



COVER SHEET

This is the author version of article published as:

Law, S.H and Eijkelenborg, M.A and Barton, G.W and Yan, Cheng and Lwin, R and Gan, J (2006) Cleaved end-face quality of microstructured polymer optical fibres. *Optics Communications* 265:pp. 513-520.

Copyright 2006 Elsevier

Accessed from <http://eprints.qut.edu.au>

Cleaved end-face quality of microstructured polymer optical fibres

SH Law¹, MA van Eijkelenborg¹, GW Barton^{1,3}, C Yan², R Lwin^{1,3}, J Gan²

¹ Optical Fibre Technology Centre, University of Sydney, 206 National Innovation Centre Australian Technology Park, Eveleigh NSW 1430, Australia, www.oftc.usyd.edu.au/mpof

² Department of Mechanical, Mechatronic and Aeronautical Engineering, The University of Sydney NSW 2006 Australia

³ Department of Chemical Engineering, The University of Sydney, NSW 2006 Australia

Abstract

The cutting of a microstructured polymer optical fibre to form an optical end-face is studied. The effect of the temperature and speed of the cutting blade on the end-face is qualitatively assessed and it is found that for fibres at temperatures in the range 70-90°C, a blade at a similar temperature moving at a speed of less than 0.5 mm/sec produces a good quality end-face. The nature of the damage caused by the cutting process was examined and found to vary with fibre temperature, blade quality and cut depth. Thermo-mechanical analysis showed that the drawn material was significantly more visco-elastic than the annealed raw material in the 70-90°C temperature range. The behaviour of the surface damage with cut-depth was found to be consistent with the behaviour of a visco-elastic material.

Introduction

Microstructured polymer optical fibres (mPOF) are a recent development that are increasingly being viewed as a realistic alternative to conventional (*i.e.* doped) polymer optical fibre, being potentially both cheaper and simpler to make while offering a diversity of optical properties through tailoring of the hole structure [1]. However a key step in the path to commercialisation is the development of a simple process to cleave such an optical fibre and produce a smooth end-face which will not only transmit light without scattering but also be amenable to some form of low-loss splicing.

The process of cleaving a material involves the production of a pair of fracture surfaces. These surfaces are produced by rupture processes due either to cutting or to crack propagation, depending upon the properties of the material being cleaved. For a hard, brittle material this cleaving is usually achieved by controlled production of a micro-crack on one side of the sample followed by the application of a force to induce crack propagation. The properties of amorphous silica are such that when the initial crack and the applied force are in the correct size range a near perfect optical end-face can be reliably produced on an optical fibre [2]. The properties of glassy polymers – in particular the role of chain alignment and crazing in crack formation – have meant that the fracture mechanics tends to be complex and messy [3-6]. Despite some success in controlling the fracture by means of differential pressure on solid fibre [7, 8] (a technique not applicable to mPOFs) polymer optical fibre must usually be either mechanically or thermally polished after cleaving at room temperature. For mPOFs such polishing processes are likely to cause significant damage.

Production of a pair of fracture surfaces of energy G_c by the application of cutting energy from the motion of a sharp blade and/or tearing energy from the stresses at the rupture tip occurs when the sum of the cutting and tearing energies exceeds the energy of formation of the surfaces [9]. In the absence of a blade the rupture is solely dependent on the stresses at the crack tip. Griffith [10] showed that the magnitude of the stress due to an applied transverse

force is greatly magnified at the tip of a sharp crack, the degree of magnification being proportional to the square root of the radius of the crack tip.

Andrews [11] however demonstrated that crack tips are blunted in a hysterical (i.e. viscoelastic) material, thus reducing the stress concentration and potentially stopping crack propagation, leading to an increase in the material's toughness. Lake & Yeoh [12] showed that the balance between cutting and tearing energies has a significant impact on the morphology of the resulting fracture surface in a rubbery material, with smooth, cut surfaces being obtained for low values of tearing energy and rough, fracture surfaces arising when the tearing energy is high. In the intermediate region they obtained a surface with transverse striations caused by the blade triggering crack propagation that is rapidly stopped by crack tip blunting due to the materials viscosity.

All the reported work on cutting has been performed on specially prepared samples, mounted to ensure constant stress and eliminate the effects of friction between the fracture surfaces and the side of the blade. In a real life situation (such as the cutting of a fibre) this is not possible. In our situation it is demonstrably impossible to eliminate friction from the cutting process [13]. One must also consider the effect of crack depth on the stress concentration. The influence of crack depth on failure behaviour has been widely investigated [14-18]. The slip-line field analysis of Matsoukas et al [19] showed that the hydrostatic stresses are larger for a deeper crack. A number of finite-element analyses [17, 18, 20] also showed that crack depth has a significant effect on the stress levels ahead of the crack tip. Tensile stress in the remaining ligament in a bend sample is elevated with increasing crack depth due to the increase of in-plane constraint [21]. This can explain why typical cleavage morphology can be observed on the fibre end surface with increase of cutting depth as a result of elevated tensile stress in front of the cutting blade.

In previous papers [13, 22] it was shown that a 'hot blade/hot fibre' system was practicable for producing an acceptable optical end-face on mPOFs. Figure 1 shows the apparatus designed to refine our understanding of the mPOF cutting process. The fibre is clamped in a vee-groove on a heated platen. At the point under the blade is a cross-groove to prevent collision damage to the heated blade. In addition to independent control of blade and platen temperature, the former is mounted on a stepper-motor driven linear stage to enable the speed and cut depth to be controlled. The step size of the motor is 2.03 μm . To eliminate the effect of changes in blade condition caused by cutting the PMMA, the fibre platen is mounted on a

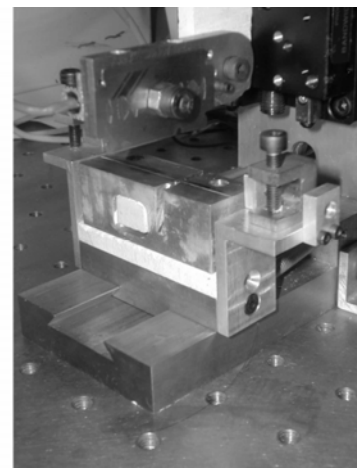
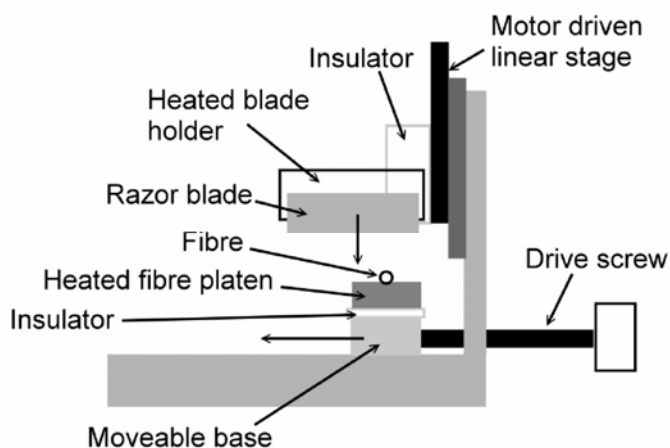


Figure 1: Controlled cutting apparatus for PMMA fibre.

screw-driven slide and moved before every cut. For the particular fibre under study it was found that:

- The hardness of the PMMA at low temperatures causes chipping of both blade and fibre making it impossible to produce clean end-faces.
- The grade of PMMA used appears to be ductile over the temperature range 25°C to 100°C.
- There appears to be a structural transition in the material at about 60°C. The best cuts are obtained with the fibre at temperatures just above this transition level.
- Blade speeds are best kept low, preferably below 1mm/sec. Generally the lower the temperature, the lower the necessary speed.
- The fibre takes approximately 90 seconds to equilibrate to the platen temperature.

This paper reports on more detailed examination of mPOF cleaving employing this apparatus. The fibre studied here was a Graded-Index Microstructured Polymer Optical Fibre fabricated from amorphous polymethylmethacrylate (or PMMA) having a viscosity molecular mass (M_v) of 7.2×10^4 and a high syndiotactic content (approx. 65%) [23]. It was fabricated by drilling the required hole pattern in a cylinder of high purity PMMA. This cylinder was then drawn to a 6mm rod and 'sleeved' with lower quality PMMA to produce a 12mm diameter preform. The latter was then drawn to fibre with an outer diameter of 400 μm at a temperature of 220°C and under 45g of tension. This high-temperature, low-tension draw gave a fibre with relatively low material anisotropies but with somewhat distorted holes and extremely fine bridges (less than 1 μm thick) between the outer holes. In this paper we first present results on the effects of blade temperature and blade speed on the cutting of such a fibre. Next analysis of the nature of the damage to the end-face is presented, while finally the results are related to relevant thermo-mechanical analysis on the PMMA used.

Impact of Blade Temperature

Figure 2 shows fibre samples equilibrated to platen temperatures of 70°C and 80°C, then cut with a blade temperature from 50°C to 90°C moving at 0.5 mm/sec. The best end-faces occur when the blade temperature is close to the fibre temperature. The 80°C fibre appears to be more sensitive to blade temperature than the 70°C fibre with core damage visible for blade temperatures of 50°C and 60°C. For a blade temperature of 90°C the core is in position indicating that the surrounding hole structure is relatively intact, but the fine bridges do not show up resulting in a black ring around the core. The reason for this is explained when SEM

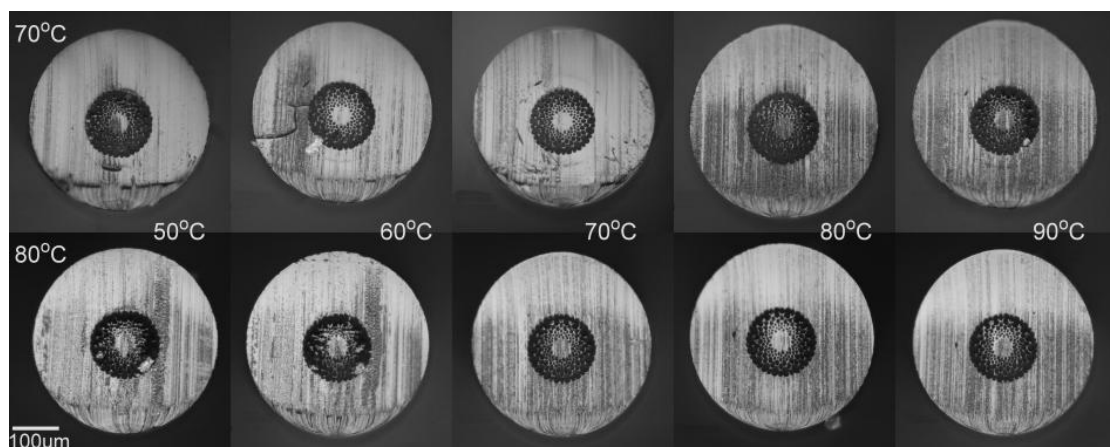


Figure 2: End faces of fibres at 70°C and 80°C cut with a blade at temperatures from 50°C to 90°C moving at a speed of 0.5 mm/sec.

images are presented. For a significant number of the end-faces there appears to be three distinct zones on the fracture surface: a pale zone indicative of a smooth surface with good back reflection; a grey zone indicative of a slightly rougher surface causing scattering of the reflected light; and a fracture zone at the lower edge.

Impact of Blade Speed

Figure 3 shows fibre samples equilibrated to a platen temperature of 70°C then cut with blade temperatures from 50°C to 90°C and moving at 0.07, 0.5 and 2.0 mm/sec. At these speeds the blade edge takes 5.7, 0.8 and 0.2 seconds respectively to traverse the fibre. Taking into consideration the presence of a ‘transition’ at 60°C, a 50°C blade might be expected to cause problems. This seems more pronounced at 0.07 mm/sec when there is more time for heat transfer between fibre and blade. There is also more mechanical damage at higher speed with an earlier onset of fracture. Unexpectedly the blade temperature also significantly affects the fracture onset, the effect being most pronounced at 0.07 mm/sec. The simplest explanation for this would be that there is significant heat transfer between the blade and the surface layers of the fibre being cut. Once again there are ‘black-ringed’ cores at higher blade temperatures, particularly 90°C, though the structure is still in place.

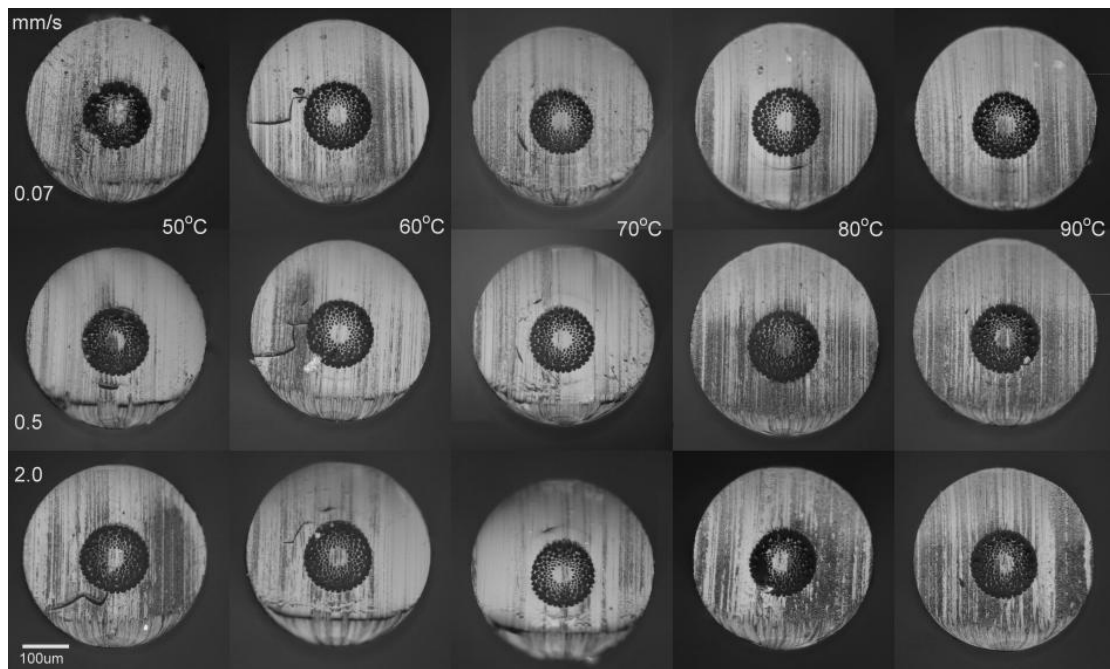


Figure 3: End faces of 70°C fibre cut with blade temperatures ranging from 50°C to 90°C and blade speeds of 0.07, 0.5 and 2.0 mm/sec.

Combining these results with previous work [13, 22] we can conclude that for the fibre under study good cleaving can be obtained when the fibre is raised to a temperature between 70°C and 90°C and cut with a blade at the same (or slightly lower) temperature moving at a speed below 0.5 mm/sec. Under these conditions the bulk of the fracture surfaces are produced by the blade cutting through the PMMA rather than by propagation of a crack some distance ahead. Such behaviour is not typical of an amorphous, glassy polymer, and has not previously been observed in PMMA. To understand why a fibre made from a material notorious for crazing and cracking should cut cleanly under the right conditions, a detailed study of the nature of the surface damage was performed in conjunction with thermo-mechanical analysis of the PMMA in both its annealed and drawn state.

Nature of the Surface Damage

Scanning electron microscopy (SEM) was used to examine the fine detail of the damage to the end-faces. Figure 4 shows fibres equilibrated with the platen at temperatures from 60°C to 100°C. The fibres were cut with a 60°C blade at a speed of 0.05 mm/sec. The images show that all the end-faces were perpendicular and relatively flat with little longitudinal damage, the exception being the dislodgement of the cores for the 60°C and 100°C samples and a spine at the lower edge of the 60°C sample. For these two samples there is also significant damage to the end surface of the fibre, across both the core and cladding at temperatures of 60°C and 100°C, but reasonably good cuts were obtained for the temperatures in between. The damage seems restricted to a thin layer on the surface. Qualitatively the damage at 60°C and 100°C is

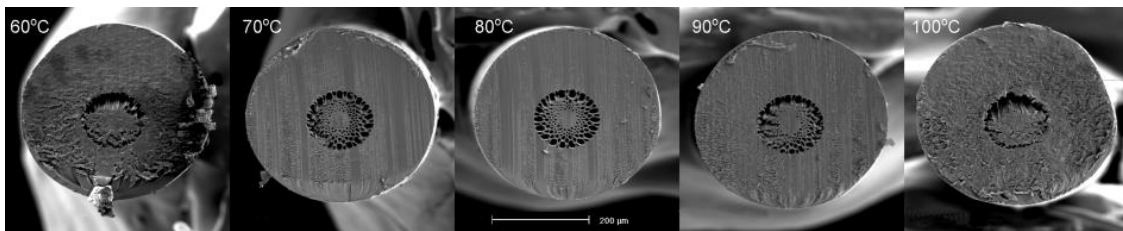


Figure 4: Scanning Electron Micrographs of fibre end faces cut at temperatures from 70 to 100°C with a 60°C blade moving at 0.05 mm/sec.

very similar and appears to indicate the presence of some coherent structure in the material with a transverse dimension of the order 10-20 µm.

Figure 5 shows high resolution SEM images of the upper and lower sections of the 70, 80 and 90°C samples. The upper sections of all three are relatively smooth with small-scale surface damage in the form of transverse striations obvious on the lower sections indicating that this damage worsens down the cut, despite the fact that the upper surface has the blade sliding across it during the later stages of the cut. The spacing of the damage in the mid-fibre region is $2.15 \pm 0.05 \mu\text{m}$, close to the step size of the motor. Towards the lower edge, just above the fracture initiation point, the spacing occasionally increases to $3.8 \pm 0.2 \mu\text{m}$. The sample at 80°C is the 'best' result, though allowance should be made for the effect of the increasing difference in temperature between blade and fibre. The onset of fracture at the lower edge occurs later in the hotter samples. There are steps visible in the fracture zone consistent with the formation of shear bands in the material prior to fracture. These three zones on the end face bear a remarkable similarity to the three types of rupture observed by Lake & Yeoh during the cutting of rubber under transverse stress [12].

While the boundary between the high purity core and the low purity sleeve PMMA is sometimes visible, particularly in the images of the lower part of the surface, there is no change in the behaviour of the surface damage across this boundary indicating that the materials exhibit very similar properties.

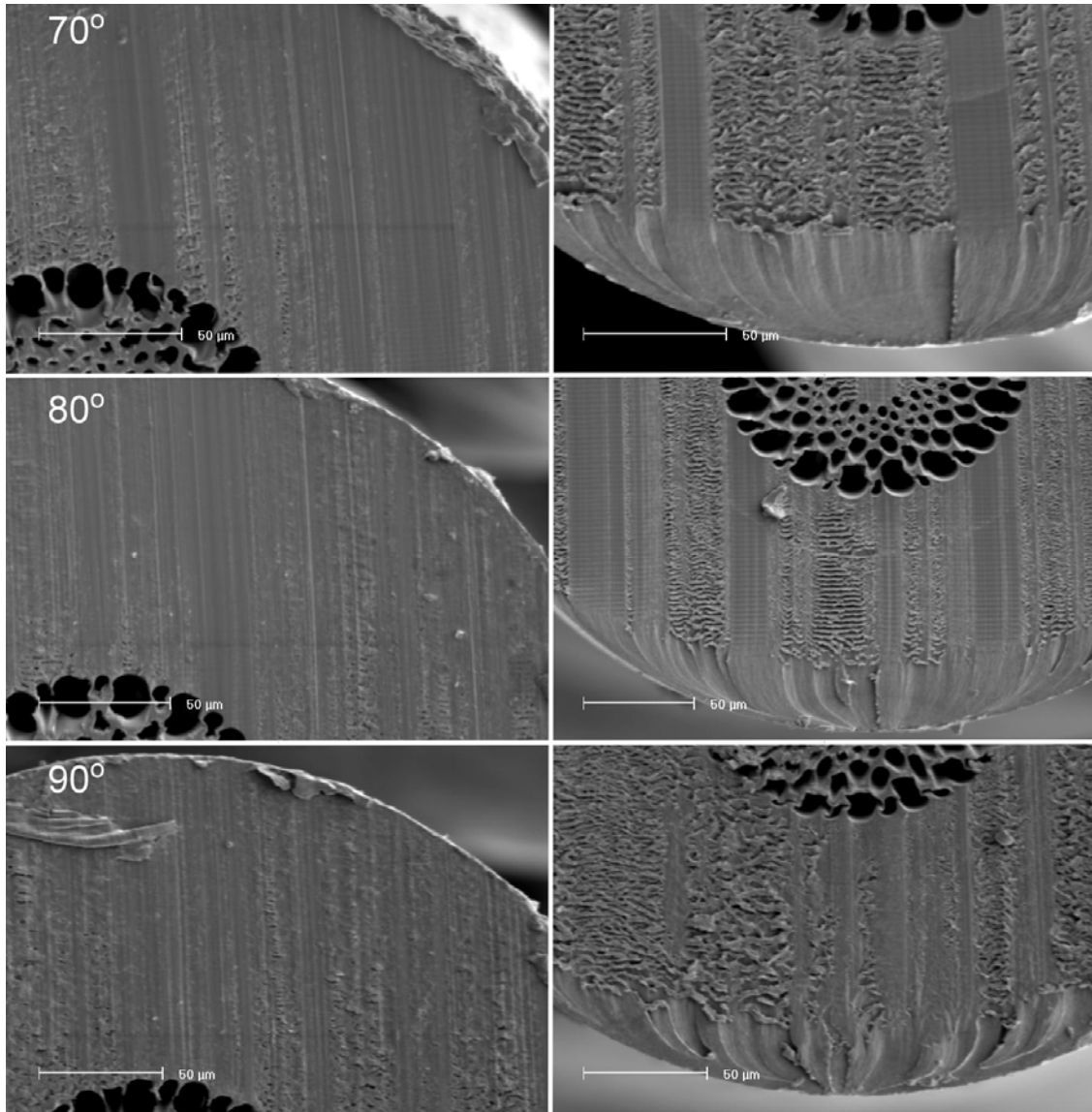


Figure 5: Details of the surface damages of fibre samples cut at temperatures of 70, 80 and 90°C.

Figure 6 shows details of fibre equilibrated to the platen at a temperature of 70°C and cut with an 80°C blade at speeds of 0.07 mm/sec, 0.5 mm/sec and 2.0 mm/sec. In each case the arrow indicates the direction of cutting. The damage is again periodic and consistent with the step size of the motor. The degree of damage increases with increasing blade velocity. It is possible that chain scission continues to occur during the pause between steps at low speeds resulting in less material being dragged forward during the subsequent step.

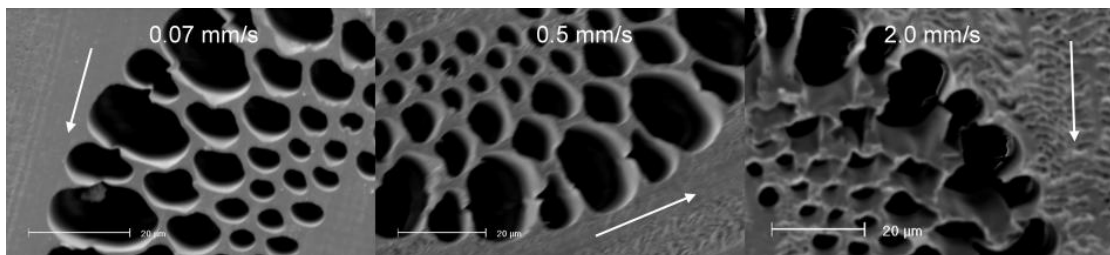


Figure 6: Details of surface damage for blade speeds of 0.07, 0.5 and 2.0 mm/sec.

Figure 7 shows detailed SEM images of the core of a fibre equilibrated with the platen at 70°C and cut with a blade at 70°C and 90°C at a speed of 0.5mm/sec. Again the white arrows indicate the direction of cutting. For the fibre cut with a 70°C blade there is little evidence of surface damage. The majority of the bridges are cleanly cut with a definite angle at the edges of the holes. The very fine bridges are somewhat stretched and bent. In contrast, not only is there significant surface damage in the sample cut with a 90°C blade but the ends of the bridges are smoothly rounded, consistent with melting of the material by the blade. These bridges would not be visible under an optical microscope, leading to the aforementioned 'black' areas in Figs. 2 and 3.

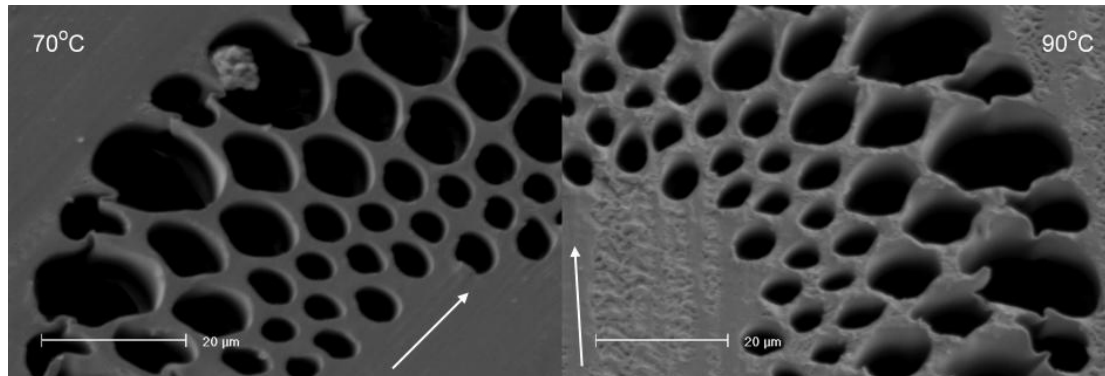


Figure 7: Details of surface and bridge damage for blade temperatures of 70 and 90°C.

In conclusion there appear to be a number of different types of damage which can occur on the end-face of an mPOF during cutting:

- Longitudinal separation between structural elements in the material close to the transition temperature.
- Abrasion by the rough surface of the blade causing longitudinal scoring.
- Lateral striations in the mid to lower section of the end face.
- The melting of parts of the fibre when the blade is too hot.

There are also similarities in between zones of the cut surfaces of the fibre and observations of rubber cut under transverse stress. Clearly an understanding of the material properties of the PMMA fibres and how these vary with temperature is necessary for a more complete understanding of the cutting process and how it produces acceptable end-faces.

Mechanical properties of drawn fibre

The viscosity molecular weight of the raw PMMA places it in the transitional region between brittle and ductile behaviour [24]. To determine whether the material is more brittle or ductile after drawing, mechanical testing was performed on solid fibre drawn under similar conditions to the mPOF (200°C, 65g). Figure 8 shows the results of two tensile tests performed on an Instron 5567 using test method ASTM 3379-75. Samples of fibre were prepared on paper tabs with a gauge length of 100 mm and tested at room temperature with an extension rate of 1 mm/min. The results are consistent and confirm that the fibre displays some ductile characteristics, yielding at a stress of about 40 MPa and deforming up to a strain of some 10% before stress-hardening sets in. Thus it is not surprising that a fibre drawn at a tension of 50g should cut like a ductile material rather than undergo brittle fracture.

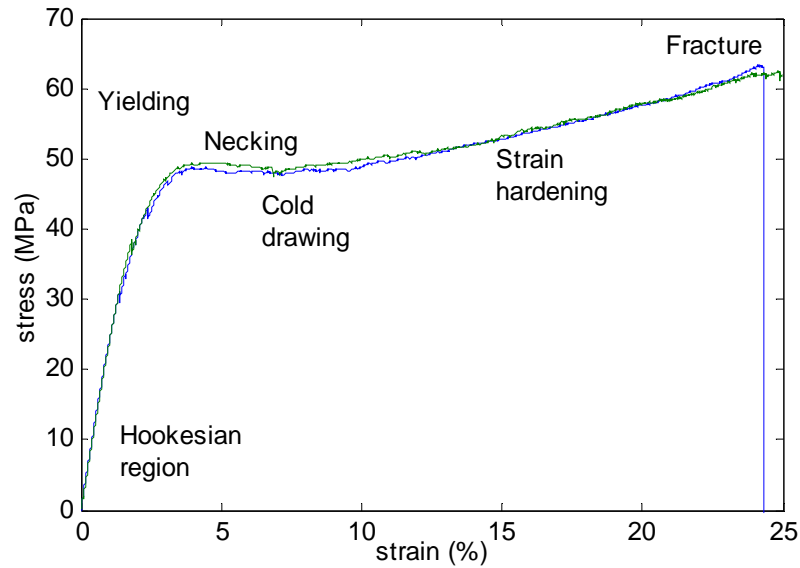


Figure 8: Results of tensile tests on the fibre

Thermo-mechanical analysis was also performed on a solid fibre sample drawn under similar conditions to the mPOF tested (200°C, 65g). Differential scanning calorimetry (DSC) measures the rate of energy input needed to raise the temperature of a sample relative to a standard sample [25, 26]. It provides a measure of the heat capacity of a material, a parameter which is sensitive to changes in molecular mobility. Figure 9 shows the results of a DSC scan for a 13 mg sample performed using a TA Instruments Model 2920. The band between the dashed lines indicates the temperature range over which successful cutting has been observed. The sample was equilibrated at 30°C for one minute, then heated at a rate of 10°C/min to a temperature of 120°C. The curve displays two ‘thermal events’. The inflection points for these were found to be $80\pm 2^\circ\text{C}$ and $115\pm 3^\circ\text{C}$, respectively. The second inflection point is in the range expected for the α -relaxation (or glass transition temperature) of syndiotactic

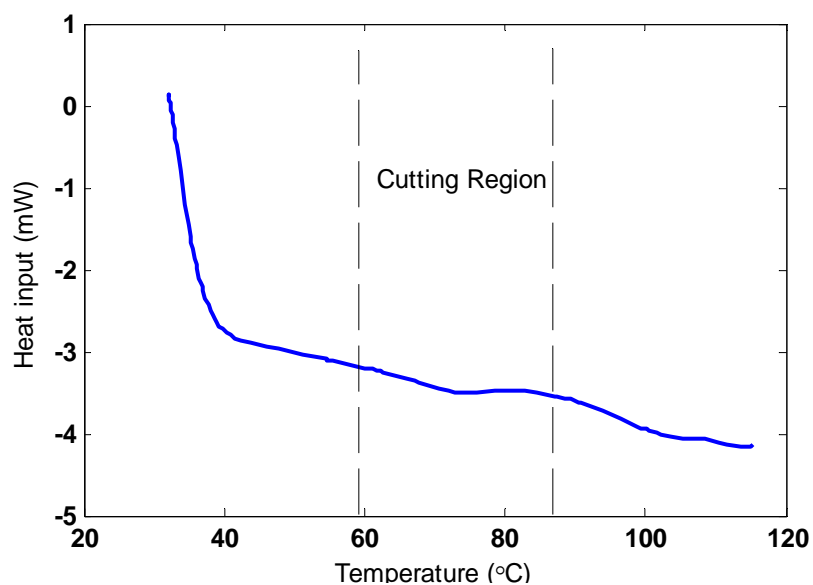


Figure 9: Result of differential scanning calorimetry on a sample of solid PMMA fibre drawn at 200°C under 65g of tension.

PMMA [23, 27]. The first however is too high for either the β -relaxation (expected at a temperature around 20°C) or for the α -relaxation of isotactic PMMA (expected at a temperature around 50°C). The results indicate a ‘thermal event’ in the temperature range within which cutting is possible.

Dynamic mechanical analysis (DMA) is a technique for determining the relative proportions of viscous to elastic behaviour. A small oscillatory force is applied to a sample (well within the Hookean regime) and the phase shift of the resulting deformation relative to the applied force is measured as a function of temperature [25, 28, 29]. Fibre samples are clamped at both ends with the oscillatory force applied as an extension. For bulk materials a small plank is fixed by one end (via a cantilever mount) and a transverse oscillatory force is applied to the other end. Figure 10 shows the results of a DMA scan performed on a 10 mm fibre sample in a TA Instruments 2980 DMA (solid lines). A 10 μ m extension was applied to the sample at a frequency of 1 Hz while the temperature was raised at a rate of 1°C/min to 120°C. Also shown are the results of a cantilever test on a 30x10x3 mm sample of annealed, bulk PMMA preform (shown as dashed lines). After clamping this produced a 17.93 mm long cantilever to which a 10 μ m, 1 Hz oscillation was applied. Once again the temperature was raised at a rate of 1°C/min. The two vertical dashed lines indicate the range over which cutting had previously been successfully achieved.

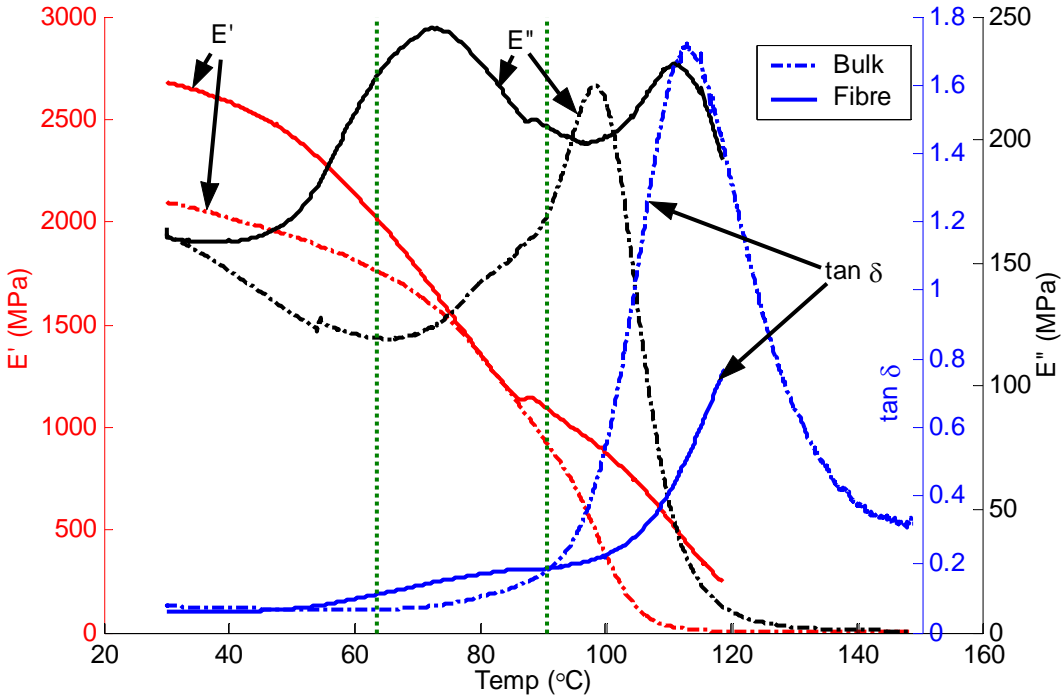


Figure 10: DMA results for the fibre (drawn curves) compared with the results for undrawn, annealed PMMA (dashed curves).

There is a clear and significant change in the properties between the bulk material and the drawn fibre. In particular the loss modulus (E''), a measure of the deformability of the material has developed a double-peak dependence with maxima at 73.0°C and 111.5°C, the first being close to the mid-point of the temperature range for which successful fibre cleavage was previously achieved.

Drawing a polymer to fibre involves very high draw ratios (between 10 and 20). The effects of such a pronounced distortion on the material properties have not been investigated in detail [25]. Since low draw ratios (up to about 3) are known to create significant anisotropies in the material [30-32], it is possible that this increase in viscoelasticity is associated with an anisotropy due to chain alignment.

Optimum Conditions for cleaving mPOF

A total of 91 samples of GImPOF were cut with platen temperatures ranging from 25°C to 100°C, blade temperatures ranging from 50°C to 100°C and blade speeds from 0.03 mm/sec to 7 mm/sec. The end-faces were assessed as ‘good’ or ‘bad’ depending upon the integrity of the core region and the degree of damage in the cladding area. Figure 11 shows this end-face

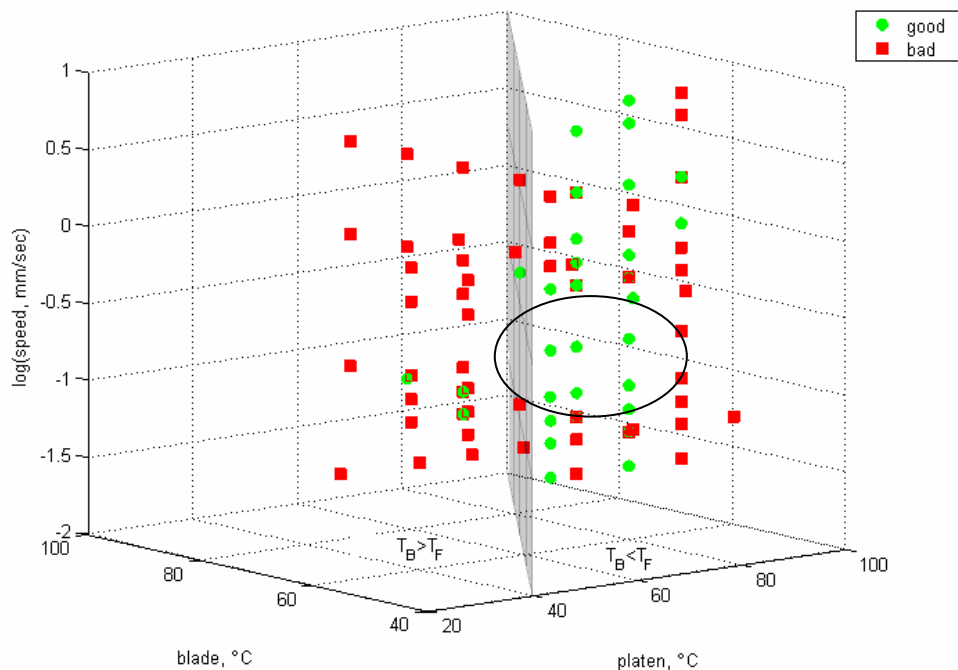


Figure 11: Cutting parameter space for the GImPOF with plane of equal fibre and blade temperature indicated.

quality assessment plotted against platen temperature, blade temperature and blade speed (as a logarithmic variable). Also shown is the plane where platen and blade temperatures are equal, from which it seems clear that the cutting process proceeds more smoothly when the blade temperature is less than the platen temperature. There is a region of consistent ‘high quality cleavage’ corresponding to a platen temperature in the range 70-80°C, a blade temperature in the range 60-70°C and a blade speed from 0.07 to 0.5 mm/sec.

Conclusions

It has been demonstrated that it is possible to cut a PMMA fibre with a hot blade and produce an end-face that is both flat and free of crazing or fibrils (Figure 12). The best results are obtained for fibre temperatures in the range 70°C to 80°C with the blade temperature close to (or slightly below) the fibre temperature. Since the cleaving process is one of cutting rather than crack propagation, lower blade speeds are generally more effective.

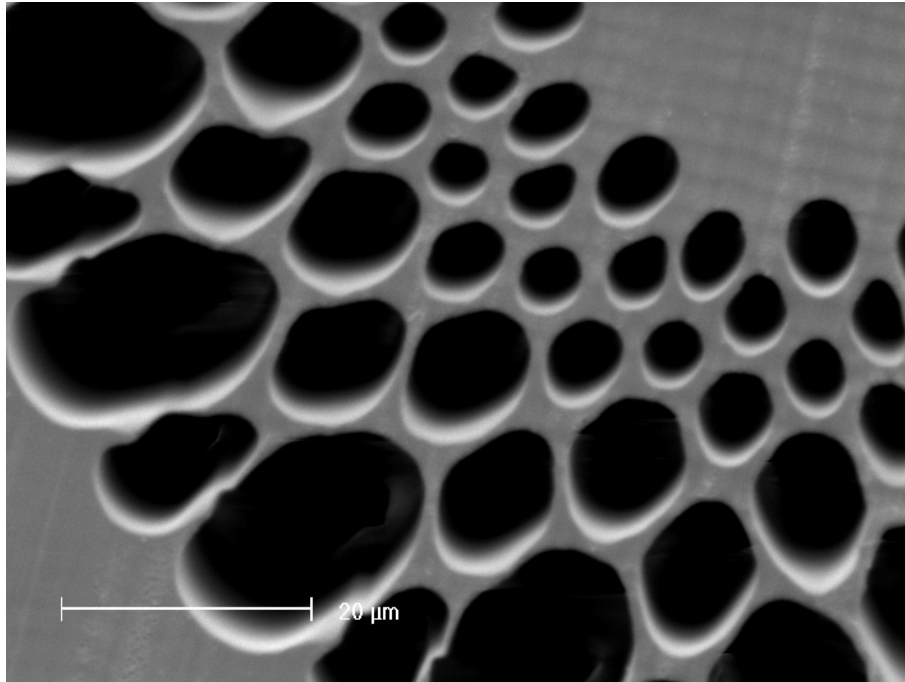


Figure 12: End face of the core region of a well-cut mPOF.

Several distinct types of end-face damage have been identified that can be associated with different aspects of the overall cutting process: lateral striations indicative of limited crack propagation as the cut depth increases; ductile fracture in the final stage of cleaving; melting of bridges when the blade is too hot. The existence of a ‘good’ temperature range for cleaving would appear to be related to structural changes and material anisotropies caused by the fibre drawing process. In particular the increased viscosity of the PMMA in the 70-80°C region would appear to inhibit crack propagation by enabling distortion and blunting of the crack tips.

Further studies are needed to elucidate the effect of draw conditions on both the material properties and the cutting process, as well as determining the effect of the different types of damage on optical transmission through the end-face which is the ultimate test of the quality of any cleaved surface.

Acknowledgements

This work was supported by the Australian Research Council and the Bandwidth Foundry Pty Ltd, the latter being a Major National Research Facility supported by both the Australian and New South Wales Governments.

References

- [1] M. A. van Eijkelenborg, A. Argyros, G. Barton, I. M. Bassett, M. Fellow, G. Henry, N. A. Issa, M. C. J. Large, S. Manos, W. Padden, L. Poladian, and J. Zagari, *OPT FIBER TECHNOL*, 9 (2003) 199-209.
- [2] T. A. Michalske, "Fractography of Optical Fibers," in R. C. Bradt and R. E. Tressler, (Ed) *Fractography of glass*. New York: Plenum Press, 1995.
- [3] J. W. Curtis, *J PHYS D APPL PHYS*, 3 (1970) 1413-1422.
- [4] D. Hull, "Nucleation and Propagation Processes in Fracture," *Polymer Materials*. Ohio: American Society for Metals, 1975, pp. 487-550.
- [5] H. H. Kausch, *Polymer fracture*. Berlin ; New York: Springer-Verlag, 1978.

- [6] E. Passaglia, J PHYS CHEM SOLIDS, 48 (1987) 1075-1100.
- [7] D. Moll and H. Poisel, "Polymer Optical Fiber Termination - A Never Ending Story?," presented at International Conference on Polymer Optical Fiber, Boston, 2000.
- [8] H. Poisel, O. Ziemann, and K. F. Klein, Trends in polymer optical fibers, 5131 (2003) 213-19.
- [9] A. N. Gent, S. M. Lai, C. Nah, and C. Wang, RUBBER CHEM TECHNOL, 67 (1994) 610-618.
- [10] A. A. Griffith, PHILOS T ROY SOC A, 221 (1921) 163-198.
- [11] E. H. Andrews, J MECH PHYS SOLIDS, 11 (1963) 231-242.
- [12] G. J. Lake and O. H. Yeoh, J POLYM SCI POL PHYS, 25 (1987) 1157-1190.
- [13] S. H. Law, J. D. Harvey, R. J. Kruhlak, M. Song, E. Wu, G. W. Barton, M. A. van Eijkelenborg, and M. C. J. Large, OPT COMMUN, 258 (2006) 193-202.
- [14] B. Cotterell, Q. F. Li, D. Z. Zhang, and Y. W. Mai, ENG FRACT MECH, 21 (1985) 239-244.
- [15] Q. F. Li, L. M. Zhou, and S. R. Li, ENG FRACT MECH, 23 (1986) 925-928.
- [16] S. X. Wu, Y. W. Mai, B. Cotterell, and C. V. Le, ACTA METALL MATER, 39 (1991) 2527-2532.
- [17] W. A. Sorem, R. H. Dodds, and S. T. Rolfe, INT J FRACTURE, 47 (1991) 105-126.
- [18] R. H. Dodds, T. L. Anderson, and M. T. Kirk, INT J FRACTURE, 48 (1991) 1-22.
- [19] G. Matsoukas, B. Cotterell, and Y. W. Mai, J MECH PHYS SOLIDS, 34 (1986) 499-510.
- [20] C. Ruggieri and R. H. Dodds, INT J FRACTURE, 79 (1996) 309-340.
- [21] C. Yan and Y. W. Mai, INT J PRES VES PIP, 77 (2000) 313-319.
- [22] J. D. Harvey, R. J. Kruhlak, M. Song, E. Wu, S. H. Law, G. W. Barton, M. A. van Eijkelenborg, and M. C. J. Large, "Cleaving Microstructured Polymer Optical Fibre," presented at 14 International Conference on Polymer Optical Fibre, Hong Kong, 2005.
- [23] J. A. Brydson, "15: Acrylic Plastics," *Plastics materials*, 3rd ed. London: Newnes-Butterworths, 1975, pp. 328-346.
- [24] R. P. Kusy, J NON-CRYST SOLIDS, 24 (1977) 141-4.
- [25] E. A. Turi, "Thermal characterization of polymeric materials," 2nd ed. San Diego: Academic Press, 1997.
- [26] R. B. Cassel, "Measuring the Glass Transition of Amorphous Engineering Thermoplastics," TA Instruments, New Castle, DE, USA TA-309.
- [27] F. E. Karasz and W. J. MacKnight, MACROMOLECULES, 1 (1968) 537-540.
- [28] J. Foreman, "Dynamic mechanical analysis of polymers," TA Instruments, New Castle, DE, USA TA-236, 1997.
- [29] A. Franck, "Viscoelasticity and dynamic mechanical testing," TA Instruments, New Castle, DE, USA AN004.
- [30] C. B. Bucknall, *Toughened plastics*. London: Applied Science Pubs, 1977.
- [31] L. J. Broutman and F. J. McGarry, J APPL POLYM SCI, 9 (1965) 589-608.
- [32] L. J. Broutman and F. J. McGarry, J APPL POLYM SCI, 9 (1965) 609-626.