Novel thermal annealing methodology for permanent tuning polymer optical fiber Bragg gratings to longer wavelengths

A. Pospori,[1,*] C. A. F. Marques,[2] G. Sagias,[3] H. Lamela-Rivera,[3] and D. J. Webb,[1]

[1]*Aston Institute of Photonic Technologies, Aston University, Aston Triangle, Birmingham, B7 4ET, United Kingdom*
[2]*Instituto de Telecomunicações and Physics Department & I3N University of Aveiro, Campus de Santiago, 3810-193 Aveiro, Portugal*
[3]*Opto-Electronics and Laser Technology Group, Universidad Carlos III de Madrid, Edificio Sabatini, Leganés Madrid, 28911, Spain*
**andreas.pospori@gmail.com*

Abstract: The Bragg wavelength of a polymer optical fiber Bragg grating can be permanently shifted by utilizing the thermal annealing method. In all the reported fiber annealing cases, the authors were able to tune the Bragg wavelength only to shorter wavelengths, since the polymer fiber shrinks in length during the annealing process. This article demonstrates a novel thermal annealing methodology for permanently tuning polymer optical fiber Bragg gratings to any desirable spectral position, including longer wavelengths. Stretching the polymer optical fiber during the annealing process, the period of Bragg grating, which is directly related with the Bragg wavelength, can become permanently longer. The methodology presented in this article can be used to multiplex polymer optical fiber Bragg gratings at any desirable spectral position utilizing only one phase-mask for their photo-inscription, reducing thus their fabrication cost in an industrial setting.

OCIS codes: (060.3735) Fiber Bragg gratings, (060.2310) Fiber optics, (060.4230) Multiplexing, (130.5460) Polymer waveguides.

References and links

1. D. J. Webb, "Fibre Bragg grating sensors in polymer optical fibres," Meas. Sci. Technol. **26**(9), 092004 (2015).
2. M. C. J. Large, J. H. Moran, and L. Ye, "The role of viscoelastic properties in strain testing using microstructured polymer optical fibres (mPOF)," Meas. Sci. Technol. **20**(3), 034014 (2009).
3. C. A. F. Marques, A. Pospori, D. Sáez-Rodríguez, K. Nielsen, O. Bang, and D. J. Webb, "Aviation Fuel Gauging Sensor Utilizing Multiple Diaphragm Sensors Incorporating Polymer Optical Fiber Bragg Gratings," IEEE Sens. J. **16**(15), 6122-6129 (2016).
4. T. X. Wang, Y. H. Luo, G. D. Peng, and Q. J. Zhang, "High-sensitivity stress sensor based on Bragg grating in BDK-doped photosensitive polymer optical fiber," Proc. SPIE 8351, 83510M (2012).
5. C. Broadway, D. Gallego, A. Pospori, M. Zubel, D. J. Webb, K. Sugden, G. Carpintero, and H. Lamela-Rivera, "Microstructured polymer optical fiber sensors for opto-acoustic endoscopy," Proc. SPIE 9886, 98860S (2016).
6. W. Zhang, D. J. Webb, and G. D. Peng, "Investigation Into Time Response of Polymer Fiber Bragg Grating Based Humidity Sensors," J. Lightwave Technol. **30**(8), 1090-1096 (2012).
7. K. O. Hill, B. Malo, F. Bilodeau, D. C. Johnson, and J. Albert, "Bragg gratings fabricated in monomode photosensitive optical fiber by UV exposure through a phase mask," Appl. Phys. Lett., **62**(10), 1035-1037 (1993).
8. I. P. Johnson, D. J. Webb, and K. Kalli, "Utilisation of thermal annealing to record multiplexed FBG sensors in multimode microstructured polymer optical fiber," Proc. SPIE 7753, 77536T (2011).
9. D. Bosc, and C. Toinen, "Tensile mechanical-properties and reduced internal stresses of polymer optical-fiber," Polym. Compos. **14**(5), 410-413 (1993).
10. 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 **24**(2), 1206-1213 (2016).
11. J.J. Tribone, J.M. O'Reilly, and J. Greener, "Analysis of enthalpy relaxation in poly (methyl methacrylate): effects of tacticity, deuteration, and thermal history," Macromolecules **19**(6), 1732-1739 (1986).
12. P. Stajanca, O. Cetinkaya, M. Schukar, P. Mergo, D.J. Webb, and K. Krebber, "Molecular alignment relaxation in polymer optical fibers for sensing applications," Opt. Fiber Technol. **28**, 11-17 (2016).

13. A. Pospori, C. A. F. Marques, D. Sáez-Rodríguez, K. Nielsen, O. Bang, and D. J. Webb, "Thermal and chemical treatment of polymer optical fiber Bragg grating sensors for enhanced mechanical sensitivity," Opt. Fiber Technol. **36**(7), 68-74 (2017).
14. K. E. Carroll, C. Zhang, D. J. Webb, K. Kalli, A. Argyros, and M. C. Large, "Thermal response of Bragg gratings in PMMA microstructured optical fibers," Opt. Express **15**(14), 8844-8850 (2007).
15. A. Abang, and D. J. Webb, "Effects of annealing, pre-tension and mounting on the hysteresis of polymer strain sensors," Meas. Sci. Technol. **25**(1), 015102 (2014).
16. 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. **38**(19), 3769-3772 (2013).
17. A. Pospori, C. A. F. Marques, O. Bang, D. J. Webb, and P. André, "Polymer optical fiber Bragg grating inscription with a single UV laser pulse," Opt. Express **25**(8), 9028-9038 (2017).
18. K. Schmidt-Rohr, A. S. Kulik, H. W. Beckham, A. Ohlemacher, U. Pawelzik, C. Boeffel, and H. W. Spiess, "Molecular nature of the beta-relaxation in poly(methyl methacrylate) investigated by multidimensional NMR," Macromolecules **27**(17), 4733-4745 (1994).
19. K. Fukao, S. Uno, Y. Miyamoto, A. Hoshino, and H. Miyaji, "Dynamics of α and β processes in thin polymer films: Poly(vinyl acetate) and poly(methyl methacrylate)," Phys. Rev. E **64**(5), 051807 (2001).
20. W. Zhang, D. J. Webb, and G. D. Peng, "Enhancing the sensitivity of poly(methyl methacrylate) based optical fiber Bragg grating temperature sensors," Opt. Lett. **40**(17), 4046-4049 (2015).
21. M. B. J. Diemeer, "Polymeric thermo-optic space switches for optical communications," Opt. Mat. **9**(1-4), 192-200 (1998).

1. Introduction

Polymer optical fibers (POFs) exhibit different mechanical and optical properties compared with silica optical fibers [1]. POFs have higher flexibility in bending, higher fracture toughness, higher failure strain, and lower Young modulus [2]. The latter characteristic causes POF Bragg grating (POFBG) sensors to have higher sensitivity in pressure [3], stress [4], and acoustic-wave detection [5]. POFBGs made of hydrophilic polymers, such as poly(methyl methacrylate) (PMMA), can be also used for humidity monitoring [6].

POFBGs are usually photo-inscribed with the phase-mask technique, which is the most reliable and simplest method [7]. However, for a particular fiber, the phase-mask can inscribe a grating structure only at a specific Bragg wavelength, since the period of the grating equals the half period of phase-mask [7]. To inscribe a Bragg grating at a different spectral position, a new phase mask with different pitch is required. Considering that the phase-masks are expensive, the Bragg grating multiplexing can be a very costly process. In 2011, the thermal annealing method was utilized to demonstrate the first multiplexed POFBGs using only one phase-mask for their recording [8]. The authors annealed the POF by exposing it above its β-transition temperature, in which the polymer molecules start to become mobilized, the fiber shrinks in length and the Bragg grating period becomes shorter. The fiber shrinkage possibly occurs due to the removal of residual internal stress, which was introduced during the POF drawing stage [9]. The rate of fiber shrinkage depends on the annealing conditions (duration, temperature and humidity), chemical composition of polymer material, and thermal processing history, including the POF drawing conditions [10–12].

A number of POFBG annealing experiments have been reported since 2011, not only for multiplexing but also for other purposes such as strain, stress, pressure and humidity sensitivity enhancement of POFBG sensors [10, 13], longer operational range in temperature detection applications [14], and hysteresis effect reduction of sensors under mechanical cycling loading [15]. Climatic-controlled chambers are usually used to anneal the POFs with pre-defined annealing conditions (temperature and humidity) and the process takes between few hours and several days [8, 10, 12, 14, 15]. Recently, a simpler and cost effective annealing method was demonstrated, in which the POFs were annealed in heated water (100% humidity) for few minutes [13]. This method was also used in the work presented here.

In all the reported annealing experiments, the POFs were loose, without any external force being applied on them during the annealing process. Therefore, the POFs shrank in length and

the Bragg wavelength of POFBGs blue shifted permanently after the annealing process. The permanent shifting can be an issue in cases where annealing is used for purposes other than multiplexing and the Bragg wavelength is desired to be kept at its original spectral position. Until now, there was no method of tuning the Bragg wavelength to longer wavelengths, thus the multiplexing of sensors is feasible only at wavelengths below the original spectral position of Bragg grating. In this article, a novel annealing methodology is demonstrated, which utilizes the fiber axial strain or stress during the annealing process to tune the Bragg wavelength at any desirable spectral position over a spectral range that extends above the recorded Bragg wavelength. Similar experiments were performed by two different research groups to prove the concept; the POFBGs were placed in heated water for annealing and the POFs were kept stretched during the process. The results show that fiber stretching is an important parameter to consider during the annealing process, since it determines the direction and degree of Bragg wavelength shifting.

2. Fabrication of Bragg gratings

POFBGs have been inscribed with 325 nm He-Cd (Kimmon IK3301R-G) and 248 nm KrF (Coherent Bragg Star Industrial-LN) laser systems by Aston University (group 1) and University of Aveiro (group 2), respectively. Both research groups inscribed the gratings in a single-mode PMMA microstructured fiber, having a core doped with benzyl dimethyl ketal for photosensitivity enhancement [16]. The diameter of fiber is 130 μm and the core size is 8 μm. The POF was fabricated in-house and it has diameter fluctuation more than 20 μm, as a result the fiber operation in the 850 nm wavelength region becomes sometimes few-moded. The research groups used the phase mask technique to fabricate the POFBGs as depicted in Fig. 1. Additional details about the fabrication setup for each group can be found in references [13] for group 1 and [17] for group 2. Group 1 used a phase-mask with a pitch of 558 nm and group 2 used a phase-mask with pitch of 568 nm, which inscribe Bragg gratings centered at 829 nm and 844 nm respectively, since the refractive index of PMMA is 1.486 in this wavelength range. In the following experiments, the POFBGs were interrogated in reflection and not in transmission; the reflectivity strength of each grating does not influence the experimental results obtained in this work. To monitor the POFBGs in reflection, a super luminescent diode (Superlum SLD-371 for both groups) and an optical spectrum analyzer (HP 86142A for group 1 and Yokogawa AQ6373B for group 2) were connected with the POF via a 50:50 optical coupler as shown in Fig. 1.

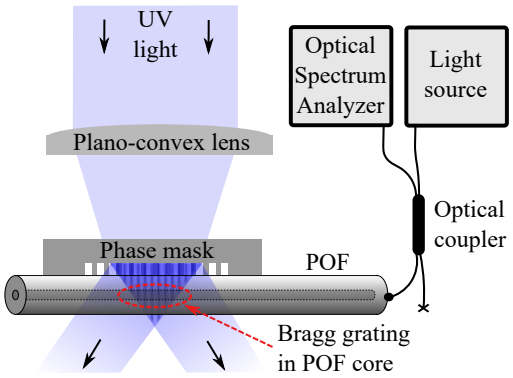

Fig. 1. Setup of POFBGs fabrication.

3. Experimental details and results

3.1. Motivation and initial testing

The motivation of carrying out the experiments below was the need to produce POFBGs centered at 850 nm for a specific application. Considering that the available phase-masks produce gratings with Bragg wavelengths only below 850 nm, the hypothesis studied here was that it should be possible to imitate the fiber drawing process and permanently elongate the POF. During the fiber drawing, the molecular chains of the polymer are stretched and aligned along the fiber axis [9]. After it is drawn from the oven, the POF is rapidly cooled down in room ambient conditions and the molecules become immobilized. Without having enough time to return to their amorphous state, the stretched molecules render the POF longer in physical length than would be the case with the molecules in a relaxed state. By performing thermal annealing without applying a force on the fiber axis, the POF can shrink in length, since the molecules relax and return to their original amorphous state [18]. However, by annealing with some stretching, the intention was to investigate whether the fiber length could be permanently increased.

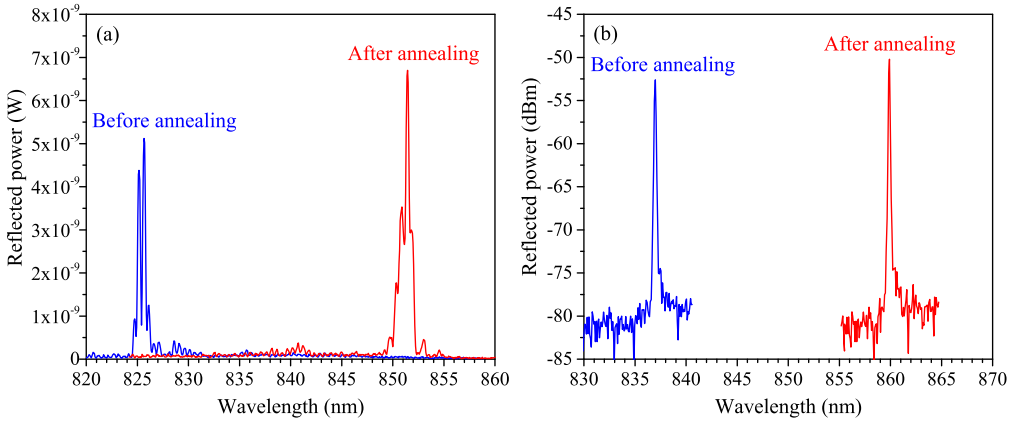

Fig. 2. Reflection spectrum of POFBG before and after the annealing process obtained by (a) group 1 and (b) group 2.

Initially, to test the concept, the POF was randomly pulled by hand and it was placed for 2 seconds on a hot-plate, which was heated between 70 °C and 75 °C. The β-transition temperature of PMMA is approximately at 50 ± 5 °C and above that temperature, the molecules start to become mobilized [19]. At the first trial, the Bragg wavelength permanently shifted to shorter wavelengths because the pulling force was not enough. Therefore, the process was repeated with higher pulling force. After 5 trials with higher pulling force, the Bragg wavelength was permanently shifted to longer wavelengths. Fig. 2 shows the reflection spectrum of a POFBG before and after annealing as obtained by the two research groups. Due to the unknown pulling force that was applied on the previous experiment, it was unknown if the POF exceeded the elastic limit during its straining, although the strain response over modest strains was linear after the annealing process (see Fig. 3). The obtained strain sensitivity was 0.77 ± 0.01 pm/με, which is similar to the other reported sensitivities using the same POF [13].

3.2. Annealing with constant strain

To investigate our hypothesis more quantitatively, a new experiment was conducted in order to control the annealing conditions. The experimental setup is illustrated in Fig. 4. First, a non-annealed POFBG was placed between a high-precision movable stage and a fixed support in order to strain it to 1%, which is well below the elastic limit. While being strained, the POF was

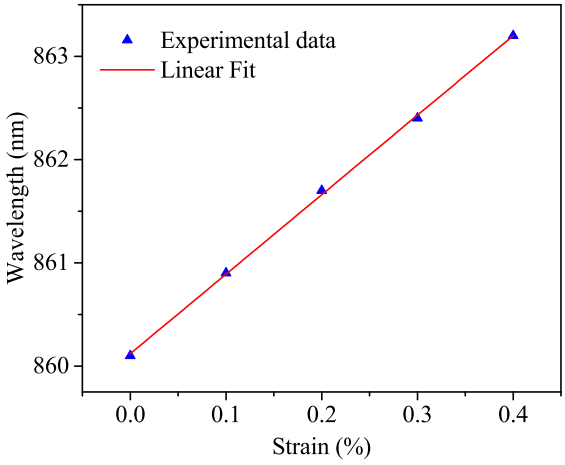

Fig. 3. Strain response of POFBG after the annealing process as obtained from group 2.

positioned in a container filled with water to ensure that the ambient relative humidity remains constant (100%) during the whole annealing process. The container had two openings for the fiber, which were closed with plasticine to keep the water in the container. The POFBG was kept in the water at room temperature (25 ± 2 °C). After 40 minutes, the Bragg wavelength had stopped shifting due to water absorption. At this point, the annealing process was begun by turning on the hot-plate, which was underneath the container (see Fig. 4). The water temperature was monitored with a mercury thermometer. After 45 minutes, the water was removed instantly from the container, thus the strained POF was cooled down at room temperature. Then, the POF was removed from the setup and remained under room ambient conditions for more than 1 hour in order to release the absorbed water.

Fig. 5 shows the Bragg wavelength shift with temperature during the annealing process. In temperatures well below the β-transition, the change of Bragg wavelength ($\Delta\lambda_B$) due to temperature change (ΔT) can be expressed as

$$\Delta\lambda_B = \lambda_{B_0}\left(\alpha + \frac{\xi}{n_{eff}}\right)\Delta T. \tag{1}$$

where λ_{B_0} is the initial Bragg wavelength, α is the thermal expansion coefficient, ξ is the thermo-optic coefficient and n_{eff} is the effective refractive index of the POF core. The thermo-optic coefficient of PMMA is negative and usually larger than the thermal expansion coefficient [20]; therefore, the Bragg wavelength shifts to shorter wavelengths as the temperature increases. In general, during the annealing process, the shrinkage of POF (and consequently the period of POFBG) follows an exponential decay, which is influenced by the annealing conditions (temperature and humidity) and the thermal history of the polymer [13]. However, if the POF is strained (as in Fig. 5), its thermal expansion or contraction is restrained in the axial direction [21]. Therefore, the POFBG cannot shrink freely during annealing and the change of Bragg wavelength is not as much as in the case of loose fiber. This is the reason for the more “linear” behaviour of Bragg wavelength during POFBG annealing in comparison with the other reported annealing experiments. However, although the Bragg wavelength shifted to shorter wavelengths during the annealing process (see Fig. 5), at the end of the experiment it had not returned to its spectral position before strain was originally applied. Fig. 6 shows the spectrum of POFBG before and after the thermal annealing with 1% fiber strain. In the case of group 1, the Bragg wavelength

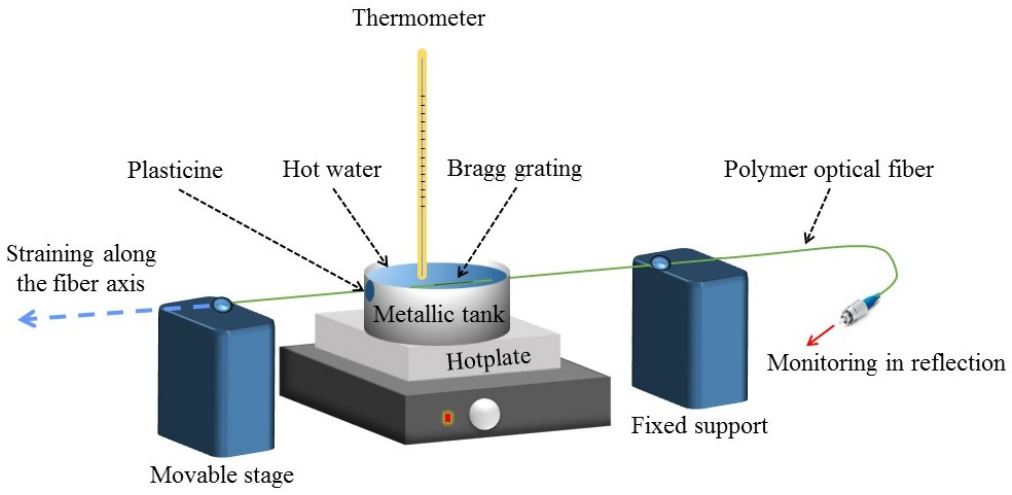

Fig. 4. Experimental setup to strain and anneal the POFBG.

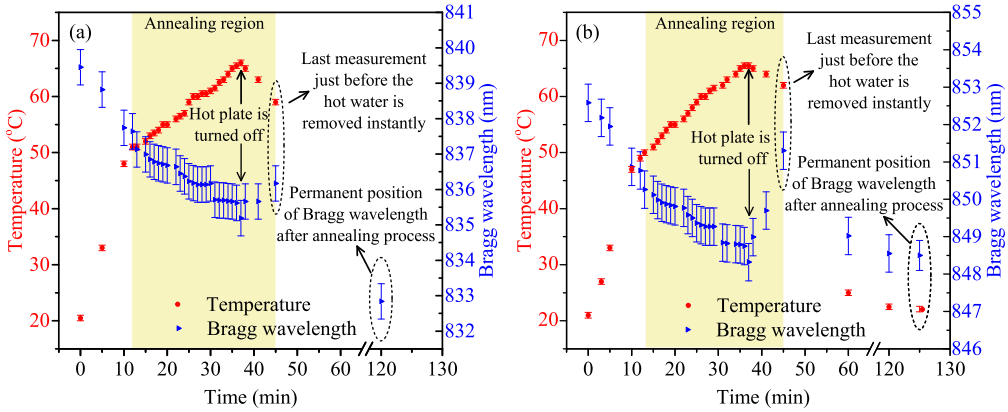

Fig. 5. Bragg wavelength shift during annealing with 1% strain as obtained from (a) group 1 and (b) group 2.

was permanently tuned from 828.7 nm to 832.8 nm, while for group 2, the shifting was from 844.2 nm to 848.5 nm.

The same POFBG was placed again in the experimental setup (see Fig. 4) to repeat the annealing experiment, but with 2% strain in order to investigate the influence of fiber strain on the total Bragg wavelength tuning. This time the annealing duration was only 13 minutes. Note that the annealing duration and temperature in all experiments was chosen arbitrarily, because we are just investigating the possibility to tune the POFBG to longer wavelengths. Fig. 7 shows the Bragg wavelength shift with temperature during annealing and Fig. 8 depicts the spectrum of POFBGs before and after the annealing process. The spectral position of Bragg wavelength was tuned from 832.8 nm to 840.6 nm by group 1 and from 848.5 nm to 858.7 nm in the case of group 2. Fig. 9 summarizes the results of the two annealing experiments and indicates that the degree of Bragg wavelength tuning is strongly depended on the level of fiber strain.

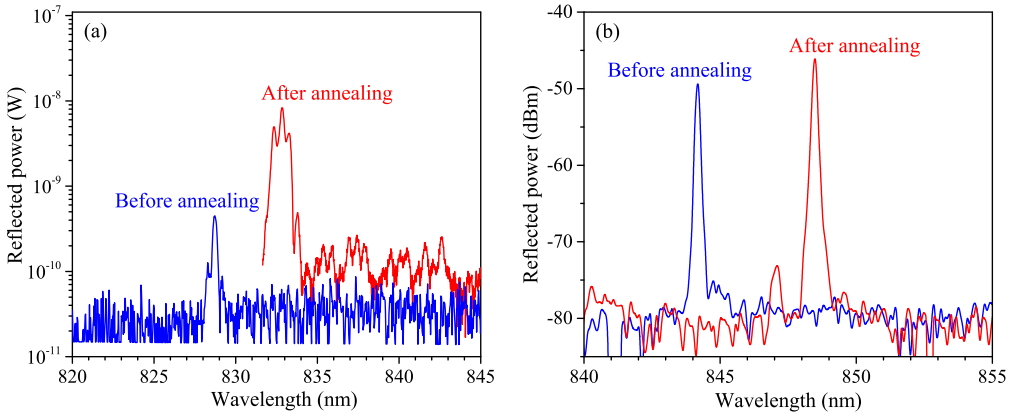

Fig. 6. Reflection spectrum before and after annealing with 1% strain as obtained from (a) group 1 and (b) group 2.

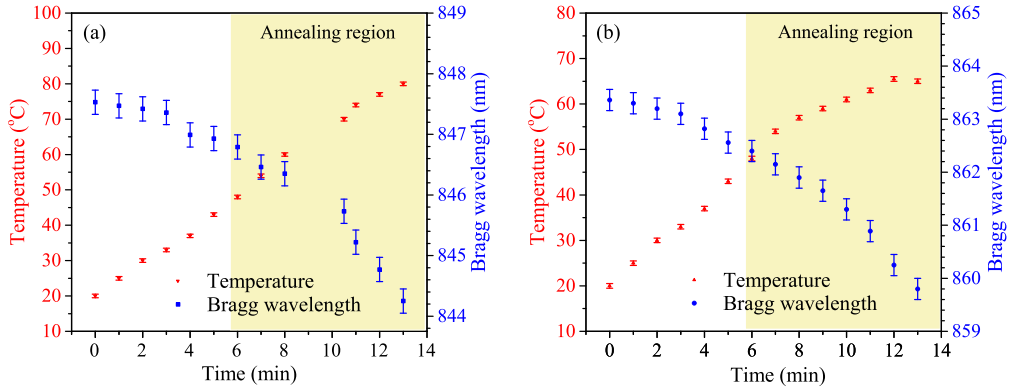

Fig. 7. Bragg wavelength shift during annealing with 2% strain as obtained from (a) group 1 and (b) group 2.

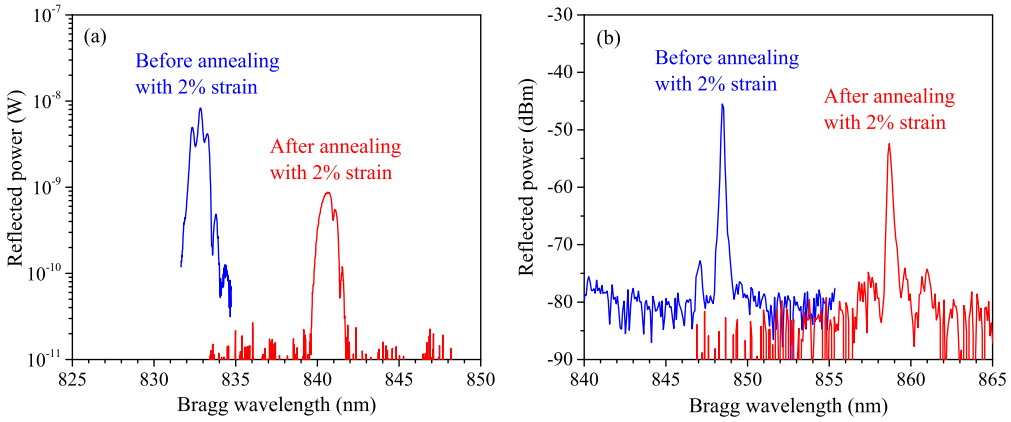

Fig. 8. Reflection spectrum before and after annealing with 2% strain as obtained from (a) group 1 and (b) group 2.

As a practical example, the annealing methodology presented in this article was used by

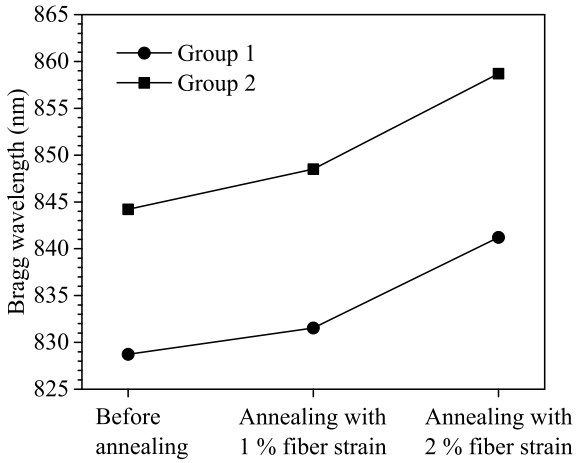

Fig. 9. Bragg wavelength shift before and after annealing with 1% and 2% strain.

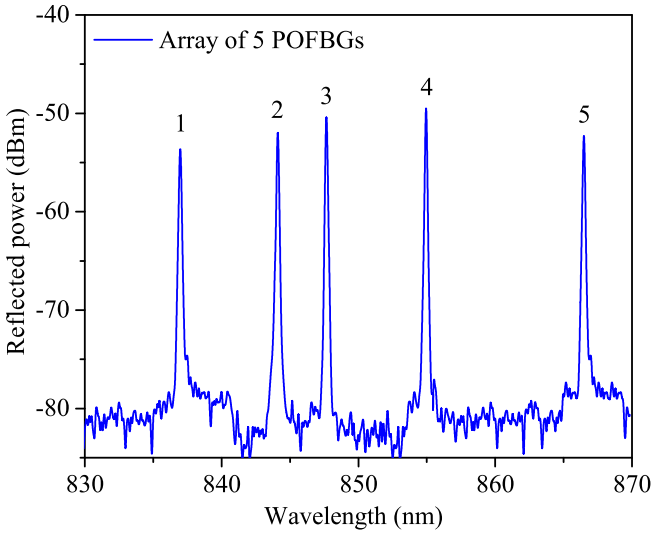

Fig. 10. Reflection spectrum of 5 POFBGs multiplexed along the fiber length.

research group 2 to develop an array of 5 POFBGs along the same fiber piece. The 5 POFBGs were inscribed with the same phase-mask (568 nm pitch) and Bragg wavelength centered at 844.2 nm. However, each POFBG was annealed with a different strain percentage immediately after its inscription in order to be placed at a specific spectral position, as shown in Fig. 10. The first POFBG was tuned from 844.2 nm to 837.0 nm, because it was annealed without applying any fiber strain. The second POFBG was not annealed and it remained at its original spectral position (844.1 nm). The third, forth, and fifth POFBG were annealed with 0.65%, 1.3% and 2.3% strain, respectively. Consequently, their Bragg wavelengths were tuned from 844.2 nm to 847.7 nm, 854.9 nm, and 866.5 nm, respectively. In conclusion, Fig. 10 demonstrates the concept presented in this work and shows the ability to tune the Bragg wavelengths to any desirable spectral position (negative and positive wavelength tuning) by appropriately selecting the degree of fiber strain during the annealing process.

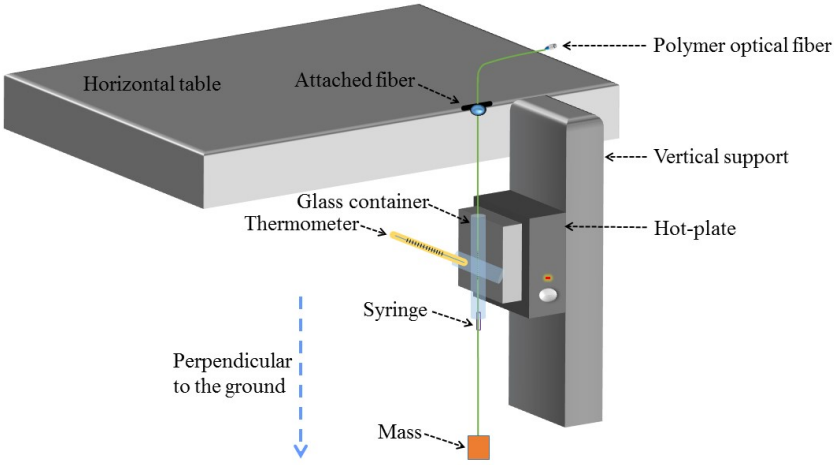

Fig. 11. Experimental setup to stress and anneal the POFBG.

3.3. Annealing with constant stress

The idea of imitating the POF drawing process to stretch the polymer molecules and elongate the POF is more closely followed when annealing with constant fiber stress instead of constant fiber strain, because the polymer chains are under constant pulling force during the fiber drawing stage. Therefore, research group 2 performed two additional experiments to demonstrate that the POFBGs can be also permanently tuned to longer wavelengths by applying constant stress rather than constant strain. To apply a constant stress, a mass with a known value was attached to one end of the POF and it was held perpendicular to the ground in order to use gravitational force to stress it along its length, as shown in Fig. 11. The applied stress, which is defined as the gravitational force F divided by the cross-sectional area A of the POF, is equal to

$$\sigma = \frac{F}{A} = \frac{mg}{\pi \left(\frac{d}{2}\right)^2}, \tag{2}$$

where m is the added mass, g is the gravitational acceleration of the Earth (9.8 m/s^2) and d is the fiber diameter at the location of POFBG. As shown in Fig. 11, the POFBG was placed in a sealed glass container (tube-shaped) filled with tap water to provide constant ambient relative humidity at 100% during the annealing process. At the bottom of the container, there was a needle with internal diameter similar with the POF diameter. A small amount of plasticine was also added in order to restrict the water as much as possible without restricting the movement of POF. There was some water leakage, but the amount of water in the container was always covering the POFBG. To anneal the POFBG, a hot plate, which was attached to the container, was used to raise the water temperature up to 65 °C. The added mass used to stress the POFBG was 7.80 ± 0.05 g for the first experiment and 18.10 ± 0.05 g for the second, which provided 5.8 ± 0.9 MPa and 13.4 ± 2.1 MPa constant mechanical stress, respectively. To perform the experiment, the POFBG was placed in the water for more than 40 minutes to fully absorb it and then the mass was added to stress it. In the next step, the hot-plate was turned on for annealing. After a half hour, the hot water was removed instantly in order to rapidly cool the POFBG in room conditions and then the mass was removed from the POF to release the stress. After two hours, the final Bragg wavelength position was determined. Fig. 12 depicts the change of Bragg wavelength during annealing for both experiments. Applying a constant stress during annealing, the thermal expansion of polymer allows the fiber to elongate, which is the reason for the positive shifting

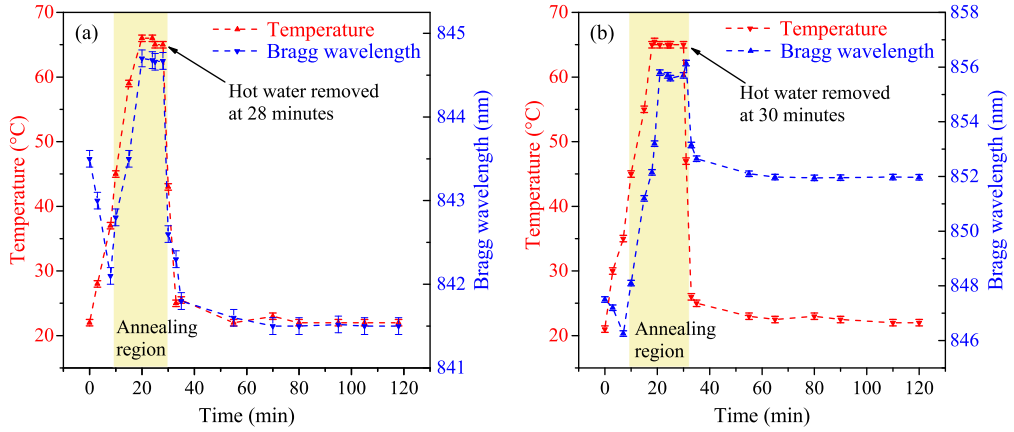

Fig. 12. Bragg wavelength shift during annealing with constant stress of (a) 5.8 ± 0.9 MPa and (b) 13.4 ± 2.1 MPa.

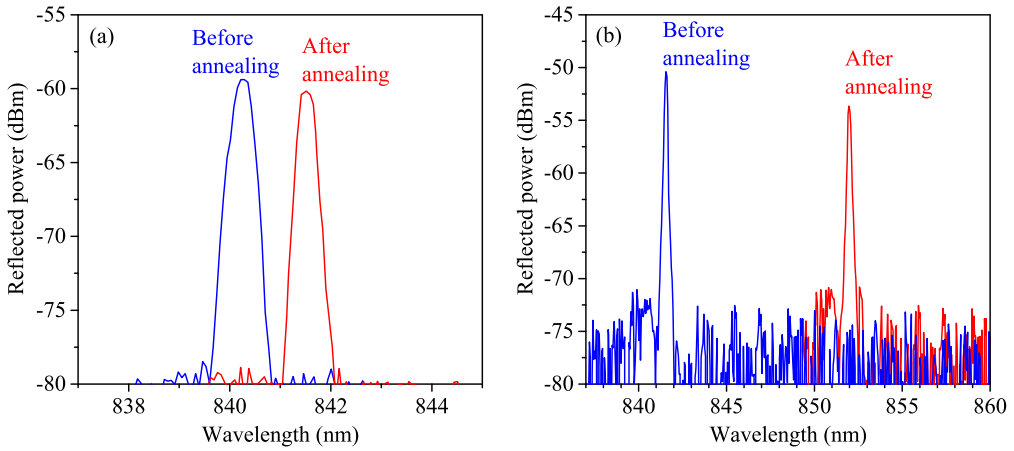

Fig. 13. Reflection spectra before and after annealing with constant stress of (a) 5.8 ± 0.9 MPa and (b) 13.4 ± 2.1 MPa.

Table 1. Bragg wavelength at each stage for both experiments.

Experimental stage	**Bragg wavelength of first experiment ±0.1 (nm)**	**Bragg wavelength of second experiment ±0.1 (nm)**
Before placed in water	840.3	841.6
After 40 minutes in water	841.4	842.4
After adding the mass	843.5	847.5
At the end of the annealing process	844.7	855.7
Just after removing heated water	842.3	852.7
After 2 hours in room ambient conditions	841.5	852.0
	1.2 (total shift)	10.4 (total shift)

of the Bragg wavelength when the grating enters the annealing temperature region (>45 °C) in comparison with Fig. 5 and Fig. 7. The reflection spectra of both POFBGs before and after the process are shown in Fig. 13. Table 1 shows the spectral position of Bragg wavelengths at various key experimental stages throughout the process.

Note that the initial Bragg wavelength for both experiments is less than 844.2 nm, because both POFBGs were placed on the inscription setup with some strain (for easier fabrication purposes). Therefore, after the inscription process, the POFs were returned to their original length and the period of the inscribed POFBGs became shorter. However, the main point is that the total Bragg wavelength tuning was 1.2 nm and 10.4 nm in the case of the 5.8 ± 0.9 MPa and 13.4 ± 2.1 MPa experiments, respectively. Results demonstrate that the degree of fiber stress during the annealing process strongly influences the total Bragg wavelength tuning.

4. Conclusion

This paper demonstrates for the first time a novel methodology to permanently tune POFBGs to longer wavelengths. Combining thermal annealing and fiber stretching, the POF can be elongated and consequently the period of the POFBG can become longer. The POF can be stretched by applying either a constant strain or constant stress along its length. Both methods are suitable to permanently red-shift the Bragg wavelength, as long as the annealed POFBG is cooled down while being stretched – a similar phenomenon observed during its drawing stage. Results show that the degree of fiber stretching (strain or stress) determines the total Bragg wavelength tuning. The paper also demonstrates an application of the technique by producing an array of 5 POFBGs along the same POF, which were inscribed with one phase-mask, with their Bragg wavelengths being tuned both below and above their original spectral position.

Funding

People Programme (Marie Curie Actions) of the European Union's Seventh Framework Programme FP7/2007-2013 (608382); National funding agencies FCT/MEC and FEDER-PT2020 (UID/EEA/50008/2013); National funding agency FCT (SFRH/BPD/109458/2015).

Acknowledgments

The authors acknowledge Prof. Ole Bang and Sáez-Rodríguez for providing the optical fiber used in this work.