

The Properties of Polymer Protective Coatings of Optical Fibers. I. The Influence of Active Diluent Concentration on the Properties of UV-Cured Epoxyacrylate Coatings

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SYNOPSIS

The strong relationship between the properties of UV-cured epoxyacrylate coatings of optical fibers and their compositions was found. The epoxyacrylate oligomer-to-acrylate monomer active diluent ratio was used to give a simple explanation of the mechanism of polymerization reaction of UV-curable epoxyacrylate compositions. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

The integral part of the optical fiber is its protective coating. This polymer layer decides the mechanical strength of the fiber as well as its resistance against the influence of environment.¹⁻³ Protective coatings consist of one or two layers, according to the assignment of the fiber. The materials most frequently used as the protective coatings are polymers of different kinds, usually the UV-curable acrylate compositions.^{4,5}

The protective coatings of optical fibers perform a few important functions. First, a protective coating must ensure an appropriate mechanical resistance of the optical fiber (it must be emphasized that, due to the water corrosion, quartz optical fiber cannot exist without the protective coating); second, it must harden the fiber against the energy transmission losses caused by microbendings; and, third, the polymer used as a protective coatings must meet some optical requirements.⁵ Furthermore, because the protective coating is laid onto the fiber in the time of its drawing, the curing process should be quicker than the drawing one for economical reasons.

The requirements mentioned above are well met by the UV-curable formulations. Such a typical formulation contains usually three main components:

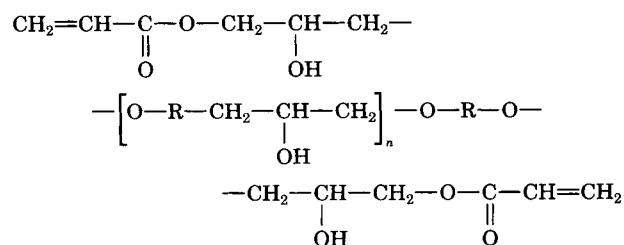
the basic oligomer; the monomer, which is an active diluent of the oligomer; and the photoinitiator beginning the reaction of photopolymerization. The composition of the UV-cured formulation influences both the curing rate and the properties of the created polymer.^{6,7}

In this study, the influence of the active diluent concentration in the UV-curable epoxyacrylic formulation on the properties of optical fiber protective coatings was investigated. We have tested the properties directly related to the polymer structure (e.g., degree of polymerization) as well as the mechanical properties of protective coatings (Young's modulus, relative elongation).

EXPERIMENTAL

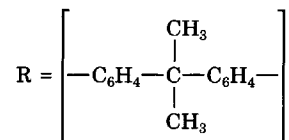
Materials

The basic components of the formulations investigated were epoxyacrylate resins obtained by the reaction of Polish epoxy resins Epidian-2 and Epidian-5 with acrylic acid. As a result of esterification,⁶ obtained were two products of the general formula



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where



and $n < 1$ for ADGD-5, and $1 < n < 2$ for ADGD-2.

The product obtained from Epidian-2 was denoted ADGD-2, and from Epidian-5, ADGD-5. The average molar weight was assumed to be equal to 904 for ADGD-2 and 589 for ADGD-5. To prepare the UV-curable composition, an ADGD-2 and ADGD-5 mixture was used, always in the weight ratio 1 : 1. As the active diluent, ethylhexyl acrylate (AEH), and as the photoinitiator, 2,2-dimethoxy-2-phenylacetophenone (G-651) were applied.

The weight ratios of the epoxyacrylate resin mixture (ADGD-2,5) and AEH in the liquid formulations used in the reported investigations are given in Table I. The photoinitiator concentration in these mixtures was constant and equal to 1.4% w/w. We have found in separate experiments that such a concentration of G-651 is optimum.

METHODS AND APPARATUS

The degree of polymerization of UV-cured polymers was measured as follows: A foil of cured polymer (0.2 mm thick) was placed in a Soxhlet apparatus and extracted with acetone for 6 h. 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 percent of the initial weight, was assumed as the degree of polymerization (gel content).

The measurements of mechanical properties of the cured polymers (Young's modulus, relative elongation, and breaking strength) were performed

with Tiratest tester at strain rates of 1 and 100 mm/min. The specimens of the polymers were prepared as strips of 130 × 8 × 0.2 mm.

The coefficients of water vapor diffusion through the polymers were measured using an instrument constructed in our laboratory. The details concerning this instrument and the method of measurement were described previously.^{8,9}

All specimens of cured polymers were produced as follows: A liquid formulation was poured into the form milled in the Teflon matrix. This formulation was next cured using a 400 W UV lamp, always maintaining the same distance between the lamp and the specimen, equal to 30 cm. The irradiation process was carried out in argon atmosphere for 30 s.

RESULTS AND DISCUSSION

The results of the investigations of the UV-cured polymers are presented in Table II. Their properties are compiled according to the increasing content of active diluent (AEH) in the liquid formulation.

The most interesting dependence in Table II is the influence of AEH concentration on the degree of polymerization (gel content). This parameter reaches a maximum at an AEH concentration equal to 30% w/w. A further increase of AEH concentration leads to a decrease of the degree of polymerization. The mechanical properties of UV-cured polymers depend on the AEH concentration in the same manner—the Young's modulus as well as the breaking strength attain their maxima also at 30% w/w of AEH concentration. Only the relative elongation, the value of which diminishes with AEH concentration increase, namely, with increase of the degree of polymerization, reaches the minimum earlier, at 25% AEH in the liquid formulation.

It seems that the relationships described above may be explained as follows: At 30% AEH concentration, the network obtained by the UV-curing polymer is cross-linked to the highest degree. This means that at a 7 : 3 oligomer-to-monomer weight ratio the photopolymerization reactions probably run stoichiometrically. The analysis of the water vapor diffusion coefficient dependence on AEH concentration in the obtained polymers confirms the supposition that at 30% AEH concentration the degree of polymerization of these polymers attains maximum: The value of this coefficient is minimal just at 30% w/w of AEH. This means that the polymer structure is then the most dense (the most

Table I The Composition of UV-Cured Epoxyacrylate Formulations

Formulation	ADGD-2,5 (% w/w)	AEH (% w/w)	G-651 (% w/w)
I	83.6	15	1.4
II	78.6	20	1.4
III	73.6	25	1.4
IV	68.6	30	1.4
V	63.6	35	1.4

Table II The Composition of UV-Cured Epoxyacrylate Formulations

AEH Concentration (% w/w)	Gel Content (%)	Young's Modulus (N/m ²)	Breaking Strength (N/m ²)	Relative Elongation (%)	Water Vapor Diffusion Coefficient ($\frac{\mu\text{g mm}}{\text{m}^2 \text{ s}}$)
15	72.7	80	5.2	36.4	—
20	89.9	510	15.2	14.1	23.4
25	88.7	729	18.8	4.8	19.8
30	91.3	833	33.5	5.4	15.4
35	83.1	719	17.7	5.7	16.9

compact) and resists most of the penetration of water molecules into the polymer.

It seems that the dependencies presented in Table II can be easily explained by a simple model of reaction between the epoxyacrylate oligomer and AEH. Each molecule of epoxyacrylate oligomer, irrespective of its molecular weight, possesses two unsaturated bonds (see Materials). Therefore, each molecule is able to introduce four electrons into the reaction. Two of them are used up in the generation of new bonds between the oligomer molecules and, as a result, the polymer chain grows longer, whereas the next two can generate bonds with AEH molecules.

Let us assume that the molecular weights of ADGD-5, ADGD-2, and AEH are 589, 904 and 142, respectively, and that the concentration of photoinitiator in each liquid formulation is constant and equal to 1.4% w/w. Let us also assume that the presence of photoinitiator does not influence the structure and properties of polymers originated as a result of photopolymerization. With these assumptions, one may calculate, for each composition

of epoxyacrylic formulation (Table I), a number of electrons participating in the curing reaction, coming both from oligomers and AEH molecules.

The results of these calculations, related to 100 g of liquid formulation, are listed in Table III. These data show that the same number of electrons is delivered by epoxyacrylate oligomers and AEH molecules while the concentration of AEH in formulation is about 28% w/w. This result is in excellent agreement with the experimental ones, presented in Table II. Therefore, it seems that the simple stoichiometric model of reaction can be applied in the case of UV photopolymerization of epoxyacrylates.

The similar relationship concerning the dependence of photosensitivity of modified polysiloxanes on the molar percentage of photosensitive groups was found by Lemaitre et al.¹⁰

The results presented above are rather obvious and may be predicted on the basis of a simple theory of chain polymerization.¹¹ It seems, however, that they may be useful for practical designs of UV-cured epoxyacrylate coatings.

Table III Comparison of a Number of Electrons Delivered by Epoxyacrylate Oligomers (A) ADGD-5 and (B) AEH in 100 g of Liquid Formulations Characterized by Different AEH Concentration

AEH Concentration (% w/w)	A	B	A : B
20.0	$1.31 \cdot 10^{23}$	$0.85 \cdot 10^{23}$	1.549
25.0	$1.24 \cdot 10^{23}$	$1.06 \cdot 10^{23}$	1.172
27.5	$1.20 \cdot 10^{23}$	$1.17 \cdot 10^{23}$	1.029
28.5	$1.18 \cdot 10^{23}$	$1.21 \cdot 10^{23}$	0.979
30.0	$1.16 \cdot 10^{23}$	$1.27 \cdot 10^{23}$	0.910
35.0	$1.07 \cdot 10^{23}$	$1.48 \cdot 10^{23}$	0.742

CONCLUSION

The results of the investigations of UV-cured epoxyacrylate protective coatings of optical fibers as well as the stoichiometric model of the curing reaction may be of great importance for optical fiber technology. They show that properties of these coatings may be regulated in a rather wide range of values by a simple change of active diluent concentration in the liquid formulation and that the degree of this regulation may be predicted.

The authors wish to thank W. Podkościelny, W. Charmas, and B. Tarasiuk for the synthesis of the epoxyacrylates used in this study.

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Received July 14, 1992

Accepted November 13, 1992