UV-Curable, Special Coding Inks for Optical Fibers

Gexing Shen, Wanneng She, Xiouning Qu, Xiaomeng Yu, Qunzhen Sun, Wei Liu, and Giachen Ron—Hubei Research Institute of Chemistry*

A UV-curable, special coding ink for optical fibers consists chiefly of UV-curable prepolymers, coloring materials, and a photoinitiator. The UV-curable prepolymers are silicone epoxy benzoic acrylate (SEBA) and alicyclic hydrocarbon epoxy acrylate (ACEA). The coloring materials are disperse red urethane acrylate (RUA), disperse blue urethane acrylate (BUA), acridine yellow urethane acrylate (YUA), or their mixtures. The relationships of component-property of UV-curable, special coding inks were studied. The typical UV-curable, special coding inks were used to color the optical fibers.

INTRODUCTION

UV-curable, special coding ink[1-4] is used for coloring the surface of optical fibers. Optical fibers used in the optical cable usually need connecting. Different colored optical fibers are useful to distinguish between the various optical fibers in the cable. The need for optical fiber identification increases dramatically when optical fiber counts per cable increase from tens to hundreds or even thousands. UV-curable ink can provide a quick cure rate, excellent gel resistance, and good adhesion to the surface of the optical fibers. This kind of ink usually consists of a UV-curable prepolymer, pigment or dye, photoinitiator, and other additives.

In this study, a silicone epoxy benzoic acrylate (SEBA) and alicyclic hydrocarbon epoxy acrylate (ACEA) were synthesized and mixed in proper proportion for the reactive prepolymer of UV-curable inks. Disperse red urethane acrylate (RUA), disperse blue urethane acrylate (BUA), and acridine yellow urethane acrylate (YUA) were also synthesized. These photocurable dyes can take part in the cure reaction of the special coding ink. The color of the cured inks would not transfer or be removed by organic compounds. In addition, these photocurable dyes possess comparative translucence that is advantageous to melt-connecting optical fibers. The coding inks were used to manufacture optical cable.

EXPERIMENTAL

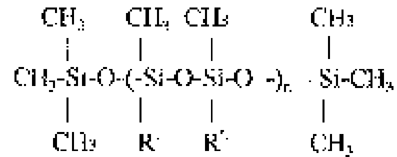
The prepolymers and UV-curable colorants were prepared and tested with the following commercially obtained materials.

Materials and Reagents

(1) Photoinitiator BK (benzoin dimethyl ether)
(2) Sensitizer (diphenyl ketone/triethyl amine = 1/1)
(3) Stabilizer (p-hydroxyanisole)
(4) WS-1, loose tube-filling gel for optical fibers (Hubei Research Institute of Chemistry, Wuhan, China).
(5) WS-2, loose tube-filling gel for optical fibers (Hubei Research Institute of Chemistry).
(6) Syncofox 415, loose tube-filling gel for optical fibers (Cynco Inc. USA).
(7) Unigel 435, loose tube-filling gel for optical fibers (BP, Inc., England)

Syntheses

SEBA Prepolymer: This prepolymer was synthesized by reacting a silicone epoxy with benzoic acid and/or acrylic acid derivatives. The structural formula is:



wherein $R^1 = -(CH_2)_{1\sim6}OCH_2CH(OH)CH_2OOC\text{-}Ph$

$R^2 = -(CH_2)_{1\sim6}-OCH_2CH(OH)CH_2OOCCH{=}CH_2$

*No. 30 Guan Shan Rd., Wuhan 430074, P.R. China.

Table 1—Composition Ratio of a Series of Color UV-Curable Special Coding Inks

Color of Ink	Composition Ratio (wt. %) Red	Blue	Yellow
Red	100	0	0
Orange	27	0	73
Yellow	0	0	100
Green	0	22	78
Blue	0	100	0
Indigo	0	8	92
Purple	55	45	0
Brown	50	27	23
Gray	22	38	40

ACEA Prepolymer: ACEA was synthesized by reacting an alicyclic hydrocarbon epoxy with an acrylic acid derivative. The structural formula is:

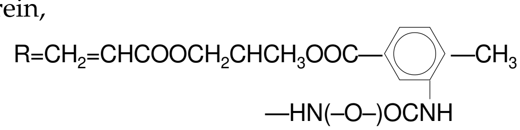
$$CH_2 = CHCOOCH_2CH(OH)CH_2OOC–R–$$
$$COOCH_2CH(OH)CH_2OOCCH = CH_2$$

wherein R=cyclopentyl or cyclohexyl group.

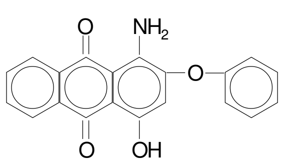
Photocurable Dyes: Disperse red urethane acrylate (RUA), disperse blue urethane acrylate (BUA), and acridine yellow urethane acrylate (YUA) were synthesized by reaction of the disperse dyes with toluene diisocyanate and hydroxypropyl acrylate. The structural formulas are as follows:

R—Dye—R

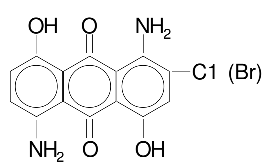
Wherein,



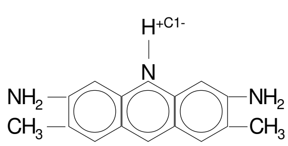
and the dyes are:



Disperse Red 3B



Disperse Blue 2BLN



Acridine Yellow

Preparation of UV-Curable Special Coding Inks

All of the following components were mixed and mulled in a circulating muller, and the individual special red, blue, and yellow coding inks were prepared. They were stored in opaque containers at 25°C. Formulations of UV-curable special coding inks are: SEBA 60, ACEA 40, Photoinitiator 5, Photosensitizer 3, Stabilizer 0.1, and Photocurable dye 2.

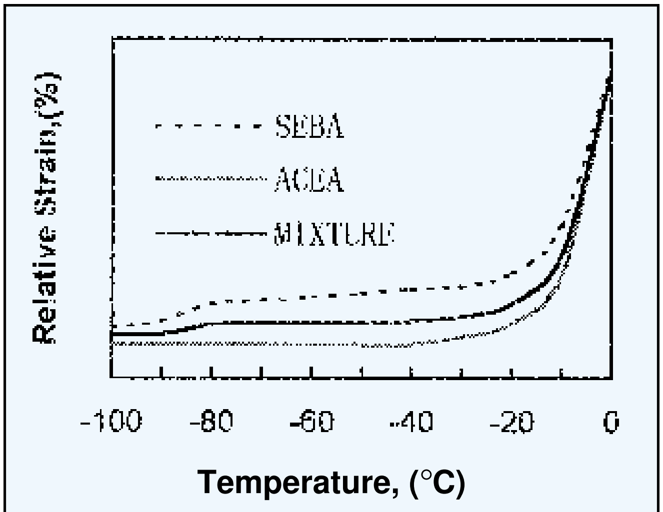


Figure 1—Thermomechanical behavior of SEBA, ACEA, and the mixture (60/40) in Table 3.

When the three UV-curable special coding inks were mixed in different proportions (see *Table* 1) a series of various colored special coding inks were prepared. In addition, the white UV-curable, special coding ink is made by exchanging photocurable dyes with titanium dioxide (TiO_2).

Preparation of Cured Films

Glass plates were cleaned and dried and the films, approximately 0.1 mm in thickness, of the inks were cast onto the plates with a Bird-type applicator. The films were then irradiated under a high pressure mercury lamp* (25 watts/cm) for 30 sec. After exposure, the cured films were stored in a vacuum desiccator until tested.

*The wavelength distributions of UV-lamp are at 250-400 nm.

Table 2—Properties of Prepolymers

Properties (25°C, 50% RH)	SEBA	ACEA
Liquid Prepolymer		
Density, g/cm	1.11	1.05
Viscosity, mPa.s	3,000	50,000
Refractive index	1.51	1.50
Cure time, sec.	2	2
Cured film		
Tensile strength, Mpa	1.7	8.3
Tensile modulus, Mpa	8.5	36.1
Elongation, %	20	23
T_g, °C	–81,–11	–11

Table 3—The Characteristics of Mixture

Properties	Mixture ratio, SEBA/ACEA, (w/w) 80/20	60/40	50/50	40/60
Viscosity, mPa.S	6,800	9,700	12,200	15,300
Tensile strength, MPa	2.9	4.3	5.5	6.3
Elongation, %	22	23	23	23
Modulus, MPa	13.8	19.1	24.2	29.7

Table 4—Mechanical Properties of Cured Films of Different Colored Inks[a]

Color of Inks	Tensile Strength MPa	Elongation %	Modulus MPa
Colorless	10.89	26.0	43.2
Yellow	9.92	22.0	43.8
Blue	9.32	22.9	40.8
Red	5.79	19.2	30.2
Orange	8.34	20.3	36.2
Green	5.05	20.5	30.5
Gray	4.25	19.8	21.5
Purple	6.61	20.9	32.4
Indigo	5.92	18.7	31.7
Brown	5.07	17.7	29.6
White	4.33	28.4	14.4

(a) Liquid films were irradiated for 30 sec. All tests are at 25°C, 50% RH.

RESULTS AND DISCUSSION

Effect of UV-Curable Prepolymer Compositions on Properties

The characteristics of the two UV-curable prepolymers studied are given in *Table* 2.

From the data in *Table* 2, it is apparent that the prepolymers have rapid cure rates; SEBA has a low glass transition temperature (T_g), low viscosity, low tensile strength, and low elongation; ACEA has good mechanical properties, high viscosity, and a poor low temperature characteristic. When the two prepolymers were mixed in different proportions and cured, they had the properties given in *Table* 3.

Based on the results given in *Table* 3, it can be seen that when the ratio of SEBA:ACEA is 60:40, the mixture has proper viscosity, tensile strength, and modulus. Therefore, this mixture was used as the basic material for the special coding inks.

The T_g of prepolymers and SEBA/ACEA = 60/40 mixture were determined by the thermomechanical method (see *Figure* 1). From the thermomechnical curves, it is apparent that the relaxation maxima temperatures of SEBA occur at –81° and –10°C; of ACEA at about –11°C; and of the mixture at about –81° and –11°C.

Effect of Photocurable Dyes on Properties

When the colorant is added to the UV-curable oligomeric materials, the cure rate and mechanical properties of ink are altered because the colorant obstructs or ab-

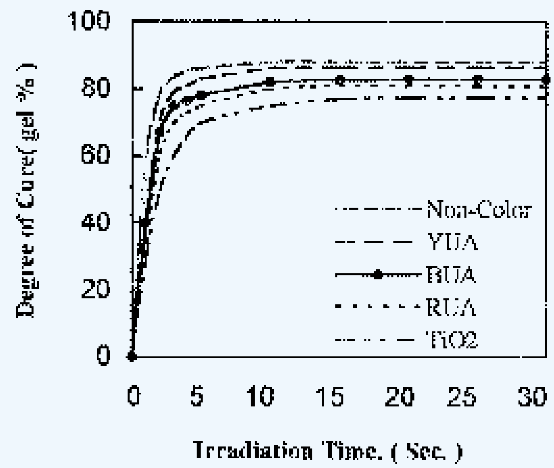


Figure 2a—Degree of cure (gel %) as a function of irradiation time in using different color materials.

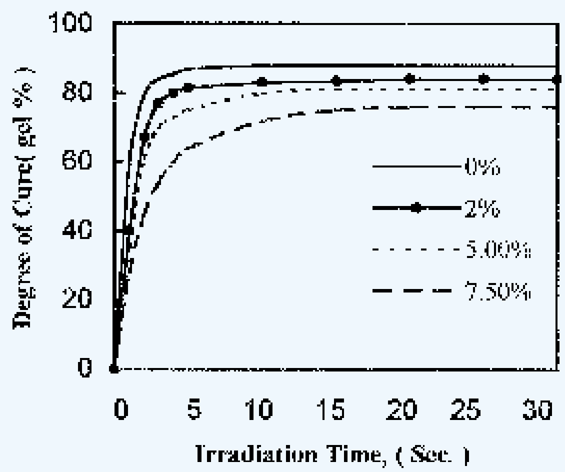


Figure 2b—Degree of cure (gel %) as function of irradiation time in using different contents of YUA color materials.

Table 5—Results of Filling Gel Resistance and Color Migration of Cured Film[a]

	Weight Change (%) and Color Migration of Cured Film (Y or N)				
Inks	WT-102	WS-1	WS-2	Syncofox 415	Unigel 435
Colorless	–18.3/N	–16.5/N	–18.7/N	–17.6/N	–20.6/N
Yellow	–22.7/N	–20.2/N	–21.3/N	–21.9/N	–22.5/N
Blue	–22.7/N	–20.2/N	–21.3/N	–21.9/N	–22.5/N
Red	–22.3/N	–22.5/N	–23.1/N	–22.5/N	–23.6/N
White	–22.0/N	–20.5/N	–22.5/N	–22.2/N	–24.8/N
	–21.0/N	–16.9/N	–22.2/N	–19.3/N	–21.6/N

(a) Cured films were soaked in different filling gels at 88°C for 70 days. Y=Migration, N=No migration.

Table 6—Typical Properties of UV-Curable Special Coding Inks for Optical Fibers

Characteristics	Test Data			
	Yellow	Blue	Red	White
Liquid ink, 25°C, 50% RH				
Density g/cc	1.12	1.15	1.17	1.21
Viscosity mPa.s	8,850	9,720	9,210	9,000
Refractive index	1.51	1.51	1.51	1.51
Cure time (touch) sec	2	3	4	5
Storage time in months	>12	>12	>12	>12
Cured ink, 25°C, 50 RH				
Tensile strength MPa	9.92	9.32	5.79	4.09
Tensile modulus MPa	43.8	40.8	30.2	14.4
Elongation %	23.1	22.9	19.2	28.4
Water absorption (24 hr) %	3.60	4.20	4.50	4.70
T_g °C	–81,–11	–81,–11	–81,–11	–81,–11
Weight loss (200°C, 40 min) %	11.70	13.10	12.50	11.40
Hydrogen generation µl/g	2.3	2.3	2.3	2.3
Oil[a] absorption (88°C, 70 days) %	–21.90	–22.50	–22.20	–19.30

(a) Poly-θ-olefine oil.

sorbs ultraviolet radiation. These effects are different and dependent on the content and kind of colorant used. The test results are shown in *Figures* 2a and 2b.

From the curves shown in *Figure* 2a, it is apparent that the colorants decrease cure rate. Inorganic pigments (TiO_2) have a larger effect than the photocurable dyes. The effect of these systems on the cure rate is in the order: TiO_2>RUA>BUA>YUA. From the results given in *Figure* 2b, it can be seen that increasing the content of color material also decreases the cure rate. However, at a level of two percent of colorant, the effect on the cure rate was not very great.

Colorants also affect mechanical properties of UV-curable inks. The mechanical properties of a series of cured inks were tested, and the results are shown in *Table* 4. Based on the results of *Figures* 2a and 2b, and data in *Table* 4, it is apparent that the effect of colored materials on mechanical properties is the same as on the cure rate. For example, the effect on decreasing tensile strength is also TiO_2>RUA>BUA>YUA.

Gel and Solvent Resistance of UV-Curable Ink

UV-curable, special coding inks for optical fibers offer advantages in gel and solvent resistance. Special photocurable dye substitutes for pigments improve the UV-curable ink by allowing improved light penetration and therefore, improved gel and solvent resistance. In addition, it is also very important that the colorants do not migrate and fade into the components of cable. The results are shown in *Table* 5.

Based on the data in *Table* 5, it is apparent that all cured films had a weight loss from 15 to 20% when soaked at 88°C for 70 days. It is shown that a few of the substances in inks were extracted. However, the inks' color did not migrate, and the surface of the cured films remained smooth and did not peel off after soaking.

Adhesion of UV-Curable Ink to Optical Fibers

Adhesion of UV-curable inks to optical fibers is an important characteristic. Nearly 100% of the world's optical fiber coatings are UV-curable. Since the UV-curable ink is similar in composition to the UV-curable optical fiber coating, there may even be some actual chemical bonding between the layers depending on cure conditions. Therefore, UV-curable inks have the potential to improve adhesion to optical fibers. After the colored optical fibers were tested by the methods in *Table* 5, the phenomena of colored layers removing and peeling was not found.

Typical Characteristics of UV-Curable, Special Coding Inks for Optical Fibers

The basic formulation of UV-curable, special coding inks for optical fibers is based on the result obtained. Typical characteristics of coding inks of basic colors such as red, yellow, blue, and white are shown in *Table* 6.

CONCLUSION

UV-curable prepolymers, a silicone urethane acrylate (SUA), and an epoxy urethane acrylate (EUA) were synthesized. Photocurable dyes, disperse red urethane acrylate (RUA), disperse blue urethane acrylate (BUA), and acridine yellow urethane acrylate (YUA) were also synthesized. When 60 parts by weight of SUA and 40 parts by weight of EUA were mixed, two parts of a coloring material such as RUA, BUA, YUA, or TiO_2, five parts of benzoin dimethyl ether photoinitator, and three parts of diphenyl ketone and triethyl amine (1:1 by weight) photosensitizer were added with mulling. In this way the UV-curable, special coding inks for use on optical fibers were prepared. This kind of UV-curable, special coding ink for optical fibers is advantageous and has performance characteristics such as rapid cure rate, good low temperature performance, 100% solids, and good solvent resistance.

References

(1) Fouassier, J.P., 20th FATIPEC-Kongr, 206-8, 1990.
(2) Kobayashi, M. (to Gooh Chemical Industry Co. Ltd.), JP03-31310, February 12, 1991.
(3) May, P., Eur. *Polymer Paint Color J*., 183 (1993).
(4) Vannais, S., co-author, *Ultraviolet Color of Optical Fibers—A Comprehensive Study* (to be published), Nokia-Maillefer, South Hadley, MA.