Organically modified silicate coatings for optical fibers

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ABSTRACT

Three kinds of UV-curable organically modified silicates have been prepared to be used as protective coatings for optical fibers. The synthesis involves the reaction of the thiol group of 3-mercaptopropyltrimethoxysilane with a C=C bond in one of the acrylic groups of three commercially available aliphatic triacrylates. The methoxysilyl groups of the synthesized diacrylate methoxysilanes were subjected to hydrolysis and condensation to form Si–O–Si units. Transparent, viscous, solvent-free resins were obtained that hardened in seconds when exposed to UV radiation. The coating derived from the reaction with glycerol propoxy triacrylate (GPTA) proved to adhere the best of the three to both plastic and glass substrates. It was then tested as a protective coating for silica fibers. Reliability tests were carried out including bending strength and fatigue tests at pH 7 and 10. The results show improved water resistance of the coated fiber in neutral conditions.

2. INTRODUCTION

Present formulations for UV-curable coatings applied to protect optical fibers consist of several components. Generally, the formulations include (1) a high viscosity reactive oligomer (epoxy acrylate, urethane acrylate, polysiloxane acrylate), (2) a reactive diluent (mono or multiacrylate monomers), (3) a photoinitiator, and (4) an adhesion promoting agent. The final properties of the cured coating such as hardness, flexibility, toughness, abrasion, optical transparency, adhesion and glass transition (T_g) are determined directly by the chemistry and composition of the liquid formulation. There are several commercially available UV-curable materials to satisfy a variety of applications. All of these materials are highly toxic in the liquid state. We are therefore investigating formulations which contain no volatile components in order to reduce the hazards related to their removal.

Ideally, a coating formulation would be one component, nonvolatile, highly reactive, sufficiently viscous, with good wetting to the substrate. In addition, the resulting coating should have the desired mechanical, optical and physical properties after curing under dynamic conditions (in a high speed fiber drawing operation). We would like to be able to tailor these properties simply by controlling the synthesis parameters of this one component system. A promising class of materials for this kind of "ideal" coating is inorganic-organic hybrid materials with organics chemically linked to inorganics. In particular, organically modified silicates were investigated.

In the search for new UV curable materials combining both good optical and protective properties, we synthesized three different types of diacryloalkoxysilanes. Upon hydrolysis and partial condensation of alkoxysilyl groups, they formed viscous, one component UV-curable liquids containing photoinitiator. The acrylosilicate coatings were synthesized by the method used previously by Wolter *et al.*[1] in which 3-mercaptopropyltrimethoxysilane was coupled via its S–H group to the C=C bond of the acrylic group of aliphatic triacrylate. Three commercially available triacrylates commonly used as reactive diluents in UV curing technology were

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used. They were glyceryl propoxy triacrylate (GPTA), trimethylolpropane triacrylate (TMPTA) and pentaerythritol triacrylate (PETA). The GPTA derived acrylosilicate was applied on silica fibers during a fiber drawing process. This paper discusses the properties of the UV curable acrylosilicate coatings, as well as the results of fatigue and aging testing of the coated fibers.

3. SYNTHESIS AND CHEMISTRY OF THE MATERIALS

The chemical structures of the triacrylates are shown in Fig. 1. Samples of all three triacrylates were supplied by Radcure Specialties, Inc., Louisville, KY. Diacrylate trimethoxysilanes were synthesized using 3-mercaptopropyltrimethoxysilane. This was coupled to the triacrylate by a Micheal addition, under basic conditions, as shown in Fig. 2, using GPTA as an example.

Typically, 0.1 moles of triacrylate were dissolved in 75 ml of ethyl acetate with a small amount of basic catalyst. To this mixture, 0.1 moles of 3-mercaptopropyltrimethoxysilane was added slowly while mixing under nitrogen. Mixing was continued for 30 minutes and then 2.5 ml of 5N HCl were added to hydrolyze the methoxysilyl groups to Si–OH. Then, the mixture was stirred at room temperature for 24 hours and stored in darkness for another 48 hours. During this time the silanol groups condensed to form Si–O–Si units. The next step was evaporation of all volatile components (water, solvent and alcohol) by attaching a rotational evaporator. The viscous transparent liquid was no longer diacrylomethoxysilane but diacrylosilicate resin. This resin will now be referred to as the "DAS" material. The DAS resin containing photoinitiator cured when exposed to UV radiation.

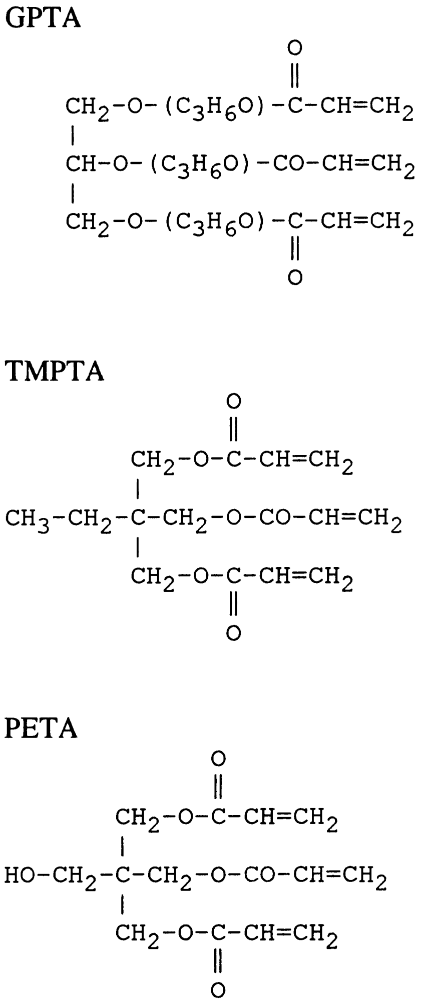

Fig. 1: Chemical structures of GPTA, TMPTA and PETA triacrylates.

4. PROPERTIES OF THE DIACRYLATE SILICATES (DAS)

The three types of diacrylate-silicate resins varied slightly in viscosities and refractive indices. The refractive indices found for the resins before curing were: GPTA - 1.475, TMPTA - 1.501 and PETA - 1.518.

Several tests of curing under static conditions were carried out using 2,2-dimethoxy-2-phenylacetophenone (0.2 wt%) as photoinitiator and UV intensities of 2000 mW.cm^{-2} on both plastic and glass plates.

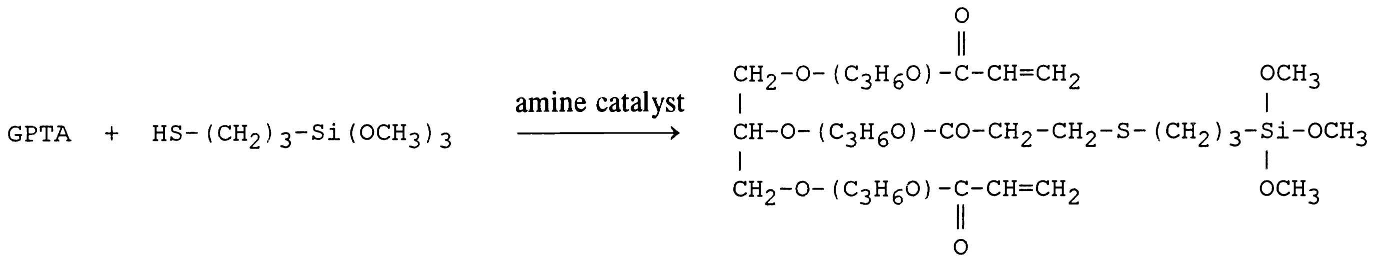

Fig. 2: Reaction scheme for the synthesis of diacrylate trimethoxysilane

Table I: Refractive index, n_D, elastic modulus, E, and strain to failure, ε_f, for GPTA-derived DAs (I and II) and GPTA cured films.

	I	II	GPTA
n_D	1.475	1.473	1.485
E	8.3 MPa	60.7 MPa	215 MPa
ε_f	41%	32%	10%

All three types of acrylosilicate coating adhered well to the substrates after curing. The 0.2 mm films were tack-free indicating that no oxygen inhibition had taken place even though the samples were cured in air. The reason for this is probably the presence of amine radicals from the amine-type catalyst in the formulation which is known to prevent oxygen inhibition by consuming oxygen radicals while accelerating the curing process.

The best adhesion was found for GPTA derived coating. Curing time was the shortest for this coating at about 10 s, compared to longer than 15 s for TMPTA and PETA derived coatings. Considering that GPTA is a propoxylated acrylate ester of glycerol, it is expected that oxyalkylation, especially ethoxylation or propoxylation of acrylates, occurs more completely during photopolymerization than the parent acrylates.[2] Moreover, propoxylation improves physical properties of the acrylates (lower toxicity) and favorably affects their coating properties such as adhesion, flexibility and solvent resistance. More complete curing for GPTA resin can be explained by the longer spacer arms between reactive double bonds, which makes these double bonds more accessible.

Some properties of the 0.40 mm thick films were measured for GPTA-derived DAS with condensation times prior to the evaporation of solvent equal to one day (I) and to three days (II) and compared to the cured GPTA (Table I). Longer condensation times resulted in increases of elastic modulus and strain. This means that controlling the extent of condensation, *i.e.* conversion of Si–OH groups to Si–O–Si units, affects the mechanical properties of the coating. Further control of these properties is possible by increasing the concentration of the Si–OH species through cocondensation of methoxysilyl groups of the DAS with silica precursors like tetraethylsilane (TEOS).

For applications on fiber, we selected GPTA-derived diacrylosilicate resin. Silica fibers were drawn at 1950°C. An open cup with a silicone tip was used as the coating applicator. The coating cup was cooled to 0°C to achieve the desired viscosity. The coating was not applied under pressure because too little coating material was available. For this reason the coating was not always applied uniformly along the length of the fiber. There is therefore a possibility that the coating adhesion varied along the length. The fiber diameter was 125 μm and the outer coating diameter was approximately 202 μm. For convenience, the GPTA-derived diacrylosilicate (DAS) coating will be referred to as the DAS coating and the fiber coated in it as the DAS fiber.

5. MECHANICAL TESTING

The strength and fatigue behavior of the fiber with the DAS fiber was characterized using uniaxial tension and two-point bending. Zero-stress aging experiments were also performed. The results have been compared with data from similar experiments performed on another fiber for reference purposes. This reference fiber had the same diameter and was coated with a commercially available single UV-curable acrylate coating. The comparison is made only to obtain a rough idea of how some aspects of the behavior of our material compares with those of a typical commercially available material. The reader should not make conclusions about the comparative merits of the two coatings since only some of their properties are investigated.

5.1 Strength

The strength of the DAS fiber was measured using uniaxial tension and two-point bending methods. Twenty specimens were tested using each technique. Fig. 3 shows the Weibull distribution of the strengths obtained from the tensile test for both the DAS and reference fibers. Samples with a gauge length of 300 mm were broken in air at a constant crosshead speed of 30 mm.min^{-1} (corresponding to a loading rate of 120 MPa.s^{-1}); the relative humidity during the test was about 30%. The average strength was 5.21±0.36 GPa for the DAS fiber and 4.80±0.08 GPa for the reference; the Weibull moduli, m, were 11 and 68 respectively. Although the mean strength of the DAS fiber is slightly higher than the reference fiber strength (but consistent with strength values commonly obtained when freshly drawn pristine silica fiber is tested under similar conditions), bimodal behavior was observed. The low strength mode is probably due to particulate contamination in the coating which was not filtered prior to application. It may also be due to the non uniformity of the coating and its adhesion. By filtering the coating and applying it uniformly under pressure, the occurrence of weak defects should be eliminated. The high strength mode is substantially stronger than the reference fiber and has a similar Weibull modulus, m. The strain to failure in liquid nitrogen, *i.e.* under inert conditions, measured in two-point bending is 17.83±0.24% (m = 47) for the reference fiber and 17.29±0.38% (m = 28) for the DAS fiber which are approximately the same (the failure stress can not be calculated since the elastic modulus at such high strain is unknown). Therefore, the improved (high mode) strength of the DAS fiber measured in ambient is not because it is intrinsically stronger, but results from an enhanced resistance to the fatigue that occurs during the tests in ambient.

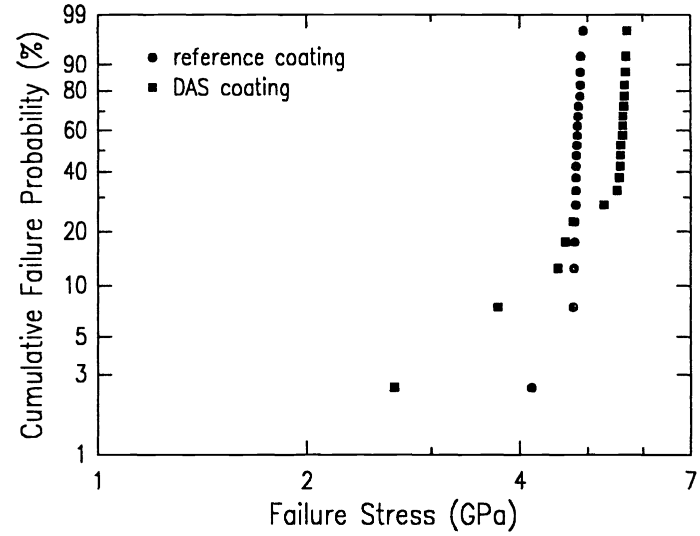

Fig. 3 Weibull distribution of the strengths of the DAS coated fiber (■) and the reference fiber (●) measured in uniaxial tension at 120 MPa.s^{-1} in ambient. The gage length was 300 mm.

Weak defects were detected only by testing relatively long lengths of fiber. The scatter in the results was much smaller when using the two-point bending technique in which the effective tested length is a few tens of microns.[3] In particular, the average strength measured for 20 specimens in two-point bending at a constant stress rate of 60 MPa.s^{-1} was 5.60±0.04 GPa with a value of m = 60 for the DAS fiber and 4.85±0.04 GPa, m = 58 for the reference. The environment in this case was pH 7 buffer solution at room temperature.

5.2 Static Fatigue

Static fatigue experiments were performed using the two-point bending technique described by Matthewson *et al.*.[4] The fiber specimens are bent double inside a precision diameter glass tube which is subsequently immersed in the test environment. The diameter of the tube determines the constant applied strain and the specimen failures are detected acoustically. In this case, at least 20 samples were loaded in each tube; the testing was performed under accelerated conditions of 90°C in pH 7 buffer solution.

The DAS fiber was found to exhibit unusually large scatter in the time of failure and this was again due to bimodal behavior. Fig. 4 shows the static fatigue results for both the DAS and reference fibers; the short and long times to failure modes have been analyzed separately. Considering the long lifetime mode, the DAS fiber exhibits substantially longer lifetimes than the reference fiber both before and after the fatigue "knee" with a maximum lifetime ratio of ~50 before the knee and ~12 after the knee. The fatigue parameter, n, measured from the slope of the line fitted to the data in the log/log plot in Fig. 4, was approximately 18.5 before the knee (compared to the generally reported value of ~20), and about 0.75 after the knee. The short time to failure mode has lifetimes comparable to the reference fiber and may be a result of the non uniform coating and its adhesion.

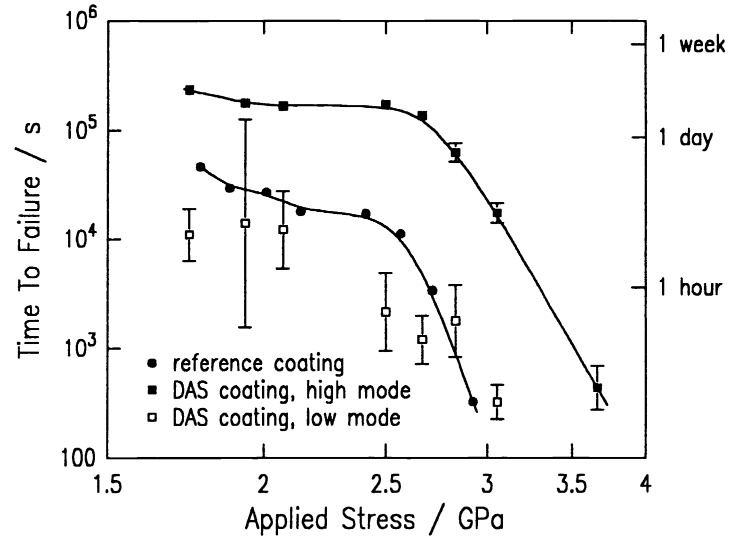

Fig. 4. Static fatigue of DAS fiber (■ - high failure time mode, □ - low failure time mode) and the reference fiber (●) in 90°C pH 7 buffer solution.

The reasons for the general improvement in both the strength and fatigue of the DAS fiber are not clear. The two fibers have a similar inert (liquid nitrogen) strength so that the improved ambient strength and fatigue behavior of the DAS fiber is because the DAS coating slows the fatigue processes. This could be due to the different chemical nature of the two coatings. Our observations could be explained if the DAS coating produced a lower pH at the fiber surface or reduced the water activity there. Alternatively, the DAS coating is expected to have good adhesion to the fiber which might partially passivate the fiber surface.[5]

It should be mentioned that it has been found that adding silica particles to the polymer coating dramatically delays the onset of the fatigue knee.[6-9] The DAS coating contains siloxane bonds and it might be thought that it provides protection in an analogous fashion to the silica particles. However, this is unlikely since the silicon atoms in the coating are bonded to carbon and so are not readily hydrolyzed to form free dissolved silica (which is thought to be the active agent in coatings containing particles). Also, the silica particles were not found to affect the fatigue before the knee, only after the knee; this is in marked contrast to the results for the DAS coating presented here.

5.3 Zero-Stress Aging

Fig. 5 shows the residual strengths of the DAS fibers measured using two-point bending[3] at a constant stress rate of 60 MPa.s^{-1} after aging under zero stress at 90°C in pH 7 and pH 10 buffer solutions. Data for the reference fiber in pH 7 are also shown for comparison. Each point represents the average of 20 specimens and the error bars are a 95% confidence interval. The samples were tested in the same environment in which they had been aged; in the case of the unaged measurements, the samples were soaked in the test environment at room temperature for at least 48 hours in order to equilibrate the fiber surface with the environment.[10]

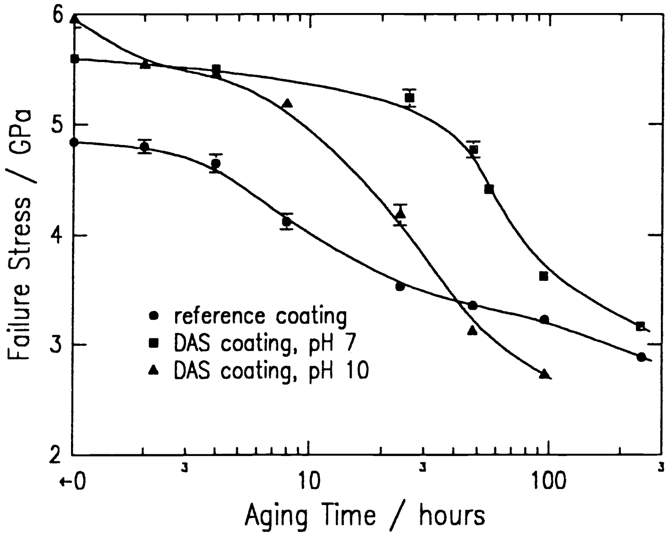

Fig. 5. Residual strength after aging in 90°C pH 7 buffer solution of the DAS coated fiber (■), the reference fiber (●) and the DAS fiber aged in 90°C pH 10 buffer solution (▲).

The DAS fibers exhibit higher post-aging residual strength than the reference. Again, as in the case of the static fatigue experiments, the improvements are more significant on a relatively short time scale and tend to be smaller for the longest aging time. This confirms that the beneficial action of this coating formulation tends to be exhausted at long experimental times, although the fiber retains a higher resistance to strength degradation than the reference throughout all the aging times and environments examined. Oddly, the unaged strength of the DAS fiber is higher in pH 10 than in pH 7. The cause of this is not known but it presumably must be due to how the coating interacts with the buffer solution. Normally the strength decreases with increasing pH.

6. CONCLUSIONS

We have produced a coating formulation for optical fibers that is a single component system without volatile solvents or diluents. The formulation is therefore expected to have much lower toxicity than typical commercial formulations that do have volatile components. In particular, our formulation is expected to have a reduced risk of allergic reaction in users of the coating.

The results show that our diacrylosilicate (DAS) coating formulation gives improved strength and aging characteristics when compared with one particular commercially available coating. The DAS coating is in effect a silane coupling agent owing to Si–O and possibly Si–OH units in its structure reinforcing the bonding between the surface of the silica fiber and the resin matrix. Silane coupling agents having a functional (methacryloxy, glycidyloxy, propylamino, *etc.*) group substituted alkoxysilane are known to promote adhesion between the silica substrates and the polymeric coating. It is also well known that the beneficial action of silane coupling agents depends on its amount and the adsorption behavior of its silyl species.[11] In our case, the DAS coating has these species distributed uniformly throughout the matrix. This uniformity must reflect in the nature of the fiber–coating interface. While good adhesion is thought to improve fatigue resistance, it must be noted that excessive adhesion is undesirable in some applications because the coating must be strippable for making splices and connections.

Organically modified silicates have already been reported to exhibit enhanced water resistance and stability against bases, when applied as coatings for some substrates.[12] In particular, resistance toward bases is unusual for silicate based materials. The aging results presented here confirm the water resistant behavior of our coating in comparison with one acrylate coating. The aim of our future work will be to determine the nature and mechanisms for such behavior, but it can already be concluded that our coating is especially promising for applications demanding higher performance in the protection of optical fibers. However, we recognize that fatigue and aging resistance are only two of many properties required for successful commercial use.

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