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Solution-Mediated Annealing of Polymer Optical Fiber Bragg Gratings at Room Temperature

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Solution-mediated annealing of polymer optical fiber Bragg gratings at room temperature

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Abstract—In this letter we investigate the response of poly(methyl methacrylate) (PMMA) microstructured polymer optical fiber Bragg gratings (POFBGs) after immersion in methanol/water solutions at room temperature. As the glass transition temperature of solution-equilibrated PMMA differs from the one of solvent-free PMMA, different concentrations of methanol and water lead to various degrees of frozen-in stress relaxation in the fiber. After solvent evaporation, we observe a permanent blue-shift in the grating resonance wavelength. The main contribution in the resonance wavelength shift arises from a permanent change in the size of the fiber. The results are compared with conventional annealing. The proposed methodology is cost-effective as it does not require a climate chamber. Furthermore, it enables an easy-to-control tuning of the resonance wavelength of POFBGs.

Index Terms—Annealing, Plastic optical fiber, Optical fiber sensors, Bragg gratings, Polymers, Absorption.

I. INTRODUCTION

SENSING devices such as fiber Bragg gratings (FBGs) based on polymer optical fibers (POFs) bring about various advantages over their counterparts made of silica. They offer an increased sensitivity to stress due to a considerably lower Young's modulus and a wider range of strains available [1-2]. Also, polymer optical fibers are ideal candidates for *in-vivo* biosensing applications [3-5] due to their non-brittle nature, flexibility in bending and biocompatibility. Further advantages are ease of handling, low densities, and low processing temperatures, as well as flexibility in the production process (choice of functional group, polymerization method, etc.) [1-2]. Poly(methyl methacrylate) (PMMA) is the most common material for polymer optical fiber Bragg gratings (POFBGs) [6-8].

However, for more specific purposes, such as humidity insensitivity, low attenuation, and high-temperature resistance, TOPAS (COC, cyclic olefin copolymer) [9], CYTOP (an amorphous fluoropolymer) [10], and polycarbonate (PC) [11] POFBGs, respectively, have been developed.

One particular problem associated with the use of POFBGs is their limited thermal stability at temperatures even much lower than their glass transition temperature (T_g) [12]. To overcome this problem, proper annealing is typically required. Annealing of POFs and POFBGs has recently been the subject of an increasing number of studies [12-16]. This process has proved well in enhancing the thermal stability and widening the range of linear temperature response of POFBGs [12-13]. The recently published papers by Woyessa *et al.* [15] and Stajanca *et al.* [16] focus on how the particular value of relative humidity (RH) at which annealing is carried out can in fact affect the properties of PMMA POFs and POFBGs. The RH effect is due to the fact that water acts as a plasticizer for PMMA and lowers its T_g [16-17]. Such investigations consider the effect of RH when the annealing temperature is itself particularly high, about 80-90 °C. This effect is huge because of the elevated annealing temperature [15-16]. Zhang *et al.* [8] also studied the effect of RH on the wavelength drift of PMMA-based POFBGs, but this mechanism was caused by the optical absorption increasing with RH, which led to an increase in internal temperature due to photothermal effect.

Early investigations showed that, when PMMA is at equilibrium with water, the T_g of the polymer is lowered by approximately 20 °C compared to the dry one [17]. Given that the T_g of PMMA is typically 105-115 °C [14,16], its minimum actual T_g at saturation ranges between 85 °C and 95 °C. Similar considerations apply to several other polymer-solvent combinations. Indeed, the T_g of a polymeric material equilibrated with one or more solvents may be different from that of the pure polymer. To an extent that depends on the specific way polymer and solvent/solution interact. For instance, if a swelling agent for PMMA is used, such as methanol, the actual T_g of the polymer-solution system at equilibrium can go down to room temperature [18].

The present work is based on the following idea: why not to generate an effect equivalent to conventional annealing simply by lowering the actual T_g of the polymer to such an extent that room temperature 'matters' energetically? In other words, immersing a PMMA fiber in methanol/water solutions at room temperature may have an effect akin to annealing a solvent-

free fiber at high temperature and controlled humidity. Therefore, instead of increasing the local temperature to approach T_g in a climate chamber at controlled RH, here we want to observe a comparable effect by using a suitable T_g–lowering solution. In particular, the specific aim of this work is to investigate the relaxation of PMMA microstructured polymer optical fiber Bragg gratings (mPOFBGs) when immersed in methanol/water solutions. As a consequence of the solution concentration dependence of the T_g, varying methanol/water ratio implies changing the T_g of the PMMA fiber when equilibrated with the solution, which results in different degrees of frozen-in draw stress relaxation. The solution-based annealing is cost-effective as it does not require a climate chamber. It would reduce the overall cost of POFBG sensor development and it is also better suited for large-scale production processes than annealing in a climate chamber.

II. SOLUTION-MEDIATED ANNEALING METHOD

Early studies by Williams *et al.* focused on the effect of the presence of methanol on the T_g of PMMA [18]. Depending on the weight-average molecular weight (M_w), for methanol-equilibrated PMMA systems they found a T_g ranging from 20 °C (M_w = 23500 g/mol) to 30 °C (M_w = 550000 g/mol). The weight-average molecular weight can be thought of as an average polymer chain length. Since PMMA polymers optimal for the fiber draw process have an M_w being within this range [14,19], the T_g of a PMMA-based optical fiber equilibrated in methanol corresponds to room temperature. When heated up close to its actual T_g, a polymer fiber tends to relax frozen-in draw stresses. This can affect the dimensional stability of the fiber and therefore limit its operating temperature to values well below the theoretical ones. Heating up an unannealed fiber to even modest temperatures during operation can yield a permanent blue-shift in the resonance wavelength of Bragg gratings [12]. Furthermore, their optical and mechanical properties may also be affected [14,16]. As a result of the polymer fiber draw process, polymer chains are aligned along the drawing direction, which leads to the formation of frozen-in stress in the fiber. Such degree of alignment depends on the draw stress applied to the preform (1-stage drawing) or both preform and cane (2-stage drawing) [14,16,19]. After drawing, polymer chains are in a non-equilibrium configuration and have the tendency to move back toward the original state as soon as they are provided with enough energy to do so. The higher the temperature, the greater the rearrangement of the polymer chains relaxing the frozen-in draw stresses. The relaxation is typically accompanied by a change in dimension of the fiber, i.e. shrinkage in the axial direction as well as an increase in diameter [12,14,16]. Considering that the relaxation occurs when the local temperature approaches T_g, we can theoretically obtain an effect similar to annealing if we simply lower the T_g of a PMMA fiber by immersing it in a methanol-based solution at room temperature. The literature reports the use of methanol to facilitate the doping of PMMA canes for fiber drawing with various compounds, e.g. benzyl dimethyl ketal (BDK) [20] and rhodamine 6G [21]. However,

pure methanol cannot be directly used for fibers, since the very low T_g would lead to an excessive draw stress relaxation in PMMA mPOFBGs. This effect is much less pronounced at the cane level, as at this stage the polymer canes are thicker and the polymer chains are less oriented than in the final fiber.

The best way to obtain a sufficiently low T_g but not too close to room temperature is to use a proper diluent, similarly to what is done in annealing using a climate chamber where the temperature is high but lower than T_g [15-16]. Water represents a good candidate in this regard, as it is miscible with methanol and, as already mentioned, the T_g of water-saturated PMMA is known from the literature to be about 20 °C lower than that of the pure polymer [17]. As a result, the addition of water to a methanol-based solution is expected to increase the T_g of PMMA fibers equilibrated with the solution.

III. EXPERIMENTS AND RESULTS

An in-house made 2-ring PMMA mPOF was used in the experiments. The microstructured fiber was manufactured at DTU Fotonik from GEHR PMMA rods (glass transition of the bulk material being 106 °C) by using the drill-and-draw technique [19]. It had an average diameter of approximately 150 µm and an 8-µm core. The average draw temperature and draw stress were 190°C and 10 MPa, respectively. The hole diameter and pitch size were 2 µm and 5 µm, respectively. The resulting hole to pitch ratio of 40% ensured that the fiber was endlessly single mode [22]. Bragg gratings were inscribed into the fiber by using a CW HeCd laser operating at 325 nm (IK5751I-G, Kimmon). We used the phase mask method for grating writing and an inscription setup being the same as the one reported in Bundalo *et al.* [23]. For inscription, a laser power of 20 mW and a custom-made phase mask by Ibsen Photonics A/S, optimized for writing at 325 nm and having a uniform period of 572.4 nm, were used. Six FBGs were inscribed in six PMMA mPOFs from the same fiber draw and tested in solutions at three different volumetric concentrations (v/v) of methanol/water, 50:50%, 60:40%, and 70:30% (uncertainty of 1% v/v). The grating behavior in each solution was tested with two different FBGs. The initial resonance wavelength of the gratings used in the experiments is reported in Table I. Note, the small differences in initial Bragg wavelength are due to the slightly different pre-strain levels

TABLE I
INITIAL BRAGG WAVELENGTH FOR THE DIFFERENT EXPERIMENTS

Methanol/water v/v [%]	Initial Bragg wavelength [nm]
50/50	847.3 (grating 1); 845.5 (grating 2)
60/40	846.2 (grating 1); 846.6 (grating 2)
70/30	847.3 (grating 1); 847.4 (grating 2)

applied during the grating inscription. CHROMASOLV methanol (Sigma-Aldrich, purity ≥ 99.9% by weight) and Milli-Q water were used. In both cases, 10 ml solutions were prepared in 10 ml graduated cylinders that were sealed at the top with Parafilm to avoid evaporation during the measurements. We used a supercontinuum source (SuperK Compact, NKT Photonics) as the light source and a spectrometer (CCS175 – Compact Spectrometer, Thorlabs) to track the reflection peak continuously throughout the
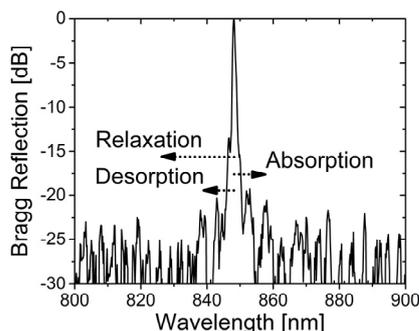
Fig. 1. Normalized Bragg reflection spectrum monitored throughout the experiments at room temperature. Stress relaxation and solution absorption-desorption phenomena interplay and contribute to the observed overall shift.

experiments. The FBGs were immersed and kept in the respective solutions as long as the relaxation continued. Fig. 1 shows an example of a Bragg grating peak monitored during the experiments. Three different phenomena were expected to occur: solution absorption (red-shift) and frozen-in stress relaxation (blue-shift) while the grating was immersed in the solution, and desorption (blue-shift) as well as some residual relaxation (blue-shift) once the fiber was removed from the solution. The FBGs were taken out of the solution once the rate of Bragg reflection wavelength blue-shift was ~ 0.4 nm/hour (absolute value), after which the desorption-evaporation of the solution was monitored.

Fig. 2 shows an example of the Bragg grating wavelength as a function of time for a PMMA mPOFBG immersed in a solution of methanol and water 50:50% for 64 hours (stopping criterion met), after which the grating was removed from the solution and monitored for further 13 hours to study the grating response during solvent evaporation. In this experiment the overall resonance wavelength shift obtained after solvent evaporation was -50.0±3.0 nm (error expressed in terms of standard deviation). The absorption of the methanol/water solution changed both refractive index and fiber size. Since the shift was large and permanent (same value after one week), the observed behavior must be due mainly to a permanent change in the size of the fiber, as already seen in high-temperature annealing of polymer optical fibers and sensors [12,14,16]. An initial red-shift in Bragg wavelength was observed, with a maximum of 1.5±0.1 nm after approximately 100 minutes, because of the swelling dominating the chain alignment relaxation at the beginning of the experiment. This was the result of a temporary positive balance between red-shift due to solution-mediated swelling and blue-shift caused by chain alignment relaxation. However, after about 8 hours the total shift referred to the initial Bragg wavelength became constantly negative. This corresponded to the tendency towards relaxation becoming stronger and stronger after an initial lag phase due to the initial diffusion of the solution into the fiber. However, the real contribution due to absorption-swelling, which would lead to a much greater red-shift than the observed one, was hidden by the incipient relaxation (blue-shift). This can easily be seen in Fig. 2, where the rapid solvent evaporation upon FBG removal from the solution corresponds to a sudden and sharp blue-shift of the resonance wavelength. The fast evaporation process was

facilitated by the small diameter of the fiber. The further down-shift occurred after removal of the Bragg grating from the solution was measured to be -15.0±1.6 nm at the end of the experiment. The shift was toward blue as the evaporation implied further fiber shrinkage. The mild decrease observed after the sharp downward jump in resonance wavelength was due to solvent evaporation and some residual relaxation becoming less and less important as the evaporation went on.
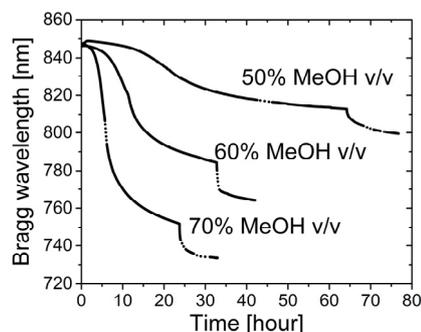

Fig. 2. Fiber Bragg grating wavelength versus methanol (MeOH) volumetric concentration. Note, a few experimental data were missing due to high reflection noise and were recovered by fitting (represented by dotted lines).

To obtain a measurement of the corresponding fiber shrinkage, we repeated the in-solution annealing experiments applying similar conditions to four PMMA mPOFs from the same draw. Fig. 3 shows the permanent values of both shrinkage (stars) and Bragg wavelength shift (circles). At 50% v/v of methanol the average fiber shrinkage was 5.25±0.20%.

Fig. 2 further shows the Bragg grating wavelength as a function of time for two PMMA mPOFBGs being immersed in a solution methanol/water 60:40% v/v and 70:30% v/v for 33 hours and 24 hours, respectively, and further monitored for 9 hours during desorption-evaporation of the solution once the gratings were removed from the solution. Three main differences with respect to the case 50:50% can be noticed. First, the relaxation process was clearly faster than in the previous case due to the higher concentration of methanol, since methanol is a stronger swelling agent for PMMA than water. In particular, the relaxation speed increased with methanol concentration. Second, as expected the overall Bragg wavelength shifts were considerably higher in absolute value, being -80.3±2.4 nm and -111.6±3.2 nm for 60% and 70% v/v of methanol, respectively (Fig. 3). The dispersion in the data can be due to the uncertainty in solution concentration as well as to fluctuations in room temperature and fiber diameter. Fig. 3 shows that also the fiber shrinkage increased with methanol concentration, being 8.13±0.25% and 12.69±0.13% for the experiments at 60% and 70% v/v, respectively. Third, probably because of the relaxation occurring very fast, in these two cases only a slight initial red-shift in Bragg wavelength was observed, although the desorption curves during solvent evaporation were steeper, as can be easily seen in Fig. 2. Note, the final Bragg wavelength shifts obtained in the cases 60% and 70% v/v are comparable with the ones obtained by annealing at 80 °C in a climate chamber at 30% RH (-76.2 nm [15]) and 70% RH (-136.5 nm [15]), respectively. Also, similarly to conventional annealing [15], in all the three cases
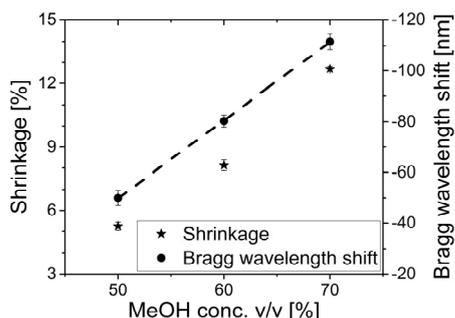
Fig. 3. Shrinkage and Bragg wavelength shift versus MeOH concentration. The fibers and gratings were checked after one week and both shrinkage and resonance wavelength shift were permanent. The dotted line represents the trend of the rate of Bragg wavelength shift within the range 50-70% v/v.

(50%, 60% and 70% v/v of methanol) there was no significant loss in grating strength, as it was lowered by 2 dB at the most.

In Fig. 3 it can also be seen that a decrease in resonance wavelength by about 3 nm can be expected if we run the experiment with a methanol concentration being increased by 1% within the range 50%-70% v/v (dotted line). This value can be used to calculate the solution concentration approximately required to tune the resonance wavelength of PMMA POFBGs down to a specific spectral region of interest.

We further tested the previously treated fibers together with four PMMA mPOFs from the same draw in a climate chamber (CLIMACELL, MMM Group) at 80 °C and 50% RH for 48 hours. The length of each fiber was measured before and after the experiment. The results are reported in terms of shrinkage in Table II. The shrinkage was significantly lower for the fibers annealed in solution compared to unannealed fibers, and it decreased with increasing methanol/water ratio used for the in-solution treatment. This shows that the proposed method can lead to enhancing the thermal stability of PMMA fibers.

TABLE II
IMPROVED THERMAL STABILITY OF IN-SOLUTION ANNEALED PMMA MPOFS

Methanol/water v/v [%]	Fiber shrinkage [%]
Unannealed	8.13±0.32
50/50	5.41±0.27
60/40	4.29±0.13
70/30	3.08±0.14

IV. CONCLUSION

The possibility of relaxing stresses frozen in the PMMA fibers by using methanol/water solutions was demonstrated. By immersing two-ring PMMA mPOFBGs in solutions at various concentrations of methanol and water, it was possible to obtain significant and permanent Bragg wavelength blue-shifts at room temperature. The thermal stability of the PMMA mPOFs was seen to be improved as a consequence of the solution-mediated annealing. This technique does not require the use of a climate chamber, and it is easy to control and implement. In addition, if an appropriate combination of solvents is used, the solution-based annealing method may also be applied to other polymers such as TOPAS and PC.

REFERENCES

[1] D. J. Webb, "Polymer Fiber Bragg Grating Sensors and Their Applications," in *Optical Fiber Sensors: Advanced Techniques and Applications*, G. Rajan, CRC Press, 2015, pp. 257-276.

[2] K. Peters, "Polymer optical fiber sensors — a review," *Smart Mater. Struct.*, vol. 20, no. 1, p. 013002, 2011.

[3] J. B. Jensen, P. E. Hoiby, G. Emiliyanov, O. Bang, L. H. Pedersen, and A. Bjarklev, "Selective detection of antibodies in microstructured polymer optical fibers," *Opt. Express*, vol. 13, no. 15, pp. 5883–5889, 2005.

[4] G. Emiliyanov, P. E. Høiby, L. H. Pedersen, and O. Bang, "Selective serial multi-antibody biosensing with TOPAS microstructured polymer optical fibers," *Sensors*, vol. 13, no. 3, pp. 3242-3251, 2013.

[5] H. U. Hassan, K. Nielsen, S. Aasmul, and O. Bang, "Polymer optical fiber compound parabolic concentrator tip for enhanced coupling efficiency for fluorescence based glucose sensors," *Biomed. Opt. Express*, vol. 6, no. 12, pp. 5008-5020, 2015.

[6] G. D. Peng, Z. Xiong, and P. L. Chu, "Photosensitivity and gratings in dye-doped polymer optical fibers," *Opt. Fiber Technol.*, vol. 5, no. 2, pp. 242-251, 1999.

[7] Z. Xiong, G. D. Peng, B. Wu, and P. L. Chu, "Highly tunable Bragg gratings in single-mode polymer optical fibers," *IEEE Photonics Technol. Lett.*, vol. 11, no. 3, pp. 352–354, 1999.

[8] W. Zhang, A. Abang, D. J. Webb, and G.-D. Peng, "Wavelength Drift of PMMA-Based Optical Fiber Bragg Grating Induced by Optical Absorption," *IEEE Photonics Technol. Lett.*, vol. 27, no. 4, pp. 336-339, 2015.

[9] I. P. Johnson, W. Yuan, A. Stefani, K. Nielsen, H. K. Rasmussen, L. Khan, D. J. Webb, K. Kalli, and O. Bang, "Optical fibre Bragg grating recorded in TOPAS cyclic olefin copolymer," *Electron. Lett.*, vol. 47, no. 4, pp. 271–272, 2011.

[10] A. Lacraz, M. Polis, A. Theodosiou, C. Koutsides, and K. Kalli "Femtosecond Laser Inscribed Bragg Gratings in Low Loss CYTOP Polymer Optical Fiber," *IEEE Photonics Technol. Lett.*, vol. 27, no. 7, pp. 693-696, 2015.

[11] A. Fasano, G. Woyessa, P. Stajanca, C. Markos, A. Stefani, K. Nielsen, H. K. Rasmussen, K. Krebber, and O. Bang, "Fabrication and characterization of polycarbonate microstructured polymer optical fibers for high-temperature-resistant fiber Bragg grating strain sensors" *Opt. Mater. Express*, vol. 6, no. 2, pp. 649-659, 2016.

[12] K. E. Carroll, C. Zhang, D. J. Webb, K. Kalli, A. Argyros, and M. C. J. Large, "Thermal response of Bragg gratings in PMMA microstructured optical fibers," *Opt. Express*, vol. 15, no. 14, pp. 8844–8850, 2007.

[13] W. Yuan, A. Stefani, M. Bache, T. Jacobsen, B. Rose, N. Herholdt-Rasmussen, F. K. Nielsen, S. Andresen, O. B. Sørensen, K. S. Hansen, and O. Bang, "Improved thermal and strain performance of annealed polymer optical fiber Bragg gratings," *Opt. Commun.*, vol. 284, no. 1, pp. 176–182, 2011.

[14] C. Jiang, M. G. Kuzyk, J.-L. Ding, W. E. Johns, and D. J. Welker, "Fabrication and mechanical behavior of dye-doped polymer optical fiber," *J. Appl. Phys.*, vol. 92, no. 1, pp. 4-12, 2002.

[15] G. Woyessa, K. Nielsen, A. Stefani, C. Markos, and O. Bang, "Temperature insensitive hysteresis free highly sensitive polymer optical fiber Bragg grating humidity sensor," *Opt. Express*, vol. 24, no. 2, pp. 1206-1213, 2016.

[16] P. Stajanca, O. Cetinkaya, M. Schukar, and K. Krebber, "Molecular alignment relaxation in polymer optical fibers for sensing applications," *Opt. Fiber Technol.*, vol. 28, pp. 11–17, 2016.

[17] L. S. A. Smith and V. Schmitz, "The effect of water on the glass transition temperature of poly(methyl methacrylate), " *Polymer*, vol. 29 no. 10, pp. 1871-1878, 1988.

[18] D. R. G. Williams, P. E. M. Allen, and V. T. Truong, "Glass transition temperature and stress relaxation of methanol equilibrated poly (methyl methacrylate)," *Eur. Polym. J.*, vol. 22, no. 11, pp. 911-919, 1986.

[19] M. C. J. Large, G. W. Barton, L. Poladian, and M. A. van Eijkelenborg, *Microstructured Polymer Optical Fibres*, Springer, 2008.

[20] D. Sáez-Rodríguez, K. Nielsen, H. K. Rasmussen, O. Bang, and D. J. Webb, "Highly photosensitive polymethyl methacrylate microstructured polymer optical fiber with doped core," *Opt. Lett.*, vol. 38, no. 19, pp. 3769-3772, 2013.

[21] M. C. J. Large, S. Ponrathnam, A. Argyros, N. S. Pujari, and F. Cox, "Solution doping of microstructured polymer optical fibres," *Opt. Express*, vol. 12, no. 9, pp. 1966-1971, 2004.

[22] B. Kuhlmey, R. C. McPhedran, and C. M. de Sterke, "Modal cutoff in microstructured optical fibers," *Opt. Lett.*, vol. 27, no. 19, pp. 1684–1686, 2002.

[23] I.-L. Bundalo, K. Nielsen, C. Markos, and O. Bang, "Bragg grating writing in PMMA microstructured polymer optical fibers in less than 7 minutes," *Opt. Express*, vol. 22, no. 5, pp. 5270–5276, 2014.