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GI-POF: from Preform to coated fiber

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Abstract

The high bandwidth, Graded Index Polymer Optical Fiber (GI-POF) makes it possible to transmit high-speed optical signals along short-ranged optical network systems. A rod type polymer preform, with a radially-varying refractive index, is useful for preparing low-loss and high-bandwidth GI-POF and can also be used in the manufacture of Polymer Optical Rod Lenses.

We have successfully manufactured a polymer rod with good mechanical properties by utilizing ultra-centrifugal force and by varying concentrations of the monomers with different reactivity. This process could avoid the excess heating during the reaction phase and maintain a stabilized, decreasing refractive index profile from the center axis to the periphery, with minimal fluctuations. The technique could be applicable for a preform with larger diameters and with controlled reproducible properties at higher producing speed.

POF were drawn from thus produced GI-POF using 8m long drawing tower with IR furnace and then also coated with various UV curable coating materials (tight buffer coatings, colored coatings, flame retardant coatings, ribbon coatings, etc), thereby increasing the mechanical reliability, providing improved transmission performance, and increased bending and tensile strength properties.

1. Introduction

At present, the Polymer Optical Fiber (POF) market is focused on short distance communication networks for fiber-to-the-home (FTTH), fiber-in-the-home (FITH), and automotive data communications in accordance with IEEE 1394b.[1-2] Graded Index Polymer Optical Fiber (GI-POF) has recently attracted extensive attention in optical fiber communication network systems and MEMS micro-optic applications. The refractive index varies continuously within the graded index polymeric materials. This variation allows them to have unique optical properties that conventional optical materials with constant refractive index cannot achieve.

The refractive index distribution can be expressed by Equation (1):

$$n(r) = n_0(1-1/2Ar^g)^{0.5} = n_0(1-1/2A'(r/R_p)^g)^{0.5} \qquad (1)$$

Where n_0 is the refractive index at the center axis, n(r) is the refractive index at a distance r from the center axis, R_p is the radius of the rod, g is the power law index, and A and A' are constants of the refractive-index distribution.

Several synthetic approaches have been used to prepare the GI-POF preform materials, e.g. two-stage copolymerization [3], photo copolymerization [4-5], interfacial gel copolymerization [6], centrifugal polymerization [7], vapor phase diffusion copolymerization [8], etc.

However, the bare POF does not perform well when directly exposed to harsh environmental conditions, mechanical stress or extreme bending of the fiber. The outer coatings must withstand the above conditions, i.e., demonstrate oxidative and hydrolytic stability, high resistance to moisture and organic solvents, so that these coatings could promote the long term reliability in the POF application.

Through elaborately-controlled copolymerization processes in a centrifugal field utilizing the differences in reactivity, refractive index, and the density of the constituent monomers and polymers, a polymer rod preform with a radially varying refractive index profile could have been prepared. With this technique, it is possible to mass produce fibers and achieve optimal refractive index distribution. We have also gone further on manufacturing processes with thus prepared preform: Fiber drawing process using IR furnace, and UV curable coatings applications on GI-POF (e.g., tight buffer coating, colored coatings, flame retardant coatings, and ribbon coating).

2. Experiment

Preparation of POF Preform

The basic principle of our preform fabrication is to utilize the ultra-centrifugal force and the difference in the reactivity of monomers which are mixed in a rotating tube. The liquid materials with different reactivity and refractive indices were fed into a heated rotating tube, and polymers rich in higher reactivity constituent were generated, which went to the outer layer due to the ultra-centrifugal force. The materials rich in the other constituents remained at the center of the rotating tube. After a few hours of polymerization process, the remaining reactants would be

polymerized progressively in a controlled way that we came up with, until the required graded index profile is completed. The composition of the monomers fed into the tube was made to change gradually over time, so that the composition of the polymer preform in the tube also gradually changes in the radial direction. Therefore, by controlling the amounts and the ratios of the materials being fed into the tube over a specific time period, a varying refractive index profile of the polymer preform could be obtained in the rotating tube.

The main advantages of this process are the controllability of the desired refractive index profile and the production capability of the large preforms without sacrificing the ideal shapes of index profile.

We have designed and constructed a reaction system which consists of an electric oven, a rotating tube-holding apparatus, polymer and monomer feeding pumps, and a specialized reactant feeding nozzle. A positive nitrogen atmospheric environment was maintained inside the oven.

The glass tubes were designed with various dimensions of inner diameter, outer diameter, and the length (500 mm). After the material was charged into the tube (as shown in Fig. 1), the polymerization reaction was induced at a reaction temperature of 60°C while rotating the tube at a rate of 12,000 rpm. When the viscosity of the materials increased to about 100,000 cPs, the polymerization reaction proceeded, and the reaction temperature was raised gradually to 100 °C. When the viscosity of the material reached about 200,000 cPs with further reaction, the reactor temperature was lowered to 60 °C. The materials were further polymerized after the monomer feeding. After polymerization, the preform was annealed at 110 °C under reduced pressure for 12 hrs. This preform was used to draw into GI-POF by IR furnace.

A schematic drawing of the experimental setup is shown in Fig. 1. A tube with an inner diameter of 43 mm was rotated about its central axis. The maximum attainable rotation speed is approximately 12,000 rpm; consequently, the centrifugal field varied from 0 at the center of the tube to about 2,100 G-force (unit normalized relative to the Earth's gravitational field) at the inner wall of the tube.

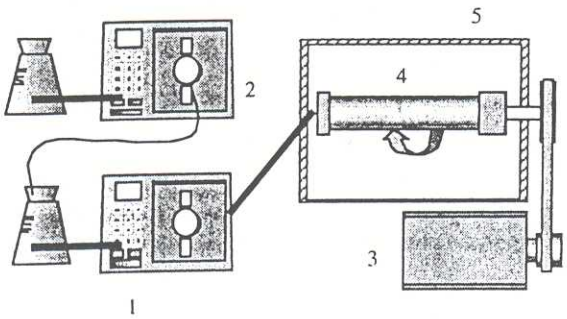

Fig. 1. The scheme of reactor for manufacturing polymer rod;

1, 2: Liquid pump for injection, 3: AC Motor for centrifugal force, 4: Glass tube, and 5: Electrical Oven

POF drawing

We designed and constructed an 8 meter drawing tower. It consists of the preform feeding parts, furnace, diameter gauge, capstan, dancer, and take up system.

The research was conducted to test the possibility of high speed drawing with a large diameter preform. In order to overcome the overall disadvantage of heating with the conventional electric resistance furnace, mainly the problem associated with heat transfer, an IR furnace with the wavelength range of 1-2 μm was designed and fabricated. Since radiation energy generated from the IR furnace could directly reach the inner region of the preform, the temperature gradient in the preform would be reduced. The IR furnace was made of several circular halogen lamps each with a power rating of 1,000 Watts and the wavelength of the center of the radiation was 1.5 μm. From our positive results, we have determined that the IR heating system in the drawing process is at least as suitable for high-speed drawing of large preforms as conventional methods.

POF coating application

The POF coating materials were mainly composed of oligomer, monomer, pigment and photoinitiators. The oligomeric component of base composition can include a single type of oligomer or it can be a combination of two or more oligomers. The oligomeric material is preferably an unsaturated urethane acrylate. Urethane oligomers provide an aliphatic or aromatic di-isocyanate groups which react with dihydric polyether or polyester. Typically a polyoxyalkylene glycol is formed, such as a polyethylene glycol. This oligomer usually has 4-10 urethane groups with the molecular weights ranging 3000 ~ 6000g/mol.

Also single monomeric component or a combination of two or more monomers was also included. This monomer is an unsaturated acrylate, which contains various functional groups to induce cross-linking reaction.

For most acrylate-based coating formulations, conventional photo initiators such as ketonic photoinitiator and phosphate oxide additives were used (less that 10 percent by weight). The photo initiators were chosen to provide reasonable curing speed without causing premature gelation of the coating materials.

The coating materials also contain additives, which include antioxidants, catalysts, lubricants, low molecular weight non-cross linking resins, adhesion promoters and stabilizers. Some additives influence the photo polymerization process, thereby affecting the physical properties of the coating.

From the urethane oligomer (54%), monomers (36%), cross-linkers (3%), photoinitiator (5%) and additives (pigment, antioxidants, UV stabilizer, etc), the coating material of POF exhibited desirable bending or tensile strength characteristics. [11-12] Materials were cured with a UV lamp (600 W / inch, D type bulb, Model No. VPS

600I made by FUSION) at the line speed 50-100 m/min. The 1 mm diameter POF passed through a 1.5 mm long coating die and UV curing zone.
The tight buffer coating, color coated fiber, flame retardant coated fiber, and ribbon coated fiber could also be prepared in conventional coating line in our lab using suitable coating materials developed for these purposes. Some of their results will be presented here.

Characterization

The molecular weight of the polymer samples used in this study was measured by gel permeation chromatography (GPC). GPC measurements were performed with a Waters GPC calibrated with narrow-distribution and polystyrene standards. Tetrahydrofuran was used to dissolve the polymer samples and as an efluent. The polymer possessed a weight-average molecular weight of about 100 kg/mol.

Differential scanning calorimetry measurements were performed on a Perkin-Elmer DSC-7 calorimeter at a standard heating rate of 10 °C/min.

The refractive index profiles of the polymer rod were measured with a preform analyzer (Nettest P104), and it was possible to compare the bandwidth predicted of GI-POFs with the normal quadratic index profiling. The effect of the shaped index profile on the bandwidth can be theoretically analyzed by this approximation process.

The viscosity of uncured POF coating composition was measured by a Brookfield viscometer, model RV II+, 1.5 rpm, #41 spindle, at 25 °C. The refractive index of uncured composition was measured by an Abbe refractometer at room temperature.

Films (75 μm thick) of the coating material were prepared on microscope slides and then UV cured by exposing the films to D type Lamp, (120 W / cm) at 1.0 J cm^{-2} in a nitrogen controlled atmosphere. Complete curing of the sample films was determined using an IL-390 radiometer manufactured by International Light Inc.

The tensile strength, elongation and secant modulus of the cured samples (films and fiber) were tested using a universal testing instrument, Instron Model 4201; the load cells used were 2 and 20 pound capacity (ASTM D638M).

The bend radius is defined as the radius of the drum or mandrel on which the fiber is to be wound or bent.

3. Results

The refractive index profiles (RIP) of polymer rod used are shown in Fig. 2. The monomers used were acrylate and fluoroacrylate. The materials were copolymerized in five steps (five discontinuous injections) and the result is shown in line A. The undesirable line shape is evident. In line B and C, the composition of the feeding monomers changed continuously over all injection period (1hr and 6 hrs, respectively).

Optimal conditions for the RIP which causes minimal fluctuation and quadratic without flatness at the center so that results in the least dispersion, could be obtained by continually injecting and varying the concentration elaborately for 6 hours to achieve the GI-POF as a light carrier with a high bandwidth.

The approximate value of exponent g in index profile power-law equation shown in Equation (1) was determined. The values of g extracted from lines B and C were about 4 and 2. These profiles could also be changed by varying composition ratios and injection times over various ranges. The numerical aperture (NA) estimated from the index profile (n_0 and n_1) was approximately 0.23 in line C.

The bandwidth characteristic of the polymer rod was calculated by the Wentzel-Kramers-Brillouin (WKB) numerical computation method. The results were that the calculated bandwidth in line B was 0.8 GHz and the one in line C was 3.5 GHz. Attenuation of approximately 150 dB/km could also be obtained at 650 nm. Optical loss was measured by cut-back method.

With a conventional electric furnace, drawing speeds was limited only 50 m/min due to the large temperature gradients. While the outer surface is melting, the heat was not transferred enough to the central regions. Therefore, we designed our own IR furnace system which could reduce the temperature gradient problems within the preform. The POF preform was drawn using one IR lamp at a line speed of 50~100 m/min. The POF with diameter of 1 mm could be drawn, fluctuation of which could be kept less than 50 μm.

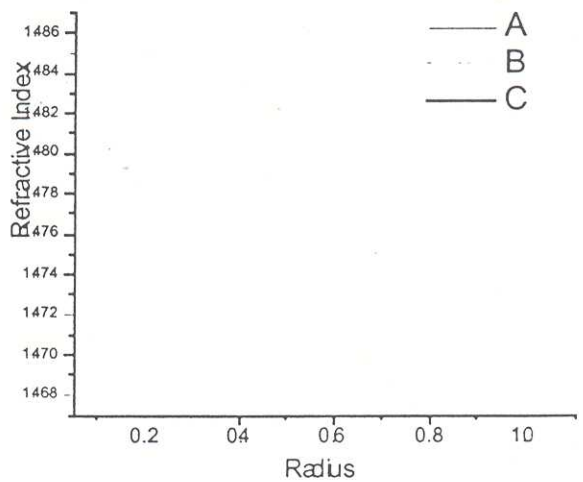

Fig. 2. Refractive index profile of preforms (A: 5 step injection, B: 1 hr continuous injection, C: 6 hr continuous injection)

Table 2. The General Properties of Coating materials for POF

Liquid viscosity cPs @ 25 °C	4,000 ~ 6,000
Elongation (%)	15 ~ 30

Tensile Strength (Mpa)	10 ~ 20
Young's Modulus (Mpa)	120 ~ 200
DMTA T_g ℃	60 ~ 70

The general properties of coating materials for POF are shown in Table 2. These coating materials were designed for achieving optimal bending and tensile strength characteristics. These were applied to the POF fiber at the line speeds 50 ~ 100 m/min, thickness of which was determined to be about 200 μm. Fig. 3 shows the fibers when POF was coated with tight buffer coating materials and coloring (violet) materials.
The tight buffer coating provides an additional protection for the POF. These coatings prevent the fiber from being oxidatively degraded and also improved resistance to moisture and organic solvents. Long term reliability testing of our POF is underway.

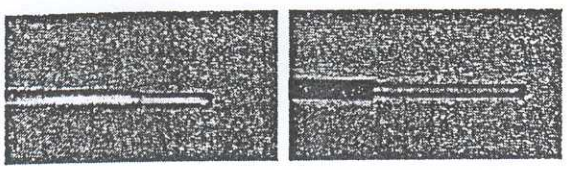

Fig. 3. POF Coated with Tight buffer and Coloring

A comparison of properties of bare POF and coated POF are also shown in Table 3. These results show that the attenuation has not been significantly changed by the coatings, while the mechanical properties have been demonstrated to be improved.

Table 3. Comparison of properties of Bare POF and coated POF

	Optical Loss [dB/km]	Tensile [N]	Bending R [mm]
Bare POF	150	2.7	5
Tight buffer	150	3.3	4
Coloring (Violet)	151	3.2	4

The quadratic refractive index profile of our GI-POF allows it to be utilized as optical fiber in high-speed data transmission applications. The controlled manufacturing processes investigated in this study indicate that the specialty fiber with appropriate index profile, for example depressed clad fiber or W-shaped fiber, can also be obtained with changing composition ratio.

4. Conclusion

We have developed the technique for manufacturing GI-POF which uses copolymerization process with the incorporation of ultra-centrifugal force, established the drawing process parameters, and determined the UV curing characteristics for the coating of thus drawn fiber (e.g., tight buffer coatings, colored coatings, flame retardant coatings, ribbon coatings, etc).

Projects presently underway:

1) POF flame-retardant coating meeting UL 94 standards.
2) Ribbon matrix coating for multi-fiber applications.
3) Environmental long term reliability testing.

5. Reference

1. C. Emslie, J. Mater. Sci. **23**, 2281(1988)
2. W. Groh, D. Lupo, and H. Sixl, Angew. Chem. Int. Ed. Engl. Adv. Mater. **28**, 1548(1989)
3. Y. Ohtsuka, T. Sugano, and Y. Terao, Appl. Opt., **20**, 1319(1981)
4. Y. Ohtsuka, H. Hatanaka, and Y. Koike, Appl. Opt. **23**, 1779(1984)
5. Y. Koike, H. Hatanaka, and Y. Ohtsuka, App. Opt. **23**, 1779(1984)
6. Y. Koike, E. Nihei, N. Tanio, and Y. Ohtsuka, App. Opt. **29**, 2686(1990)
7. F. G. H. van Duijnhoven, (1999)
8. Yamatomo T., Mishina Y., Oda M. U.S. Patent 4,852,982 (1989)
9. T. Ishigure, E. Nihel, and Y. Koike, App. Opt. 33, 4261(19[illegible])
10. T. Ishigure and Y. Koike POF 2001, 293(2001)
11. Blyer, et al., Optical Fiber Telecommunications, 299(19[illegible])
12. Morikawa et al., Chemical Abstract, 11536(1988)