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UV-radiation curing of acrylate/epoxide systems

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Abstract

Interpenetrating polymer networks (IPNs) have been synthetized by light-induced cross-linking polymerization of a mixture of acrylate and epoxide monomers. The consumption of each monomer upon UV-irradiation in the presence of radical and cationic-type photoinitiators was monitored in situ by real-time infrared spectroscopy. The acrylate monomer was shown to polymerize faster and more extensively than the epoxy monomer, which was further consumed upon storage of the sample in the dark, due to the living character of cationic polymerization. Curing experiments carried out in the presence of air and under air diffusion-free conditions indicate that the radical polymerization of the acrylate monomer is hardly affected by the oxygen inhibition effect, while the cationic polymerization of the epoxy monomer is enhanced by the atmosphere humidity. The addition of a photosensitizer, like isopropylthioxanthone, was shown to speed up substantially the polymerization of the epoxide, with formation within seconds of two fully cured IPNs. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: UV-curing; Acrylates; Epoxides

1. Introduction

Interpenetrating polymer networks (IPNs) form a special class of polymer blends in which both polymers generally are in network form [1,2]. They can be synthesized by cross-linking polymerization of two multifunctional monomers or telechelic oligomers that polymerize by different mechanisms, e.g. radical and cationic types. The main advantage of IPNs is that they combine the properties of the two kinds of polymer networks. An easy way to produce IPNs is by photoinitiated polymerization of a monomer mixture, in particular by combining the two types of monomers, which are the most widely used in UV-radiation curing: acrylates, which polymerize by a radical mechanism, and epoxides, which polymerize by a cationic mechanism.

UV-radiation has already been used to produce semi-IPNs or IPNs by photopolymerization of acrylate monomers in various polymer matrixes [3–9] or in epoxidized polyisoprene [10], respectively. The main interest of using UV-light to induce the polymerization reaction lies in the high polymerization rates, which can be reached under intense illumination, together with the advantage of a solvent-free formulation curable at ambient temperature. As a result, the UV-curing technology has found a large variety of applications, in particular to achieve a fast drying of varnishes and printing inks, and a quick setting of adhesives and composites materials [11–12].

The monomers selected for this study are compounds, which are typically used in UV-curable resins, namely a bisphenol A based diacrylate and a biscycloaliphatic epoxide. Phase separation does not occur in this particular mixture, which remains perfectly transparent, before and after UV-curing. Acrylate monomers, which are known for their high reactivity, polymerize rapidly in the presence of photogenerated free radicals. Epoxides, which undergo polymerization by a cationic mechanism, are less reactive but they are insensitive to oxygen inhibition. A hydroxyphenylketone and an aryliodonium salt were used as photoinitiators because these compounds are known to generate upon UV exposure free radicals and protonic species, respectively, with high quantum yields [13]. This hybrid formulation contains no volatile acrylate diluent and therefore it does not show the strong odour and irritating character typically found in acrylate-based UV-curable formulations.

The objective of this work was to study the kinetics of such ultrafast polymerization processes in order to assess both the reactivity of the two monomers and the efficiency of the photoinitiators. It was achieved by using real-time infrared (RTIR) spectroscopy as analytical tool [14].

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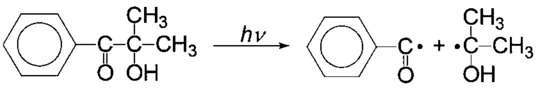
Indeed, this technique is unique as it allows one to monitor in situ the polymerization of each monomer of the mixture and to record directly the conversion versus time profiles in a timescale as short as 1 s. The important kinetic parameters can thus be determined, in particular the actual polymerization rate and the final cure extent, a quantity which governs the physico-chemical characteristics of the IPN formed.

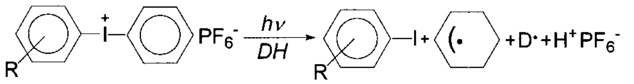
2. Experimental

2.1. Materials

A hydroxyphenylketone (Darocur 1173 from Ciba Specialty Chemicals) was used to generate the free radicals that are to initiate the polymerization of the acrylate monomer. The photocleavage of this molecule produces a benzoyl radical and an α-hydroxyalkyl radical, both of which are capable to react with the acrylate double bond [13]:



A diaryliodonium hexafluorophosphate salt (DAI from Ciba Specialty Chemicals) was used to generate the protonic acid, which will initiate the cationic ring-opening polymerization of the epoxy monomer. It should be noted that the photolysis of this compound in the presence of a hydrogen donor molecule (DH) produces both protonic species (Brönsted acid) and free radicals [15]:



The monomer polymerizing by a radical mechanism was a diacrylate bisphenoxy-A derivative (BPDA) (Ebecryl 150 from UCB). The monomer polymerizing by a cationic mechanism was a biscycloaliphatic diepoxide (BCDE) (Araldite CY-179 from Ciba Specialty Chemicals).

The two polymer networks generated upon UV-curing are represented schematically in Chart 1.

2.2. Kinetic analysis of the photopolymerization

A 1/1 mixture (by weight) of the two monomers containing 3 wt% of each photoinitiator was applied onto a silicon wafer, at a typical thickness of 24 μm. In some experiments a 15 μm thick transparent polypropylene film was laminated on top of the liquid resin to prevent the diffusion of oxygen. The sample was placed in the compartment of an infrared spectrophotometer where it was exposed to the UV radiation of a medium pressure mercury lamp. The light intensity at the sample position could be varied between 20 and 60 mW cm^{-2}, as measured by radiometry (IL-390 radiometer).

The polymerization of the sample exposed to both the excitation UV beam and the analysis IR beam was followed in situ by RTIR spectroscopy. The disappearance of each one of the two functional groups was monitored continuously by setting the wave number of the IR detection at the proper value: 795 cm^{-1} for the epoxy ring and 1411 cm^{-1}

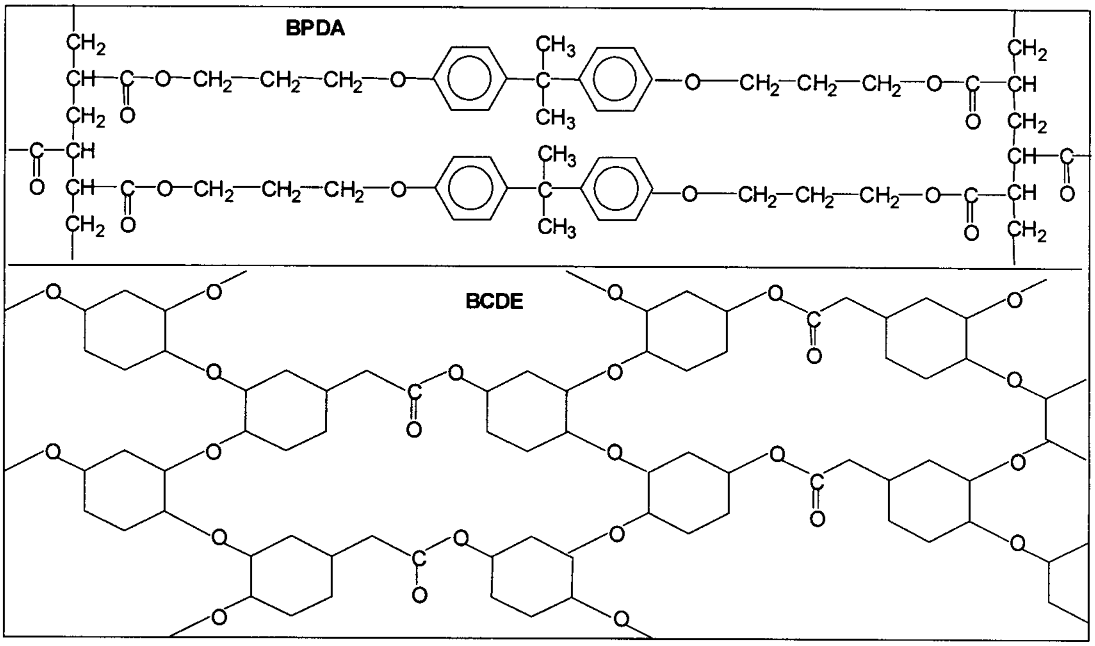


Chart 1. Polymer networks formed by photoinitiated polymerization of a bisphenol A diacrylate derivate (BPDA) and of a biscycloaliphatic diepoxide (BCDE).

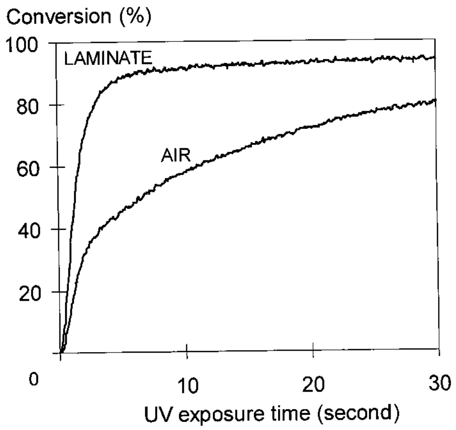


Fig. 1. Photoinitiated radical polymerization of a bisphenoxy diacrylate monomer. Photoinitiator: [Darocur 1173] = 3 wt%; light intensity: 20 mW cm^{-2}; film thickness: 30 μm.

for the acrylate double bond. By operating the IR-spectrophotometer in the absorbance mode, conversion versus time curves were recorded, as shown in Fig. 1 for the acrylate monomer. From the maximum slope of this curve, the formulation reactivity, ratio of the rate of polymerization (R_p) to the monomer concentration ($[M_0]$), can be evaluated for each monomer. The amount of unreacted functionalities in the UV-cured polymer was determined from the value of the final conversion reached at the end of the UV exposure.

The hardness of the UV-cured polymer was evaluated by monitoring the damping of the oscillations of a pendulum placed onto a glass plate coated with a 30 (m thick film (Persoz hardness). The polymer hardness was shown to be strongly dependent on the glass transition temperature [16]. Persoz values, expressed in seconds, are typically ranging from 30 s for soft elastomeric materials up to 400 s for very hard and glassy polymers.

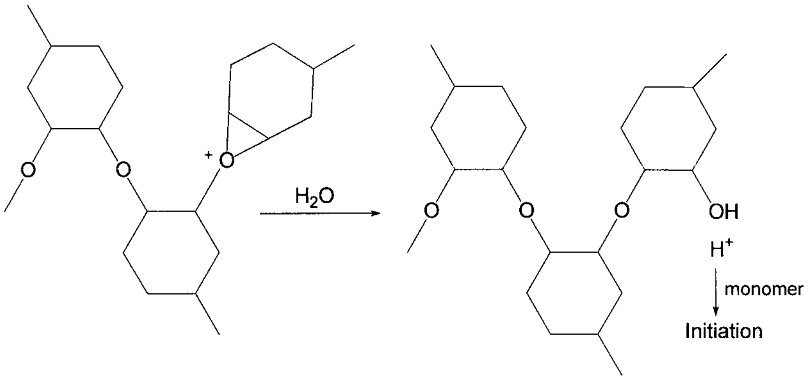
3. Results and discussion

The photoinitiated polymerization of each monomer alone has first been examined, before studying the photopolymerization of the monomer mixture, which generates the IPNs, and in particular the effect of atmospheric oxygen and of the type of photoinitiator used. We have also examined the influence of a photosensitizer and of light-stabilizers on the polymerization kinetics, and on some of the polymer properties as well.

3.1. Photopolymerization of the acrylate and epoxy monomers

The BPDA monomer polymerizes readily when it is exposed to UV radiation in the presence of a radical-photoinitiator under O_2 diffusion-free conditions (laminate), as shown in Fig. 1. After a short induction period (0.2 s) due to the oxygen dissolved in the monomer, the cross-linking reaction proceeds rapidly ($R_p/[M_0] = 1\ s^{-1}$) and reaches 90% conversion within 5 s. This value hardly changes upon further exposure because of the severe mobility restrictions brought upon by the build-up of the glassy polymer network. In the presence of air, the polymerization proceeds initially less rapidly ($R_p/[M_0] = 0.2\ s$) and is progressively slowing down because of the inhibitory effect of atmospheric oxygen on this radical-induced polymerization (Fig. 1). The conversion value levels off at 87% after a 1 min exposure, so that the coating UV-cured in the presence of air contains a significant amount of unreacted acrylate double bonds (13% of the original amount, i.e. 0.5 mol kg^{-1}).

The BCDE undergoes polymerization at a slower pace than the acrylate monomer, as observed in previous studies [17] (Fig. 2). The ring-opening polymerization proceeds faster and more extensively for the sample in contact with air than in the laminated sample, and even more so in thin films. This thickness effect, which was not observed in a dry atmosphere and under air-free conditions (laminate), was attributed to a catalytic effect of humidity on the ring-opening polymerization of the epoxide, probably through a chain transfer reaction involving the hydroxyl groups of water:



The build-up of hydroxyl groups upon UV-curing of this epoxide was confirmed by IR spectroscopy and shown to be more important in samples cured in the presence of air than in laminated samples. Moreover, an increase of the atmosphere relative humidity leads

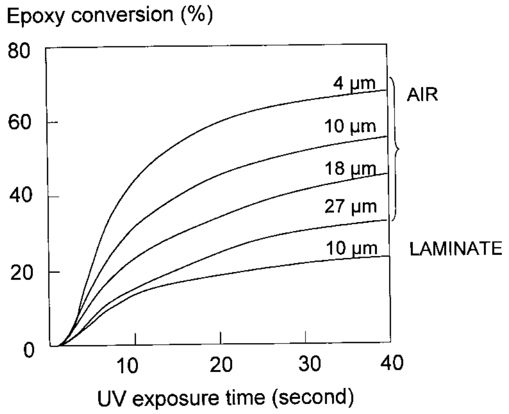


Fig. 2. Photoinitiated cationic polymerization of a biscycloaliphatic diepoxide monomer. Photoinitiator: [DAI] = 2 wt%; light intensity: 20 mW cm^{-2}.

to an increase of both the epoxy consumption and the OH group formation.

It should be emphasized that this chain transfer reaction, which consumes rapidly the epoxy groups is actually detrimental to the curing process because it generates hydroxyl end groups instead of ether cross-links. The atmospheric conditions will therefore have a drastic effect on the physico-chemical and mechanical properties of the final product. The polymer formed by UV-curing in a humid atmosphere was indeed found to be softer and less resistant to solvents than the glassy polymer formed by UV-curing in a dry atmosphere. The experiments reported in this article have all been performed at a relative humidity of 30 ± 5%.

3.2. Photopolymerization of the acrylate/epoxide system

When the diacrylate/diepoxide monomer mixture (BPDA/BCDE: 1/1 by weight) was exposed to UV radiation in the presence of the diaryliodonium salt under air-free conditions (laminate), the polymerization of both monomers occurred simultaneously, as shown in Fig. 3. The fast polymerization of the acrylate monomer is a clear demonstration that free radicals are formed by photolysis of this cationic photoinitiator. As expected, the dicycloepoxide polymerizes less rapidly and less extensively, the conversion versus time curve being very similar to the one recorded upon UV-irradiation of the neat monomer (Fig. 2).

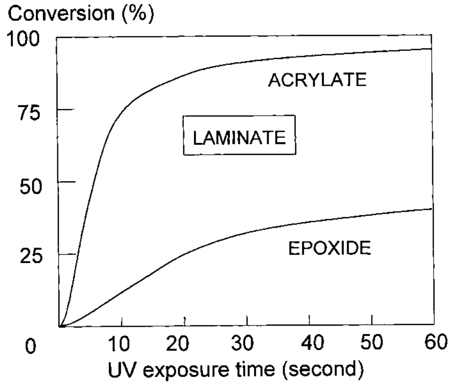


Fig. 3. Photoinitiated polymerization of an acrylate/epoxide hybrid system. BPDA/BCDE = 1/1 by weight under laminate conditions. Photoinitiator: [DAI] = 2 wt%; light intensity: 20 mW cm^{-2}; film thickness: 10 µm.

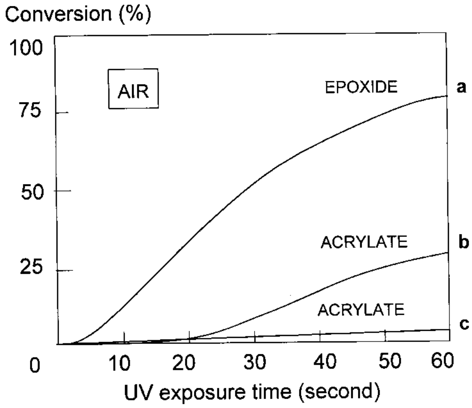


Fig. 4. Photoinitiated polymerization of an acrylate/epoxide hybrid system. BPDA/BCDE = 1/1 by weight in the presence of air. Photoinitiator: [DAI] = 2 wt%; light intensity: 20 mW cm^{-2}; film thickness: 13 µm; curves a and b: acrylate/epoxide mixture; curve c: neat acrylate monomer.

A quite different behavior was observed by performing the same experiment in the presence of air, as shown in Fig. 4 for a 13 µm thick coating. While the polymerization of the epoxide was, found to be enhanced by the presence of air (curve c), probably because of the humidity effect, the acrylate monomer started to polymerize only after 20 s of UV exposure, to reach hardly 25% conversion after 1 min (curve b). In thinner samples, the acrylate polymerization was completely suppressed. It was also the case when the neat acrylate monomer was UV-irradiated in the presence of the iodonium photoinitiator (Fig. 4, curve c). Such a drastic effect was attributed to the inhibitory effect of atmospheric oxygen on radical-initiated polymerization. It is particularly pronounced in the present case because of the too slow production of free radicals upon photolysis of the aryliodonium salt. These radicals must first react with the O_2 dissolved in the sample to reduce its concentration low enough ($\sim 10^{-5}$ M) to allow the acrylate monomer to compete successfully with O_2 for the scavenging of the initiating radicals [18]. The fact that the acrylate monomer starts to polymerize in the hybrid system after a certain induction period was explained by the build-up of the epoxy network and the resulting increase in viscosity, which slows down the diffusion of atmospheric O_2 into the sample.

Several strategies can be used to minimize the inhibitory effect of oxygen:

- increase the film thickness, so as to reduce the rate at which atmospheric oxygen diffusing through the surface is dissolved into the sample;
- increase the light intensity, thus speeding up the initiator

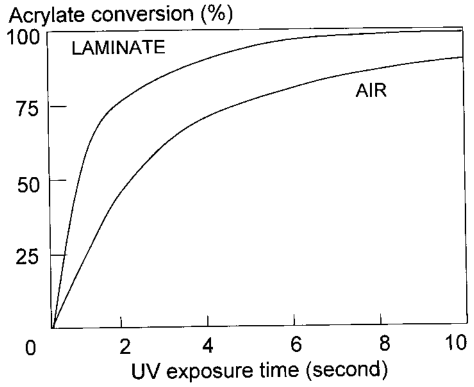


Fig. 5. Acrylate polymerization upon UV irradiation of an acrylate/epoxide (1/1) mixture. Photoinitiators: [DAI] = 2 wt%; [Darocur 1173] = 2 wt%; light intensity: 20 mW cm^{-2}; film thickness: 13 μm.

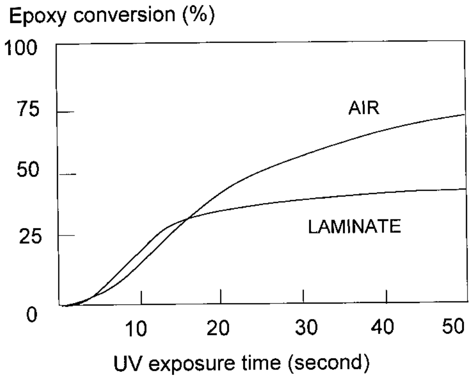


Fig. 6. Epoxy polymerization upon UV irradiation of an acrylate/epoxide (1/1) mixture. Photoinitiators: [DAI] = 2 wt%; [Darocur 1173] = 2 wt%; light intensity: 20 mW cm^{-2}; film thickness: 13 μm.

photolysis and consequently the production of free radicals; this will also decrease the exposure time during which oxygen diffuses into the coating;

- increase the rate of free radical formation by introducing a radical-type photoinitiator into the formulation.

The latter strategy proved to be, by far, the most effective. Indeed, by adding a hydroxyphenyl ketone photoinitiator ([Darocur 1173] = 2 wt%) the polymerization of the acrylate monomer was found to proceed within seconds upon UV exposure, even in the presence of air. Fig. 5 shows typical polymerization profiles recorded by RTIR spectroscopy for a 13 μm thick sample UV-irradiated either in the presence of air or under laminate conditions. It should be noted that a nearly complete polymerization of the acrylate double bond was achieved after a 10 s UV-irradiation of the monomer mixture, while the conversion value was levelling off at 90% in the neat monomer (Fig. 1). This behavior can be accounted for by considering that the epoxy co-monomer acts as a plasticizer during the early polymerization of the acrylate monomer: 80% conversion of the acrylate after 3 s, compared to only 5% conversion of the epoxide which is still liquid at that stage. The beneficial effect of the co-monomer is even more apparent for polymerizations carried out in the presence of air: 90% acrylate conversion in the hybrid system compared to only 60% for the neat acrylate after a 10 s UV exposure.

The polymerization quantum yield (Φ_p), i.e. the number of acrylate double bonds polymerized per photon absorbed, can be evaluated from these kinetic data by using the following equation:

$$\Phi_p \frac{[\text{Acrylate}]_{0(\text{mol/kg})}\,\tau l_{(\text{cm})}}{I_{0(\text{Es}^{-1}\ \text{cm}^{-2})}\,t_{(\text{s})} \times 1000f},$$

where τ is the acrylate conversion after an exposure time t at a light intensity I_0 in a sample of thickness l absorbing a fraction f of the incident light. Under air diffusion-free conditions, a Φ_p value of 1500 mol E^{-1} was obtained. The kinetic chain length of the acrylate polymerization was calculated, from the ratio Φ_p to the initiation quantum yield ($\Phi_i = 0.5$ radical E^{-1}), to be on the order of 3000 mol radical^{-1}. This relatively high value shows how effectively the chain reaction develops in this system, even in a short timescale.

The polymerization of the epoxide which occurs later on is only slightly affected by the previous build-up of the acrylate polymer network, as shown in Fig. 6. Here again, the epoxy polymerization was found to proceed more extensively in the presence of air than in the laminated sample: 70% conversion after 1 min, compared to 35% in O_2-free conditions. It should be noted that the remaining epoxy groups continue to react slowly upon storage of the sample in the dark because of the living character of cationic polymerization (see below). From the amount of epoxy groups polymerized, the quantum yield was calculated to be on the order of 200 mol E^{-1}.

Similar results have been obtained by performing the polymerization at a higher light intensity (55 mW cm^{-2}), with the expected increase in reaction rates. Fig. 7 shows the polymerization profiles recorded for the two functional

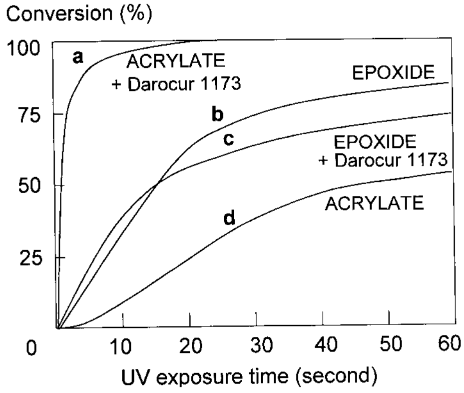


Fig. 7. Influence of a radical photoinitiator ([Darocur 1173] = 2 wt%) on the photopolymerization of an acrylate/epoxide mixture in the presence of air. [DAI] = 2 wt%. Light intensity: 55 mW cm^{-2}; film thickness: 10 μm.

Table 1
Performance analysis of UV-curable acrylate/epoxide systems (film thickness: 10 μm)

Formulation	Ebecryl 150 (wt%)	Araldite CY-179 (wt%)	DAI (wt%)	Darocur 1173 (wt%)	Monomer	Reactivity $R_p/[M]$ in s^{-1}		Conversion after 10 s (%)	
						Air	Laminate	Air	Laminate
$I = 20$ mW cm^{-2}									
A	49	49	2	–	Epoxy	0.025	0.02	75	35
					Acrylate	0.01	0.1	26	93
B	48	48	2	2	Epoxy	0.028	0.03	71	45
$I = 55$ mW cm^{-2}									
A	49	49	2	–	Epoxy	0.045	0.05	75	35
					Acrylate	0.02	0.2	50	95
B	48	48	2	2	Epoxy	0.05	0.06	75	40
					Acrylate	0.8	1.2	100	100

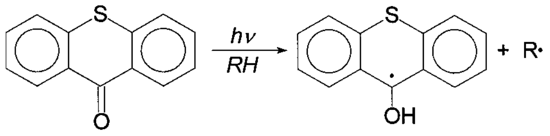
groups upon UV-irradiation of the monomer mixture, with and without radical-type photoinitiator, in the presence of air. The great influence of this initiator on the build-up of the two IPNs is clearly apparent. Its presence is essential to achieve an adequate curing of the acrylate monomer. If necessary the gap between, the two polymerization profiles (curves a and c in Fig. 7) can be reduced by lowering the Darocur 1173 concentration down to 0.5 wt%. When the two polymer networks are generated simultaneously, the plasticizing effect of the epoxy monomer becomes less pronounced so that complete polymerization of the acrylate monomer is more difficult to achieve and requires longer exposure times. The value of the monomer reactivity and of the conversion reached after a 60 s UV exposure are reported in Table 1 for the two formulations (A and B) polymerized either in the presence of air or as laminated samples.

3.3. Photosensitized polymerization of the acrylate/epoxide system

One of the reasons of the slower UV-curing of epoxy monomers lies in a poorly efficient initiation process, which is partly due to the low UV absorbance of aryliodonium salts. To overcome this limitation small amounts of a photosensitizer are usually introduced in the UV-curable formulation. This will shift the absorption spectrum in the 350–400 nm range where the mercury lamp has its maximum emission. With isopropylthioxanthone ([ITX] = 0.5 wt%), the polymerization rate of the dicycloaliphatic epoxide was increased by a factor 3.

The UV-curing experiments of the BPDA/BCDE mixture described previously have been repeated with formulations containing 0.5 wt% ITX (formulations C and D). Fig. 8 shows the polymerization profiles of the epoxy and acrylate groups which were recorded with formulation C (containing only the diaryliodonium salt as photoinitiator) upon UV-irradiation in the presence of air or under laminate conditions. As expected, the cationic polymerization of the epoxy monomer proceeds much faster than in the absence of ITX sensitizer, as it now reaches over 70% conversion after only 5 s. The acrylate monomer is also undergoing a fast and extensive polymerization, even in the presence of air, to reach a 98% conversion value after 10 s. The drastic increase observed in the acrylate polymerization rate when the photosensitizer is introduced in the monomer mixture is a clear indication that initiating radicals have been produced more effectively under those conditions. It can be accounted for by considering that the two following processes occur in the presence of ITX:

- the sensitized photolysis of the iodonium salt which produces larger quantities of free radicals, at the same time as the protonic acid;
- the photolysis of ITX in the presence of a hydrogen donor molecule, which produces directly a donor radical capable to initiate the acrylate polymerization.



The fact that oxygen inhibition is less pronounced in such hybrid systems than in typical acrylate resins could be due to the simultaneous polymerization of the epoxide which makes the viscosity rise, thus slowing down the diffusion of atmospheric oxygen into the coating. The more complete polymerization of the acrylate monomer (98% conversion in the mixture versus 87% in the neat monomer) was attributed here again to the plasticizing effect of the epoxide co-monomer. From the amount of acrylate and epoxy groups polymerized, the cross-link density of the IPN formed was calculated to be on the order of 5 mol kg^{-1}.

When Darocur 1173 (2 wt%) was introduced in the monomer mixture (formulation D), the polymerization rate of the acrylate monomer was increased by a factor

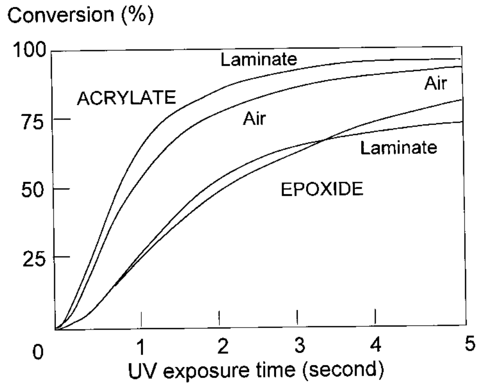


Fig. 8. Photosensitized polymerization of an acrylate/epoxide hybrid system. Photoinitiators: [DAI] = 2 wt%; [Quantacure ITX] = 0.5 wt%; light intensity: 60 mW cm^{-2}; film thickness: 30 μm.

1.8, a complete cure being reached within 5 s, as shown in Fig. 9. It should be noted that, under the given experimental conditions, identical kinetic profiles were recorded with the laminated sample and the coating UV-irradiated in the presence of air, for both types of monomers. Oxygen inhibition has been completely suppressed in the acrylate polymerization.

For the epoxy monomer, the cationic polymerization remains essentially unaffected by the addition of the radical-type photoinitiator, and it proceeds about one third as fast as that of the acrylate monomer. Therefore, only half of the epoxy groups have reacted after 2 s when the polymerization of the acrylate is almost completed.

The values of the monomer reactivity and of the conversion reached after a 10 s UV exposure are reported in Table 2 for the various formulations polymerized either in the presence of air (coatings) or as laminates (adhesives). A comparison with similar data reported in Table 1 clearly shows the superior performance of the formulations containing the ITX photosensitizer (C and D).

3.4. Dark polymerization

A distinct characteristic of cationic-type polymerization is that the propagating polymer cations (oxonium ions in the present case) are not reacting among themselves, unlike the propagating polymer radicals. Once initiated, the ring-opening polymerization will therefore continue to proceed after the UV-exposure upon storage of the sample in the dark. This post-polymerization reaction can be easily visualized by RTIR spectroscopy, simply by continuing to record the decay of the epoxy IR band after the UV-irradiation.

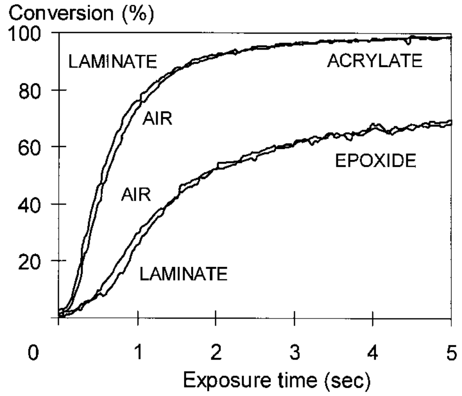


Fig. 9. Photosensitized polymerization of an acrylate/epoxide hybrid system. Photoinitiators: [DAI] = 2 wt%; [Darocur 1173] = 2 wt%; [Quantacure ITX] = 0.5 wt%; light intensity: 60 mW cm^{-2}; film thickness: 30 μm.

Fig. 10 shows some typical polymerization profiles recorded for an acrylate/epoxide mixture (formulation C) exposed for only 1 s to UV-radiation. It can be seen that the epoxy monomer continues to polymerize slowly after the light has been switched off (from 40 to 55% within the first 20 s), while the acrylate conversion stays constant at 50%. In spite of the short UV exposure (a UV dose of 60 mJ cm^{-2} only), a complete reaction of the epoxy groups was achieved after storing the sample for 1 h in the dark. (Fig. 10). This behavior can be explained by the uncomplete polymerization of the acrylate monomer (55% conversion) which leaves a greater molecular mobility to the epoxy monomer within the IPN formed.

In this respect, it should be noted that a more complete

Table 2
Performance analysis of photosensitized UV-curable acrylate/epoxide systems Light intensity: 60 mW cm^{-2}; film thickness: 30 μm

Formulation	Ebecryl 150 (wt%)	Araldite CY-179 (wt%)	DAI (wt%)	ITX (wt%)	Darocur 1173 (wt%)	Light stabilizer	Monomer	Reactivity $R_p/[M]$ in s^{-1}		Conversion after 10 s (%)	
								Air	Laminate	Air	Laminate
C	48.75	48.75	2	0.5	–	–	Epoxy	0.31	0.43	83	74
							Acrylate	0.57	0.75	98	100
D	47.75	47.75	2	0.5	2	–	Epoxy	0.4	0.38	75	73
							Acrylate	1.06	1.2	100	100
E	47.5	47.5	2	0.5	2	T-384 (1 wt%)	Epoxy	0.15	0.13	70	65
							Acrylate	0.4	0.54	96	97
F	47.5	47.75	2	0.5	2	(1 wt%)	Epoxy	0.03	0.05	34	45
							Acrylate	1.1	1.3	100	100

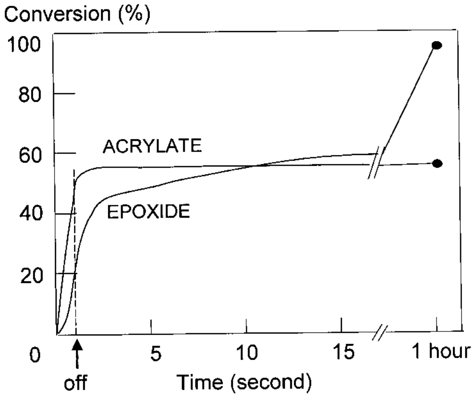


Fig. 10. Dark polymerization after a 1 s UV exposure of an acrylate/epoxide hybrid system. Photoinitiator: [DAI] = 2 wt%; [Quantacure ITX] = 0.5 wt%; light intensity = 60 mW cm^{-2}; film thickness: 30 μm; atmosphere: Air.

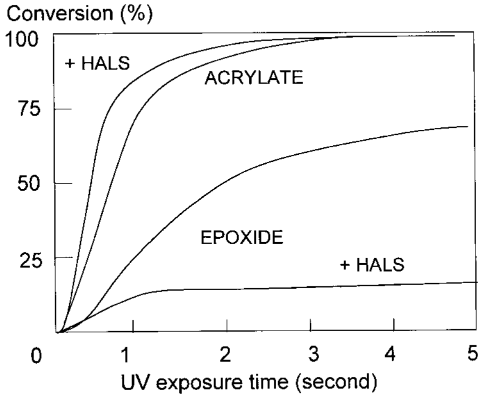


Fig. 12. Influence of HALS radical scavenger on the photopolymerization of an acrylate/epoxide hybrid system in the presence of air. [Darocur 1173] = 2 wt%; [Quantacure ITX] = 0.5 wt%. HALS: [Tinuvin 292] = 1 wt% Light intensity: 60 mW cm^{-2}. Film thickness: 30 μm.

cure of both monomers can be achieved by a thermal treatment at 80°C of a sample UV-irradiated for 5 s at $60\,\text{mW cm}^{-2}$. While the acrylate conversion stayed at 100%, the epoxy conversion increased from 75 to 90%. The long term properties of the fully cured IPN thus obtained are expected to remain unchanged upon usage.

3.5. Influence of light stabilizers on the curing process

If UV-cured coatings are to be used in exterior applications it is necessary to introduce light stabilizers to improve there weathering resistance [19]. These additives are mainly UV absorbers, which screen the harmful UV solar radiation and hindered amines (HALS) radical scavengers [20,21]. From a practical point of view, it is important to know how much these compounds do affect the UV-curing process.

Fig. 11 shows clearly that the polymerization of both monomers is hindered by the introduction of a hydroxy-benzotriazole UV absorber ([Tinuvin 384] = 1 wt%) into formulation D. This slowing down effect is due to the competition, which exists between the photoinitiator and the UV-absorber for the scavenging of the incident photons, with the resulting decrease in the initiation rate. For the epoxy monomer, the presence of the phenolic OH group of the benzotriazole may also affect the cationic polymerization by promoting chain transfer reactions. To reach a certain degree of conversion in the stabilized sample, the UV exposure time had to be increased by a factor 3.

HALS radical scavengers have a contrasted effect on the photopolymerization of the acrylate/epoxide hybrid system, as shown in Fig. 12 in the case of Tinuvin 292 (1 wt%). On one hand, this type of light stabilizer does not affect at all the radical polymerization of the acrylate monomer. This unexpected behavior, which has been previously described [22], was explained by considering that the nitroxyl radicals, which act as scavengers, are not produced upon UV-curing in air, because the acrylate polymerization can only proceed in an O_2-depleted medium. Indeed, the addition of a stable

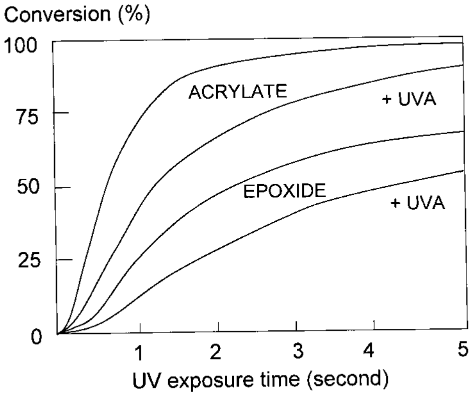


Fig. 11. Influence of a UV-absorber on the photopolymerization of an acrylate/epoxide hybrid system in the presence of air. Photointiators: [DAI] = 2 wt%; [Darocur 1173] = 2 wt%; [Quantacure ITX] = 0.5 wt%; UV-absorber: [Tinuvin 384] = 1 wt%; light intensity: 60 mW cm^{-2}; film thickness: 30 μm.

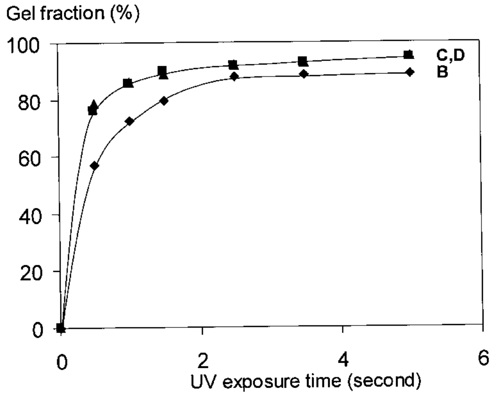


Fig. 13. Insolubilization profiles of the acrylate/epoxide hybrid formulations B, C and D exposed to UV-radiation.

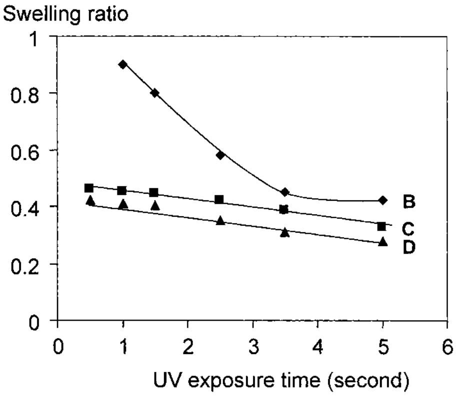


Fig. 14. Swelling profiles of the acrylate/epoxide hybrid formulations B, C and D exposed to UV-radiation.

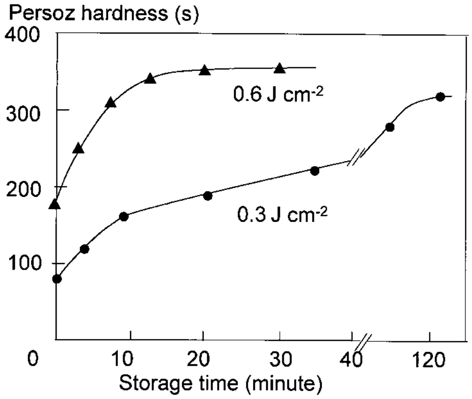


Fig. 16. Hardening of a UV-cured acrylate/epoxide polymer (formulation C) upon storage in the dark at ambient. UV dose: 0.3 and 0.6 J cm^{-2}.

nitroxyl radical (TEMPO) was shown to suppress totally the polymerization reaction.

On the other hand, the ring-opening polymerization of the epoxy group is adversely affected by the presence of HALS, with a five-fold drop in the polymerization rate (Fig. 12). Hindered amines are actually expected to interact with the initiating protonic species because of their basic and nucleophilic character. The UV-curing of the epoxy monomer will require not only a longer exposure but also an increase in the diaryliodonium salt concentration. The use of a less basic HALS (Tinuvin 123) was found to minimize this detrimental effect, the conversion value of the epoxy group rising up to 70% after a 30 s UV exposure and reaching nearly 100% upon storage. It is therefore still possible to get a fully cured acrylate/epoxide IPN in the presence of a HALS and a UV absorber. The kinetic data obtained from these UV-curing experiments performed in the presence of light stabilizers are reported in Table 2 (Formulations E and F).

3.6. Properties of UV-cured acrylate/epoxide IPNs

The perfectly transparent polymer obtained after UV-curing of the BPDA/BCDE mixture is a clear indication that phase segregation has not occurred upon photopolymerization and that the two polymer networks are well compatible and tightly interpenetrated. This type of material can therefore be utilized as clear coat to protect various substrates (metal, plastics, wood), and also as organic glass to produce optical components by a cold process.

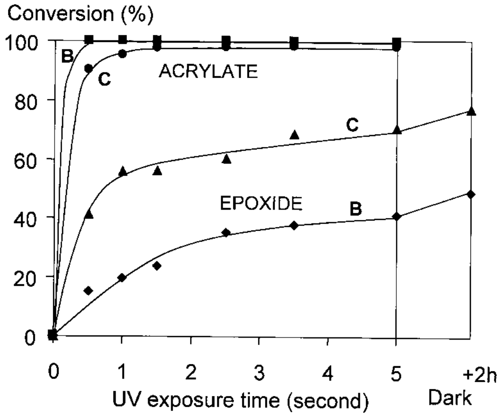


Fig. 15. Influence of the ITX photosensitizer (formulation C) on the UV-curing of an acrylate/epoxide hybrid system.

The chemical resistance of the UV-cured IPNs was evaluated by gel fraction and swelling measurements carried out 3 h after the UV exposure to take the dark polymerization into account, chloroform being used as solvent. Samples were passed repeatedly under a high intensity mercury lamp (80 W cm^{-1}) of an industrial-type UV-line at a web speed of 10 m min^{-1}. Fig. 13 shows the insolubilization profiles obtained with formulations B, C and D. A faster and more complete insolubilization was achieved with the formulations containing the ITX sensitizer. Swelling measurements also show that a tighter network is formed under those conditions, with a swelling ratio on the order of 0.3 (Fig. 14). This low value confirms that highly cross-linked polymer networks have been formed upon photopolymerization of the two monomers. The better performance of formulations C and D was attributed to a more efficient polymerization of the epoxy monomer in the presence of the photosensitizer. This was confirmed by IR measurements (Fig. 15) which show a more complete cure of the epoxide in the formulation C containing ITX: 76% conversion versus 48% for formulation B after a 5 s UV exposure and 3 h storage in the dark. In the three formulations the polymerization of the acrylate monomer proceeds very fast and extensively, reaching 100% conversion within 0.5 s for the hybrid systems containing Darocur 1173 as radical photoinitiator (formulations B and D).

It is important to note that, because the cationic polymerization of the epoxy group continues to proceed in the dark after the UV-exposure, the sample emerging from the UV oven will further harden upon storage at ambient temperature. This process can be monitored quantitatively by measuring repeatedly the pendulum hardness (Persoz) of

Table 3
Performance analysis of UV-cured acrylate and epoxy monomers

Monomer	Photoinitiator	T[a] (S)	$R_p/[M]$[b] (s^{-1})		Hardness[c] (s)
			Epoxide	Acrylate	
BCDE (epoxide)	DAI + ITX	2	0.4	–	340
BPDA (acrylate)	D-1173	1.5	–	0.5	250
BCDE/BPDA	DAI + D-1173	1.0	0.05	0.8	360
BCDE/BPDA	DAI + ITX	0.5	0.31	0.57	360

[a] Exposure time for getting a tack-free sample.
[b] Reactivity at 60 mW cm^{-2} in air.
[c] Maximum Persoz hardness.

the polymer, coated onto a glass plate, after the UV exposure upon storage in daylight. Fig. 16 shows how the Persoz hardness increases with time for an acrylate/epoxide IPN exposed for 0.5 s to the UV radiation of a high intensity mercury lamp. Upon storage in air, the sample reached its maximum hardness at a value of 340 s after about 30 min. On the Persoz scale, which goes up to 420 s for mineral glass, such a high value indicates the formation of a hard and glassy material. Maximum hardness can be reached more rapidly by extending the UV exposure time up to 4 s (Fig. 17), or even 2 s for the sample containing the ITX photosensitizer, as shown in Fig. 18.

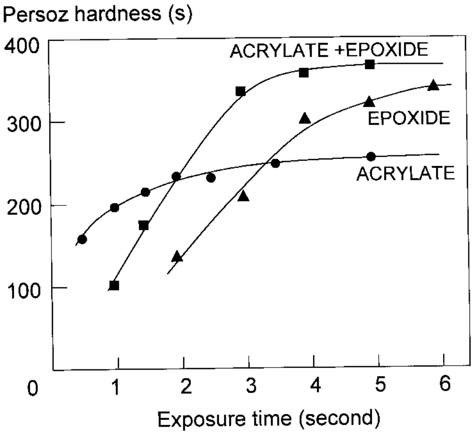


Fig. 17. Hardening of an acrylate/epoxide coating and of the neat acrylate and epoxide monomers upon UV irradiation.

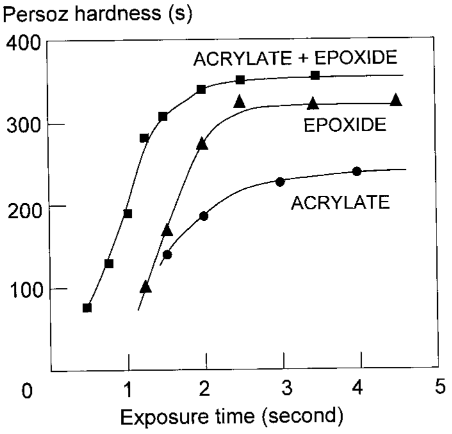


Fig. 18. Hardening of an acrylate/epoxide coating and of the neat acrylate and epoxide monomers upon UV irradiation in the presence of a photosensitizer. [DAI] = 2 wt%; [Quantacure ITX] = 0.5 wt%.

Also reported on these graphs are the hardness profiles of the epoxy and acrylate monomers photopolymerized separately. It can be seen that the epoxy polymer requires a longer exposure (7 s) to reach its maximum value (340 s), while the diacrylate monomer yields a softer polymer (250 s Persoz hardness after a 5 s exposure). The hybrid system shows superior performance in both the unsensitized (Fig. 17) and the sensitized (Fig. 18) formulations. The difference in reactivity between the various UV-curable formulations can also be quantified, by measuring the exposure time needed to get a tack-free coating. The data reported in Table 3 are in good agreement with the conclusions of our kinetic study by IR spectroscopy. One can notice that the acrylate/epoxide hybrid system requires a shorter exposure to be cured than either one of the two monomers taken separately.

For all the formulations containing the diepoxide, the relative humidity of the atmosphere was found to have a substantial effect on the curing process, specially on the post-polymerization of briefly irradiated samples. For the neat BCDE epoxide UV-irradiated for 2 s in the presence of air, the Persoz value increased from 100 to 320 s upon storage in a dry atmosphere, but only to 170 s in a 100% humid atmosphere. This behavior was also observed with the acrylate/epoxide system, but to a lesser extent (Persoz hardness of 280 s in a humid atmosphere), most probably because of the presence of the acrylate polymer network, which is not affected by humidity. It was attributed to the moisture-driven chain transfer reaction, which converts epoxy groups into hydroxyl end groups instead of ether cross-links. It is therefore important to perform the photocuring processing under well-controlled humidity conditions to obtain polymer materials showing always the same properties.

4. Conclusion

Photoinitiated polymerization of a mixture of difunctional monomers reacting by different mechanisms is one of the most efficient methods to generate rapidly IPNs. Such ultrafast polymerization is best followed by real-time infrared spectroscopy, a technique that records directly conversion versus time curves for each one of the two monomers. In the case of the epoxide/acrylate combination, UV-irradiated in the presence of both cationic and radical-type photoinitiators, the polymerization of the acrylate monomer proceeds faster than the cationic polymerization of the epoxide, to reach 100% conversion within seconds. This is in marked contrast with the photopolymerization of the neat acrylate monomer where mobility restrictions in the glassy polymer formed lead to incomplete cure.

The living character of the cationic polymerization is beneficial for it allows the unreacted epoxy groups to further polymerize upon storage of the sample in the dark, thus leading to a fully cured IPN polymer. The formation of the two polymer networks yields a hard and solvent resistant material because of its high crosslink density. Owing to their performance regarding both processing and properties, UV-cured acrylate/epoxide polymers are expected to find their main applications as fast drying protective coatings and for the rapid manufacture of composite materials and optical components at ambient temperature.

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