The Effect of Urethane Acrylate Structure on the Fracture Toughness and Puncture Resistance of Optical Fiber Coatings

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Introduction and Background

Optical fibers are typically coated with a dual layer acrylate coating system, the main purpose of which is to protect the glass fiber from optical, environmental and mechanical failure modes. The coating system consists of a soft inner coating, commonly referred to as the "inner primary" or "primary" coating, and a hard outer coating, commonly referred to as the "outer primary" or "secondary" coating. The properties and dimensions of the coating system are designed to minimize microbend induced attenuation losses[1] while maximizing the mechanical protection of the fragile glass surface. The need for mechanical protection has increased in recent years with the advent of photonic devices. Fiber in these applications is handled significantly more than in typical fiber cabling operations.[2] It is generally believed that a secondary coating with a high modulus is advantageous for increased protection of the glass fiber from mechanical damage during processing and handling. That said, increasing the modulus of these cross-linked acrylate coatings is often accompanied by a reduction in the elongation to failure and brittleness becomes a concern. A better understanding of coating toughness and the factors that contribute to toughness is needed in order to design coatings that provide increased mechanical protection for the glass optical fiber.

Urethane acrylate oligomers are commonly used in optical fiber coatings to impart toughness to the cured coating. These oligomers are synthesized through the reaction of a polyol with a diisocyanate to yield an isocyanate terminated oligomer. These oligomers are then reacted with a hydroxyethyl acrylate monomer to yield the desired urethane acrylate oligomer. Because there are a wide variety of polyols available, oligomers can be made with many different structures which will result in coatings with different cured properties.[3]

The resistance of a brittle material to cracking is described by the material property known as fracture toughness, K_C. Fracture toughness is related to the amount of energy required to propagate a flaw to failure. For the case of linear elastic fracture mechanics the fracture toughness of a flaw in tension is given by,

$$K_{IC} = Y\sigma_f \sqrt{a} \qquad\qquad (1)$$

where Y is a parameter describing the geometry of the flaw and the loading condition, σ_f is the tensile strength at failure, and a is the flaw depth at failure. Thus, for a given flaw size, a, a higher fracture toughness allows for greater stress before failure. Equation (1) pertains to fracture in a brittle fashion, without yielding. However, if the flaw is small

enough, secondary coatings can yield prior to failure. A parameter that captures both the fracture toughness and the ability to yield is known as the ductility factor.[4]

$$D = [1/\pi(K_{IC}/ \text{ yield stress})^2] \qquad\qquad (2)$$

A larger ductility factor indicates a larger plastic zone in front of a stressed flaw, but, more practically, indicates reduced sensitivity of the coating to defect formation and propagation.

In this study, the relationship between the structure of the urethane acrylate oligomer and the resulting fracture toughness and ductility of the secondary coating is investigated. Oligomers with a variety of structures were synthesized and formulated into secondary coatings. In addition to toughness testing, select coatings were then put onto optical glass fiber and tested for puncture resistance as direct puncture through the coating is one of the common failure modes for optical fiber coatings. The purpose of this paper is to present our findings on the relationship between the oligomer structure, the fracture properties of the coating, and the resulting puncture resistance of the coated optical fiber.   We will also demonstrate that conventional fracture mechanics can be used to guide the formulation of optical fiber coatings with increased damage resistance.

Initial work showed that linear oligomers based on rigid block polyols, such as alkoxylated bisphenol A, resulted in coatings with both higher modulus and toughness values as compared to the control coatings. Similar results were also seen with oligomers based on propoxylated glycerol.[5] A portion of these initial findings is included in this paper. These initial results served as the basis for the work reported herein whereby oligomers were prepared from various multi-functional polyols and then modified by the incorporation of different types of rigid urethane "arms" – mostly based on bisphenol A. In addition, several new linear oligomers incorporating bisphenol A were studied.   The bisphenol A group, which is known for its strength and rigidity, is also the basis for the monomer that was used in the formulations.

Experimental
Oligomer Synthesis

The di-functional and multi-functional urethane acrylate oligomers were prepared using well established synthetic procedures.[6] Details of the individual oligomer preparations have been previously published.[5] In general, stoichiometric quantities of polyols, diisocyanate and hydroxyl functional acrylate were reacted together to give oligomeric mixtures having an average structure corresponding to that given in the text. Due to the highly viscous nature of the oligomers, most were prepared as 50% solutions in Photomer® 4028 from Cognis Corporation as a non-reactive diluent to facilitate synthesis and subsequent handling. All of the starting materials were used as received. The starting materials have been abbreviated in the data tables as follows; GP is propoxylated glycerol with a molecular weight of either 725 or 1500, BPA is bisphenol A, $(PO)_2BPA$ is propoxylated bisphenol A, $PErythPPG_{426}$ is propoxylated pentaerythritol, $TMP(PO)_3$ is propoxylated trimethylolpropane, PPG_{425} is polypropylene glycol with a molecular weight of 425, T650 is poly(tetramethylene glycol) (Terathane®650), CHDM is cyclohexane dimethanol, $H_{12}MDI$ is 4,4-methylenebis(cyclohexylisocyanate) (Bayer

Desmodur® W), TDI is toluene diisocyanate, IPDI is isophorone diisocyanate, HEA is hydroxyethyl acrylate, and CLA is caprolactone acrylate.

Coating Formulation Preparation

The coating formulations were prepared using a high speed mixer and a jacketed beaker heated to 65ºC. The formulation components were weighed into the beaker and mixed until the photoinitiators were completely dissolved and the mixture appeared to be homogeneous. The coatings were then poured into black plastic containers and allowed to cool. With the exception of Control 1, all of the coatings contain Photomer 4028® from Cognis Corporation as the monomer component. The oligomer to monomer ratio was kept constant in all cases.

Coating Sample Preparation for Tensile and Fracture Testing

Rods were prepared for tensile property measurement by injecting the formulations into non-stick tubing with an inner diameter of approximately 625 microns. Films were prepared for fracture toughness testing by drawing down the formulations on a glass plate at a thickness of approximately 250 microns. Both rods and films were cured using a Fusion D lamp with a nitrogen purge. The rods received a dose of approximately 2700 mJ/cm^2 and the films received a dose of approximately 1350 mJ/cm^2. The samples were then allowed to condition overnight in a controlled environment at 23ºC and 50% relative humidity prior to testing.

Tensile Property Measurements

The rod samples described above were used for tensile property measurement. Tensile testing was conducted using a universal testing machine with a specimen gauge length of 5.1 cm and a speed of 2.5 cm/minute. A total of 10 samples were tested for each coating. The yield stress was determined from the stress strain curve using established methods.[7] The Young's modulus value was also recorded.

Fracture Toughness Testing

Fracture toughness was measured on the films described above by preparing specimens with a center cut notch as shown in Figure 1 and then pulling to failure in tension. The specimen width was 52 mm with a thickness of about 250 microns. Using a template, notches of 18, 24, and 30 mm were carefully placed in the center of the specimens using a sharp blade. The K_{IC} and ductility values for the coatings were calculated using the equations described above. For a sheet or film with through flaw of 2a, the geometry factor Y is $1.77 - 0.177(2\lambda) + 1.77(2\lambda)^2$ where $\lambda = a/$sample width.[8]
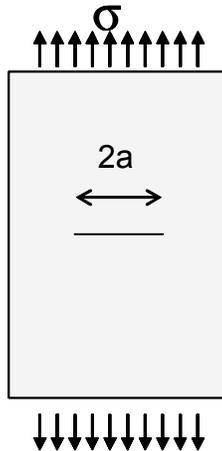
Figure 1. Illustration of Sample used for K_{IC} Measurements

Optical Fiber Preparation

Fibers with select formulations were made on an optical fiber draw and screened at the usual 100 kpsi prior to puncture resistance testing. The nominal fiber geometry was 125 micron diameter glass, 190 micron diameter primary coating, and a 245 micron diameter secondary coating.

Puncture Resistance Testing

This test method is explained in detail in reference 2. A 4-centimeter length of fiber is placed on a 3 mm-thick glass slide. This fiber is examined at 100X magnification using transmitted light and is rotated until the secondary coating wall thickness is equivalent on both sides. In this position, the secondary coating will be thickest at the top or bottom and equal on the sides.
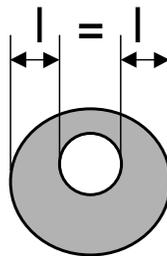
Figure 2. Orienting the fiber for indentation testing.

In this orientation, the coating is indented with a 75° diamond wedge indenter until it punctures through the coating. The peak load at puncture is recorded for ten such measurements. The fiber is then rotated 180° so that the other extreme for the secondary wall thickness can be tested in the same manner. Thus, twenty measurements are obtained for a given section of fiber.

Figure 3 shows previously published puncture resistance results of the Control 1 coating.[2] The puncture load scales linearly with the cross-sectional area of the secondary coating with the softer primary coating playing almost no role.
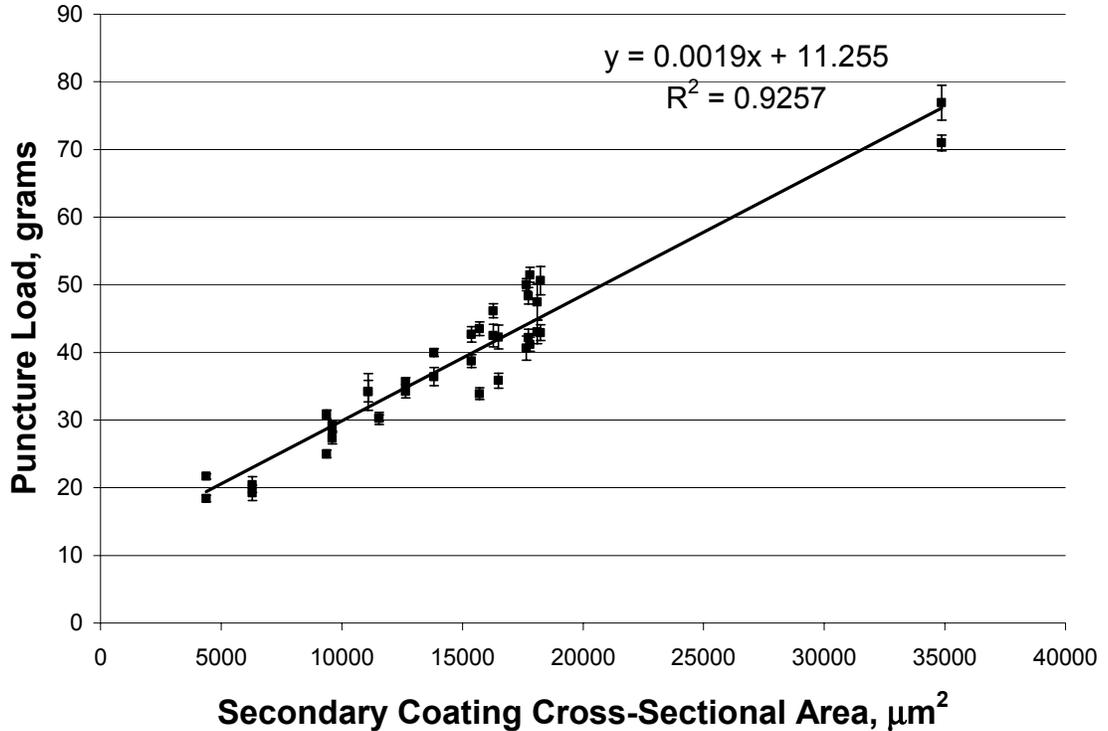
Figure 3.   The puncture resistance of optical fiber with Control 1 as the secondary coating.[2]

Results and Discussion
Coating Tensile and Fracture Properties
Table 1 contains the tensile and fracture data for the two control coatings. Control 1 is a commercial coating of moderate modulus and toughness. The second coating, Control 2, is based on Photomer® 4028 and contains a commercially available aliphatic polyether based urethane acrylate oligomer. The second control coating has a higher Young's modulus and ductility value than the first control, as well as a slightly higher toughness value. The higher ductility value can be attributed mainly to the lower yield stress value this coating exhibits. Because the composition of Control 1 is unknown, it is difficult to postulate as to why Control 2 is a tougher coating.

The data in Table 2 is for coatings based on three of the first generation experimental oligomers and is meant to serve as a reference against the data presented in Tables 3,4,5, and 6. All of these coatings have modulus values which are higher than either of the controls, with Coating 1 and Coating 2 also exhibiting higher fracture toughness values. Coating number 3 has been included as an example of a coating

which was noted to be brittle due to the high modulus and fairly low fracture toughness values. This behavior explains the failure of rods prior to yielding. With the high crosslink density associated with the use the tetrafunctional oligomer, this is not unexpected. The fact that Coating 2 has the highest fracture toughness value of all of these coatings is thought to be due to the presence of the propoxylated bisphenol A in the oligomer. It is postulated that the bisphenol A, due to its hard and compact nature, may serve as loci to absorb and dissipate energy that would otherwise result in catastrophic failure of the coating through fracture processes.

The data for oligomers based on propoxylated glycerol appears in Table 3. All of the coatings exhibited higher modulus and fracture toughness properties as compared to the control coatings in Table 1. They also exhibited slightly higher K_{IC} and ductility values than for the oligomer used in Coating 2. Like Coating 2, they all exhibited clear yielding behavior in the tensile test. When comparing all of these coatings, there does not seem to be any effect from changing the diisocyanate used in the oligomer preparation nor from modifying the number of BPA groups in the "arm" of the oligomer. Likewise, changing the molecular weight of the propoxylated glycerol, replacing the BPA with the rigid 1,4 cyclohexane dimethanol (CHDM), or replacing the hydroxyethyl acrylate cap with the potentially crystalline caprolactone acrylate cap also had no significant effect on these properties of interest.

The data in Table 4 represents oligomers based on propoxylated pentaerythritol. As is the case with the data shown in Table 3, there was no significant effect when the diisocyanate was changed or when comparing the effect of one BPA group in the "arm" to two BPA groups. The biggest difference was seen when the rigid BPA based "arm" was replaced with a polyol "arm". While Coatings 13 and 14 both have modulus values akin to the rest of the coatings in this grouping, replacing the BPA "arm" with the polyol "arm" resulted in a coating which exhibited no yield point in tensile testing.

The data for oligomers based on propoxylated trimethylolpropane appear in Table 5. The use of polyol "arms" resulted in coatings which exhibited no yielding behavior in the tensile test. Increasing the molecular weight of the polyol in Coating 20 resulted in a slightly lower modulus value as well. The only coating to exhibit yielding was Coating 21 which contained a BPA based "arm".

Data for several linear oligomers appear in Table 6. These oligomers were synthesized based on the results seen for the oligomer used in Coating 2. All of the coatings in this group exhibited modulus values which were not significantly different. Changing the diisocyanate used in the synthesis of the oligomer had no effect on the properties, nor did replacing the BPA group with the CHDM group.   The oligomers in Coatings 22, 26, and 28 contain both a BPA block and a polyol block. In all of these cases, the coatings exhibited clear yielding behavior and high toughness.   It appears that the presence of the rigid block is an important factor in achieving high toughness.

Table 1. **Tensile and Fracture Data for Reference Coatings**

Coating	Young's Modulus (MPa)	Yield Stress (MPa)	K_{IC} (MPa·m$^{1/2}$)	D (μm)
Control 1	1050 +/- 40	44.5 +/- 5.1*	0.67 +/- 0.04	72
Control 2	1450 +/- 20	40.1 +/- 0.75	0.75 +/- 0.05	111

* This coating did not exhibit as clear of a yield point as Control 2.

Table 2. **Tensile and Fracture Data for First Generation Oligomers**

Coating	Oligomer Structure	Young's Modulus (MPa)	Yield Stress (MPa)	K_{IC} (MPa·m$^{1/2}$)	D (μm)
Coating 1	GP$_{725}$(H$_{12}$MDI-HEA)$_3$	1915 +/- 30	45.3 +/- 0.9	0.920 +/- 0.088	131
Coating 2	HEA- H$_{12}$-(PO)$_2$BPA- H$_{12}$-HEA	1979 +/- 44	55.6 +/- 1.41	1.252 +/- 0.099	161
Coating 3	PErythPPG$_{426}$(H12-HEA)$_4$	1975 +/- 55	No Yielding	0.797 +/- 0.104	No Data

Table 3. **Tensile and Fracture Data for Propoxylated Glycerol Based Oligomers**

Coating	Oligomer Structure	Young's Modulus (MPa)	Yield Stress (MPa)	K_{IC} (MPa·m$^{1/2}$)	D (μm)
Coating 4	GP$_{725}$ (H12MDI-BPA-H12MDI-HEA)$_3$	2090 +/- 80	57.5 +/- 1.4	1.32 +/- 0.09	168
Coating 5	GP$_{725}$(IPDI-BPA-IPDI-HEA)$_3$	2210 +/- 100	63.4 +/- 0.8	1.40 +/- 0.05	153
Coating 6	GP$_{725}$(TDI-BPA-TDI-HEA)$_3$	2200 +/- 50	59.4 +/- 0.7	1.44 +/- 0.07	188
Coating 7	GP$_{725}$(H12MDI-BPA-H12MDI-BPA-H12MDI-HEA)$_3$	2340 +/- 100	61.2 +/- 1,9	1.51 +/- 0.07	194
Coating 8	GP$_{725}$(IPDI-BPA-IPDI-BPA-IPDI-HEA)$_3$	2450 +/- 60	63.4 +/- 2.1	1.39 +/- 0.10	152
Coating 9	GP$_{725}$(TDI-BPA-TDI-BPA-TDI-HEA)$_3$	2290 +/- 50	61.7 +/- 1.3	1.55 +/- 0.10	200
Coating 10	GP$_{725}$(TDI-CHDM-TDI-HEA)$_3$	2200 +/- 60	60.5 +/- 1.1	1.38 +/- 0.06	164

Coating		Young's Modulus (MPa)	Yield Stress	K_IC	D (μm)
Coating 11	GP$_{725}$(TDI-BPA-TDI-CLA)$_3$	2150 +/- 50	59.9 +/- 1.0	1.35 +/- 0.03	161
Coating 12	GP$_{1500}$(TDI-BPA-TDI-HEA)$_3$	1960 +/- 130	57.1 +/- 3.2	1.22 +/- 0.06	144

Table 4. Tensile and Fracture Data for PErthy(PO)$_5$ Based Oligomer Formulations

Coating	Oligomer Structure	Young's Modulus (MPa)	Yield Stress (MPa)	K$_{IC}$ (MPa$^.$m$^{1/2}$)	D (μm)
Coating 13	PErythPPG$_{426}$(IPDI-T650-IPDI-HEA)$_4$	1950 +/- 60	No yielding	No data	No data
Coating 14	PErythPPG$_{426}$(IPDI-PPG425-IPDI-HEA)$_4$	2110 +/- 70	No Yielding	No Data	No Data
Coating 15	PErythPPG$_{426}$(IPDI-BPA-IPDI-HEA)$_4$	2260 +/- 40	66.5 +/- 7.3	1.43 +/- 0.07	166
Coating 16	PErythPPG$_{426}$(TDI-BPA-TDI-HEA)$_4$	2260 +/- 130	65.3 +/- 1.7	1.33 +/- 0.07	135
Coating 17	PErythPPG$_{426}$(TDI-BPA-TDI-BPA-TDI-HEA)$_4$	2650 +/- 30	73.3 +/- 0.4	1.46 +/- 0.05	126

Table 5. Tensile and Fracture Data for TMP(PO)$_3$ Based Oligomer Formulations

Coating	Oligomer Structure	Young's Modulus (MPa)	Yield Stress (MPa)	K$_{IC}$ (MPa$^.$m$^{1/2}$)	D (μm)
Coating 18	TMP(PO-IPDI-PPG425-IPDI-HEA)$_3$	2120 +/- 70	No Yielding	No Data	No Data
Coating 19	TMP(PO-IPDI-T650-IPDI-HEA)$_3$	2070 +/- 70	No Yielding	No Data	No Data
Coating 20	TMP(PO-IPDI-PPG1000-IPDI-HEA)$_3$	1530 +/- 110	No Yielding	No Data	No Data
Coating 21	TMP(PO-IPDI-BPA-IPDI-HEA)$_3$	2570 +/- 50	64.6 +/- 0.9	1.41 +/- 0.8	151

Table 6. Tensile and Fracture Data for Linear Oligomer Formulations

Coating	Oligomer Structure	Young's Modulus (MPa)	Yield Stress (MPa)	K_{IC} (MPa·m$^{1/2}$)	D (μm)
Coating 22	HEA-H12-BPA-H12-PPG425-H12-BPA-H12-HEA	2250 +/- 60	63.1 +/- 1.1	1.42 +/- 0.06	159
Coating 23	HEA-IPDI-BPA-IPDI-BPA-IPDI-HEA	2340 +/- 80	64.0 +/- 1.4	1.40 +/- 0.07	152
Coating 24	HEA-TDI-BPA-TDI-BPA-TDI-HEA	2320 +/- 50	62.2 +/- 1.0	1.39 +/- 0.08	159
Coating 25	HEA-TDI-CHDM-TDI-CHDM-TDI-HEA	2340 +/- 30	66.1 +/- 1.0	1.41 +/- 0.06	144
Coating 26	HEA-TDI-BPA-TDI-PPG425-TDI-BPA-TDI-HEA	2270 +/- 80	62.7 +/- 1.2	1.36 +/- 0.08	151
Coating 27	HEA-H12-BPA-H12-BPA-H12-HEA	2370 +/- 150	64.0 +/- 2.8	1.38 +/- 0.14	148
Coating 28	HEA-TDI-BPA-TDI-T650-TDI-BPA-TDI-HEA	2370 +/- 110	62.4 +/- 1.6	1.23 +/- 0.14	124

Puncture Resistance Testing

The results of the puncture resistance testing on Controls 1 and 2 along with the selected experimental coatings are shown in Figure 4. The two control coatings have about the same puncture resistance at the same coating cross sectional area even though Control 2 has a significantly higher modulus than Control 1. This is likely due to the fact that these two coatings do not have significantly different fracture toughness values. The experimental coatings all exhibit higher puncture values as compared to either Control 1 or Control 2. Comparing the experimental coatings, Coating 2 appears to provide slightly higher puncture resistance than Coating 1 at the same coating cross sectional area which may be attributed to its slightly higher ductility factor. Because the fibers with Coatings 6, 8, and 15 had lower coating cross sectional area values, the puncture results

look slightly lower than for Coating 1. However, because the puncture resistance increases linearly with coating cross sectional area, it can be inferred that the puncture resistance of Coatings 6, 8, and 15 is not significantly different from that of Coatings 1 and 2.
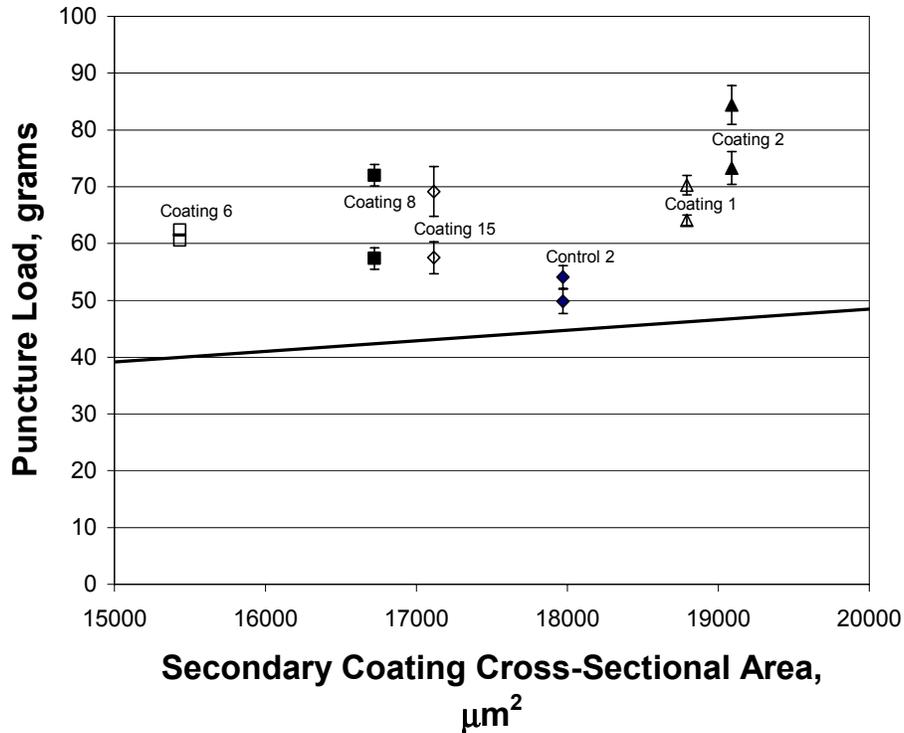
Figure 4. Puncture resistance of toughened coatings compared to that of the Control 1 fiber (line).

In Figure 5 the practical test of puncture resistance is plotted versus the more fundamental ductility factor and there appears to be reasonable agreement. This suggests that the process of puncturing through an optical fiber coating during typical processing events can be represented by the coating's resistance to brittle fracture and ability to yield.
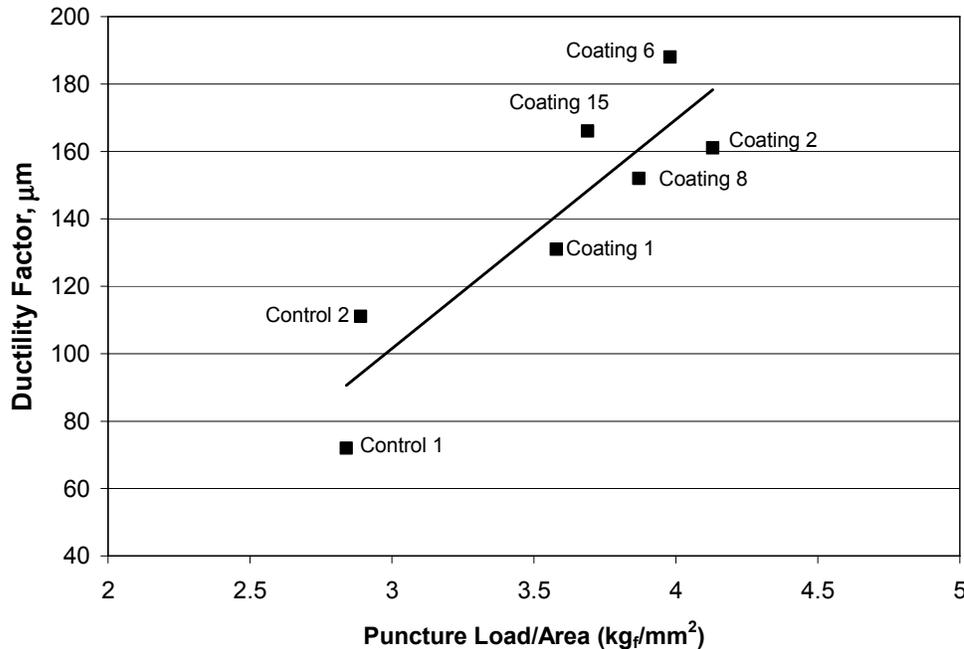
Figure 5. Puncture resistance and the coating ductility factor for a range of coating compositions.

Conclusions and Future Work

New urethane acrylate oligomers were prepared and evaluated for their ability to provide increased modulus and toughness in optical fiber secondary coatings. With few exceptions, the coatings with the new oligomers all exhibited increased modulus and toughness as compared to the control coatings. A clear correlation of oligomer structure with modulus and toughness properties was not apparent. However, it appears that a rigid group such as bisphenol A or cyclohexane dimethanol contributes to yielding. This would be consistent with results reported for cross-linked epoxy coating networks in which the presence of a yielding mechanism to absorb energy was found to increase toughness.[9] A clear connection between coating structure, yielding, and toughness still needs to be established, particularly in regard to the role of the bisphenol A group which was present in all of these coatings either from the oligomer or the Photomer® 4028 monomer. Additional structure/property studies to explore these connections are on-going and will be reported in the future.

Coatings with enhanced toughness were put onto optical fiber and the resulting puncture resistance was improved over that of the two control coatings. This is consistent with the higher ductility factor measured for the experimental coatings. The correlation between the ductility factor and the puncture resistance for these coatings demonstrates that conventional fracture mechanics can be used to guide the development of optical fiber coatings with increased mechanical protection.

Acknowledgements

References

1. Gloge,D. The Bell System Technical Journal 1974, 54(2), pgs 245 – 262.
2. G. Scott Glaesemann and Donald A. Clark, "Quantifying the Puncture Resistance of Optical Fiber Coatings" Proceedings of the 50th Internationl Wire and Cable Symposium, 240 – 248, Orlando, FL, 2001.
3. Z. Wicks, F. Jones, S.P. Papas Organic Coatings Science and Technology Volume1 pg 215.
4. D.R. Moore and S.Turner, *Mechanical Evaluation Strategies for Plastics,*CRC Press, Boca Raton, FL, 2001.
5. M.D. Fabian, G.S. Glaesemann, D.N. Schissel US 6,862,392 Coated Optical Fiber and Curable Compositions Suitable for Coating Optical Fiber.
6. For general reviews and leading references on urethane/acrylate oligomer synthesis and properties see P. Santhana, G.Krishnan, V.Choudhary, I.K. Varma, *J. Macromol. Sci. Rev. Macromol. Chem. Phys.,* C33(2), 147 – 180 (1993); J.A. McConnell and F.K. Willard in *ACS Symp. Ser.,* 417, 272 – 283 (1990); G.K. Noren, J.M. Zimmerman, J.J. Krajewski, and T.E. Bishop in *ACS Symp. Ser.,* 417, 258 – 271 (1990); B. Martin, *Radiation Curing,* Aug. 1986, 4 -15; H.C. Miller, *Radiation Curing,* May 1984, 4 – 7.
7. *R.J. Young and P.A. Lovell, Introduction to Polymers, 2nd Edition, 2001 Chapman & Hall, London*
8. ASTM E 1820-99a Standard Test Method for Measurement of Fracture Toughness and ASTM D5045-99 Standard Test Methods for Plane-Strain Fracture Toughness and Strain Energy Release Rate of Plastic Materials.
9. See A.J. Lesser and K.J. Calzia, Journal Polymer Science: Part B: Polymer Physics, 42, 2050-2056(2004) and references cited therein.