

# Organic Polymeric Coatings for Silica Fibers. I. UV-curing Epoxy Acrylate (V1F)

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## Synopsis

Coated optical fibers ( $\sim 100\ \mu\text{m}$ ) were prepared exhibiting fracture strengths in excess of 750 ksi ( $5.3\ \text{GN/m}^2$ ) for lengths up to 100 meters. To achieve this we have developed a novel coating and coating application process. The coating is an epoxy acrylate, cured by UV irradiation, which may contain a multifunctional silane coupling agent. The coating liquid was applied to the fiber prior to solidification by an applicator, which facilitates centering of the fiber in the coating. Our coating system offers advantages in that there is no solvent to remove, thereby avoiding possible surface "corrosion" of the glass fiber. The reasonably low viscosity of the coating formulation allows for the extensive wetting of the fiber surface irregularities prior to solidification.

## INTRODUCTION

Recent improvements in the optical characteristics of glass fibers has tended to shift the critical problem in optical fiber development from optical quality to mechanical quality.<sup>1</sup> Since glass is a brittle material, failure at stresses considerably less than the theoretical stress is probably largely due to surface defects rather than bulk defects. In general, the fracture behavior of glass can be divided into two parts—instantaneous and long-time fracture. Long-time failure or fatigue is presumably the result of the slow growth of cracks at a value of stress lower than  $\sigma_i$ , the instantaneous fracture strength.

It would be desirable to measure the strength of long lengths of pristine fiber (uncoated) so as to isolate the fiber properties from the coating properties. This is exceedingly difficult in lengths greater than a few centimeters because of the extreme susceptibility of pristine fiber to mechanical and chemical degradation. To maintain the pristine strength of glass fibers, it is imperative that the surface of the glass be protected during the drawing process to preclude the adsorption of hostile agents which will facilitate premature failure of fibers at low levels of stress.<sup>2-11</sup>

Although it has been shown repeatedly that short lengths of pristine fibers are of considerable strength,<sup>12</sup> it has become clear that the manner in which protective coatings are applied may be responsible for the significant decrease in fracture strength observed with long lengths of fiber ( $> 1\ \text{m}$ ). Optimization of the protection of glass fibers (mechanical and environmental) requires that suitable coatings be applied immediately after drawing the fiber from the melt, while precluding prior contact of the fiber with any hard solid surface. Closely allied to the problem of protection is the assurance of extensive interfacial contact

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(wetting) between the fiber and the coating phase prior to solidification of the coating. Interfacial voids may act as sites for the adsorption and collection of water, leading to stress corrosion and ultimately failure at low levels of stress.

Although a variety of options are available in choosing a coating system (e.g., thermoplastic, thermoset, polymer-solvent, vapor-phase deposited, thermally or radiation crosslinked, etc.), a desirable coating should promote adherence, particularly with respect to hostile environment, and offer sufficient mechanical protection immediately after coating to preserve the pristine nature of the glass surface. The functioning of the coating may also be associated with its ability to minimize the effect of surface flaws that are intrinsic to the drawing process or are present in the bulk of the preform as voids and brought to the surface during fiber drawing. Finally, the coating should have a fracture strain in excess of the fracture strain of the glass fiber. Other factors, such as the cleanliness of the fiber drawing facility, are independent of the coating process but may contribute significantly to surface damage of the glass.

We have explored a new method for applying an organic polymeric coating to an optical fiber so as to preserve the pristine fracture strength up to lengths in excess of 1 km.<sup>13</sup> Kilometer lengths tested in short sections (20 m) exhibit minimum strengths of 620 ksi (4.35 GN/m<sup>2</sup>). Thus far, we have used a UV-cured epoxy acrylate.<sup>14-16</sup> This coating formulation, which may contain a silane coupling agent,<sup>17,18</sup> has shown promising capacities for maintaining the high fracture strength of the pristine glass fiber in hostile environments.<sup>19</sup>

## EXPERIMENTAL: RESULTS

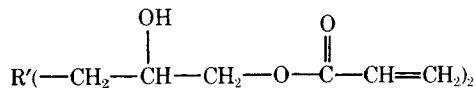
### Drawing of Optical Fibers

The optical fibers were drawn vertically from a variety of glasses using a 250-W CO<sub>2</sub> laser<sup>20</sup> and a graphite resistance furnace, both with appropriate fiber diameter controls. Spurious contamination from the graphite resistance furnace tended to obscure strength results, therefore we report only strength data for the laser-drawn fiber. The diameter of the fiber was maintained at  $110 \pm 5 \mu\text{m}$ . We used a coating applicator<sup>21</sup> modified with a compliant exit port<sup>22</sup> to facilitate self-alignment of the fiber during the coating operation. The opening of the exit port of the compliant applicator was varied to control the coating thickness. The UV-curing epoxy acrylate liquid (V1F) was applied and cured at rates up to 25 m/min by passing between two 12-in.-long 200 W/in. medium-pressure mercury UV lamps to ensure a well-cured coating. Longer lamps or better utilization of the lamp energy would facilitate more rapid drawing of the fibers, provided the increased drawing speed does not affect the fiber strength.

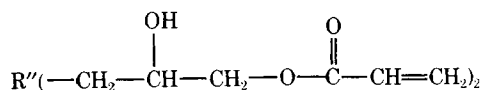
The coated fibers were collected on a 10<sup>5</sup>/<sub>8</sub>-in.-diameter anodized aluminum drum. We found that the coated fibers did not require the storage precautions that had to be exercised with uncoated fibers and that the surface quality of the drum, barring any obvious rough surface imperfections, did not seem to affect the overall strength of the fiber.

## UV-Cured Epoxy Acrylate Coating Formulation

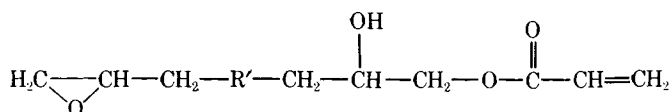
Table I gives the composition of the prepolymer of this coating system (V1F). The constituents are reacted until an acid value less than 1 is achieved. The prepolymer contains approximately 90% of the following species:



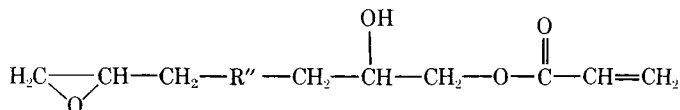
and



The remaining 10% consists of



and



The above prepolymer blend may be polymerized to a flexible film by electron or UV radiation. Extremely rapid curing can be obtained by UV radiation when a sensitizer such as benzoin or its ether derivative is added to the formulation.<sup>16</sup> Our present formulation contains 0.50% of the isobutyl ether derivative of benzoin, Vicure 10 (Stauffer Chem. Corp.). The temperature dependence of the viscosity of the prepolymer blend is illustrated in Figure 1.

TABLE I  
Prepolymer Composition of V1F Coating System

Component	Chemical Structure	Manufacturer	Composition, %
LY8161	$(\text{H}_2\text{C} \begin{array}{c} \diagup \\ \text{---} \text{CH} \text{---} \\ \diagdown \\ \text{O} \end{array} \text{---CH}_2)_n R'$	Ciba-Geigy Co.	45.4
RD-2	$(\text{CH}_2 \begin{array}{c} \diagup \\ \text{---} \text{CH} \text{---} \\ \diagdown \\ \text{O} \end{array} \text{---CH}_2)_n R''$	Stauffer Chemical Corp.	27.6
Acrylic acid	$\text{CH}_2=\text{CH}-\text{COOH}$		$\frac{27.0}{100.00}$
where	$R' = -\text{O}-\text{C}_6\text{H}_4-\text{C}(\text{CH}_3)_2-\text{C}_6\text{H}_3(\text{Br})-\text{O}-$		
and	$R'' = -\text{O}-(\text{CH}_2)_4-\text{O}-$		

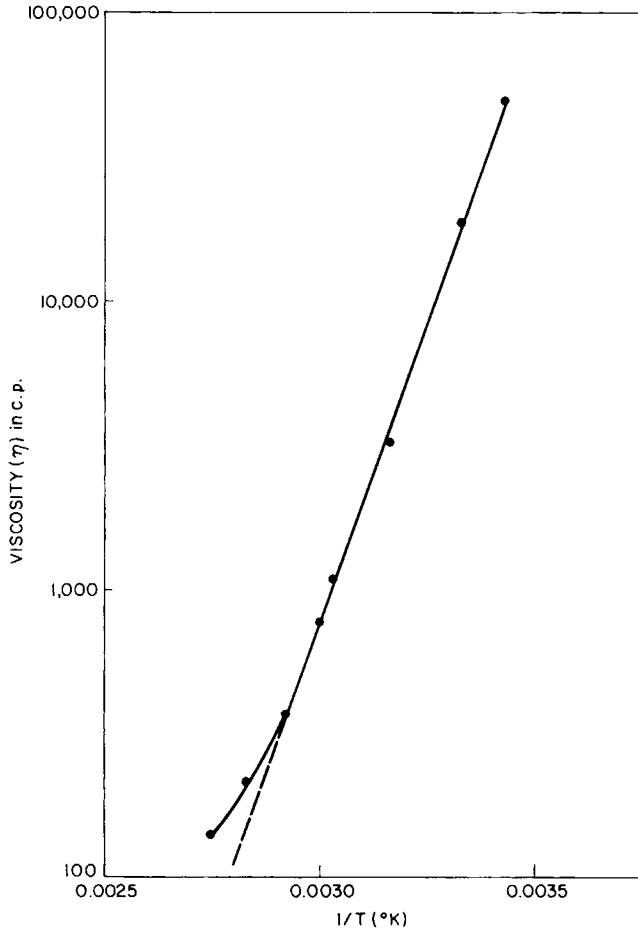
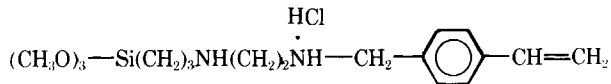


Fig. 1. Viscosity of the epoxy acrylate as function of temperature.

We have chosen for the present investigation a styrene-functional amine hydrochloride silane designated Z-6032 (Dow Corning Corp., Midland, Mich.) having the following structural formula:



For ease of application, we have incorporated approximately 0.5% of this silane coupling agent directly into the resin mixture. This procedure eliminates the need for multiple coating processes. Further, it obviates the use of solvents. The choice of this particular silane coupling agent was dictated by the following considerations:

The literature data in Table II clearly indicate that the adsorption of certain liquids on glass fibers lowers the surface free energy of the glass,  $\gamma$ , and decreases the fracture strength (the greater the reduction in  $\gamma$ , the weaker the fiber). It also shows that water is the most hostile liquid. Traditionally, in the production of glass fibers, finishes that lower the critical surface tension of glass to  $\leq 35$  dynes/cm have improved their wet strength performance<sup>23</sup> by preventing the

TABLE II  
Surface Free Energy Lowering  $\Delta\gamma$  of Quartz and Fracture Strength of Silica Glass Rods (0.10 cm)  
in Various Saturated Vapors<sup>a</sup>

Saturated vapor	$\Delta\gamma$ , ergs/cm <sup>2</sup>	Average fracture strength, psi
Vacuum	0	13,200
Benzene (dried)	52	13,600
Benzene (< 0.02% H <sub>2</sub> O)	52	10,200
Acetone	85	11,900
<i>n</i> -Propyl alcohol	110	9,600
Water	244	8,000
Water (100 min)	244	6,600

<sup>a</sup>  $\Delta\gamma = \gamma_s - \gamma_{sv}$  from reference 3; fracture strength from reference 4. Exposure time to vapors 10 min, except where noted.

adsorption of water. Figure 2 illustrates a mechanism for the stress corrosion cracking of a silanol-containing glass surface.<sup>24</sup> The adsorption of water is able to cleave highly strained Si—O—Si linkages that appear at the tip of micro-cracks<sup>24,25</sup> which presumably are generated in the formation of the glass fiber.<sup>26,27</sup> Surface attachment of silanes or functionalities in the resin formulation would modify the silanol surface to preclude the incursion of bulk water. It may, however, be difficult to prevent hydrolysis of the surface by the presence of water vapor. This is prevented by using multifunctional coupling agents that require the simultaneous hydrolysis of two or three bonds, a highly unlikely situation. Although the mechanism for the action of the silane is not well understood, Plueddemann<sup>28</sup> envisions the adsorption of the cationic styryl-functional coupling agent to occur as shown in Figure 3.

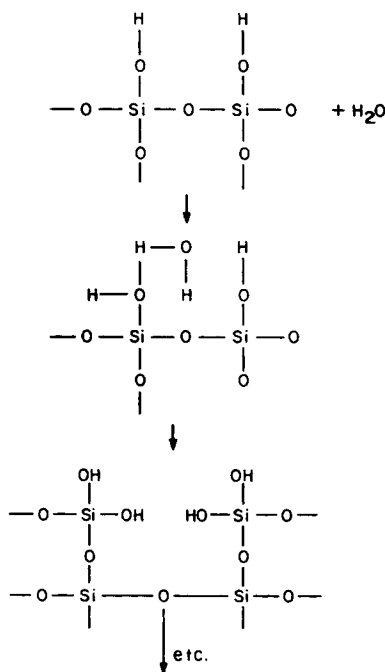


Fig. 2. Schematic diagram of the adsorption of water onto a silanol surface with subsequent scission of a Si—O—Si linkage.

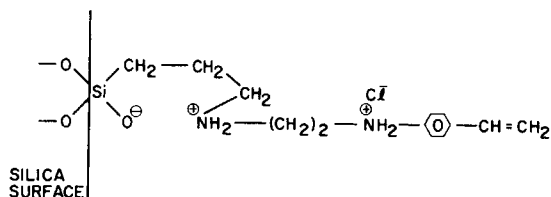


Fig. 3. Schematic representation of the adsorption of the styryl-functional silane coupling agent Z-6032 onto a quartz surface.

We do not exclude from the above considerations that residual hydroxyl functionality on the prepolymer may react with the silanol groups (hydrogen or covalent bonding) on the glass surface. A schematic for this possible reaction is shown in Figure 4. Initial studies concerned with exposure of the coated fibers to accelerated aging (simultaneous high humidity, temperature, and stress) have not provided definitive enough results to permit a clear choice of possible mechanisms. We present both possibilities as viable models for improved permanence. Current efforts are directed toward elucidating interfacial reaction between coating liquid and glass.

The physical properties of the cured coating are given in Table III. The cured polymer is a highly crosslinked material which does not fuse, even at temperatures as high as 325°C. The material when exposed to such elevated temperatures for short times remains quite flexible. Figure 5 shows a thermogravimetric analysis of the employed coating system (V1F) after curing. The bottom curve shows a scan at 10°C/min, and the top curve corresponds to 100°C/min in air.

INTERACTION OF RESIN  
WITH GLASS SURFACE

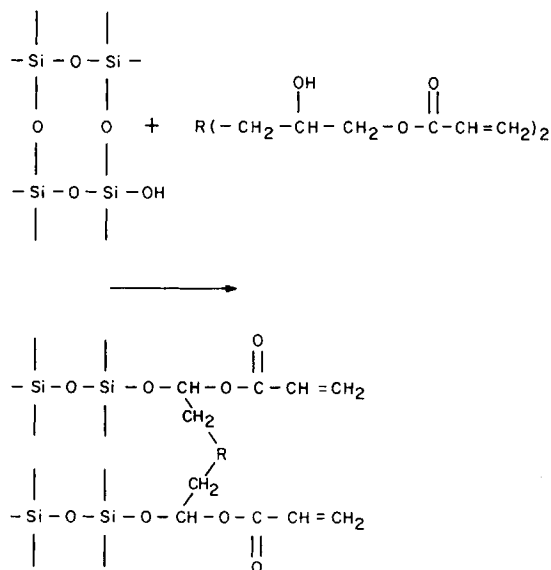


Fig. 4. Schematic for the chemisorption of functionalities on the epoxy acrylate to the silanol groups of the silica surface.

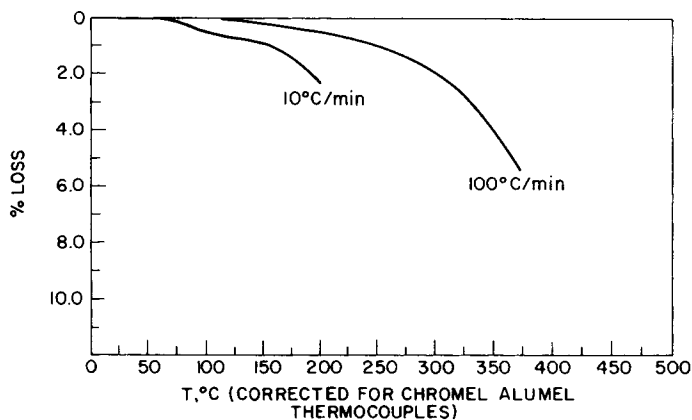


Fig. 5. Thermogravimetric analysis of V1F in air at heating rates of 10° and 100°/min. For the short time exposure to UV radiation encountered in the fiber drawing process, a minimum weight loss is expected.

TABLE III  
Physical Properties of Free Film of Cured Epoxy Acrylate-Silane Coating

Tensile strength	1010 psi
Young's modulus	3390 psi
Elongation at break	28%

These curves show that for heating rates of 10° and 100°C/min there is a loss ~2.3% and 0.4%, respectively, at 200°C. In commercial processing, e.g., coating fiber, the coating is expected to be exposed to a temperature of ~200°C for a duration of only a few seconds. Under these conditions the heating rate is expected to be of the order of greater than 1000°C/min, thereby minimizing polymer degradation.

In an experiment designed to measure the effectiveness of the coating system in the presence of water, we prepared a variety of prepolymer-coupling agent mixtures, UV cured them on quartz plates, and examined their stability in water. Table IV summarizes our observations. Clearly, the use of selected coupling agents has a positive influence on the wet strength performance of the laminate. It is speculated that the alkoxy functionality covalently bonds to the silanol groups on the glass surface while the styryl functionality enters into covalent bonding with the prepolymer phase. Furthermore, according to Plueddemann,<sup>28</sup> there is evidence that other functionalities on the glass surface appear to interact

TABLE IV  
Prepolymer-Silane Coupling Agent Mixtures UV Cured on Quartz Plates. Delamination Tendency in Water

System	Time to delaminate <sup>a</sup>
Prepolymer + 0.5 part Vicure 10	<1 hr
Prepolymer + 0.5 part A174 + 0.5 part Vicure 10	<1 hr
Prepolymer + 0.5 part A187 + 0.5 part Vicure 10	<1 hr
Prepolymer + 1.0 part Z-6032 + 0.5 part Vicure 10	>7 days

<sup>a</sup> Cured film is difficult to remove from glass, but is easily peeled from substrate after the composite is submerged in water.

strongly with the Z-6032. Since these results may not be directly related to the fiber coating process, some reservations should be exercised. However, trends may be significant.

### Control of the Coating Thickness

In the course of this experimental investigation, we have controlled the coating thickness  $h_\infty$  by means of the empirical relationship<sup>21</sup>

$$h_\infty = \chi(r_2 - a)$$

which applies for the case in which the radius  $r_2$  of the capillary of the applicator is not much greater than the radius  $a$  of the fiber. Preliminary evidence suggests that the coefficient of discharge,  $\chi$ , for our particular coating formulation is proportional to the dimensionless parameter  $\beta (= \gamma/\mu v_0)$ , where  $\gamma$  is the surface tension of the coating liquid,  $\mu$  its viscosity, and  $v_0$  the velocity at which the fiber is drawn. Figure 6, illustrating our experimental results, clearly shows that by varying the annular aperture ( $r_2 - a$ ) one can predict the coating thickness  $h_\infty$  only on the basis of the velocity  $v_0$  of the fiber, since  $\gamma$  and  $\mu$  are constant at a particular temperature. We plan to investigate the relationship  $\chi$  versus  $\beta$  further.

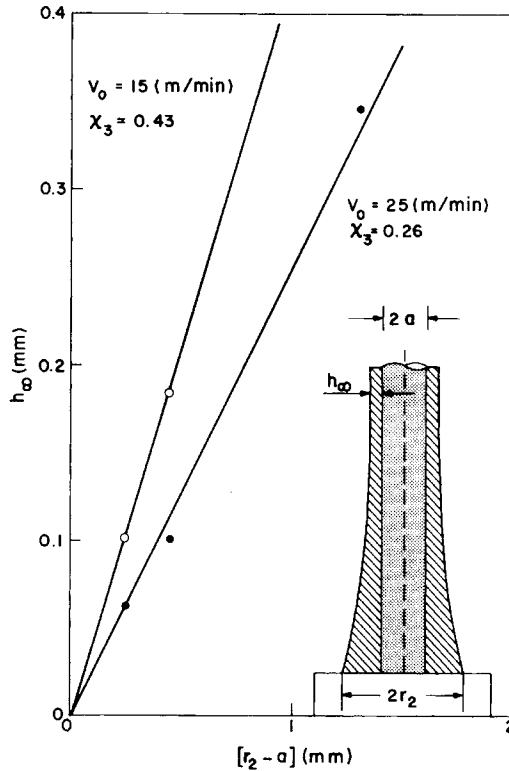


Fig. 6. Graph of the coating thickness  $h_\infty$  as function of the radius of the exit part of the capillary and the fiber radius for constant viscosity and surface tension of the coating liquid.



**Fracture Strength of Coated Optical Fibers**

The strengths of coated fibers were measured in an Instron. Clearly, with coated fibers the precautions normally exercised in the testing of pristine fibers may be relaxed a great deal. Short coated fibers ( $\leq 0.6$  m) were tested vertically at a strain rate of  $\sim 0.2/\text{min}$  at  $23^\circ\text{C}$  and 50% R.H. For lengths of  $\geq 1$  m, a load cell was mounted horizontally and the stress applied manually. The results for the fracture strength as a function of gauge length are shown in Figures 7 and 8. It would appear that for lengths up to 100 m, no serious decay in fracture strength is observed.

The centering of the fiber in the coating is a crucial parameter, since this is translated immediately into a markedly lowered fracture strength if there is insufficient coating to encapsulate the fibers. Reasonably well-centered fibers yielded the data shown in Figures 7 and 8.

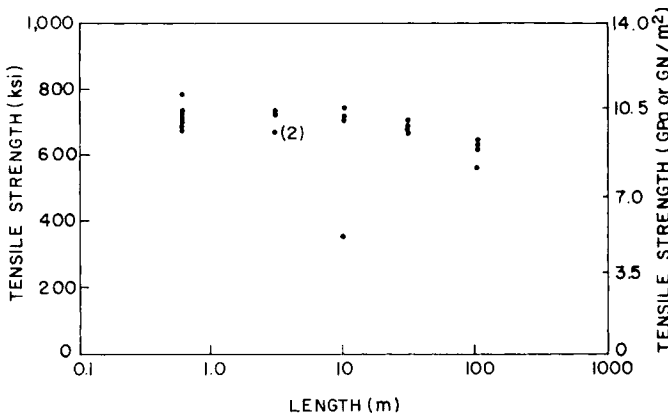


Fig. 7. Tensile strength of laser-drawn optical fiber coated with V1F vs length of specimen tested.

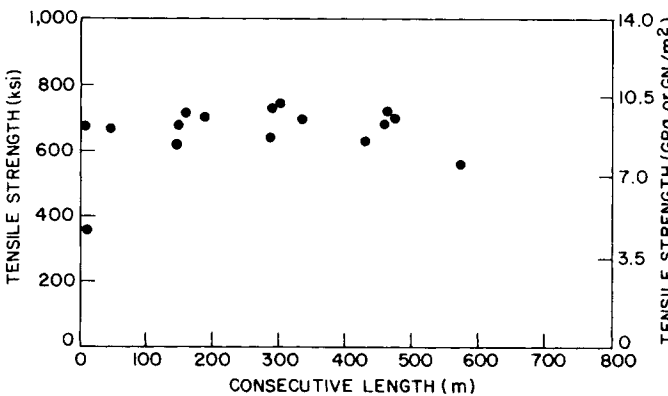


Fig. 8. Tensile strength of laser-drawn optical fiber (clad glass) coated with V1F. Tested in lengths varying from 0.6 to 100 m consecutively. Total length prepared and tested is approximately 600 m.

## CONCLUSIONS

The manner in which a coating is applied and the type of coating liquid appear to be crucial in order to preserve the properties of the pristine fiber during the coating application. Once the fiber is coated, these stringent handling measures can be relaxed without loss in fiber strength properties. Well-protected fibers were obtained by the use of the UV-curing formulation applied by a compliant applicator and the liquid cured with the use of commercially available medium-pressure lamps. With this system we achieved extensive adhesion at the polymer/glass interface. The penetration and collection of water vapor at the interface which would tend to delaminate the composite was prevented by the use of a proper surface modifier and the chemical constitution of the epoxyacrylate.

Employing the above considerations, long lengths (> 1 km) were prepared with minimum strengths in excess of 620 ksi (4.35 GN/m<sup>2</sup>). In shorter lengths (~100 m), we obtained fracture strengths in excess of 750 ksi (5.3 GN/m<sup>2</sup>).

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