Fabrication of a Graded-index Polymer Optical Fiber Preform by Using a Centrifugal Force

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Abstract—We have investigated a fabricating method for a graded index polymer optical fiber preform using a centrifugal force. When two monomers with different densities and refractive indices are polymerized under a centrifugal force, a concentration gradient is generated due to their density difference. Therefore, a graded refractive index can be obtained according to the concentration gradient. When a monomer is polymerized under a centrifugal force, a preform with a hollow is obtained because of volume shrinkage. To compensate for this practically, additional monomer should be filled into the hollow. Monomer should be fed to obtain a continuous gradient of refractive index at the interface before the first polymerized product is perfectly glassified. Two different types of feeding additional monomer were experimented with: monomer-monomer pair (case I) and monomer-polymer pair (case II). The graded index profile with a proper Δn (about 0.01) was successfully obtained in either case.

Key words: Graded Index, Polymer Optical Fiber Preform, Centrifugal Force, Volume Shrinkage

INTRODUCTION

As industries related with multimedia and data transmission are booming, the need for optical fibers is increasing. In 1966, Kao and Hockham performed a study on optical fibers using silica glass. Optical fibers have provided a base of wave guiding media because these fibers can satisfy requirements such as high bandwidth and low attenuation or loss, which is necessary for high performance communication. Over the years, many studies have been performed that helped make mass production of glass optical fiber possible. Furthermore, optical fibers have enabled data communications to grow rapidly owing to higher data transmission rate than that of copper cable [Hecht, 1990].

Optical fibers consist of core and cladding [Emslie, 1988]. Core is a part of propagating light and cladding is a part of reflecting light totally. Optical fibers can be divided into single-mode and multi-mode according to the transmission type. They can also be divided into step index (SI) and graded index (GI) according to the index profile of the core part. Fundamentally, GI-optical fibers can transfer 10-100 times as much information as SI-optical fibers. Currently, silica glasses are used for data communications. The diameter of glass optical fibers should be very small, typically 125 μm, to allow them to be flexible due to their inherent brittleness. The inherent brittleness of glass fibers requires a more elastic polymer coating to protect their surface and to prevent the growth of Griffiths cracks and consequent fracture. The small diameter of the fibers, although advantageous in saving both space and weight, creates

connecting problems in some applications. The mismatch of connection causes serious optical loss, which means that connections require very costly, time consuming and complicated work. On the other hand, polymer optical fibers can be made with a relatively big diameter such as 1mm. Therefore, connections could be easier and require lower cost. The transmission loss of GOF is about 0.2-0.3 dB/km at 1,330 nm, but that of POF is about 200 dB/km at 650 nm. It is caused by difference of scattering loss in each material. GOF is good for long distance communication with low attenuation while POF is a better candidate for a short distance network such as local area network (LAN). SI-POF can be used as illumination parts due to low transmission rate, while GI-POF can be used as short distant communications. Now, demand of short distance communications is increasing rapidly since local area networks are being set up in the home. It is worthwhile to substitute GI-POF for GOF in a short distance network because numerous and complicated connections are necessary in such cases.

Until now, known GI-POF fabrication methods could be classified into batch and continuous processes. Developed at Keio University, the typical batch process is known as interfacial gel polymerization [Koike et al., 1998; Koike and Nihei, 1991; Ishigure et al., 1995]. The continuous one, known as co-extrusion, was developed at the University of Florida [Park et al., 2000]. These processes have some disadvantages. The former has low reliability, low yield and low long-term stability, and the latter has ease of contamination and difficulty in obtaining a reliable preform due to many control variables. The other process is a centrifugal force method in which a graded index profile is obtained according to the density gradient by a centrifugal force [van Duijnhoven et al., 1999]. This method has some advantages such as good reliability and ease of

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Table 1. Characteristics of materials used

Materials	Density (g/cm³)	RI
MMA	0.936	1.14
SM	0.909	1.547
PMMA	1.190	1.490
PS	1.05	1.591

control of a graded index profile by controlling rpm or material composition. However, it has the disadvantage that a preform with hollow is obtained by volume shrinkage due to the density difference between monomer and polymer. This problem should be resolved by compensating with an additional monomer of as much as the portion of shrunk volume.

In this study, a GI-POF preform has been fabricated under a centrifugal force and the volume shrinkage problem has been successfully resolved by compensating with an additional monomer. To obtain a graded index profile, monomer-monomer pair (case I) and monomer-polymer pair (case II) were used.

EXPERIMENTAL

1. Materials

Styrene monomer (SM) and methyl methacrylate (MMA) was copolymerized to fabricate a GI-POF preform. The properties of the used monomer and polymer are listed in Table 1. 0.4 wt% benzoyl peroxide was used as an initiator.

2. Volume Shrinkage

When a monomer is polymerized under a centrifugal force field, a tube type preform is produced due to volume shrinkage. Generated copolymers move outward and lead to generating a vacancy at the center because centrifugal force overcomes gravity. The shrunk
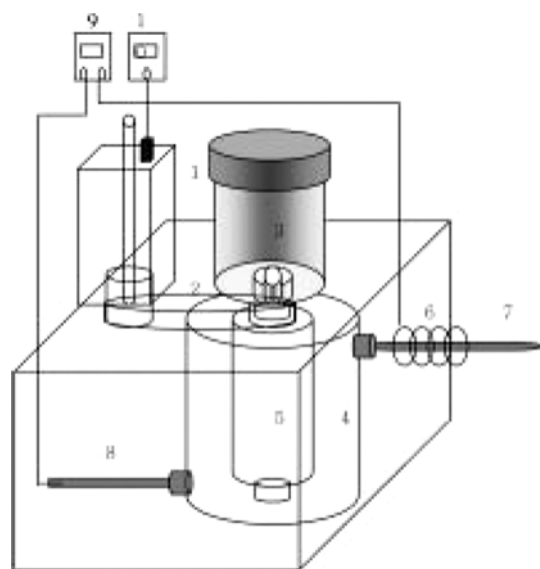
Fig. 1. The structure of a reactor.

1. Motor
2. Belt
3. Feeding inlet
4. Insulated outer cylinder
5. Reactor
6. Air inlet
7. Heating band
8. Air outlet
9. Temperature controller
10. Rpm controller
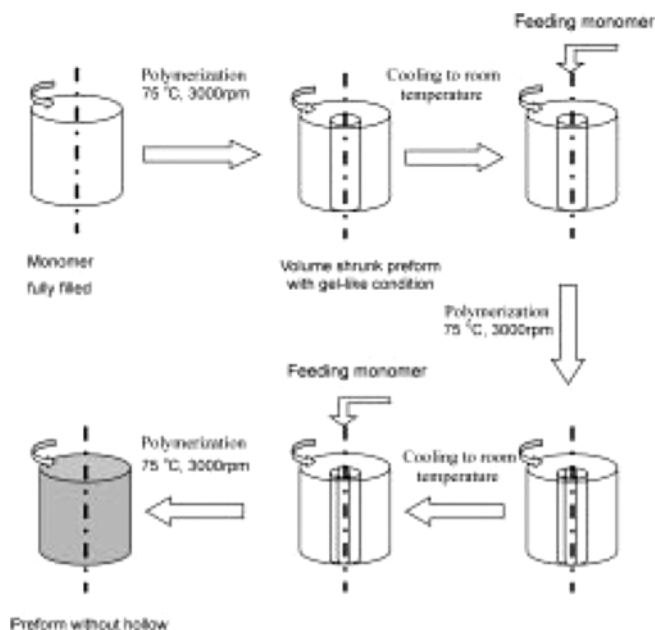
Fig. 2. Procedure of case I.

volume should be compensated because a tube type preform could not be used practically. The quantity of a monomer fed additionally can be decided by measuring the amount of volume shrinkage. In this study, the experiment was carried out as follows: A solution [SM : MMA=50 : 50 (wt/wt%)] containing 0.4 wt% BPO filled a capillary tube. The sample was polymerized at 75 °C in a convection oven. Volume shrinkage was measured by examining the change of height of sample at 75 °C in the convection oven.

3. Fabrication Methods of a GI-POF Preform

To obtain a graded index, the experiment was performed in case I and case II. The structure of the reactor is shown in Fig. 1.

3-1. Case I

Experimental procedure is shown in Fig. 2. A prepared solution (80 g) whose composition is SM : MMA (40 : 60 wt/wt%) with 0.4 wt% BPO was placed in a glass reactor. Polymerization was performed at 75 °C, 3,000 rpm for 7 hr. In order to prevent creating bubbles or voids in the preform, the temperature of the reactor was slowly cooled to room temperature. After cooling to room temperature, monomer whose composition was SM : MMA (50 : 50 wt/wt%) and with 0.4 wt% BPO was fed in a rotating reactor. Again, temperature was elevated to 75 °C and reaction was performed for 7 hr. After the same process was repeated twice, a preform without hollow was obtained.

3-2. Case II

Experimental procedure is shown in Fig. 3. Copolymer (40 g) whose composition is PS : PMMA (40 : 60 wt/wt%) was swelled with monomer (40 g) whose composition was SM : MMA (60 : 40 wt/wt%) for 24 hr. And then this was polymerized at 75 °C, 3,000 rpm for 7 hr. Then, the temperature of the reactor was cooled to room temperature and monomer whose composition was 60 : 40 wt/wt% with 0.4 wt% BPO was fed in a rotating reactor. Again the temperature was elevated to 75 °C and the reaction was performed for 7 hr. After the same process was repeated two times, a preform without hollow was obtained. This method has advantages in compari-
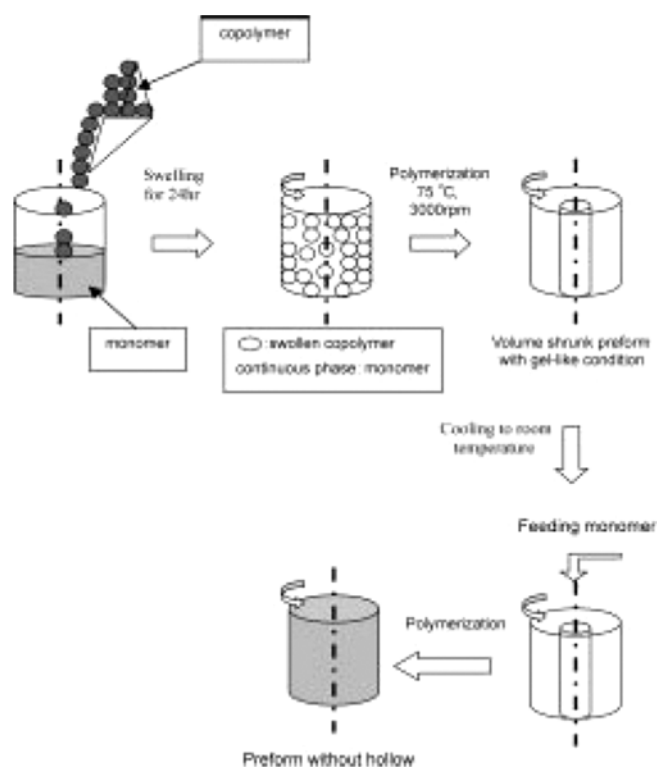
Fig. 3. Procedure of case II.

Fig. 5. Change of volume shrinkage with conversion.

son with case I. First, the material selection width becomes wide, because materials satisfy only one condition--that one polymer or copolymer is higher density and lower refractive index than monomer. Second, volume shrinkage is lower than case I, because volume doesn't shrink as much as the portion of copolymer. This allows for the reduction of additional feeding process in comparison with case I.

change of volume shrinkage with conversion is shown in Fig. 5. Monomer is expanded in the early stage. This phenomenon is caused by thermal expansion of monomer. Theoretical volume expansion in the early stage is written as

$$\frac{V_{Total}(75\,^{\circ}C)}{V_{Total}(25\,^{\circ}C)} = \frac{V_{SM}(75\,^{\circ}C)}{V_{SM}(25\,^{\circ}C)} \times x + \frac{V_{MMA}(75\,^{\circ}C)}{V_{MMA}(25\,^{\circ}C)} \times (1-x)$$

where,

$\dfrac{V_{Total}(75\,^{\circ}C)}{V_{Total}(25\,^{\circ}C)}$ is total volume expansion ratio

$\dfrac{V_{SM}(75\,^{\circ}C)}{V_{SM}(25\,^{\circ}C)}$ is SM volume expansion ratio

$\dfrac{V_{MMA}(75\,^{\circ}C)}{V_{MMA}(25\,^{\circ}C)}$ is MMA volume expansion ratio

x is volume fraction of SM

In this experiment, x is 0.5, $V_{SM}(75\,^{\circ}C)/V_{SM}(25\,^{\circ}C)=0.0431$ and V_{MMA} $(75\,^{\circ}C)/V_{MMA}(25\,^{\circ}C)=0.0741$. Thus, theoretical volume shrinkage is 0.0586. The volume expansion is 0.054 in the early stage and this is consistent with theoretical result.

Volume shrinkage ($V_{volume\ shrinkage}$) increases with time and is saturated with the value of 0.17. This value is consistent with following calculated value:

RESULTS AND DISCUSSION

1. Volume Shrinkage

Change of volume shrinkage with time is shown in Fig. 4, and

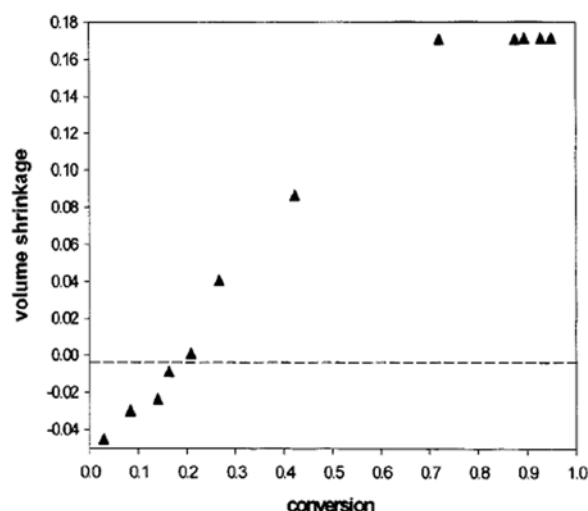**Fig. 4. Change of volume shrinkage with time.**

$\rho_{SM}=0.909$ g/cm^3 $\rho_{MMA}=0.936$ g/cm^3 $\rho_{monomer}=0.9225$ g/cm^3

$\rho_{PS}=1.05$ g/cm^3 $\rho_{PMMA}=1.190$ g/cm^3 $\rho_{polymer}=1.12$ g/cm^3

$$\frac{M}{V_{monomer}} : \frac{M}{V_{polymer}} = \rho_{monomer} : \rho_{polymer} = 0.9225 : 1.12$$

$$\frac{V_{polymer}}{V_{monomer}} = 0.837, \quad V_{cal.volume\ shrinkage} = 0.163$$

The volume shrinkage of preform under centrifugal force field is shown in Fig. 6. The volume shrinkage of a preform ($V_{preform\ volume\ shrinkage}$) is 0.193 and it is higher than $V_{volume\ shrinkage}=0.17$ which is created without centrifugal force field. This is because the created copolymer is compressed by centrifugal force. Because additional monomer will be fed after volume shrinkage, this is not a serious problem.
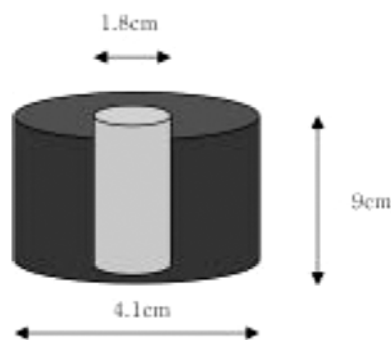
2. Refractive Index of Preform

Fig. 6. Volume shrinkage of preform fabricated under centrifugal force field.

To evaluate the refractive index of a preform, the composition of preform along radial direction was analyzed by H^1-NMR, because the refractive index is proportional to the composition ratio. The refractive index of a preform was calculated by using the correlation between the refractive index and the copolymer composi-
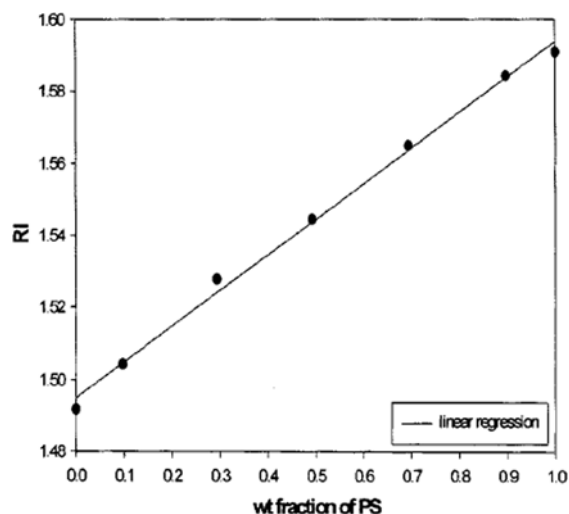

Fig. 7. Change of refractive index with wt fraction of PS.
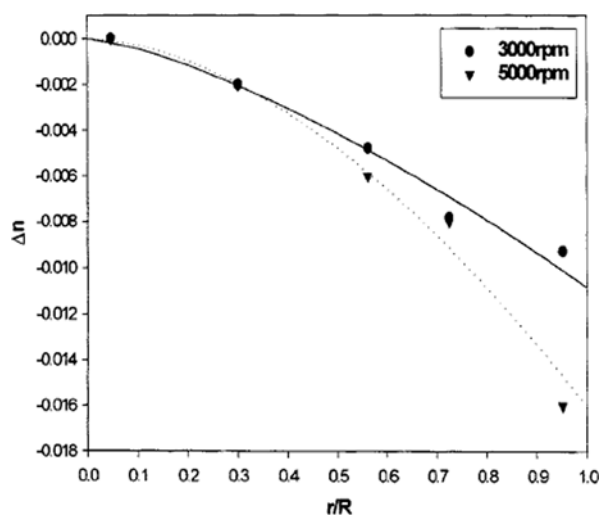

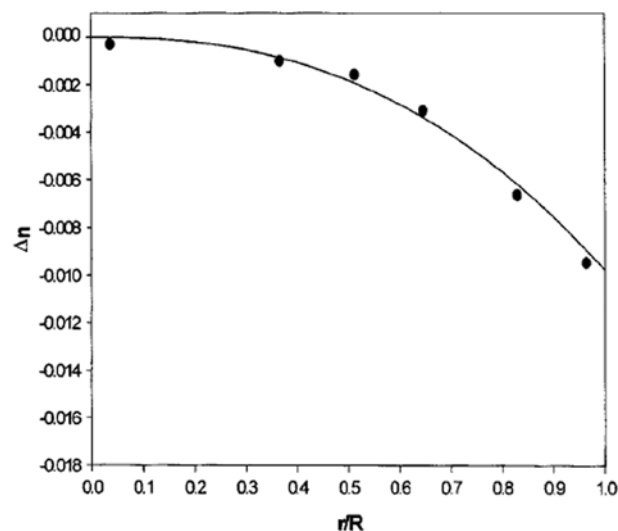Fig. 8. Distribution of refractive index in preforms made by case I.

Fig. 9. Distribution of refractive index in preforms made by case II.

tion ratio. Refractive index according to the polymer composition ratio was measured by Abbe's refractometer and is shown in Fig. 7. The results of each case are shown in Figs. 8 and 9.

In case I, when the reactor is rotating at 3,000 rpm, the difference of refractive index between the center axis of core and periphery is about 0.008. RI difference is about 0.016 when the reactor is rotating at 5,000 rpm. The solid and dotted lines represent the shape of the index profile of the preform. Generally, the GI-profile of core can be written as [Keiser. 2nd Ed.]

$$n(r) = n_0 \sqrt{1 - 2\Delta \left(\frac{r}{R}\right)^\alpha}$$

Here r is the radial distance from the center axis of core, R is the core radius, n_0 is the refractive index at the center axis of core, n_2 is the refractive index at periphery of the core and the dimensionless parameter α defines the shape of the index profile. The index difference Δ for the graded index fiber is given by

$$\Delta = \frac{n_0^2 - n_1^2}{2n_0^2} \approx \frac{n_0 - n_1}{n_0}$$

It was known that the α value is related to transmission rate. Transmission rate became maximum when α was about 2. To evaluate Δ and α value by using the measured data, $\log\{1-n(r)^2/n_0^2\}$ was plotted with $\log(r/R)$. The slope is α value and interpolated value is $\log 2\Delta$. The values of each case are shown in Fig. 10. α is 1.53 and Δ is 0.007 when the reactor is rotating at 3,000 rpm. α is 1.82 and Δ is 0.011 when the reactor is rotating at 5,000 rpm. Here, we can know that the α profile could be adjusted by rpm. Higher rpm is required to obtain an optimal α value of about 2.

In case II, RI difference is about 0.01. α is 2.292 and Δ is 0.006. To obtain a proper α profile, rpm, monomer composition, or copolymer composition should be controlled. If rpm is increased, a higher α value can be obtained; and if rpm is decreased, a lower α value can be obtained. In this experiment, 60 : 40 (SM : MMA wt/wt%) monomer and 40 : 60 (PS : PMMA wt/wt%) copolymer were used. Under the same rpm, the higher α value will be obtained if the concentration of SM is higher than 60 wt%. Furthermore, under the same rpm and monomer composition, a higher α value will be obtained
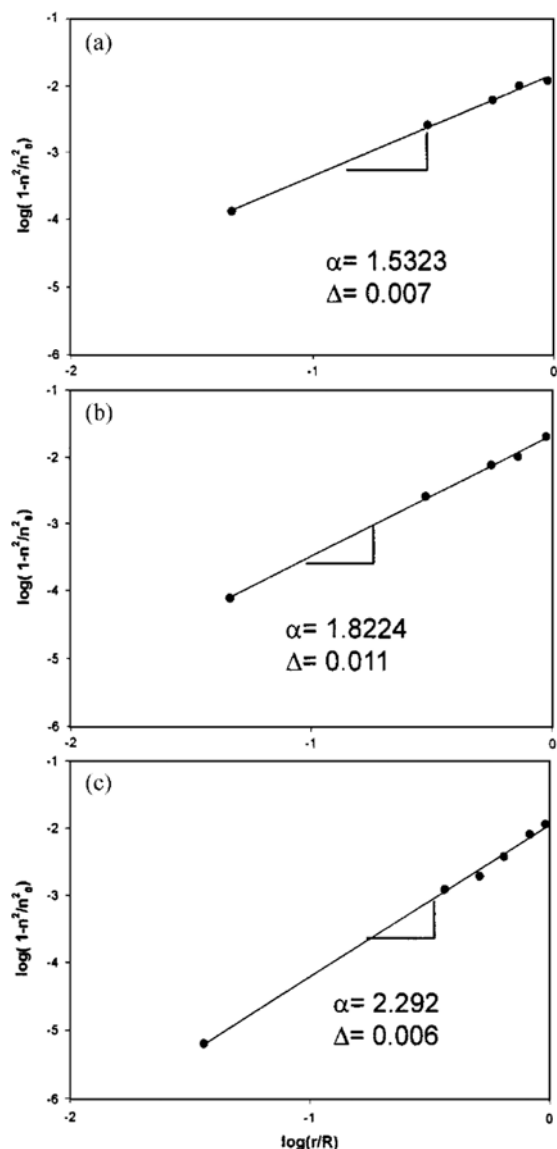
Fig. 10. log (r/R) vs log $\{1-n(r)^2/n_0^2\}$, (a) case I, 3,000 rpm (b) case I, 5,000 rpm (c) case II.

if the PS composition of copolymer is higher than 40 wt%.

CONCLUSIONS

PS/PMMA blend with a graded index profile was obtained by using centrifugal force. When polymerization was done under centrifugal force, a preform with hollow was usually obtained due to volume shrinkage. To resolve this problem, additional monomer with different composition was successfully fed to match the refractive index at the interface. A GI-POF preform without hollow and with a proper Δn (about 0.01) was fabricated with either monomer-monomer pair or monomer-polymer pair. It is expected that these GI-POF preforms can be used either in polymeric lens, LAN or image guide systems [Koike et al., 1994; Lee and Kim, 1991; Tagaya et al., 1997]

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