

The Properties of Polymer Protective Coatings of Optical Fibers. II. The Influence of Curing Time on Adhesion of UV-Curable Coatings to Fused Silica Surface

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SYNOPSIS

The dependence of adhesion of four various UV-curable protective coatings of optical fibers to the surface of fused silica on the time of UV irradiation was investigated. The maxima of adhesion were observed in short periods of time of curing. Comparison of adhesion values to the hardness, gel content, and contact angles of water measured on the polymer surface revealed that adhesion of epoxyacrylate protective coatings of optical fibers depended on the inner structure of the polymer rather than on its surface properties. This observation was confirmed by IR studies. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

The mechanical strength of high-silica lightguide fibers is, besides their optical properties, the most important parameter determining applicability of these fibers. Beginning from the articles by Maurer,¹ Olshansky and Mauer,² and Kalish and Tariyal³ reporting the first results of the investigations of static and dynamic fatigue of optical fibers, many efforts have been made to understand the dependencies between the mechanical strength of the fibers and their construction and the influence of the environment.⁴ It appeared soon that the strength of optical fibers depend essentially on the properties of their polymer protective coatings.

The polymer coating secures an appropriate mechanical resistance of the optical fiber in two different ways: It protects the surface of silica fiber against water corrosion⁵ and, because of the polymer coating adhesion to the fiber surface, prevents the enlargement of the microcracks and flaws on its surface when the fiber is under strain. The first task is accomplished if the chemical composition and inner structure of the polymer causes a small permeability of water (vapor or liquid) through the thin layer of

the polymer coating the fiber and if adhesion of the polymer to fused silica is complete.⁶

The analysis of the physicochemical phenomena taking place on the polymer-fused silica interface leads to the assumption that the mechanical strength of optical fibers depends to a great extent on the adhesion but not on the water diffusion through the polymer coating, because a well-adhering polymer coating prevents silanol group formation on the silica surface.⁷

Besides, the optical fiber can be considered as a type of composite material composed of a hard glass core and softer polymer coating. Then, the mechanical properties of such a material depend not only on the properties of the glass and polymer but also on adhesion of the polymer to the glass surface.

In the case of the optical fiber, the term "adhesion" should be interpreted not as "ideal" adhesion in its explicit thermodynamic sense but rather as "practical adhesion" in the sense proposed by Adamson.⁸ In our opinion, such an interpretation of the adhesion phenomenon permits one to take into account the properties of fiber components as well as the phenomena accompanying the curing process of the liquid lacquer composition on the fiber.

In a previous article,⁹ we showed that the mechanical properties of UV-cured epoxyacrylic coatings of optical fibers might be regulated by the

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change of their chemical composition, e.g., by the change of the active diluent concentration in the liquid formulation. The second factor regulating the properties of UV-curable coatings may be the dose of UV radiation causing polymerization of the liquid composition. In this study, the influence of the curing time (which is, of course, proportional to the UV dose if the curing process is carried out under stable conditions) on the adhesion of the UV-curable formulation to the fused silica surface was investigated. The measured adhesion values were correlated with the mechanical properties of cured polymers and with the properties of their surfaces.

EXPERIMENTAL

Materials

For the fused silica specimens, 3 mm diameter rods, freshly drawn from the thicker preform in the optical fiber oven, were used. The fused silica was from Carl Zeiss, Jena, Germany.

For the investigated coatings of the optical fibers, four UV-curable formulations were used:

1. Epoxyacrylate formulation ADGD-2,5.⁹
2. Urethanoacrylate formulation ME-82.¹⁰
3. Formulation composed of epoxyacrylates and urethanoacrylates mixed in the weight ratio 4 : 1, ADGD-2,5 + ME-82.
4. Formulation from by DeSolute (DSM Resins International, The Netherlands) as 950-0.175 lacquer.

The properties of the polymers obtained from these formulations are presented in Table I.

METHODS AND APPARATUS

Determination of Adhesion

The term "adhesion" used in this article should be understood as the energy of adherence of a polymer

ring to the fused silica rod but not as adhesion in its explicit thermodynamic sense. The wider discussion of this problem as well as the details of the method of adhesion determination were previously published.¹¹ Generally, the ring of the investigated polymer 1.2 mm thick was cured on a fused silica rod and, next, torn off from the rod using a tensile tester, Tiratest 2200 (Berlin, Germany). It was assumed that adhesion of the investigated polymer to the fused silica surface was equal to the highest strain force registered by the tester, divided by the surface area of contact between the polymer ring and the fused silica rod.

Hardness of Polymer Protective Coatings

Hardness of cured polymers, expressed in Shore degrees, was measured using the Karl Frank hardness tester 38008/38009 (Karl Frank, Weinheim-Birkenau, Germany). The specimens for hardness measurements were produced as follows: A liquid formulation was poured into the PTFE matrix and cured using a 400 W lamp, always maintaining the same distance between the lamp and the specimen, equal to 30 cm. The irradiation process was carried out in an argon atmosphere. The thickness of cured foils was 3 mm.

Degree of Polymerization

The degree of polymerization (gel content) of UV-cured polymers was measured by a 6 h extraction with acetone of a foil of cured polymer in a Soxhlet apparatus. The extracted foil was then dried for 18 h at ambient temperature and then for 6 h at 70°C. The weight loss caused by extraction, expressed as a percent of the initial weight of a foil, was assumed as a degree of polymerization (gel content).

Contact Angle Measurement

The contact angle of water on the foils of cured ADGD-2,5 was measured as follows: A droplet (1 μ L) of water was placed on the surface of cured foil

Table I The Properties of UV-cured Protective Coatings of Optical Fibers

Formulation	Young's Modulus (N/mm ²)	Relative Elongation (%)	Breaking Strength (N/mm ²)	Hardness (° Shore)
ADGD-2,5	729.0	4.8	18.8	75D
ME-82	3.1	52.0	1.1	53A
ME-82 + ADGD-2.5	550.0	28.0	15.0	71D
950-0.175	2.2	125.0	1.9	48A

and the contact angle was measured after 10 min using a telescope-goniometer constructed in our laboratory with precision $\pm 1^\circ$. We found, in the separate experiments, that the stability of water contact angle on the investigated polymers is attained after 5 min of equilibration.

IR Measurements

The IR transmission spectra, obtained before and after UV irradiation of the investigated formulations, were recorded with a double-beam spectrometer Specord M80 (Carl Zeiss) within the range $1800\text{--}1300\text{ cm}^{-1}$. The data obtained were manipulated by an IBM PC computer using a commercial software. The investigated sample was put on the surface of the KRS-5 window and next in a special frame in the sample compartment of the spectrometer. Construction of the frame assured the same position of the investigated sample after UV irradiation.

RESULTS AND DISCUSSION

In Figure 1, the dependencies of adhesion of four UV-curable polymers to fused silica surface in UV-irradiation times are presented. The shape of these

diagrams is rather unexpected: For all four formulations, one may observe the maxima of adhesion. The maxima for epoxy- and urethanoacrylate compositions (diagrams 1 and 2) occur in a very short time of curing, which is equal to 1–2 min, and for the DeSolite one the maximum occurs in 10 min of UV irradiation.

The shape of discussed diagrams for the time of curing longer than necessary for the maximum of adhesion shows that adhesion depends probably on the chemistry of investigated formulations. One can observe the decrease of adhesion for ADGD-2,5 and for the formulation containing 80% w/w ADGD-2,5 down to the level reached in the curing time of 0.5 min only (Fig. 1, diagrams 1 and 3). Adhesion of urethanoacrylate composition (diagram 2) does not depend on the curing time, whereas the adhesion of the DeSolite formulation decreases slowly.

Two questions arise from the data presented above: What is the reason for the adhesion maximum of polymer coatings to the surface of fused silica and why, in the case ADGD-2,5, ADGD-2,5 + ME-82, and DeSolite formulations, adhesion decreases with the increase of the curing time?

The answer to these questions should be researched, taking into account the "ideal" adhesion as well as the "practical" one, thus, the interactions between the surfaces of polymer and fused silica and

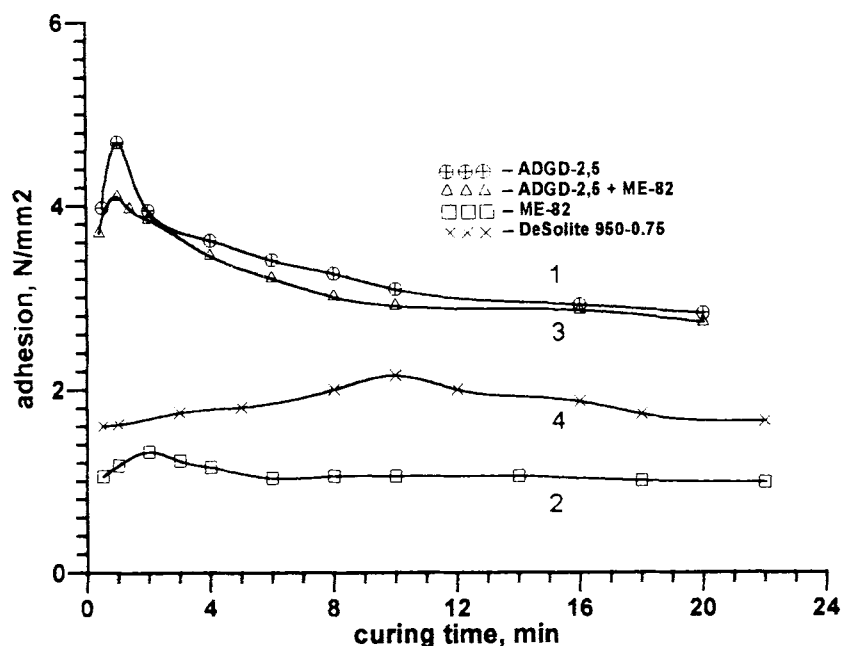


Figure 1 Variation of polymer protective coatings adhesion to fused silica surface with time of UV-curing: (1) ADGD-2,5; (2) ME-82; (3) ADGD-2,5 + ME-82; (4) DeSolite 950-0.75 lacquer.

the properties of a "bulk" polymer, especially the changes of its rheological and viscoelastic properties depending on the UV-curing time. The hardness of cured polymers was chosen as the value representative for these properties, and the relationships between the hardness and the curing time are graphed in Figure 2. One can also observe the maxima in the diagrams presented in Figure 2, but the close correlation of the maxima position in Figures 1 and 2 occurs only for the urethanoacrylate composition. The further run of the hardness - curing time relationship for this polymer (Fig. 2, curve 2) is very interesting: The hardness of ME-82 decreases slowly with the curing time increase, but after 15 min, the hardness decrease is very sudden. The epoxyacrylate coating reaches the maximum of its hardness in 4 min of curing (Fig. 2, curve 1) — at this time, adhesion of this polymer decreases distinctly (Fig. 1, curve 1). Addition of urethanoacrylate oligomer to ADGD-2,5 leads to the shift of the hardness maximum up to 6 min and a more sudden decrease of the hardness with the increase of the curing time (Fig. 2, curve 3). Hardness of the DeSolite coating reaches the maximum in 1 min of curing and, after a small decrease, does not change in the investigated range of curing time (curve 4).

The relationships presented above show that for all investigated compositions the most favorable curing time may be ascribed in which their hardness is the highest. However, it is not clear why the hardness of epoxy- and urethanoacrylates decreases in a longer time of curing, since the shape of the relationship between the gel content and curing time for ADGD-2,5 shows that the process of polymerization follows up to about 15 min of UV irradiation (Fig. 3). Perhaps, the process of polymerization is accompanied by the competitive one: partial degradation of the polymer network which begins just after the time of curing necessary to obtain the maximum hardness. The products of degradation are not extracted with acetone in a Soxhlet apparatus.

Some additional data concerning the photopolymerization process of protective coatings of optical fibers are obtained from IR spectroscopy. For these studies, ADGD-2,5 was chosen because of its relatively simple structure and because this material was most often used in our laboratory as a protective coating of optical fibers.^{9,10}

In Figure 4, the IR spectrum of a liquid composition (a) and spectra of this composition after 2 and 10 min of UV irradiation (b and c, respectively) are plotted. The main changes caused by UV irradiation are observed as the shift to higher frequen-

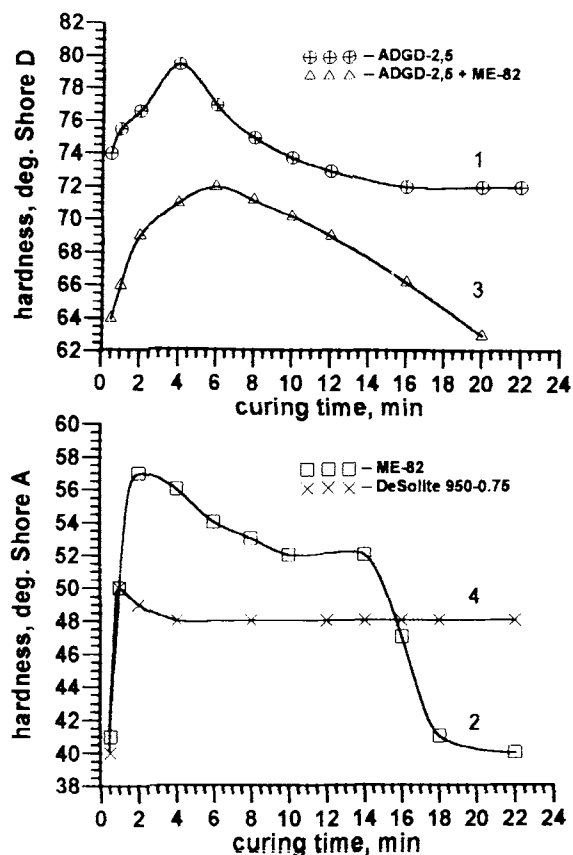


Figure 2 Variation of polymer hardness with the time of UV-curing: (1) ADGD-2,5; (2) ME-82; (3) ADGD-2,5 + ME-82; (4) DeSolite 950-0.75 lacquer.

cies (from 1718 to 1734 cm^{-1}) of a strong band associated with the $\text{C}=\text{O}$ group and the intensity decrease of the bands 1635 and 1408 cm^{-1} . The two last bands are assigned to the $\text{C}=\text{C}$ (1635 cm^{-1}) and $\text{CH}_2=\text{CH}$ (1408 cm^{-1}) vibrations.¹²

In Table II, the changes of frequencies of the bands chosen from Figure 4 are set up, whereas in Figure 5, the changes of the 1635 and 1408 cm^{-1} band intensities caused by the UV are presented.

We propose the following explanation of the changes observed in the IR spectra: The unsaturated bonds occur in the epoxyacrylic oligomer and in the ethylhexylacrylate molecules which are the main components of the liquid formulation. This fact is revealed by high-absorption intensity bands at 1635 cm^{-1} ($\text{C}=\text{C}$) and 1408 cm^{-1} ($\text{CH}_2=\text{CH}$) (Fig. 4). We also observed the absorption bands in the 900–1000 cm^{-1} region (e.g., 984 and 916 cm^{-1}) which could be related to the out-of-plane vibrations of the vinyl groups. The beginning of the photopolymerization is connected to the diminution of the amount of the unsaturated bonds; therefore, the intensity of

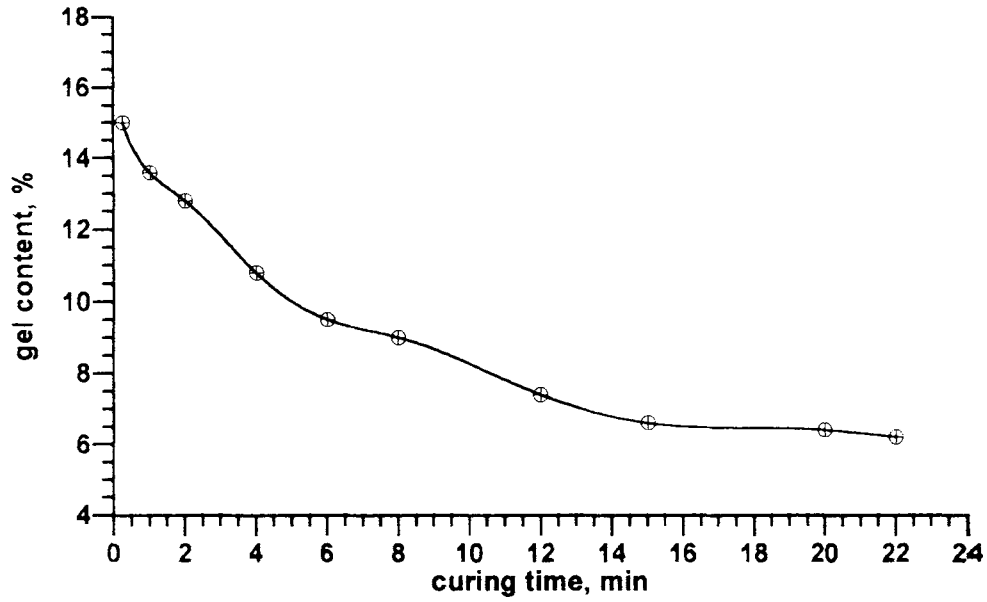


Figure 3 Dependence of gel content on curing time for ADGD-2,5 coating.

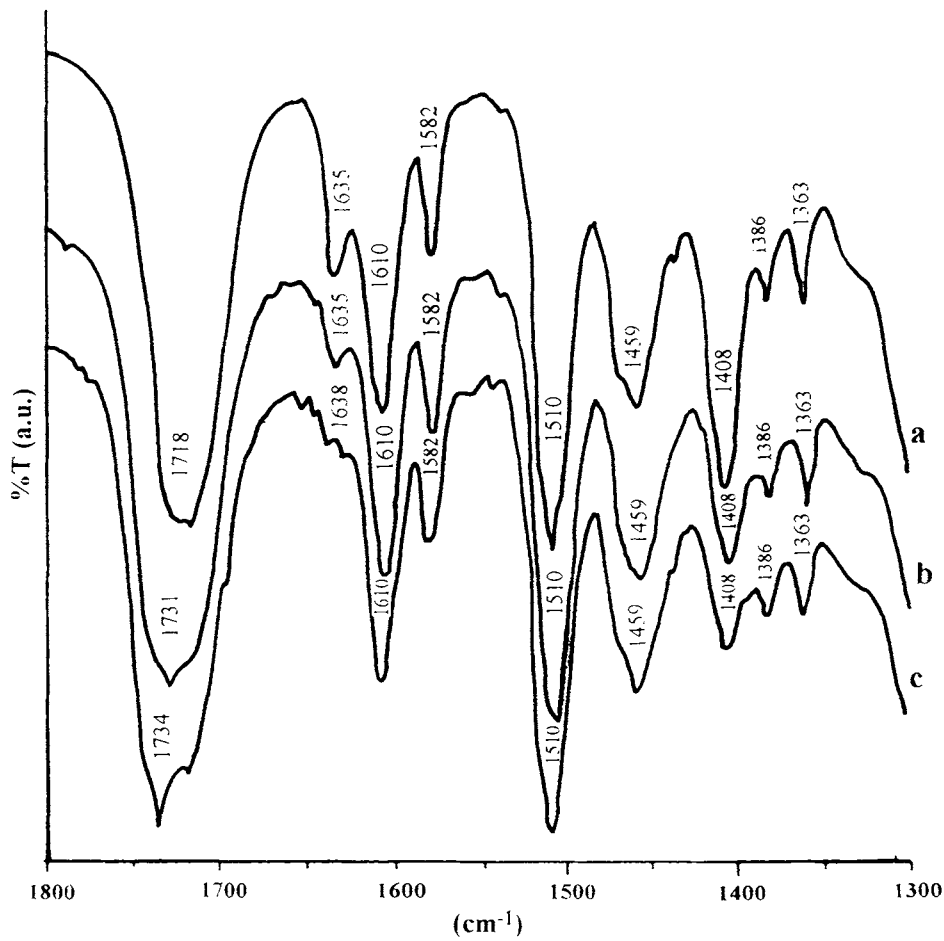


Figure 4 IR spectra of ADGD-2,5 sample (a) without and (b) after 2 min and (c) 10 min UV irradiation.

Table II The Frequencies of Significant Bands in the IR Spectra

Assignment	Band Position in Spectrum (cm^{-1})		
	<i>a</i>	<i>b</i>	<i>c</i>
C=O	1718	1731	1734
C=C	1635	1635	1638
CH ₂ =CH	1408	1408	1408

the bands at 1408 and 1635 cm^{-1} must decrease [Fig. 5(a)]. The diminution of the amount of unsaturated bonds causes also the shift of vibrational modes associated with the C=O group to the higher frequencies (Table II).

The data presented in Figure 5 give ground to the assumption that the photopolymerization is very quick — probably, the majority of unsaturated bonds are used up in the generation of the polymer network during the first minute of UV irradiation. Nevertheless, the intensity of the absorption band at 1635 cm^{-1} decreases slowly but continuously also in a longer time of curing. It means that the number of unsaturated bonds also decreases slowly. Therefore, the IR data confirm the conclusion resulting from the gel content vs. the curing time relationship (Fig. 3) that the polymerization process follows up to 15 min of curing.

As seen in Figure 6, where the water contact angle on the ADGD-2,5 surface was plotted vs. the time of curing, not only the properties of the bulk polymer but also its surface properties depend on the time of UV curing. The initial increase of the contact angle value means that the polymer surface becomes more hydrophobic. This phenomenon may be explained by the decrease of the number of unsaturated bonds in the mixture of the epoxyacrylic oligomer and the active diluent and by a possible depolarization of the oxygen-containing moieties of the reacting molecules. The maximum of the contact angle value is reached in 2 min of curing time. As was shown by the IR measurements, at this time, the polymerization process is almost finished. However, the increase of curing time leads to the decrease of contact angle — the polymer surface becomes more hydrophilic. After about 10 min of curing, the value of the contact angle stabilizes at 55°C. Similar values of water contact angles were found for poly(methyl methacrylate), poly(vinyl chloride), and agarose.¹³

It is generally accepted that the adhesion of two substances being in contact is high if their surfaces can interact specifically, e.g., if the polar interactions contribute to the interfacial energy.¹⁴ It seems that this is not the case for fused silica optical fibers. The silanol groups practically do not occur on the surface of fused silica fibers drawn at the temperature of about 1800°C.¹⁵ Then, the surface of such a fiber

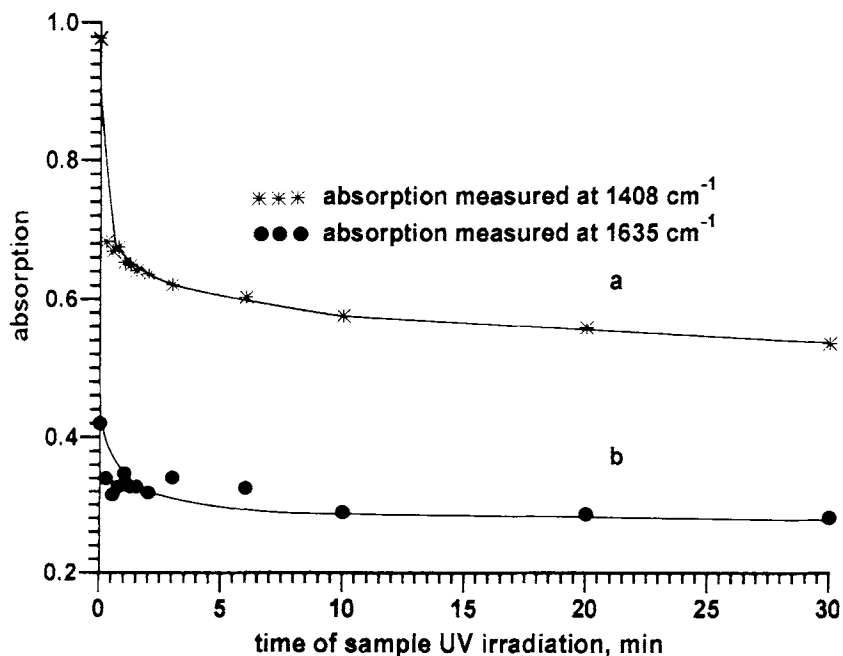


Figure 5 Influence of the ADGD-2,5 UV irradiation on the change of absorption intensities at 1635 and 1408 cm^{-1} .

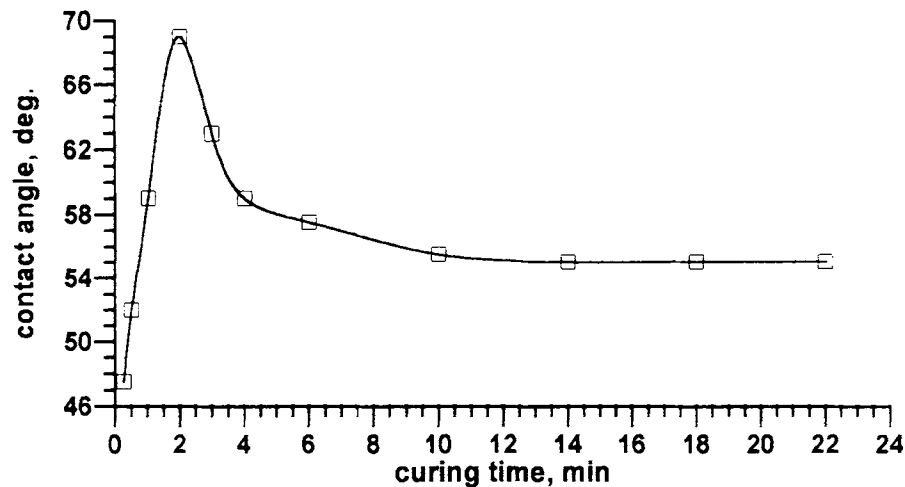


Figure 6 Dependence of water contact angle on the curing time of ADGD-2,5.

(and the surface of fused silica rods used in the reported experiments) is almost totally dehydroxylated and contributes to the interfacial energy by dispersive forces only. The hydrophobic character of ADGD-2,5 cured 2 min (Fig. 6), i.e., near the maximum of adhesion (Fig. 1, curve 1), shows that this surface also does not contribute to interfacial energy by the polar interactions. Therefore, it seems that the change of the ADGD-2,5 character, caused by UV irradiation, is not the main reason for the adhesion maximum of the epoxyacrylate coating in 1 min of curing and the decrease of adhesion in longer times of curing. Probably, this is caused by the changes of the inner structure of polymer formed during UV curing and connected with this phenomenon, e.g., shrinking of the polymer coating.

CONCLUSIONS

The results of the investigations of the UV-cured polymer adhesion on the fused silica surface may be of great importance for optical fiber technology. They show that the adhesion of protective coatings depends on the chemistry of these coatings as well as on the UV-curing time. The latter factor may be used in order to regulate the mechanical properties of optical fibers.

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