

NOTE

Effect of cladding layer glass transition temperature on thermal resistance of graded-index plastic optical fibers

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INTRODUCTION

Graded-index plastic optical fibers (GI POFs)¹ are a highly competitive transmission medium for short-range communications such as local area networks and interconnections. Because GI POFs have a parabolic refractive index profile in the core region, modal dispersion is minimized and high-speed data transmission of over a gigabit per second is possible. Currently, most suppliers produce GI POFs via coextrusion and a dopant diffusion method;² the core polymer, which contains a diffusible dopant that has a higher refractive index than that of the base polymer, and the cladding polymer are concentrically extruded. The core and cladding polymers flow together into a diffusion zone, and the dopant from the core layer diffuses toward the cladding layer, forming the GI profile. The polymer then flows into an exit die and is drawn into a fiber.

The biggest issue in GI POF fabrication is that the dopant significantly decreases the glass transition temperature T_g because of the plasticization effect. The operating temperature of GI POFs was previously considered to be limited by the lowest T_g , which is usually that of the core center where the dopant concentration is the highest, and thus, considerable effort has been invested in developing high- T_g core materials to enhance the thermal resistance of GI POFs. Recent studies have mainly focused on two approaches: employing high- T_g polymers as the core base material^{3–9} and reducing the dopant concentration (which determines the refractive index change between the core and cladding) by designing high-refractive-index dopants^{10–13} or by choosing combinations of core and cladding base polymers that have certain refractive index differences.^{5,7,9,13} In other words, little attention has been paid to the cladding layer.

Here, we report the first observation of the effect of the cladding T_g on the thermal resistance of GI POFs. We recently developed a three-layered GI POF by coextrusion^{8,9} and used this method to fabricate the GI POFs for this study. The core was a copolymer of 2,2,2-trichloroethyl methacrylate (TCIEMA) and *N*-cyclohexyl

maleimide (cHMI) doped with diphenyl sulfide, and the cladding and over-cladding polymers were poly(methyl methacrylate) and poly(carbonate), respectively. In this study, we used two types of commercial poly(methyl methacrylate) resins with different T_g values and compared the long-term thermal reliability of the GI POFs in terms of fiber attenuation.

EXPERIMENTAL PROCEDURE

Materials

TCIEMA and cHMI were purchased from Osaka Organic Chemical Industry (Osaka, Japan) and Nippon Shokubai (Osaka, Japan), respectively. Diphenyl sulfide and lauryl mercaptan were purchased from Sigma-Aldrich Japan (Tokyo, Japan), and di-*tert*-hexyl peroxide was purchased from NOF Corporation (Tokyo, Japan). Poly(methyl methacrylate) (Acrypet TF8 and VH5 Grades) and poly(carbonate) (LEXAN HFD1810 Grade) resins were purchased from Mitsubishi Rayon (Tokyo, Japan) and Saudi Basic Industries Corporation (Tochigi, Japan), respectively. The TCIEMA was freshly distilled, and the cHMI was dried under vacuum before use. All other chemicals were used as received.

Fabrication of GI POFs

The general extruder setup and fabrication details are described in Nakao *et al.*⁹ The core polymers were prepared using di-*tert*-hexyl peroxide (0.03 mol%) and lauryl mercaptan (0.12 mol%) as the free-radical initiator and chain transfer agent, respectively, according to Nakao *et al.*⁸ The TCIEMA/cHMI copolymer composition was modified to be 96.3/3.7 mol% so that the core T_g decreased and the effect of the cladding T_g on the thermal resistance would be clearly observed. The materials for the core, cladding and over-cladding layers and the corresponding T_g values are summarized in Table 1. Fiber A and Fiber B differ only in terms of the cladding polymer.

Measurements

The T_g values were determined using a differential scanning calorimeter (DSC220C, Seiko Instruments, Chiba, Japan) at a scan rate of 10 °C min⁻¹ in a dry nitrogen atmosphere. The T_g values were measured during the second

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heating scan at the midpoint of the heat capacity transition between the upper and lower points of the deviation from the extrapolated rubber and glass lines.

Cross-sectional images of the fibers were taken using a digital microscope (VHX-1000, Keyence, Osaka, Japan) while illuminating the other end of a 5-m fiber with a white light-emitting diode.

Attenuation spectra were measured by employing the cutback method.¹⁴ A tungsten lamp (AQ-4303B, Ando Electric, Tokyo, Japan) and optical spectrum analyzer (AQ-6373, Yokogawa Electric, Tokyo, Japan) were used as the light source and detector, respectively.

The dry-heat and damp heat resistance performances were evaluated by monitoring the change in the attenuation in a drying oven with forced convection (OF-450, AS ONE, Osaka, Japan) and a thermo-hygrostat (HIFLEX-FX424P, Kusumoto Chemicals, Tokyo, Japan), respectively, according to IEC 60793-1-46. The light source was a light-emitting diode with an emission wavelength of 650 nm, and a multichannel optical power meter (OP710, OptoTest, Camarillo, CA, USA) was used as the detector. A 13-m fiber was first placed in the oven, and 1.5-m lengths at both ends of the fiber were ferruled. The ends of the fiber were passed through small holes on the side walls of the oven and coupled to the source and detector. To minimize the effect of a fluctuating input power, a 1-m multimode silica fiber was also coupled to the source, and the output power was measured as the reference. The attenuation increment over time was determined by the difference in the output powers in units of decibelmilliwatts divided by the length (10 m) of the fiber that was exposed to the test temperature.

Table 1 GI POF materials and glass transition temperatures (T_g)

	Core		Cladding		Over-cladding	
	Material	T_g (°C)	Material	T_g (°C)	Material	T_g (°C)
Fiber A	TCIEMA/cHMI 96.3/3.7 mol% DPS 4.0 wt%	107	PMMA (Acrypet TF8 Grade)	105	PC (LEXAN HFD1810 Grade)	130
Fiber B			PMMA (Acrypet VH5 Grade)	115		

Abbreviations: cHMI, cyclohexyl maleimide; DPS, diphenyl sulfide; GI POF, Graded-index plastic optical fibers; PC, poly(carbonate); PMMA, poly(methyl methacrylate); TCIEMA, trichloroethyl methacrylate.

RESULTS AND DISCUSSION

Cross-sectional views of Fiber A and Fiber B are shown in Figure 1. The three-layered structures were precisely aligned, and the core, cladding and over-cladding layer diameters were 0.20, 0.28 and 1.00 mm, respectively. Figure 2 shows the attenuation spectra of Fiber A and Fiber B, and we found that the cladding polymer did not affect the fiber attenuation. The predominant factor affecting the attenuation in the visible to near-infrared region is the stretching overtone absorptions of C–H bonds.¹⁵ Molecular vibration absorptions are typically observed at infrared wavelengths, which correspond to the resonance frequencies of fundamental molecular vibrations. Because of the molecular potential anharmonicity, however, overtone and combination absorption bands also appear at visible and near-infrared wavelengths. The lowest attenuations of Fiber A and Fiber B were 120 and 123 dB km⁻¹ at 654 nm, which is located between the fifth and sixth overtones of the C–H stretching vibrational absorptions.

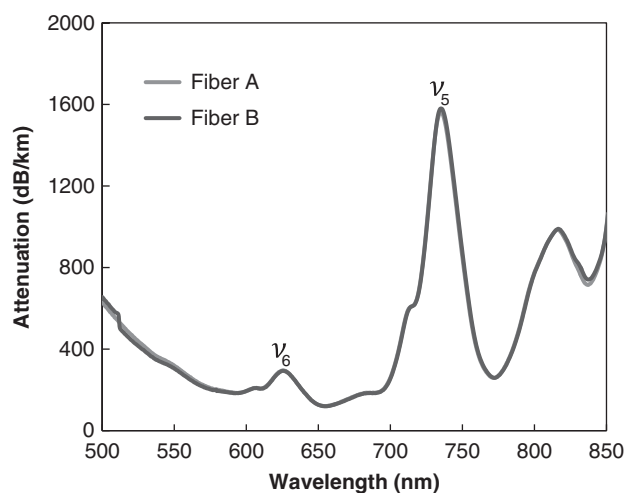


Figure 2 Attenuation spectra of Fiber A and Fiber B; ν labels the C–H vibrational absorptions of the core polymer and the subscript is the vibrational quantum number. A full color version of this figure is available at *Polymer Journal* online.

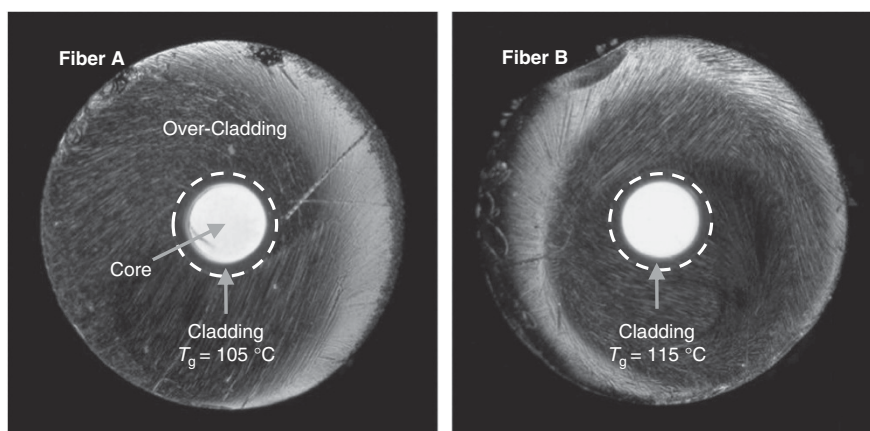


Figure 1 Cross-sectional views of Fiber A (left) and Fiber B (right). Core, cladding and over-cladding layer diameters for both fibers are 0.20, 0.28 and 1.00 mm, respectively. A full color version of this figure is available at *Polymer Journal* online.

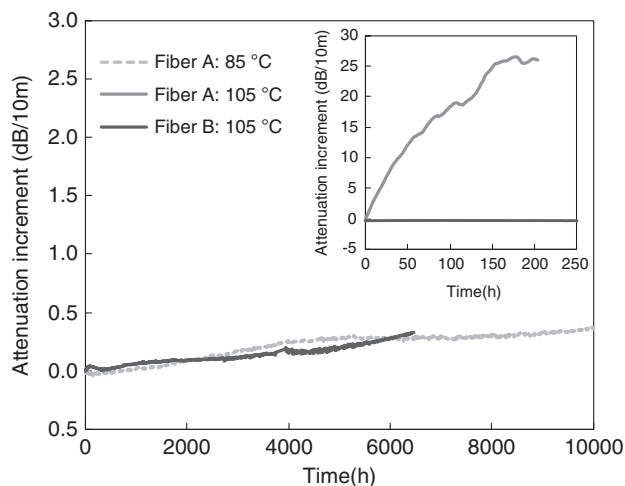


Figure 3 Temporal changes in the fiber attenuation at 650 nm under 85 or 105 °C dry conditions. Note that different scales are used for the inset showing the data for Fiber A tested under 105 °C dry conditions. A full color version of this figure is available at *Polymer Journal* online.

The long-term thermal reliability of these fibers was evaluated in terms of the fiber attenuation, and Figure 3 compares the temporal attenuation changes at 650 nm. The dashed blue line represents the behavior of Fiber A at 85 °C, which is a common heat aging test condition standardized by IEC 60793-2-40. At 85 °C, which is ~ 20 °C lower than the T_g values of the core and cladding, the increment in the attenuation of Fiber A after 10000 h was 0.37 dB per 10 m. In contrast, when Fiber A was at 105 °C (solid blue line), which is nearly identical to the core and cladding T_g values, the fiber attenuation drastically increased from the beginning of the test, and the increment after 200 h was 26 dB per 10 m. However, if the cladding T_g was 115 °C (Fiber B: solid red line), the fiber attenuation was stable, and the increment after 6000 h was only 0.28 dB per 10 m.

The large increase in the fiber attenuation of Fiber A is considered to be caused by a structural imperfection at the core-cladding boundary. When both the core and cladding layers are between glassy and rubbery states, it seems reasonable to suppose that the boundary surface fluctuates spatially and scatters light (this spatial fluctuation is because the residual stress formed during the fiber drawing process is partially released and the materials have different thermal shrinkage rates¹⁶). Extrinsic light scattering was believed to occur when either the core or cladding T_g was below the environmental temperature, and thus, the operating temperature of GI POFs was considered to be limited by the lower T_g , which is usually that of the core. However, these comparative experiments show clearly that maintaining a flat, smooth interface will depend on whether the cladding T_g is sufficiently high to maintain the original concentric fiber structure; the core layer is not necessarily required to be in a glassy state. To the best of our knowledge, this is the first observation of the cladding effect on the long-term stability of attenuation in GI POFs. However, the role of the dopant concentration distribution in GI POFs cannot be disregarded. Although dopant molecules are effectively immobilized in glassy polymers, they are expected to diffuse in rubbery polymers, and thus, to fully discuss the feasibility of the fiber structure considered here to enhance the thermal resistance of GI POFs, the long-term stability of the refractive index profile and bandwidth also need to be investigated.

Note that we also evaluated these fibers under damp heat conditions (standardized by IEC 60793-2-40). Figure 4 shows

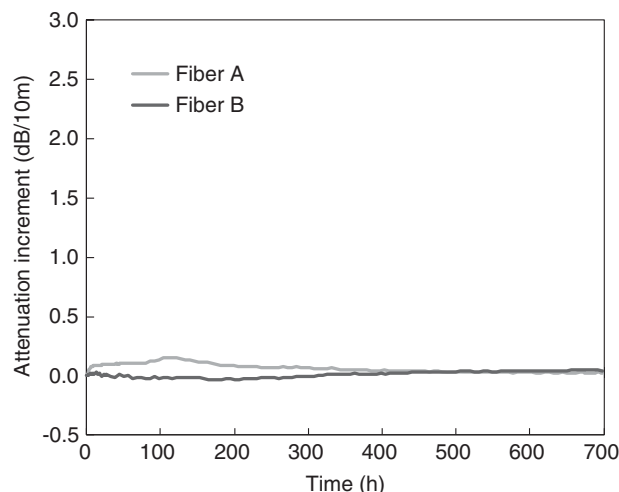


Figure 4 Temporal changes in the fiber attenuation at 650 nm under 75 °C–85% relative humidity damp conditions. A full color version of this figure is available at *Polymer Journal* online.

the change in the attenuation of Fiber A and Fiber B over time at 75 °C and 85% relative humidity. Both fibers were stable in the humid environment, and there was no dependence on the cladding layer.

CONCLUSIONS

We have investigated the effect of using high- T_g polymers as the cladding of GI POFs on the long-term thermal stability of the fiber attenuation. To identify the influence of the cladding layer, we prepared two GI POFs with the same materials and structure but with different T_g values. The difference in the cladding T_g did not affect the original fiber attenuation, as evidenced by the nearly identical spectra. When the GI POFs were exposed to a 105 °C environment, which was a temperature similar to the core T_g (107 °C), the attenuation of the GI POF with the lower T_g (105 °C) cladding increased abruptly due to light scattering at the core-cladding boundary, whereas the attenuation of the other GI POF with the higher T_g (115 °C) cladding was stable for over 6000 h. These results suggest that the long-term stability of the fiber attenuation does not depend on the core state (glassy or rubbery) but does depend on whether the cladding T_g is high enough to maintain the original flat, smooth core-cladding boundary.

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