



PROTECTIVE COATINGS FROM HIGHLY HEAT-RESISTANT SILICA OPTICAL FIBERS: FROM FUNCTIONALIZATION OF POLYIMIDES TO PHOTOPOLYMERIZING COMPOSITIONS

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Abstract

New approaches to the formation of primary protective coatings for silica optical fibers based on polyimides or their photocurable compositions with diacrylates are presented. Particular attention is drawn to improving the adhesion of the polymers to the fiber by introducing carboxyl groups or amide bonds into the polyimide. The advantages of high-temperature autocatalytic synthesis of carboxylated polyimides and the use of photocurable compositions to improve the manufacturability and properties are shown.

Key words: polyimides, polyamide-imides, diacrylates, UV photopolymerization, heat-resistant protective coating.

Introduction

Highly heat-resistant polyimides (PIs) comprise a large class of high-molecular-weight compounds which includes many representatives and is of high theoretical and practical importance. Owing to their outstanding thermal and mechanical properties and good solubility in organic solvents, PI materials are used in many high-tech areas of industry [1–4]. In particular, thin PI films with high thermal and strength properties are successfully used in information display devices, flexible solar cells, flexible printed circuit boards, touch panels, temperature-regulating and protective coatings for electronic and space devices, *etc.* [2, 3, 5, 6]. To ensure the proper quality of products, PI films must have, in addition to high glass transition and thermal degradation temperatures, good strength, adhesion, resistance to aggressive media and corrosion, and manufacturability [2, 5, 6].

Nowadays, the commercial production of PI coatings typically involves several technological steps: application of a polyamide acid (PAA) solution to a substrate, thermal imidization of PAA, and drying of the coating from the solvent and released water [2, 5, 6]. The hydrolytic and thermal instability, incomplete cyclization of PAA to PI [6, 7], and several application cycles to achieve the required thickness are serious drawbacks of this approach, limiting the use of coatings in devices that require high reliability and durability [6, 7].

Herein, we present a comparative analysis of current trends in the field of manufacturing highly heat-resistant polymeric coatings for silica optical fibers. In addition to the dependence of the stability of optical fibers on the polyimide nature (the presence of side carboxyl groups or amide bonds), special attention is drawn to improving the manufacturability of the coatings. In particular, the results of high-temperature tests of silica optical fibers with a coating based on a photocurable



Rating of polymer coatings for silica optical fibers

three-component composition consisting of fluorinated cardo copolyimide 6FDA-AFL_{0.75}:6FpDA_{0.25} dissolved in 1,4-butanediol diacrylate and a photoinitiator are presented for the first time.

Results and discussion

During the drawing process, the silica optical fibers were successively passed through a spinneret with a polymer varnish and then through a heating furnace, where they were dried [8]. The following optimal technological parameters for the formation of coatings from PI solutions were established: the molecular mass of the polymer ($M_n = 30\text{--}90$ kDa, $\eta_{inh} = 0.6\text{--}1.5$ dL/g), concentration and dynamic viscosity of the polymer solution (15–30% and 20–50 Pa·s), fiber drawing speed (~10 m/min), drying temperature (300–350 °C), diameters of the drawn fiber (100–150 μm) and the spinneret hole (250 μm), *etc.* [9, 10].

It is generally accepted that, besides the mechanical and thermal stability of a polymer, the adhesion of the coating to quartz glass is a necessary condition for maintaining the fiber strength [8–10]. It was shown that the coatings with the required adhesion to optical fibers can be formed both by adding a coupling agent to the PI solution [9] and by introducing additional functional groups into the polymer structure, for example, carboxyl [6, 11, 12] or amide units (the synthesis of polyamide-imides [10]), capable of forming hydrogen and other non-covalent bonds with the surface of a silica fiber.

The stability of the resulting coatings was assessed by two-point bending tests before and after annealing [13]. The average strength values for the fibers with different coatings (Fig. 1) are given in Table 1.

The initial strength of the fibers with the developed PI coatings was slightly inferior to the commercial analog

CeramOptec®. The annealing of the samples at 300 °C for 72 h did not significantly affect the strength of optical fibers, which indicates their stability. Only the strength of the fibers with the ODPA:AFL coating, formed by adding the coupling agent, decreased by 10% after 24 h of heat treatment. The annealing of the commercial fiber and the fiber with the polyamide-imide (6FDA:TFDB:TPC) coating at 350 °C for 24 h led to a loss of ~10–15% of strength, while the coating based on BTDA-DABA_{0.5}:AFL_{0.5} with side carboxyl groups retained the initial strength of the fiber. A slight decrease in the heat resistance of the fiber protected by 6FDA:TFDB:TPC may be due to the imperfection of the coating, namely, the presence of organic dust microparticles [10, 14]. A dramatical decrease in the strength of the commercial fiber (more than 60%) was observed only after three-day annealing at 350 °C, while the fibers with the developed PI coatings from BTDA-DABA_{0.5}:AFL_{0.5} and 6FDA:TFDB:TPC retained ~60% of their strength under these conditions.

An additional advantage of using the BTDA-DABA_{0.5}:AFL_{0.5} coating, obtained on the basis of 3,5-diaminobenzoic acid by the autocatalytic high-temperature polycondensation, is the ability to produce a coating *in situ* directly from the reaction solution, avoiding the stages of the polymer separation and purification [11].

The need to carefully remove residual solvent from the coating, the possible formation of defects due to its rapid evaporation, as well as its negative impact on the environment and health are the main drawbacks of this process. The most attractive, technological and ecologically friendly method is photocuring of a varnish applied to the surface of the optical fiber. Modern highly heat-resistant coatings made of poly(oligo)(urethane diacrylates) or silicones [15], which are

widely used in industry, are capable of withstanding prolonged heating up to 200 °C.

We have suggested an original approach consisting in the formation of photocurable coatings from a three-component composition: di(meth)acrylate, polyimide, and photoinitiator [16]. It was found that optical fibers with a coating based on poly(1,4-butanediol diacrylate) and 23 wt % of highly fluorinated cardo copolyimide (PolyBDDA/6FDA-AFL_{0.75}:6FpDA_{0.25}) after three days of annealing at 350 °C retains more than 98% of its strength, which indicates high thermooxidative stability and excellent adhesion (Table 1). To date, the presented results are record-breaking not only for photocurable coatings described in the literature, but also for coatings obtained by the traditional methods from PI.

It should be noted that maintaining the strength of the fiber after prolonged exposure to temperature can ensure its stability and durability during operation under normal conditions [17].

Conclusions

The use of organosoluble PIs with carboxyl or amide groups (polyamide-imides) allowed for eliminating most of the drawbacks of PAAs. The PI solutions are stable and do not require special storage conditions; a coating with the required thickness and adhesion to optical fibers is formed during a single application of the varnish. The developed autocatalytic synthesis of the carboxyl-containing PIs opens up the possibility of forming a coating *in situ* directly from the reaction solution. The application of alternative approaches to the formation of highly heat-resistant protective coatings, such as UV-curable compositions, accelerates and significantly simplifies the technological process, while the absence of evaporated solvents

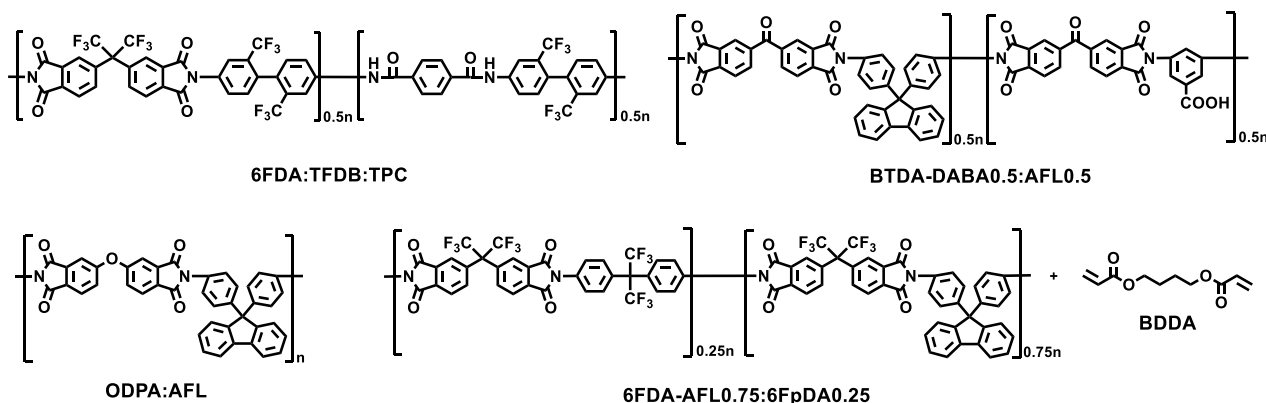


Figure 1. Chemical structures of the polyimides and photopolymerizing composition used to form the protective coatings for optical fibers.

Table 1. Two-point bend strength median data of the optical fibers protected by different polymers

| Polymer | Strength, GPa | | | | | | | Ref. |
|--|---------------|---------|---------|---------|---------|---------|---------|------|
| | Initial | 300 °C | | | 350 °C | | | |
| | | 1 h | 24 h | 72 h | 1 h | 24 h | 72 h | |
| CeramOptec® ¹ | 6.5±0.1 | 6.6±0.2 | 6.6±0.2 | 6.4±0.2 | 6.9±0.3 | 6.0±1.4 | 2.6±2.0 | [11] |
| ODPA:AFL ² | 6.0±0.1 | 5.8±0.2 | 5.3±0.5 | — | — | — | — | [9] |
| BTDA-DABA _{0.5} :AFL _{0.5} | 6.1±0.1 | 6.3±0.1 | 6.2±0.2 | 6.3±0.1 | 6.2±0.1 | 6.1±0.2 | 3.9±1.6 | [11] |
| 6FDA:TFDB:TPC | 6.0±0.6 | 6.3±0.4 | 6.2±0.8 | 5.8±1.3 | 6.0±1.2 | 4.7±1.3 | 3.1±0.9 | [10] |
| PolyBDDA/6FDA-AFL _{0.75} :6FpDA _{0.25} | 5.8±0.1 | 6.1±0.3 | 6.0±0.1 | 6.0±0.1 | 6.0±0.6 | 6.0±0.8 | 5.7±0.5 | |

^a commercial optical fiber with the PI coating;

^b 3-aminopropyltriethoxysilane (2 wt %) was added to the polymer solution as an adhesion promoter.

reduces the amount of volatile organic compounds released into the atmosphere, thereby improving work hygiene and reducing the negative impact on the environment.

In addition to significant technological advantages, the optical fibers with new coatings are superior in terms of heat resistance to the commercial analog produced by CeramOptec®, which can ensure a longer and more reliable service life of optical fiber sensors based on them

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