

Aging Behavior of Polymer Optical Fibers: Degradation Characterization by FTIR

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ABSTRACT: The optical transmission loss behavior was investigated for commercially available poly(methyl methacrylate) (PMMA) based polymer optical fibers (POFs). POFs were exposed to various climates of temperature and humidity. Optical transmission measurements using multiplexer (a prototype device) reveal that POFs exhibited an early drop-off followed by a slow decline of transmission at 100°C with low humidity and nearly 100% loss of transmission at the early stages of exposure at 92°C with 95% relative humidity (RH) and at 120°C with low humidity. Fourier transform infrared (FTIR) and gel permeation chromatography (GPC) analysis data show no significant molecular changes in the PMMA core after climatic exposures. However, the attenuated total reflection (ATR)-FTIR data shows a few molecular changes in

claddings due to degradation. Scanning electron microscopy (SEM) data illustrate the shrinkage and folding structure in claddings. The loss of the optical transmission at the early (initial) stages of exposure is attributed to the physical changes (like thermal expansion), and the same at the later stages mainly to chemical changes (e.g., oxidative degradation). The experiments conducted here show that the POFs optical transmission stability is strongly dependent on the chemical composition of claddings. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 103: 860–870, 2007

Key words: polymer optical fibers; aging; reliability; optical transmission stability; degradation; Fourier transform infrared

INTRODUCTION

Because of the large core diameter, large numerical aperture (NA), high ductility, and low cost of production, polymer optical fibers (POFs) have great potential to replace glass optical fibers and copper cables in the area of short distance optical data communication.^{1–6} The optical loss factors of POFs are grouped mainly into intrinsic and extrinsic loss factors. Table I shows the sources of the loss factors, which are discussed in more detail elsewhere.^{1,2} Amorphous glassy polymers, such as PMMA, polycarbonate (PC), and polystyrene (PS), are the traditional polymers used as core materials for fabricating step-index (SI) as well as graded-index (GI) POFs.^{1–4} The recent breakthrough in higher bandwidth achievement using GI-POFs motivated the researchers to develop new core materials. As a result, CYTOP[®], a perfluoropolymer is developed recently and is used as a core material for fabricating GI-POFs.^{7,8} Fluoropolymers are usually applied on top of the core as a cladding layer in POFs.⁹

POFs are considered as new technical products and are known to have long-term applications under various climates (e.g., high temperature, high humidity,

and combination of high temperature and humidity).^{1,10} The optical transmission stability is a key issue for POFs as well as for other polymer-based optical components. Because of the organic chemical nature of POFs, the optical transmission stability under various climates is lower than inorganic glass fibers; however, its transmission loss mechanism is not fully understood.¹ Hence, further research on the influence of climatic stress factors on the transmission stability of POFs is required to estimate their reliability for long-term applications. The optical transmission property of a POF is derived mainly by the material properties of the core and cladding. Accordingly, the POF optical performance depends strongly on the physical and chemical changes that occur in the core and cladding materials after climatic exposure. It is known that the functional property of polymeric waveguides is extremely sensitive to both physical and chemical changes of their materials.¹¹ A good number of publications report the influences of climatic parameters on optical properties of polymer optical components.^{12–15} But there are only a few reports on degradation studies of PMMA-based POFs.^{16–19} The results of these studies show that an increase in the optical loss (or attenuation) is due to increased light absorption by degradation products.

It is well-established that changes in physical and chemical properties of polymer substances take place due to degradation as a result of outdoor exposure.^{20,21} Oxidation is a typical phenomenon that takes place in

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TABLE I
Optical Transmission Loss Mechanism in POFs

Loss factors	Sources
Intrinsic	Absorption: (i) absorption overtones: C–H, O–H, C=O, C–C, C–O, etc.; (ii) electronic transitions Rayleigh scattering: fluctuations in density and refractive index, and molecular orientation.
Extrinsic	Absorption: transition metals, organic contaminants, etc. Scattering: dusts, micro- and macrovoids, microcracks, bubbles, fluctuations in core diameter, core-cladding boundary imperfections, etc.

many organic compounds and in polymers in the presence of oxygen.²¹ Climatic parameters such as temperature and humidity can invariably influence the degradation behavior of a polymer that is exposed to outdoor. FTIR is applied as a useful tool to study the degradation and water sorption processes in various polymers including PMMA and fluoropolymers.^{22–26} Such kind of FTIR studies especially on polymer films were made more effective in combination with ATR technique.^{22–24,27,28}

In this work, the optical transmission loss behavior of three POFs under three different climates was investigated. Significant changes were observed in the claddings in contrast to the cores. The data shows that the optical transmission stability of POFs under different climatic conditions is largely dependent on the chemical composition of claddings. The physical and chemical causes for the loss of transmission in POFs are discussed.

EXPERIMENTAL

Materials and aging or exposure tests

Three POFs having SI profile were used. All the POFs were 1 mm in diameter but the core diameter was about 980 μm and the cladding thickness was about 20 μm . POFs that contained the structure of core and cladding were referred to as bare fibers. Fibers and their components (core and cladding) were named as S1, S2, and S3. The fibers S1, S2, and S3 were purchased from Asahi Chemicals, Toray Industries, and Mitsubishi Rayon of Japan, respectively. The core and cladding of the above-mentioned fibers were PMMA and a fluoropolymer respectively. As these were the materials data provided by the manufacturers, the experimental findings here show that claddings possessed different fluoropolymer compositions (see FTIR Analysis, Fig. 4).

Three exposure or aging conditions were applied using a climatic chamber and an oven for a period of 30 h to 4500 h. The exposure conditions were as given below. Here low humidity means relative humidity of < 50%. An exposure condition of high

temperature with low humidity was referred to as dry condition.

1. 92°C/95%RH
2. 100°C/low humidity
3. 120°C/low humidity

Optical transmission measurements

The optical transmission of POFs was measured using a prototype multiplexer device.^{3,29} The multiplexer consists of mainly three parts; light source unit, detector unit, and positioning system. Three light emitting diodes (LEDs) were used as light sources in the visible region, 525, 590, and 650 nm, of the spectrum. A PIN photodiode followed by a low noise amplifier was used as a detector. Both the detector and the light source units were set on the adjustable platform of the positioning system. In the positioning system, a special receptacle and a stepping motor were employed for fixing POFs uniformly on a single plane and for switching light between the POFs to be tested respectively.

A 10 m length of POF was kept inside the climatic chamber, which was the exposed part of its total 12 m length. The ends of POF were connected to the multiplexer standing out side (about 1 m apart) the climatic chamber.

FTIR measurements

Spectra of POF, core, and cladding were individually recorded using a FTIR – Nexus 670 instrument (Nicolet Instruments Corp.). For obtaining spectra of cores, bare POFs were sliced into small pieces and soaked in chloroform to dissolve the cores and then the capillary films from the core solutions were placed on NaCl discs. To acquire spectra of POFs (core and cladding) and claddings only (see Cladding Separation), *smart-golden-gate-single-reflection-diamond* (L.O.T., Oriel, Germany) accessory was used as ATR unit. It consisted of an internal reflection element (prism) made out of Type-IIa-Diamond with an incident angle of 45°. The wave number range recorded using FTIR transmittance method was 4000–400 cm^{-1} and with ATR method was 4000–600

cm^{-1} . The number of scans and resolutions were 250 and 4 cm^{-1} , respectively.

Differential scanning calorimetry

The glass transition temperature (T_g) and melting temperature (T_m) of bare POFs and claddings were determined using a Seiko DSC 220C instrument. Aluminum pan served as reference. The heating and cooling rate was $10^\circ\text{C min}^{-1}$.

GPC and SEM

The molecular weight distributions of the unexposed and exposed cores were measured by the GPC method using a Polymer Lab GPC 210 instrument. Tetrahydrofuran (THF) was used as an eluent with a flow rate of 1 mL min^{-1} .

Electron microscopic pictures of POFs and claddings were taken from a Philips SEM 515 (pw6703) instrument.

Cladding separation

Bare POFs were cut into small pieces (2–3 cm in length) and soaked in chloroform for 15–20 h at ambient temperature for complete dissolution of the cores. The nondissolved claddings were separated out from core solutions by normal filtration using a Whatman filter paper, washed 3–4 times with chloroform itself, and then pressed between soft papers to remove excess chloroform. Finally, the remaining chloroform was removed by drying at below 55°C in a vacuum oven. We found this procedure as a best way of separating the cladding from the core for S2 and S3 fibers. The claddings obtained by this way appeared as hollow cylinders. As both the core and the cladding of POF S1 were found to dissolve in chloroform and in a few other laboratory solvents, it became highly difficult to separate out the cladding from the core by the above-described method.

RESULTS AND DISCUSSION

DSC and GPC analysis

Bare POFs exhibited T_g and it was found to be about 118°C . Claddings (S2 and S3) demonstrated T_m and it was found to be about 127°C . The T_g and T_m were determined by running at least two DSC measurements for each sample. Since the core diameter of bare POFs used was much larger than that of the cladding, the DSC determined T_g of bare POFs was considered as T_g of cores. This interpretation was confirmed by running DSC measurements for three more bare POFs with 1 mm diameter and found T_g in the same range. In the following sections these

DSC data were taken into account for discussing the causes for the optical transmission loss of POFs.

The determined average molecular weight (M_w) of the three unexposed cores was found to be in the order of 10^5 g/mol . This technique was extended to study degradation of POFs mainly of cores by monitoring their molecular weight distributions. As an outcome, no significant reduction or increase in molecular weight of the three exposed cores was found. The molecular weight of each core sample (exposed and unexposed) was determined by running each solution at least twice in the GPC column. GPC data suggests that no considerable degradation has taken place in cores after climatic exposures.

Optical transmission loss behavior

Although we measured transmission of POFs at three wavelengths, the data presented here is the resultant data after averaging the three wavelengths. With different loss magnitudes, very similar transmission loss behavior was found in all three POFs at three wavelengths. This allowed us to average the transmission data of three POFs measured at three wavelengths, which then allowed us to interpret data clearly. In this and subsequent sections, the term *transmission* is commonly used for representing the *optical transmission* of POFs.

Figures 1 and 3 show the optical transmission loss behavior of POFs exposed to $92^\circ\text{C}/95\% \text{RH}$ and $100^\circ\text{C}/\text{low humidity}$ respectively. Though, all of the POF cores were made of PMMA, their transmission stability was found to be not equal. They demonstrated poor transmission stability. The loss of transmission could be due to physical changes that have taken place in POFs as a result of climatic exposures and are discussed.

Exposure to $92^\circ\text{C}/95\% \text{RH}$

The data shows that the influence of high humidity is very significant to the transmission stability of POFs. The transmission of POFs reached $< 1\%$ within a span of 50 h. The transmission peaks at the very start of exposure might be related to structural relaxation of the polymer, which may improve the boundary or interface between the core and cladding.³⁰ The peaks at about 17 h might be due to undesired variation in humidity in the climatic chamber. Between the three fibers there is a marked difference in the transmission stability as each fiber took its own duration to reach 50% and $< 1\%$ transmission (Fig. 1). Their transmission loss performance appeared to be similar up to 50% loss. This transmission loss performance may be called as linear behavior. While the dissimilar performance in reaching $< 1\%$ transmission from the point of 50% may be

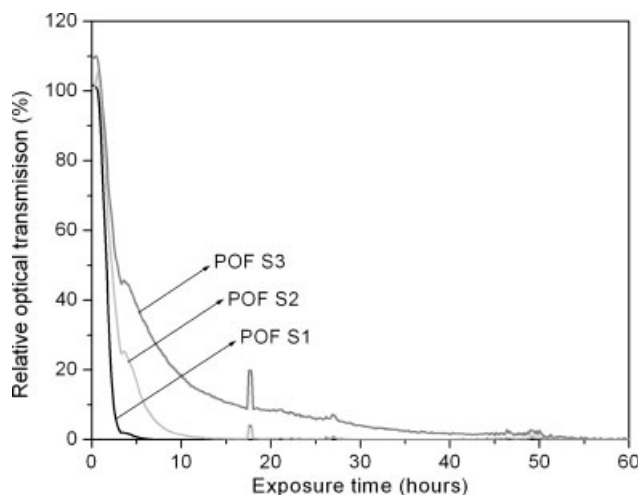


Figure 1 Relative optical transmission loss of POFs measured during exposure at 92°C/95%RH.

called as nonlinear behavior. The exposure times registered for reaching 50% transmission were 96, 127, and 168 min and for reaching < 1% transmission were 5, 12, and 60 h in S1, S2, and S3 fibers respectively. All these observations indicate that both the imposed temperature-humid condition and material properties could strongly influence the transmission stability of POFs.

The results (Fig. 1) demonstrate that the increased rate of water absorption in POFs decreases the transmission down to < 1%. This observation was confirmed by exposing all three POFs at 90°C with low humidity and found that they exhibited a maximum transmission loss of about 18% at the end of 3300 h. The water absorption could be due to the thickness of the core as it was much thicker (~ 980 μm in diameter with closed geometry) than the cladding (~ 20 μm in thickness). As already mentioned the core material of the three POFs was PMMA. Water absorption or transportation in PMMA occurs in dual mode. Part of water migrates into the polymer network and causes swelling of the polymer and part of it accumulates in the pre-existing micro voids (or cracks).³¹ The presence of defects such as micro voids, micro cracks, and dust in a POF depends on its drawing history. To

reduce the optical transmission loss as low as possible, POF manufacturers may use precise drawing methods and parameters to avoid the incorporation of aforementioned impurities that could cause a loss of transmission by scattering. Therefore, in general, the presence of defects in the fiber can be neglectable or even absent at the state of delivery, which was confirmed for the present POFs (the length of the tested samples was about 13 m) by back scattering measurements with an optical time domain reflectometer (OTDR).³ It fairly suggests that the transportation of water into defects, should insignificantly induce the transmission to < 1% in a span of few hours.

Nevertheless, water transportation into the polymer matrix induces swelling of the polymer, which has a significant effect on the transmission stability of POFs. Swelling causes volume expansion of the polymer, which is reversible in nature and it is related to phenomena of wetting (sorption) and drying (desorption).³¹ In our study, lateral swelling of all the three POFs was observed and was more in S1. Table II provides the data of diameter of POFs measured at the stages of 50% and nearly 100% loss of transmission. This swelling appeared to be irreversible because no decrease in diameter was observed after warming the samples under dry condition and moreover they became brittle after bringing down to the room temperature-humid condition. Additionally, the increase in diameter resulted in significant contraction of the fiber length. These observations suggest that the phenomenon other than swelling could be involved for causing the observed irreversible increase of diameter of POFs.

The increase in diameter of POFs it could be explained on the basis of water in polymers acting as a plasticizer accompanied by an increase in the thermal coefficient of (volume) expansion and a reduction of T_g .^{32,33} Amorphous polymers including PMMA exhibit a known order of anisotropic thermal expansion. The anisotropic nature of thermal expansion mainly depends on the polymer processing history (e.g., extrusion, injection molding, compression, and blow molding). In other words, polymers exhibit large anisotropic thermal expansion when orientation

TABLE II
Measured Diameter of the Exposed and Unexposed POFs using an Electronic Screw Gauge (Mitutoya)

Bare POF	Before exposure	Diameter (μm) (± 5)		
		At 50% loss of transmission	At nearly 100% loss of transmission	After 50 h of exposure
S1	1,000	1,090	1,200	1,460
S2	1,000	1,040	1,145	1,395
S3	1,000	1,030	1,110	1,365

A: exposed to 92°C/95%RH; B: exposed to 120°C/low humidity.

of polymer chains takes place.³⁴ Furthermore, the thermal expansion coefficient is believed to be lower in the direction of orientation than in the perpendicular direction. These effects are related to the free volume theories of glassy polymers.³⁵ Such anisotropic behavior can also be expected in the fiber cores of the present POFs. The cores of POFs exhibited a T_g of about 118°C, which suggest the possibility of occurrence of orientation. In the case of isotropic behavior, a T_g of about 105°C could be expected. Dugas et al. studied structural anomalies in PMMA core fibers and found anisotropic thermal expansion which was due to orientation.^{36,37} Therefore, in our study POFs, there might be more thermal expansion in the transversal direction than in the longitudinal direction. The anisotropic behavior of thermal expansion of polymers can be well detected upon heating up to their T_g and then cooling down to the room condition. In the case of climatic exposure, the set temperature was only 92°C which was far below the observed T_g . To cause significant thermal expansion in a duration of 60 h (within which all the three POFs had lost nearly all their transmission, Fig. 1) was far earlier than predicted by Dugas et al.^{36,37} Hence, the observed significant increase in diameter and reduction of fiber length could be due to the plasticizing effect of water in the fiber core. This also indicates that water in POFs reduced T_g by increasing the chain mobility. As a result thermal expansion occurred at a faster rate than it would take when exposed at 92°C only. Furthermore, plasticizer effect seemed to be irreversible because the observed change in diameter and brittle nature of the cooled samples provided an indication of molecular disorder. The irreversible plasticizing effect brought by water molecules in polymers may be referred to as structural relaxation.^{33,38}

As already mentioned, the optical transmission stability of the three POFs was different from each fiber. POF S1 took less time (5 h) than the other two POFs (12 and 60 h for S2 and S3, respectively) to reach < 1% transmission. This could be due to the difference in the chemical compositions of the claddings. Using FTIR, it was found that cladding S1 was a fluoroacrylate polymer whereas S2 and S3 was a fluoroolefin polymer (see FTIR Analysis, Table III, Fig. 4). This data suggest that the lowest transmission stability of POF S1 could be due to hydrophilic nature of its cladding. Also, it is known that fluoroacrylate polymers are less resistant to water as compared to fluoroolefin polymers.³⁹ As a consequence, the absorbed water in the fluoroacrylate cladding has been diffused into the core. In other words, cladding S1 supported the water absorption process of the core where as claddings S2 and S3 acted as hydrophobic barrier. This data shows that more polar the cladding, faster the migration of water into the core. Hence, POF S2 and S3 needed

longer duration as compared to S1. The difference in transmission loss rate between S2 and S3 may also be attributed to a small variation either in the chemical compositions of the claddings or due to different structural anomalies in the fiber cores.

Changes in both physical and chemical properties are common to take place in polymers as a result of water absorption.^{21,24,32,33} Most probable physical changes that could occur in POFs are volume and refractive index changes. They induce heterogeneity and/or imperfections, which are strongly responsible for increasing the optical loss by any type of light scattering. Chemical changes in POFs lead to optical loss, which could be due to molecular degradation and interaction of water molecules with the functional groups of the polymer.

In our study, the physical changes (like the observed increase in diameter and contraction of the fiber length resulting in total volume change) appeared to be the main source for the total transmission loss of POFs because the chemical changes that could be detected using FTIR and GPC were insignificant to cause the total transmission loss in <60 h (Fig. 1). A change in the fiber diameter is mainly related to change in the core diameter. This is one of the important parameters that influence the transmission by generating imperfections at the core-cladding interface of a POF.^{1,2,4,40} Therefore, this might be one of the main sources for the total transmission loss. The thermal expansion in oriented glassy polymers generally means the molecular disorder from the ordered structure. Certainly, such a process can also be expected in the present core fibers, which induces structural anomalies or heterogeneity within the core fiber resulting in decrease of transmission by scattering.

To observe the surface morphological changes of the postexposed samples, SEM studies were conducted. Figure 2 shows SEM data of both POF (core

TABLE III
Comparison of Absorption Bands of PMMA and Cladding S1

Mode of vibration	PMMA ³⁹	Cladding S1 ($\pm 1 \text{ cm}^{-1}$)
$\nu(\text{C}=\text{O})$	1,734	1,734
$\delta(\text{CH}_2)$	1,485	1,485
$\delta_a(\text{CH})$ of $\alpha\text{-CH}_3$	1,448	1,450
$\delta_s(\text{CH})$ of OCH_3	1,436	1,431 (shoulder)
$\delta_s(\text{CH})$ of $\alpha\text{-CH}_3$	1,387	1,415, 1,392
$\nu_s(\text{C}-\text{C}-\text{O})$	1,273; 1,242	1,279; 1,237
$\nu_a(\text{C}-\text{O}-\text{C})$	1,193; 1,147	1,164, doublet 1,131 and 1,019
$\nu(\text{C}-\text{C})$	1,063	1,030
OCH_3 rock	989	965
$\alpha\text{-CH}_3$ rock	966	May be overlapped at 965
CH_2 rock	843	834
$\nu_a(\text{C}-\text{C})$	754	747

ν and δ represents the stretching and bending vibrations, respectively. Subscripts s and a represents the symmetric and asymmetric vibrations, respectively.

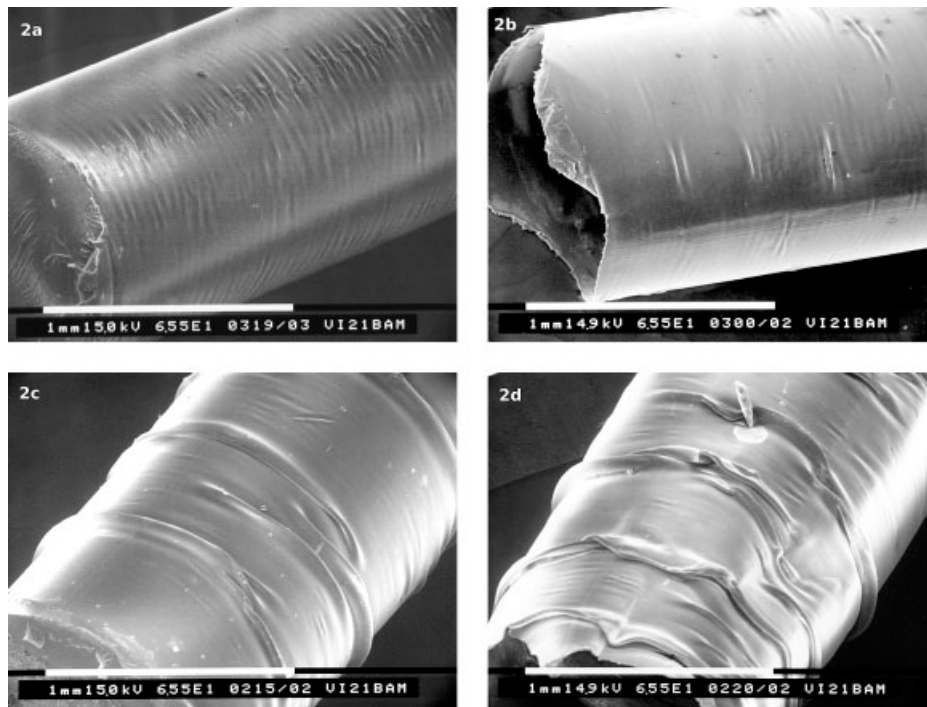


Figure 2 SEM photographs of the exposed POFs (a, c) and claddings (b, d) of S2. (a, b) Exposed to 92°C/95%RH; (c, d) exposed to 120°C/low humidity.

and cladding) and the cladding of S2. Shrinkage/folding was observed on the surface of POF S2 and S3. An identical shrinkage/folding was also observed in claddings [Fig. 2(b, d)]. It was found that the shrinkage/folding structure was mainly in the cladding but not in the core. One cause for this could be that the applied high temperature-humid condition (92°C/95%RH) might have approached the softening point of claddings. This could be possible because the same fibers exposed to 120°C under very low humid condition showed the more pronounced shrinkage/folding structure [Fig. 2(c, d)]. Also, the (volume) thermal expansion coefficient mismatch between the core and cladding could result in the formation of such a structure on the polymer surface.⁴¹ The shrinkage/folding structure was not observed in the POF S1 under SEM. It may be due to similarity in the chemical composition of the core and cladding. Using FTIR it was found that the chemical composition of cladding S1 was much comparable as compared to claddings S2 and S3 to that of the PMMA core (Figs. 4 and 5 and Table III). From this data it can be assumed that the thermal coefficient of expansion of both the core and cladding could fall in the same region, which can result in no shrinkage/folding structure. This assumption was supported by a large increase in diameter of POF S1 compared to other two fibers (Table IIA). This kind of effect was observed more clearly in samples that were exposed to 120°C/low humidity (Table IIB). Nevertheless, changes like folding/shrinkage in POFs could create physical structure imperfections mainly at the

core-cladding interface during the early stages of exposure, which could lead to increased optical loss due to scattering. Hence, the formation of the shrinkage/folding structure was one of the main sources for total the transmission loss of POFs.

Previous investigations showed that PMMA and fluoropolymers can exhibit negative thermo optic coefficient (TOC) which describes a change in refractive index n with temperature T .⁴² Prod'homme have derived an equation that relates dn/dT to volume expansion (or density) and electronic polarisability of materials.⁴³ According to this theory, TOC depends on temperature coefficient of electronic polarisability (ϕ) and volume expansion coefficient (β). Most of the optically transparent polymers exhibit negative TOC (e.g., PMMA shows negative TOC in the order of $10^{-4}/^{\circ}\text{C}$), where β dominates over ϕ . In view of the Prode'homme theory it can be postulated that POFs may exhibit a negative change in n . At the exposure condition 92°C/95%RH, the temperature itself could be sufficient to influence the volume expansion that can be enhanced by the water absorption. Thus a considerable variation in n may be expected to take place in POFs. This can happen within the fiber and can generate heterogeneity mainly in the core causing more microscopic scattering loss (e.g., Rayleigh scattering). Furthermore, a deviation in n results a in variation of numerical aperture (NA) which governs the optical transmission property of a POF. Therefore, a significant contribution to the total transmission loss from digression in n of both the core and cladding is possible.

It was observed that all three POFs exhibited almost equal rate of transmission loss at all the three wavelengths. This suggests that scattering occurred under heterogeneous conditions with extensions much larger (geometrical optics) or much smaller (Rayleigh scattering) than the wavelength. This is an additional evidence which supports the transmission loss is primarily due to physical changes of POFs. Thus, physical changes appear to play an important role to cause the total transmission loss of POFs under the climate 92°C/95%RH. Finally, under this exposure climate, the transmission stability of the three POFs can be characterized in the following order: POF S3 > POF S2 > POF S1.

Exposure to 100°C/low humidity

Figure 3 shows the transmission data of POFs that were exposed to 100°C with low humidity. The results show a strong initial drop-off of the optical transmission as soon as temperature reached 100°C (linear behavior). The optical transmission of POFs was stable after an initial drop-off when the set temperature became stable (nonlinear behavior). The linear behavior of the transmission loss of POFs was quite different; fiber S1 exhibited more loss (about 65%) than S3 and S2 fibers (about 25%). This linear loss in transmission is attributed mainly to physical changes. Since the exposure temperature was near to T_g of the core, molecules can set-in motion which influences the polymer physical structure significantly. Molecular motion of polymer chains perhaps cause softening and change in volume of the polymer, which could result in imperfections in the core as well as at the core-cladding interface. The temperature dependence of initial transmission loss was verified by exposing the POFs to 95°C/low humidity

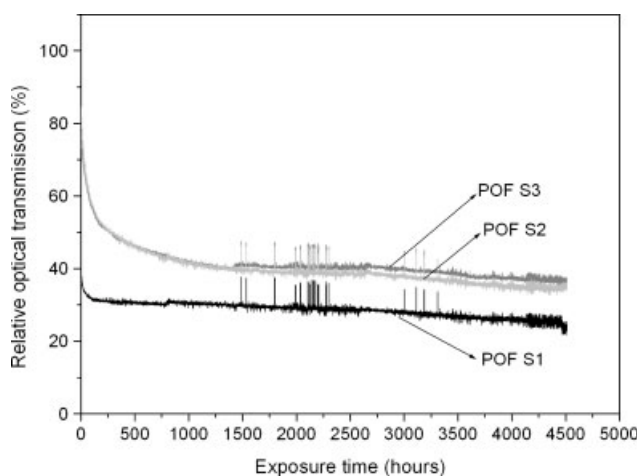


Figure 3 Relative optical transmission loss of POFs measured during exposure at 100°C/low humidity.

and found very similar linear- and nonlinear-loss behavior. But here the loss was much lower than observed at 100°C/low humidity. The low transmission stability of POF S1 can be explained in the following way. The S1 cladding was found to have a chemical composition similar to that of the core (PMMA). It can be assumed that T_g of the cladding could recline in the same region as that of the core (at about 118°C). As a result, T_g of both the core and the cladding of POF S1 was in the vicinity of the experimental temperature. Consequently, a cooperative softening process might take place between the core and the cladding, which induced more imperfections in the physical structure of the fiber, leading to faster degradation of optical transmission of POF S1.

Additionally, the volume change due to thermal expansion can account for a change in n of the polymer, which could lead to a transmission loss due to scattering.^{42,43} Another process that might have taken place in POFs could be the polymerization of active oligomers and these oligomers which will get trapped unreacted in the polymer matrix during the manufacturing process.⁴⁴ Such a reaction can cause material heterogeneity in POFs especially in the core that could promote transmission loss to a higher extent. The quantity of oligomers present in the fiber depends on polymer manufacturing conditions and fiber processing history.

We believe that once the physical changes are set-in at the initial stages (i.e., an initial drop-off of the transmission) and with stable temperature, the transmission loss of POFs becomes nonlinear. The nonlinear behavior of transmission loss results essentially from chemical changes due to occurrence of chemical reactions like oxidative degradation, in addition to loss owing to the physical changes. From the data it was clear that the nonlinear transmission loss was mainly from thermo-oxidative degradation of POFs. Under the exposure of climate 100°C/low humidity, almost an equal transmission stability of POFs S2 and S3 and a least stability of S1 was detected (Fig. 3).

Exposure to 120°C/low humidity

To accelerate the transmission loss behavior (aging behavior), POFs were exposed to 120°C with low humidity. They exhibited total loss of transmission as soon as the temperature reached the set point (hence no data is presented). This could be due to mechanical softening of both the core and the cladding. A significant increase of diameter and brittleness and the formation of the shrinkage/folding structure were observed, which were similar to the data obtained from the test of exposure to 92°C/95%RH. However, the changes were more pronounced under the exposure condition 120°C/low humidity [Fig. 2(c, d)]. An additional exposure test was conducted at 110°C

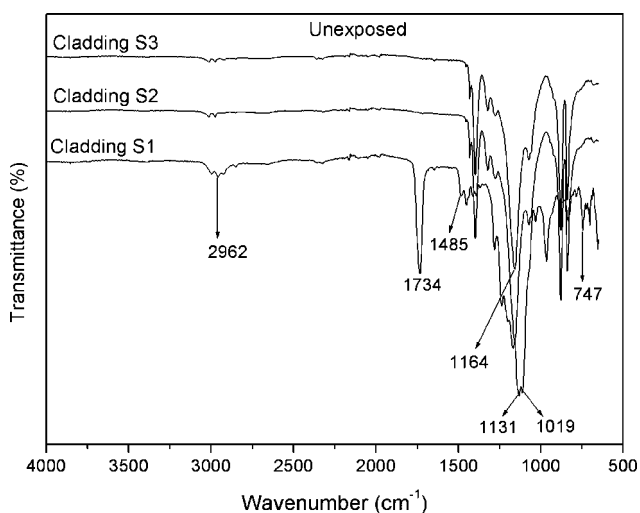


Figure 4 ATR-FTIR spectra of the unexposed claddings S1, S2, and S3.

with low humidity for all the three POFs to ensure our interpretation that the transmission loss was mainly due to physical changes. We observed very similar transmission loss behavior as in the case of exposure at 92°C/95%RH but with higher magnitude in the time scale. We also observed the physical changes however in this case the effects were more pronounced than at 92°C/95%RH and less pronounced than at 120°C/low humidity. Obviously, in the former case, humidity played a major role in bringing those observed effects.

FTIR analysis

Characterization of the unexposed POFs

Figure 4 shows the ATR-FTIR spectra of the unexposed claddings S1, S2, and S3. It was found that the spectrum of a bare POF (sample was placed horizontally in the sampling chamber) was equivalent to the spectrum of its cladding only when it was measured using ATR unit. This was due to the fact that the penetration depth of the IR beam (a maximum of 5 μm) was much smaller than the thickness of the cladding ($\sim 20 \mu\text{m}$).

With this advantage of ATR, the spectrum of cladding S1 was recorded by placing the POF, because it was not removed from the core by the method followed for removing claddings S2 and S3. To maintain the uniformity, the spectra of claddings measured by placing POFs are presented here. In the subsequent text, unless it is mentioned as cladding only spectrum (measured by placing cladding only) then it should be understood as cladding spectrum measured by placing the POF.

The spectrum of S1 cladding shows more similarity with that of the PMMA core (Figs. 4 and 5). The

absorption bands of S1 were compared with that of PMMA and are presented in Table III. A shift in the position of absorption bands was observed, which was due to fluorination. The broad and small absorption bands in the region between 1060 and 1300 cm^{-1} show a big influence of C—F groups. The absorption bands of PMMA provides further evidence that fluorination is most likely be at the O—CH₃ group of PMMA like polymer because there was no shift in the position of the C=O band (Table III).⁴⁵ Fluorination might be the substitution of a hydrogen atom by a linear fluorinated alkyl chain. These results support that the cladding S1 should be a poly(fluoroalkyl methacrylate) (PFMA) but the extent of fluorination was found difficult to assign. It could also be possible that a copolymer or a blend of nonfluoroacrylate and fluoroacrylate polymers might be the material of the cladding.

Very similar spectra of S2 and S3 (Fig. 4) show strong absorption bands in the region between 1100 and 1400 cm^{-1} , which suggests the characteristic stretching vibrations of C—F groups in the polymer chain. This direct interpretation was made with the information that claddings were fluoropolymers as disclosed by vendors. Very small absorption bands in the region between 2970 and 3015 cm^{-1} reveal the presence of a few C—H groups as this region is the characteristic absorption of C—H stretching vibrations. Two absorption bands in the lower wavenumber region between 835 and 880 cm^{-1} indicate the deformation vibrations of C—H.

These results suggest that the cladding material of S2 and S3 might be either a fluorinated polyolefin (polyfluoroolefin) or a copolymer of olefins and fluorinated olefins or could be a blend of polyolefins and fluorinated polyolefins. However, the most probable composition might be a copolymer of fluoroolefins because earlier studies have disclosed the

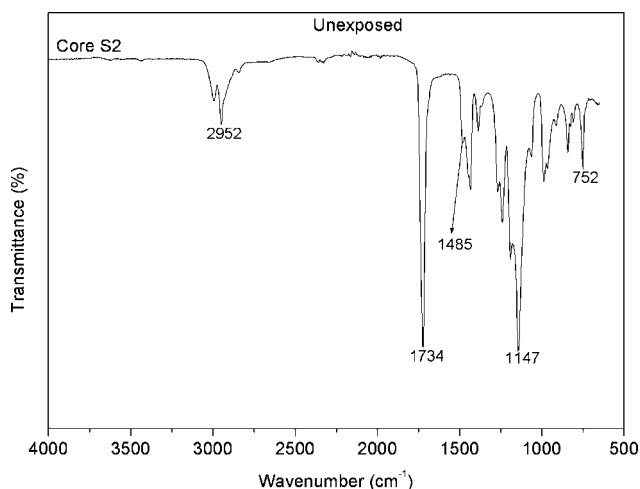


Figure 5 FTIR spectrum of the unexposed core S2.

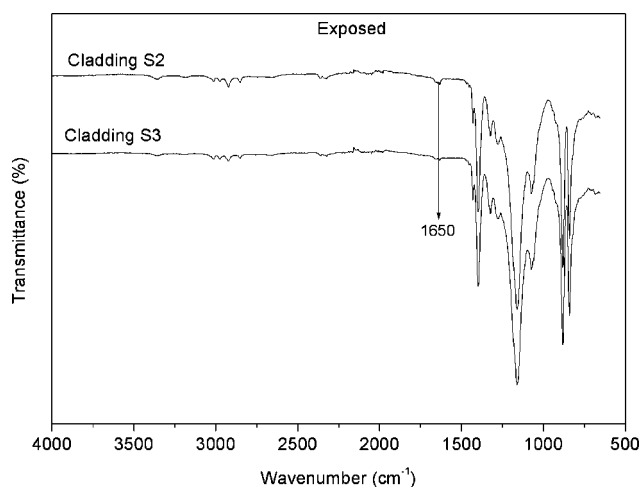


Figure 6 ATR-FTIR spectra of claddings S2 and S3 exposed at 92°C/95%RH.

possible applications of this type of material as a cladding of POFs.⁴⁶ Between cladding S2 and S3 there might be a difference in the chemical composition but was not detected with FTIR.

Spectra of all the unexposed cores were found equivalent and showed all the characteristic bands of PMMA that are reported in the literature.⁴⁷ One of the spectra of cores (S2) is shown in Figure 5 and it was used as a reference for the qualitative comparison of absorption bands of cladding S1.

Characterization of the exposed POFs

The exposed cores (92°C/95%RH) showed no significant chemical changes as in the FTIR spectra. In contrast to the cores, claddings S2 and S3 reflected a small change with a small absorption band (doublet) at around 1650 cm⁻¹ (Fig. 6). It belongs to stretch vibrations of C=C structure, which could be formed due to main chain scissions of the polymer chains as a result of exposure. However, we assume that this small chemical change is less significant as compared to the observed bulk physical changes. But the small chemical change could be an additional effect in bringing the optical transmission down to < 1% at the early stages of exposure.

Figure 7 shows spectra of claddings exposed to 100°C/low humidity. Here also the exposed cores did not show any significant changes in their spectra. However, a few small changes in claddings S2 and S3 were observed. Two new bands at around 1650 cm⁻¹ (doublet) and 3360 cm⁻¹ were detected. These bands are assigned to stretching vibrations of C=C structure and OH groups of hydroperoxides respectively. Recently, Nasef et al.²⁶ reported in their FTIR study that the C=C structure was formed due to main chain scissions and hydroperoxides were

generated after reacting with oxygen (oxidation). These two are the main reactions of photodegradation of partially fluorinated polymer films. This strongly suggests that such chemical processes might have taken place in the present samples and resulted in new absorption bands. Here, we propose that these changes can influence the core-cladding interface of POFs thus reducing the bonding or adhesion strength. Additionally, degradation reactions can result in new polymer structures and/or new products, which would bring heterogeneity, for instance, in *n*. In this way chemical changes increase the transmission loss of POFs. Using FTIR no major chemical changes were observed in cladding S1 (data not shown). But in our previous study using chemiluminescence (CL) technique we showed that climatic exposure of POFs (S1 and S3) resulted in the oxidative degradation of both cladding and core.⁴⁸

Figure 8 shows the ATR-FTIR spectra of claddings exposed at 120°C/low humidity. Significant changes were observed in all the exposed samples. The spectra of S1 [Fig. 8(a)] showed decreased intensity with a new absorption band at around 1650 cm⁻¹. The appearance of this band is attributed to stretching vibrations of C=C that has resulted mainly from the main chain scissions of the cladding polymer. This type of observation was also made with the spectrum of cladding S1 exposed to 92°C/95%RH. With S2 and S3 spectra, two new bands at around 1730 cm⁻¹ and 750 cm⁻¹ were detected [Fig. 8(b, c)]. These bands are the characteristic absorptions of the stretching vibrations of C=O and C—C (and C—H deformations vibrations) respectively. An increasing trend of band intensities of these bands was also observed. These effects result from more of physical changes rather than chemical changes in POFs. Since the temperature 120°C was just above the glass point

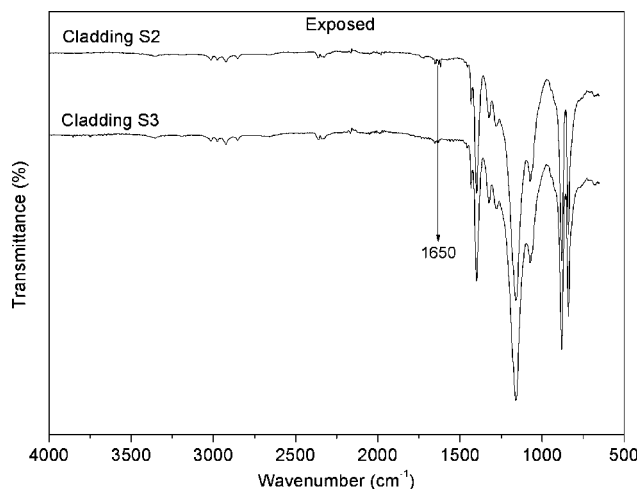


Figure 7 ATR-FTIR spectra of claddings S2 and S3 exposed at 100°C/low humidity.

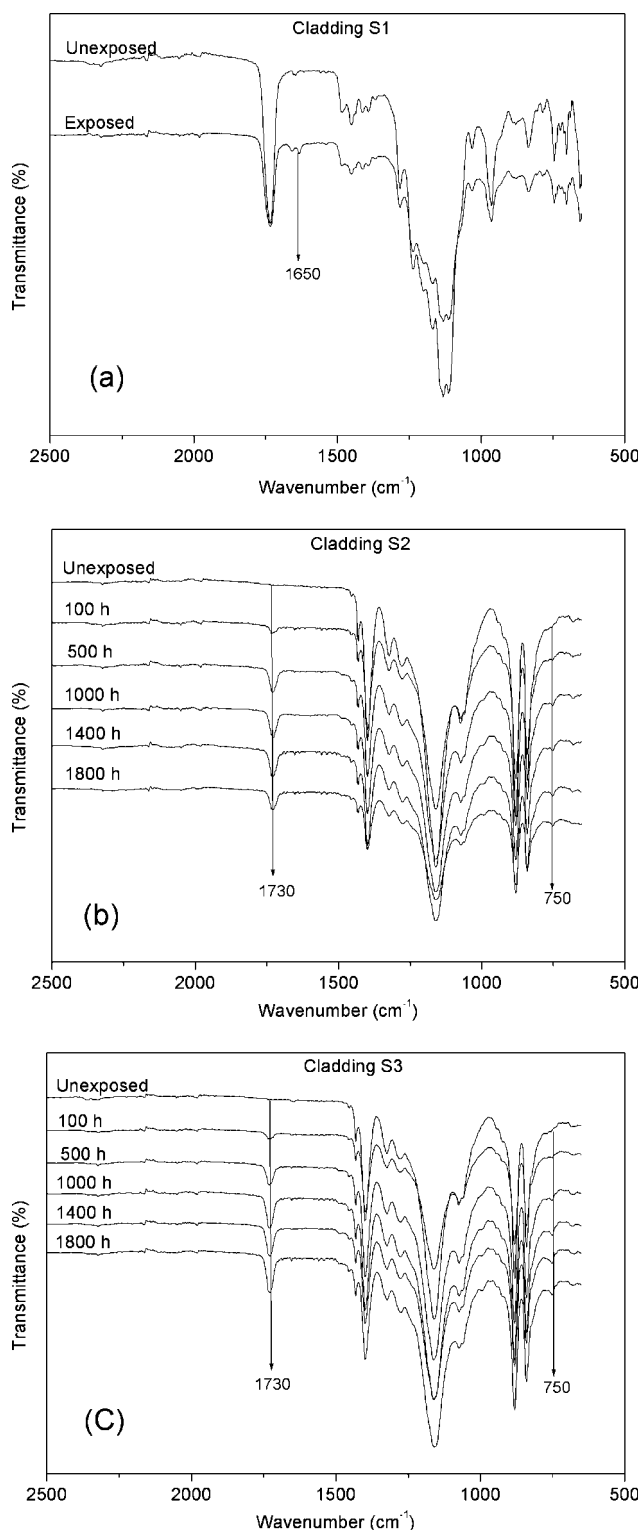


Figure 8 ATR-FTIR spectra of POFs exposed at 120°C/low humidity: (a) S1; (b) S2; (c) S3.

of POFs, a large (volume) thermal expansion of the core might have taken place by melting. As a result, IR light could enter more into the core through the cladding and detect these bands. The other absorption bands of the core (PMMA) were not detected,

which could be due to weak absorption and/or may be overlapped with strong absorption bands of C—F groups of the cladding. Cladding also exhibits thermal expansion, which additionally increases the detection of core absorption bands as a consequence of more thinning. A trace of the C=O absorption band at 1730 cm^{-1} was observed in the spectra of claddings after they were separated from the cores, which suggests that the oxidative degradation might have taken place in claddings. To confirm our interpretation for new absorption bands of claddings, we conducted an exposure test for the present POFs at 110°C/low humidity and found similar results but with lower magnitude of band intensities (data not presented).

The results observed by exposing POFs to 120°C/low humidity indicate that similar physical changes might have occurred here too but with lower magnitude than in POFs exposed to 92°C/95%RH, causing an early loss of transmission.

CONCLUSIONS

The optical measurement data shows that the optical transmission stability of the three POFs was unequal although their cores were composed of PMMA. POFs exposed to 92°C/95%RH and 100°C/low humidity showed both the linear and nonlinear behavior of transmission loss. The total transmission loss (linear and nonlinear) of POFs exposed to 92°C/95%RH was primarily due to physical changes (like thermal expansion, shrinkage/folding, and refractive index variation). The linear and nonlinear transmission loss of POFs exposed to 100°C/low humidity were due to physical changes (like softening) and chemical changes (like oxidative degradation) respectively. FTIR investigation reveals that the difference in the chemical compositions of claddings was responsible for the observed different rates of transmission loss of POFs. In contrast to the cores, claddings exhibited degradation effects as a result of climatic exposure. The observed effects were more pronounced in POFs exposed to 120°C/low humidity. All together, the results demonstrate that the optical transmission stability of POFs with nonacrylate polymer cladding is better than that of POFs with acrylate polymer cladding.

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