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SHORT COMMUNICATIONS

Gradient-Index Polymer Fibers Prepared by Extrusion

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Gradient-Index (GRIN) materials have emerged as very attractive materials because of their versatile applications in imaging, collimating, and optical communications.[1-5] The refractive index varies according to GRIN cylindrical material as shown in eq 1.

$$n(r)=n_c(1-1/2A(r/R_p)^2) \quad (1)$$

where n_c and $n(r)$ are the refractive indices at the center axis and at the distance r from the center, respectively, R_p is the radius of the rod, and A is the distribution constant. The unusual distribution of the refractive index of GRIN materials causes them to have quite different characteristics from the conventional step-index (SI) materials. They have found commercial applications in photocopy and facsimile imaging arrays, fiber couplers, and medical or industrial endoscope. GRIN polymer optical fibers have been recently demonstrated to have a large bandwidth of $2\,GHz\,km^{-1}$ and also a low optical loss of $56\,dB\,km^{-1}$ at 688 nm wavelength.[4]

Two kinds of materials are generally used as GRIN materials: glass and polymers. Several methods have been used to prepare GRIN glass materials, *e.g.*, ion-exchange,[6] sol–gel leaching,[7] glass fusing,[1] molecular stuffing,[1] chemical vapor deposition,[1] and neutron irradiation.[8] However, these methods are quite expensive and the production rate is low. Also, glass has limitations of poor flexibility and processibility, which have largely limited its applications. Polymers have the advantages of excellent mechanical properties, molecular design flexibility, good processibility, and low cost over glass. Hence, the development of GRIN polymeric materials has grown rapidly in recent years. Extrusion processes were developed to prepare GRIN polymer fibers successfully.[9-11] However, several drawbacks arise in these processes, *e.g.*, the difficulties involved with selecting optimum conditions, poor reproducibility because of the gas blowing in the diffusion zone, and the long diffusion time required which has subsequently led to long manufacturing time and low production rate.

In this study, a closed extrusion process was developed to prepare GRIN polymer fibers. Instead of obtaining a gradient-index polymer in an open system by blowing gas conventionally, a closed system is used to prepare GRIN polymer fibers by mutual diffusion of monomers with different refractive indices in a host polymer. The material systems used in this investigation are the host polymer, poly(methyl methacrylate) (PMMA) along with monomers,

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methyl methacrylate (MMA), and benzyl methacrylate (BzMA). Additionally, the compositions of BzMA and MMA inside the fiber, imaging radius R_c, and distribution constant A are estimated from the refractive index distribution. The parameters in the extrusion process which may significantly affect on the refractive index distribution are also discussed.

EXPERIMENTAL

Materials

Methyl methacrylate (MMA) (99%, Janssen Chimica) and benzyl methacrylate (BzMA) (98%, TCI) were purified by vacuum distillation. PMMA (Chi-Mei, Co., $M_w = 8.3 \times 10^4$, $M_n = 4.0 \times 10^4$)), 1-hydroxycyclohexyl phenyl ketone (TCI) and hydroquinone (99%, Janssen Chimica) were used without further purification. The monomers MMA and BzMA have similar reactivity ratios and the refractive indices of their homopolymers were 1.49 and 1.56, respectively.

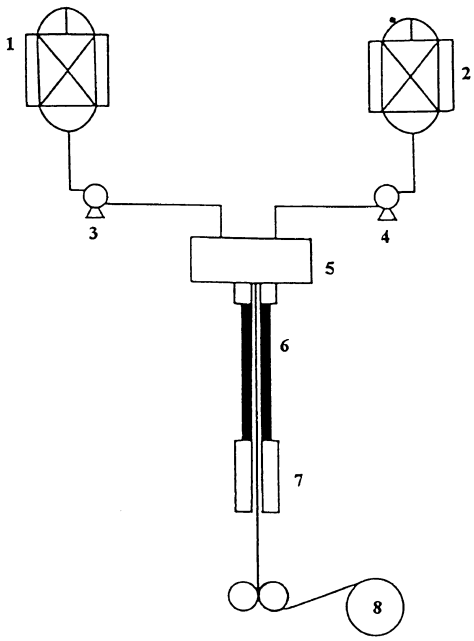

Figure 1. Experimental setup of the extrusion process for preparing GRIN polymer fibers. 1 and 2, material supply tanks; 3 and 4, gear pumps; 5, a concentric die; 6, an enclosed zone; 7, a hardening zone; 8, rolls.

Preparation of GRIN Polymer Fibers

Figure 1 shows a schematic diagram of the apparatus of the extrusion process for preparing GRIN polymer fibers. A material supply tank (1) contained the solution of a polymer (A) and at least one monomer (B) (may contain another monomer (C)); meanwhile a material supply tank (2) contained the solution of a polymer (D) and at least one other monomer (E). These two solutions were heated at 60°C. Next, gear pumps (3) and (4) with speeds of 0.5 and 1.5 ml min^{-1} were used to feed the two reactant mixtures 1 and 2 with the volume ratio of 1 : 3 into a concentric die (5), respectively. A dual-layer composite monofilament was then extruded out of the orifice of the die and fed into an enclosed zone of 45 cm (6), which was maintained at 80°C. While the monofilament went through the diffusion zone, the monomer (B) and/or (C) in the inner layer and the monomer (E) in the outer layer diffused into each other to produce the effect of a continuous distribution of refractive index in the filament. The monofilament was then fed through a hardening zone (7) where it was hardened by four UV lamps of 60W/cm each. Thus, a polymer fiber with a parabolic distribution of refractive index was taken up through rolls (8) by a take-up roll. In the present experiment, mixture 1 contained 57.4 wt% of PMMA (polymer A), 28 wt% of BzMA (monomer B), and 14 wt% of MMA (monomer C); meanwhile mixture 2 was 60 wt% of PMMA (polymer D) and 39.4% of MMA (monomer E). Both mixtures 1 and 2 contained 0.5 wt% photoinitiator 1-hydroxy cyclohexyl ketone, and 0.1 wt% inhibitor hydroquinone. The diameter of the prepared fiber was 1 mm.

Characterization

The refractive index profile of the prepared GRIN polymer fiber was measured using a Jenaval interphako interference microscopy

(Carl Zeiss Jena Gumb), in which a matching oil with a refractive index of 1.488 was used as the reference. The accuracy of this instrument was in the range of ± 0.002. The polymer thin film for the measurement of refractive index distribution was prepared by cutting the polymer fiber using a Microtome HM 350 (Microm GmbH). The film thickness was 30 μm. The polymer film was then placed on the slide and covered by a small piece of micro cover glass. A drop of embedding liquid was then placed on the slide, and the oil was diffused all over the surface of the micro cover glass. The distribution constant A and imaging radius R_c, which has the quadratic-index distribution expressed as eq 1 in the center region, was determined from the linear portion of the curve of Δn with $(r/R_p)^2$. Here, Δn is the difference of the refractive index of the center (n_c) and periphery (n_p).

RESULTS AND DISCUSSION

Refractive Index Distribution

Figure 2 shows the relationship between Δn and (r/R_p) (curve I) and $(r/R_p)^2$ (curve II) of the obtained polymer fiber. The values of n_c, n_p, and Δn determined from curve I are 1.508, 1.490, and 0.018, respectively. The distribution of the refractive index suggests that the mutual diffusion of MMA and BzMA occurred in the diffusion zone and resulted in a distribution of different compositions of MMA and BzMA inside the fiber. Since the refractive indices of PMMA and PBzMA are 1.49 and 1.56, respectively, the composition of the center and periphery of the fiber contains 25.7%, and 0% of BzMA, respectively. The imaging region R_c/R_p and distribution constant A estimated from curves I and II are 0.62, and 5.80×10^{-2}, respectively. Since the value of R_c/R_p is less than 1, the obtained polymer fiber in the present study may be suitable for optical fiber communication. However, it would not be suitable for the purposes such as an imaging lens, which would require R_c/R_p to be equal to 1.

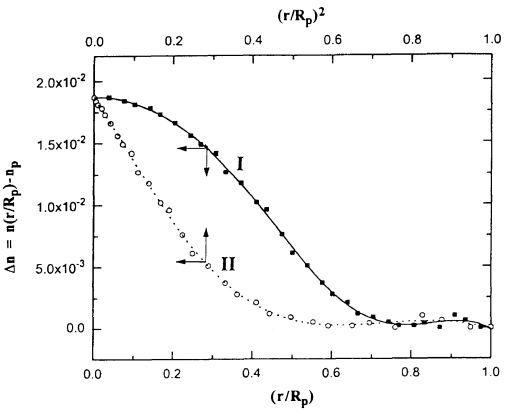

Figure 2. Relationship between the difference of the refractive index Δn with (r/R_p) and $(r/R_p)^2$ of the polymer fiber prepared by the extrusion process.

Discussion

The refractive index profile of the obtained polymer optical fiber was affected by both the formulation of the reactant mixture and the diffusion process. It can be expected that different types of monomer combinations, *e.g.*, MMA with fluoro-alkyl acrylate (FAA), BzMA with FAA, or a combination of MMA, BzMA, and FAA, would result in different shapes of refractive index profiles. Also, variation of the host polymer, *e.g.*, PMMA, PBzMA, PVB, or copolymers of BzMA and MMA, or BzMA and VB, or MMA and VB may have a significant effect on the refractive index distribution. Therefore, optical properties of the polymer fibers can be determined through molecular design. The diffusion process can also play an quite influential role in the properties of the polymer fiber. The diffusion time which would be affected by the length of the diffusion zone and feeding speeds of the two gear pumps, diffusion coefficients of monomers in host polymers, viscosities of the feeding mixtures, and temperature of the diffusion zone are important parameters in the diffusion process. The effects of these factors on the refractive index distribution will be presented on the next paper.[12]

CONCLUSIONS

A GRIN polymer fiber was successfully prepared by a closed extrusion process. The mutual diffusion of benzyl methacrylate and methyl methacrylate in a closed system resulted in quadratic distribution of refractive index up to 62% of the diameter of the obtained fiber and distribution constant A equal to 5.8×10^{-2}. The values of n_c, and n_p were 1.508, and 1.490, respectively, which correspond to 25.7% and 0% of BzMA in the center and periphery of the fiber. In further studies, the effects of formulations of the reactant mixtures, diffusion properties of monomers, temperature of the diffusion zone and feeding speed of the gear pump on the distribution of the refractive index of the resulting fibers will be examined.

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