

# Acrylic Resins Resisting Oxygen Inhibition During Free-Radical Photocuring. I. Formulation Attributes

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**ABSTRACT:** A resin system was found to be resistant to the formation of an oxygen-inhibited layer when cured in air via conventional free-radical photopolymerization. The resins, containing multifunctional acrylates and a high concentration of a photoinitiator, were applied as thin film coatings and photocured with either visible light (400–500 nm) or UV light (254 nm). Fourier transform infrared spectroscopy with an attenuated total reflection attachment and pencil hardness were used to assess the surface double-bond conversion and the surface hardness of the coatings cured in air and without air, respec-

tively. The surfaces of many tested resins could produce similar conversions under both curing conditions. Optimally formulated resins had a high conversion and hardness even when the irradiance was as low as 50 mW/cm<sup>2</sup> for the visible light and 4 mW/cm<sup>2</sup> for the UV light. The requirements for possessing such a unique curing property are presented. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 112: 1565–1571, 2009

**Key words:** coatings; FT-IR; irradiation; photopolymerization; radical polymerization

## INTRODUCTION

Oxygen inhibition (OI) in free-radical polymerization is a well-known phenomenon.<sup>1–18</sup> Oxygen molecules can promptly react with primary and chain radicals, converting them into peroxy radicals, which are much less reactive toward double bonds at a normal photopolymerization temperature.<sup>2,4,10,18</sup> They can also quickly quench the excited triplet state of Norrish type II photoinitiators,<sup>18</sup> preventing them from generating free radicals. These two processes greatly reduce the population of reactive free radicals, leading to a long induction period, slow polymerization, and polymers with a low molecular weight. If the oxygen concentration is sufficiently high, polymerization can be practically halted to a stop; this is the case when a thin film of monomers is being cured via free-radical photopolymerization.<sup>3–17</sup> On account of its proximity to the atmosphere, the surface of the film tends to have a much lower conversion because of a continuous supply of oxygen from the air, and this results in a liquidlike, tacky, or mechanically weak formation, which is commonly called the oxygen-inhibited layer (OIL).

For obvious reasons, it is essential in most applications that the OIL be eliminated or at least substantially reduced. A number of preventive techniques have been practiced or investigated to overcome OI in photocuring, including (1) adding a surface-active photoinitiator to make a higher photoinitiator con-

centration in the coating surface zone,<sup>5</sup> (2) creating a physical barrier to prevent oxygen from contacting the resin,<sup>6,7</sup> (3) resorting to chemicals to convert dissolved oxygen into the nonreactive singlet state,<sup>4,8,9</sup> (4) incorporating tertiary amines to regenerate free radicals from inactive peroxides,<sup>4,10,11</sup> (5) purging with inert gases,<sup>4,12–14</sup> and (6) using extremely high irradiance to counteract oxygen replenishment from air.<sup>15–17</sup> All these methods work to some extent but are not without their respective shortcomings, which include but are not limited to changes in the surface properties in techniques 1 and 2, potentially inferior physical properties in technique 3, discoloration in technique 4, too strict curing conditions and limited portability in techniques 5 and 6, and potential charring and overcuring in technique 6. Therefore, the search continues for a better resin formulation or curing process.

During our attempts at developing new dental sealants, we found a new way of combating OI: the use of acrylic monomer resins consisting of a significant portion of acrylates with multiple double bonds ( $n \geq 5$ ) and a high concentration of a photoinitiator. The cured resins had no discernable OIL, and the surfaces showed high hardness,<sup>19</sup> smoothness,<sup>20</sup> wear resistance,<sup>21</sup> and the ability to prevent biofilm attachment.<sup>22</sup> The distinctive nature of this approach is that it achieves the no-OIL goal with low irradiance and without resorting to additional chemicals or any special equipment. Such great flexibility and portability well suit field applications of photocuring, such as preventive and restorative dentistry at a doctor's office. Our research work will be introduced in two articles. In this article, we discuss the nature

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TABLE I  
Tested Monomers

| Trade name   | Chemical name                                       | Functionality | Purity (%) <sup>a</sup> |
|--------------|---|---------------|-------------------------|
| Acrylate     |   |               |                         |
| SR285        | Tetrahydrofurfuryl acrylate                         | 1             | ~ 100                   |
| SR495        | Caprolactone acrylate                               | 1             | 90                      |
| SR259        | Poly(ethylene glycol) 200 diacrylate                | 2             | ~ 100                   |
| SR610        | Poly(ethylene glycol) 600 diacrylate                | 2             | ~ 100                   |
| SR349        | Ethoxylated 3 bisphenol A diacrylate                | 2             | ~ 100                   |
| SR415        | Ethoxylated trimethylolpropane triacrylate          | 3             | ~ 100                   |
| SR351        | Trimethylolpropane triacrylate                      | 3             | ~ 100                   |
| SR295        | Pentaerythritol tetraacrylate                       | 4             | ≤90                     |
| SR355        | Ditrimethylolpropane tetraacrylate                  | 4             | ~ 99                    |
| SR399        | Dipentaerythritol pentaacrylate                     | 5             | ~ 100                   |
| CN975        | Hexafunctional urethane acrylate                    | 6             | ~ 100                   |
| DPCA60       | Acrylate of caprolactone modified dipentaerythritol | 6             | ~ 100                   |
| Methacrylate |   |               |                         |
| SR203        | Tetrahydrofurfuryl methacrylate                     | 1             | ~ 100                   |
| SR210        | Poly(ethylene glycol) 200 dimethacrylate            | 2             | ~ 100                   |
| SR350        | Trimethylolpropane trimethacrylate                  | 3             | ~ 100                   |

<sup>a</sup> Per Sartomer's Materials Safety Data Sheets (MSDS).

of the formulation by examining the curability of a series of acrylic resins in air via conventional free-radical photopolymerization. In another article still under preparation, we will propose the mechanism preventing OI in light of the monomer structure and efficiency of initiation.

### EXPERIMENTAL

Tables I and II list the tested monomers, including acrylates with the number of double bonds (functionality) ranging from 1 to 6 and methacrylates with the number of double bonds ranging from 1 to 3, all courtesy of Sartomer Co. (Exton, PA), and the photoinitiators, respectively. All the chemicals were used without further purification. The percentages indicated hereafter are based on mass (wt %).

Resins were formulated with three purposes in mind. Group 1 formulas, used for studying the effects of the monomer functionality and photoinitia-

tor concentration, were made through the dissolution of the photoinitiator Lucirin TPO-L (TPOL) in acrylates of functionality ranging from 1 to 6. TPOL was used in these cases because, as a liquid, it could be easily blended into the resins even at a very high concentration. In addition, some acrylates, such as hexafunctional urethane acrylate (CN975) and dipentaerythritol pentaacrylate (trade name SR399), would have been too viscous to effectively dissolve any solid photoinitiators. Group 2 formulas, used for investigating the effects of various photoinitiators, were prepared through the dissolution of 50% SR399 and 5.0% photoinitiator (based on the monomer) in acetone (99.5%; Aldrich Chemical Co., Inc., Milwaukee, WI). In addition, 5.0% (based on monomer) 4-ethyl dimethylamino benzoate (Lancaster Synthesis Inc., Windham, NH), a tertiary aromatic amine used as a cointiator, was added to the resins containing a type II photoinitiator [including phenylpropanedione

TABLE II  
Tested Photoinitiators

| Trade name    | Chemical name  | Abbreviation | Type           | Manufacturer                                   |
|---------------|--|--------------|----------------|--|
| Irgacure 819  | Bis(2,4,6-trimethylbenzoyl) phenylphosphineoxide   | I819         | I              | Ciba Specialty Chemicals Corp. (Tarrytown, NY) |
| Lucirin TPO   | 2,4,6-Trimethylbenzoyl diphenylphosphine oxide   | TPO          | I              | BASF Corp. (Charlotte, NC)                     |
| Lucirin TPO-L | Ethyl-2,4,6-trimethylbenzoyl phenylphosphinate   | TPOL         | I              | BASF   |
| —             | Camphorquinone   | CQ           | II             | Hampford Research Inc. (Stratford, CT)         |
| —             | Phenylpropanedione   | PPD          | I, II          | Aldrich Chemical Co., Inc. (Milwaukee, WI)     |
| H-Nu 470      | 5,7-Diiodo-3-butoxy-6-fluorone   | H470         | II             | Spectra Group Ltd., Inc. (Maumee, OH)          |
| —             | Phenanthrenequinone  | PAQ          | II             | Aldrich  |
| Irgacure 784  | Bis( $\eta^5$ -2,4-cyclopentadien-1-yl)-bis[2,6-difluoro-3-(1H-pyrrol-1-yl)-phenyl] titanium | I784         | — <sup>a</sup> | Ciba   |

<sup>a</sup> Neither type I nor type II. This has been called pseudo type I.<sup>23</sup>

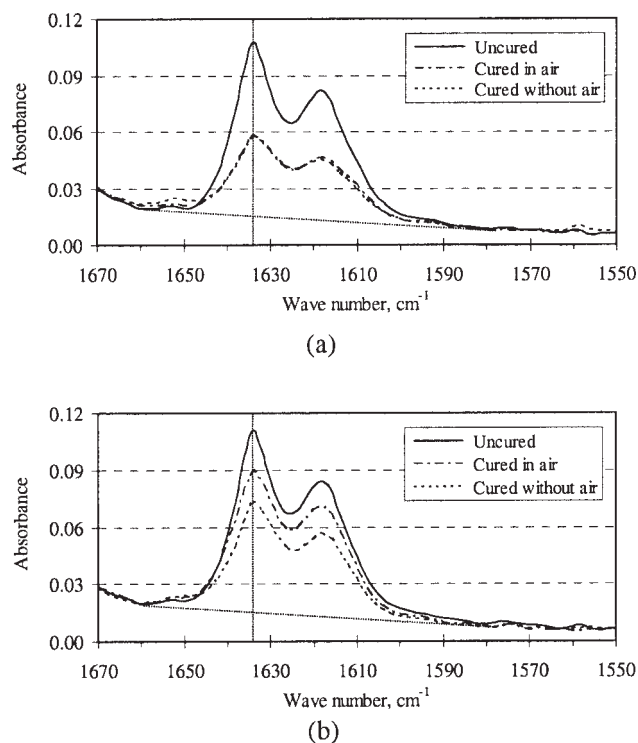
and Irgacure 784 (I784)]. The solvent acetone was incorporated to facilitate the dissolution of the solid photoinitiators. Finally, group 3 formulas, used for comparing acrylates with methacrylates, were formulated through the blending of 20% TPOL with one of the corresponding acrylate–methacrylate pairs [tetrahydrofurfuryl acrylate (trade name SR285) vs tetrahydrofurfuryl methacrylate (trade name SR203), poly(ethylene glycol) 200 diacrylate (trade name SR259) vs poly(ethylene glycol) 200 dimethacrylate (trade name SR210), and trimethylolpropane triacrylate (trade name SR351) vs trimethylolpropane trimethacrylate (trade name SR350)]. In each pair, the monomers possessed an identical ester substitute but differed in either the acryloyl or methacryloyl moiety.

For photocuring, a thin coat of a resin (20–50  $\mu\text{m}$  thick) was spread onto a clear polyester film (0.25 mm thick), beneath which was a cured tooth-colored composite as the background. The resin was either uncovered for curing with oxygen (in air) or covered with another clear polyester film for curing without oxygen (without air). The solvent in the coat of the acetone-containing resin was allowed to evaporate in the dark for at least 60 s before the resin was irradiated or covered. The resins were irradiated either with a visible light with a wavelength of 400–500 nm (VIP quartz–tungsten–halogen dental curing unit, Bisco Inc., Schaumburg, IL) or with a UV light at 254 nm (Pen-Ray lamp, UVP, Upland, CA). Because it did almost all the photocuring, visible light is the default curing unit throughout this article unless specified otherwise.

The degree of conversion (DC) of double bonds was measured with Fourier transform infrared (FTIR) spectroscopy (Spectrum 1000 FTIR spectrometer, PerkinElmer, Norwalk, CT) with an attenuated total reflectance (ATR) unit (Golden Gate P/N10500 series, Graseby Specac Inc., Smyrna, GA). The cured resin was pressed against the diamond prism, and the surface was scanned 10 times at a  $4\text{-cm}^{-1}$  resolution to generate an FTIR–ATR spectrum. The height of the aliphatic double-bond peak ( $1634\text{ cm}^{-1}$ ) was measured for both the uncured ( $H_{\text{uncured}}$ ) and cured ( $H_{\text{cured}}$ ) resins. The conversion was calculated from their ratio:

$$\text{DC}(\%) = \left(1 - \frac{H_{\text{cured}}}{H_{\text{uncured}}}\right) \times 100 \quad (1)$$

The mean of triplicates was analyzed with an analysis of variance and the Student–Newman–Keuls test. Use of the statistics was meant to show the reproducibility of the measurements only. A resin's resistance to OI was assessed either by the difference between the DCs cured in air (uncovered) and without air (covered) or by the ratio of the former to the latter (DC ratio). The OI was higher when the DC difference was smaller or the DC ratio was closer to unity.

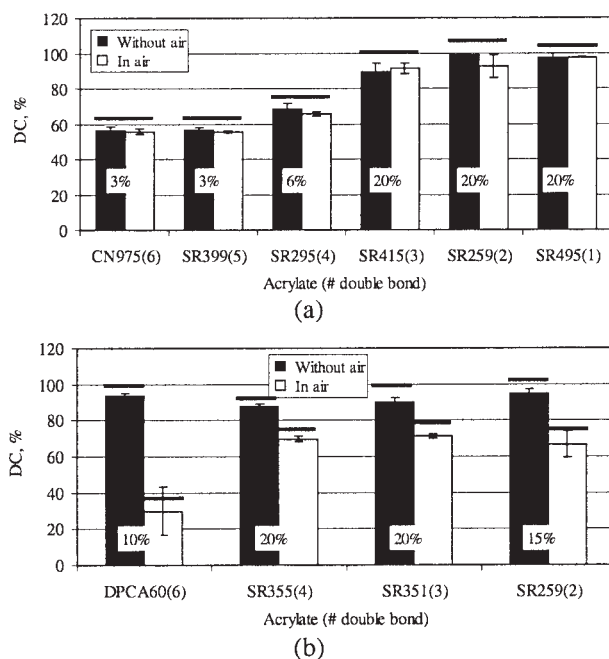


**Figure 1** FTIR–ATR spectra of the uncured and cured pentaacrylate SR399 with (a) 3.0 and (b) 1.0% TPOL. Indicated are the peaks at  $1634\text{ cm}^{-1}$  and baselines for the determination of their heights.

The surface physical properties were evaluated by the pencil hardness (ASTM D 3363-00) with a set of Kemberly graphite drawing pencils (General Pencil Co., Jersey City, NJ). The hardness of a specimen was assigned by the number of the hardest pencil not able to score any visible mark on the cured surface. The pencils used for testing were in the following ascending hardness order: 5B, 4B, 3B, 2B, B, HB, 1H, 2H, 3H, 4H, and 5H. As an approximate correlation, a cured coating surface was no longer tacky when its pencil hardness was greater than 5B, or it could not be scratched by a human fingernail when the number was greater than 1B.

## RESULTS

Figure 1 displays typical FTIR–ATR spectra of uncured and cured acrylates. The absorption band centered at  $1634\text{ cm}^{-1}$  is associated with aliphatic  $\text{CH}_2=\text{CH}-$  stretching.<sup>24</sup> The conversion of the monomer to the polymer reduces the number of aliphatic double bonds and thus the peak height. For the OI-resistant resin (with a high photoinitiator concentration), the peak height was similar for curing in air and without air [Fig. 1(a)]. Conversely, for the OI-susceptible resin (with a low photoinitiator concentration), the peak height was much higher for

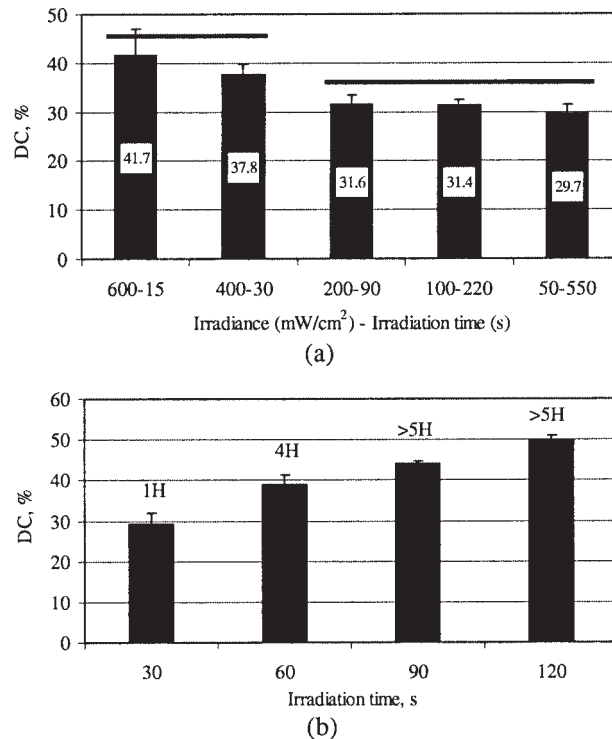


**Figure 2** DCs of acrylates with different numbers of double bonds (in parenthesis) and different concentrations of the photoinitiator TPO (numbers on the columns). The samples were photocured for 30 s at 500 mW/cm<sup>2</sup> without air or in air: (a) those showing high resistance to OI and (b) those showing low resistance to OI. DC pairs under the same bar were statistically the same ( $p > 0.05$ ).

that cured in air than for that cured without air [Fig. 1(b)].

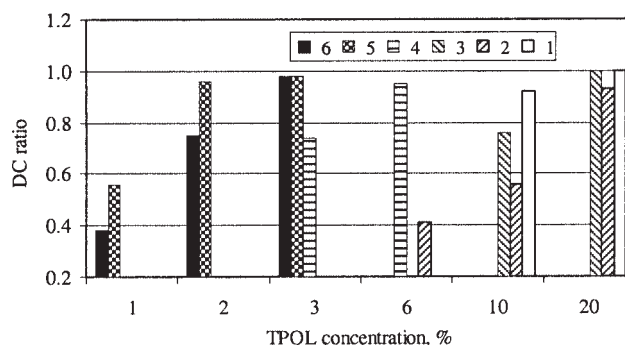
Figures 2–4 describe the curing behavior of group 1 formulas. Figure 2 presents the DCs of acrylates with the number of double bonds ranging from 1 to 6 and with the concentration of photoinitiator TPO ranging from 3 to 20%. Many of them showed considerable OI resistance [Fig. 2(a)], but some did not [Fig. 2(b)]. Figure 2 indicates whether or not being OI-resistant also depended on the concentration of the photoinitiator. Diacrylate SR259 was OI-resistant with 20% TPO but was not with 15% TPO. Although not all the tested acrylates resisted OI, those that did were all acrylates. None of the methacrylates were OI-resistant, as shown later.

Figure 3(a,b) depicts the DC of pentaacrylate SR399 with 3.0% TPO cured under 50–600 mW/cm<sup>2</sup> visible light and that of hexaacrylate CN975 with 5.0% Lucirin TPO (TPO) cured under 4 mW/cm<sup>2</sup> UV light. Even with some of the extremely low irradiance in air, the resins still achieved decent DC values when the irradiation duration was sufficiently long. Note that the DC was about 50% after the resin was irradiated 120 s with 4.0 mW/cm<sup>2</sup> UV, which is only slightly lower than the DC of 56% for CN975 in Figure 2(a), for which 30 s of 500 mW/cm<sup>2</sup> visible light was used. Figure 3(b) also includes the pencil hardness of the cured surfaces. Even when the DC

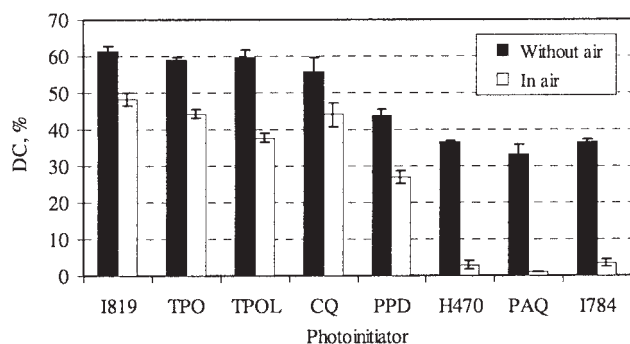


**Figure 3** DCs of (a) pentaacrylate SR399 with TPO 3.0% cured with visible light and (b) hexaacrylate CN975 with TPO 5.0% cured with UV light at 4 mW/cm<sup>2</sup>. Both were cured in air. DCs under the same bar were statistically the same ( $p > 0.05$ ).

was only about 30%, the coating surface was as hard as that of a dimethacrylate-based dental resin cured without air (HB). When it was higher than 40%, its hardness (>5H) was greater than that of cast poly (methyl methacrylate) (4H). One must understand the difference between the DC of double bonds and the DC of the monomer for a multifunctional



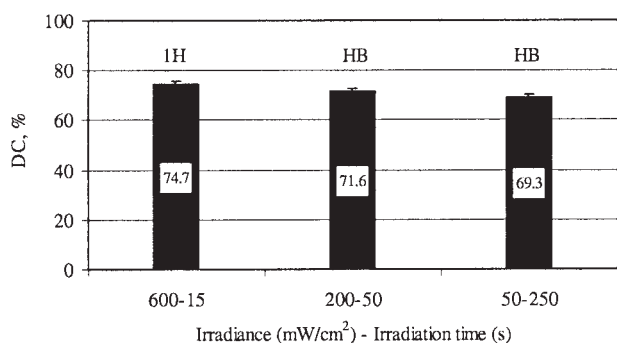
**Figure 4** DC ratio (DC cured in air vs DC cured without air) as a function of the number of double bonds per molecule (see legend) and the concentration of TPO for samples cured for 30 s at 500 mW/cm<sup>2</sup>. The number of double bonds for the associating monomers were 6 for CN975, 5 for SR399, 4 for pentaerythritol tetraacrylate (trade name SR295), 3 for ethoxylated trimethylolpropane triacrylate (trade name SR415), 2 for SR610, and 1 for caprolactone acrylate (trade name SR495).



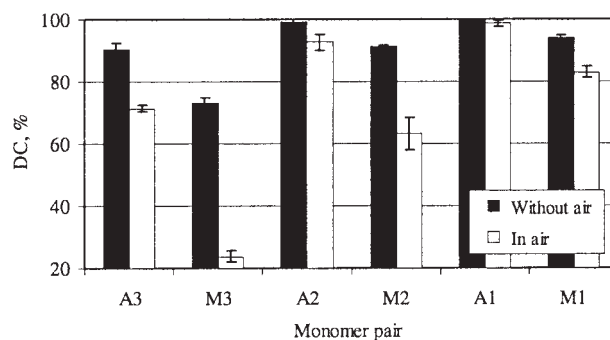
**Figure 5** DCs of the pentaacrylate SR399 with 5.0% of different photoinitiators cured for 30 s at 500 mW/cm<sup>2</sup> without air and in air.

monomer system. The monomer is converted to the polymer as long as one of the double bonds reacts. Therefore, a seemingly low DC of double bonds may in fact result in a high DC for the monomer. For instance, a DC of 40% for the pentaacrylate in Figure 3 means that on average two of the five double bonds reacted for each molecule. With such a DC, there was virtually no remaining monomer. Supporting evidence can be found from the fact that no leachable material was detected from the dental sealant comprising primarily the pentaacrylate after curing.<sup>19</sup>

Figure 4 correlates the DC ratio to the number of double bonds and photoinitiator concentration, suggesting that the resistance to OI is a function of their interplay. A higher photoinitiator concentration produced a higher OI resistance, and an acrylate with a higher functionality required a lower concentration of the photoinitiator to achieve that goal. For example, it took only 3% TPOL for the acrylates with five or six double bonds to reach a DC ratio higher than 0.95, whereas 20% TPOL was required for those with one to three double bonds. Therefore, both the pentaacrylates and hexaacrylates had already shown



**Figure 6** DCs of a blend of 28% CN975 (a hexaacrylate) and 65% SR349 and SR610 (both diacrylates) plus 7.0% TPO.



**Figure 7** DCs of corresponding acrylates and methacrylates with functionalities of 1-3 and 20% TPOL cured for 30 s at 500 mW/cm<sup>2</sup> without air and in air: (A1) SR285, (M1) SR203, (A2) SR259, (M2) SR210, (A3) SR351, and (M3) SR350.

high OI resistance with a moderate amount of the photoinitiator. Their coatings cured in air also possessed pencil hardness greater than 4H. With a sufficiently high concentration of TPOL (20%), nevertheless, all the acrylates in Figure 4 were essentially cured without OIL.

Figure 5 shows the effects of photoinitiators on the DC of SR399 (group 2 formulas) cured with 500 mW/cm<sup>2</sup> for 30 s. All three type I photoinitiators tested (Table II) were effective, whereas half of the type II photoinitiators were not. I784, a pseudo-type I, behaved just like an inefficient type II.

A coating with OI resistance as well as good surface hardness can also be attained with a blend of a multifunctional acrylate and diacrylates. As Figure 6 demonstrates, a resin with a monomer ratio of 30% hexaacrylate to 70% diacrylates cured in air at 50 mW/cm<sup>2</sup> could yield a DC close to that of a resin cured at 600 mW/cm<sup>2</sup>, although a higher radiant exposure (total energy input) had to be used. Their pencil hardnesses were also comparable. All three curing conditions in Figure 6 produced a surface too hard to be scratched with a fingernail.

Finally, Figure 7 compares corresponding pairs of acrylates and methacrylates (group 3 formulas). Despite their identical functionality and similar molecular structures, the methacrylate in each pair always had a greater DC difference. All the methacrylates cured in air possessed a tacky surface, which indicated significant OI.

## DISCUSSION

Molecular oxygen has a much higher reaction rate toward a free radical (rate constant = 10<sup>9</sup>-10<sup>10</sup>/M/s) than acrylate molecules (10<sup>6</sup>-10<sup>7</sup>/M/s).<sup>25</sup> To maintain a significant rate of chain propagation to compete with OI, the acrylic curing system has to have an oxygen concentration lower than the critical level

$(5 \times 10^{-6} \text{ M})$ .<sup>3</sup> This has to be accomplished not only by exhaustion of the predissolved oxygen molecules ( $\sim 10^{-3} \text{ M}$ )<sup>3,4,12</sup> but also by the interception of those coming from air. The latter is much more crucial for thin film coatings because of their huge surface-to-volume ratio.

One way of reducing the oxygen concentration is to use the free radicals themselves to convert dissolved oxygen molecules; this takes advantage of the aforementioned prevailing oxygen-radical reaction. In regular photocuring in air, because the generated free radicals have to instantly capture almost all incoming oxygen molecules in addition to promptly depleting most of the predissolved ones, extremely high irradiance in the UV range is needed to produce such a huge population of radicals. Such a requirement rules out the use of the technique in some areas, such as the field of dentistry, in which UV is strictly prohibited. Our approach, on the other hand, can essentially lift this restriction. With an optimal formulation, the resin can be photocured without significant OI even under very low irradiance from visible light, such as  $50 \text{ mW/cm}^2$ , or under even lower irradiance from UV light, such as  $4 \text{ mW/cm}^2$  (Fig. 3).

We used FTIR-ATR to assess the extent of the surface cure because of its surface sensitive measurement. The measured distance from the surface can be calculated by the penetration depth ( $Z_p$ ) of the evanescent field:<sup>24</sup>

$$Z_p = \frac{\lambda_0}{2n_2\pi\sqrt{\sin^2\alpha - (n_1/n_2)^2}} \quad (2)$$

where  $\lambda_0$  is the wavelength of the IR beam;  $\alpha$  is the incident angle; and  $n_1$  and  $n_2$  are the refractive indices of the sample material and the ATR prism, respectively.  $Z_p$  is around  $1.2 \mu\text{m}$  when  $\lambda_0$  is  $1600 \text{ cm}^{-1}$ ,  $\alpha$  is  $45^\circ$ , and  $n_1$  and  $n_2$  are 1.5 and 2.4 for acrylates and diamond, respectively. This is the zone in which oxygen has a major impact because of its limited diffusion length in a short time.<sup>10</sup> One advantage of using ATR was that there was no need to use an internal standard for calibration of the path length, which was nearly identical for all the samples because of the constant value of  $Z_p$ .

Similar DCs for a thin film cured in the presence and absence of air suggest adequate surface cure. Not only did many in-air cured resins show comparable DCs, but some of them also possessed other properties associated with a high DC, such as high hardness, high abrasion resistance, and no cytotoxicity in a sensitive agarose overlay method (ISO 10993-5). Pencil hardness was used as a simple and convenient way to complement the measurement of DC. Its good numbers ( $>1\text{B}$ ) support the inference of excellent surface cure.

According to this work, to achieve an adequate surface cure, three necessary conditions have to be satisfied in the resin formulation: (1) the use of acrylates, (2) a high functionality, and (3) a high concentration of the photoinitiator (preferably type I).

The first condition reflects the fact that none of the tested methacrylates showed OI resistance anywhere close to that of their acrylate counterparts (Fig. 7). Their lower polymerization rate may be one of the reasons. A typical methacrylate has a rate of polymerization 20–30 times lower than that of the corresponding acrylate.<sup>26</sup> This would make a methacrylate much less a competitor to OI. There are reports that methacrylates are more resistant to OI than acrylates in terms of the rate reduction.<sup>18,27</sup> Nevertheless, the absolute rate for methacrylates may still be too low to be competitive.

The second condition needs some elaboration. Although many acrylates of low functionality can be cured without OIL as long as a sufficient amount of a photoinitiator is present (Fig. 4), for most practical applications, acrylates have to have at least three or better four double bonds per molecule to avoid too much photoinitiator being used. The use of a photoinitiator at a concentration of 20% would not be desirable because, as low-molecular-weight species, decomposed or undecomposed photoinitiators will impair the physical, chemical, and biological properties of the cured material. Nevertheless, a modestly high concentration of a photoinitiator ( $<8\%$ ) appeared to be nondetrimental (Figs. 3 and 6). Preservation of excellent physical properties for such formulated resins<sup>19–22</sup> is likely due to their extremely high crosslinking density, which is a result of the high functionality of the monomers.

Acrylates of high functionality do not have to be the only monomers. A large portion of difunctional acrylate can be blended as well. As demonstrated in Figure 6, only 30% of the hexaacrylate CN975 was able to render the resin almost free of OIL. Such flexibility in the resin formulation is extremely useful for many applications. Acrylates of high functionality are usually accompanied by a high viscosity. Their applications are very limited without the addition of diluents. Diacrylates with a low viscosity can serve as reactive diluents to make the formula less viscous as well as nonvolatile. For instance, the viscosity of hexaacrylate CN975 was  $14 \text{ Pa s}$  at  $22.0^\circ\text{C}$ . Its blend with two diacrylates, ethoxylated 3 bisphenol A diacrylate (trade name SR349) and poly(ethylene glycol) 600 diacrylate (trade name SR610; Fig. 6), had a viscosity of only  $1.2 \text{ Pa s}$ .

The third condition seems to make sense because, after all, a high concentration of a photoinitiator can generate a large quantity of free radicals in a short period of time. As suggested in Figure 4, for OI resistance, a minimum photoinitiator concentration of

2% had to be used for any of the acrylates tested. Much more was needed if their functionality was lower than 5. An examination of Figure 5 suggests that the type I photoinitiators are much more effective than the type II photoinitiators in resisting OI. This is likely due to two reasons: different reaction rates toward oxygen in their excited states and the use of a coinitiator or lack of it. Because of its very short lifetime, the triplet excited state of type I photoinitiators is not prone to oxygen quenching.<sup>3,7</sup> On the other hand, type II initiators can be readily deactivated because of their long-lived triplet state.<sup>10</sup> Moreover, excited type II photoinitiators have to react with a hydrogen donor coinitiator to produce free radicals, and this increases their chances of reacting with oxygen molecules.

An important point to be emphasized is that the three aforementioned requirements are only necessary conditions, not sufficient ones. Resins so formulated may or may not be photocured without forming an OIL. This is clearly implicated in Figure 2(b).

How acrylates so formulated acquire such unique OI resistance is still under investigation. It is fascinating that, against our intuition, the resins are able to produce an OIL-free surface even when cured under very low irradiance. In a related study, we proposed that the rate of cure is not an important factor in determining the OI resistance.<sup>28</sup> In fact, the acrylates with higher functionality polymerized more slowly.<sup>28</sup> Nevertheless, some decent curing speed is still necessary because similar resins initiated via a redox process using a peroxide with an amine could not produce a surface without an OIL. We believe that the requirement of high functionality has something to do with the crosslinking density and presumably the rate of crosslinking site formation. A closely knitted mesh of polymerized segments may be so efficient in impeding oxygen permeation that eventually chain propagation proceeds in an oxygen-free environment. Oxygen permeation through a polymer matrix is a product of its solubility coefficient and diffusion coefficient, both being functions of the free volume.<sup>29</sup> More detailed discussion will be given in the second article of this work.

## CONCLUSIONS

This study describes a new approach to making acrylic resin formulas resistant to OI during photocuring. An optimally formulated resin can be cured to achieve similar DCs via conventional free-radical

photopolymerization in air and without air. The surface of the cured resin is not only without tackiness but also sufficiently hard to withstand pencil scoring tests. Moreover, the resin can show such OI resistance even during low irradiance curing. The essential requirements for a practically applicable formulation are the use of a portion of acrylates with at least three double bonds and a high concentration of the photoinitiator.

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