Preparation of Large-Sized Graded-Index Polymer Preform

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ABSTRACT: In this article, an improved method was put forward to overcome the defect of interfacial-gel polymerization technique. The cause of the defects was analyzed, and the factors of reaction conditions on formation of the graded-index (GI) polymer preform (i.e., reaction temperature and atmosphere pressure) were investigated. High-performance large-sized GI polymer preform was prepared by this improved technique, in which diphenyl sulfide was used as higher refractive index molecules. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 89: 817–820, 2003

Key words: polymerization; refractive-index; diffusion; optical

INTRODUCTION

Recently, even in the access area, a high-speed data communication system, such as digital in-home network and high-speed local area network (LAN), has been rapidly developed. So the development of optical fiber network, which is the most important infrastructure for high-speed data communication, has been required. Polymer optical fiber (POF) has many advantages to silica optical fiber in the short haul transmission field, such as low-cost connecting due to the large core, flexibility and toughness due to the polymer material, and so on. However, because poly(methyl methacrylate)-based step-index plastic optical fiber (PMMA SI-POF), which is available in the market, has high loss due to absorption of carbon–hydrogen bond and low bandwidth, its application field has been limited.[1] To overcome these disadvantages, graded-index polymer optical fiber (GI POF) is being developed. GI POF is one of the potential candidates providing inexpensive high-bandwidth data link for local area networks and telecommunication applications.[2,3] By far, there are many synthetic methods that have been used to prepare GI perform and the interfacial-gel polymerization technique provided by Koike et al. is considered to be one of the potent methods; the mechanism[4,5] of it is well accepted. However, there are still many problems in this method such as part opacity, bubble, and refractive index distributing asymmetric.

In this article, the reason for defects made by interfacial-gel polymerization technique was analyzed. The effects of reaction conditions on formation of the GI polymer preform (i.e., reaction temperature and atmosphere pressure) were investigated. Furthermore, an improved method to overcome the defects of interfacial-gel polymerization technique, named gradual-interfacial-gel polymerization, was put forward, by which high-performance large-sized GI polymer preform was prepared without the above disadvantage. Fiber length mainly depends on the diameter and length of the preform; therefore, it is of importance to prepare large-sized GI preform.

EXPERIMENTAL

Formation of the large-sized GI polymer preform

Diphenyl sulfide (DPS) was used as higher refractive index molecules (M_2) in our experiment. MMA was used as monomer (M_1); BPO was regarded as polymerization initiator, and *n*-LB was used as chain transfer agent (agents produced in Beijing Chemical Plant, Beijing, China). The formation was carried out as follows: the monomer, higher refractive index molecules, polymerization initiator, and chain transfer agent were purified first. Then, the MMA monomer mixture with higher refractive index molecules, polymerization initiator, and chain transfer agent was dropped into a pure PMMA tube with one end sealed gradually, and the reaction would take place gradually along the PMMA tube. The inner wall of the polymer tube was slightly swollen by the monomer mixture, and then a gel phase was formed on the inner wall of the tube. According to the accelerated polymerization

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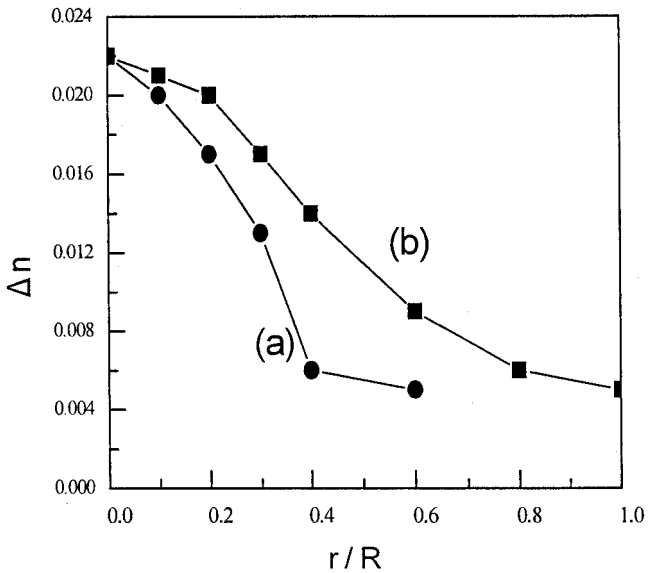

Figure 1 Refractive-index distributions of the MMA-DPS GI preform having 25 and 10 mm diameters.

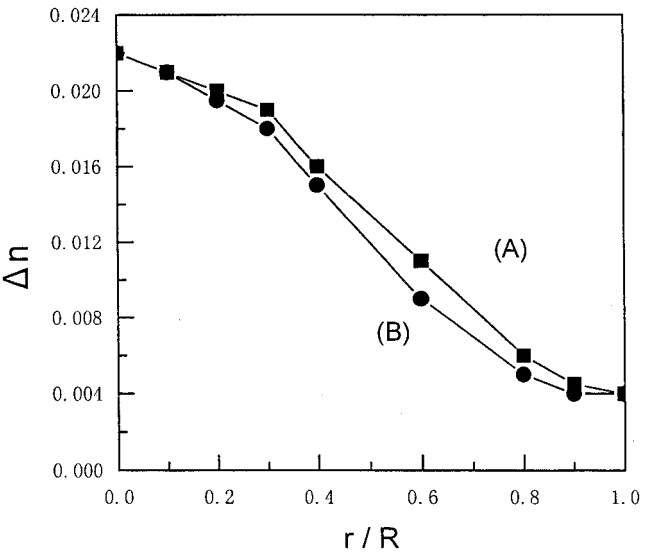

Figure 2 Refractive-index distributions of the MMA-DPS system GI preform having a radius of 25 mm, length of 30 cm: (a) top of the preform; (b) bottom of the preform.

reaction due to so-called gel-effect, the polymer was preferentially formed in the gel-phase and gradually grew to the center axis of the tube. Thus, the polymer gel phase was gradually formed from the inner wall of the tube and the content of the PMMA tube finally solidified up to the center axis of the tube. The reaction was at 60°C for 35 h and the polymer was solidified at 80°C for 4 h under 0.2 mmHg. Finally, PMMA-DSP system GI polymer preform with a diameter of 25 mm (inner diameter, 18 mm) and a length of 30 cm was obtained.

Measurement of the refractive-index distribution of the GI preform

To eliminate the defects of interfacial-gel polymerization technique and improve the performance of GI preform, the effects of the reaction conditions (i.e., reaction temperature and atmosphere pressure), polymerization initiator, and chain transfer agent were all investigated. The results will be discussed in next section. The refractive-index distribution of the various GI preform was measured by end-face reflect technique.[6] The results were shown in Figures 1-3.

RESULTS AND DISCUSSION

The contrast between interfacial-gel polymerization method and the gradual-interfacial-gel polymerization method

The mechanism of interfacial-gel polymerization method[7,8] is considered to be mainly gel-effect and the selective diffusion of the monomer and the dopant molecule into the polymer gel phase formed from the inner wall of the PMMA tube by the gel effect. Methyl methacrylate (MMA) monomer could diffuse into the gel phase more easily than dopant monomer because the MMA monomer molecular volume is smaller than that of dopant monomer. The polymerization reaction rate of MMA in the gel is much faster than the polymerization rate in the monomer liquid phase because of the gel effect. So, with the polymer phase thickened, the concentration of the dopant molecules in the monomer liquid phase gradually increased. At the center region of the PMMA tube, the concentration of dopant would increase to the maximum. Along with the polymer phase reaching the center axis of the PMMA tube, the refractive-index radius GI distribution formed, and a GI polymer rod was obtained.

The gel-effect is the reason to make the refractive index radial distributing of GI preform, but when the whole PMMA tube filled with the mixture takes gel

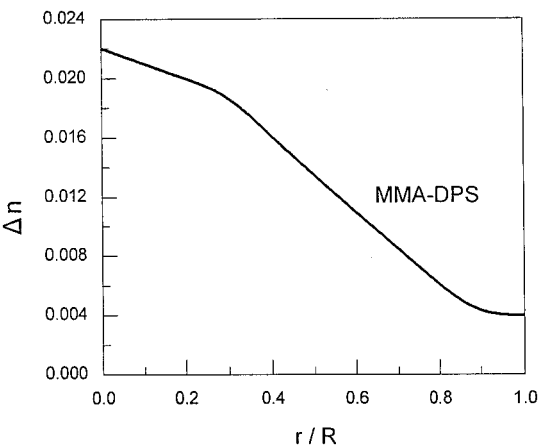

Figure 3 Refractive-index distribution of the MMA-DPS GI preform (radius 25 mm).

effect, quantities of reaction heat were released enough, which would produce bubble. When the whole tube filled with the mixture reacted, the higher refractive index molecules may deposit on the back of the tube because the higher refractive index molecule's weight is heavier than the MMA molecule's weight. Then, the refractive indexes would asymmetrically distribute along the PMMA tube and part opacity would be produced also.

The mechanism of gradual-interfacial-gel polymerization method is similar to the interfacial-gel polymerization method that the refractive index distributing formed mainly because of the gel effect and selective diffusion. However, in the gradual-interfacial-gel polymerization method, reaction occurred along the length of the PMMA tube gradually. The whole length of PMMA tube taking the gel effect would be avoided; the polymerization reaction heat release is controlled, and the bubble of the preform would be prevented. For the same reason that the reaction occurred along the length of PMMA tube gradually, the refractive-index distribution asymmetric along the length of preform caused by the higher refractive index molecules weight is heavier than the MMA molecules weight would be eliminated.

Effects of the polymerization initiator, chain transfer agent

Yang et al.[9] found that increasing the concentration of initiator from 0.5 to 1.0 wt %, and the increasing the chain-transfer agent from 0 to 1000 ppm could reduce the defect of GI polymer preform because of reducing the shrinkage of the polymers through decreasing the molecules weights of the prepared polymer. However, increasing the concentration of initiator or chain transfer would lead to increasing the impurity and optical attenuation of the GI polymer rods. In our experiment, 0.5 wt % of BPO and 0.1 wt % of *n*-LB were used, which can make GI preform have no voids and bubbles.

Effects of reaction temperature

There were two reasons for forming voids or bubbles in the GI polymer rod as we concluded. First, the rapid reaction produced lots of reaction heat. The reaction heat cannot spread out in time to make the voids and bubbles in the preform. The rapid reaction led to shrinkage of polymer for high molecular weight, so it would make voids and bubbles in the preform also. Second, there was air dissolving in the reaction mixture and carbon dioxide gas produced by initiator decomposing in the reaction mixture. They could continuously overflow with heating at first. However, when polymerization was reached to some extent, the average molecule's weight and viscosity of the reaction mixture increased, and the air and carbon dioxide could not overflow. Then, the voids and bubbles in the GI preform were formed. The experimental results revealed that the GI polymer preform prepared at 60–70°C contained less void or bubble than that at higher reaction temperature, and it did not deform at this temperature region.

Effects of reaction atmosphere pressure

In the former stage of reaction, when the reaction mixture was polymerized at 70°C under 0.2 mmHg vacuum pressure, the air and carbon dioxide could completely overflow from reaction mixture. In the later stage of reaction, the reaction mixture was polymerized under 2 mmHg high pressure, and formation of the voids and bubbles led by shrinkage of polymerization was difficult for high pressure.

PERFORMANCE OF PMMA-DPS GI PREFORM

It is well known that the index distribution of GI POF can be expressed by a power law of the form[10]

$$n(r) = \begin{cases} n_1[1 - 2(r/R)^g \Delta]^{1/2} & 0 \le r \le R \\ n_2 & r \ge R \end{cases}$$

where

$$\Delta = \frac{n_1^2 - n_2^2}{2n_1^2}$$

and where g is the exponent of the power law, R is the core diameter, and n_1 and n_2 are the refractive index of the core center and cladding, respectively.

Olshansky and Keck[11] deduced that when $g = g_{\text{opt}} = 2$, the bandwidth is maximized and

$$g = g_{opt} = 2 + \varepsilon - \Delta\frac{(4 + \varepsilon)(3 + \varepsilon)}{5 + 2\varepsilon}$$

$$\Delta = \frac{n_0 - n_1}{n_0}$$

where ϵ is the parameter of the material dispersion, and n_1 and n_2 are the refractive index of the core center and cladding, respectively. The optimizing refractive-index distribution of the polymer GI POF core is the quadratic parabolic profile.

Polymerization reaction rate is the key factor for forming the refractive index profile of the GI POF in the gradual-interfacial-gel polymerization technique. It affects the diffusion process of MMA monomer and dopant molecules into the polymer gel phase formed from the inner wall of the tube and makes different Δ, so different polymer rates make different g. There are

many factors affecting the polymerization reaction rate which will be discussed in another article.

By using the new technique, we successfully obtained the quadratic refractive index distribution even in the case of such a large diameter (25 mm) preform, just as Figures 1 and 3 show. The measurement result of the bottom and top's refractive-index distribution of PMMA-DPS GI preform is almost the same, as can be seen in Figure 2. These results indicated that gradual-interfacial-gel polymerization method could eliminate the defects that commonly exist in the interfacial-gel polymerization method and prepare the large-sized graded-index polymer preform that has high performance.

CONCLUSIONS

High-performance large-sized MMA-DPS dopant system GI preform was made by gradual-interfacial-gel polymerization method. It was experimentally confirmed that the quadratic refractive index distribution was successfully obtained even in the case of such a large diameter (25 mm) preform. The large diameter is important to polymer fiber because the fiber length possibly obtained from a preform depends on the diameter and length.

The effects of reaction condition on the formation of defects of GI polymer preform were investigated. Low temperature reduces the defects of voids or bubbles of the GI polymer preform. However, too low a temperature leads to deformation of the GI polymer preform. Vacuum takes advantage in overflowing the gas of the reaction mixture in the former stage, whereas high pressure is beneficial to compress the defects of voids or bubbles of the GI polymer preform in the later stage.

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