Thermal and Mechanical Analysis of Cross-Linked Optical Fiber Coatings

S. M. Budy, T. Hawkins, P. Foy, M. J. Matthewson, D. W. Smith Jr., and J. Ballato

***Abstract*—A convenient route to enhancing the thermal degradation on-set temperature of existing commercial optical fiber coatings is presented. UV curable acrylate coatings were modified through the addition of a multi-functional cross-linking agent and are shown to increase their degradation temperature by 65°C without any degradation in the mechanical or optical properties of the resultant fiber. Such enhanced thermal robustness in coatings is important for optical fiber applications in high energy laser (HEL) systems and selected higher temperature sensing environments.**

***Index Terms*—Mechanical testing, optical fiber, optical fiber coatings.**

I. Introduction

SILICA-BASED optical fibers, ubiquitous in telecommunication systems, are finding greater utilization in more extreme applications. Examples include down-hole monitoring of oil wells and other geophysical and geothermal exploration as well as defense and security related optical fiber lasers [1], [2]. Especially when employed in non-traditional environments, the thermal and mechanical robustness of the optical fibers is of major concern and the polymeric fiber coatings can be the limiting factor in the utility of the fiber [3].

For decades, polymeric coatings have been applied to optical fibers. The coatings provide mechanical protection to the pristine surface of the as-drawn glass [4]. With a few limited exceptions, the fiber industry has largely relied on an acrylate-based polymer system due to its relatively low cost and its ability to be cured at high speed on-line using ultraviolet (UV) light. Cross-linked polymers have been extensively studied and offer beneficial properties such as good fracture strength, high modulus, increased solvent stability, better scratch resistance, reduced oxidation, and improved thermal degradation [5].

However, as fibers are finding use in more extreme environments, there is a growing need for coatings that exhibit greater thermal stability while not adversely affecting the overall mechanical or optical properties of the fiber. Rather than introduce a new polymer into what is a well-established industry, this work takes off-the-shelf UV curable acrylates accepted by the industry and enhanced their thermal stability through a simple additive. More specifically, reported here is a method to easily modify a wide range of commercially available acrylate resins through the addition of a multi-functional cross-linker.

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II. Experimental Procedure

A. Organic Polymer Coating

Desolite single coating (#3471-3-14), a well-established optical fiber coating, was purchased from DSM Desotech, Inc. (Elgin, Ill.). Dipentaerythritol penta-/hexa-acrylate was purchased from Sigma-Aldrich, and was chosen due to a high level of cross-linking functionality. Thereby small quantities can be added with the greatest change in properties.

Preliminary tests involved blending different weight loadings (wt%) of the penta-/hexa-functional acrylate cross-linker with DSM resin at the selected amounts. Samples were mixed with a mechanical shaker for 12–24 hr to ensure proper mixing. Films were prepared by drop casting and spin casting the prepared solutions and then curing under a UV lamp for 6–8 hr to ensure complete polymerization.

Thermal stability was predicted using dynamic thermal gravimetric analysis (TGA) obtained using a TA Hi-Res TGA2950. Thermal decomposition temperatures were obtained at a temperature rate of 10 °C/min in air. The degradation temperature (T_{d}) was defined as the temperature where the onset of weight loss deviated from 100%.

The refractive index was acquired from spin cast films on glass substrates obtained at 633 nm using a Metricon Prism Coupler 2010.

Coating solutions were prepared in larger volumes for subsequent coating onto a silica optical fiber ($\sim$50 mL total volume). Mixing was ensured by a mechanical shaker overnight, followed by filtering with a 1 μm filter and centrifugation (10 000 rpm) to remove all bubbles. Solutions were taken immediately to the draw tower for use after centrifugation.

B. Fiber Fabrication and Coating

A 26 mm diameter F300 silica rod, manufactured by Heraeus Tenevo (Buford, GA), was used in all draw experiments. The optical fibers used in this study were drawn at Clemson University using a commercial grade Heathway draw tower. The following details were used on all fiber and coating draws: the draw temperature was 2025 °C, a laser gauge measured 125 ± 0.5 μm for

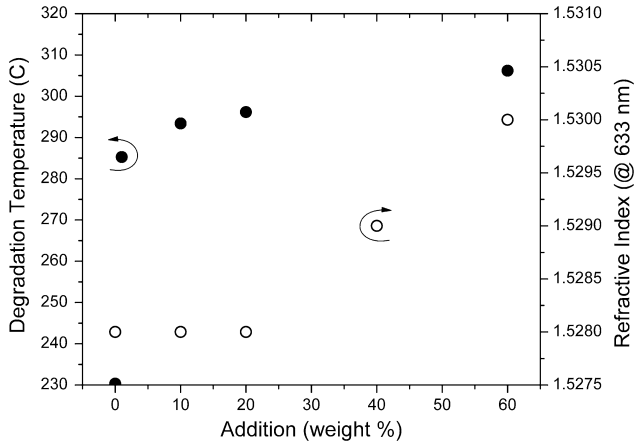

Fig. 1. Onset of degradation temperatures measured by TGA in air (•) and room temperature refractive index (○), at a wavelength of 633 nm, measured as a function of multi-functional cross-linker concentration.

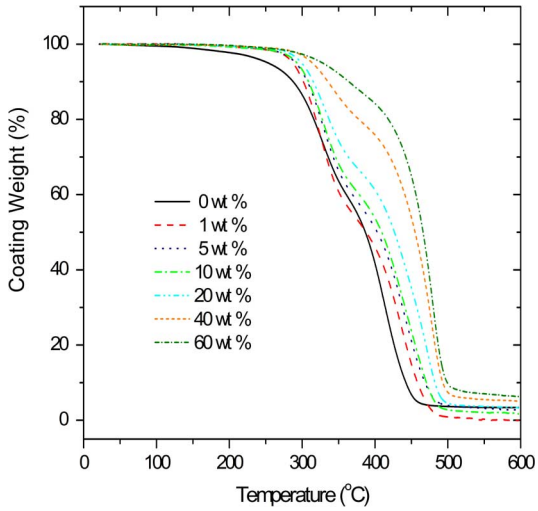

Fig. 2. Dynamic thermal gravimetric analysis curves obtained for acrylate coating with different amounts of multi-functional cross-linker (10 °C/min).

all fiber diameters, pressure driven coating system using pressures from 0.8 to 1.0 bar with coating head die sizes; 375 μm (entrance die) with either 275 μm, 325 μm, or 350 μm (exit dies) was used to apply to the fiber while drawing, a UV lamp operating at 150 to 175 Watts/inch, a second laser gauge measured the average thickness of the coating (ranged from 200.8 to 241.7 μm), and a spool to collect the fiber, from beginning to end.

C. Mechanical Testing

The strength and fatigue behavior of the fibers with zero and 20 wt% of crosslinker in the coating have been characterized with two-point bending [6] using standard test procedures [7]. In addition, the strength distributions have been measured in uniaxial tension with a gauge length of 0.5 m, also using standard test methods [8]. Coating strip force measurements have been made to characterize coating adhesion and strippability, using a standard test method [9]. Since strength and fatigue (and, to some extent, strip force) are sensitive to temperature and humidity, all measurements were made in a controlled environment of $23 \pm 0.2°$ C, $50 \pm 5\%$ humidity.

III. Experimental Results

A. Refractive Index (RI) Analysis

Spin cast films were prepared on glass substrates and fully cured under a UV lamp for each loading level. The results are shown in Fig. 1. No change in refractive index was found until a loading greater than approximately 30 wt% cross-linker was achieved.

B. Dynamic Thermogravimetric Analysis

Thermal gravimetric analysis (TGA) was used to estimate the thermal stability of the acrylate coating containing zero up to 60 wt% multi-functional cross-linker addition. Although only dynamic thermal analysis was performed, a more thorough study would entail isothermal experiments at numerous temperatures [10]. However, it is necessary to know the highest temperature at which a coating continues its efficacy. The thermal stability may be defined in many ways; the highest temperature before degradation is essential in defining an appropriate performance level for a explicit period of time. As shown in Figs. 1 and 2, the onset of thermal degradation increases with continued addition of the multi-functional acrylate cross-linker. With the addition of only 1 wt% of the multi-functional acrylate cross-linker, the thermal degradation temperature raises from 230 °C to 285 °C in air; a 55 °C increase. Thermal degradation occurs for all samples beyond 300 °C, thereby leading to catastrophic weight loss and possible separate weight loss mechanisms as seen by the multi-modal decrease. Further studies would be necessary to convolute the exact degradation mechanism. Nevertheless, at lower temperatures a smooth minimal weight loss can be observed indicating complete cross-linking and curing.

C. Strength and Dynamic Fatigue

The subcritical crack growth (fatigue) behavior of fiber coated with polymer containing zero and 20 wt% of cross-linker has been measured using two-point flexure [11]. The results in Fig. 3 show how the strength varies with loading rate (as characterized by the faceplate velocity). The slope of the log-log plot is used to determine the stress corrosion susceptibility parameter, n, which is found to be 20.6 [20.0–21.2] and 20.3 [19.6–21.0] for the zero and 20 wt% cross-linker coatings respectively; the numbers in brackets represent a 95% confidence interval for the estimates of n. While the fatigue behavior of the two specimens is statistically indistinguishable, the coating containing the cross-linker results in a somewhat higher strength fiber.

Two-point bending was used for these measurements since it has an effective test length of one to a few tens of microns [6]. As a result the occasional weak defect that is due to extrinsic processing defects are not observed and the method is more sensitive to the glass/coating interface itself, which is the topic of importance here. However, tensile measurements have also been made to ensure that the cross-linker does not cause an excessive

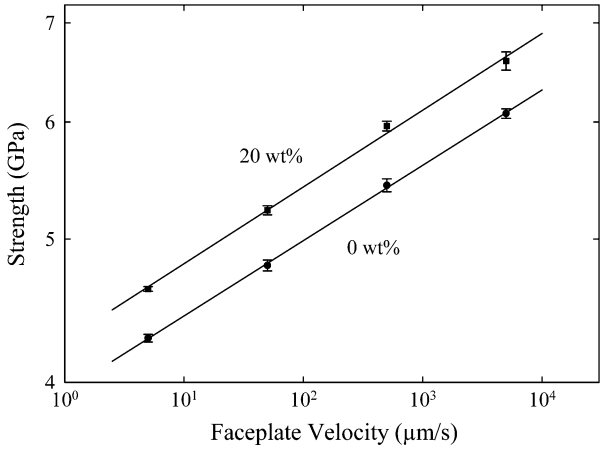

Fig. 3. Fiber strength measured in two-point bending as a function of faceplate velocity for coating with and without 20 wt% of cross-linker.

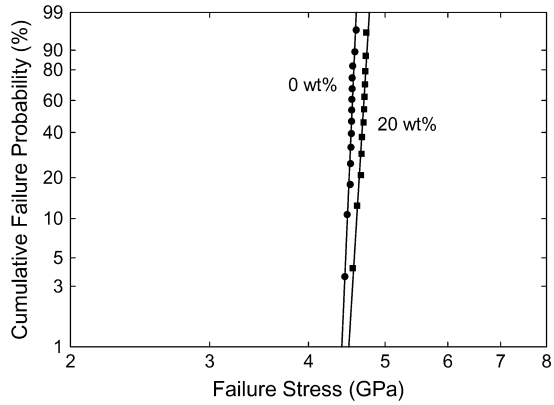

Fig. 4. Weibull plot of the strength distributions measured in uniaxial tension and a gauge length of 0.5 m at a stress rate of 30 MPa/s for fiber with coatings containing 0 and 20 wt% of cross-linker.

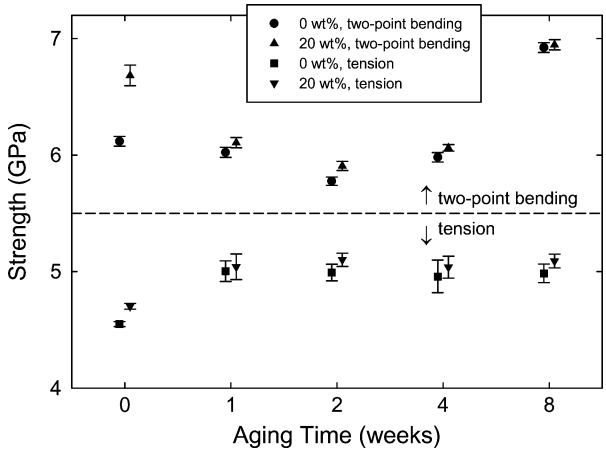

Fig. 5. Strength measured in two-point bending (faceplate speed 5000 μm/s) and tension (stress rate 30 MPa/s) as a function of zero-stress aging time in 85 °C, 85% humidity environment.

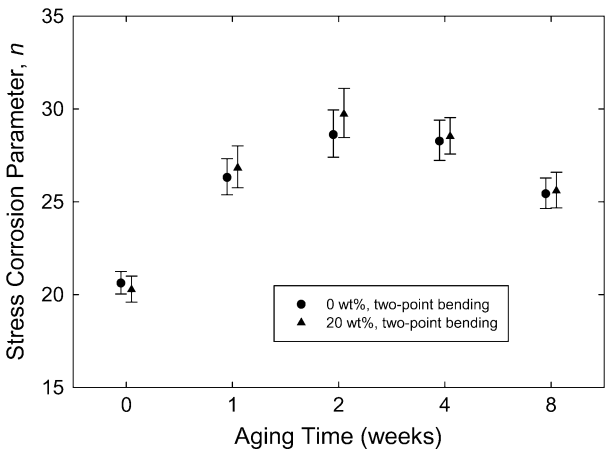

Fig. 6. Stress corrosion parameter measured by dynamic fatigue in two-point bending as a function of zero-stress aging time in 85 °C, 85% humidity environment.

number of weak failures due to, for example, incorporation of dust into the coating. Fig. 4 shows a Weibull probability plot for 0.5 m tensile specimens and it is observed that the cross-linker has an insignificant effect on the strength distribution. Overall, the cross-linker does not have any negative impact on the short term strength and fatigue behavior.

D. Zero-Stress Aging

In general, UV-curable polymer coatings do have some effect on fatigue—typical values for n are around 20 to 25 but can sometimes be as high as 30 for some coatings—but the effects are not dramatic. In contrast, the zero-stress aging behavior can be far more sensitive to the nature of the coating. During aging in aggressive environments (high temperature and/or high humidity or water activity) strength degradation can be observed to occur beyond some incubation time; degradation is caused by corrosion of the glass surface by moisture. The corrosion causes surface roughness which acts as a source of stress concentrators, thereby degrading the strength [11]. The time of onset of the zero-stress aging "knee" is known to be very sensitive to the nature of the coating. Ideally, any modification to the coating should not adversely affect the zero-stress aging behavior. Fig. 5 shows how the strength varies with aging time under zero-stress in an 85 °C, 85% humidity environment (an industry standard test condition for enhanced thermal aging) for fibers coated with polymer coating with 0 and 20 wt% cross-linker. Strength was measured in both two-point bending and 0.5 m gauge length tension. Although the results for bending and tension are significantly different (due to how the different effective test lengths interact with the somewhat sparse population of flaws) the amount of cross-linker does not affect the performance. The stress corrosion parameter, n, measured in two-point bending (Fig. 6), while increasing with aging time, is essentially independent of the amount of cross-linker. These results show that the amount of cross-linker in the coating does not adversely affect the zero-stress thermal aging behavior, at least in regard to current industry standard requirements.

IV. Conclusion

The thermal degradation temperature of commercially available acrylate-based optical fiber coatings has been improved by the addition of a single component drop-in modifier. The onset for thermal decomposition temperature increased by 65 °C through the addition of modest amounts of multi-functional

acrylate cross-linker. A range of mechanical tests showed that the overall strength, dynamic fatigue parameter, and zero-stress aging performance were unaffected by the additive or slightly improved. Additional acrylate resins are also of interest and are being explored for lower refractive index coatings.

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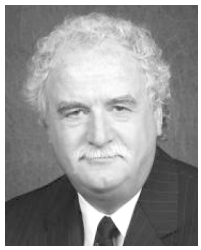

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