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Study of Adhesive Properties of Organosilicon Coatings for Fiber Optics

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The adhesive strength of various organosilicon compositions used as coatings for optical fibers is investigated. The objective of the study is to develop an understanding of the effects of chemical composition and manufacturing conditions on adhesive characteristics of the coatings.

KEY WORDS Optical fibers, coatings, organosilicons, adhesion, processing conditions.

INTRODUCTION

Organosilicon compositions with accelerated curing such as; Sylgard series in USA[1]; or, XE in Japan,[2] and SIEL in Russia[3] are commonly used as light-reflective, filtering or buffer coatings for fiber optics. In order to stabilize the fiber optics properties and to facilitate the further processing into the cable, the primary coating should be covered immediately after the application of the first coating by a secondary strengthening coating. The secondary coating should be abrasive-resistant and have high adhesive strength through the interaction with primary coating. Polyarylatesiloxane blockcopolymers (PAC) are widely used in Russia as strengthening coatings. Similar polymers are also commonly used for the same purpose in USA.[4–6] The application of the STYK-type organosilicon compounds as assembly adhesives provides the possibility of producing various structural materials from finished optical fibers.[7]

One of the main requirements of the fiber optics coatings is good adhesion of the coating to the fiber (quartz) core and high adhesive strength between the primary and secondary coatings. The coating compound should adhere well to all optical fibers components and to metal substrates. A knowledge of the mechanisms of the properties change in adhesive coatings is required to predict the optimal fiber optics production. However, fiber optics elements are frequently chosen without a proper evaluation of their adhesive properties. This is because of the lack of a technique for the determination of adhesive strength between the coatings and fibers. This article describes an attempt to develop such a technique.

Adhesive strength of SIEL, STYK and PAC compounds to fibers and elements of optical fibers and bonding strength between coatings in industrial fiber optics were investigated. The effects of; a) chemical composition of the coatings and b) conditions of formation of coatings on fibers were studied.

EXPERIMENTAL

To evaluate the adhesion of investigated compositions to the fibers surface, the strength τ of polymer-fiber joints was measured using the pull-out technique.[8] The sample scheme is shown in Figure 1a. The samples were either oven cured at elevated temperatures or by accelerated electron beam at room temperature. The joints were tested on a single-sample adhesion tester at room temperature and constant rate loading. The loading force was measured by means of pressure sensor DD-10 and pressure indicator UD-24 and recorded on a "KSP"-type recorder. The testing equipment is shown schematically in Figure 2.

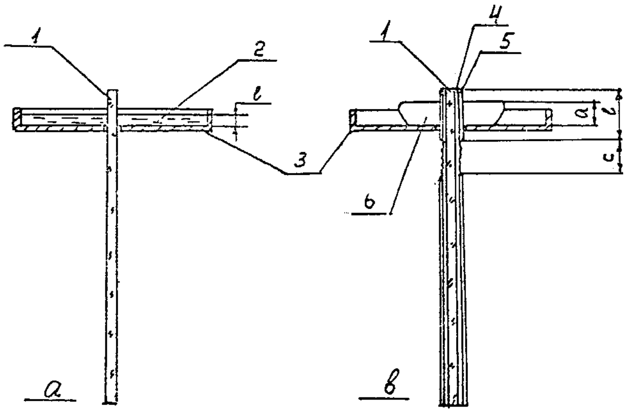


FIGURE 1 Scheme of specimens for adhesive strength determination in joints: a) polymer-fiber; b) optical fiber portion with double coating. 1—fiber; 2—polymer; 3—aluminum mould; 4—primary coating; 5—secondary coating; 6—additional layer of the secondary coating.

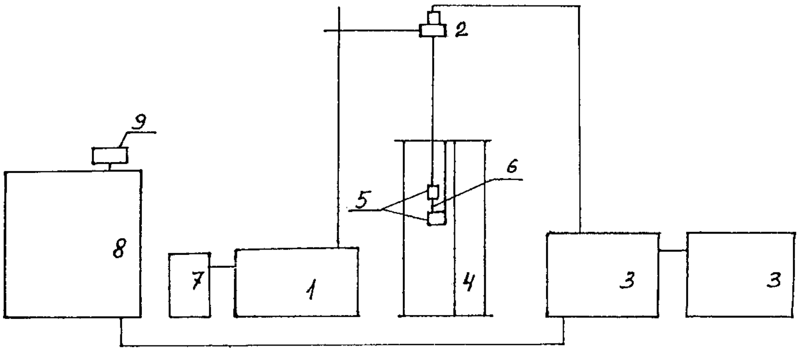


FIGURE 2 Scheme for load measuring. 1—loading block; 2—sensor "DD-10"; 3—pressure indicator "ИЛ-2И"; 4—a device for clamping of specimen; 5—movable and unmovable clamps; 6—tested specimen; 7—laboratory autotransformer; 8—recorder "KCII-4"; 9—resistance cell.

The specific preparation of the samples allowed us to apply this technique for measuring the bonding strength between coatings in industrial fiber optics τ_{1-2}.[9] The samples schematic is shown in Figure 1b. For testing, the optical fiber section with cut off secondary coating on the site "c" was inserted into an aluminum mold with a hole in the centre. Then on the site "a" an ancillary layer of the same secondary coating was applied from the solution in chloroform. The ancillary layer did not fill the entire volume of the mold but was formed only in the immediate vicinity of the fiber because of rapid evaporation of the solvent. The adhesion to newly formed ancillary layer was usually so strong, that after the load was applied to the joint the fracture took place at the interface between the primary and secondary coatings. The failure characteristic is described in detail below. The outlined technique for samples preparation allowed us to obtain adhesive joints with sufficiently small contact area "S" of polymer-to-fiber and polymer-to-polymer to avoid samples cohesive (across the fiber) failure under external loading.

Adhesive strength value of each tested joint (Figure 1a) was found from the equation $\tau = F/S$, where F is the force of fiber pull-out from the polymer layer; S is the contact area between the polymer and fiber. S was calculated as lateral surface cylinder with a diameter equal to the fiber diameter "d" and a height equal to the joint length "l," $S = \pi dl$. Fiber diameter was measured by a micrometer with an accuracy of 10 μm, and its length was measured either by a point micrometer or under the optical microscope of "MPB-2-type" with an accuracy of 20 μm. The failure characteristic was recorded simultaneously.

The failure was also supposed to occur on a cylinder with surface diameter "D" equal to the diameter of the fiber with the primary coating $D > d$ when bonding strength between optical fiber coating τ_{1-2} (Figure 1b) was calculated. SIEL, PAC and STYK compositions were used as adhesives.

1. SIEL-type compounds of accelerated curing are compositions based on low-molecular vinyl containing organosilicon rubbers and oligoorgano-hydride siloxane cross-linking agents.[10] They are cured by polyadditional reaction in presence of platinum catalysts at $T_{\text{cure}} = 150°\text{C}$. As a result of polymerization, the elastomeric coatings with the refraction index in the range of $n_D = 1.38–1.51$, were obtained capable of preventing microbending of fibers and loss of light filtering function. These coatings are efficient within a temperature range of $-80– +250°\text{C}$ and thermostable on long term ageing and exposure to radiation.[11]

We have investigated 2-component SIEL-1 and SIEL-2 compositions. SIEL-1—is a compound based on α,ω-bis(trivinylsiloxy)oligomethyl-siloxanes and α,ω-bis(trimethylsiloxy)oligomethylhydridesiloxanes; SIEL-2—is a compound where besides the components of SIEL-1 methyl-γ-trifluorpropylsiloxy units are present (see Scheme I).

The strength of joints of SIEL-quartz fiber with a diameter $d = 290$ μm was studied. The polymers were cured at the temperature $T_{\text{cure}} = 150–340°\text{C}$, curing time t_{cure} varied from one minute to 280 hours.

2. Polyarylate siloxane block-copolymers (PAC) produced by homophase polycondensation method of oligoarylate diols (OA is a copolymer of phenolphtalein and clorane hydride of terephthalic acid with MM 4650) and α,ω-bis(cloroformiato)oligoorganosiloxanes with various setting (see Scheme II). PAC

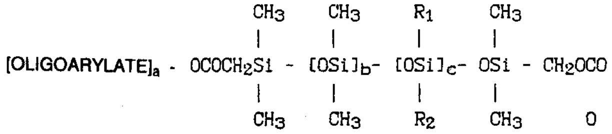
$(CH_2\text{-}CH)_3SiO\{[(CH_3)_2SiO]_m[R^1CH_3SiO]_l\}_xSi(CH\text{-}CH_2)_3$

R^1- $CH_3, CF_3CH_2CH_2$; m-100-300; l-0-70; MM-(80-100)x10^3

$(CH_3)_3SiO\{[(CH_3(H)SiO]_a[(CH_3)_2SiO]_b[R^1CH_3SiO]_c\}_ySi(CH_3)_3$

a+b+c-1; a-0.2-0.4; c-0-0.5

SCHEME I Common formula of SIEL.



$$[\text{OLIGOARYLATE}]_a\text{-}OCOCH_2\underset{CH_3}{\overset{CH_3}{Si}}\text{-}[O\underset{CH_3}{\overset{CH_3}{Si}}]_b\text{-}[O\underset{R_2}{\overset{R_1}{Si}}]_c\text{-}O\underset{CH_3}{\overset{CH_3}{Si}}\text{-}CH_2OCO$$

a-8-13; b-0-126; c-0-95; n-4-12; R_1-H, C_2H_3, C_2H_5; R_2-CH_3, C_2H_5

SCHEME II Common formula of PAC.

$\{[CH_3(H)SiO]_a[(CH_2\text{-}CH)SiO_{1.5}]_b[R^1SiO_{1.5}]_c[R^2(CH_3)SiO]_d\}_x$

a+b+c+d-1; a-b; R^1-CH_3, C_6H_5; R^2-CH_3, $CH_2CH_2CF_3$

SCHEME III Common formula of STYK.

are white powders. They are used as coating from solutions in clorinated hydrocarbons (methylene chloride, chloroform). PAC-films have good physical-mechanical properties (tensile strength is 20–40 MPa, elongation is 20–120%). They are thermostable and frost resistant (efficient within a temperature range of −60–+200°C) as well as wear resistant.[12]

The strength of joint PAC-steel fiber with a diameter d = 150 μm was investigated. Initial samples have been produced from PAC at room temperature in solvent medium. Samples, thermally treated at 200°C during 7 hours or irradiated by an accelerated electron beam in doses 250–1200 kGr, were also studied. Irradiation was carried out using electron accelerator of "ELV-8"-type. The experimental conditions were; accelerated electron energy = 165 MeV, accelerated electron current = 6,5 MA, dose range = 10–4000 kGr.

3. STYK-type compounds are compositions based on polyorganohydride-vinylsiloxanes with statistic distribution of vinyl and hydride groups vulcanizing by polyadditional mechanism (see Scheme III). After curing they become transparent solid products suitable for polishing and grinding. Being close analogs of epoxy compounds in cured state as far as physicomechanical properties are concerned, they are noted for better thermal stability (working temperature range is −60–+200°C) and minimum loss of beam flux under the operation conditions of optical fibers.[7]

We have studied the strength of STYK-steel fiber (d = 150 μm), STYK-melted quartz fiber (d = 200 . . . 300 μm) joint as well as the adhesion to optical fibers, coated by SIEL (d = 410 μm) or PAC (d = 450 μm) compounds. STYK-compounds have cured between T = 160–180°C in non-isothermal conditions (the temperature elevation rate was 1°C/min) in presence of platinum catalysts STYK-compounds were also been cured by a beam of accelerated electrons at irradiation doses of 250–1200 kGr.

TEST RESULTS

1. Adhesive Properties of SIEL

The study of the adhesion of primary coatings to quartz fibers showed that regardless of curing conditions and polymer chemical composition, the cohesive fail-

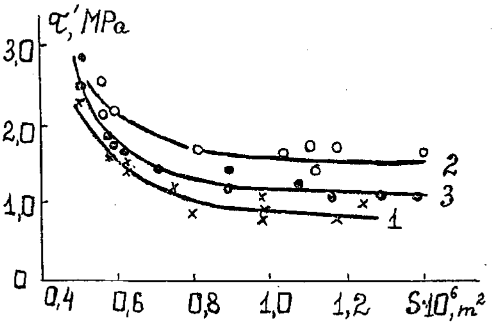


FIGURE 3 Dependences of SIEL-quartz fiber joints strength on contact area. $T_{exp} = 20°C$; $T_{cure} = 150°C$; $t_{cure} = 6$ hours; $l/d = 1.5 \ldots 5.5$; rubber molecular mass: 1—30×10^3; 2—70×10^3; 3—90×10^3.

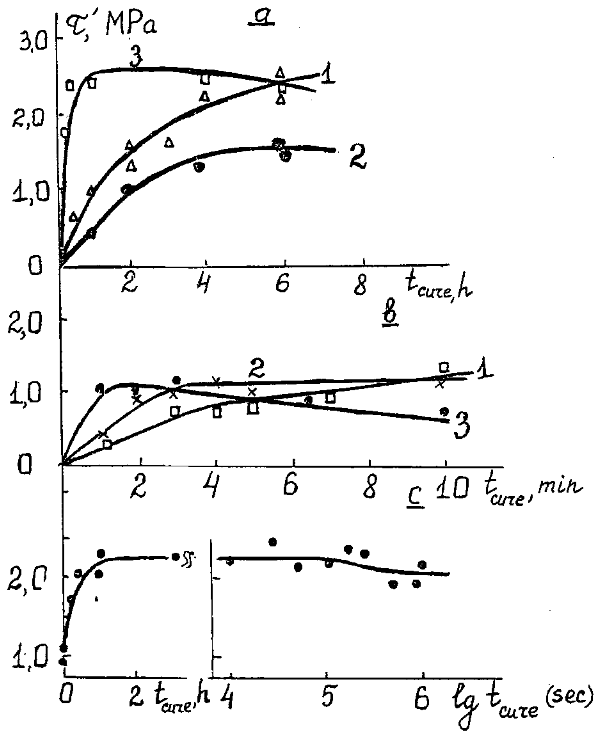


FIGURE 4 SIEL-quartz fiber joint strength as a function of cure time. Rubber molecular mass 70×10^3; $T_{exp} = 20°C$. a) $T_{cure} = 150°C$ (1,2); $T_{cure} = 200°C$ (3); 1,3—$S = 0.6 \times 10^{-6} m^2$; 2—$S = 1.2 \times 10^{-6} m^2$; b) $T_{cure} = 250°C$ (1); 300°C (2); 340°C (3); $S = 0.6 \times 10^{-6} m^2$; c) $T_{cure} = 300°C$; $t_{cure} = 3$ min; $T = 200°C$; $S = 0.6 \times 10^{-6} m^2$.

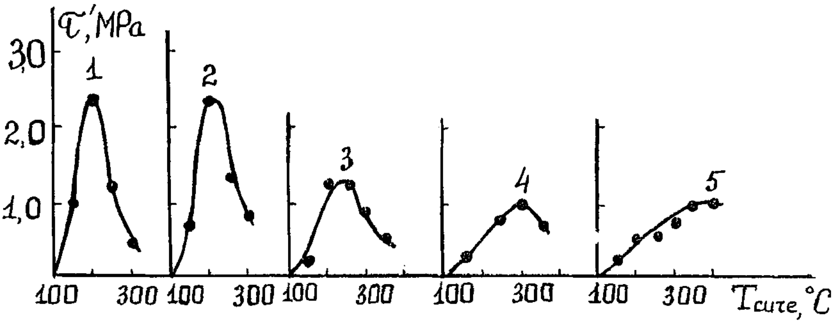


FIGURE 5 SIEL-quartz fiber joint strength as a function of curing temperature. Rubber molecular mass 70 × 10; T_{exp} = 20 C; $S = 0.5 \times 10^{-6}m^2$. t_{cure} = 1 hour (1); 30 min (2); 10 min (3); 5 min (4); 2 min (5).

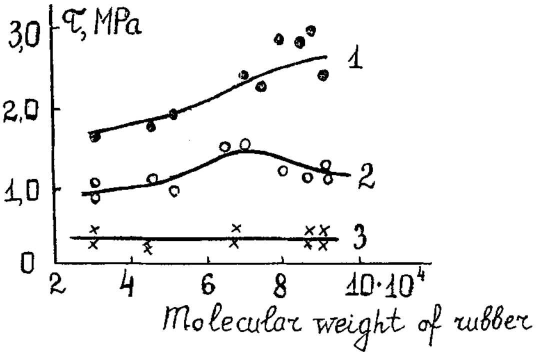


FIGURE 6 SIEL-quartz fiber joint strength as a function of rubber molecular mass. T_{cure} = 150°C; t_{cure} = 6 hours; T_{exp} = 20°C; $S = 0.6 \times 10^{-6}m^2$ (1), $S > 1.0 \times 10^{-6}m^2$ (2,3). 1,2—30% of crosslinking agent in a mixture; 3—3% (stoichiometric composition).

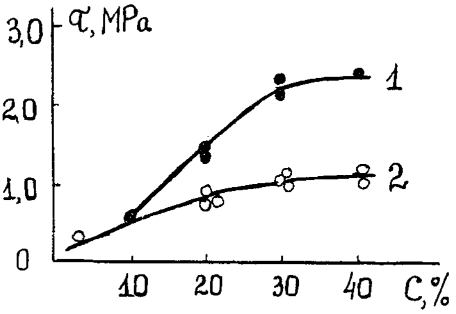


FIGURE 7 Effect of crosslinking agent quantity ($C\%$) per 100 parts by weight of mixture on SIEL-quartz fiber joint strength. T_{cure} = 150°C; t_{cure} = 6 hours; $T_{exp}O$ = 20°C. Rubber molecular mass 30 × 10^3; $S = 0.5 \times 10^{-6}m^2$ (1); $S = 1.0 \times 10^{-6}m^2$ (2).

ure within a binder took place with less than 50 μm thick polymer layer remaining on the fibers. This shows that the bonding strength between the investigated compositions and quartz fiber is rather high. We shall indicate the shear strength in the case of cohesive failure within the near-surface layer by the symbol τ^1. It turned out that strength values, calculated by means of equation $\tau^1 = F/S$ depend on joint area at small S (l/d = 1–3) (Figure 3). Such behavior is typical, as it is shown in Reference 8, for fiber-polymer joints tested at temperatures that are higher than the glass transition temperature of the adhesives which fail at the interface. Since the glass transition temperatures T_g of siloxane elastomers SIEL-1 and SIEL-2 are below −100°C, they fail in the thin near-surface layer.

The bonding strength between the investigated polymer composition and quartz fiber depends considerably on curing conditions. Figure 4a, b demonstrate that as polymerization period is increased, τ^1 values exhibit a curve with a maximum. If curing temperature is low enough and time is limited, interface strength does not reach its peak and we can see either an increasing section of a τ-T_{cure} curve or a τ^1 curve with a plateau. The higher the cure temperature, the faster the adhesive strength reaches the maximum value. For a given system this value decreases with increasing temperature of curing (Figure 5). For T = 150°C, the peak strength equals to 2.5 MPa and can be attained within one hour. When curing temperature is elevated up to 340°C, the bonding strength attains its peak of 1.2 MPa in a minute. More prolonged exposure at this temperature results in cracks when the fibers are pulled out. This indicates the polymer embrittlement took place.

Figure 4c shows the results of adhesive strength tests after long-term ageing of joints at T = 200°C. The preliminary vulcanization during 3 minutes at T_{cure} = 300°C results in τ^1 value of 1.0 MPa.

Further exposure to 200°C increases the bonding strength. Consequently, relatively low τ^1 values, attained at short-term composite exposures to high temperatures, can be increased by means of this treatment. The τ^1 values can be both dependent (Figure 6, curves 1,2) and independent (curve 3) of the molecular mass of the rubber. The absolute value of τ^1 depend on the amount of cross-linking agent (Figure 7). Note that it is inefficient to increase the amount of cross-linking agent beyond 30–35%.

II. Adhesive Properties of PAC

Twelve series of PAC containing dimethylsiloxy units (DM), methyl-hydridesiloxy units (MH), diethylsiloxy units (DE), methylvinylsiloxy units (MV) and their combinations (see Table I) have been studied to optimize the secondary (protective) coating compositions. Steel fibers with a diameter of d = 150 μm have been used as a substrate of joints to determine adhesive strength of such a large number of polymers. It is much easier to make measurements with such joints than with joints where quartz fibers coated with a SIEL film are used as a substrate. At the same time it can be assumed that the obtained relationships may be used to select the secondary coating for quartz fibers coated with the primary coating. Results of these experiments are presented in Table I. It should be noted that in general, the increase in siloxane component content in copolymer leads to a decrease in adhesive strength. The behavior is independent of the type siloxane blocks and the curing methods. However, the value of adhesive strength and its change on thermal treatment or on electron beam treatment is a function of chemical composition and the amount of siloxy units. A larger strength increase was observed with methylvinyl groups in siloxane blocks after thermal treatment, than with other compositions.

TABLE I

The effect of organosiloxane block composition, accelerated electrons and thermal treatment on PAC[x)] adhesive strength to steel fiber

Series number	Siloxane block properties		Adhesive strength б,MPa			
	$\bar{M}_n$	Siloxy units composition and quantity, mol%	Initial samples	Samples after:		
				Irradiation in doses,kGr		Thermal treatment 200°C/h
				250	1200	
1	2	3	4	5	6	7
1	Polyarylate "FV-2"-type		8.9	9.5	8.5	9.2
2	3500	DM - 100	5,0	4.7	4.0	4.8
3	7870	" - "	1.0	1.8	1.7	1.6
4	9640	" - "	0.2	0.3	0.9	0.3
5	2620	MH - 100	6.2	5.8	9.0	7.6
6	3340	" - "	2.8	1.8	2.2	3.7
7	2110	DE - 100	3.7	4.5	9.0	4.6
8	3500	MV - 100	2.5	6.0	10.5	9.0
9	5000	" - "	0.4	2.7	6.0	6.2
10	8400	" - "	0.3	0.4	3.0	2.1
11	3130	MV - 50 DM - 50	3.4	4.2	7.7	9.1
12	2660	MH - 50 DM - 50	3.9	2.6	7.7	8.6

x) $\bar{M}_n$ - oligoarylate diol 4650

The same trend is observed on radiation treatment by accelerated electrons at low dose of 250 kGr.

With the increasing dose τ value increases for all compositions and in specific cases the values exceed those achieved by thermal treatment. It should be noted that in all experiments the failure occurred along the interface. Thus, adhesive strength of PAC-steel fiber systems is a function of total siloxane component content in copolymers, of the type of siloxane block and of conditions of joints formation.

III. Bonding Strength between Coatings in Fiber Optics

As noted above, one of the principal requirements to protective-reinforcement coatings is the high bonding strength to the primary coating. The effects of chemical composition of coating and the conditions of fiber optics treatment, on bonding strength of fiber, primary and secondary coatings systems have been studied. Specimens of commercial optical fiber with SIEL-1 or SIEL-2 primary coating and secondary coating with reactive dimethyl siloxane blocks or with dimethylsiloxane block modified by MH and MV groups were studied. As shown (Table I) MV and MH-groups introduction into secondary coating improved adhesion to steel wire.

It may be expected the same PAC—will be advantageous for use in fiber optics. However, PAC containing considerable portion (more than 15 mol%) of reactive units in siloxane blocks tend to develop structures under storage. Therefore, we restricted our studies of adhesion between fiber optics polymers to polyarylate-siloxane block-copolymers containing no more than 6–12 mol% of reactive groups in siloxane block. We studied untreated specimens, as thermally treated specimens at 200°C for 1 . . . 70 hrs and radiation (accelerated electron beam) treated samples at doses up to 4000 kGr. The starting specimens are optical fiber with fiber quartz core of 125 or 250 μm diameter, obtained at drawing rate of 420 m/min. Primary coating was applied at temperatures between 300–350°C, the secondary coating was applied from chloroform solution at temperature between 100–150°C. Experimental results are given in Table II and in Figures 8 and 9. The data in Table II show that bonding strength between surfaces of starting specimens depends on the secondary coating composition. As expected, the introduction of MV groups into the secondary coating gives maximum values of bonding strength in starting specimens. This confirms the usefulness of PAC-steel fiber adhesion studies.

The thermal treatment and large dose radiation (4000 kGr) improves the adhesive interaction between coatings for all compositions under study. It should be noted, that with reactive groups in secondary coating the adhesive interaction of coatings is almost independent of the primary coating composition. In the absence of reactive groups in PAC specimens the effect of chemical composition of primary coating effect is significant, particularly after thermal treatment. For primary coatings with γ-trifluoropropyl groups τ_{1-2} values were raised by 15 to 20 and more in each experiment. This holds also for the radiation treatment (Figure 8). Prolonged heat ageing (at 200°C for 70 hrs) does not have a marked effect on τ_{1-2} (Figure 9). The change in fiber core diameter from 125 up to 200 μm has no effect on the bonding strength. The type of failure is determined by the bonding strength between coatings. The adhesive failure at coatings interface was observed with relatively low $\tau_{1-2} < 0.6$ MPa values. At $\tau_{1-2} = 0.6 + 1.2$ MPa the fracture was mainly cohesive within SIEL primary coating, but at $\tau_{1-2} > 1.2$ a combined failure involving quartz fiber interface was observed with some compounds.

Thus, in the last case interaction forces between coatings exceed those acting in SIEL-quartz fiber interface.

IV. Adhesive Properties of STYK Compounds

As noted, the compounds of STYK type must adhere well to all fiber optics elements and to metal. Results of adhesive strength studies between these compounds and quartz fibers with untreated surfaces and surfaces modified by primary and secondary coatings, and steel fibers are given in Figures 10–12 and Table III, respectively. All fiber-STYK joints were fractured along the interface.

TABLE II

Coating composition and optical fiber treatment effect on σ_{1-2} cohesive strength

Series Number	Characteristic of dimethylsiloxane block of the secondary coating		σ_{1-2} bonding strength between coatings in optical fibers, Mpa							
			Initial samples		Samples after thermal treatment at 200°C/7h		Samples after dose irradiation, 400		4000	
	$\bar{M}_n$	Modifying siloxy units composition and content, mol %	THE PRIMARY COATING							
			SIEL-1	SIEL-2	SIEL-1	SIEL-2	SIEL-1	SIEL-2	SIEL-1	SIEL-2
1	2	3	4	5	6	7	8	9	10	11
1	3190	MH-12.7	0.03	0.05	0.85	0.74	0.06	0.05	0.30	0.25
2	3320	MV-12.0	0.40	0.40	1.60	1.10	1.30	0.95	1.30	1.40
3	5660	MV-2.8	1.10	0.43	2.30	2.10	1.15	1.20	1.27	1.20
4	5780	MH-6.5	0.03	0.03	0.70	0.57	0.05	0.03	0.26	0.25
5	mixture of series 3 series 4	95 wt parts 5 wt parts	1.00	0.90	2.80	2.70	0.95	1.37	1.13	-

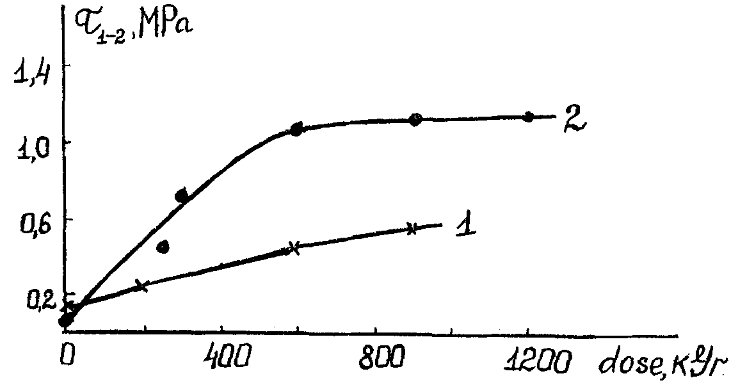


FIGURE 8 Fiber-primary coating-secondary coating system bonding strength against absorbed irradiation dose. The primary coating: 1—SIEL-1; 2—SIEL-2.

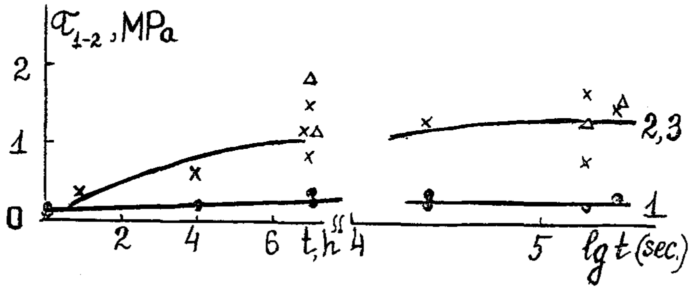


FIGURE 9 Coatings bonding strength upon optical fibers thermal ageing. $T_{\mathrm{cure}} = 200°\mathrm{C}$; PAC with DM-groups on SIEL-1 (1); on SIEL-2 (3); with MH-groups on SIEL-1 (2); $n = m = 25$; "n" and "m"—are the quantities of DM-siloxygroups and MH-siloxygroups respectively.

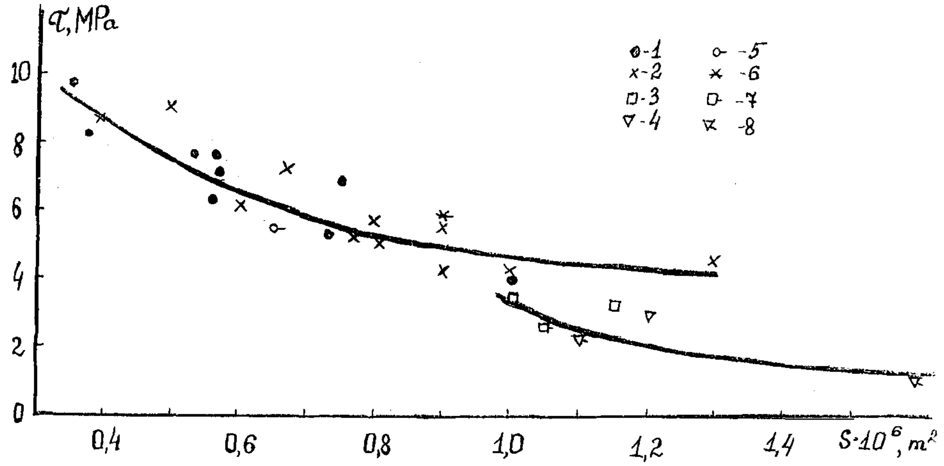


FIGURE 10 Fiber-STYK compounds joint adhesive strength against contact area. $T_{\mathrm{cure}} = 160°\mathrm{C}$; $t_{\mathrm{cure}} = 3$ hours; $T_{\mathrm{exp}} = 20°\mathrm{C}$. 1–4—STYK-DM; 5–8—STYK-FT; steel fibers—1,5; quartz fibers—2,6; quartz fibers coated with SIEL—3,7; quartz fibers coated with SIEL and PAC—4,8.

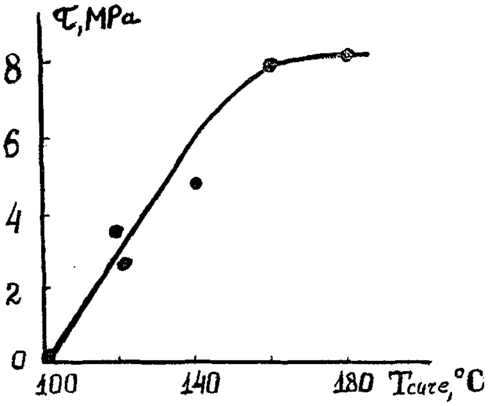


FIGURE 11 Effect of curing temperature on adhesive strength of STYK-DM—steel wire joints. t_{cure} = 6 hours; T_{exp} = 20°C; S = 0.6 $10^{-6}m^2$.

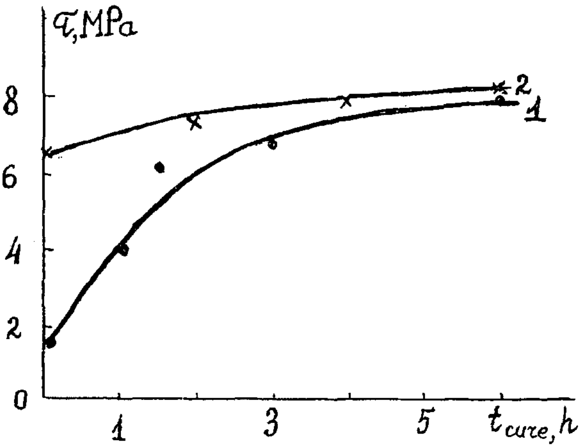


FIGURE 12 Adhesive strength of STYK-DM-steel wire joint as a function of cure time—fiber surface joint. 1—T_{cure} = 160°C; 2—T_{cure} = 280°C; T_{exp} = 20°C; S = 0.6 × $10^{-6}m^2$.

Therewith, for all investigated systems the size effect in markedly manifested (Figure 10). With other conditions equal, the adhesive strength of STYK-fiber joints with high surface energy (steel, quartz) is higher than in joints with low-energy surface (SIEL and PAC coated)—see Figure 10.

The τ values for compounds, containing dimethylsiloxy units and for STYK-FT, wherein part of DM units is replaced by methyl-γ-trifluoro-propylsiloxy units, are essentially equal. The data points fall essentially on the same τ-S curve. However, the introduction of methylphenylsiloxy units (STYK-MPh) to composition increases the strength up to 12.5 MPa (at S = 0, 4 × 10^{-6} m^2, T_{cure} − 160°C, t_{cure} − 6 hrs). At high levels of Si-H group content, the transition to a two-part system does not affect the adhesive strength of STYK-DM-steel fiber joints. The addition of mineral fillers (TiO_2, $BaSO_4$) to STYK-Ph composition has no effect on τ values.

As indicated illustrated by the curves in Figure 10 a weak link (i.e. a site wherein a failure is likely to begin) of articles based on quartz fiber optics, may be the

TABLE III

STYK-steel fiber surface connection adhesive strength dependence on irradiation dose

Composition	Irradiation dose, kGr	τ, MPa x) without catalyst	with catalyst-traces
STYK-DM	250	4.8	10.5
STYK-FT	250	5.0	10.5
STYK-MF	250...1200	0	0

x) S-$0.6\times10^{-6}m^2$

interface between STYK and coatings (SIEL, PAC). This must be taken into account in designing of devices. It should also be noted that the τ values are temperature and curing time dependent. Thus, after 6 hours of isothermal curing at $T = 100°C$, τ values are practically equal to zero (Figure 11) but under a non-isothermal process with a temperature rise up to 160°C or 180°C (at a heating rate of about 1°C/ min), the τ values reach 1.5 and 6.5 MPa respectively (Figure 12). Under isothermal curing (or postcuring) the strength follows a curve with a plateau. The τ values attained at 160°C and 180°C after 6 hrs are practically identical.

In Table III are presented the values of STYK compounds adhesive strength cured by accelerated electron beam. It is apparent that the effectiveness of such curing is a function of the nature of siloxy units. STYK-MPh is not cured even at 1200 kGr dose, while for STYK-DM and STYK-FT a 5-times smaller curing dose is sufficient. In the absence of a catalyst the τ values for these compounds reached 5 MPa. But in the presence of platinum catalyst, the adhesive strength is doubled. The τ values for STYK-DM and STYK-FT cured by electron beam are identical. It can also be seen (see Table III and Figures 11 and 12) that the curing with accelerated electrons allows us to achieve higher values of adhesive strength than with thermal curing.

DISCUSSION

We found that the joints elastomeric coatings of SIEL type with quartz fibers failed within a thin layer near surface or within the interphase. Therefore, the cohesive and adhesive characteristics of failure are displayed. The joint strength increases with polymerization time and increasing rubber molecular mass; the growth of τ^1 is accelerated at elevated temperatures. This is typical for a cohesive mode of failure. In addition, the joint strength decreases with contact area increase. This is typical for an adhesive mode of failure. Such behavior may be presented as follows. Studied elastomeric coating is a product of vulcanization obtained by polyadditional reaction of vinyl containing silicone rubbers with oligoorganohydridesiloxane crosslinking agent.

$$\sim\mathrm{Si} - \mathrm{CH} = \mathrm{CH_2} + \mathrm{H} - \mathrm{Si}\sim \xrightarrow{t,\ Pt} \sim\mathrm{Si} - \mathrm{CH_2} - \mathrm{CH_2} - \mathrm{Si}\sim \qquad (1)$$

However, a number of side reaction with moisture and oxygen in air runs parallel to basic polyaddition reaction at crosslinking agent excess.[13]

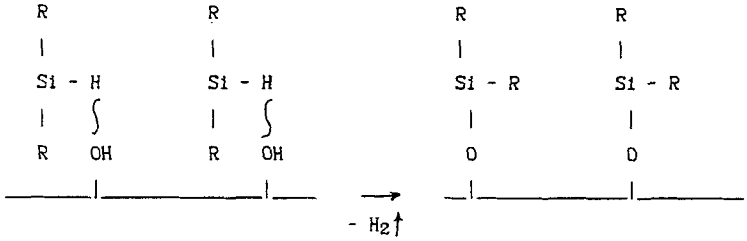
$$\sim\mathrm{SiH} + \mathrm{H_2O} \rightarrow \mathrm{n\ SiOH} + \mathrm{H_2}\uparrow \qquad (2)$$

$$\sim\mathrm{SiH} + \mathrm{HOSi} \rightarrow \sim\mathrm{Si} - \mathrm{O} - \mathrm{Si}\sim + \mathrm{H_2}\uparrow \qquad (3)$$

$$2\sim\mathrm{SiH} + \mathrm{O_2} \rightarrow 2\sim\mathrm{SiOH} \qquad (4)$$

$$2\,\mathrm{SiOH} \rightarrow \sim\mathrm{Si} - \mathrm{O} - \mathrm{Si}\sim + \mathrm{H_2O} \qquad (5)$$

Proceeding of side reactions plays a double role. On one hand, the system is reinforced because it leads to microheterogeneity,[14] on the other hand, the hydrogen evolution may also weaken the system. The reaction (2) involves formation of chemical bonds with air moisture and the polymer. Therefore, the chemical interaction on glass fiber surface, where absorbed moisture is present, is enhanced. The reactions of coatings with air moisture on the fiber surface can proceed according to the following scheme:



The hydrogen evolution loosens the subsurface layer along which the fracture can take place.

Under the conditions of preparation of optical fibers, the residence time of SIEL coating applied on fiber in the high temperature zone between 300–350°C is very short. Therefore, the polyadditional reaction is incomplete and a large number of reactive groups is retained in the polymer. Since the surface of cured coatings of SIEL type is of low energy (surface tension γ = 15–25 dyne/cm), the application of protective films based on thermodynamically incompatible polymers such as polyamides, polyacrylates, polycarbonates, flouroplastics is not effective. However, in the case of polyacrylates with incorporated siloxane part as secondary coatings (PAC), the polymers of primary and secondary coatings proved to be semi-compatible and intersoluble, which promotes the adhesion.

On additional thermal treatment, post curing of SIEL may take place along with increases in interaction between SIEL and the quartz fiber. Fiber-STYK joints and fiber-SIEL joints differ not only in the absolute values of bonding but also in the failure mode. This can be explained on the basis of polymer structure. STYK molecule is shorter, with statistical distribution of vinyl and hydride groups. The vulcanization possibly leads to a complete consumption of vinyl double bonds. Polymerization reaction proceeds according to reaction scheme 1. All STYK compounds have dense packing and regular structure providing conditions for effective interaction with the substrate surface. High values of adhesive strength obtained with PAC, STYK fiber optical and by accelerated electron beam cure are attributed to "cleaving" of double bonds in vinyl group. This generates new active centers for initiation of polyadditional reactions, chemical interaction of coupling agent with substrate, and interaction of polymeric coatings with each other. As a consequence, curing of some compositions and formation of strong composites become possible without high temperature heating. The resistance of STYK-MPh compositions to be cured on radiation is explained by the presence of phenyl radicals with high absorption characteristics.[15] This feature of phenyl-containing organosilicon polymers makes this composition suitable for applications with exposure to elevated radiation.

SUMMARY AND CONCLUSIONS

1. A technique has been developed to determine the bonding strength for coated optical fibers. The adhesive properties of the organosilicon polymeric materials—fiber optics joints have been studied.
2. It is shown that the primary coatings of SIEL type develop a high bonding strength with quartz fibers. Its value is a function of starting rubber molecular mass, amount of crosslinking agent, time and temperature of curing process. The joints are failing cohesively close to the surface layer.
3. Optimal PAC-based secondary coatings compositions have been chosen, which provide a high bonding strength between the primary coating of the optical fiber and "joining" material. PAC containing methylvinylsiloxy units in the siloxane chain offers the maximum adhesion. The strength of bonding decreases as content of siloxane in block copolymer increases and is slightly affected by the type of side chain groups and application conditions.
4. The high strength thermosetting compounds of STYK type provide high adhesion to all components of fiber optics parts. The adhesive properties of STYK are superior to those of SIEL. STYK performance is dependent primarily on the conditions of adhesive joint formation.
5. Curing of PAC and STYK by accelerated electrons beam leads in specific cases to compounds with higher bonding strength than thermal curing.

6. The established relationships permit us to predict and control adhesion to fiber optics materials.

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