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In situ synthesis of copolymers based on polyvinylpyrrolidone and condensation polymers and their use as optical fiber coatings

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ABSTRACT

The copolymers of *N*-vinyl-2-pyrrolidone (N-VP) and condensation cardo and/or fluorinated condensation polymers (aromatic polyamide, polyimide and polyarylate) were synthesized by free radical *in situ* polymerization. The partial formation (14–61 wt%) of polivnylpyrrolidone (PVP) homopolymer upon the polymerization of N-VP containing dissolved condensation polymer was stated. Synthesized (*co*)polymers are differed in heat resistance and solubility from neat PVP. Using relevant copolymers solutions in *N*-methyl-2-pyrrolidone the optical fiber coatings having good adhesion properties were fabricated. Such coatings demonstrate high stability at elevated temperatures. A substantial number of defects on coatings and a slight decrease in bending strength are observed only on exposure at 200 °C for 72 h. Simultaneously holding for 1 and 24 h at the same temperature leads to hardening of the fibers: bending strength changes from ~5 up to 6 GPa.

1. Introduction

Optical fiber polymer coatings as a rule are based on acrylic polymers, silicones or polyimides (PI) [1]. Each type of coatings has its advantages and drawbacks. UV-curable polyacrylates are used for a majority of applications including transmit light over long distances. However they are sensitive to many chemicals and most polyacrylates can be used only up to 85 °C. Especially modified polyacrylate coatings can withstand a temperature of 150 °C [2]. Using relatively inexpensive silicone rubber allows increase working temperature to 200 °C [3] but several application spheres are needed in coatings that withstand temperatures of 300 °C and above. One solution is to use coatings from PIs which also conventionally apply to harsh environmental conditions (*e.g.* oil and gas, nuclear, medical, and aerospace applications) [4,5]. The technology PI's coatings formation includes utilization of poly(amic acid) precursor which poses a problem of incomplete imidization [6] and subsequent stability of the final coating. Only quantitative cyclization of the relevant polyamic acid allows getting stable at high temperature coatings. It's not easier to achieve in the rapid formation of the optical fiber coating. As a rule, polyimide structure formation in the fiber drawing process can only be ensured when the final coating thickness does not exceed 1.5–2 μm. To formulate 5–10 μm coverage coatings a few deposition cycles are needed.

Probably, most commercially available polyimide-coated fibers start to degrade from relatively low temperature (200–250 °C) owing to the presence of amic acid moieties which also significantly reduces coating durability [5]. Moreover, majority of PI's coatings has insufficient adhesion to the fiber that forces by use of additional coupling agents or synthesize polymers with specific functional groups [7,8].

Previously [9] we have demonstrated the new method of PI's coatings formation. This approach relies on the application of preparing copolyimide's solution to coatings formulation and excludes the conventionally used polyamic acid. This ensures the absence of amic acid groups in the formed coating. The strength of optical fibers with the described coating has no more than 10% after holding for 30 s, 1 h and 24 h at 430, 350 and 300 °C, respectively. Meanwhile the fluorinated copolyimide has insufficient adhesion to the fiber and is quite expensive.

Despite the long history of polymers based on polyvinylpyrrolidone (PVP) [10,11] it gains new uses. (*Co*)polymers and composites based on PVP have many applications in different fields: from conventional, such as medicine, cosmetics, textile *etc.* [10–13], to membrane [14,15], nanoparticles coordination [15–17], adhesives [11], coatings [10,11,18], *etc.* Due to its good adhesive properties these (*co*)polymers are used for dressing of fiberglass to create glass-reinforced plastics, prepregs, laminates [19]. Probably this

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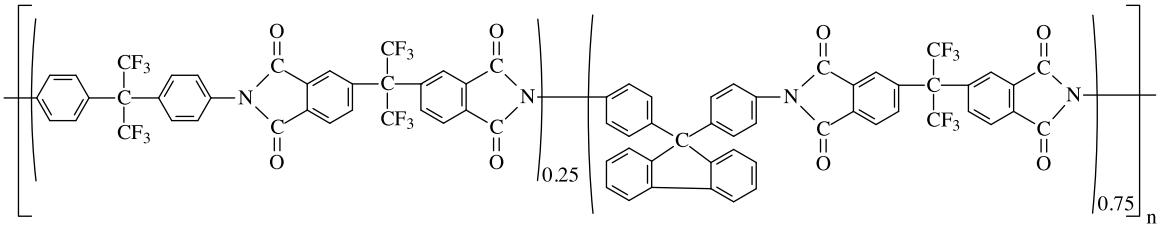
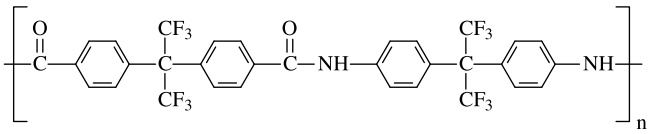


PI



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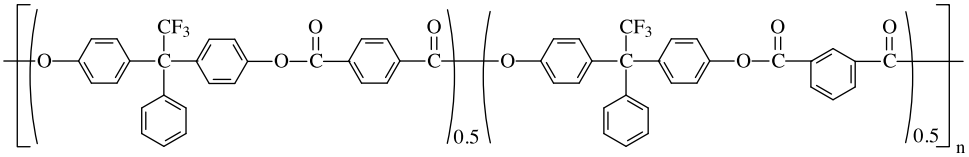

PAR

Scheme 1. Chemical structures of condensation polymers: polyimide (PI), polyaramide (PA) and polyarylate (PAR).

property of PVP (*co*)polymers can be used upon the optical fiber coatings fabrication.

This paper presents the approach for copolymers synthesis by *in situ* free radical polymerization of *N*-vinyl-2-pyrrolidone (N-VP) containing dissolved condensation polymers and their application for optical fiber coatings production. Such copolymers should have good adhesion to fibers, relatively low costs and thermal stability greater than polyacrylates. They can also be used in the membrane's manufacture [15]. For comparison among the used condensation polymers there was not only PI tested but other aromatic condensation aromatic polymers, such as polyaramide (PA) and polyarylate (PAR), have been used as well.

The possibility to forming molecular composites of PVP and PI with tuned properties using polycondensation *in situ* method [20] is an additional reason to perform this study.

2. Experimental

2.1. Materials

4,4′-(Hexafluoroisopropylidene)diphthalic anhydride, 9,9-bis (4′-aminophenyl)fluorene, 4,4′-(hexafluoroisopropylidene)dianiline (98–99%, Sigma-Aldrich, Germany), 1,1-bis(4′-hydroxyphenyl)-1-phenyl-2,2,2-trifluoroethane, tere-, isophthaloyl chloride, N-VP, N-MP, *m*-cresol, 1-chloronaphtalene, diethyl ether and azobisisobutyronitrile (AIBN) were purified by common procedures (vacuum distillation, vacuum sublimation, crystallization). 2,2-Bis(4′-carboxyphenyl)hexafluoropropane dichloride was synthesized by common method. Constants (m.p., b.p.) of the compounds correspond with literature data.

2.2. Condensation polymers synthesis

PI based on 4,4′-(hexafluoroisopropylidene)diphthalic anhydride (1.00 mol), 9,9-bis(4′-aminophenyl)fluorene (0.75 mol) and 4,4′-(hexafluoroisopropylidene)dianiline (0.25 mol) was synthesized by one-step polycyclization in *m*-cresol medium [21]. The reaction proceeds at 180 °C for 5 h under Ar. PI was isolated by the precipitation into methanol excess, washed and dried in vacuo at 70–150 °C. h_{inh} = 0.72 dL/g (DMF)

PA was prepared by low temperature polycondensation of 2,2-bis(4′-carboxyphenyl)hexafluoropropane dichloride (1.00 mol)

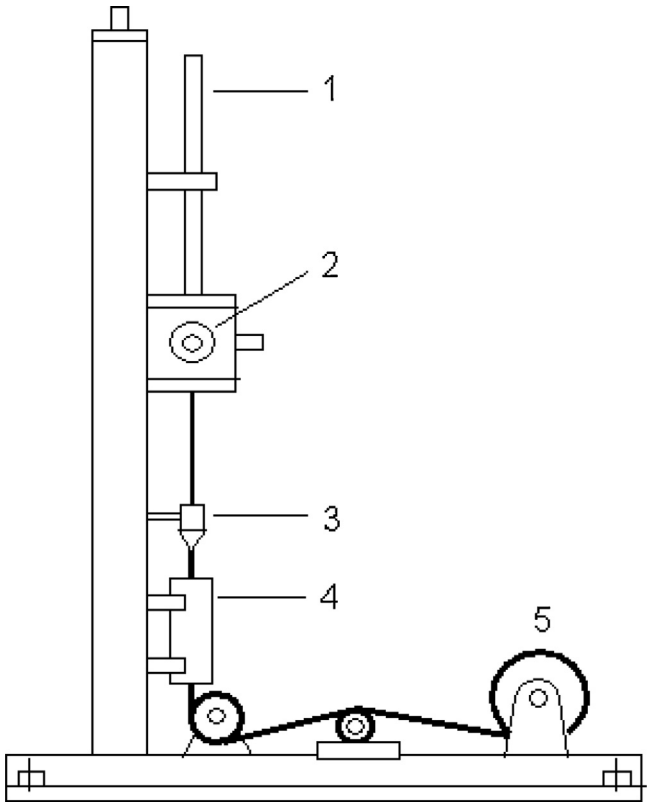

Fig. 1. Fiber drawing that includes a conventional coating process (1–preform, 2, 4–furnace, 3–die, 5–capstan).