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# Study of doping non-PMMA polymer fibre canes with UV photosensitive compounds

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**Abstract:** We propose a solution doping method for polycarbonate (PC) and TOPAS polymer optical fibre (POF) canes using different UV photosensitive dopants aiming to reduce the fibre Bragg grating inscription time at the typical Bragg grating inscription wavelength (325nm). Three-ring solid-core PC mPOF canes and hollow-core TOPAS canes were doped with a solution of dopants in acetone/methanol and hexane/methanol, respectively. Doping time, solvent mixture concentration and doping temperature were optimised. A long and stepwise drying process was applied to the doped canes to ensure complete solvent removal. This is required to avoid the formation of any bubbles during the fibre drawing process.

**Key Words:** Microstructured polymer optical fibre cane, UV inscription, Polycarbonate, TOPAS.

## 1. Introduction

Polymer optical fibres (POFs) can be used for different sensing applications. One of the advantages of polymer fibres over conventional silica glass fibres is their small Young modulus compared to silica. For instance PMMA's Young modulus is typically 2-3 GPa, which is about 30 times smaller than that of silica (72 GPa) [1]. Lower Young modulus implies a higher sensitivity to stress. Furthermore, polymer fibres are biocompatible and potentially cheap to manufacture. These properties make them very attractive for different sensing applications such as structural health monitoring and biomedical sensing devices, e.g. glucose sensors [2]. Polymer optical fibres can be made from different materials, such as PMMA (polymethyl methacrylate), Zeonex [3], et cetera. The most commonly used is PMMA (polymethyl methacrylate). However, interest has recently developed in polycarbonate (PC) mPOFs due to the fact that PC has good mechanical properties as well as high operating temperature range due to its high glass transition temperature of 144 °C. Fibre Bragg gratings (FBGs) can be inscribed in PC fibres and can be used for sensing applications [4]. One limitation in the manufacture of POFBGs is typically represented by the FBG inscription time. One of the ways to reduce the fibre Bragg grating inscription time is to dope the polymer with the photosensitive materials before fibre drawing. E.g. Benzyl Dimethyl Ketal (BDK) is used to dope PMMA [5]. The reduced inscription time may help in the commercialization of POFBG sensors. Polycarbonate has been shown to be photosensitive at typical inscription conditions and to have shorter inscription time compared to PMMA at same inscription wavelength [4]. Doping PC with different photosensitive dopants can further increase its photosensitivity and therefore reduce the grating inscription time. Another non-PMMA material that has drawn attention in recent years is TOPAS, which is a cyclic olefin copolymer used for many applications in healthcare, optics, packaging and electronics applications. The main advantage of TOPAS over PMMA is its humidity insensitivity which is highly desirable for some sensing applications [6-7]. In this work we investigate solution doping methods for mPOF cane doping. We test several UV photosensitive dopants. The aim is to reduce the fibre Bragg grating inscription time at the typical Bragg grating inscription wavelength (325nm).

## 2. Doping

The doping experiments involved the use of various photosensitive compounds, such as BDK, coumarin and the recently developed monomer 2,7-NAF.DM [8], at various dopant concentrations. Two different solution-

based doping techniques were investigated. The first was applied to PC and was similar to the one adopted by Large et al. [9], as displayed in Figure 1(a). Polycarbonate mPOF canes were left in a solution containing the dopant for a time ranging from hours to days - depending on the solution concentration – until the solvent/dopant diffusion had met around the core. At this point we tried out two different routes, both of which were proposed in [9]. We either left the mPOF canes in the solution until the diffusion fronts met in the core or we applied heat to them in order to facilitate further diffusion of the dopant towards the core. Also, the drawing conditions themselves can facilitate further diffusion because of the elevated temperature involved. Note that in Figure 1(a) the inward diffusion of the solvent/dopant solution occurring through the outer wall of the cane is not shown for the sake of clarity. Figure 1(b) shows the alternative doping technique that was developed. A hollow-core polymer cane was initially doped with a solution of the desired dopant for a limited time in order to allow a mild inward diffusion to occur. This method was applied to TOPAS 5013 POF canes. The single-hole can then be collapsed by fibre drawing to obtain a doped solid core. Notice, the latter step has not been tested yet.

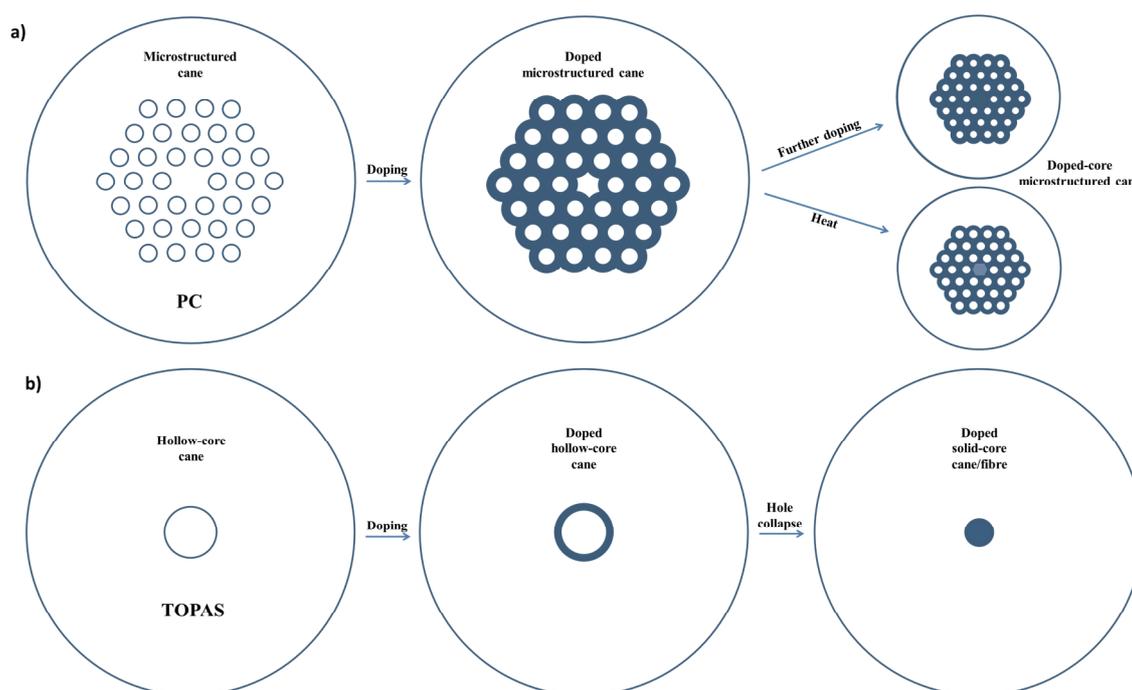


Figure 1. (a) Doping method used for PC mPOF canes. (b) Hollow-core TOPAS POF cane doping technique with further suggestion of hole collapse to obtain fibres with a doped solid core.

In both PC and TOPAS cane doping techniques, a swelling agent was required to open the structure of the polymer and allow an easier and rapid diffusion of dopant into the cane. In PC, acetone represented a good candidate for such purpose. Acetone can indeed diffuse very rapidly, but the fast swelling brings about environmental stress cracking [10]. Therefore, a proper diluent such as methanol was required. Methanol indeed diffuses much slower into PC than does acetone as the former is a relatively poor solvent for PC [10]. We conducted a series of preliminary experiments with methanol/acetone solutions aiming to optimise the swelling of polycarbonate but, at the same time, avoiding stress cracking issues. Short samples of the canes with a length of approximately 10-15mm were left in a mixture acetone/methanol ranging from 20% to 50% v/v for about 2 days at room temperature. The canes used for drawing the fibers are needed to be one order magnitude longer than the samples. Nevertheless, the results from short samples can be related to the real canes where the required doping time is expected to be longer. At concentrations of acetone around 40% v/v the PC mPOF canes lost their original transparency irreversibly, as shown in Figure 2. The best result for rather fast diffusion without losing transparency was obtained for a solution acetone/methanol 33:67% v/v. This may be seen in Figure 3, which shows the diffusion pattern for shortsamples from the same mPOF cane left at various acetone/methanol mixture concentrations for the same doping time. The percentage refers to the

volumetric concentration of acetone. For 25 %, the diffusion was too slow as confirmed by the diffusion area, i.e. the ring around the holes, being very small. At higher concentrations of acetone the diffusion speed increased with increasing acetone concentration as expected.



Figure 2. Preliminary test for solution concentration optimisation.

At 34-35% the diffusion speed was therefore relatively fast. However, the canes started to lose some transparency, while, for a concentration of 33%, no significant decrease in transparency was observed. At 33% the swelling action, mainly due to the acetone, was still adequate, and considerably higher than at lower acetone concentrations.

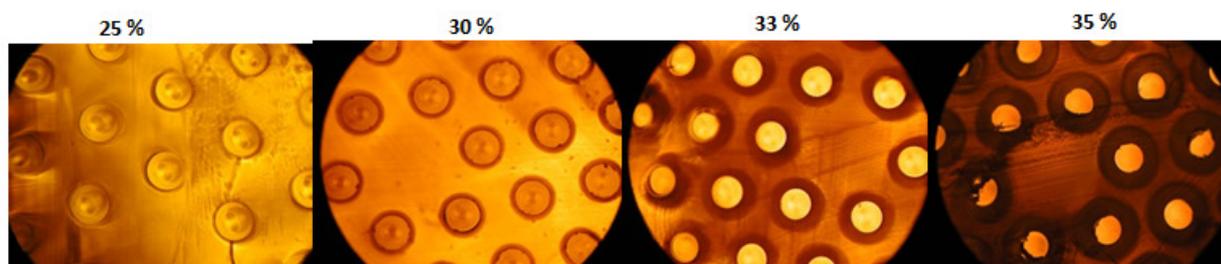


Figure 3. Diffusion pattern for a PC 3-ring mPOF cane at different acetone/methanol concentrations where the same doping time is applied.

Notice, acetone/methanol 33:67% v/v was the optimum for doping at room temperature, i.e. 25 °C. For higher temperatures the optimal condition was found to vary. In particular, the optimum shifted towards lower concentrations when the doping temperature was increased. For instance, at 40 °C the optimal acetone/methanol concentration was found to be 30:70% v/v.

A similar procedure was carried out for hollow-core TOPAS 5013 canes. We used a solution methanol/n-hexane where the latter acts as the swelling agent. Since mixtures methanol-hexane present partial miscibility at around room temperature, the maximum concentration of hexane in methanol considered in our experiments was 40% v/v, i.e. below the solubility limit of 41.34% v/v, 46.32% v/v and 53.97% v/v at 20 °C, 25 °C and 30 °C, respectively, reported in [11]. As done for PC, the doping conditions were optimized by varying the concentration of hexane in methanol in order to maintain a high clarity of the cane after doping with the best doping speed possible. The optimum concentration was found to be 70% methanol and 30% hexane v/v.

### 3. Drying

Drying resulted to be the most critical step before drawing the fibre from the doped canes. Evaporation of acetone/methanol solutions from PC canes was rather difficult and required the application of a long and stepwise drying process. Likewise, also drying TOPAS canes after doping with hexane/methanol solutions required a treatment similar to that of PC. All canes were dried first at room temperature for at least one day and then in an oven for several days where the temperature was gradually increased from 40 °C up to 110 °C (TOPAS) or 120 °C (PC). The canes were weighted before and after the doping to ensure complete solvent removal. Ideally, to have an easier drying process, the doping time – and therefore the absorption/swelling –

should be fairly limited. Figure 4 shows an example of what may happen during the drying process when the solvent content is too high.



Figure 4. Bubble formation in a TOPAS cane after drying above 70 °C.

#### 4. Conclusion

Until now the main limitation has been the significantly higher loss introduced by the combination of doping-drying process. One doped PC mPOF with reasonable transmission loss was produced, but it did not show any significant increase in photosensitivity. This may be due to insufficient concentration of dopant in the core, which still requires optimisation. Moreover, a few rather transparent doped canes were obtained, but the fibre transmission loss after fibre drawing was very high, probably because of the formation of small bubbles during the drying and drawing stages. In this regard, work is in progress to optimise the drying process for complete removal of the solvent without creating bubbles in the polymer cane. This is needed to make sure that there is no bubble formation during fibre drawing. In addition, the introduction of photosensitive compounds in the core itself tends to increase transmission loss due to higher scattering loss and the transparency of the dopant being typically lower than that of the host polymer. This may represent an intrinsic limitation in doping PC and TOPAS, where the fibre losses are in general higher than those of PMMA.

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