

Chemiluminescence Investigation of High Temperature and Humidity Aging of PMMA Based Polymer Optical Fibres (POF)

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Abstract

We discuss the aging behavior of polymethyl methacrylate (PMMA) based bare POFs, which were exposed at three various climatic conditions. We relate the changes in optical transmission to the thermo-oxidative degradation of the polymer. We used the chemiluminescence (CL) technique as a sensitive tool to investigate the thermo-oxidative degradation behavior of the POFs. The optical measurements results show an early drop in optical transmission followed by a long slow decline afterwards. Extent and rate of transmission loss depend on humidity and temperature as well as the material. As the CL shows no indication of degradation products formed during early transmission loss this is attributed to physical effects. However, the slow decline afterwards followed by the CL in parallel to the optical transmission loss is attributed to chemical degradation.

I. INTRODUCTION

Several advantages such as low cost of production, more flexibility in handling and ease of fabrication of their connectors etc. have opened the POFs many applications areas: for example in local area networks (LANs), in automotive industry, in sensors and lighting, etc. [1]. A main limitation of the POFs is less stability compared to the silica optical fibres in long-term optical applications.

A POF comprises the core, the cladding and the jacket, which are entirely made up of organic materials (e.g. for core materials: PMMA, Polycarbonate, Polystyrene, etc., e.g. for cladding materials: fluorinated acrylate polymers [2], e.g. for jacket materials: polyethylene, polyamide, etc.). The stability of a POF in terms of its optical transmission properties depends on both physical and chemical changes of these materials. A general optical loss mechanism in POFs is discussed in [3].

While the poor long-term performance exhibited by the POFs under various climatic conditions is known [1] the chemical aging behavior of the POFs under these conditions is less understood. To estimate their reliability in long-term applications it is relevant to carry out further research on the aging of POFs in response to various climatic exposure conditions.

It is known that the organic materials in contact with air can react with oxygen and then form oxidation products. The classical mechanism of polymer oxidative

degradation (in particular PMMA) has been discussed elsewhere [4]. The thermo-oxidative degradation or stability of polymers can be monitored using the chemiluminescence (CL) technique. The CL emission derives from electronically excited states of oxidation products, which are usually carbonyl compounds [5]. It has been proved that CL can perform as a sensitive tool to record even very weak light emission by the polymers during the oxidative degradation [6]. In CL research, so far most of the work has been dedicated to study the thermo-oxidative stability of polyolefins and polyamides [7]. Only one paper deals with degradation of PMMA based optical cables using CL [6].

In the present work, by applying the CL technique, we investigated the thermo-oxidative degradation behavior of some POFs, which were exposed to two various climatic conditions, at 92 °C / 95 % relative humidity (RH) and at 100 °C with low humidity.

II. EXPERIMENTAL

Ila. Materials

Three different PMMA based POFs were studied. POFs were received from Mitsubishi Rayon Co. Ltd. (Eska CK-40), Toray Industries Inc. (PGU-FB 1000), and Asahi Chemicals Co. (Luminous TB-1000). In addition to the POFs, optical grade PMMA (Acrypet grade V, received from Mitsubishi Rayon America Inc.) in the form of granules was studied in parallel to be compared with the POFs.

Iib. Climatic Exposure /Aging Conditions

The applied climatic exposure conditions were:

1. 92 °C / 95 % RH (800 hPa water vapor),
2. 100 °C / 2 hPa water vapor,
3. 120 °C / 1 hPa water vapor.

At the above-mentioned conditions, POFs were exposed up to 2000 hours using climatic chambers and ovens. Both ends of the POFs were connected to a multiplexer device [1] to measure the relative optical transmission at three wavelengths regions (525nm, 590nm and 650nm) during the aging.

Iic. Eska Cladding Preparation

By treatment of POF with trichloromethane solvent, only the core was dissolved and the non-dissolved cladding was separated from the core solution. Using dioxane

solvent the POF cladding was swelled and then it removed, the core was separated.

IIIc. Chemiluminescence (CL)

Instrumentation: A simple, self-constructed computer controlled CL setup was used for the present investigation. The main parts consist of a gas tight sample chamber with thermostat heater, photo multiplier (Hamamatsu R1527P) and single photon counting detector (EG & G / ORTEC) [7].

Sampling: we chose samples in the form of fibre itself (core with cladding). POFs were cut in to pieces of 2-3 mm length and then placed in a horizontally mounted aluminum pan in the CL sample chamber. Since it has been demonstrated that the PMMA based POFs show comparatively weak CL emission at temperatures below glass transition temperature (T_g) [6], as much samples as possible were placed in to the aluminum pan. Almost the same weight (or surface to volume ratio) was maintained through out our CL measurements.

Measurements: we chose temperature ramping (310 K to 450 K) measurement for all the samples. The CL emission was recorded under a constant flow rate of pure oxygen.

III. RESULTS AND DISCUSSION

IIIa. Optical Measurements

Optical transmission measurement results show highest stability for Eska-CK-40 POF and lowest stability for Luminous TB-1000 POF at exposure conditions 1 and 2. At condition 1, POFs lost more than 50 % transmission in less than 5 hours and complete loss of transmission occurred in less than 60 hours. At condition 2, the POFs lost some transmission (≈ 60 % in Luminous, ≈ 20 % in Eska and ≈ 15 % in PGU-FB POFs) as soon as the condition was reached. However, POFs showed quite good stability as the condition was stable (≈ 30 % in Luminous POF and ≈ 40 % in Eska and PGU-FB POFs, at the end of 2500 hours). The temperature in condition 3 was higher than T_g (the DSC determined T_g for all the three unaged POFs was about 118 °C), POFs lost all the transmission as soon as the set temperature was reached.

IIIb. Chemiluminescence (CL) Measurements

First, we investigated separately the thermo-oxidative degradation behavior of the unaged POF (core with cladding), the core, and the cladding and PMMA. Fig. 1 represents the recorded CL emission of Eska CK-40. The results show that the cladding contributes to the total CL of the bare POF in a higher extent than the core. The CL of the POF core and the PMMA gave consistent results. Both behaved similarly in the thermo-oxidative degradation as the CL emission of them was almost in the same range. However, both the POF core and the PMMA showed much lower CL emission than the cladding or the bare POF. This clearly indicates the important role of the

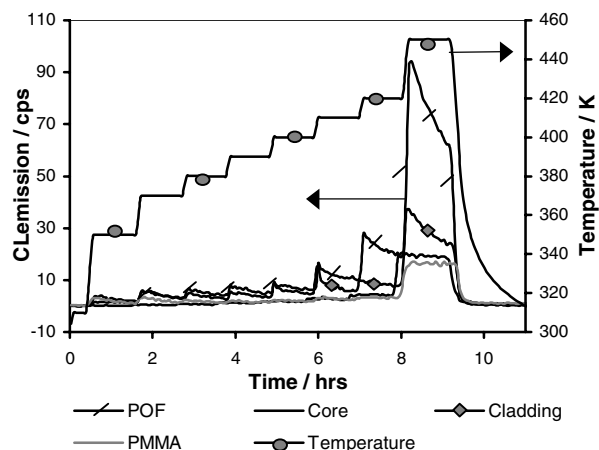


Figure 1: CL spectra of unaged Eska CK-40 (POF, core and cladding) and PMMA (granules)

cladding in the thermo-oxidative degradation of the POFs. Of course, many factors are involved in the cladding CL. An example is the hollow cylindrical structure of the isolated cladding, which allows oxygen to diffuse more efficiently into the cladding. Consequently it is more prone to oxidative degradation. The CL results of Eska CK-40 are consistent with the CL of PGU-FB 1000, which confirmed the thermo-oxidative degradation of the core and the cladding as well. We did not record the CL separately for the core and the cladding of Luminous TB-1000 POF, as we could not separate them out.

Thermo-oxidative stability of the unaged POFs and PMMA were investigated in comparison. Fig. 2 shows the respective CL curves. We observed a CL emission difference between the unaged POFs. Unaged Eska POF showed higher CL emission than the unaged Luminous POF suggesting lower stability. Although both POFs consist of a PMMA core they showed marked differences in the height of their CL emission. The only difference we found (at this point of investigation) between these two POFs was a different composition of the cladding. Using

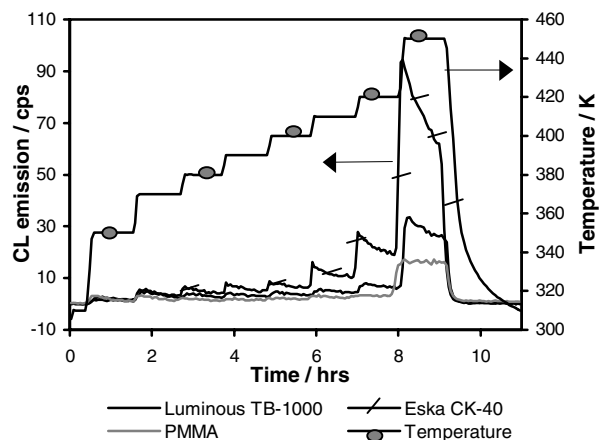


Figure 2: CL spectra of unaged POFs and PMMA

Fourier transform infrared (FTIR) spectroscopy a highly fluorinated polyolefin polymer cladding in Eska POF and a fluorinated acrylate cladding in Luminous POF could be analyzed. Therefore, it can be stated that the difference found in the CL emission of the two unaged POFs was mainly due to the different composition of the cladding of the POFs. No FTIR evidence could be found for a difference in core materials. Unaged PMMA showed lower CL emission than both the unaged POFs, but in a similar range as Luminous POF. The CL measurement results show a higher thermo-oxidative stability of Luminous POF than Eska POF.

Fig. 3 and 4 show the recorded CL curves at 380 K of Eska CK-40 POF and Luminous TB 1000 POF (core with cladding) respectively, exposed under 92 °C / 95 % RH. A decrease in CL emission was observed for the subsequently exposed POF samples (Fig. 3 and 4). The different behavior observed between the two POFs will be explained in terms of the water absorption by the POFs. Both POFs showed a decrease in CL emission for the samples exposed up to their 50 % optical transmission (opt.tra.). At this point it clearly indicates that absorbed water in POFs decreases the CL emission as had been found earlier [6]. For an exposure that resulted in an optical transmission loss of 50 % the observed CL emission drops to remarkable values than for the unaged sample. The subsequent exposure of Eska POF samples to about 0 % transmission and further to 1600 hours shows a trend for an increase of the CL emission almost up to the initial unaged POF sample level (Fig. 3). The opposite trend was observed with Luminous POF. As the water absorption increases the CL emission decreases (Fig. 4).

In Eska POF, the core rather than the cladding mainly influences the absorption of water because the cladding consists of a highly fluorinated polymer, which is known to be hydrophobic [8]. This means that in the cladding almost no water molecules can be accommodated, and hence almost no influence or a very less influence of the

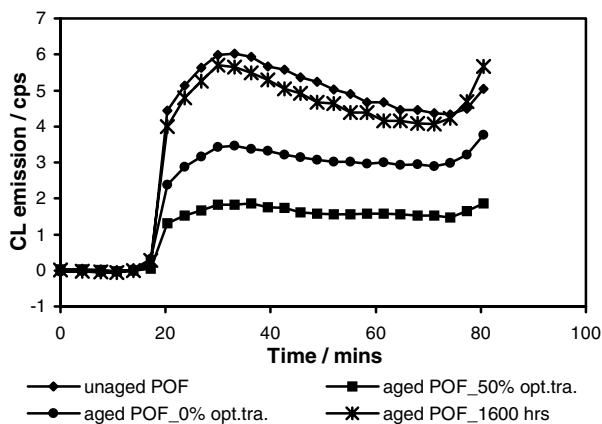


Figure 3: CL spectra at 380 K of Eska CK-40 POF aged under the condition 1

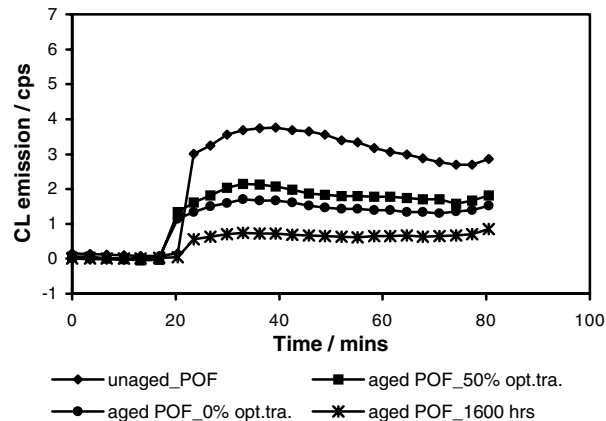


Figure 4: CL spectra at 380 K of Luminous -TB 1000 POF aged under the condition 1

water to the cladding in its thermo-oxidative degradation is to be expected. Therefore, the increasing trend of the CL emission (in comparison to the CL of aged POF_50% opt.tra.) observed in the POFs (aged POF_0% opt. tra. and aged POF_1600 hrs) could be mainly due to the cladding CL emission. This means an increasing rate of degradation of the cladding.

In Luminous POF, the water absorption by the core is more influenced by the cladding. As already mentioned above, Luminous POF cladding consists of fluoro acrylate polymer. The acrylate groups can act as hydrophiles to absorb water, which then can diffuse into the core. Hence, absorbed water in both the core and the cladding influence the CL emission, which decreases as the absorption proceeds (Fig. 4). It shows absorption of water in acrylate polymers has a significant influence on CL emission. It can modify the oxidative degradation reaction scheme during humidity aging of the POFs.

As already discussed above, Luminous POF showed less optical stability than Eska POF. At the condition 1, POFs lost the transmission as the absorption of water increased. Acrylate cladding POF shows faster rate of water absorption than Eska POF. As a result, Luminous POF transmission drops to 0 % earlier than Eska POF. The loss of optical transmission may not be primarily due to thermo-oxidative degradation of the polymer (degradation products cause more absorption of light) [6]. It could also be caused by physical changes (causing scattering loss, e.g. Rayleigh scattering, scattering at the interface, etc.) [1]. One of the properties, which control the transmission of the POFs, is the core diameter [1]. We observed an increase in diameter of the POFs especially of Luminous POF at the aging condition 1, which suggested physical changes also contributed to the total transmission loss of the POFs.

Fig. 5 and 6 represent the CL of the POF samples exposed at 100 °C. Here, too, both the POFs show a decrease in CL emission for the samples that were exposed up to 50%

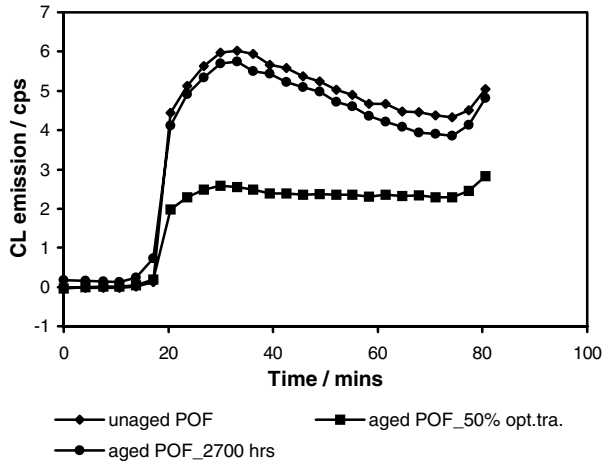


Figure 5: CL spectra at 380 K of Eska CK-40 POF aged under the condition 2

of their optical transmission (aged POF_50% opt.tra.). This decrease in CL emission is proposed for any kind of chemical reaction in competition to oxidative degradation. A possible competing reaction of this kind could for instance the polymerization of monomers, which have remained unreacted in the POFs. Koike et. al. have investigated the scattering loss due to polymerization of the trapped monomers in purified PMMA glass [9]. This suggested an early drop in optical transmission could be due to any sort of scattering of light in POF rather than absorption of light by oxidative degradation products. A small difference was observed in decrease of the CL emission between the two POFs. Luminous POF shows a stronger decrease compared to Eska POF. On the other hand, optical measurement results showed the time to drop off to 50 % transmission in Luminous POF was about 4 hours where as in Eska POF it was about 300 hours. It is reasonable to state that oxidative degradation occurred in Eska POF during this period of time as a

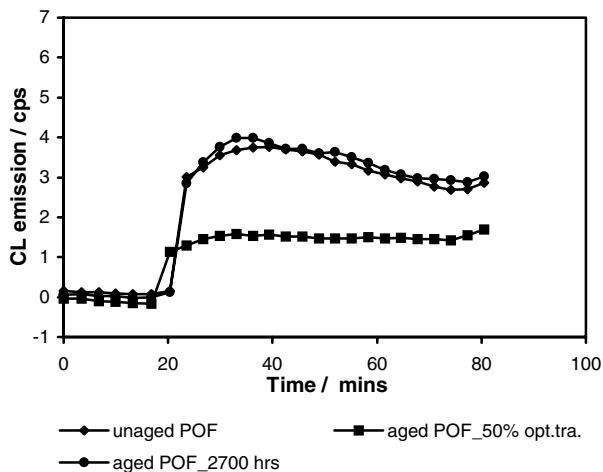


Figure 6: CL spectra at 380 K of Luminous-FB 1000 POF aged under the condition 2

result it showed an increase of CL emission compared to Luminous POF. Further, as the aging time increased more diffusion of oxygen and then oxidative degradation began to occur. Consequently, POFs exposed for 2700 hours showed an increase in the CL emission (Fig. 5 and 6). The cladding contributed to the total CL emission of the POFs. Optical measurement results showed Luminous POF lost more transmission than Eska POF in the early stages of aging at the condition 2. We assume that the early drop off in optical transmission showed by POFs is caused mainly by physical changes (light scattering due to refractive index change, scattering at the core-clad interface, etc.). Then our CL investigation results are in good agreement to the optical transmission measurement results.

IV. CONCLUSION

Optical measurement results show POFs transmission stability of Eska CK-40 is better than Luminous TB 1000 at the aging conditions 92 °C / 95 %RH and 100 °C / low humidity. Thermo-oxidative degradation of the POFs involves both the core and the cladding. Thermo-oxidative stability of Luminous TB 1000 is better than Eska CK-40 as investigated by CL. Absorption of water in POFs reduces the CL emission of POFs. Physical changes (e.g. changes in the core diameter, refractive index changes, and the core-clad boundary imperfections) significantly contribute to the total of transmission loss in POFs. CL can be recommended as a sensitive tool to test the thermo-oxidative stability of the POFs.

REFERENCES

- [1]. W. Daum, J. Krauser, P.E. Zamzow and O. Ziemann, *Polymer Optical Fibres for Data Communication*, ISBN 3-540-42009-6 Springer-Verlag, 2002.
- [2]. Savu, M. Patricia, McAllister, W. Jerome, *U.S. Patent 5,148, 511*, September 1992
- [3]. J. Zubia and J. Arrue, *Optical Fiber Technology*, Vol.7, 101-140, (2001)
- [4]. W. Schnabel, *Polymer Degradation: Principles and Practical Applications*, Hanser Gardner, 1982
- [5]. A. K. Campbell, *Chemiluminescence: Principles and Applications in Biology and Medicine*, Ellis Horwood Ltd., U.K., 1988
- [6]. B. Schartel, S. Krüger, V. Wachtendorf and M. Hennecke, *J. Lightwave Technology*, Vol. 17, No. 11, Nov. 1999
- [7]. V. Wachtendorf, *Untersuchung thermooxidativer Veränderungen an Polymeren durch Chemilumineszenz*, Verlag Dr. Köster, Berlin, Germany, 1997
- [8]. C. A. Sperati, *Polymer Handbook*, ed.: J. Brandrup and E.H. Immergut, Wiley-Interscience, 1989
- [9]. Y. Koike, S. Matsuoka and H.E. Bair, *Macromolecules*, Vol.25, PP 4807-4815, 1992