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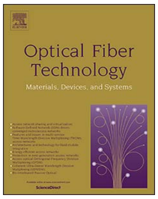

Regular Articles

Solution-mediated cladding doping of commercial polymer optical fibers

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ABSTRACT

Solution doping of commercial polymethyl methacrylate (PMMA) polymer optical fibers (POFs) is presented as a novel approach for preparation of custom cladding-doped POFs (CD-POFs). The presented method is based on a solution-mediated diffusion of dopant molecules into the fiber cladding upon soaking of POFs in a methanol-dopant solution. The method was tested on three different commercial POFs using Rhodamine B as a fluorescent dopant. The dynamics of the diffusion process was studied in order to optimize the doping procedure in terms of selection of the most suitable POF, doping time and conditions. Using the optimized procedure, longer segment of fluorescent CD-POF was prepared and its performance was characterized. Fiber's potential for sensing and illumination applications was demonstrated and discussed. The proposed method represents a simple and cheap way for fabrication of custom, short to medium length CD-POFs with various dopants.

1. Introduction

In number of applications, polymer optical fibers (POFs) may represent a preferable choice over their silica-based counterparts [1–3]. Polymer materials offer higher chemical flexibility and simpler processing [4,5], which is typically associated with lower POF manufacturing costs. Most common commercial POFs are large-diameter multi-mode (MM) fibers based on polymethyl methacrylate (PMMA). These fibers can be fairly cheap, very robust but flexible, plus they are easy to handle and connectorize [6,7]. Among other advantages, POF technology also allows incorporation of different organic dopants, such as fluorescent dyes, into the fiber material. Fluorescent POFs (F-POFs) have attracted considerable attention in different fields over the years. They have been originally developed in 1980's for scintillation detectors in high energy physics experiments [8,9]. However, since then, F-POFs have been exploited for various tasks in fiber sensing [10], lasing and amplification [11], or illumination [12,13] applications.

Depending on the POF manufacturing procedure, different approaches can be used to incorporate the dopant into the fiber material. Most commonly, the doping is performed on the chemical level, when the dopant is added to the monomer mixture before fiber preform polymerization [14,15]. Alternatively, the dopant can be physically mixed with the polymer melt if the extrusion or casting is used to produce the preform [13]. Finally, solution doping technique has been used to introduce the dopant into the bulk fiber preform [16]. For the vast majority of produced F-POFs, only the core of the fiber is doped. Limited selection of core-doped F-POFs is available also commercially. Cladding doping is in principle possible, however, no cladding-doped POF (CD-POF) is available commercially. Few experimental CD-POFs have been fabricated and explored for different applications. Pun et al. prepared PMMA-based POF with Rhodamine 640-doped cladding and investigated its potential as a side-pumped intrinsic fiber light source [17]. Narro-Garcia et al. fabricated POF with pure PMMA core and THV-Rhodamine 6G cladding for use in illumination applications [12]. Muto et al. used POF with Fluorescein-doped cladding as an optical humidity sensor for breathing condition monitoring [18]. CD-POFs can be of high interest especially in sensing applications. Over the years, numerous fluorescence-based POF sensing schemes have been explored. These include sensors for gamma or UV radiation [19,20], partial discharges [21], humidity [18], position [22], oxygen [23], pH factor [24] and others. Many of these sensing schemes rely on attaching the sensing dye to the side of the fiber. In order to excite and/or collect the light from the dye, some sort of local fiber modification, e.g. tapering, etching or removal and recoating of the cladding, is typically required [20,25]. This sort of local modification usually deteriorates fiber mechanical integrity, increases its loss and offers only limited interaction lengths. Incorporation of the suitable dye directly into the fiber cladding can facilitate efficient interaction between the light propagating inside of the fiber core and the surrounding environment. This could be potentially exploited for construction of various chemical or environmental fiber sensors [26–28].

All of the above-mentioned F-POF manufacturing techniques rely on a doping in a pre-drawing stage. Fabrication of F-POFs in this way, therefore, represents technically demanding process requiring suitable

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high-cost equipment and facilities. Recently, solution doping technique was suggested for post-fabrication doping of cladding layer of commercial PMMA POFs [29]. In this work, we present more detailed analysis of solution doping of large-core PMMA POFs as a novel mean for CD-POF fabrication. The technique is studied and optimized in terms of suitable selection of used POF, doping conditions and time. We show that this method may represent rather cheap and straightforward way for preparing custom CD-POFs with short to medium lengths.

2. Doping procedure optimization

POF solution doping technique relies on soaking of a bulk polymer component, e.g. fiber preform, in a suitable solvent-dopant mixture [16]. Successful doping requires selection of the right solvent suitable both for the doped material and the used dopant. In the case of PMMA, methanol is typically used. The technique is commonly employed for doping of microstructured POF preforms either with fluorescent compounds [16,30], or with dopants for increasing fiber photosensitivity [31,32]. The solvent gradually penetrates the bulk polymer and induces its osmotic swelling [33]. At ambient temperatures, ingress of methanol into PMMA exhibits Case II diffusion behavior [34,35], which is characterized by a sharp boundary between the intact inner PMMA region and the swollen outer layer. Due to the solvent-induced swelling, even larger molecules such as organic dyes can diffuse into the PMMA molecular structure. Nevertheless, the mobility of larger dyes is significantly lower than for small solvent molecules and their penetration into the material lags behind the solvent. Similarly as for in-diffusion, also out-diffusion of the solvent is significantly faster than for larger dopant molecules. After the solvent is removed, the dopant molecules are left in the material and their distribution remains stable even at elevated temperatures [30].

Instead of doping bulk polymer elements, we use the solution doping technique directly with commercial PMMA fibers. Various factors such as temperature, specimen geometry or thermal history may influence the diffusion process in PMMA [33,34,36,37]. Therefore, this section is aimed at the basic investigation and optimization of the doping procedure on a small scale, i.e. using short fiber samples and small solvent-dopant mixture quantities.

2.1. Methods and materials

Following the previous studies discussed above, we chose methanol as the suitable doping solvent in this work. LC-MS grade methanol (≥99.95%) from Th. Geyer (Berlin, Germany) was used. The work is focused on the technological aspect of the novel cladding-doping procedure for commercial PMMA POFs. Therefore, we limited this study to using a common and affordable dopant; powdered Rhodamine B (≥95%) from Sigma-Aldrich (Munich, Germany). Nevertheless, we managed to successfully use the presented technique also with several other dopants including Fluorescein, Rhodamine 6G or Alizarin Yellow R. The technique was tested with three different commercial PMMA POFs of similar characteristics; ESKA CK-40 and ESKA GK-40 from Mitsubishi Rayon (Tokyo, Japan) and RAYTELA PGU-FB1000 from Toray (Tokyo, Japan). Some of the main fiber properties extracted from their respective datasheets are listed in Table 1. All the fibers are 1 mm step-index POFs with PMMA core and cladding from perfluorinated polymer.

The doping solution was prepared by dissolving 25 g of Rhodamine B in 75 ml of methanol. This relatively high dopant concentration was chosen in order to facilitate better visibility of the Rhodamine B (RhB) ingress into the fibers. The prepared solution was distributed into multiple small laboratory glass bottles. The tested POFs were cut into short 4 cm pieces. Three fiber pieces were inserted in a bottle with the doping solution, separately for each fiber type. The bottles were closed and stored in a climate chamber at specified temperature for a given time. After the specified time, the samples were taken out of the solution, thoroughly rinsed and dried. The process is schematically illustrated in Fig. 1. The doping procedure was repeated for different doping temperatures and times.

Table 1
Main characteristics of the PMMA POFs used in the study.

	Eska CK-40	Eska GK-40	RAYTELA PGU-FB1000
Fiber diameter [μm]	1000	1000	1000
Core diameter [μm]	980	980	980
Numerical aperture	0.5	0.5	0.5
Operation temperature range [°C]	−55–70	−55–85	−55–70
Transmission loss at 650 nm [dB/km]	≤200	≤150	≤150
Minimum bending radius [mm]	25	20	9

To monitor the lateral ingress of methanol and dye into the fibers, cross-section of the obtained doped samples was investigated with an optical microscope. One end of a doped sample was cut roughly 2 mm away from the original end face. This end of the fiber was inserted in an SMA connector and polished with the help of polishing paper and puck. The connectorized fiber piece was kept in the polishing puck and place on the sample holder of the optical microscope. This helps to keep the fiber in straight upright position so the image of the fiber cross-section can be taken. Inspection of the samples and their cross-sectional images allow us to assess the dynamics of the solvent-dye penetration into the fiber in order to determine the most suitable doping conditions.

2.2. Doping process dynamics

The progress of lateral penetration of methanol-RhB solution into the fiber is illustrated in Fig. 2 for the case of ESKA CK-40 doping at 30 °C. The figure depicts cross-sectional microscope images of the fiber samples that were left in the solution for progressively increasing doping times. The images were taken in the transmitted light mode. Lateral view of each sample is depicted under the corresponding microscope image. The ingress of methanol into the fiber is clearly visible already for the sample with 3 h doping time. The obvious boundary between an intact inner region and a thin swollen outer ring penetrated by methanol can be noticed in the cross-sectional image. As the doping time increases, methanol penetrates deeper into the fiber and the ring gets thicker until the full methanol penetration is reached. The doping series depicted in Fig. 2 serves as an example for illustrating the doping procedure progress. Nevertheless, analogical behavior with different dynamics can be observed for all three tested fibers and different doping temperatures.

To evaluate the progress of methanol front, diameter of the whole fiber D and the inner unpenetrated region d was measured from the microscope images for all the samples. To account for diffusion inhomogeneities, the measurement was performed along four different radial directions. The values were then averaged and used to calculate the relative methanol penetration $P = (D-d)/D$ of the given sample. The final P value of the fiber doped under given conditions was calculated as an average from the three individual fiber samples doped under the same conditions. Fig. 3 shows the time progress of relative methanol penetration into all three tested fibers at 20 °C. We found out that the experimentally measured data (solid points) can be best approximated by a power function fit (solid lines) in a form $P(t) = at^b$. Here, t is the doping time, a and b are the scaling factor and the exponent of the power function, respectively. The power function dependence of $P(t)$ observed in our experiment contradicts previous works [16,34,35]. Methanol ingress into PMMA at ambient temperatures typically exhibits Case II diffusion behavior and the methanol front should progress with a constant velocity. This means that the