

Use of Laser Spallation to Measure the Adhesion of Optical Fiber Coatings

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ABSTRACT: The correlation between chemical effects of some typical optical fiber coating formulations and adhesion to glass was studied by the use of laser spallation. The technique was able to show verifiable differences between dissimilar materials and demonstrated a good correlation to adhesion values determined by mechanical peel testing, and

to pullout values measured on coated optical fiber. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 93: 2459–2468, 2004

Key words: laser spallation; adhesion; coatings; pull-out testing; peel testing; optical fiber

INTRODUCTION

Optical fiber has become an integral part of life in the last two decades. The ability to deploy the fiber is due, in no small measure, to the polymeric coatings which are applied to the glass fiber, to protect and preserve the optical properties of the fiber.¹ Typically, the coatings are applied as a dual layer, consisting of a soft, low-modulus primary coating and a stiff, higher modulus secondary coating.² Because the softer primary coating is applied directly to the glass, an understanding of the interfacial properties (particularly the adhesion) between the coating and glass surface is necessary to properly evaluate the coating. Peel testing has proven to be a time-tested technique for evaluating adhesion and certainly provides very useful and trustworthy data.³ Similarly, the use of the fiber pull-out test has proven itself as a measure of dry adhesion in both composite materials and coated optical fiber as well.⁴

In recent years, the use of laser spallation to measure adhesion between a film and a substrate has been applied across a wide variety of materials, both organic and inorganic in nature.⁵ This method is intriguing as a measure of optical fiber coating adhesion because it may allow measurements on the optical fiber itself, as well as address potential issues that exist in some optical fiber applications. Laser spallation functions as an adhesive test by the generation of photo-acoustic waves which impact the film interface with short pulses of high-energy light from a laser. This impact originates a pressure wave by the heating,

and, in some cases, even vaporization of materials on the substrate. The generated heat creates shock waves, which then propagate through the substrate and impact the coating, causing it to snap back in tension. The force of the pressure wave is dependent upon the laser pulse power and amount of light absorbed by the sample. For the purposes of our study, the laser adhesion device seemed to hold the most promise.⁶ In this description of laser spallation, laser pulses of known power are directed at a substrate coating, generating a separation between the substrate and coating. The separation of the film from substrate creates a very distinctive diffraction pattern at the far field of the acting laser beam, which can be easily captured by a detector. This method requires that at least one of the layers be transparent to the wavelength of laser light being used. This requirement is almost always possible to satisfy by selecting an appropriate laser wavelength. We have found this method to be useful as a measure of optical fiber coating adhesion and herein report our efforts to use this method on typical optical fiber formulations cured on flat glass surfaces.

EXPERIMENTAL

General considerations

Ethoxylated nonylphenol acrylate (Photomer® 4003) was obtained from Cognis Corp. (Ambler, PA). Caprolactone acrylate (Tone® M-100) was obtained from Dow Chemical (Midland, MI). Lauryl acrylate (Ageflex® FA 12) was purchased from CPS Chemical (Tarrytown, NY). Diacetoneacrylamide, *N,N*-dimethylacrylamide, *N*-isobutoxymethylacrylamide, *N*-vinyl-2-pyrrolidinone, and acrylic acid were obtained from Monomer-Polymer and Dajac Laboratories Inc. (Feasterville, PA). All photoinitiators, UV absorber, and

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TABLE I
Compositional Information and Average Threshold Adhesion Values of Optical Waveguide Formulations

Formulation no.	Comonomer 1	Adhesion promoter, additive	Threshold adhesion
1	Ethoxylated nonylphenol acrylate—20%	2 pph bis AP, ^a 0.5 pph Tegorad 2200	1.667
2	Caprolactone acrylate—20%	2 pph bis AP, 0.5 pph Tegorad 2200	1.829
3	Ethoxylated nonylphenol acrylate—20%	No adhesion promoter	1.630
4	Diacetone acrylamide—20%	2 pph bis AP, 0.5 pph Tegorad 2200	4.348
5	<i>N,N</i> -Dimethylacrylamide—20%	2 pph bis AP, 0.5 pph Tegorad 2200	3.745
6	Acrylic acid—20%	2 pph bis AP, 0.5 pph Tegorad 2200	17.931
7	<i>N</i> -(Isobutoxymethyl) acrylamide—20%	2 pph bis AP, 0.5 pph Tegorad 2200	2.885
8	Ethoxylated nonylphenol acrylate—20%	1 pph methacrylo-silane ^b	1.818
9	Lauryl acrylate—20%	2 pph bis AP, 0.5 pph Tegorad 2200	1.993
10	Caprolactone acrylate—20%	No adhesion promoter	1.738
11	Ethoxylated nonylphenol acrylate—20%	2 pph bis AP, 0.3 pph mercapto-AP ^b	2.008
12	Ethoxylated nonylphenol acrylate—20%	0.3 pph mercapto-AP	1.890
13	Ethoxylated nonylphenol acrylate—20%	1 pph methacrylo-silane 0.3 pph mercapto-AP	1.961
14	<i>N</i> -vinylpyrrolidinone—20%	2 pph bis AP, 0.5 pph Tegorad 2200	2.540
15	<i>N</i> -vinylpyrrolidinone—5%	2 pph bis AP, 0.5 pph Tegorad 2200	1.022
16	<i>N</i> -vinylpyrrolidinone—10%	2 pph bis AP, 0.5 pph Tegorad 2200	1.960
17	<i>N</i> -vinylpyrrolidinone—15%	2 pph bis AP, 0.5 pph Tegorad 2200	2.261
18	Ethoxylated nonylphenol acrylate—25%	2 pph bisAP, 0.5 pph Tegorad 2200	1.047
19	Ethoxylated nonylphenol acrylate—25%	No adhesion promoter	0.7
20	Ethoxylated nonylphenol acrylate—25%	1 pph mercapto-AP	1.562
21	Ethoxylated nonylphenol acrylate—25%	1 pph acrylo-silane ^d	1.164
22	Ethoxylated nonylphenol acrylate—25%	1 pph methacrylo-silane	1.08
23	Ethoxylated nonylphenol acrylate—25%	1 pph glycido-silane ^e	1.157

Comonomer 2 in all formulations is ethoxylated nonylphenol acrylate.

^a Bis AP = 1,4-Bis(trimethoxysilylethyl)benzene.

^b Methacrylo-silane = γ -methacryloxypropyltrimethoxysilane.

^c Mercapto AP = (3-mercaptopropyl)trimethoxy silane.

^d Acrylo-silane = γ -acryloxypropyltrimethoxysilane.

^e Glycido-silane = γ -glycidoxypropyltrimethoxysilane.

antioxidants were obtained from Ciba Specialty Chemicals (Tarrytown, NY). The adhesion promoters 1,4-bis(trimethoxysilylethyl)benzene, γ -glycidoxypropyltrimethoxysilane, γ -methacryloxypropyltrimethoxysilane, and γ -acryloxypropyltrimethoxysilane were obtained from Gelest Inc. (Tullytown, PA). The adhesion promoter γ -mercaptopropyltrimethoxysilane was obtained from Sigma-Aldrich Corp. (St. Louis). All chemicals listed above were used as received without further purification. Tegorad 2200 additive was obtained from Degussa Goldschmidt AG (Essen, Germany) and was filtered through a 0.45- μ m polypropylene filter cartridge prior to use. Urethane acrylate oligomers were obtained from a variety of commercial sources and used without further purification.

Tensile tests were accomplished by using a MTS Sintech 1/G tensile tester. Films were cured on a Fusion UV curing belt operated by using the following conditions: 600 W/in D-bulb, 50% lamp power, 40 rpm belt speed, N₂ purge, four passes per film (average dose = 1.7–1.8 J/cm²). These conditions allowed us to achieve 100% conversion of the polymer film.

General procedure for preparing formulations

Urethane acrylate oligomer and monomer were added to a 4-L glass kettle, heated to 50–60°C by a heating

mantle, and stirred by an overhead stirrer with a stainless steel blade for 1 h at 250 rpm. Then, the addition of the photoinitiator and antioxidant was made, and the resulting mixture was stirred for an additional 1 h. The mixture was then cooled to room temperature, and an optional organofunctional silane and optional Tegorad 2200 were added, and the mixture stirred for an additional 1 h at room temperature. The resulting coating was removed to an opaque Nalgene® bottle and stored in a location that was shielded from light. Relevant compositional information on the formulations prepared by this method is given in Table I.

Procedure for 180° peel test

The general procedure used to conduct peel testing was described previously by Satas.^{3a} Borosilicate glass plates (15 × 30.5 × 10.3 cm) were allowed to soak in a bath of KOH dissolved in isopropanol overnight. The glass plates were rinsed with deionized water, blotted with lint-free wipes, and further dried with a stream of nitrogen gas. The liquid urethane acrylate was then cast as a 254- μ m-thick layer on the glass slide by the use of a draw down box. The film was next cured on a Fusion UV curing belt by using the conditions described in the general experimental section. Complete

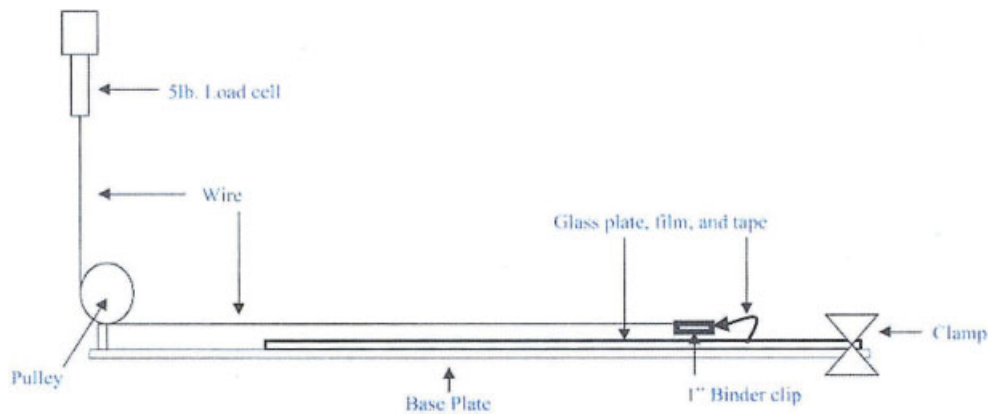


Figure 1 Apparatus for 180° peel adhesion test.

through-cure was verified by means of FTIR. Following curing, the films were allowed to condition in a temperature- and humidity-controlled room (23°C, 50% relative humidity) for at least 16 h, after which time 2.5-cm-wide fiberglass filament backing tape (Manco Inc.) was applied to the top surface. The tape and film were again conditioned in a humidity-controlled room, using the conditions described above, for at least 16 h. After this time had passed, the films were trimmed to obtain a 2.5-cm sample width. The glass slide was then mounted horizontally in a tensile tester, which was equipped with a metal plate to which the film and slide were clamped, as well as a flexible steel wire and a pulley. The wire was then connected to the tester load cell by the use of a binder clip (see Fig. 1). The tester was then operated at a rate of 12.7 cm/min until a total of 10–13 cm of film was peeled from the glass. The average peak load was then calculated from the load versus displacement curve.

Description of laser system

The setup of laser experiment is shown in Figure 2. All laser adhesimeter measurements were accomplished

on a Lambda Physik Starline Nd:YAG laser running at 355 nm in burst mode. The laser is capable of operating with a repetition rate of a few Hz to 1 kHz. The laser pulse duration is 10 ns with an energy of 3.5 mJ at a 1-kHz repetition rate. The radiation mode is 99% TEM₀₀. In the burst mode, the laser may give an output from one to several hundred shots per burst. In this experiment, a burst of 20 shots was used.

Laser delamination test

A series of 50- μ m-thick urethane acrylate coating films were cast on a glass microscope slide by using a draw-down box and cured on a Fusion curing belt as described above. These films were then placed into the beam path of a Lambda Physik StarLine Nd:YAG laser running at 355 nm in the burst mode for a fixed number of pulses at the repetition rate of 10 Hz. The film was exposed to the laser light until the film was delaminated from the slide, as evidenced by the appearance of interference patterns. This period of time to delamination corresponds to the time when the amount of pumped laser energy is equal to the attach-

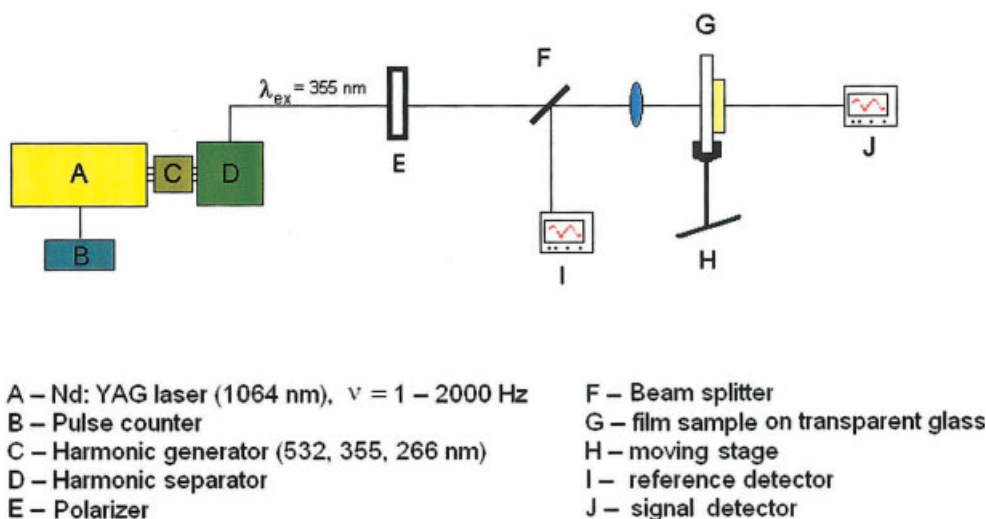


Figure 2 Principal setup of the laser spallation method.

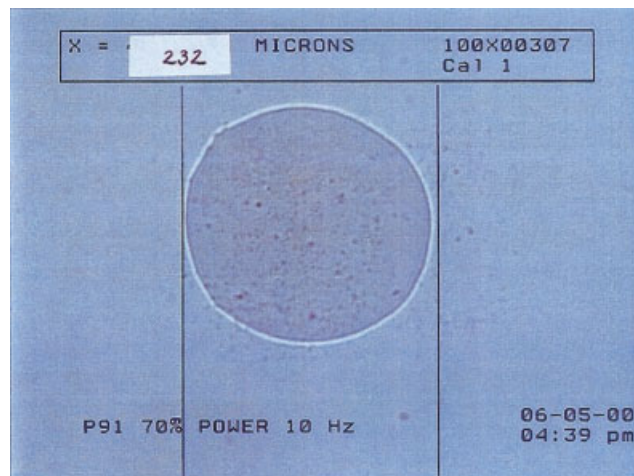


Figure 3 Microphotograph of the polymer film irradiated at 70% of the maximum laser power at 10 Hz repetition rate (taken 10 min after the irradiation).

ment forces holding the film to the glass plate (E_{debond}).

RESULTS AND DISCUSSION

Demonstration of suitability

Due to the possibility of film damage occurring prior to debonding, it was necessary to demonstrate that the technique was suitable for these types of materials. The feasibility of the laser adhesimeter with urethane acrylate coatings adhered to glass was proven by the exposure of several films to the laser beam by the method described in the Experimental. Representative microphotographs of the delaminated film are displayed in Figures 3 and 4 below. As may be observed, it was possible to obtain debonding of the film from the glass without visible damage to the coating such as burning or charring.

Theoretical model

With suitable conditions in hand, it then became necessary to develop a numerical model to describe the threshold adhesion, which would allow the quantitative evaluation of various coating samples. The physical mechanism of coating delamination may be tied to the theory of the laser-induced shock wave which originates during the vaporization of the polymeric material. The pressure generated by this wave causes the weakly bound coating to be separated from the glass substrate. The amount of pressure generated by this wave is dependent on the laser power and the amount of light absorbed by the sample. The physical model which describes the breakdown of the adhesive bond between the glass and film may be rationalized as follows: photons from the excitation beam are absorbed either by the material itself or by a defect

present in the material. This leads to the generation of a free electron, which, in turn, is accelerated by the interaction with another photon. Upon collision of the free electron with the material, an avalanche of free

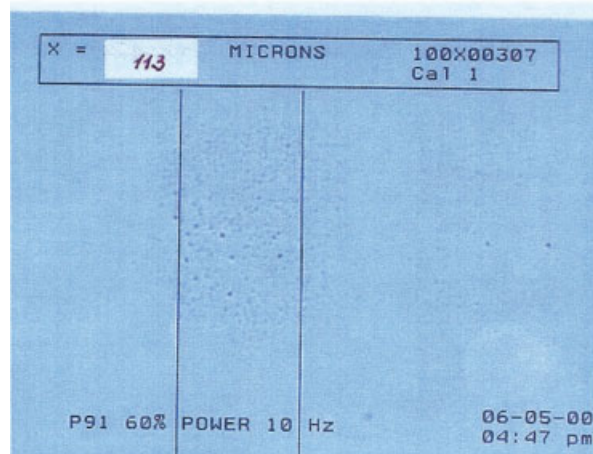
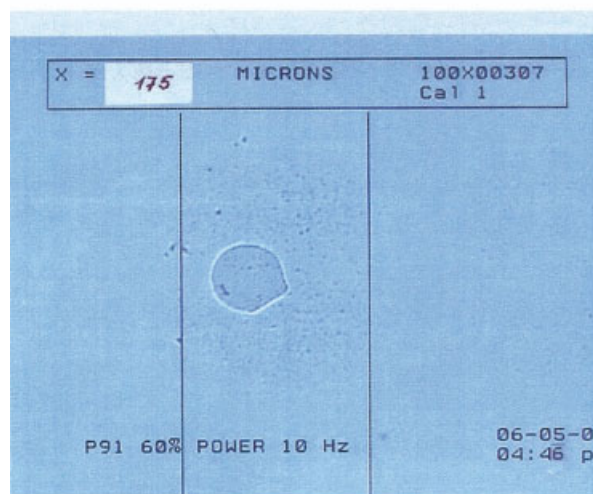
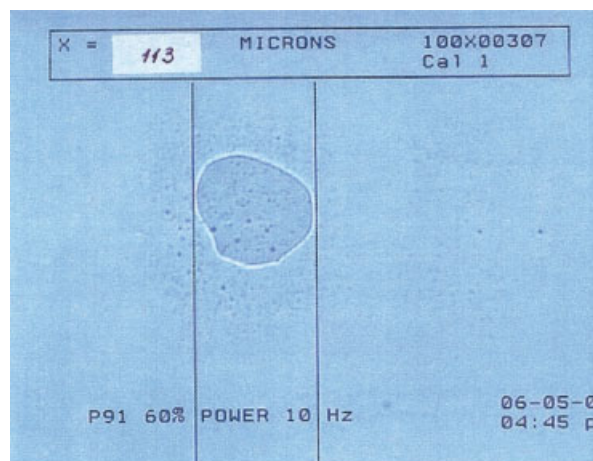


Figure 4 Microphotographs of the polymer film irradiated at 60% of the maximum laser power at 10 Hz repetition rate (taken 15 min after the irradiation with 1-min intervals between each).

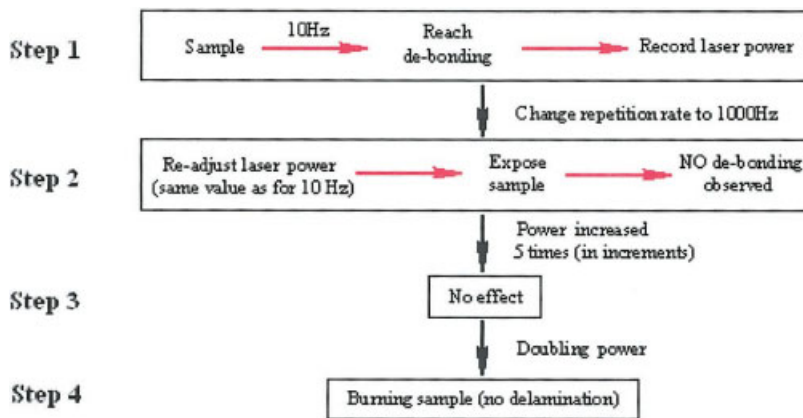


Figure 5 Schematics of continuous wave experiment.

electrons is generated. The resultant plasma microexplosion leads to the generation of a shock wave.

Alternatively, the observed delamination of polymer film from the glass substrate may be explained in terms of simple degradation of polymer material. To verify the mechanism and establish the phenomenological model of the debonding process, a series of experiments was carried out.

Continuous wave (CW) simulated experiment

The question of whether the debonding of the film from the glass was solely a thermally driven event was addressed by a simulated CW experiment. If the adhesive bond breaking is a simple thermal degradation (i.e., $E_{\text{debond}} = kT$), the adhesion will depend only on the amount of laser energy, and not the pulse frequency. The experimental scheme is shown in Figure 5. As described in the experimental section, a 10-Hz pulse rate was used to generate debonding. By increasing laser frequency to a quasi-continuous pulse rate (1000 Hz) to simulate a continuous light wave source, and by reducing individual pulse energy, the same average power was delivered. The experiment demonstrated that when the same laser power that generated a debond at 10 Hz was used in the CW-like experiment, debonding of the film did not occur even after five incremental increases in laser power. When the laser power was increased to 10 times the initial value, film delamination was not observed, but instead sample burning was noted. These results are a clear indication of a high peak intensity effect being necessary to cause a breakdown in the polymeric coating adhesive bond.

Dependence of the debond energy on energy density

A goal of this study was to ultimately verify whether the laser adhesimeter method can be extended to mea-

surements of coating to glass adhesion on optical fiber. Because conducting such measurements will require a tight focus and small spot size, it is important to define the limits on these two parameters. The laser was shown to have a linear dependence of beam size as a function of focus distance (data not included). Consequently, the debonding energy of films of formulation 4 (see Table I) was measured as a function of the focus distance. The debond energy values obtained for this experiment are shown in Figure 6. This data was obtained for two principal regions: with the sample holder in (within 6 mm) and out of focus. It is clear that in both of these cases the debonding energy is directly proportional to the beam area, and it is not a function of energy density. This further indicates that there is no qualitative change in the delamination mechanism when the spot size is changed; therefore, experiments with tight focusing (such as on fiber samples) are feasible.

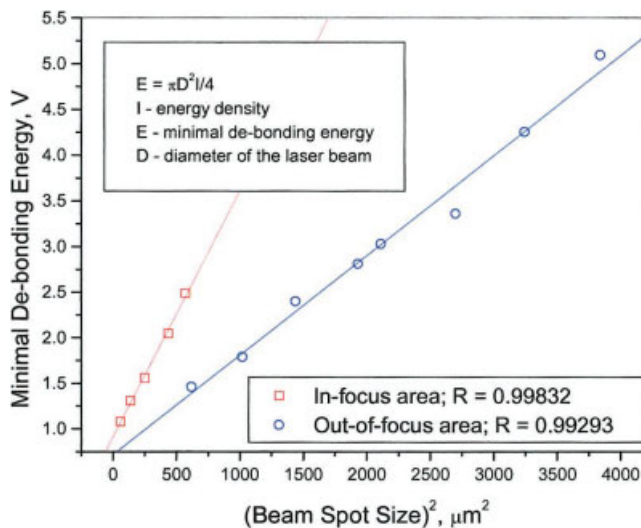


Figure 6 Minimum debonding energy as a function of beam spot size for formulation no. 4.

Mathematical expressions for the calculation of threshold adhesion

The debonding mechanism described in previous sections stipulates that absorption and laser power density are critical variables in the adhesimeter measurements. These two variables are also (to a first approximation) acting independently, and to differing degrees. Combining them leads us to a value called the Threshold Adhesion, which may be thought of as the product of the corrected absorbance of the sample times the energy necessary to cause debonding. Taking all the above into account leads to the equation

$$\text{Threshold Adhesion} = (E_{\text{debond}})^y \times \varepsilon^x \quad (1)$$

where E_{debond} is the debonding energy required to remove film from glass; y is the correction factor for debonding energy; ε is the absorbance of sample at the wavelength of irradiation; and x is the correction factor for sample absorbance.

To obtain the values of x and y , additional steps were required. First, the x/y ratio was calculated by measuring the threshold adhesion for two formulations which have different absorbance at the wavelength of interest, but the same adhesive properties. For that purpose, formulation 4 was spiked with two differing levels of a commercially available UV absorbing compound Tinuvin® 1130 which is not surface active with respect to glass and does not have any major effect on physical properties such as Young's modulus, tensile strength, glass-transition temperature (T_g), etc.⁷ In this case, eq. (2) can be applied

$$(E_{\text{debond}1})^y \times \varepsilon_1^x = (E_{\text{debond}2})^y \times \varepsilon_2^x \quad (2)$$

Solving for x/y gives

$$x/y = \alpha = \frac{\log(E_2/E_1)}{\log(\varepsilon_1/\varepsilon_2)} \quad (3)$$

The debonding energy E_{debond} was measured for formulation 4 with and without the addition of the Tinu-

TABLE II
Adhesion and Absorbance Values for Film Samples Modified with UV Absorber Tinuvin® 1130

Sample no.	Batch	ε_{355}	$E_{\text{debonding}}$ (V)	α_{av}
1	Formulation #4	0.084	3.372	
2	#4 + 0.2 wt % Tinuvin 1130	0.246	2.185	0.389
3	Formulation #4	0.0855	3.7865	
4	#4 + 0.1 wt % Tinuvin 1130	0.1762	3.030	0.394
5	#4 + 0.2 wt % Tinuvin 1130	0.2660	2.469	

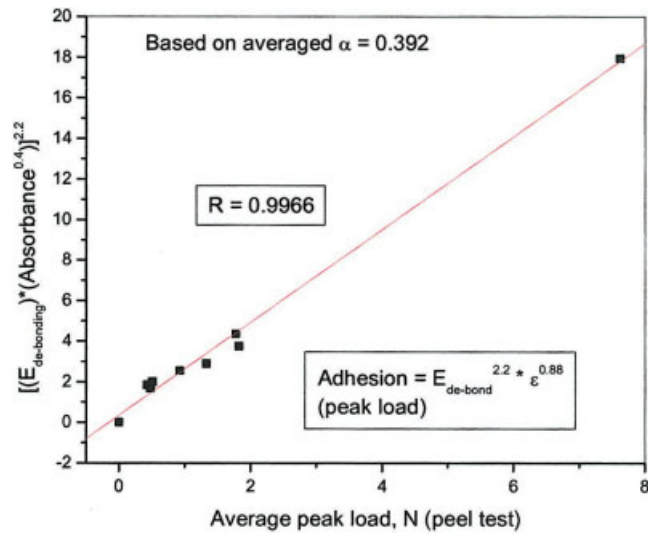


Figure 7 Calculation of y -value from peel test and laser spallation test data.

vin® 1130 in the amount of 0, 0.1, and 0.2 wt % (see Table II).

It may be seen from Table II that the values of α obtained for different loading levels of UV absorber are in close agreement. The final value of α was determined to be equal to 0.392 ± 0.061 after several replications. Equation (1) can now be rewritten as

$$\begin{aligned} \text{Threshold Adhesion} &= (E_{\text{debond}})^y \times \varepsilon^x \\ &= (E_{\text{debond}})^y \times \varepsilon^{\alpha y} = [(E_{\text{debond}}) \times \varepsilon^{0.392}]^y \quad (4) \end{aligned}$$

To calculate y , it was necessary to use the values of threshold adhesion obtained independently by another test method. Peel testing, described in Experimental, was proven to provide reliable data for the coatings of interest. Although the mechanisms of delamination are different for the peel test versus laser spallation, the quantitative ranking of formulations obtained from peel testing should be applicable to generate the value of y . Although an exact calculation from peel test data would be meaningless, it was estimated by plotting data from the laser experiment, $[(E_{\text{debond}}) \times \varepsilon^{0.392}]^y$, versus adhesion data from peel testing (see Fig. 7). This data was then manipulated by choosing arbitrary values of y until the best linear fit with highest regression was obtained. This was accomplished by using the data displayed in Table III, from the formulations listed therein, and graphically in Figure 7. The value of y obtained by this method equals 2.2 and allows one to rewrite eq. (4) as

$$\begin{aligned} \text{Threshold Adhesion} &= [(E_{\text{debond}}) \times \varepsilon^{0.392}]^{2.2} \\ &= (E_{\text{debond}})^{2.2} \times \varepsilon^{0.86} \quad (5) \end{aligned}$$

Bearing in mind the error bars for both laser spallation and peel tests, one can round the values for the two

TABLE III
Calculation of γ -value from Peel Test and Laser Test Data

Formulation no.	Average peak load (N)	$E_{\text{debonding}}$ (V)	ϵ_{355}	$E_{\text{debond}}^{2.2} \times \epsilon^{0.86}$
6	7.61977	9.947	0.081	17.93082
5	1.82426	4.922	0.0793	3.74494
4	1.77944	4.922	0.0943	4.34841
7	1.33122	3.946	0.103	2.88547
14	0.92334	3.815	0.0968	2.53926
9	0.50649	3.194	0.115	1.99289
1	0.4796	2.997	0.11	1.66728
2	0.43029	3.195	0.104	1.82863

exponents in eq. (5), resulting in the value of 1 for absorbance, and the value of 2 for the debonding energy. Given the squared function for the power term, it indicates that the film delamination is a two-photon process. This is a very fair assumption which seems physically reasonable and fits in well with the known general concepts of laser light interactions with organic material.⁸ This phenomena can be explained by the first photon creating a plasma within the material, which then absorbs the second photon. Obviously larger power densities could change this situation, with three or higher photon processes becoming possible, but a two-photon process seems to be likely under our conditions.

Analysis of threshold adhesion data

Measuring the adhesion of the coatings to glass is a worthy goal, but understanding the chemistry which underpins it is of great importance when evaluating coatings, designing new coatings, and understanding fiber performance under field conditions. Assuming that physical contact between the UV crosslinked polymers and the glass substrate is not a variable for these systems, adhesion performance is dominated by the chemistry at the interface, that is, by the ability of the polymer to form strong covalent and noncovalent bonds with the glass surface. This can be accomplished through the incorporation of polar moieties that can form strong polar or hydrogen bonding interactions with the also polar glass surface, and through the incorporation of organofunctional silane coupling agents that can form covalent bonds between the glass and polymer.⁹ Various UV-curable coating formulations were prepared to examine how formulation variables influence adhesion to glass (Table I). The data from Table I is discussed in the following sections as a series of three sets of experiments. In one set of experiments, the coating formulation variable was comonomer polarity. In a second experiment, the effect of varying concentrations of *N*-vinyl-2-pyrrolidinone (NVP), a polar monomer which contains a hydrogen bonding acceptor group, was examined. In addition, organofunctional silane chemistry was ex-

plored. We make no attempt to draw comparisons to the peel test data in this section, as the threshold adhesion calculation incorporates data from the peel test.

Formulation entries **1, 2, 4, 5, 6, 7, 9,** and **14** show the effect of polymer polarity on the adhesion, which was modified by the addition of various comonomers of differing polarity to a formulation. The general trend in adhesive strength observed for this series appeared to roughly follow hydrogen bonding strength.¹⁰ As is apparent from Figure 8(A), entry **6** of Table I afforded the highest value for threshold adhesion in this series and contained the most polar comonomer, acrylic acid, examined in this study. Because acrylic acid contains a carboxylic acid functionality, a known very strong hydrogen bonding group, it would be expected to form the strongest hydrogen bonds with the glass surface. Formulations **1, 2,** and **9** displayed the lowest threshold adhesion, and quite unsurprisingly also contained the least polar molecules: ethoxylated nonylphenol acrylate, caprolactone acrylate, and lauryl acrylate. Although these formulations were expected to have relatively low adhesion to glass compared to **6**, it was anticipated that there would be a slight trend with hydrogen bonding with the following order: **2 > 1 > 9**. Lauryl acrylate contains no hydrogen bonding functional groups, other than the acrylate ester, and would not be expected to have strong interactions with the polar glass surface, whereas the caprolactone acrylate group has multiple ester groups in addition to a hydroxyl functional group, and was expected to impart higher adhesion to glass. The ethoxylated nonylphenol acrylate monomer contains an aromatic group and ether groups which can form weak hydrogen bonding, noncovalent interactions. It may be that the laser spallation method was at the sensitivity limit for these measurements, and, therefore, the expected trend was not observed for this weakly bonding series. The middle portion of the adhesion ranking was held by the formulations which contained amide-bearing monomers of intermediate polarity (i.e., formulations with diacetoneacrylamide, *N,N*-dimethylacrylamide, *N*-isobutoxymethylacrylamide, and *N*-vinyl-2-pyrrolidinone). Within this set of formulations, significant

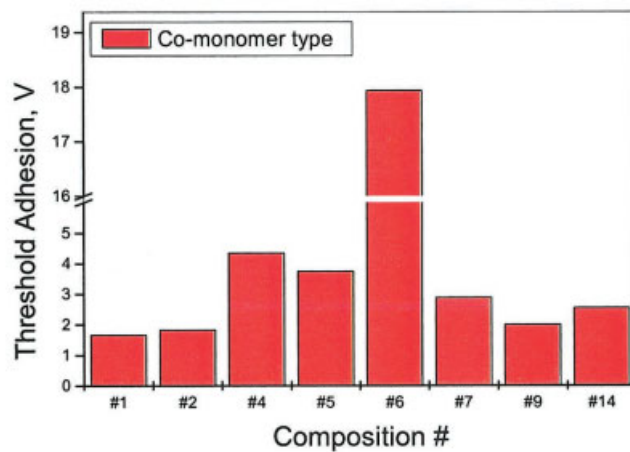
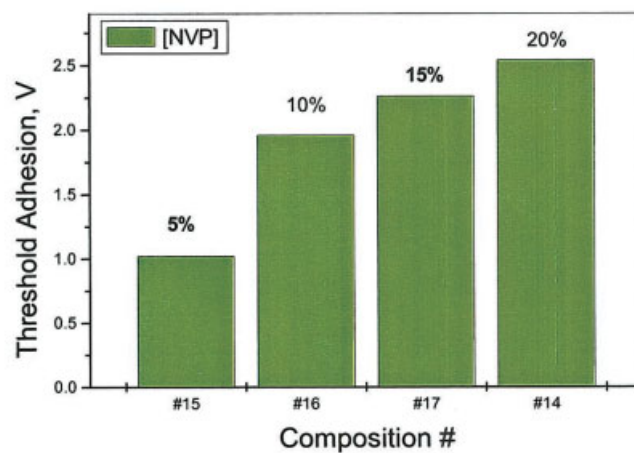
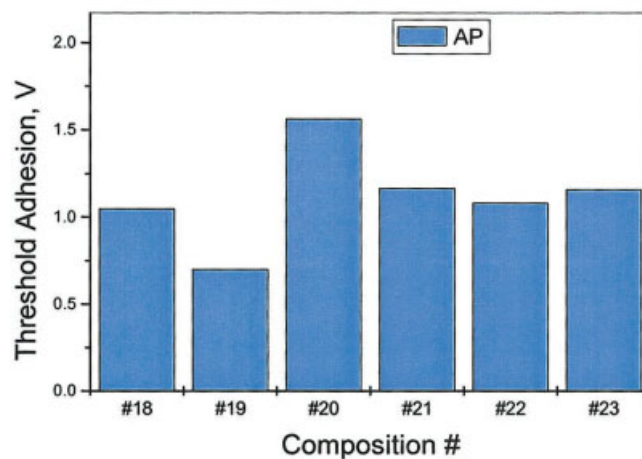
(A) Monomer loading**(B) *N*-vinyl-2-pyrrolidinone (NVP) loading****(C) Adhesion promoter loading**

Figure 8 Dry threshold adhesion as a function of various formulation constituents. (A) Monomer loading; (B) *N*-vinyl-2-pyrrolidinone (NVP) loading; (C) Adhesion promoter loading.

adhesion differences were observed with the following adhesion trend: **4** > **5** > **7** > **14**. Differences in adhesion performance within these formulations are likely due to subtle differences in steric and electronic factors.

Copolymers of NVP were known to improve adhesion properties of adhesive formulations.¹¹ NVP was also commonly used to affect other desirable properties including cohesive strength, T_g , viscosity, water permeability, etc.^{10,12} We were interested in how the concentration of NVP in a UV-curable coatings affected adhesion strength to glass. When the NVP level in a series of UV-curable formulations (see formulations **14**, **15**, **16**, and **17**) was varied from 5 to 20%, the adhesive strength was seen to increase also, as shown in Figure 8(B). The change was not linear, however, with a step increase being observed between 5 and 10%. This implies that once a certain critical concentration of NVP is reached at the glass surface, marked improvements in adhesion may be obtained.

The addition of organofunctional adhesion promoters to coating formulations can provide a method for forming covalent bonds between the glass substrate and the polymer coating or adhesive. Covalent bonding is more effective than noncovalent bonding, such as hydrogen bonding, in providing chemical adhesion to a surface.^{9a} Organofunctional silanes are often incorporated as additives to coating formulations to improve glass adhesion, yet these silanes are added in small quantities so as not to negatively impact other essential coating properties.^{9b-d} Because different organofunctional silanes have different propensities for reacting with glass surfaces and polymers, we examined a variety of silanes for adhesive strength by using laser spallation. For the silane adhesion promoter series, the control formulation **19**, which contained no adhesion promoter, gave a threshold adhesion value of 0.70, the lowest of the series, as shown in Figure 8(C). Formulation **18** contained the bis(trimethoxysilylethyl)benzene (bis AP), which showed a 30% increase in adhesion compared to **19**. In this case, the bis AP cannot form covalent linkages to the polymer network but does promote polymer adhesion to glass. Formulations **20**, **21**, **22**, and **23**, which contained silane adhesion promoters γ -mercaptopropyltrimethoxysilane, γ -acryloxypropyltrimethoxysilane, γ -methacryloxypropyltrimethoxysilane, and γ -glycidoxypropyltrimethoxysilane, respectively, showed significantly improved adhesion over control formulation **19**. γ -Glycidoxypropyltrimethoxysilane in formulation **23** can form linkages by reacting with nucleophilic formulation constituents, thus improving the adhesion. Formulations **20**, **21**, and **22** contain silanes that can form covalent linkages between the glass and polymer, resulting in enhanced adhesion compared to **19**. Nonetheless, these formulations had significantly lower threshold adhesion values than formulations that contained strong hydrogen-bonding monomers, such as

formulations **4-7**. This is likely due to a number of important factors. First, the organofunctional silanes are usually incorporated into formulations in small quantities compared to monomers. Second, organofunctional silanes need to react with water (i.e., become hydrolyzed) that is either already present in the liquid coating, is absorbed on the surface of the glass substrate, or is absorbed into the cured coating from the atmosphere, to condense efficiently with silanols on the glass surface. Although the glass treatment and aging time was kept the same for each series of tests, the process was not optimized specifically for the adhesion promoter study. Third, when added at such low levels, these additives will likely be distributed throughout the coating where only some fraction of the total added amount reaches the glass surface and reacts.

It was sometimes observed that coating formulations with and without silane adhesion promoter had similar adhesion performance as measured by laser spallation. For example, formulations **1** and **3** had essentially the same threshold adhesion values, 1.667 and 1.630, respectively (see Table I). In addition, formulations **2** and **10** indicated only a slight influence of adhesion promoter on threshold adhesion values, 1.829 and 1.738, respectively (see Table I), where only a 5% improvement was observed with the addition of the organofunctional silane. The organofunctional silane of formulations **1** and **2** does not contain a functional group that can covalently bind to the polymer network, which may explain the observed results. However, this particular silane, bis AP, was found to be particularly useful in maintaining coating adhesion to glass in high humidity environments.¹³ Instead of forming covalent bonds with the polymer, the bis AP may promote adhesion through formation of an interpenetrating polymer network.

In addition to silane type, we examined the effect of silane loading on adhesion performance. Formulations **12** and **11** had 0 and 2 pph of bis(trimethoxysilylethyl)benzene and both contained 0.3 pph γ -mercaptopropyltrimethoxysilane. A small dependence on bis AP silane loading was observed based on the laser spallation results with formulation **11** having higher threshold adhesion than **12**. Comparison of formulations **8** and **13** shows the effect of the γ -mercaptopropyltrimethoxysilane loading on adhesion, where both formulations contained 1 pph γ -methacryloxypropyltrimethoxysilane. Formulation **13**, which contained 0.3 pph γ -mercaptopropyltrimethoxysilane in addition to 1 pph of γ -methacryloxypropyltrimethoxysilane, had slightly higher adhesion to glass.

In addition to applying the laser spallation test method to better understand the chemistry of adhesion of polymer coatings to glass, we were interested in relating the laser spallation adhesion test to optical fiber tests used to assess coated optical fiber attributes. We observed that the threshold adhesion obtained

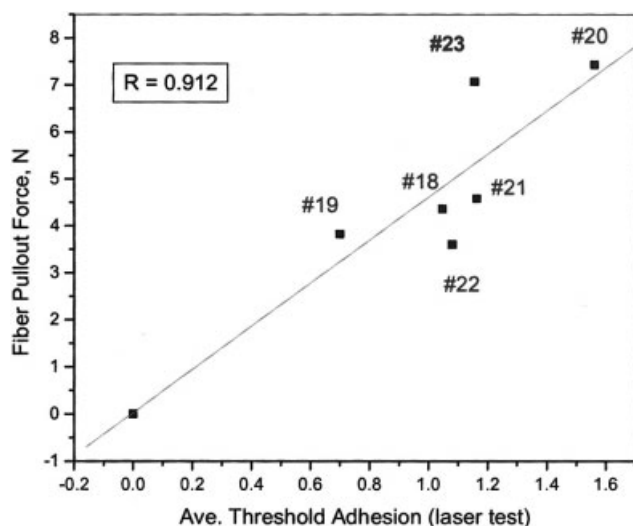


Figure 9 Correlation between laser adhesion data for films and fiber pullout force in the adhesion promoter loading experiment.

from laser spallation was found to correlate with the fiber pull-out test commonly used in the optical fiber industry. Typically this test is used as a measure of adhesive and frictional characteristics of a given coating, although the validity of this test as a true measure of adhesion has been questioned.⁸ The data shown in Figure 9 for formulations 18-23 demonstrated a ball-park correlation between the fiber pull-out results and the threshold adhesion. Scatter in the data could be due to other factors that affect fiber pull-out force, such as coating tensile properties, coating shrinkage, and coating thickness variations.

CONCLUSION

A new method is proposed for measuring coating to glass adhesion on films. Measurements of the adhesive force of a coating film to a glass substrate by a laser delamination technique allow quantification of various factors, such as chemical nature and concentration of monomer, oligomer, and adhesion promoter, on the resulting coating-to-glass adhesion. Obtained values of threshold adhesion are in reasonable agreement with peel testing and fiber pull-out force data.

It appears that the dry adhesion of polymer coating films to glass is largely dominated by the type and

concentration of the comonomer, and, to a lesser extent, by type and concentration of the silane adhesion promoter when the latter is used as an additive at relatively low levels, and is not allowed sufficient time to hydrolyze.

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