

Designing UV-Curable Materials for High-Temperature Optical Fiber Applications

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Coatings for optical fiber have traditionally had stringent requirements regarding resistance to a number of environmental factors including humidity and extremes of temperature. In addition to this, the cure speed demands of the fiber draw process have been among the most stringent in the UV&EB-curing industry, often with line speeds exceeding 1,500-2,000 meters per minute. Industry standards are in place for accelerated aging performance of fibers in telecommunications cable at 85°C, 85°C/85% relative humidity, and temperature cycling from -65 to 85°C.

Among the main properties being monitored in these aging tests is how resistant the fiber is to transmission or “attenuation” loss after aging. Stresses in the coatings due to thermal transitions, embrittlement or polymer chain scission due to thermo-oxidation, and/or volatilization of unbound components can lead to small-radius bends in the fiber or micro-bending, which can result in a less than ideal path for light transmission. In addition to this, certain polymeric materials used as protective coatings on the fiber or in the cable can generate hydrogen gas at higher temperatures, and if the hydrogen is allowed to migrate into the glass itself, can create areas that actually absorb the wavelengths of

light being transmitted. This process is known as darkening of the fiber. These and other factors make the design of rapidly curing coating materials a challenge for higher temperature applications.

New Application for Optical Fiber

A newer application for optical fiber is in the subterranean exploration of oil deposits. These are commonly referred to as “downhole” or “geophysical” applications. Since 1993, optical fiber has been used to sense conditions such as temperature, pressure, and chemical environment (pH) in oil wells at distances up to at least 30 kilometers. In the past, performing these measurements with standard electrical sensing technology has proven difficult, due to the need of regenerating the electrical power for these distances. There were an estimated 200 fiber optic P&T (pressure and temperature) gauges installed as of the early part of 2007.¹ Fiber optic sensors have improved the ability to “see” oil deposits from the surface and have enabled more efficient draining of the deposits once found.

In a downhole fiber application, the well temperatures can range from near ambient to between 90-250°C.² As

such, standard acrylate-coated optical fiber will not work for this entire service range, as much of the typical communications-grade fiber is rated at below 100°C operating temperature. The bare silica glass in downhole optical fibers is typically sealed with a carbon or hermetic coating, which is extremely resistant to hydrogen migration. On top of this hermetic coating, different chemistries are used which dramatically influence the final operating temperature of the fiber. Typically, acrylate coatings are used for applications from 85-150°C. From 150-200°C, silicones and fluorinated materials such as PFA (tetrafluoro-ethylene perfluoroalkyl-vinylether copolymer) are used, and for applications demanding 200-300°C, a polyimide coating is used.³⁻⁵

In these sensor applications, as well as in more typical telecommunication environments, the coating will preferably be strippable from the underlying

glass in order to splice, or connect, to other optical fibers or directly to instrumentation. The ease with which the stripping can be performed is a key factor in how practical they are to use in the field. Acrylate coatings typically can be stripped by mechanical methods either at ambient temperature or by using a heated tool. One issue with using the more heat resistant chemistries is the difficulty in removing them from the fiber. For instance, polyimide coatings often require a very strong acid in order to achieve removal. This is time consuming and involves special handling techniques.

As a class, acrylate coatings tend to outperform other chemistries for cost, ease of processing, cure speed, and commercial availability. Silicones and polyimides are typically slower curing, in many cases are solvent-borne, and often are incompatible with other components in the liquid form.

The purpose of this paper is to present some of the work conducted to maximize the operating temperature range of acrylate coatings in these types of applications. As part of this work, six outer or “secondary” coatings for optical fiber were tested for changes in weight loss, color, and tensile properties after aging at progressively higher temperatures. Secondly, a number of monomeric and oligomeric components were cured and heat aged to assess resistance to weight loss as baseline information for further coating development.

Experimental

Table 1 gives a breakdown of the different components present in the six optical fiber coatings tested. Nine different types of urethane acrylate (UA) oligomers, one bisphenol-A epoxy diacrylate oligomer, and various acrylate monomers are present in these

TABLE 1

Secondary coating chemistries

ID	SC-1	SC-2	SC-3	SC-4	SC-5	SC-6	Description
UA-1	•						Aliphatic Polyether No. 1
UA-2	•						Aliphatic Polyether No. 2
UA-3		•					Aliphatic Polyether / Polyester
UA-4				•			Isocyanate / Hydroxyethyl Acrylate
UA-5			•				Isocyanurate
UA-6			•				Aliphatic Polycarbonate
UA-7						•	Aliphatic Polyether No. 3
UA-8				•			Aliphatic Polyether No. 4
UA-9					•		Aliphatic Polyether No. 5
EA-1				•	•		Bisphenol-A Epoxy Diacrylate
AM-1	•						IBOA
AM-2	•	•	•	•			HDODA
AM-3				•			Propoxylated NPGDA
AM-4						•	DPGDA
PI	•	•	•	•	•	•	Alpha-hydroxy ketone photoinitiator
AO	•	•	•	•	•	•	Bis-phenolic antioxidant

FIGURE 1

Secondary coating weight loss after 24 hours at various temperatures

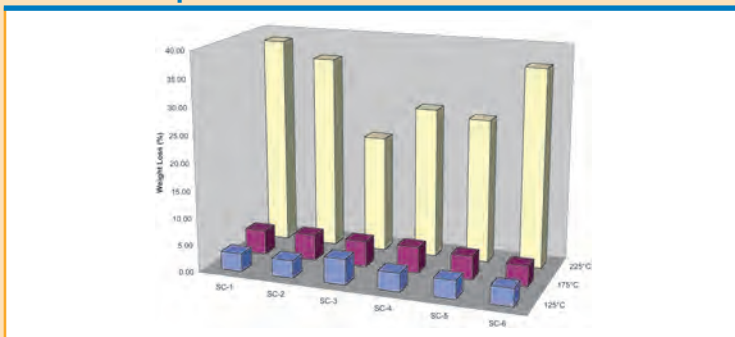


FIGURE 2

Secondary coating weight loss vs. exposure time at 225°C

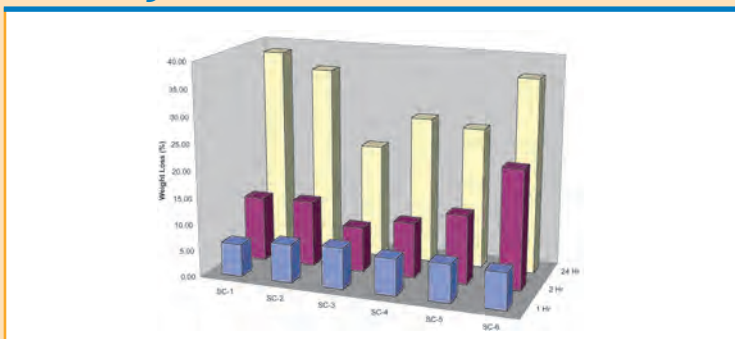
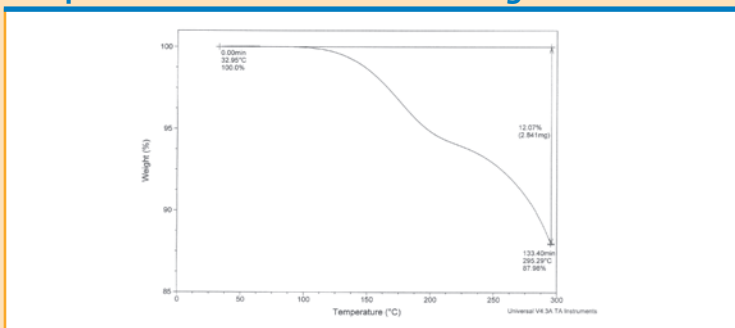


FIGURE 3

Typical TGA plot of a UV-cured film similar in composition to formulas SC-1 through SC-6



chemistries. An alpha-hydroxy ketone photoinitiator and a standard bisphenolic antioxidant are present in each of these as well. These coatings were cured using a Fusion UV 600 Watt/inch irradiator with an “H” bulb. The radiant energy density used to cure these coatings was 1,000 mJ/cm² as measured by an EIT radiometer. A 3-mil bird applicator was used to apply the films to the glass. The coating, glass and applicator were all allowed to equilibrate to 85°C before curing in order to minimize vitrification effects, as these coatings have glass transition temperatures well above room temperature, typically >75°C. After curing, the films were removed from the glass and allowed to equilibrate in a 23± 2°C/50±5%RH environment before subjecting them to aging at 125, 175 and 225°C heating in forced air ovens.

Results & Discussion

Figure 1 shows the weight loss of these coatings after 24 hours at 125, 175 and 225°C. Figure 2 shows weight loss after 1, 2 and 24 hours at 225°C. From this data, it is clear they lose a significant fraction of their weight at 225°C after only a short period of time. Exposure to this condition can serve as a quick screening process for relative heat resistance, but the data at 125 and 175°C may provide a better metric as to continuous service temperature. The SC-3 formula has a slightly higher weight loss than the other formulas at 125°C, but also contains the highest level of photoinitiator in the set, much of which is not actually bound into the crosslinked structure. At higher temperatures, the weight loss of SC-3 is significantly lower than that of the other formulas. The best weight loss resistance appears to be with the SC-3, 4 and 5 formulas.

Weight loss at elevated temperature is theorized to be due to both (a) the loss of volatile components in the film such as unreacted photoinitiators,

monomers, oligomers antioxidants, and other additives, and (b) the thermally-initiated scission of covalent bonds, producing lower molecular weight materials that eventually migrate to the surface of the film and volatilize. Figure 3 shows a typical TGA plot of a UV-cured film similar in composition to that of formulas SC-1 through SC-6. This plot was obtained by heating a cured film at a rate of 2°C/minute and measuring weight loss. Two distinct regions can be identified in this plot. At approximately 100-125°C the onset of weight loss occurs. The rate of weight loss becomes steady from approximately 150- 200°C before beginning to plateau. The onset of a second transition occurs at approximately 200°C and the weight loss rate again becomes steady from 250-275°C. The first transition is likely the volatilizing of unbound components, as the weight loss approaches a plateau value of 6%, which is similar to the weight of unreacted photoinitiator and other unbound additives in the system. The second transition is more likely due to that of thermal decomposition and becomes more enhanced at higher temperatures.

The color and tensile property changes were also evaluated for the SC-1 through SC-6 compositions. These results are shown in Figures 4 and 5. Measuring the Delta E of the aged films over a standard white background tile assesses the color change. All of the films will approach a similar Delta E value with enough exposure time at 225°C, but the rate of discoloration is clearly slower for the SC-3 than with the other formulas. Tensile property change with temperature was measured via the secant modulus at 2.5% strain measured at 85°C. This temperature was chosen to give an idea of whether the films were increasing in crosslink density. The modulus of these materials as a function of temperature will

FIGURE 4

Delta E values after aging at 225°C

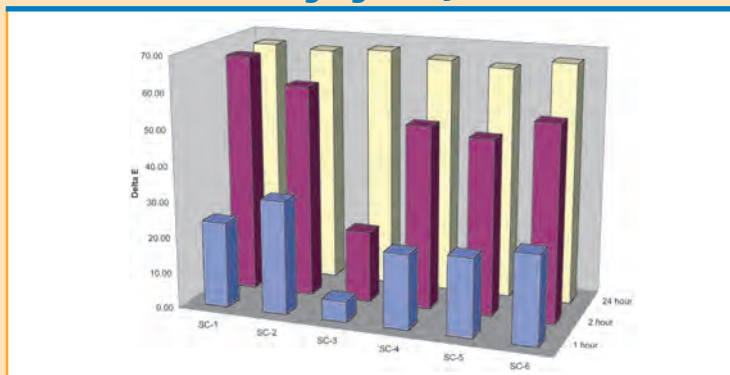


FIGURE 5

Change in 85°C modulus after exposure at 225°C

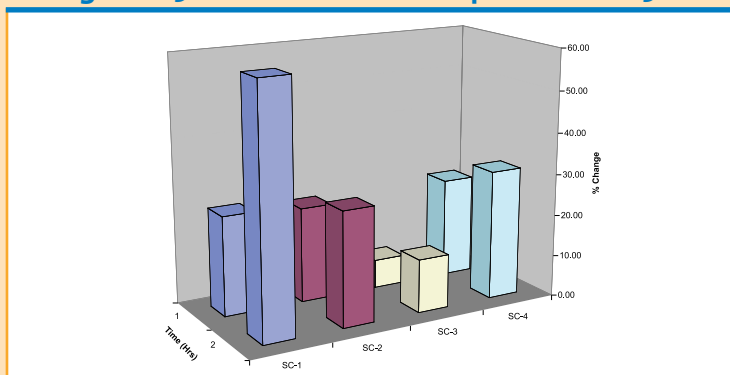


FIGURE 6

Weight loss of acrylate diluents after 24-hour heat exposure

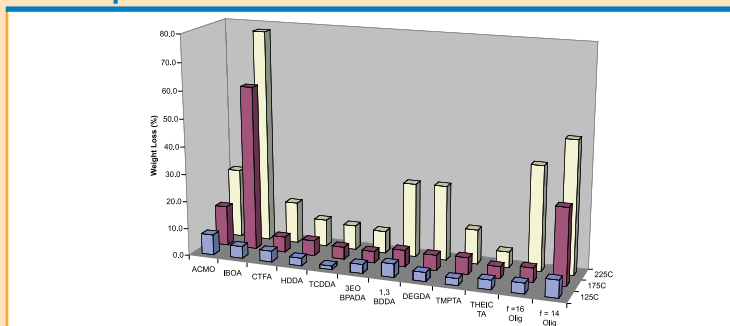


TABLE 2

Soft segment oligomers

Oligomer ID	Description
UA-6	Aliphatic Polycarbonate (Urethane Acrylate No.6)
UA-8	Aliphatic Polyether (Urethane Acrylate No. 8)
UA-11	Polyimide modified (Urethane Acrylate No. 11)
SA	Silicone Acrylate
SUA-1	Silicone Modified Urethane Acrylate No. 1
SUA-2	Silicone Modified Urethane Acrylate No. 2

decrease until they reach a plateau or equilibrium value. As the crosslink density increases, the modulus at this elevated temperature will also increase. Of the six formulas tested, only SC-1 through SC-4 had enough elongation to give a modulus value at 2.5% strain. The other two formulas were too brittle to be tested. As can be seen in Figure 5, the 85°C modulus, and thus crosslink density of the systems is increasing. The SC-3 formula appears to be most resistant to this change.

Investigations were further made into suitable faster-curing, high-temperature

materials for optical fiber applications. Various monomeric components were cured using a loading of 4% alpha hydroxy ketone photoinitiator and 1% bis-phenolic antioxidant. These films were prepared using a 1.5-mil wire-wound rod at 60°C on glass and 1,000 mJ/cm² of UV energy using the same curing lamp mentioned previously. The cured material was removed from the glass and heated at 125, 175 and 225°C to assess weight loss. Results are shown in Figure 6. Of the three-monofunctional diluents tested, the cyclic trimethylol-propane formal acrylate

(CTFA) appeared to have the best resistance to weight loss. It is very apparent the use of isobornyl acrylate (IBOA) results in dramatic weight loss at elevated temperatures. The weight loss resistance of the various difunctional monomers was very similar. Perhaps of most significance is the similarity in performance of hexanediol diacrylate (HDODA) to that of tricyclodecane-dimethanol diacrylate (TCDDA) and 3-mole ethoxylated bisphenol-A diacrylate (3EO BPADA). Of the higher-functional diluents, the tris-hydroxyethyl isocyanurate triacrylate (THEIC TA) was the best performing. Two highly functional (f = 14 and 16) polyester acrylates with low viscosity were also tested for this study. These are both based on highly branched backbones. Both of these polyesters gave higher weight loss at the 225°C exposure than most of the di- and tri-functional monomers and would not appear to be suitable as temperature-resistant diluents.

Various oligomer chemistries were also tested in a separate study. In this case, blends were made with acrylated oligomer, 4% photoinitiator and no antioxidant. Some glycidyl ether-based epoxy oligomers were also cured using a blend of 1.5% iodonium cationic photoinitiator and 0.7% ITX photosensitizer. These were all cured on glass at 85°C with a UV energy of 1,000 mJ/cm². A longer-term weight loss study was performed out to five days at 225°C. The descriptions of these experiments are listed in Tables 2 and 3 and the weight change data is plotted in Figures 7 and 8. This study looked at both softer segment oligomers to enhance flexibility and also harder segment oligomers, which traditionally give better heat resistance.

The best performing soft segment material was a silicone-modified urethane acrylate, SUA-1. This material retained nearly 80% of its

TABLE 3

Hard segment oligomers

Oligomer ID	Description
UA-5	Isocyanurate (Urethane Acrylate No. 5)
UA-10	Low MW Polyester / THEIC TA (Urethane Acrylate No. 10)
EA-1	Bisphenol A Epoxy Acrylate (Epoxy Acrylate No. 1)
EA-2	Acrylated Epoxy Novolac / TMPTA (Epoxy Acrylate No. 2)
BPF	Bisphenol F Epoxy
EN	Epoxy Novolac
EPN	Epoxy Phenol Novolac
MA-1	Melamine Acrylate No. 1 (Low MW)
MA-2	Melamine Acrylate No. 2 (Medium MW)

weight after five days exposure. The polycarbonate-based urethane acrylate had the most weight loss, followed by the polyether urethane UA-8 and the silicone-based materials SA and SUA-2. The polyimide-modified urethane acrylate UA-11 showed marginal improvement, but was still much less resistant than SUA-1.

The hard segment oligomers with the best heat resistance were based on the epoxy structures. The novolac epoxy as well as bis-phenol F, bis-phenol A epoxy acrylate, novolac epoxy acrylate, and phenol-modified epoxy novolac all retained 75% or greater of their weight after five days. After these, the most stable oligomer was a low-molecular weight polyester urethane acrylate blended with THEIC TA (UA-10). An isocyanurate-based urethane acrylate (UA-5) and the melamine acrylate oligomers lost approximately 45% of their weight after five days.

Based on this work, a final set of formulas (XN1, 2, 3, and 6) were made utilizing the SUA-1 oligomer in combination with harder segment oligomers, along with similar photo-initiator and antioxidant used in the previously tested secondary coatings. Films were cured and aged at 225°C vs. the SC-3 secondary coating. Results are listed in Figure 9. The incorporation of the heat resistant silicone urethane acrylate provided formulas that even after 24 hours had nearly 90% weight retention.

Conclusion

A number of acrylate-based secondary optical fiber coatings have been evaluated for property changes upon exposure to elevated temperatures. Of the materials tested, a coating consisting of specific types of urethane acrylate oligomers and hexanediol diacrylate diluent was the most resistant to weight loss, color change,

FIGURE 7

Soft segment oligomers—weight change at 225°C

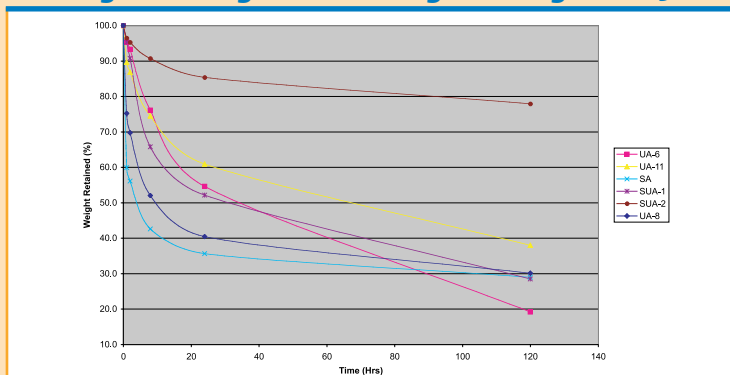


FIGURE 8

Hard segment oligomers—weight change at 225°C

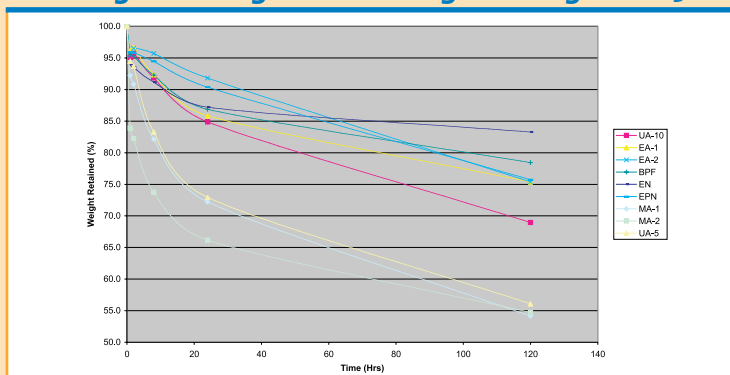
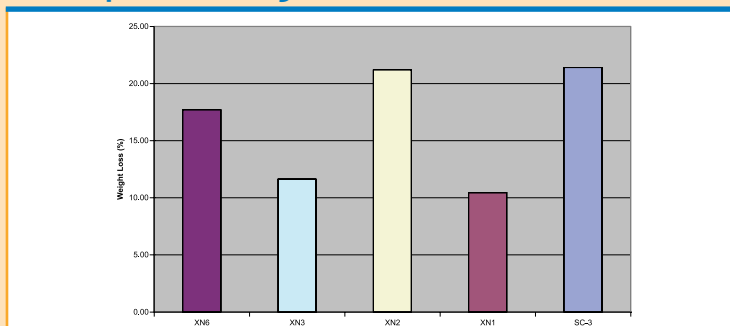


FIGURE 9

Experimental coating weight loss after 24 hours at 225°C



and increases in crosslink density upon exposure to temperatures from 125-225°C. In addition, monomeric and oligomeric materials were also cured in neat form and aged at elevated temperatures. Oligomeric materials have been found, which possess enhanced thermal resistance over that of the urethane and HDODA-based coating. These results are part of the ongoing development of fast-curing technologies for higher temperature optical fiber applications. ▸

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References

1. Hansen, Henning, "History of Downhole Permanent Monitoring," www.seafom.com, Subsea Fiber Optic Monitoring Group.
2. Homa, Daniel, et al., U.S. Patent Application 2006/0222306, paragraph 5.
3. Corning Hermetic Single-Mode Specialty Fiber-Technical Bulletin, January 2007, www.corning.com/specialtymaterials.
4. Shimizu, et al., U.S. Patent 6,711,335.
5. Li, Jie, et al., "Advances in Design and Development of Optical Fibers for Harsh Environments," OFS Specialty Photonics White Paper www.specialtyphotonics.com.

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