Climatic Exposure of Polymer Optical Fibers: Thermooxidative Stability Characterization by Chemiluminescence

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ABSTRACT: The optical transmission stability was investigated for commercially available polymer optical fibers (POFs) which were exposed to a climate of 92°C and 95% relative humidity for about 3300 h. The optical transmission stability of POFs was correlated to their thermooxidative stability. POFs possessed identical core material, poly(methyl methacrylate), but they differed in the materials used for the claddings. The optical transmission was measured online using a prototype device called multiplexer. The chemiluminescence (CL) technique was applied to characterize the thermooxidative stability and degradation of POFs. CL analysis reveals the thermooxidative degradation of bare POFs (core and cladding), predominantly of the claddings, as a result of climatic exposure. Ultraviolet–visible transmittance measurements demonstrated more changes in the claddings as compared to the cores due to degradation. The CL and optical measurements data indicated that the optical transmission stability of POFs was dependent mainly on the thermooxidative stability of the claddings and their chemical compositions. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 103: 1593–1601, 2007

Key words: ageing; polymer optical fiber; degradation; chemiluminescence; transparency

INTRODUCTION

Polymer optical fibers (POFs) have been demonstrated as an alternative medium for glass and copper fibers in the area of short-haul optical data communication.[1–3] Despite high attenuation (optical transmission loss) of POFs, they offer a few great advantages such as large core diameter, large numerical aperture, high ductility, and low cost of production. The commercially available step-index (SI) POFs are poly(methyl methacrylate) (PMMA), polystyrene, and polycarbonate based fibers. The graded-index (GI) POFs have gained much attention because of their high optical transmission performance. In recent years, researchers have focused on high-bandwidth and low-attenuation POFs; as a result, the GI fiber Lucina™ has been developed. This specialty POF is based on Cytop®, which is a cyclic perfluoropolymer.[4] Various fluoropolymers are known to use claddings in SI POFs.[5]

The optical transmission loss in commercially available POFs is a contribution of both intrinsic and extrinsic loss factors. Table I shows sources of the loss factors, which have been explained in detail else-

where.[2,3] POFs are employed under various industrial environmental conditions such as high temperatures, high humidity, combination of temperature and humidity, and repeated bending. The optical transmission stability is a key issue under such conditions for long-term applications of POFs and other polymer-based optical components. It is known that the long-term optical transmission performance of POFs under various climatic aging conditions is unsatisfactory as compared to glass fibers.[1] However, the real causes for an increase in the optical transmission loss due to climatic exposure are still not clearly understood, and so this subject is still under debate. In general, any small physical and chemical changes can largely influence the optical transmission stability of POFs. However, in long-term applications, the optical transmission stability is most likely governed by the oxidative stability of polymers that are used for the fabrication of POFs. The core and cladding are the chief components, which have a large influence on the optical transmission of the POF. Therefore, in this work, much attention is paid to study the thermooxidative stability of these components.

The utility of the conventional methods such as Fourier transform infrared (FTIR) coupled with thermogravimetry and differential scanning calorimetry is limited by lack of sensitivity for monitoring the thermooxidative degradation of polymers. On the other hand, the chemiluminescence (CL) technique has been known for many years for monitoring the thermal oxi-

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TABLE I
Optical Transmission Loss Factors of POFs

Loss factor	Source
Intrinsic	Absorption overtones (higher harmonics) and electronic transitions: C—H, C=O, C—C, C—O, C=O, and C=C
	Rayleigh scattering: fluctuations in the density and refractive index, and molecular orientation
Extrinsic	Absorption: transition metals (e.g., Fe and Co), and organic contaminants (e.g., chain-transfer agents)
	Scattering: dust, microvoids and macrovoids, microcracks, bubbles, fluctuations in the core diameter, and core–cladding boundary imperfections

dation in many organic compounds and organic polymers.[6–8] According to the most commonly accepted mechanism, the CL emission is the result of the decay of an electronically excited state carbonyl (ketone) molecule produced during the oxidation. However, as far as the precise molecular pathway to the excited carbonyl is concerned, more than one mechanism has been discussed,[6] but without implications for our current interest. The CL emission is proportional to the oxidation reaction rate, a higher emission meaning lower thermooxidative stability and lower emission meaning higher thermooxidative stability of the polymer under investigation. Since the development of the single-photon-counting technique, CL has been demonstrated to be a powerful tool for investigating the thermooxidative stability of many commodity and engineering polymers especially of polyolefins[9] and polyamides.[10] Recently, it has been successfully extended to study the thermooxidative degradation behavior of PMMA-based POFs[11] and conjugated polymers.[12,13]

This study is focused on correlating the optical transmission loss behavior with the thermooxidative degradation of POFs. As a new effort, by applying the CL technique, the thermooxidative stability before and after exposure to 92°C and 95% relative humidity (RH) has been characterized for bare POFs (core and cladding) and claddings individually. A good correspondence between CL and climatic exposure has been found that the lower the thermooxidative stability of POFs the higher the degradation. The experiments here have demonstrated that the probability of claddings degradation is more as compared to cores. The optical transmission stability of POFs could depend mainly on the chemical compositions of claddings.

EXPERIMENTAL

Materials and climatic exposure/ageing

Two SI POFs with PMMA core were investigated. The fibers were named as S1 and S2. These samples consisted of core, cladding, and jacket. Fibers with this structure are called cables; those without the jacket are called bare fibers. The specifications of the POFs are presented in Table II. With a climatic chamber (VCS 4034-5/S, Vötsch Industrietechnik GmbH, Berlin, Germany), POF cables were exposed to a climate of 92°C and 95% RH for about 3300 h. For chemical investigations, the jackets of POFs were mechanically removed using a wire stripper.

Optical transmission measurements

The optical transmission of POFs was measured during exposure and using multiplexer. The optical transmission at 525, 590, and 650 nm was recorded online. Light-emitting diodes were used as light sources in the multiplexer. The working principle of the multiplexer can be found in refs. 1 and 14. For the present exposure test, 12 m as a standard length of POF cables was selected. Out of 12 m length, 10 m was placed inside the climatic chamber for exposure, whereas the ends (each 1 m length from the chamber) were connected to the multiplexer standing outside the chamber.

Cladding extraction

To separate the cladding from the rest of the POF, first, jackets of POFs were removed manually using a wire stripper. Then, bare POFs were cut into small pieces (2–4 cm long) and soaked in chloroform for 15–20 h at ambient temperature for the complete dissolution of the core. We found this as the best way of separating the cladding from the core. The nondissolved claddings were separated from the core solutions by the ordinary filtration using a Whatman filter paper, washed three to four times with the same solvent and then pressed between soft papers to remove the excess solvent. Finally, the remaining solvent was removed via drying at below 55°C in a vacuum oven. In this way, the obtained claddings appeared as hollow cylinders.

CL

Instrumentation

A computer-controlled, self-constructed, and simple setup was used for the present investigation. The

TABLE II
Specifications of POFs

POF	Manufacturer	Core	Cladding[a]	Jacket
S1	Toray Industries, Inc. (Osaka, Japan)	PMMA	Highly fluorinated polyolefin or copolymer of olefins	PA12
S2	Mitsubishi Rayon Co., Ltd. (Tokyo, Japan)	PMMA	PFA	PE

[a] Experimental findings.

block diagram of the CL instrumentation is shown Scheme 1. It consisted mainly of an airtight sample chamber coupled to a thermostat heater, which was controlled within ±0.1 K using a temperature controller (Model 340, Lake Shore Cytronics Inc., Westerville, OH), a photomultiplier tube (PMT) (Model R1527P, Hamamatsu Photonics K. K., Hamamatsu, Japan), and a single-photon-counting detector (EG&G/Ortec, Oak Ridge, TN). A detailed instrumentation of the CL setup can also be found in ref. 15.

Sampling

Both, bare POFs and claddings, were cut into 2–3 mm pieces and horizontally mounted on a clean aluminum pan in the sample chamber. Almost a constant weight (equivalent to a constant volume-to-surface ratio) was maintained for all the samples.

Measurements

Temperature ramp measurements were conducted in a temperature range of 107°C (380 K) and 177°C (450 K). CL curves were recorded under a constant flow rate of pure oxygen gas. Blank CL measurements for the empty aluminum pan were conducted to ensure that the background emission would not reach sample emission levels.

Ultraviolet–visible (UV–vis) transmittance measurements

UV–vis transmittance spectra were recorded with a Varian Cary 300 instrument. To register the spectra of the cores, solutions were prepared using a spectrograde dichloromethane. Claddings prepared as previously described above (see the Cladding Extraction section) were directly used for recording the spectra.

RESULTS AND DISCUSSION

Optical transmission loss behavior

The results of the optical transmission measurements are depicted in Figure 1. The presented data were obtained by the averaging of the three wavelength transmissions measured as a function of time during exposure of POFs to 92°C and 95% RH. The data clearly evidence a difference in the optical transmission stability between S1 and S2, although they possessed identical core material, PMMA. S2 exhibited higher stability than S1. Additionally, the transmission loss behaviors displayed by these two were dissimilar. In this and subsequent paragraphs, the term *transmission* is used instead of *optical transmission* of POFs for easy understanding.

Within about 50 h of exposure, the transmission of both POFs decreased to a certain extent (ca. 6%), and during this reduction, they exhibited a similar loss behavior (Fig. 1). These observations are similar to the findings of Daum and coworkers,[1,16] who attributed this initial transmission reduction to a fluctuation of humidity in POFs. Schartel et al.[11] attributed it to chemical changes by the oxidation of low-molecular-weight species present in the fiber. In our previous work, a similar exposure experiment on various bare POFs with a PMMA core showed that physical influences such as shrinkage and an increase in diameter of POFs, were most likely to cause the initial transmission reduction.[17] However, CL experiments carried out here to the unexposed samples indicate the presence of low-molecular-weight species or chemisorbed water (see the CL of the unexposed POFs). Hence, the observed initial transmission reduction is attributed to primarily physical changes and secondarily to chemical changes.

After the small transmission reduction at the start of exposure, the transmission loss behavior of POFs
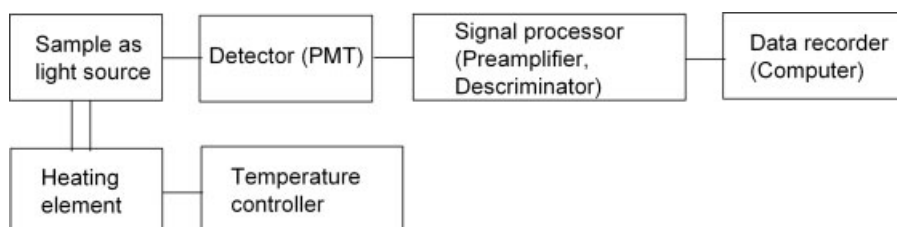
Scheme 1 Block diagram of the CL instrumentation.
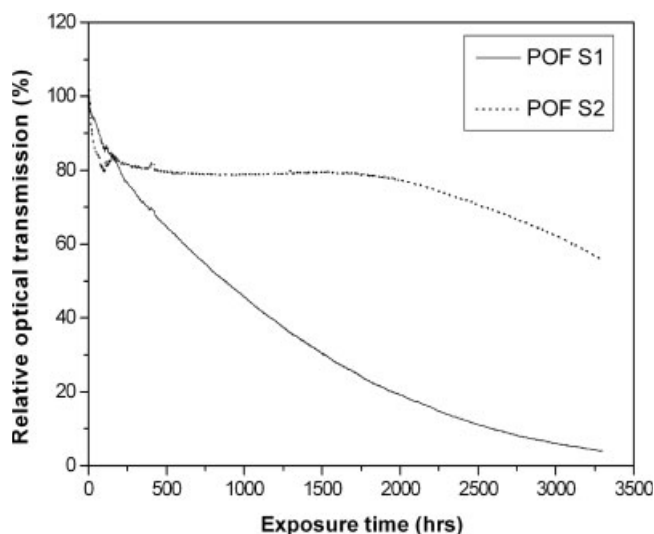
Figure 1 Relative optical transmission of POFs measured during exposure to 92°C and 95% RH.

was different (Fig. 1). Both exhibited a continuous decrease in transmission, but S1 registered a higher time dependency than S2. At some point in the initial stages, S2 displayed a reversible increase and decrease to a certain level and then a very slow decrease, whereas S1 demonstrated a continuous fast decrease with the exposure time. The variation of transmission of S2 is assigned to mainly physical changes, as chemical reactions alone would show a monotonic decrease in transmission. Physical changes are most likely due to the presence of humidity, and the extent of a reversible transmission change could depend on material properties of the core, the cladding, and the jacket. However, from the position of the slow decrease and continuous fast decrease of transmission of S2 and S1 respectively (Fig. 1), the changes are attributed to mainly the thermooxidative degradation of the polymer.

CL

The investigated bare POFs as well as claddings exhibited CL with no induction period in the selected temperature range. Because the CL emission is proportional to the rate of the oxidation, it can directly measure the thermooxidative stability of a sample under investigation. Because for the investigated samples the original physical form and a constant initial weight were maintained, the results are comparable. In our previous work, we demonstrated that the total CL emission from the bare POF was the contribution of both core and cladding.[18]

CL of the unexposed bare POFs

CL curves for the unexposed bare POFs S1 and S2 were recorded separately and are presented in Fig-

ure 2. Although both samples possessed the PMMA core, they evidenced unequal thermooxidative stability (Fig. 2). The investigated samples showed similar characteristics with respect to the initial peak and plateau behavior. Schartel and coworkers[11,13] reported similar results, showing the consistency of the CL method. At the initial temperature step (107°C), the CL peak emission from S2 was more or less equal to that of S1. However, the observed initial peak behavior of both samples can be attributed to the extent of consumption of low-molecular-weight species such as monomer present in the polymer matrix reacting with oxygen and/or to the reaction of a fraction of the polymer accessible in excess with already available or trapped oxygen. This reaction may be independent of the diffusion of surrounding oxygen. Strlic et al.[19] studied CL of cellulose and reported such an initial peak, which was mainly due to chemisorbed water in the polymer. If the second interpretation is adopted, the observed initial peak would represent an amount of the absorbed humidity in the present samples. Out of the pathways of both interpretations (monomer or chemisorbed water), it can be concluded that a small difference in the CL emissions from S1 and S2 was due to fiber processing and conditioning histories.

In the subsequent temperature steps, the CL plateau emission from S2 was greater than that of S1, but both showed an increasing trend. The CL plateau emission can be regarded as the availability of polymer molecules to the thermally activated oxidation, given that the oxygen diffusion is constant. The possible explanations for the increasing trend are, an increase in the mobility of the polymer chains that are spatially separated and an increase in the diffusion or dissolution of oxygen in the polymer matrix. The chain mobility could be additionally increased by the plasticizing effect of degradation products. At higher temperatures (167°C and 177°C), the plateau behavior
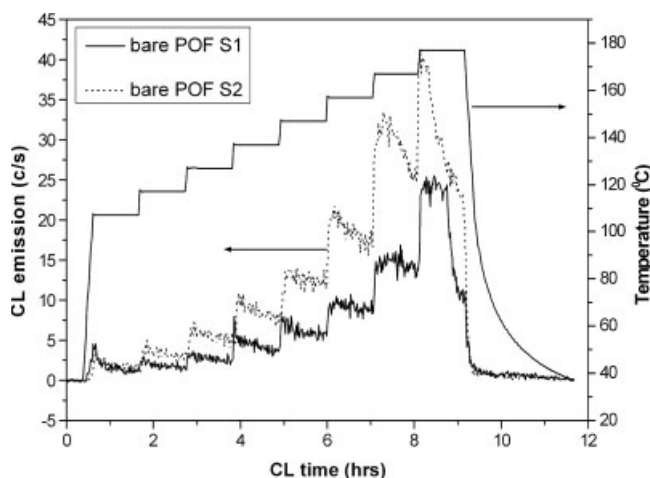
Figure 2 CL of the unexposed bare POFs.

of S2 was marked to vanish but attained a broad maximum and then decreased. This may not be surprising because higher temperatures could result in accumulation of reaction products that can quench the excited-state carbonyls; as a result, a fast decay rate of the CL emission can be expected.[20] The decay rate could be enhanced by the mobility of both excited-state molecules and oxidation products, due to melting of the polymer. The influence of temperature on the decay rate can be seen in Figure 2 that S2 showed CL emission with less pronounced declining slope at 167°C than at 177°C. However, a detailed investigation has to be carried out to confirm these characteristics.

The CL emission from S2 was higher, and it appeared less thermooxidative stable than S1. The difference in the CL emissions between the two samples is attributed to predominantly a difference in the chemical compositions of the claddings because the core polymer of both fibers was PMMA. Additional influencing factors could be the polymer formulation and polymer manufacturing and fiber drawing conditions. However, these issues are less significant because POF producers can use similar formulations and drawing conditions to achieve transparency as high as possible. Hence, the claddings should be responsible for the observed difference in CL of bare POFs. We also believe that the CL behavior of a bare POF is almost a model of its cladding CL, except for the lower emission, mainly because of the sample physical structure. CL of the claddings is discussed in the subsequent sections. It is well known that the core (950–980 μm in diameter with closed geometry) is a major part of the bare POF. But, oxidation (with new oxygen from the surrounding) of a bare POF starts first at the cladding (20–50 μm thick) and then at the core because the cladding acts also as a protective layer. Therefore, it is possible to assume that the thermooxidative degradation of the core should depend mainly on the oxygen diffusion constant of the cladding material. The subsequent results indeed demonstrate the importance of claddings in the thermooxidative degradation of POFs.

CL of the unexposed claddings

CL of the unexposed claddings S1 and S2 is presented in Figure 3. For both samples, similar CL characteristics (peak and plateau behavior) were observed as in the case of bare POFs. The CL emission from cladding S2 was higher, showing its lower thermooxidative stability as compared to cladding S1. These results are consistent with CL of bare POFs. Hence, it can be a qualitative but clear indication that the CL emission from the bare POF results mainly from the cladding. These results are in good agreement with our previous results obtained for various POFs.[18]
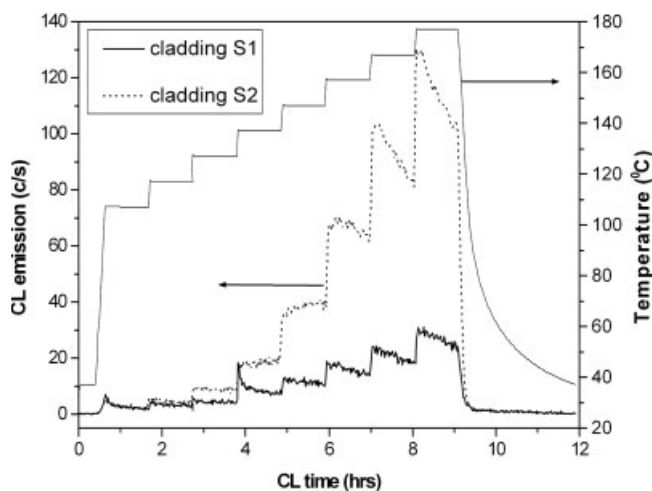

Figure 3 CL of the unexposed claddings.

Comparing the CL of the unexposed bare POFs and their corresponding claddings, it was observed that the total CL emission from the claddings was all the time higher than that of bare POFs. A few factors are involved, regardless of the chemical composition difference between the core and cladding. The physical factors that strongly appear could be the hollow structure with cylindrical geometry and the thickness. Because of the hollow structure, the diffusion of oxygen from all directions appears to be more efficient to the sample. Because of the smaller thickness of the cladding as compared to the core, the dissolution of oxygen can be promoted by the efficient diffusion. Therefore, these factors could largely influence the degradation rate of the cladding. The influences seemed to be more effective at higher temperatures (Fig. 3), implying an increase in the diffusion rate and chain mobility.

While assuming that the physical structural factors are the major causes for the higher CL emission from the claddings as compared to bare POFs, the difference in the CL emissions between the claddings could be due to a difference. Using FTIR spectroscopy, the chemical compositions of the unexposed claddings were characterized. It was found that cladding S1 should be either a highly fluorinated polyolefin or a copolymer of fluoroolefins, and cladding S2 should be a poly(fluoroalkyl acrylate) (PFA). The CL data revealed that the PFA polymer was more prone to the oxidative degradation than a highly fluorinated polyolefin or a copolymer of fluoroolefins. One primary reason could be the availability of C—H groups (number or —I, inductive effect of groups at the α position) for the subsequent oxidation. Additionally, other factors such as chain branching and functional groups could influence the CL emission and its behavior as well.[21,22] Thus, different cladding materials oxidize to different levels; as a result, POFs could ex-

hibit uneven thermooxidative stability despite their identical core material. Accordingly, the extent of oxidative degradation of the core depends mainly on the material types as well as the thickness of the cladding, which is the starting component in the oxidative degradation of the bare POF.
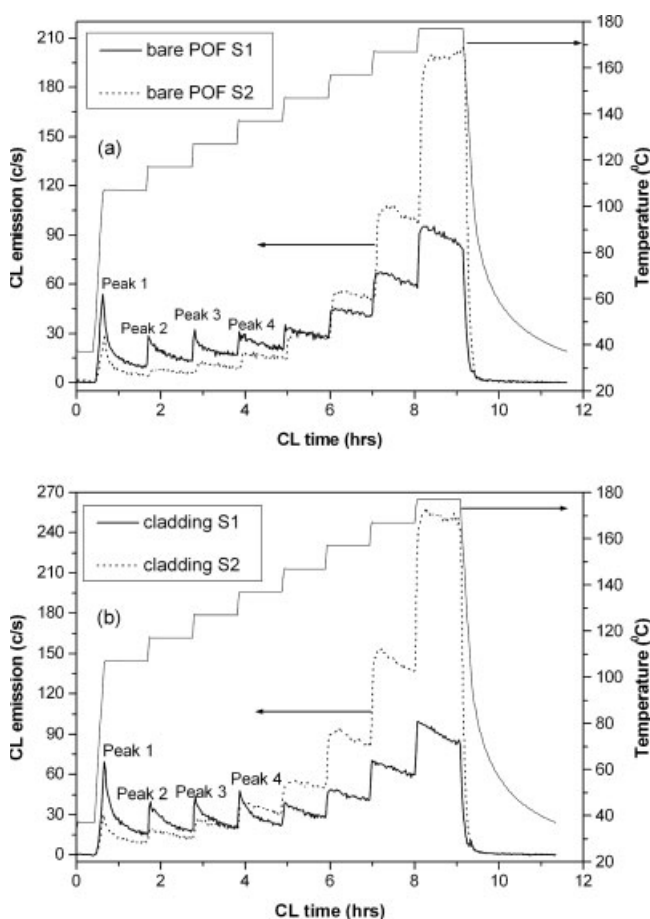
CL of the exposed bare POFs and claddings

The exposed bare POFs as well as claddings exhibited a few changes due to climatic exposure. Figure 4(a,b) shows the respective CL curves. The results indicate that the CL emission was much higher for the exposed samples than for the unexposed ones. This undoubtedly evidences that the taking place of degradation was a result of climatic exposure. CL of the exposed bare POFs as well as claddings showed an intense, sharp peak at 107°C (peak 1, Fig. 4). However, exposed POF S1 exhibited continuous peaks (peaks 2–4) in contrast to plateaus of POF S2 at the subsequent temperature levels (117°C, 127°C, and 137°C). The CL peak behavior clearly implies that one of the reactants was consumed during the oxidation process. The reactants could be one or more of the involved low-

molecular-weight degradation products formed as a result of thermooxidative degradation. The different peaks (peaks 1–4) could be interpreted as being due to the difference in the oxidizing abilities of various degradation products. The CL emission of peak 1 may be independent of the diffusion of external oxygen because, in the polymer matrix, using up the dissolved oxygen itself may still be adequate to generate peroxy radicals. To study the potential influence of the external oxygen, we investigated CL of the exposed bare POFs under nitrogen atmosphere instead of oxygen. The reappearance of peak 1 was found, though with a lower emission and a much lower emission of all subsequent peaks and plateaus. This shows that the requirement of enough oxygen is necessary to oxidize reactants completely. Nevertheless, the exposed samples peak behavior can be a direct indication of readily oxidizable products, and so the peak intensity could be a measure of the extent of consumption of these products at a particular temperature.

The evaluation of the CL emission from the exposed samples shows that S2 (both bare POF and cladding) demonstrated a lower emission than S1 at the initial four temperature steps (Fig. 4). In the subsequent temperature steps, S2 exhibited much higher emission than S1. This suggests that CL of S2 might involve one or more degradation mechanisms. The thermal aging of polymers can lead to both degradation and crosslinking reactions.[23] In view of this fact, the intensity of peak 1 of S2 could be explained by the decomposition of the degradation products that are accumulated only at the surface of the sample. Consequently, the first three plateaus can be attributed to primarily the thermally activated oxidation of the available part of the crosslinked polymer, and their emission rate is controlled by the diffusion rate of oxygen. Because the crosslinks reduces the diffusion rate, the emission for the first three plateaus was lower than S1. However, it was higher than the corresponding unexposed samples, probably due to the decomposition of residual surface accumulated degradation products. For the subsequent temperature levels (from 147°C to 177°C), the CL emission from S2 started increasing and was much higher than S1. This can be attributed to the decomposition of dissolved degradation products in the polymer matrix and an increased rate of oxygen diffusion. Because of the high temperature, the polymer can melt. As a result, the plasticizing effect of the polymer melt could additionally influence the diffusion rate.

On the basis of the above discussion, the interpretation of the CL data so far can be summarized as follows. Up to the temperature level of 140°C, S1 exhibited four consecutive peaks with higher emission and following plateaus with lower emission than S2. Degradation is evidenced by the fact that the CL emission

Figure 4 CL of the exposed (a) bare POFs and (b) claddings.

from the exposed samples was higher than the corresponding unexposed ones. The CL peaks imply mainly the consumption of available readily oxidizable active species that newly become accessible upon a new, higher temperature level first being reached. The following plateaus emissions are derived mainly from the oxidation of an available part of the polymer under stationary conditions and is governed by the individual diffusion rate of (new) oxygen in the sample. In comparison with the variation (first decrease and then increase) of the CL emission displayed by exposed S2, S1 furnished no such results. Therefore, this suggests that the thermooxidative degradation could be the main result of climatic exposure of S1 in contrast to both thermooxidative degradation and crosslinking of reactions in S2.

The comparison of the total CL emission (integration over time) shows a higher value for S2 than for S1. It clearly evidences that the extent of the thermooxidative degradation of S2 was higher than S1. This outcome is in agreement with CL of the unexposed samples; that is, S2 exhibited lower thermooxidative stability as compared to S1.

Of course, other factors such as humidity and POF jacket were not taken into account in the CL experiments of the unexposed samples, although the actual climatic exposure test was conducted in the presence of them. These factors could influence CL of the bare POF and the cladding as well. Not much data is available regarding the influences of the aforementioned factors. However, Schartel et al.[11] found a decrease in CL emission as a result of water absorption in POFs. This was not found in the present CL experiments. Nevertheless, it is known that the water absorption in polymers such as acrylate polymers can lead to both physical and chemical changes.[24,25] Polymer swelling can be a physical change, for instance. No considerable swelling was observed in the present POFs. Water can be chemically interacted via hydrogen bonding and can very slowly hydrolyze functional groups such as esters. These changes may be expected in these samples, more particularly in cladding S2 (PFA) and in the PMMA core and only to a much lower extent in cladding S1 (a highly fluorinated polyolefin or a copolymer of fluoro-olefins). Such chemical changes could lead to a complex thermooxidative degradation mechanism that ultimately results in the formation of complex degradation products. Accordingly, an exact qualitative explanation for CL of the exposed samples may be very complicated. Nonetheless, our CL experiments show that the absorption of water in POFs results in an increased rate of degradation.

The POF jacket could also influence the rate of thermal oxidation by controlling the rate of oxygen diffusion and water vapor during exposure. Therefore, the materials of the jacket could play an important role in the thermooxidative degradation of the core and cladding. Polyamide 12 (PA 12) and polyethylene (PE) were the jacket materials of POFs S1 and S2 respectively (Table II). It is known that the oxygen diffusion coefficient of PE is higher than PA 12, whereas the water absorption rate in PA 12 is higher than PE.[26] Although this information provides a broad idea about the potential influences of jackets on degradation of POFs, the real effects were found to be difficult to assign because the cladding materials used here were different. Additionally, jackets themselves can degrade by climatic exposure; as a result, their material properties will vary to different extents. Nevertheless, the real causes of individual factors, the humidity and jacket remain challenging for a future research.

It was found in CL of the unexposed samples that CL of bare POFs (Fig. 2) was almost a replica of CL of cladding (Fig. 3). Extremely consistent qualitative results were obtained from CL of the exposed samples (Fig. 4). Hence, our CL results strongly support the statement that climatic exposure of POFs leads to the thermooxidative degradation predominantly of the cladding and only to a minor degree of the core.

UV–vis transmittance

The exposed bare POFs, especially S2, appeared yellowish, in contrast to the colorless unexposed ones. This was thought to be a change of the color mainly in the cores. But the separation of the claddings from the cores by the solution method revealed a yellowish color of the claddings. The UV–vis transmittance measurements clearly evidenced large changes in the claddings and only small changes in the cores as a result of climatic exposure (Figs. 5 and 6). This data clearly showed the higher degradation of the claddings as compared to the cores. However, the small transmittance change between the cores was considerable, showing that core S2 was more affected than core S1 [Fig. 5(a,b)]. Both claddings showed more changes in the far-UV and near-visible regions of the spectrum (Fig. 6). Cladding S2 showed a big drop of the transmittance in the region between 220 and 500 nm, which strongly suggested that this new absorption of light should be due to a variety of chromophores formed due to degradation. Overall, the UV–vis experiments data is in accordance with the CL experimental results with respect to climatic exposure of POFs results in more probable degradation of claddings.

Optical transmission loss: possible explanations

CL and UV–vis experiments evidenced the thermooxidative degradation of POFs, predominantly of claddings as a result of climatic exposure. We propose
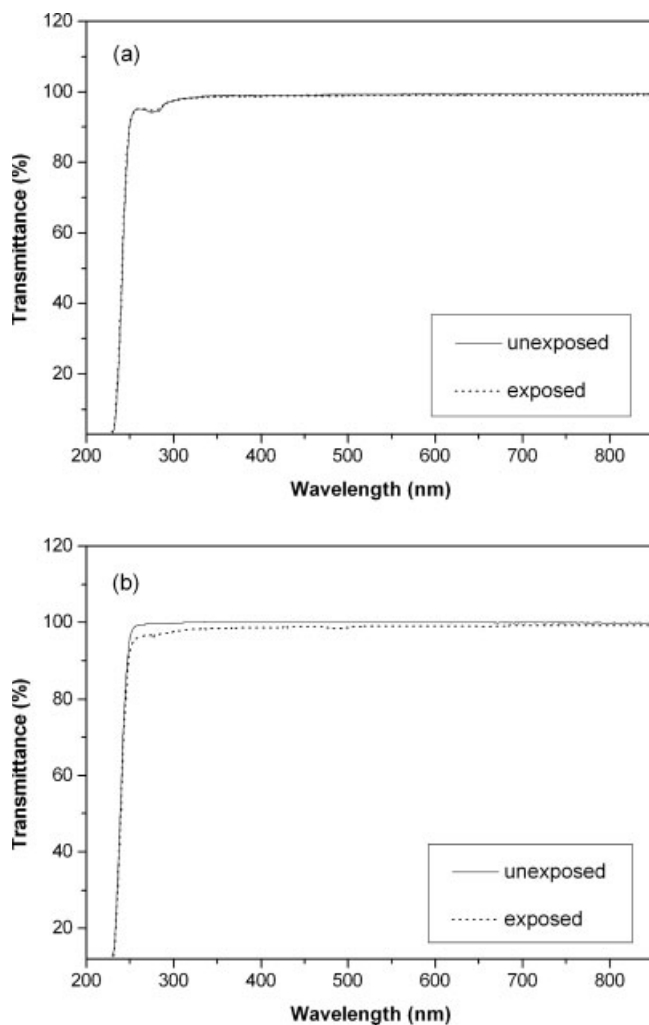
Figure 5 UV–vis transmittance spectra of the unexposed and exposed cores: (a) S1 and (b) S2.

that the observed loss of optical transmission of POFs could be derived chiefly from an increase in the light absorption by degradation products of the cladding and light scattering due to core–cladding boundary imperfections. However, we also do not omit the fact that a small degradation of the core could lead to an increase in the optical transmission loss.

Takezawa et al.[27] reported that aging of (cross-linked) PMMA-based POFs at 150°C resulted in thermooxidative degradation of the core, due to which a significant loss of the transmission was observed. They proposed that the loss of transmission was mainly due to an increase in light absorption by the conjugated carbonyl compounds as degradation products.

This strongly agrees with our hypothesis that a loss of transmission of POFs is due to increased light absorption by mainly the cladding and to a minor extent the core. As the cladding is more degraded than the core, it can contribute to a large extent to the total loss. This can be explained in the following way: both evanescent light and refracted light due to

imperfections (e.g., by degradation) at the core–cladding boundary can be absorbed in the cladding. As a result, the basic fiber-optic phenomenon, total internal reflection, within the fiber might be substantially reduced, and this causes a significant transmission loss.

On the other hand, degradation of the cladding also could lead to a change in the adhesion strength, the extent of which may depend on cladding materials. It is known in the POF technology that one of the main requirements for cladding is good adhesion, as this significantly determines the functional property of the POF.[2,28] Therefore, improper adhesion could lead to core–cladding boundary imperfections causing scattering of light resulting in an increase in the transmission loss. Accordingly, climatic exposure could decrease the adhesion strength of the cladding of both POFs. Although more degradation of cladding S2 as compared to S1 was found, contrary in transmission loss was exhibited by the POFs. That is, POF S1 registered higher transmission loss than POF S2 (Fig. 1).
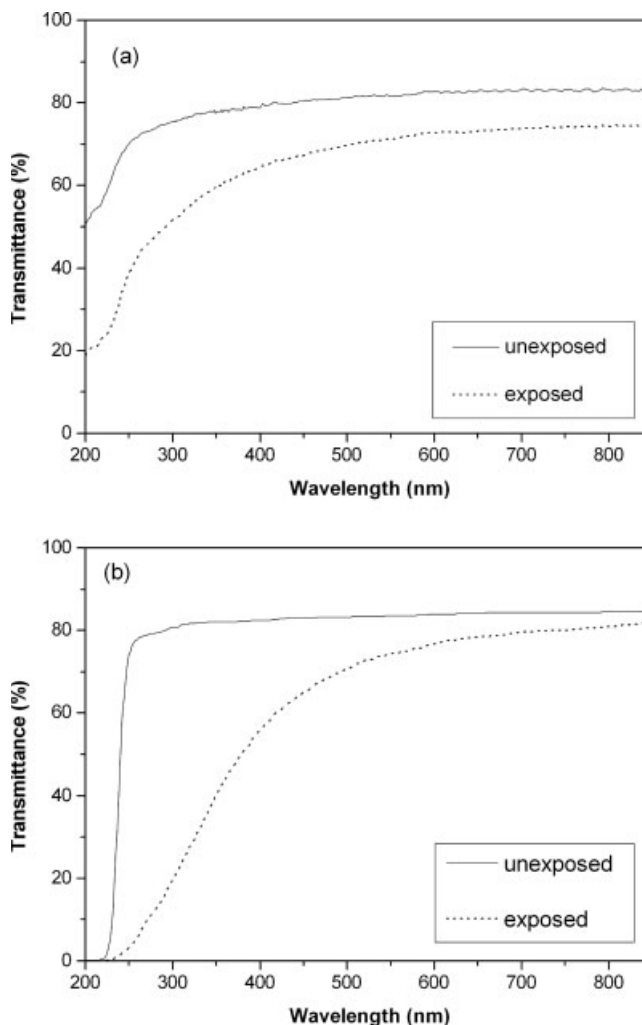
Figure 6 UV–vis transmittance spectra of the unexposed and exposed claddings: (a) S1 and (b) S2.

Therefore, it is highly possible that the adhesion strength of cladding S1 should be decreased to a larger extent than S2 because both POFs had the identical core material. It becomes obvious that mainly the chemical nature of the cladding materials determines the adhesion property of the cladding. However, the respective quantitative contributions of each source to the total transmission loss remains to be studied in a future research.

CONCLUSIONS

We successfully applied the CL technique to characterize the thermooxidative stability and degradation of POFs that were exposed to 92°C and 95% RH for about 3300 h. Very consistent results were obtained from CL and UV–vis transmittance experiments. The climatic exposure of POFs resulted in a larger extent of degradation of the claddings and a smaller extent of degradation of the cores. The thermooxidative stability and therefore the optical transmission stability of POFs were found to depend primarily on the materials used for the claddings. However, the extent of degradation of the POFs could depend largely on the jacket materials and surrounding humidity. An increase in light absorption due to electronic transitions within the degradation products is proposed to be the major cause for the optical transmission loss. It can be suggested that a loss of adhesion strength of claddings could further significantly increase the transmission loss of POFs. But, the degree of the optical transmission loss could depend chiefly on the cladding chemical composition. With these findings, we propose that CL can be used as a sensitive tool to investigate the relative thermooxidative stability of POFs.

References

1. Daum, W.; Krauser, J.; Zamzow, P. E.; Ziemann, O. Polymer Optical Fibers for Data Communication; Springer-Verlag: Berlin, 2002.
2. Kaino, T.; Koike, Y.; Thesis, J.; Brockmeyer, A.; Groh, W.; Stehlin, T. F. In Polymers for Lightwave and Integrated Optics; Hornak, L. A., Ed.; Marcel Dekker: New York, 1992.
3. Zubia, J.; Arrue, J. Opt Fiber Technol 2001, 7, 101.
4. Murofushi, H. Proceedings of the 5th International Conference on Polymer Optical Fibers (POFs), and Applications, Paris, France, Oct 22–24, 1996; p 17.
5. Savu, P. M.; McAllister, J. W. U.S. Pat. 5,148,511 (1992).
6. Campbell, A. K. Chemiluminescence: Principles and Applications in Biology and Medicine; Ellis Horwood: Chichester, England, 1988.
7. Ashby, G. E. J Polym Sci 1961, 50, 99.
8. Zlatkevich, L.; Geroge, G. A. In Luminescence Techniques in Solid State Polymer Research; Zlatkevich, L., Ed.; Marcel Dekker: New York, 1989.
9. Kohler, D. R.; Kröhnke, C. Polym Degrad Stab 1999, 63, 165.
10. Lanska, B.; M-Rychla, L.; Rychly, J. Polym Degrad Stab 2001, 72, 249.
11. Schartel, B.; Krüger, S.; Wachtendorf, V.; Hennecke, M. J Lightwave Technol 1999, 17, 2291.
12. Wachtendorf, V. Untersuchung Thermooxidativer Veraenderungen an Polymeren Durch Chemilumineszenz; Verlag Dr. Köster: Berlin, 1997.
13. Schartel, B.; Hennecke, M. Polym Degrad Stab 2000, 67, 249.
14. Günther, B.; Czepluch, W.; Mäder, K.; Zedler, S. Proceedings of the 9th International Conference on POFs, Boston, MA, Sept 5–8, 2000; p 209.
15. Wachtendorf, V.; Jansen, K.; Schulz, U.; Tjandraatmadja, G. Proceedings of the 9th International Conference on the Durability of Building Materials and Components, Brisbane, Australia, March 17–21, 2002; p 239.
16. Ziemann, O.; Daum, W.; Brauer, A.; Schlick, J.; Frank, W. Proceedings of the 9th International Conference on POFs, Boston, MA, Sept 5–8, 2000; p 173.
17. Appajaiah, A.; Kretschmar, H.-J. Proceedings of the 3rd International IEEE Conference on Polymers and Adhesives in Microelectronics and Photonics, Montreux, Switzerland, Oct 21–23, 2003; p 57.
18. Appajaiah, A.; Wachtendorf, V.; Jankowski, L. Proceedings of the 12th International Conference on POFs, Seattle, WA, Sept 14–17, 2003; p 152.
19. Strlic, M.; Kolar, J.; Philar, B.; Rychly, J.; M-Rychla, L. Polym Degrad Stab 2001, 72, 157.
20. Broska, R.; M-Rychla, L.; Rychly, J.; Mendenhall, G. D. J Photochem Photobiol A 1997, 109, 101.
21. Schard, M. P.; Russell, C. A. J Appl Polym Sci 1964, 8, 985.
22. Yoshinaga, T.; Tanaka, Y.; Ichimura, T.; Hiratsuka, H.; Kobayashi, M.; Hoshi, T. J Lumin 1998, 78, 221.
23. Schnabel, W. Polymer Degradation: Principle and Practical Applications; Hanser Gardner: Berlin, 1981.
24. Turner, D. T. Polymer 1982, 23, 197.
25. Ping, Z. H.; Nguyen, Q. T.; Chen, S. M.; Zhou, J. Q.; Ding, Y. D. Polymer 2001, 42, 8461.
26. Pauly, S. In Polymer Handbook, 3rd ed.; Brandrup, J.; Immergut, E. H., Eds.; Wiley-Interscience: New York, 1989.
27. Takezawa, Y.; Tanno, S.; Taketani, N.; Ohara, S.; Asano, H. J Appl Polym Sci 1991, 42, 2811.
28. Kaino, T.; Fujiki, M.; Nara, S.; Oikawa, S. U.S. Pat. 4,381,269 (1983).