New Developments in UV-Curable Urethane Acrylate Coatings

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Introduction

Radiation curable coatings based on urethane acrylate (UA) oligomers represent the major class of coatings widely used in industry.[1] Such coatings are used for protection of articles and objects as well as in such applications as printing (inks), lithography, and as adhesives. Cured coatings tend to give films with a good combination of toughness and elasticity, and other valuable properties. Study and improvement of properties of urethane acrylate coatings (UAC's) are of permanent interest. There is a demand for UAC's capable of cure under low radiant excitance ("intensity") and/or low radiant exposure ("dose"). Light absorbing and light scattering compounds, which may be present in a UAC, attenuate radiant intensity. In another situation, an object to be cured moves with a high speed in a process, and the coating has a very brief exposure to curing radiation. The present paper addresses this issue. We were also looking for a UAC that consists of only one oligomer, as well as a UAC with good adhesion to glass and other substrates.
This paper presents results of our study of UAC's, which are summarized in ten recent patents and patent application publications.

Techniques

We studied kinetics of UV-cure of coatings by real time, fast acquisition of IR spectra using a Nicolet 870 FTIR (ATR regime, rapid scan), with photoDSC (Perkin-Elmer DPA-7), and with a cure monitor CM 1000 (Spectra Group). The UV light source was a Lightingcure 200 (Hamamatsu). The UV intensity on samples in the experiments employing the Lightingcure instrument described in this work was 20 mW/cm^2. Devices and techniques for kinetic measurements are described in more detail in ref. 2, 3. In particular, the rate of cure was monitored by the disappearance of the absorption peak in the area with wavenumber ca. 812 cm^{-1} during UV irradiation. In the present work we deal with UV-A light (i.e., λ 320-390 nm). Measurements of physical properties of cured coatings as well as their adhesion to glass are described in ref. 4-7.

Reagents

Darocur$^®$ and Irgacure$^®$ brand photoinitiators were provided by Ciba Additives. Materials abbreviated as SRxyz were provided by Sartomer. We used several hydroxyl functionalized acrylates, in particular "caprolactone" acrylate SR495. UAC's were additionally stabilized by ionol (2,6-di-*tert*-butyl-4-methylphenol); commercial acrylates have hundred(s) of ppm of an inhibitor already. Benzoin, styrene, isophorone diisocyanate (IPDI), ionol, catalyst dibutyltin dilaurate ("Sn"), propan-2-ol (i-PrOH), vinyl acrylate were obtained from Aldrich. Fullerenes C$_{60}$ came from the MER Corporation. 4,4'- methylenebis(cyclohexyl isocyanate) (Desmodur W) and Acclaim 2220N (hereinafter "Acclaim") were from Bayer. The flow control additive BYK 331 from BYK Chemie USA was used at a level of ~ 200 ppm in all UAC's prepared in house. UCT 7840 KG, which is 3-isocyanopropyltriethoxysilane, was from United Chemical Technology. This compound was used as a functionalized adhesion promoter. All chemicals were used as received.   We also worked with an experimental UV-curable coating, UAC-

SEC, provided by a commercial vendor. UAC-SEC *base* was obtained from the vendor as well. UAC-SEC *base* is the UAC-SEC coating without photoinitiator. All chemicals were used as received. The synthesis and measured properties of radiation-curable coatings with good adhesion to polyolefins are described in ref. 8.

Results and Discussion

"All-in-one" coating

UA oligomers were prepared in the usual way: by a reaction of IPDI or Desmodur W with polyol in the presence of "Sn". Oligomer obtained this way was endcapped with SR495, cf. the previous section. In a number of experiments, photoinitiators with hydroxyl groups (benzoin, Darocure 1173, Irgacure 184, Irgacure 2959, some others) were reacted with diisocyanate as well. In our syntheses, functionalized adhesion promoters trialkoxysilanes with isocyano-, amino-, or thiol terminal group were reacted either with polyol or with NCO. Thus, we prepared oligomers end-capped not only with acrylate (or methacrylate) groups, but also endcapped with photoinitiator and with adhesion promoter. Usually less than ten percent of the end groups had a photoinitiator or an adhesion promoter moiety. Our experiments demonstrate that such oligomers represent coatings with good properties, *vide infra*. These oligomers turn out to be pourable at room or slightly elevated temperatures (30 - 45 ^{0}C). One may or may not add reactive diluents to such oligomers.

Oligomers with grafted photoinitiators are evidently light sensitive (LS). LS-UA oligomers possess several beneficial properties. The rate of cure of LS-UA oligomers is usually higher than the rate of cure of similar UA oligomers with dissolved photoinitiator. Figure 1 demonstrates kinetic curves of the cure of an oligomer with a grafted initiator (benzoin) and the analogous oligomers with dissolved benzoin, employing the real time IR measurement of the disappearance of the 812 cm^{-1} peak.[5]

Correct?
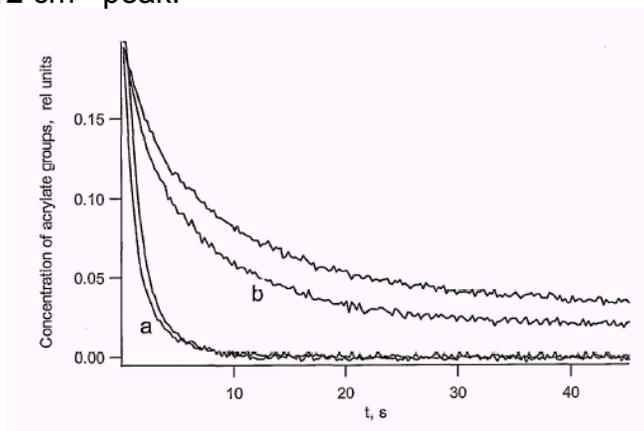
Figure 1. Kinetics of UV- cure of UA oligomer at 40 ^{0}C initiated by benzoin, which is (a) chemically-tethered, or (b) dissolved in the oligomer, see the text.

The level of benzoin was the same in both oligomers. In case (b) the coating had an endcapping agent i-PrOH in the same molar amount as benzoin in the first coating. The composition of these two UAC's are presented in the Table 1.

Table 1. Formulations of "light-sensitive" (a) and conventional (b) coatings

Input, mass percent	a	b
IPDI	14.9	14.7
ionol	0.2	0.2
benzoin	5.2	5.1
"Sn"	0.4	0.4
Acclaim	61.8	61.0
UCT 7840 KG	0.4	0.4
SR495	17.0	16.8
i-PrOH	0	1.4

It follows from the Figure 1 that the oligomer cures faster with benzoin *grafted* to the backbone compared to the cure of the oligomer with benzoin *dissolved* at the same level. The cure kinetics satisfactorily followed the first order law. We obtain rate constants k = 0.65±0.1 and k= 0.13±0.02 s^{-1} for traces (a) and (b), respectively, cf. Figure 1. (Four curves taken in different experiments are presented in Figure 1 and in Figure 2 below in order to demonstrate experimental error.)

We speculate that formation of two C-centered radicals under photodissociation of initiator bound to the oligomer results at the first moment in the advanced stage of polymerization compared to a common photopolymerization. At the first moment after absorption of light and the primary photo-physical processes, an *oligomeric free radical* is produced accompanied by a *low MW radical*. On the other hand, a standard photolysis of initiator dissolved in oligomer results at the first moment in a formation of *two low MW radicals*. In this instance, only those low MW radicals that have escaped diffusion-controlled self-termination in the solvent bulk react with oligomer to form an oligomer free radical.

Similarly, we have an experimental demonstration that an adhesion promoter tethered to a polymer chain anchors the polymer more strongly to a substrate than adhesion promoter dispersed in the polymeric media, other conditions being very similar.[9,10]

Oligomers endcapped only by photoinitiator and by adhesion promoter can be prepared separately and after that added to the main "usual" oligomer endcapped by acrylate groups.[9] That is another way to prepare a LS oligomer.

All of the LS oligomers discussed above have the following generic structure:

$$\mathbf{A^1-D^1-P-D^2-A^2},$$

where $\mathbf{A^1}$ and $\mathbf{A^2}$ are oligomer termini, which may be the same or different, $\mathbf{P}$ is oligomer backbone (usually a polyol), $\mathbf{D^1}$ and $\mathbf{D^2}$ are carbamate (urethane) linking groups, which may be the same or different. As it was stated above, $\mathbf{A^1}$ and $\mathbf{A^2}$ are, in the main, acrylate groups.

A common formulation of a UV-curable UAC consists of the principal oligomer and a photoinitiator or mixture of photoinitiators, that is, it has *at least two* ingredients. We suggest a formulation consisting *of only one component,* the LS oligomer. This difference distinguishes our UAC from all others, and it is important from the intellectual property standpoint.[5] Usually common UAC's also have one or more reactive diluents in their formulations (a third/fourth, etc., component). The user may add reactive diluent to LS oligomers; such a UAC will still be a novel UV-curable coating lacking a dissolved photoinitiator.[5]

Vinyl acrylate as a promoter of cure

It is known that vinyl acrylate is a light-sensitive compound that polymerizes under irradiation with UV-light.[11] It is not surprising that an addition of vinyl acrylate can provide an acceleration of cure of coatings. Such experiments were done with the UAC-SEC coating and other coatings.[4,11] Vinyl acrylate has a low viscosity and serves as an excellent reactive diluent. At the same time the low b.p. of vinyl acrylate is an issue. C. Hoyle, et al, have noticed that compounds of similar structure, viz. vinyl crotonate and vinyl cinnamate, initiate polymerization under irradiation. Vinyl crotonate has a higher b.p. than vinyl acrylate (133 vs. 91 ^{0}C).

Fullerenes as promoters of cure

Fullerenes possess electron-accepting properties in the excited triplet state, and they produce reactive free radicals under photo-reduction. A solution of fullerenes has a pink color, though we note that fullerenes have low solubility in most solvents. Desmodur W dissolves C_{60} in a relatively high concentration of 3%. Two UAC's based on Desmodur W were prepared in the same manner, with the only difference being the presence or absence of C_{60} in Desmodur. The UAC containing C_{60} cures ~30% faster than the analog UAC without C_{60} under our experimental conditions.[12] The kinetics of cure of the Desmodur W UAC's were measured by real time IR.

We added 4 wt.% of Darocur 4265 and 1.5 wt.% of styrene to UAC-SEC *base* (cf. Reagents section above). We named this "Coating A". "Coating B" was almost the same as Coating A with the exception that we added not styrene but a saturated solution of fullerenes in styrene in the same level of 1.5 wt.%. Cure profiles of Coatings A and B obtained with a cure monitor are presented on Figure 2.[12]
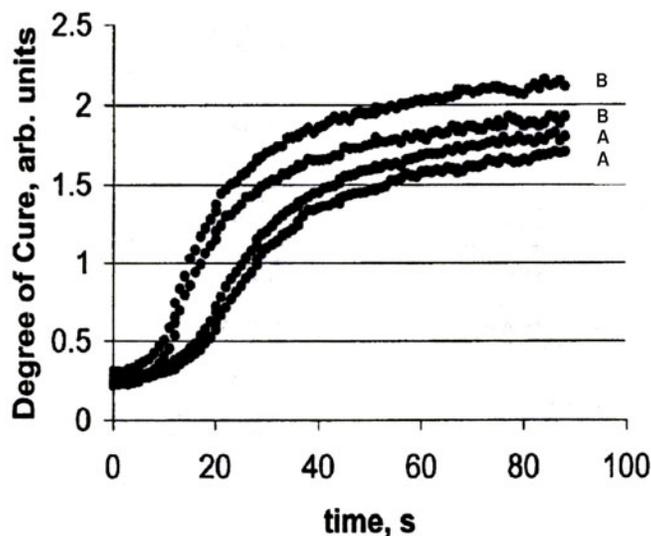
Figure 2. Kinetics of UV- cure of coatings A and B, cf. the text.

It follows from Figure 2 that the presence of fullerenes accelerates cure. Pink C_{60} additionally harvests visible light from the lamp and serves as type II photoinitiator.

Multifunctional acrylates as promoters of cure

We have observed that an addition of low MW multifunctional acrylate with functionality of three to five results in an acceleration of cure of many UAC's.[13]   In particular, an addition of low MW multifunctional acrylate SR355 (tetra acrylate) or SR399 (penta acrylate) in a level of 1-2% to UAC-SEC leads to an acceleration of cure without detrimental effect on mechanical properties of a soft cured coating.   Such a low level of multifunctional acrylates can be added without a significant reduction of elongation to break of coatings.[13]

It is well understood that the rate of cure decreases with conversion due to several factors: decrease of concentration of acrylates, decrease of concentration of photoinitiator and the radical cage-escape value.[1-3]   Chain entanglements and a reduced mobility of macroradicals at a high degree of polymerization leads to retardation of polymerization as well. We assume that low MW acrylates have a high diffusion coefficient compared to macroradicals, and they have a high probability of a reaction upon encounter with entangled macroradicals.   Multifunctional acrylates apparently serve as chain transfer agents.   They "rescue" a free valence of entangled macroradical and continue polymerization.

Adhesion to substrates.

Coatings containing vinyl acrylate demonstrate improved adhesion to glass.[4]

A selection of novel chemistries has been explored in an effort to find solutions to various common problems with coating oligomer performance, including adhesion to a substrate.[8]   To achieve tenacious adhesion to polyolefins and other low surface tension substrates, a UA oligomer of high MW and low functionality has been evaluated.   In initial studies, this oligomer shows excellent adhesion to treated polyethylene and polypropylene, and it shows these same qualities in formulations prepared to coat untreated polyethylene.   A ladder study of concentration vs. adhesion indicates that co-oligomers for alternative film properties (hardness, abrasion resistance) can be included.

In evaluating oligomers of very low viscosity for use in flexo, gravure, spray coatings, inkjet applications, and other areas requiring low viscosity, a series of developmental dendritic polyester acrylates was reviewed.   Prepolymers prepared had a wide range of functionality and very low viscosity (η), typically 250 to 350 cps neat at 25 °C.   Variations in functionality showed adhesion affinity for different substrates, with an excess of residual hydroxyl sites giving greater adhesion to metals.   These products exhibited good hardness and abrasion resistance.   An addition of acrylate reactive diluents resulted in formulations of very low η, though high oligomer content, which are easily sprayed.   As an example, a 50:50 blend of one dendritic polyester acrylate with tripropylenglycol diacrylate (TPGDA) has $\eta \approx 45$ cP at 25 °C.

Lastly, an example of a telechelic acrylated polymer in a monomer solution was evaluated.   The polymer backbone under scrutiny was a high polymer of bisphenol A and epichlorohydrin, commonly referred to as a phenoxy resin.   A quantity of acrylate functionality was imparted to the resin, allowing it to participate in crosslinking reactions.   While high in viscosity, there is an impressive range of substrates to which this material can adhere to, presumably due to a large number of secondary hydroxyls, along with low shrinkage resulting from high molecular weight per acrylate group.   Coatings and adhesives using this material are surprisingly hard (greater than 80D durometer hardness) considering the low crosslink density.[8]

Hybrid coatings

There is another avenue to modify the properties of UAC's.   One can add oxiranes

(epoxides) and run cationic photocure of oxiranes simultaneously with free-radical cure of acrylates.[6] Cationic photoinitiators as well as free-radical photoinitiators are added to a typical formulation. Thus a hybrid coating is obtained. Often two independent polymerizations result in an interpenetrating network (IPN). A special study is required if one is to claim the formation of an IPN system.

   We present below two chemical structures of commercially available compounds (dioxirane and diacrylate TPGDA) that we used in our work.

$$CH_2=CH-\overset{\overset{O}{\|}}{C}-O-(C_3H_6O)_3-\overset{\overset{O}{\|}}{C}-HC=CH_2$$
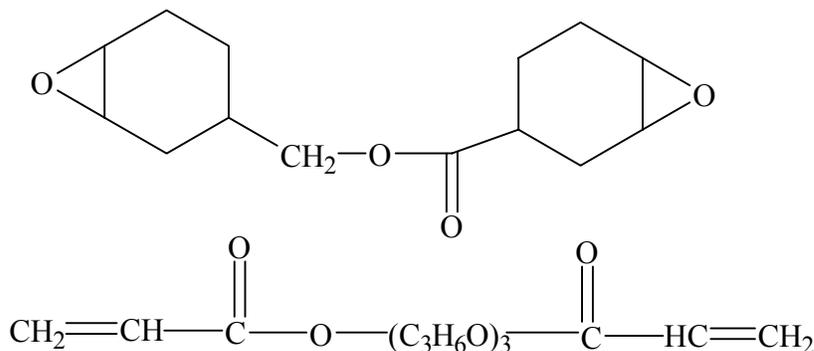
Coatings incorporating these types of acrylates and oxiranes demonstrate very good properties.[6]

Direct vs. Reverse Addition

   A UA oligomer is usually prepared by a reaction of diisocyanate (**D**) with difunctional polyol (**P**), **D+P**, followed by a reaction of residual isocyanate groups with hydroxy-functionalized acrylate (**A**). This sequence of reactions is usually called "a direct addition." It is common to use as **A** 2-hydroxyethyl acrylate or SR495, see above. We have compared properties of UA oligomers obtained in two ways:

$$\textbf{UA = (D+P) + A} \text{ vs. } \textbf{UA = (D+A) + P}$$

The latter sequence of reactions is often called "a reverse addition." We have found that the reverse addition leads to lower MW and to a lower η of the UA oligomer compared to the direct addition, stoichiometry of reagents and reaction conditions being the same. A reaction of **D**, especially non-symmetrical **D**, with polyol **P** has a lower selectivity than that of a reaction between two low MW compounds **D + A**. The latter reaction leads to a high concentration of mono isocyanates **D**-**A**. Mono isocyanates react with for example diol **P** with a formation of **A-D-P-D-A** as the main product. In a common method, a reaction of **D+P** leads to **D-P-D** and a significant contribution of products of higher MW like **D-P-D-P-D**. In this manner, the direct addition results in a higher MW and higher η of oligomers compared to similar oligomers synthesized by the reverse addition.[14]

Miscellaneous

   In some cases it is necessary to cure two different layers of coatings applied "wet-on-wet" on top of a substrate. The top-most layer attenuates the UV-light required to initiate cure of the bottom layer. A possible solution is suggested in ref.15. We have selected pairs of commercial photoinitiators suitable for this task. We suggest having a photoinitiator in the

bottom-most compound which absorbs strongly in the visible part of the spectrum. The top coating has a photoinitiator, which exhibits a hipsochromic shift of the absorption spectrum. For example, one can use yellow phosphine oxide photoinitiators in the bottom coating and colorless Irgacure 184 or Irgacure 651 in the top coating.

We suggest use of a continuous wave UV-laser with a proper arrangement in order to cure coating on very thin or narrow objects like optical fiber. It is impossible to focus a significant quantity of energy from a normal processor lamps, having a diameter of *ca.* 10 mm, onto a very narrow object like an optical fiber even if one uses perfectly elliptical reflectors with the lamp in one focus and the fiber in the other focus.[16]

There are reasons to believe that ultrasound accelerates free-radical polymerization (i.e., cure) as well.[17]

It is possible to apply two liquid UACs with essentially different properties, say "soft" and "hard", to a surface in such a way that properties of cured coatings will gradually change from the "soft" an a substrate to hard at the outside. A coatings applicator for this purpose was suggested in ref. 18.

Acknowledgements

Conclusions

Oligomers with grafted photoinitiators and adhesion promoters demonstrate, in many cases, superior properties compared to similar oligomers with dissolved photoinitiators and dissolved adhesion promoters. "All-in-one" LS oligomers undergo faster cure, they do not have leach-able additives (residual free photoinitiators), and they have strong adhesion to glass. Different photoreactive additives, which harvest UV- and visible light, can be used to accelerate the cure of coatings.

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