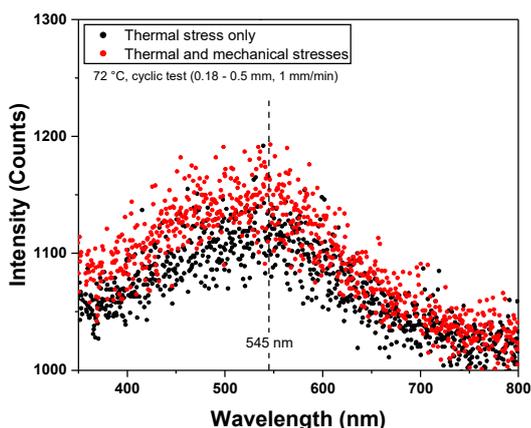


Fig. 5 Typical spectra under thermal or both thermal and mechanical stresses at 72 °C for Epoxy 2 in air. Integration time was 30 min.

C. Influence of the atmosphere

The atmosphere has been identified as a crucial parameter for mechanoluminescence. Tests were performed in air and in nitrogen to study the influence of an oxidative or an inert atmosphere.

For Epoxy 1, the spontaneous luminescence level is seen to decrease drastically in a nitrogen atmosphere, reaching significantly lower levels compared to its behavior in air. For instance, at 104 °C, in air the spontaneous luminescence after stabilization was about 900 cps, while only reaching 10 cps in nitrogen (Fig. 6).

The mechanoluminescence was also largely decreased in nitrogen, with an increase of only 30 cps under mechanical stress, compared to 200-400 cps in air.

The luminescence of Epoxy 2, however, was not impacted as much by the absence of oxygen. At 70 °C the spontaneous luminescence level in nitrogen remains at about 100 cps.

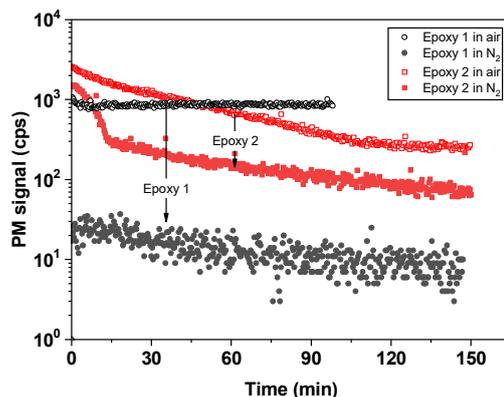


Fig. 6 Spontaneous luminescence signals of Epoxy 1 and 2 when heated respectively at 100 °C and 70 °C in air or in nitrogen. Samples heated in nitrogen were degassed prior to heating in secondary vacuum for two days.

IV. DISCUSSION

A. Mechanism of mechanoluminescence

Spectral measurements clearly indicate that adding a mechanical component to a thermal stress leads to the same excited groups than for pure thermal solicitation, showing that mechanisms of light emission must be similar. The role of the atmosphere and oxygen is also apparent, at least for Epoxy 1.

Studies of stress induced (chemi-)luminescence have been conducted in conventional polymers such as PA 66 fibers, polypropylene, HDPE and epoxy resins [2-6]. They generally attribute this phenomenon to the radiative de-excitation of chemical groups formed by the reaction of ambient oxygen and free radicals created by bond scissions in the polymer network by the applied stress. This mechanism is analogous to chemiluminescence under oxidative atmosphere, but in the case of mechanoluminescence, radicals are generated both mechanically and thermally.

The ML observed in these experiments could then be explained with established chemiluminescence mechanisms. Oxidative chemiluminescence in epoxy resins and other conventional polymers has been extensively studied. Light emission is believed to originate from oxidative reactions forming ketones in excited triplet states. The excited groups are thought to be formed through either a Russel mechanism or an energy transfer mechanism [7].

In (chemi-)mechanoluminescence, the actual role of mechanical bond scission remains unclear [4]. The applied stress on the bonds could make them weaker to oxidation, without necessarily breaking them. Both mechanisms (scission or weakening) would explain the increase in luminescence observed when applying stress. In both cases

however, mechanoluminescence allows to study the role of external stress in the thermal-oxidative degradation.

In the case of a chemically crosslinked network, bond scission seems mandatory when samples are sufficiently strained. Though efforts were made to study cyclic mechanical properties in the linear regime it is clear that plastic deformation occurred during the mechanical tests, so bond scissions probably took place during testing. However, luminescence increases almost as soon as stress is applied on a sample. A such low stresses and elongations (at the very beginning of the mechanical test), it seems rather unlikely that bond scission would occur to a substantial degree, as evidenced with simulation studies which showed that bond scission occurred mostly during plastic deformation [9]. A combination of both mechanisms is then probable.

This stress induced chemi-luminescence would then originate from the surface of the sample and be dependent on oxygen diffusion. Contribution from the bulk could also happen from dissolved oxygen molecules until their depletion.

By integrating the spectra, an increase in luminescence of 5 %, 31 % and 49 % was calculated at respectively 90 °C, 115 °C, 130 °C. The total integrated signal under thermal stress shows an Arrhenius behavior with an apparent activation energy of about 35 kJ/mol. This could mean that chemi-mechanoluminescence could be a way to monitor the acceleration of degradation by the action of mechanical stress in an oxidative atmosphere. The influence of stress is more pronounced the higher the temperature.

The stress-luminescence time delay decreases as temperature gets closer to T_g . This could be due to oxygen diffusion in the network (that would react with free-radicals), which is a thermally activated process.

B. Comparison of the two epoxy resins

In air, both resins give very similar results. First, under cyclic load, both materials exhibit a similar time delay between the applied stress and the recorded luminescence. The delays decrease as the temperature gets closer to T_g .

The spectra are also relatively similar, showing the same shape and a similar maximum around 550 nm. This would indicate that similar molecular groups are at the origin of light emission.

A previous study on the curing chemiluminescence of Epoxy 2 has shown that oxidation of the anhydride hardener was responsible for a peak at 560 nm [8]. Similar experiments were performed (not included in this article) and showed that the oxidation spectra of the base resin 1 or the catalyst 1 (of Epoxy 1) at 100 °C are different than that of the crosslinked resin. Thus, groups similar to the chemical groups responsible for luminescence in Epoxy 2 would be formed in Epoxy 1 during crosslinking and be responsible for the observed light emission.

This is also consistent with the hypothesis presented in this article that mechanoluminescence is arising from broken/weakened stressed bonds, since the luminescent groups formed during crosslinking of Epoxy 1 would be formed at the crosslinks and hence be highly stressed.

In nitrogen, Epoxy 1 shows a very weak spontaneous luminescence and mechanoluminescence, clearly indicating that ML mechanisms are similar to oxidation mechanisms.

The influence of oxygen on the luminescence of Epoxy 2, however, is not fully understood yet. It seems that Epoxy 2 is able to luminesce without reacting with oxygen, suggesting either that a lot of oxygen is dissolved in the material or that mechano-radicals are able to form luminescent excited groups upon recombination through an internal reaction pathway. Indeed, Epoxy 2 was studied at lower temperatures than Epoxy 1 to study the mechanical behavior below T_g . At those temperatures it is unlikely that oxidation is happening to a substantial degree and even a low oxygen concentration would suffice for the recombination of most of the radicals, which could explain the behavior observed in this article.

V. CONCLUSION

Mechanoluminescence (or stress induced chemiluminescence) of two epoxy resins under combined thermal and cyclic mechanical stresses or pure thermal stress was characterized through temporal and spectral acquisitions.

ML has been attributed in part to the recombination of thermo-mechano-radicals with ambient oxygen. ML showed a time delay with the applied stress attributed to oxygen diffusion in the network. The two epoxies showed almost identical spectra under thermal or thermal and mechanical stresses. This observation leads to the conclusion that similar molecular groups are at the origin of light emission, probably groups formed at the crosslinks during the curing reaction.

The relatively strong luminescence exhibited by the anhydride cured epoxy in nitrogen might be due to a large amount of dissolved oxygen or an internal reaction pathway.

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