Mechanical behavior of silica optical fibers coated with low index, low surface energy perfluorinated polymer

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ABSTRACT

Two formulations based on perfluorinated polymer were prepared for use as UV-curable optical cladding for silica fibers. In the first formulation an adhesion promoting agent based on fluoroacrylate resin was synthesized and mixed with the experimental product Defensa 7702‡ in order to promote wetting and chemical adhesion to the silica fibers. In the second formulation, wetting and physical adhesion between the liquid coating and the silica fibers were achieved by increasing the viscosity of the starting coating by addition of unsaturated perfluorinated polymer into Defensa. Both formulations were used as primary coatings on dual coated silica optical fibers. The mechanical behavior of the formulations was characterized by the strip test, the pull-out test and zero stress aging in 90°C pH 7 buffer. The results show that both formulations exhibit better wetting-adhesion characteristics than unmodified starting coating and that the strength degradation during zero-stress aging was lower for the fiber coated with the formulation of higher viscosity.

Keywords: optical fibers, coatings, strength, fluoropolymers, perfluoroalkylsilane (FAS), adhesion, aging.

1. INTRODUCTION

Single mode silica fibers, with a core doped with rare earth elements, could potentially be used as laser fibers but require special optical cladding. This cladding should have a low refractive index, low modulus of elasticity and should adhere well to the silica surface. Excellent adhesion and a refractive index of <1.39 are required for adequate fiber laser performance. Polydimethylsiloxane-based commercially available UV-curable formulations are known to exhibit adequate wetting and adhesion characteristics on silica surfaces; however, their refractive index after curing is above 1.40. A lower refractive index is only exhibited by UV-curable formulations which are based on the perfluoroalkyl acrylates. Although there are several sources of the perfluoroalkyl acrylate monomers and oligomers, there is no commercially available UV-curable coating which would satisfy the above requirements. After searching for a suitable coating to be used as optical cladding for erbium doped silica fibers, we selected Defensa 7702,‡ an experimental product based on perfluoroalkyl acrylates whose characteristics are shown in Table 1.

Adhesion and wetting are crucial issues when a UV-curable coating has to be applied to the surface of optical fibers. The rate of wetting is critical due to the short contact time between coating application and curing.

Table 1. Properties of Defensa 7702 coating material.

Before Curing	
Viscosity (25°C)	2.26 Pa.s
Refractive index, n_D^{25}	1.364
Density (25°C)	1500 kg.m^{-3}
Surface Tension	18.4 mN.m^{-1}

After Curing	
Refractive index, n_D^{25}	1.383
Tensile Strength	5.7 MPa
Elongation at Break	48.7 %
Young's Modulus	94 MPa
Shore hardness	A78
Surface Energy	13.9 mJ.m^{-1}

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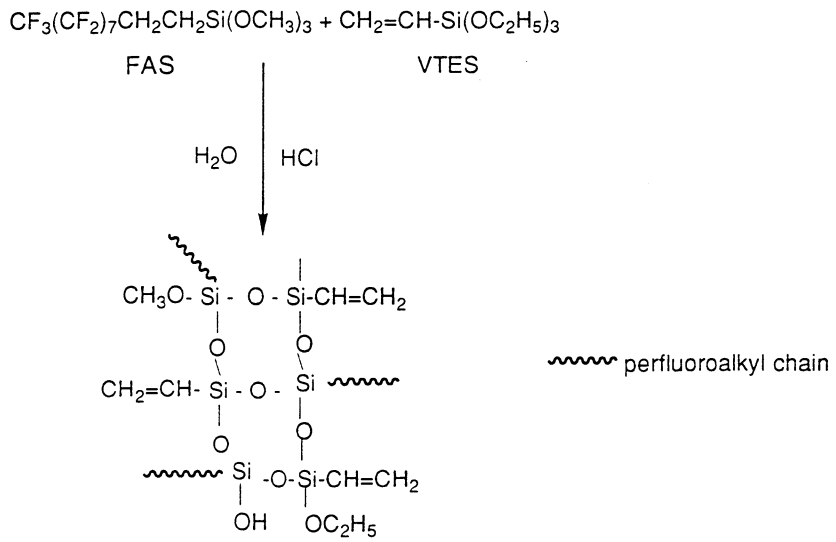

Fig. 1. Precondensation scheme of FAS and VTES into viscous, soluble oligomer functionalized with vinyl groups.

Failure to wet the surface will cause defects in the cured coatings known as fish eyes, crawling and orange peels, and will cause poor adhesion. Adhesion will result when the liquid coating and substrate surface are brought together into intimate intermolecular contact. The adhesion is then a consequence of the forces of intermolecular attraction between those surfaces and include chemical bonding (ionic, covalent) and physical bonding based on van der Waals forces or actual anchoring of the coating. The adhesion of a coating to a substrate depends upon achieving this contact by a wetting mechanism. Factors governing the rate of wetting include:

- viscosity of the liquid coating,
- surface roughness of the substrate,
- surface energy of the liquid coating (surface tension),
- surface pre-treatment of the substrate.

When the surface tension of the liquid is much lower than the surface energy of the substrate one can expect good wetting. The smooth, non porous, high energy surface of silica fiber is a substrate that is easy to wet but it is difficult to achieve good adhesion. Theoretically, the low surface tension coatings based on fluoroalkyl acrylates should easily wet the silica fibers, but in practice this is not always the case.

Experiments with Defensa showed that its viscosity is too low, even at 0°C, to allow sufficient wetting of and adhesion to the thin, elliptical section silica fiber used for erbium doped lasers. Improved wetting can be accomplished by reinforcing the intermolecular attractions either by increasing the van de Waals forces or chemical interactions. The first route can be accomplished by addition of a high viscosity polymer into the formulation, whereas the second approach requires addition of an adhesion promoting agent. This paper describes the use of both these methods in the preparation of two formulations based on Defensa. The mechanical behavior of silica fibers using these formulations as a primary coating is characterized.

2. SYNTHESIS AND CHEMISTRY OF THE MATERIALS

2.1. Synthesis of the adhesion promoting agent and preparation of formulation 1

One major disadvantage of the perfluoroalkyl acrylate and methacrylate monomers and oligomers is their incompatibility with non fluorinated organic compounds. This is why none of the available silane coupling agents known to promote adhesion in UV-curable formulations could be dissolved in Defensa. Therefore we synthesized a promoting agent which can be compatible with any perfluorinated compound. The synthesis involved the condensation of the perfluoroalkyl silane (FAS), which was heptadecafluorodecyltrimethoxysilane of formula $CF_3(CF_2)_7CH_2CH_2Si(OCH_3)_3$, with the vinyltriethoxysilane according to the scheme shown in Fig. 1. Typically,

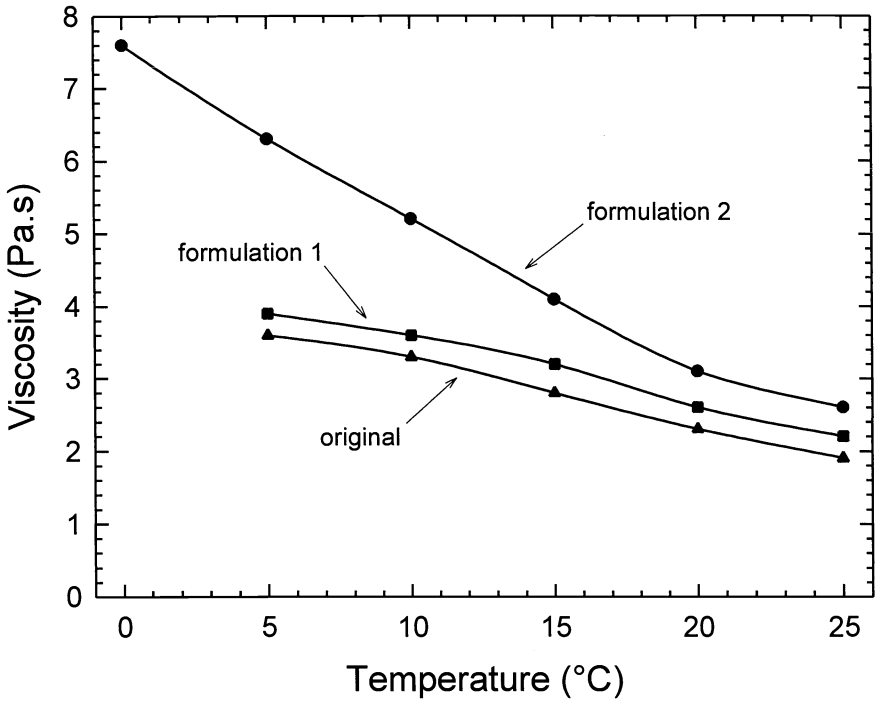

Fig. 2. Temperature dependence of viscosity for the original Defensa and formulations 1 and 2.

FAS and VTES were mixed in the volume ratio 2:1. Anhydrous ethanol, in volume equal to that of FAS+VTES, was used as solvent. 2N HCl was used as the source of water and acid catalyst and the water to alkoxy groups ratio of combined FAS and VTES was 1:2. After 24 hours mixing, the ethanol was removed and a viscous clear liquid was obtained. The liquid was chemically dried to remove traces of water and the liquid which constitutes the FAS-VTES oligomer was filtered off through a 0.2 μm syringe filter.

The FAS-VTES oligomer was readily soluble in Defensa and formulation 1 was prepared by adding 10 wt% of the oligomer to the Defensa. The viscosity of formulation 1, measured a few days after mixing, proved to be slightly higher than the original Defensa (Fig. 2). The vinyl group of the copolymer can readily be cured with the unsaturated bonds in the Defensa resulting in covalent linkage between the cured Defensa and the adhesion promoter molecule, whereas the silanol and alkoxysilyl groups of the promoter should interact with the silica surface forming either hydrogen or covalent bonding.

2.2. Synthesis of perfluorinated oligomer and preparation of formulation 2

The primary components of UV-curable coatings are multifunctional monomers, reactive oligomers and photoinitiators. However, it is possible to include resins and polymers containing no unsaturated bonds. Incorporating the unsaturated oligomer into the liquid resin should result in considerable increase of the system viscosity, especially when the introduced polymer is a high molecular weight solid. Since saturated materials are polymerized before incorporation into UV coatings, they would not contribute to coating shrinkage during cure, so the shrinkage of the system should be reduced. Shrinkage of UV coatings occurs because lower density carbon-carbon double bonds are quickly replaced by single bonds during UV cure. Levels of shrinkage from 10% to 30% are usually observed when monomers are polymerized. Shrinkage builds up stresses in the coating that result in deformation of flexible substrates and loss of adhesion to rigid substrates. Thus, introducing the saturated resin into the UV-curable formulation will result in an increase in the formulation viscosity (which should enhance wetting and adhesion) and a decrease in the shrinkage of the cured coating.

The other phenomenon worth considering is the behavior of saturated resins exposed to UV radiation. Some saturated resins undergo chain scission when exposed to ultraviolet light while others crosslink. However, both types of saturated resins should crosslink with the unsaturated components of the UV formulations during cure. Generally, saturated resins containing chromophoric groups absorb UV light above 200 nm, while those that do not absorb below 200 nm. As PMMA exhibits significant UV absorption around 250 nm, one can expect that any perfluoroalkyl methacrylate-based polymer would also absorb UV in a similar range.

The increase in viscosity of Defensa could be achieved by addition of a high viscosity oligomer which should, of course, be soluble in the original formulation. To prepare such an oligomer, we selected 1,1-dihydroperfluorooctyl methacrylate (DHPFOMA) monomer, $C_7F_{15}CH_2OCOC(CH_3)=CH_2$, of refractive index 1.332 and which provides a 60.9% fluorine contribution to the molecular weight. DHPFOMA was purified by distillation under reduced pressure and polymerized in the presence of a photoinitiator (2,2-dimethoxy-2-phenyl-acetophenone) under UV-irradiation. The resulting transparent solid homopolymer of DHPFOMA was dissolved in Defensa in the amount of 7 wt%. The effect of polymer addition on the formulation viscosity is shown in Fig. 2. The resulting formulation 2 was used as a primary buffer coating in the preparation of dual coated silica fibers.

2.2. Fiber drawing

Silica fibers were drawn from a fire polished 20 mm diameter Suprasil† rod. The silica core diameter was 125 μm and the fiber diameter coated with Defensa-based primary buffer was 175 μm. DeSotech 950044‡ secondary coating was used as the secondary buffer; the overall diameter of the dual-coated fiber was 240 μm. The fibers where formulations 1 and 2 were used as the primary buffers are denoted as fibers 1 and 2, respectively. It transpired that the viscosity of formulation 1 was still too low so that the coating did not correctly wet the fiber and so the secondary coating was not concentric with the fiber.

2.3. Fiber Characterization

2.3.1. Optical Measurements

Optical measurements to determine the numerical aperture and optical loss were not possible for fiber 1, due to the non-concentricity of the coating. The numerical aperture and optical loss were found for the fiber 2 and are shown in Figs. 3 and 4, respectively.

2.3.2. Mechanical Measurements

The adhesion of the coatings was characterized using the pullout test.[1] The strip test[2] was also used for fiber 2, but not for fiber 1 due to the non-concentric coating on this fiber. The results of the adhesion tests are shown in Table 2. The fibers were aged under zero stress in 90°C pH 7 buffer. The post-aging residual strength was measured using the two-point bending technique described elsewhere.[3] The fibers were broken at room temperature at a loading rate of 1000 $\mu m.s^{-1}$ in the same environment in which they were aged in order to avoid concerns of equilibrating the fiber with the test environment. Fig. 5 shows the residual strength of fibers 1 and 2 after aging for various times in 90°C pH 7 buffer solution.

Table 2. Pullout and strip force measurements.

	Pullout Force (N)	**Strip Force (N)**
Fiber 1	10.3 ± 1, max. 12.6	–
Fiber 2	8.6 ± 0.6, max. 11.8	1.38 ± 0.02, max. 1.4

† Heraeus Amersil Inc., Buford, Georgia.
‡ DSM Desotech Inc., Elgin, Illinois.

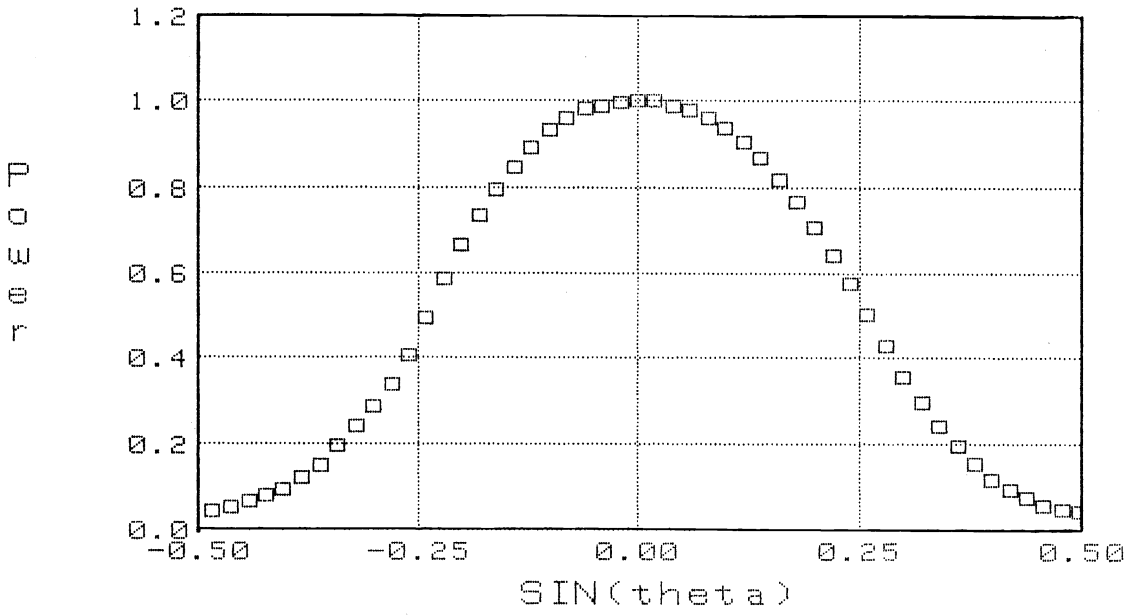

Fig. 3. Numerical aperture scan of fiber 2 using 830 nm LED light source indicating NA = 0.47 and the relative power detected from –30 to +30° for 1 m fiber sample.

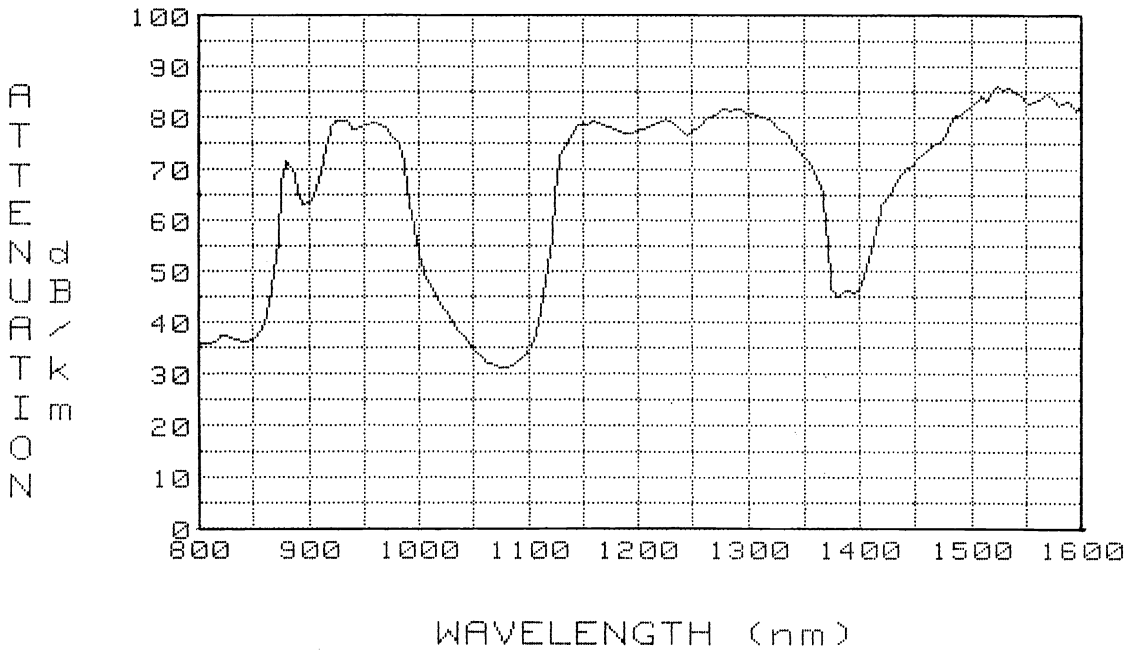

Fig. 4. Spectral attenuation of fiber 2.

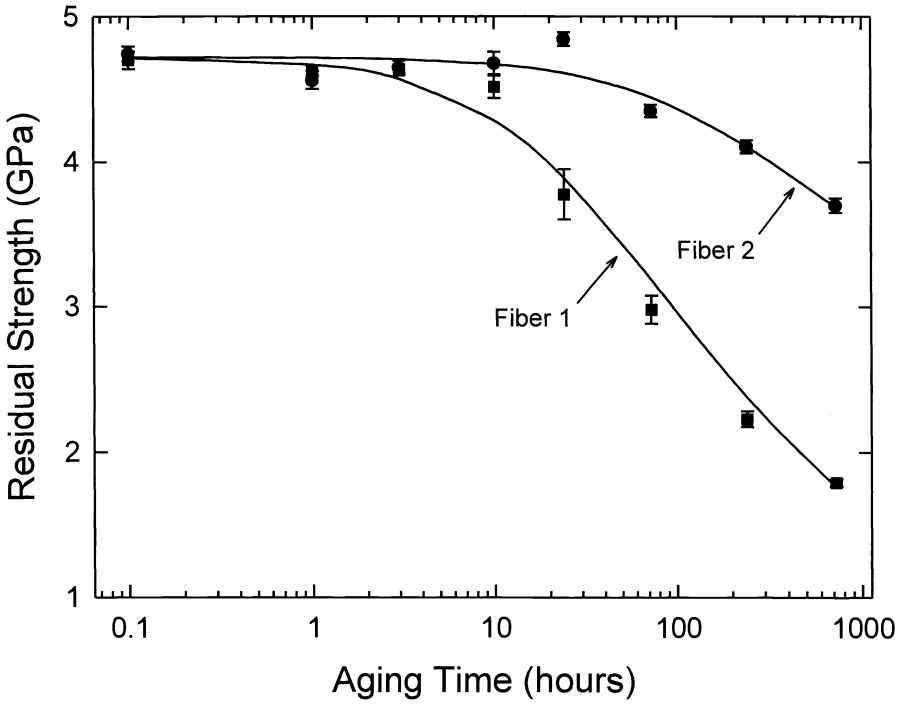

Fig. 5. Residual strength as a function of aging time in 90°C, pH 7 buffer solution.

3. RESULTS AND DISCUSSION

The pullout test results showed that the adhesion of the primary coating of fiber 1 is a little higher than that for the fiber 2, which means that there is chemical adhesion due to the action of the FAS-VTES copolymer, which contributes to the total adhesion of the primary buffer to the silica surface. The zero stress aging results, however, revealed that fiber 2 retains its strength longer than fiber 1, and this higher durability must be related to the difference between formulations 1 and 2. One difference is the higher concentration of the unsaturated bonds, due to addition of the FAS-VTES oligomer, which ultimately upon curing should result in a higher crosslink density in formulation 1. On the other hand, an increase in crosslink density is also expected for formulation 2 due to the effect of UV radiation on DHPFOMA homopolymer. Its is probable that upon curing, formulation 2 has a higher crosslink density than formulation 1. The onset of strength loss under zero stress aging is thought to be initiated by adhesion loss between the coating and the glass.[4] The higher crosslink density may slow the overall hydrolysis rate of the coating.

It is well known that so-called "high polymers" exhibit much better general protective properties than those of low molecular weight. Unfortunately, high polymers are too viscous to be used in UV-curable formulations on a large scale. The addition of the solid saturated polymer into Defensa acts as if to increase the molecular weight of the fluorocarbon polymer backbone while decreasing its reactivity by lowering the concentration of reactive groups. As a result we can expect an increase of van der Waals interactions between formulation 2 and the silica surface, accompanied by a lower shrinkage than pure Defensa. These factors could explain the improved durability of fiber 2 under hydrolyzing conditions.

It is noted that the refractive index of cured formulation 2 was below 1.39 and resulted in the fiber NA = 0.47. Also, the optical loss for fiber 2 was low for a 125 μm core, polymer clad waveguide, and formulation 2 used as optical cladding greatly contributed to this performance. It is also noted that both formulations are low surface energy (low surface tension) materials (<20 $mN.m^{-1}$) and as such should wet and adhere well to the high

energy surface of the silica fiber in order to minimize the total energy of the system, although in practice this is not always the case.

Low surface energy fluorocarbon compounds are known to exhibit water repellent properties which means that their water absorption is low. We did not measure the final surface tension of the formulations 1 and 2 but it is improbable that these values differ much from the surface tension of Defensa, namely 18.4 $mN.m^{-1}$ (Table 1). However, one can expect that the water repellent properties of formulation 1 should be weakened by the presence of hydrophilic silicate particles and alkoxy or hydroxy silyl groups. As a consequence the water penetration through the cured formulations might be quicker for fiber 1 than for fiber 2 during the aging process. This phenomenon may also explain the difference in the observed residual strength behavior from Fig. 5.

4. REFERENCES

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