# MANUFACTURING METHODS FOR MULTI STEP INDEX PLASTIC OPTICAL FIBER MATERIALS

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## *Abstract*

*Plastic optical fibres (POF) are often used in telecommunication, consumer electronics and automotive applications. Measuring and control devices used for POF are already standardised procedures. To meet the requirements of the IEEE 1394 standard for data transfer rates up to 800Mbps requires increasingly improved performance of POF. POFs which offer high bandwidth, total electromagnetic immunity and simple handling are considered as an alternative to noisy copper cables (cat 5) and high performance glass optic fibres for of a data highway. The market requires a simple and inexpensive alternative that would not be a technical overkill. The target of the study carried out in the Institute of Fibre Materials Science at Tampere University of Technology was to evaluate manufacturing methods which would allow this. This is a summary article of the results of manufacturing step index and multi-step index POF by preform manufacturing followed by fibre drawing as well as the extrusion method.*

## *Keywords*

*polymeric optical fibre, copolymerisation, extrusion, fibre drawing in IR-radiation.*

## Introduction

The working principal of plastic optical fibres is based on the phenomenon of total internal reflection, which can confine light within an optical waveguide, i.e. a material surrounded by other materials with lower refractive indices [8]. On this basis, a common optical fibre consists of a highly transparent core with a refractive index (RI) of $n_{core}$ and a surrounding cladding with a RI of $n_{cladd}$. To ensure that a light ray that has entered the fibre can be guided along it, the following must be true: $n_{core} > n_{cladd}$ [3].

Optical fibres where the RI changes in discrete steps are called step-index (SI) optical fibres, whereas those with a gradual RI change are called graded-index (GI) optical fibres. Following the many technological problems experienced in the production of GI fibres with an optimum index profile that remains stable for the duration of its service life, an attempt was made to approach the desired characteristics with the multi-step index profile fibre (MSI-POF). In this case the core consists of many layers (e. g. four to seven) that approach the required parabolic curve in a series of steps. Here a 'merging' of these steps during the manufacturing process may even be desirable. In this case, light beams do not propagate along continually curved paths as in the GI-POF, but on multiply diffracted paths. However, given a sufficient number of steps, the difference to the ideal GI is relatively small, so that large bandwidths can nevertheless be achieved [3].

The important characteristics of POF from the point of view of telecommunications applications can be divided into two categories: physical properties such as refractive index, birefringence, geometry, strength on one hand, and transmission properties such as attenuation and dispersion on the other hand.

The refractive index (n) of an isotropic material is defined in terms of the speed of the light in that material (c) and the speed of light in vacuum ($c_0$): $c = c_0 / n$. RI is related to the free volume (packing

density), the polarisability of the material, and the difference between the optical wavelength used and the maximum absorption wavelength of the material [6]. Usually dense packing or large polarisability results in an increase in the refractive index. At optical frequencies, only electronic polarisation occurs, and the refractive index can be fine-tuned through structure modification, physical aging, and guest doping of polymers. In general, aromatic polymers have higher RIs than aliphatic ones due to better packing and electronic polarisability. The incorporation of highly $\pi$-conjugated dyes raises a polymer's RI. The RI of plastic optical materials can be influenced by temperature and humidity [16].

Birefringence is the effect of variation of RI of a material when measured in different directions. It can occur even in amorphous plastics where polymer chains orientate during moulding [7]. Light scattering will occur at the interface between structures aligned in different directions [2]. Unlike inorganic crystals or glasses, polymers can be molecularly engineered to achieve low birefringence. The birefringence can be extremely low ($10^{-5}$ to $10^{-6}$, the limit of measurement) in polymers that undergo little molecular orientation during processing [19]. Usually, a lower injection speed and a longer holding time are factors which guarantee this effect [7].

The attenuation of POF means the reduction of light power in function to its wavelength during propagation in POF. The attenuation of optical fibres is caused by intrinsic and extrinsic losses. The intrinsic causes include absorption through electronic transitions (UV range), molecular vibrations (in POF, for example C-H molecules) (IR range), and Rayleigh scattering, which changes proportionately to $1/\lambda^4$. The extrinsic losses are caused through absorption by doping atoms/molecules and through scattering at impurities (particles, voids, cracks and bubbles) in the fibre, imperfections at the core/cladding interface, fluctuations in the core diameter, and through microbending. The intrinsic losses, on the other hand, are for the most part caused by the material and can hardly be influenced by manufacturers, as optimising process parameters can minimise the extrinsic losses [3].

The other characteristic influencing transmission properties is dispersion. The dispersion of a POF consists of different parts, such as modal, material and waveguide dispersion. Modal dispersion is related to the RI profile of the fibre and to the distance that light has to cover in a material with a different RI. Material dispersion is caused by the fact that the RI of the material depends on the wavelength [17]. Waveguide dispersion is caused by the fact that light waves project into the fibre cladding to various depths, depending on the wavelength of the light wave [3].

## Manufacturing methods of POF

There are basically two distinct methods used for polymeric optical fibre manufacture: fibre drawing from the preform, and the extrusion method. The extrusion process can be both continuous or batch extrusion.

### *Preform manufacturing*

POF manufacturing by preform drawing consists of three different steps: purification of initial materials, fabrication of the preform with the desired refractive index profile, and finally fibre drawing. Due to purity demands, the preferred method for synthesising polymer material for optical fibres is bulk polymerisation.

The most common causes of contamination in the initial materials are inhibitors that are added to commercial monomers to prevent premature polymerisation. They may also contain water, metal and dust particles [17]. To avoid the reduction of the transmission properties of POF polymerisation catalysts, the monomers and other additives should by purified by distillation, filtration with a membrane filter, or sublimation.

There is a large number of different methods for preform manufacture, including diffusion, chemical vapour deposition (CVD), outside vapour deposition (OVD), vapour phase axial deposition (VAD), gel polymerisation and photo copolymerisation methods.

The basic premise of the exchange diffusion method is as follows. At first, a cylindrical partially polymerised matrix with a high refractive index is made. Next, it is immersed into the bath with a monomer of a low RI. After a certain period of time, necessary for monomer diffusion to reach some

depth, the preform is taken from the bath and subjected to complete polymerisation, thus fixing the RI profile [1].

The essence of the CVD-process is that a reaction mixture as a vapour is fed into a rotating tube fixed in a horizontal position. In the beginning, the mixture contains more compounds with low RI, and in the end it contains more with high RI. If necessary, each layer is polymerised up to a certain conversion, and then the next is applied [1]. One modification of this method is outside vapour deposition (OVD). In this case, a reaction mixture is applied to the outer surface of a start rod with a high RI.

In the method of VAD process, an organic material is sprayed onto the horizontal surface of a supporting rod rotating about the vertical axis. The material is deposited and dried, forming a cylindrical preform. Several polymer solutions with different RIs are used in this method. They are sprayed from several nozzles placed at different angles in such a way that the material with the maximum RI is deposited in the centre, and with the minimum RI in the periphery [1].

The gel polymerisation process is an imitation of gel-effect conditions, when at high viscosity of the reaction medium the rate of chain breaks falls considerably, caused because the rate of polymerisation increases abruptly. This phenomenon enables an RI gradient to be created to a satisfactorily large depth at quick speed. The stages of this process include making a tube of a polymer with low RI. Next, the mixture of monomers with a different RI is poured into the tube and held for swelling. After that, the polymerisation starts from the tube walls. The completely polymerised preform is drawn to fibre [1].

A common feature of the different photopolymerisation methods is the fact that polymerisation is initialised by UV-radiation that penetrates into the mixture while being polymerised to little depth. It is absorbed by the polymerisation initiator, monomers etc. Since with the development of polymerisation the concentration of absorbing centres falls, the UV-light penetrates deeper and deeper, initiating polymerisation in ever deeper layers of the reaction mixture. Usually photopolymerisation is followed by thermal after treatment at high temperature. Finally, the created preform may be held in a vacuum of the order of magnitude of $10^{-3}...10^{-4}$ mmHg at about $50^0$C for a couple of days [1].

### Fibre drawing

After making a preform, it is drawn at 190-230$^0$C. An essential moment is the tension of the fibre during the spinning process. It must be within 50-100g. If it is higher, an over-oriented fibre is made; therefore when heating at an elevated temperature (~80$^0$C), it shrinks considerably and the losses increase [11].

The traditional way of heating the preform has been to use an electric resistance furnace. For economic reasons, it is better to use large diameter preforms; but as the thermal conductivity of POF materials is low, the conventional heating method is accompanied by an unavoidably large temperature gradient along the radial direction of the preform. To overcome these difficulties, an IR furnace working at a wavelength range of 1…2 μm could be used. At such wavelengths, the radiation energy could directly reach the inner region of the preform, and the temperature gradient would be reduced [9].

### Extrusion of POF

The extrusion of POF can be performed by a co-extrusion of multi-layered fibre, or by co-extruding the thick preform fibre at first and then drawing it to the desired diameter [14] MSI fibres can also be produced by conical extrusion. The latter method is the most favourable, because it enables multi-layered fibre structures to be produced in one process. One of the basic differences between conical extrusion and single-screw extrusion is that in the first case the production speed is regulated by the material feeding speed and does not depend on the speed of the rotors.

The co-extrusion of POF can be achieved by concentrically multi-arranging two or three extrusion nozzles whose injection ports are sequentially located from the upstream side to the downstream side. The RI profile is built up step-by-step. From the upmost nozzle emerges the cylinder of the first melt transparent polymer. From the next nozzle a melt mixture of polymer and/or diffusible non-polymerising additives with a RI different from the first polymer is injected into the central part of the

cylinder. That allows the non-polymerising material to diffuse into the cylinder. The extrusion melt moulding of the cylinder results as a POF with a region in which the RI continuously varies [15].

One way to obtain multi-layered optical fibres is by an extrusion apparatus consisting of at least one multi-layer conical extruder unit with which a fibre is extruded close to its correct diameter. The fibre is then drawn to the final diameter immediately after the multi-layer conical extruder unit. The number of the layers can be high (10 … 50), and the structure can be modified easily. Such a technique ensures a multi-layered fibre structure with no weld lines between the different layers. Other important properties achieved are controlled RI distribution, a stable fibre structure and good centricity [18].

## Experimental

### PMMA copolymerisation

PMMA copolymerisation was used to manufacture the step index preform by the thermal and photopolymerisation method. Additionally, we attempted to create a multi-step index preform by thermal polymerisation.

### *Purification of initial materials*

The initial materials used in the PMMA co-polymerisation process were as follows: MMA (methyl metacrylate) monomer with 99% purity, EA (ethyl acrylate) monomer as a plasticiser with 99.5% purity, MN-2 (2,2,3,3-tetrafluoropropyl methacrylate) as a cladding monomer with purity of 99%, AIBN (2,2' – azobisisobutyronitrile) as a polymerisation initiator, and GDMA (glycol dimercapto acetate) as a chain transfer agent with 97% purity [10].

The MMA and EA monomers were rinsed with aluminium oxide to reduce the amount of water molecules or other possible polar groups present in the initial material. Aluminium oxide was separated from monomers by centrifugation. To remove the polymerisation inhibitor from the monomers, MMA was successfully distilled with a conventional still. During EA and MN-2 distillation, the problem of polymerisation of the distilled monomer arose. The process would have demanded extra configurations like low-pressure equipment [10].

The purity of initial materials was evaluated by FTIR (Fourier transform infrared spectroscopy). Both distilled and undistilled MMA samples were observed. No major impurities were seen in the commercial MMA. The difference between spectra showed that during distillation some polymerisation of MMA takes place, so vacuum distillation is preferable.

### *Thermal polymerisation*

The method used for preform copolymerisation was partly based on an expired US patent [12]. The step index preform was manufactured in four different ways. The cladding of the step index preform was fabricated with a system based on a glass tube wedged into the wood lathe. The support end of the lathe was equipped with a duct that enabled material injection and nitrogen feeding into the glass tube. At the other end was the outlet for nitrogen. A heating device/jacket with a thermostat was set up in the lathe's horizontal axis around the glass tube. The rotation speed of the lathe was 960 rpm. For the cladding formation, pure and untreated MN-2 was injected into the glass tube, and the rotation of the lathe and the nitrogen feeding was started.

The cladding formation was fluent enough, except in the case of the second polymerisation route where the nitrogen feeding was improperly controlled because of the faulty valve of the nitrogen bottle, which led to local unhomogenities in the thickness of the cladding layer. The cladding formation conditions are listed in Table 1.

After the cladding formation, four different methods of core polymerisation were used. The combination of MMA and additives was chosen from 10 different mixtures according to pre-tests of polymerisation. The final mixtures used contained 9 ml of MMA, 5.214 mg of AIBN, 49.153 mg of GDMA and 171.295 mg of EA. According to the GPC (gel permeation chromatography) analysis of this test polymerisation, the molecular weight of the resulting PMMA copolymer was 107,590 g/mol,

the polydispersity value was 2.016 and the intrinsic viscosity was 2.224. The different routes of polymerisation and their process parameters are listed in Table 2.

**Table 1.** The cladding formation of SI POF [10]

| Route | MN-2 amount, ml | Rotation time, h | Heating time, h | Temperature, $^0$C | Nitrogen feeding time, h | Quality of the cladding |
|---|---|---|---|---|---|---|
| 1 | 1.5 + 3 | 17.5 + 8 | 17.5+72 | 75 | 1.5+3.25 | Cladding was polymerised and even |
| 2 | 2 | 17 | 17 | 75 | 5 | Cladding had thicker regions at the left end (near stopper 1) |
| 3 | 2 | 17 | 17 | 75 | - | Cladding was polymerised and even |
| 4 | 1.5 | 17 | 17 | 75 | 6 | Cladding was polymerised and even |

All preforms were kept at low pressure for two days after the temperature of the polymerised preforms was reduced, to avoid cracking or other defects that could have been caused by too sudden cooling.

The bubbles formed in the preform were most probably caused by vaporisation of chemicals in the monomer mixture, or by the solution of gas into the monomer during the polymerisation. Another influential factor on the preform construction is mould shrinkage. To prevent bubble formation caused by the residual monomer, polymerisation should take place under pressure. Elevated pressure also enables better control of the mould shrinkage, because it reduces the shrinkage inside the preform, and induces the shrinkage to occur on the top of the sample.

**Table 2.** Polymerisation routes of SI POF [10]

| Route | MMA distillation | Nitrogen feeding time, h | Heating time, h | Temperature, $^0$C | Polymerisation equipment | Comments |
|---|---|---|---|---|---|---|
| 1 | No | 17 | 24 | 75 | Vertically fixed heating jacket | Bubble formation |
| 2 | Yes | - | 24 | 75 | Heating chamber | Bubble formation more than in route 1 |
| 3 | Yes | 24 h at 5 bar | 24 | 60 | Pressurised reactor with heating chamber | At the removal from the reactor the preform was fine, but during further thermal treatment, bubbles were formed |
| 4 | Yes | 24 h at 25 bar | 24 | 90 | Pressurised reactor inlaid to heated water bath | The preform was fine |

It is preferable to form the preform in a rotation process. This means that an additional collapsing process is needed, because of the hole left in the longitudinal axis of the preform. Collapsing could be performed as in the case of glass preforms, or at the stage of fibre drawing.

*Photopolymerisation*

The aim of the photo initialised polymerisation test was to determine the optimum wavelength, intensity and time of applied UV light to achieve a certain percentage of conversion to polymer.

Two kinds of UV sources were used for photopolymerisation. The first of them was an F600 industrial lamp (supplied by Fusion UV Systems, Inc.), whose working wavelength was selected at 313 nm. The test setup is shown in the following picture. A monomer mixture consisting of 1.4 mg of AIBN, 0.02 ml of GDMA, 0.05 ml of EA and 9 ml of MMA was placed into a test tube made of borosilicate glass. The test tube was mounted into the UV-box, and the total planned radiation time of 30 seconds was given in pulses of 5 seconds. After 30 s of total radiation time, no sign of initiation of polymerisation was observed. Another radiation pulse of 30 seconds was given to the sample, but it caused the vaporisation of the whole mixture, as the sample's boiling point was reached. The reason for the unsuccessful UV-polymerisation was probably the absorption area of the borosilicate glass, which is 300-320 nm, so the UV radiation of 313 nm was absorbed by the glass tubes used.

**Table 3.** The composition of polymer mixtures used for photopolymerisation [10]

| Number of the mixture | AIBN, mg | GDMA, ml | EA, ml | MMA, ml |
|---|---|---|---|---|
| 1 | 1.4 | 0.02 | 0.05 | 9 |
| 2 | 2.1 | 0.02 | 0.05 | 9 |
| 3 | 2.7 | 0.02 | 0.05 | 9 |
| 4 | 1.4 | 0.01 | 0.05 | 9 |
| 5 | 1.4 | 0.03 | 0.05 | 9 |
| 6 | 2.1 | 0.03 | 0.05 | 9 |

Another source of UV radiation used was a Kinsten KVB-39 Exposure Unit (supplied by Kinsten Industrial Corporation) with an emission wavelength of 365 nm. At first, the monomer mixture with the same chemical composition as in the previous attempt at UV polymerisation was placed into the borosilicate glass tube. The test specimen was placed into the KVB-39 device, and radiation pulses of 15, 30, 60 and 120 seconds were applied to it. The total time of radiation was 225 seconds, which was not enough to initiate the polymerisation of the sample. After that, quartz glass tubes were used as polymerisation vessels because quartz glass is definitely permeable for UV radiation. 6 monomer mixtures were prepared, according to Table 3.

One millilitre of those mixtures was put into the test tubes, which were then put into the UV device. Nine radiation pulses of 600 seconds each were applied to the specimens, so that the total exposure time was 1.5 hours. According to the test results, bulk photopolymerisation could not be carried out. Additionally about 0.8 ml of mixture 2 was put on a borosilicate bubble tray and radiated for 600 s. In this case polymerisation occurred. This enabled the energy needed for polymerisation to be evaluated. This phenomenon could be explained with a comparison of the energy required for polymerisation and the cohesion energy of PMMA. Further investigation of the samples showed that the MMA monomer was polymerised 2 or 3 days after UV radiation. Obviously some polymerisation takes place, but the number of growing chains is markedly too low for industrially interesting polymerisation rates. The polymerisation conversion is low, at around 80 … 85%.

*Formation of multi-step index (MSI) preform*

According to the literature, a suitable way of providing a plastic optical fibre preform, wherein the refractive index gradually decreases with the distance from the centre toward the periphery, is to apply plastic layers containing a polymer with a certain refractive index and a refractive index adjusting agent by chemical vapour deposition or a coating method on the inner surface of a hollow cylindrical body rotating on its axis. The proportion of the polymer and the refractive index adjusting agent in the plastic layers can be varied so that the refractive index may gradually increase [4]. The RI modifier may be a monomer or a mixture thereof, oligomer, or polymer; $|n_1 - n_2|$ should be 0.01 or more [13]. For the experiments discussed in this article, a copolymer with a lower refractive index was chosen. The difference between the RIs of the monomers used was 0.047.

The plan for preparing the MSI preform was as follows. Firstly, the monomers which should form the polymer layer with the lowest refractive index were supplied into a horizontally placed glass tube, and after the injection, the tube was rotated with the help of the lathe used in previous tests. The refractive index was thereafter to be increased layer-by-layer by alternating the MMA/MN-2 ratio. The final cavity left in the centre axis of the tube was to be cast with the mixture forming the highest refractive index polymer, and allowed to polymerise in closed conditions. We planned to fabricate a MSI preform consisting of five layers with different refractive indexes. We did not plan to form any cladding additionally. The model of the layers is described in Table 4.

The layers of different refractive indexes may be prepolymerised to reach the gel point of the monomer, and thereafter the next layer may be injected. Confusion of the interface of the layers is not deleterious. The confusion may bring the construction of the MSI perform even closer to the construction of the graded index perform.

**Table 4.** Preliminary composition of the MSI POF [10]

| Number of layer (core) | MMA/MN-2 (wt-%) | Refractive index | External diameter of layer (% of layer 5 external diameter) |
|---|---|---|---|
| 1 | 97/3 | 1.4880 | 21.8 |
| 2 | 95/5 | 1.4865 | 54.5 |
| 3 | 93/7 | 1.4850 | 68.5 |
| 4 | 90.5/9.5 | 1.4835 | 82.2 |
| 5 | 88.5/11.5 | 1.4820 | 100 |

The polymerisation test was conducted. The MN-2 monomer of 1.5 ml was polymerised on the surface of the glass tube. Then, 10 ml of MMA monomer mixture was injected into the glass tube at a steady horizontal stage. Approximately half of the monomer mixture flooded from the glass tube, and hence the amount of the injection left inside the tube which retained the dimensions of the tube and the stoppers was maximal. The geometry of the polymerisation vessels used was not satisfactory. The main part of the device that needed improvement was the injection, which should have been conducted under rotation. The other option of the monomer feeding would be to move the injection nozzle along the lathe axis during feeding to ensure even distribution of the monomer.

## Extrusion of optical polymers

The extrusion tests were made with different kind of POF materials such as PMMA and PC. The aim of these tests was to find out the best processing temperature for different materials, and to obtain fibre of the maximum possible diameter. Three different ways of extrusion were tested: single-screw extrusion, conical extrusion and two-layered extrusion for creating step-index fibre.

### Single-screw extrusion

The testing apparatus consisted of a Fourné laboratory extrusion machine and a take-up spool specially designed for POF material extrusion. The melt pump-equipped extruding device of the Fourné machine worked as a single-screw extruder. The length of the screw was 27 D, and its compression was 1.75. The diameter of the nozzle used was 1.5 mm. The take-up speed was 250 rpm. The distance between the nozzle and take-up spool was 1.41 m. Cooling of the fibres was performed all the way from the nozzle to the take-up.
Before extrusion, the PMMA and PC pellets were dried for 17 hours at $60^0$C and 3 hours at $70^0$C respectively in the heating cabinet.

According to the test runs with this equipment, the optimal extruding temperature at the nozzle achieved for PMMA was $248^0$C. The average breaking force of the PMMA was 70.97 MPa/mm$^2$. The maximum diameter of 415 µm was achieved at a pump speed of 23 rpm. In the polarising microscope, some impurities were observed together with some bubbles. The scanning electron microscopy (SEM) images of the same fibre type showed that the fibre surface was even [5].

The optimal extruding temperature at the nozzle for PC was $280^0$C. The fibre diameter was 311 μm and its breaking force was 61.87 MPa/mm$^2$. The maximum value of the diameter, 398.8 μm, was achieved at the pump speed of 22 rpm. In the polarising microscope, a line along the fibre was seen in places, which was probably caused by the nozzle. Some impurities were observable on the fibre surface, but otherwise the fibre was clean and no particles or bubbles were seen inside it [5].

## Conical extrusion

The conical extruder used was borrowed from VTT (Technical Research Center of Finland). The rotor of the conical extruder was double-sided, forming two layers. The cone angle of the nozzle was $30^0$, the rotor diameter was 180 mm, and the diameter of the outlet was 1.4 mm. The take-up spool was the same as in the melt spinning tests. The distance between from nozzle to the take-up was 1.43 m. The cooling of the fibre was carried out by a fan that was placed on the path of the fibre, approximately 50 cm from the nozzle.

The drying of the pellets was carried out in exactly the same way as in the case of single-screw extrusion.

The optimal processing temperature for PMMA was $236^0$C, but the fibre fabricated at this temperature was rather uneven in its diameter. The average breaking force for this fibre was 101.39 MPa/mm$^2$. Raising the processing speed did not necessarily result in any growth in the fibre diameter. The maximum diameter achieved was 538.8 μm. The polarising microscopy of the samples showed dirt particles in the fibre derived from the machine parts, but no air bubbles were seen. In the SEM images, we observed traces caused by the soft fibre being taken up, which led to the fibre deformation.In addition, the line along the fibre was caused by the spinneret of the extruder [5].

The cone extrusion of PC was carried out without significant difficulties. The optimal processing temperature according to the test runs was $268^0$C. The largest fibre diameter was 625 μm, and it was achieved at the screw speed of 31.8 rpm. The breaking force of this fibre was 72 MPa/mm$^2$. Microscopy images showed the presence of impurities on the surface and inside the fibre. No bubbles were discovered [5].

## Two-layered extrusion

The aim was to produce a step-index optical fibre with the PMMA cladding and PC core. For that purpose, the above-mentioned Fourné device and conical extruder were connected by a special joint, so that the first formed the core and the latter formed the cladding. The toolings of both devices were situated at the same plane.

The PC mass temperature at the nozzle was $280^0$C; the processing temperature for PMMA was at first $260^0$C, but was raised for further attempts to $270^0$C. During the first test the speed of the Fourné feeding pump was 22 rpm and the speed of the conical extruder feeding screw was 9 rpm. The microscopy studies showed that the fibre produced in these conditions was not centred satisfactorily, and the PMMA cladding contained a large number of impurities. The two layers were not mixed, and their interface was easily observed. During this test overpressure developed in the Fourné feeding pump, and this lead to its speed being lowered to 16 rpm. Nevertheless the construction of the Fourné spinneret caused a situation where the whole amount of the molten PMMA could not fall off the conical extruder spinneret but was glutted instead. One solution could be longer distances between two spinnerets [5].

Fibres made by conical extrusion are mechanically stronger due to the short residence time at the selected temperature. In order to avoid any pollution of the products, ram extrusion feeding of bulk polymerised polymer to the extruder and immediate secondary coating is preferable. Extrusion of the SI fibre straight to the desired fibre diameter is complicated or even impossible, and it is obvious that achieving the MSI fibre by the same method would be even more difficult. The most convenient solution would be co-extrusion of the fibre with a large diameter and drawing it up to its final diameter immediately after extrusion. This enables us to control the layer thickness in a markedly easier way. Simultaneously, the problems of tooling the backpressure are solved.

**Fibre drawn in IR (infrared) radiation**

The drawing test of different PMMA-based performs were carried out with the help of a semi-automatic drawing-tower. The main parts of the test assembly were the preform-feeding device, the preform rotation unit, IR lamps, an extension tube, fibre guides and a take-up spool. The feeding speed of the preform could be regulated. A preform rotation unit fixed at the speed of 20 rpm ensured the even heating of the material. This was carried out in two steps: two lamps for preheating (max power of 1 kW each) and two lamps heating to melt at the perform tip (max power of 3 kW each). A Duran glass extension tube (outer diameter 54 mm, wall thickness 2.5 mm, length 1016 mm) shielded the whole neck -down area from the turbulence caused by the IR lamps' blowers. For the test carried out, the take-up speed was set at 10.5 m/min.

Two tube preforms (see the description in Table 5) were used for drawing tests. The preform A was tested at the preheating intensity of 30% and melting intensity of 35%. As soon as the early stage (4.5 min from the beginning) of the heating, the materials' tendency to create bubbles was observed. This kind of phenomenon had previously been registered in the case of preforms containing residual monomer over 1.5%. According to the physical data available for the tested preform, that should not have been the reason for such behaviour. The bubbles had mainly occupied the outer parts of the preform cross-section, and no significant bubble formation was observed inside the preform. A test drawing of about ten metres of fibre was made for reference from the preform A. Actual measurements of optical properties of the fibre were not performed. The cross-section of the fibre was not round. One reason for that was the uneven heating of the tube perform. In fact, a collapsing of the tube-like preform was observed, enabling the formation of hollow fibre. But in other extensions, the preform can be collapsed and the fibre drawn immediately thereafter in one phase.

**Table 5.** Physical data of the tested preforms

| Parameter | Preform A | Preform B |
|---|---|---|
| Diameter, mm | 42 (hole 13) | 42 (hole 13) |
| Length, mm | 400 | 400 |
| Material | PMMA | PMMA |
| $T_g$, $^0$C | 75 – 85 | 100 – 110 |
| Content of residue monomer, % | <1 | <1 |
| $M_w$, g | 100 000 – 200 000 | 50 000 – 100 000 |
| Polydispersity | <2 | <2 |
| Visual quality | Bad, presence of bubbles | Good |

During the test drawing of perform B, the lamp powers were lowered to 20% for preheating and 30% for the melting section. The temperature of the preform surface was measured at the melting zone with an IR-temperature probe. It was determined that visible bubbling was initiated at a surface temperature of 130 … 150$^0$C. Afterwards, the visual inspection of the preform showed that bubbling had occurred on both the surface of the preform as well as inside the material in a band from about half of the preform thickness inwards. A bubble ring with the diameter exceeding the extension tube's diameter was formed at the preform head. The fibre draw was begun by manually forcing the bubble ring to collapse, which allowed the starting drop to fall through the extension tube.

Despite the extensive bubble formation, it was possible to stabilise the drawing to steady conditions with a line speed of 10.5 m/min, a preform feeding speed of 3.5 mm/min and the temperature of the molten region of 184 ± 2$^0$C (the power of the melting lamp was 33…34%). The diameter of the resulting fibre was nominally 760 μm. The cross-section of the fibre was not round because of the uneven neck-down shape.

Small samples of both the tested preforms were further dried at different temperature, pressure and time conditions in order to investigate the change in mass. The results for preform A are gathered in Table 6. The results for preform B were similar to preform A.

Samples A2, A5 and A8 were also studied by thermogravimetry. The mass loss of all samples was registered at $180^0$C. The results of thermogravimetry were as follows: A2 – 0.41%; A5 – 0.25 %; A8 – 0.29%.

After thermal treatment, all samples were melted by IR radiation at a wavelength of 1200 nm, again in order to observe their behaviour. During the heating time of 15 minutes, the samples were overheated and bubble formation took place. The results are gathered in Table 7, where 'bubble size' means the maximum observed bubble diameter in microns, and 'surface contamination' refers to the amount of bubbles on the outer surface of the sample. The reference sample was the initial material without any thermal treatment.

**Table 6.** Thermal treatment of preform A

| Sample | Temperature, $^0$C | Time, h | Pressure, bar | Loss of mass, % |
|--------|-------------------|---------|---------------|-----------------|
| A1 | 50 | 4 | 1 | 0.04 |
| A2 | 50 | 8 | 1 | 0.04 |
| A3 | 50 | 16 | 1 | 0.05 |
| A4 | 75 | 4 | 1 | 0.09 |
| A5 | 75 | 8 | 1 | 0.09 |
| A6 | 75 | 16 | 1 | 0.12 |
| A7 | 50 | 4 | 0.1…0.2 | 0.10 |
| A8 | 50 | 8 | 0.1…0.2 | 0.09 |
| A9 | 50 | 16 | 0.1…0.2 | 0.09 |

It is obvious that thermal treatment has removed some of the low evaporating phase, and therefore the bubble formation has reduced. The best results were achieved in the case of sample A9, but sample A1 also showed quite good behaviour. Generally it can be said that thermal treatment under lower pressure (approximately 50mbar) would be preferable.

**Table 7.** Bubble formation in after treated samples of preform A

| Sample | Bubble size, µm | Number of bubbles (estimate) | Surface contamination, % |
|--------|-----------------|------------------------------|--------------------------|
| A1 | 60 | 28 | 0 |
| A2 | 380 | 65 | 80 |
| A3 | 200 | 60 | 10 |
| A4 | 190 | 55 | 10 |
| A5 | 270 | 75 | 60 |
| A6 | 220 | 40 | 25 |
| A7 | 170 | 47 | 5 |
| A8 | 250 | 50 | 50 |
| A9 | 50 | 20 | 1 |
| Reference | 7500 | 500 | 100 |

## Results and discussion

According to the test results, it can be said that monomers used for preform manufacturing have to be purified. The polymerisation process and the handling of the materials should be carried out in special conditions. The most feasible method for GI POF manufacturing should include the following steps: preform manufacture, the removal of the residual monomer under vacuum, the preheating and collapsing of the preform and finally fibre drawing.

The tests showed that bulk photopolymerisation of MMA can be carried out only with difficulty, and is more time-consuming than would be reasonable in manufacturing applications.

The co-extrusion method would enable SI or MSI fibres to be produced. This process should start with the polymerisation of the purified monomer in the feeding cylinders. In the case of conical extrusion, two different materials with different refractive indexes could be mixed in various layers. The fibre core should be extruded separately. The product of the conical extruder should be a preform of the diameter of approximately 5-10 mm, which would be drawn onto the desired diameter immediately after extrusion, without additional cooling.

The fibre drawing in IR radiation was performed, and intensive bubbling of preforms was observed before a low viscosity region was achieved for drawing purposes. Thermal after-treatment of preforms showed that the reason for bubbling was the low molecular weight components, which were partly removed at higher temperature and conditions of lower pressure.

## *Acknowledgements*

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