Study of UV-Curable Coatings for Optical Fibers

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Three kinds of UV-curable prepolymers, urethane acrylate (UA), polysilicone acrylate (SA), and epoxy acrylate (EA) were prepared. These prepolymers were mixed in different proportions to modify the properties of an optical fiber coating. The relationships of component-property and structure-property of the mixture coatings were studied. When the proportion was SA:UA:EA=5:4:3, it was used for a single coating, however, the proportion SA:UA:EA=6:5:2 was used for a primary buffer coating. These mixture coatings were applied to optical fibers.

INTRODUCTION

Ultraviolet (UV) light-curable coatings are used for optical fiber coatings because of their excellent performance and rapid curing rate.[1-6] Optical fiber coatings can be classified as one of two types: a combination of a primary buffer coating and a secondary buffer coating, or a single coating[7] that combines the characteristics of the primary and secondary coating. Primary coatings must have excellent elongation, low glass transition temperature (T_g), and a low modulus at low temperatures. Secondary buffer coatings must have higher tensile strength than primary coatings along with the other characteristics of these coatings. Single coatings must combine all of these characteristics.

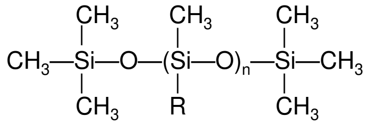
Urethane acrylates, epoxy acrylates, and silicone acrylates are UV-curable prepolymers that have very different structures, and the coatings based on these oligomeric materials have markedly different properties. In this study, these prepolymers were mixed in various proportions with other ingredients to form UV-curable coating systems that resulted in cured coatings with different properties. The goal was to develop coatings that could be used as the primary buffer coating and as the single coating for optical fibers.

EXPERIMENTAL

Epoxy acrylate (EA), urethane acrylate (UA), and silicone acrylate (SA) prepolymers were prepared. Three-component mixtures of the prepolymers (EUS) were formulated into coatings, and the structure-property relationships of the cured coatings were determined and evaluated in view of their use as optical fiber coatings.

Preparation of the Prepolymers

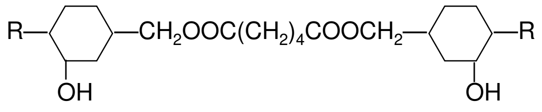
Silicone Acrylate: The SA was prepared by reacting allyl acrylate with hydrosilicone in the presence of a platinum catalyst.[8]



$$CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{Si}}-O-(\overset{\overset{CH_3}{|}}{\underset{\underset{R}{|}}{Si}}-O)_n-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{Si}}-CH_3$$

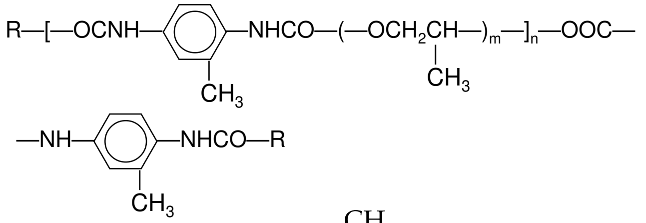
wherein R = H or $CH_2 = CHCOOCH(OH)CH_2CH_2$– and n = ~300.

Epoxy Acrylate: The EA was prepared by reaction of an aliphatic epoxy compound with acrylic acid.



wherein R = CH_2 = CHCOO–.

Urethane Acrylate: The UA was prepared by reaction of toluene diisocyanate with terminal-dihydroxy polyepoxy propane and β-hydroxypropyl acrylate.[9]



wherein R = $CH_2 = CHCOOCH_2\overset{\overset{CH_3}{|}}{CH}O$–; m = 20~40; n = 3~5.

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Table 1—Physical Properties of Prepolymers

Properties	(25°C)	SA	UA	EA
Viscosity	mPa.S	3,000	50,000	5,000
Molecular wt.	Mn	45,000	2,500	1,200
Index of refrac.	N_D	1.492	1.485	1.496
Density	D^{25}	1.113	1.080	1.256

Table 2—Properties of UV-Cured Prepolymers

Properties[a]	SA	UA	EA
Cure time, Sec .... (figure touching)	1-2	8-10	1-2
Tensile strength, Mpa	7.00	3.14	8.47
Elongation, %	20	40	23
Glass transition, °C	-57	-19	-11
Hardness, shore	18	12	19
Modulus, Mpa	35.09	7.86	56.82

(a) Tested at 25°C, 50% relative humidity.

The physical properties of three prepolymers are given in *Table* 1.

Formulation of UV-Curable Coatings

As indicated in *Table* 2, various amounts of the three prepolymers were blended to yield 100-part-by-weight batches of each mixture. Then five parts by weight of benzoin dimethyl ether photoinitiator,[10] three parts by weight of a 1/1 diphenyl ketone/triethylamine photosensitizer mixture, and one part by weight of p-hydroxyanisole stabilizer were mixed, melted, and added to each batch of prepolymer mixture. These blends were then mechanically mixed to blend the ingredients. The UV-curable coating formulations were stored in opaque containers. Each prepolymer was also formulated in this manner and tested.

Preparation of Cured Film

Glass plates were cleaned and dried, then films approximately 0.1 mm in thickness were cast onto the plates with a "bird type applicator." The films were then irradiated under a high-pressure mercury lamp* (25 watt/cm) for either 2 or 30 sec as indicated in *Table* 3. After exposure, the cured films were stored in a vacuum desiccator until tested.

RESULTS AND DISCUSSION

Inter-Solubility of Prepolymers

Thermodynamic inter-solubility of the three prepolymers is necessary for the mixture to be useful. Since the silicone acrylate is very different from the epoxy acrylate and urethane acrylate, a number of hydroxyl ester acrylate groups were grafted onto the silicone acrylate backbone. In addition, the urethane acrylate was designed in such a manner that the various prepolymers would approach each other's structures. As a result of this design, when EA, UA, and SA were mixed, they appeared to be miscible in each other. To qualitatively test the miscibility, the mixtures were stored under quiescent conditions for three months, and after this time period no phase separation was apparent.

Cure Rate and Mechanical Properties of UV-Cured Prepolymers

Cure rate and mechanical properties are important characteristics of materials to be used as optical fiber coatings. Such characteristics for each of the UV-cured prepolymers are given in *Table* 2.

From these data, it is apparent (in a relative sense) that SA has a rapid cure rate, high tensile strength, low T_g, and low elongation; UV has a slow cure rate, low tensile strength, high T_g, and good elongation; and EA has a rapid cure rate, high tensile strength, high T_g, and low elongation. These results suggest that if properly mixed, combinations of three prepolymers could yield coatings that have properties useful for optical fiber.

Cure Rate and Mechanical Properties of UV-Cured Formulated Prepolymers

Based on the results given in *Table* 2, a series of prepolymer mixtures was designed and formulated as described in *Table* 3. Their mechanical properties and cure rate were ascertained and are described in *Tables* 3 and 4. It is apparent from the data in *Table* 4 that:

Table 3—Typical Properties of Mixture of Three Prepolymers[a]

Mixture Number	Component Ratio[b], w: w: w:			Tensile Strength Mpa	Elongation (%)	Modulus Mpa	Gel Ratio[c] (%)
	SA	UA	EA				
1	5 (1)	3 (1)	2 (1)	10.3	30.0	27.2	37.7
2	6 (2)	3 (1)	3 (2)	8.2	25.3	25.9	50.9
3	7 (3)	3 (1)	4 (3)	12.7	34.3	29.6	54.2
4	5 (1)	4 (2)	3 (2)	10.2	48.5	21.2	55.0
5	6 (2)	4 (2)	4 (3)	8.0	26.0	24.6	56.8
6	7 (3)	4 (2)	2 (1)	8.9	41.0	21.5	56.6
7	5 (1)	5 (3)	3 (3)	8.9	41.5	21.4	57.9
8	6 (2)	5 (3)	2 (1)	8.0	46.8	17.0	37.4
9	7 (3)	5 (3)	3 (2)	6.9	29.5	21.0	50.1

(a) Every mixture coating was prepared according to the method mentioned. Cast films were irradiated 30 sec.
(b) The weight ratios of components are outside the parentheses. The test levels are the numbers inside parentheses.
(c) Films were irradiated by UV-lamp for two seconds.

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*The wavelength distribution and relative strength of the high-pressure mercury lamp are shown in *Figure* 4.

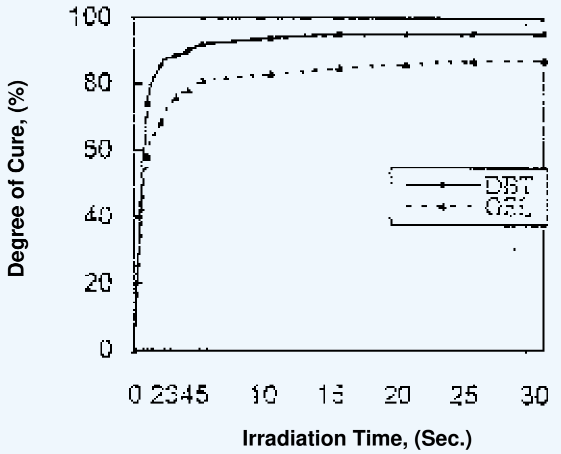

Figure 1—Degree of cure as a function of irradiation time.

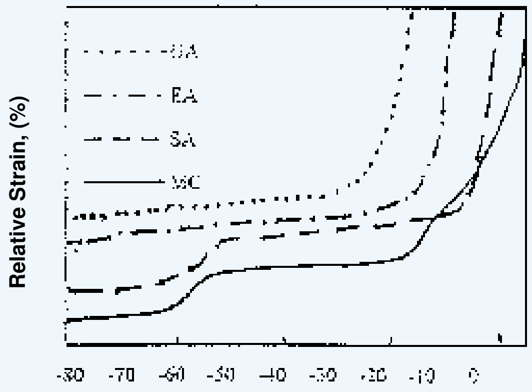

Figure 2—Thermomechanical behavior of UA, EA, SA prepolymers and mixture coating (MC) No. 4 in Table 3.

- Increasing the amount of SA improves cure rate but decreases elongation.
- Increasing the amount of UA increases elongation and decreases modulus, but does not improve tensile strength and cure rate.
- Increasing the amount of EA increases tensile strength and cure rate, but decreases elongation and modulus.

Determination of Cure Rate

The rate of cure can be represented in different qualitative and quantitative ways such as the time to dry by finger touch, gel percentage determined by solvent extraction, and double bond disappearance percentage as determined by IR spectra. The cure time by finger touch is not very exact, but it is convenient. The other tests mentioned are more exact but are time consuming.

The No. 4 mixture described in *Table* 3 was selected for study of cure rate. Films of this formulation were cast, and then the films were irradiated for a series of times from 2 to 30 sec. *Figure* 1 is a description of the cure when determined by double bond transition (DBT) percentage and gel percentage (GEL) as a function of irradiation time. The results indicate that a gel percentage greater than 66% and a double bond transition percentage of about 85% were obtained after an irradiation time of two seconds. After irradiating for 10 sec, both of these parameters approached their maximal values.

Glass Transition Temperature and Viscoelastic Behavior

As mentioned earlier, excellent low temperature properties are an important requirement for optical fiber coatings. It is particularly important that only small modulus changes take place between 40°C and -40°C. The thermomechanical behavior of the three prepolymers and mixture No. 4 (*Table* 3) is given in *Figure* 2. From these data, it can be seen that the T_g of SA is about -57°C, of UA is about -20°C, and of EA is about -10°C. The T_gs of the mixture were approximately -60° and -20°C. When the data for the mixture are compared with data for the individual prepolymers, it is apparent that the mixture's plateau region where modulus would be expected to be relatively constant is considerably broadened and partially shifted over that of the individual prepolymers. The same general characteristic of the mixture over the prepolymers is apparent in its viscoelastic behavior, which is given in *Figures* 3a-b. A series of sharp shifts in the loss modulus, E", is apparent in the -60°C region. It is felt that this is related to the morphology of the mixture coating in which there is some phase separation after cure and is a contribution from the silicone portion of the coating. In addition, the broadened peak of the loss modulus indicated by the change from -60°C to +20°C can be attributed to the ester acrylate groups in the cured mixture. According to the storage modulus, E', temperature data, *Figure* 3b, the storage modulus is 1.08×10^9 dyn/cm^2 at 40°C

Table 4—Data Analyses for Table 3

Properties	Levels	SA	UA	EA
Tensile Strength	1	29.4	31.2	27.2
(Mpa)	2	24.2	27.1	25.3
	3	28.5	23.8	29.6
	Δ=3-1	-0.9	-7.3	2.4
Elongation (%)	1	120.0	89.0	117.8
	2	98.0	115.5	103.3
	3	104.8	117.8	101.8
	Δ=3-1	-15.2	28.8	-16
Modulus (Mpa)	1	69.8	82.8	65.6
	2	67.5	67.3	68.1
	3	72.1	59.4	75.6
	Δ=3-1	2.3	-23.4	10.0
Cure rate	1	150.0	142.8	130.7
(gel percent) (%)	2	145.1	168.4	156.0
	3	160.9	145.0	168.0
	Δ=3-1	15.8	-23.0	12.9

Table 5—Typical Properties of Mixture Coatings

Typical Properties		Single		Primary	
Liquid coating	**25°C**	**M**	**+A**	**M**	**+F**
Density	g/cc	1.33	1.27	1.11	1.00
Viscosity	mPa.S	5,000	4,500	4,500	4,100
Cured coating, 25°C, 50% relative humidity					
Tensile strength	MPa	10.2	12.5	8.0	4.3
Elongation	%	48	56	47	156
Tensile modulus Mpa		30.9	38.6	17	2.81
Shrinkage on curing %			5.7		5.4
Refractive index			1.53		1.51
Water absorption % (24 hr)			1.81		4.76
Glass transition	°C		-81, -21		-81, 21
Coefficient expansion (-40- + 40°C) x 10^5 cm/cm.C			4.6		4.2

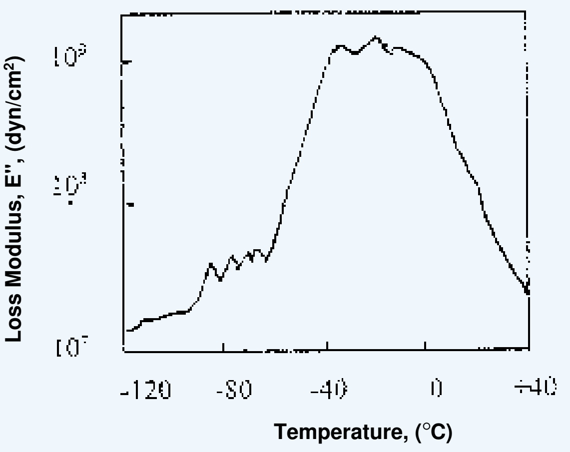

Figure 3a—Dynamic viscoelastical behavior (loss modulus E'') as a function of temperature for mixture coating No. 4 in Table 3.

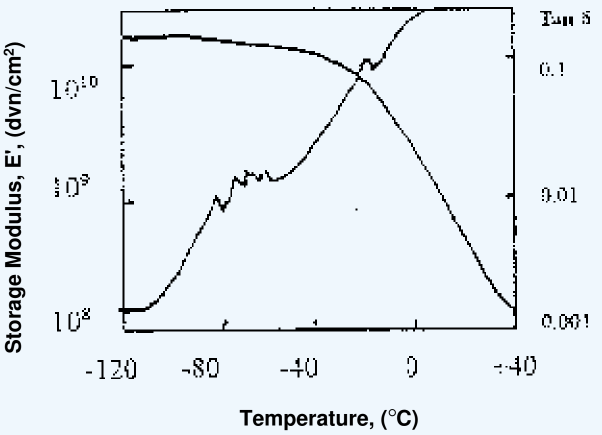

Figure 3b—Dynamic viscoelastical behavior (storage modulus, E', loss tangent, tan δ) as a function of temperature for mixture coating No. 4 in Table 3.

and 1.37 × 109 dyn/cm^2 at -40°C—a 12.7 times change in modulus.

Preparation and Properties of Coating Formulations for Optical Fibers

From the data in *Table* 4, coating mixture No. 4 in *Table* 3 was selected as a candidate for a single coating for optical fibers. To this mixture, 10% by weight of a crosslink adjuster such as trihydroxypropyl triacrylate, diglycol diacrylate, or triethylene glycol diacrylate was added. It is apparent from the data in *Table* 5 that a crosslink adjuster was added, therefore, the mechanical properties of the mixture coating were obviously improved. In addition, such a formulation should be a good starting point system for a single coat optical fiber coating. Such coatings make optical fiber manufacture easier and less expensive than processes involving a primary and a secondary coating.

Again from the data in *Table* 4, coating No. 8 in *Table* 3 was selected as the candidate for a primary buffer coating. To this mixture, 10% by weight of a flexibility adjuster such as vinyl pyrrolidone or 2-ethylhexyl acrylate was added. The properties of these modified mixture coatings are given in *Table* 5.

When the two coatings, Single, +A; Primary, +F, described in *Table* 5 were used to coat optical fibers, a fiber drawing rate of 100 meters per minute was achieved.

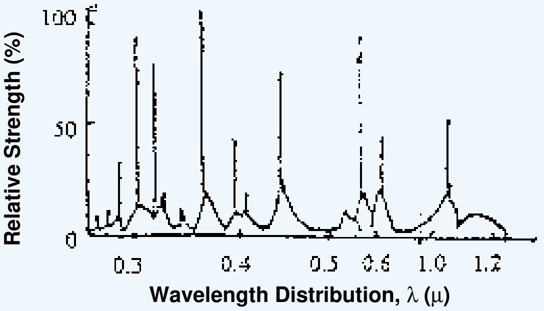

Figure 4—Wavelength distribution and relative strength of the high-pressure mercury lamp.

The IR reflection spectra of the coated and UV-cured fibers indicated that the absorption bands at 1620, 1635, 1400, and 1300 cm^{-1} were absent indicating a high degree of cure. The surface of coated optical fiber is very dry and smooth.

CONCLUSIONS

UV-curable prepolymers, a silicone acrylate, urethane acrylate, and an epoxy acrylate that have good inter-solubility were synthesized. The inter-solubility allowed broad formulating latitude with the prepolymers. Mixtures of the prepolymers in various proportions resulted in markedly different mechanical properties. When the ratio of SA:UA:EA is 5:4:3, the mixture is useful as a single coating for optical fibers. When the ratio of SA:UA:EA is 6:5:2, the mixture is useful as a primary buffer coating for an optical fiber coating system. The formulated system selected from the study had a rapid cure rate, good mechanic properties, and excellent low temperature characteristics.

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