

High-temperature polyimide coating for optical fibres

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Abstract. We present our first results on the fabrication of new, high-performance polyimide coatings. The key components of the coatings are polyimides containing various cardo and/or fluoroalkylene groups, which allows the coatings to retain their high-temperature stability and facilitates the storage of the starting polymer and the optical fibre coating process owing to the good solubility of such copolymers in many organic solvents. Annealing for 30 s, 1 h and 24 h at temperatures of 430, 350 and 300 °C, respectively, reduces the strength of optical fibres having such coating by no more than 10 %.

Keywords: optical fibre, heat-resistant coating, polyimide.

The main factor limiting the use of optical fibres in a number of application areas, in particular in the oil and gas industry, chemical industry and medicine, is their insufficient resistance to the aggressive attack of the ambient medium and temperature, which is determined primarily by the properties of their protective coating. It should protect the surface of optical glass fibres against mechanical damage and direct contact with the ambient medium. Standard (acrylate-based) protective polymer coatings allow optical fibres to be employed at temperatures no higher than 85 °C. They are sensitive to the presence of many chemicals in the ambient medium. Modified polyacrylate coatings can work at temperatures of up to 150 °C [1], and the use of silicone rubber allows the working temperature to be raised to 200 °C [2]. However, to further extend the application field of optical fibres, these should be able to operate at temperatures of up to 300 °C and above. One approach to this problem is to use protective coatings from polyimides, which offer unique thermal stability [3, 4].

At present, coatings on optical fibres are produced using solutions of polyamic acids, which undergo further chemical transformations (imidisation) after the coating process. As a rule, drying and polyimide structure formation in the fibre drawing process can only be ensured when the final coating thickness does not exceed 1.5–2 µm. To produce coatings 5–10 µm in thickness, several deposition cycles (three to five layers) are needed, which should be carried out before fibre winding onto a spool. This significantly complicates the drawing tower design: to draw polyimide-coated fibres, one has to significantly change it.

An extremely annoying limitation related to the use of currently available polyamic acid varnishes is that they should be transported and stored at reduced temperatures. Because of this, the polymers (manufactured mostly by HDMicrosystems, USA) should be delivered from the manufacturer as rapidly as possible and in a specially designed, thermally insulated container with an internal source of cold (for example, dry ice).

In this paper, we present our first results on the fabrication of new, high-performance polyimide coatings. A process proposed previously by Vinogradova et al. [5] for the synthesis of polymers through single-step high-temperature polycondensation in solution offers the possibility of obtaining various structures of cardo poly(heteroarylenes), which possess a combination of valuable properties and allow one to dispense with the polyamic acid formation step, conventionally used in the synthesis of polyimides. It has also been demonstrated that the anionic or radical polymerisation of some monomers containing dissolved polyimides yields graft copolymers with improved performance characteristics [6]. Moreover, with this approach there is no need to store polymer solutions at low temperatures before the fibre coating process.

The copolyimide whose structure is shown in Fig. 1 was synthesised through one-step high-temperature polycondensation in *m*-cresol ($T = 180$ °C, $t = 5$ h, argon). Its properties are indicated in Table 1. To coat an optical fibre, we prepared a solution of the polyimide (3.8 g) in freshly distilled, dried cyclohexanone (38 mL). To the polymer solution was added γ -aminopropyltriethoxysilane (2 wt%) as an adhesion promoter.

We checked the compatibility of the resultant material with the optical fibre drawing process and tested optical fibres coated with the new polymer.

The fibre was drawn on a specially designed drawing tower 9 m in height. After preselection of the process conditions, we drew a 140-µm-diameter fibre for testing. On its way from the drawing furnace to the drawing capstan, the fibre passed at a speed of 15 m min⁻¹ through a specially designed drawing die (a small vessel having a calibrated 200-µm-diameter

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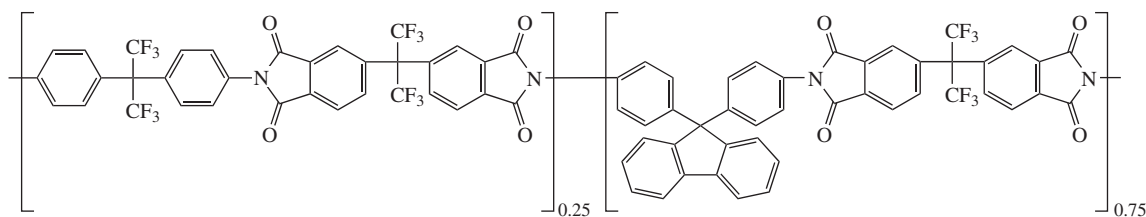


Figure 1. Structure of the copolyimide.

Table 1. Properties of the copolyimide based on 6F-dianhydride, 6F-diamine and aniline fluorene.

| Inherent viscosity of the polyimide [dL g^{-1} (NMP)] | Glass transition temperature/ $^{\circ}\text{C}$ | 10% weight loss temperature/ $^{\circ}\text{C}$ (in air) | Film | | |
|---|--|--|---------------------|----------------|-------------------|
| | | | σ/MPa | E/MPa | ε (%) |
| 1.25 | 355 | 525 | 87 | 1200 | 10 |

Note: σ is the tensile strength, E is the tensile modulus, and ε is the elongation at break.

hole in its bottom) containing a solution of the copolyimide (based on 6F-dianhydride, 6F-diamine and aniline fluorene). The difference in diameter between the die hole and fibre determined the thickness of the resultant liquid coating ($\sim 30 \mu\text{m}$). Mounted behind the die were two controlled-temperature 50-cm-long vertical tube furnaces, in which the coating was dried. The temperature in both furnaces was 350°C . After drying and imidisation, the thickness of the coating (produced as one layer) was about $3 \mu\text{m}$ (Fig. 2).

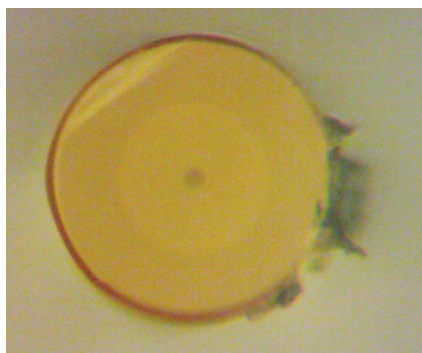


Figure 2. Image of the end face of a 140- μm -diameter optical fibre coated with a 3- μm -thick polyimide layer.

The fibre thus produced was exposed to elevated temperatures in air in a temperature controlled chamber. The strength of the fibre before and after the test was determined under laboratory conditions by two-point bend tests [7] at a face-plate velocity of 0.1 mm s^{-1} . This method is better suited to operation conditions at elevated temperatures, where the main mechanical effect is related to the bends resulting from the fibre laying process before service. The strength data are presented in Fig. 3. The state of the coating on the test samples was also examined visually (using an optical microscope).

The as-prepared fibre had a smooth colourless coating, without any visible inhomogeneities or flaws. It had high bending strength ($\sim 6 \text{ GPa}$), with small scatter. Its tensile strength was measured to be $\sim 5 \text{ GPa}$. In tension tests, we used

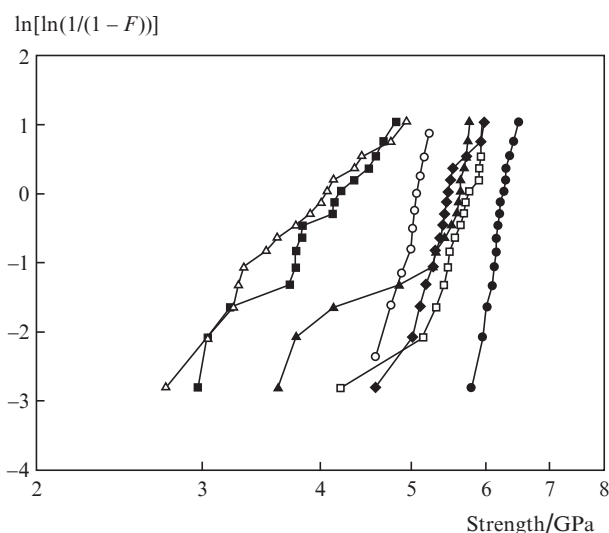


Figure 3. Measured strength of fibre samples (the vertical axis represents the Weibull function; F is the cumulative fibre failure probability): initial tensile strength (○), initial bending strength (●) and strength measured after 30 s at 430°C (◆), 1 h at 350°C (□), 24 h at 350°C (■), 24 h at 300°C (▲) and 170 h at 300°C (△).

0.5-m-long samples and a crosshead speed of 20 mm min^{-1} . The results thus obtained correlate with the strength of standard fibres at the same temperature and humidity ($\sim 25^{\circ}\text{C}$, $\sim 30\% \text{ RH}$). Thus, the coating demonstrated a wear resistance sufficient for withstanding the fibre laying process before service at elevated temperatures.

In the next test, we examined the behaviour of the coating at a temperature of 430°C over a period of 30 s [4] in order to model the fabrication conditions of a high-temperature cable based on polyimide-coated optical fibres. During the fabrication of such a cable, the fibre may be subjected to brief heating to a temperature of $\sim 400^{\circ}\text{C}$ when passing through an extruder that produces cable coatings. After such testing, the fibre was light goldish in colour, but the coating had no visible inhomogeneities or flaws, i.e. favourable test results were obtained, even though the strength dropped slightly (by $\sim 10\%$). After 1 h of annealing at the temperature in question, the samples were dark brown in colour and so brittle that strength measurements were impossible. Examination under a microscope revealed marked inhomogeneities in the coating and uncoated areas (Fig. 4a).

We also made tests at temperatures of 350 and 300°C . As follows from the data in Fig. 3, the samples tested for 1 h at 350°C and for 20 h at 300°C were in similar states, as were those tested for 24 h at 350°C and for 170 h at 300°C . After the former two tests, the samples were light goldish in colour, but the coating had no visible inhomogeneities or flaws and

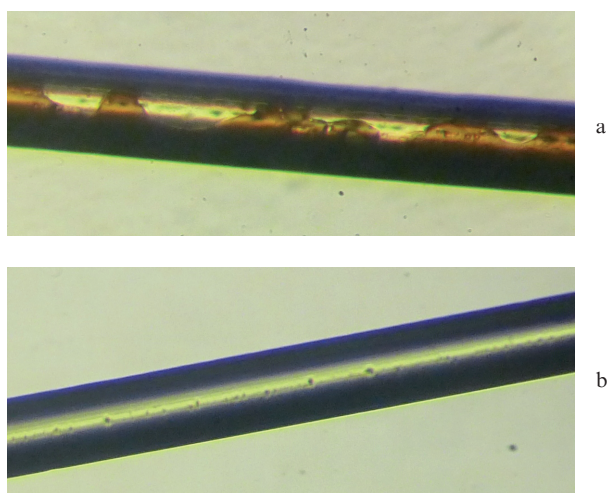


Figure 4. Fibre samples after annealing in air (a) for 1 h at 430 °C and (b) for 24 h at 350 °C.

the strength of the samples decreased by just $\sim 10\%$ with respect to its original level. In the case of the latter two tests, the strength of the samples dropped by more than a factor of 1.5, the coating became deep goldish in colour, and microscopic examination revealed point defects (Fig. 4b) or small cracks in the coating.

In our opinion, one possible cause of the defect formation in the coating and the associated early strength loss is the low elasticity of the polymer under consideration (10% elongation at break). Near the decomposition temperature of the coating, its elasticity may be even lower, which would lead to the formation of cracks and other flaws. Further structure optimisation is expected to improve the elasticity of the coating under development.

Thus, the proposed approach to the synthesis of the copolyimide, which excludes the conventionally used polyamic acid formation step, allowed us to produce materials stable during storage (in contrast to existing polyamic acid solutions). The enhanced solubility of the synthesized polyimide facilitates the optical fibre coating process, because the thickness of the coating produced in one deposition cycle has been increased to 3 μm .

Further research aimed at improving the elasticity of the new coating and optimising its adhesive properties by varying the polymer structure will enable an increase in the service life of fibres at elevated temperatures (up to 400 °C).

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