

Photoinitiated cationic polymerization of epoxides

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Abstract: Difunctional epoxy monomers have been polymerized cationically by UV irradiation in the presence of a triarylsulfonium photoinitiator. The curing process was followed quantitatively by monitoring the disappearance of the epoxy group by infrared spectroscopy and the insolubilization and hardening of the resin upon UV exposure. The addition of epoxidized soyabean oil (ESO) to an aromatic diepoxyde was shown to accelerate the crosslinking reaction with formation of a tight polymer network. The photoinitiated copolymerization of ESO with a cycloaliphatic diepoxyde proceeds extensively and leads within seconds to a fully cured insoluble material showing increased hardness, flexibility and scratch resistance. Interpenetrating polymer networks have been generated by a short UV-irradiation of blends of acrylate and epoxy monomers.

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INTRODUCTION

UV-radiation curing is used in various specific applications, mainly in the coating industry and in the graphic arts, because it is the most efficient technology presently available to transform quasi-instantly a liquid resin into a solid material.^{1,2} Under intense illumination, reactive species such as free radicals or cations can be generated in high concentrations by photolysis of an initiator, and thus promote the polymerization of multifunctional monomers. Most of the UV-curable resins currently used are based on free radical polymerization, mainly of very reactive acrylate monomers, which proceeds extensively within a fraction of a second. The less utilized cationic polymerization of monomers such as epoxides or vinyl ethers still presents a number of advantages, in particular lack of inhibition by atmospheric oxygen, post-polymerization in the dark, low shrinkage, high mechanical performance of the UV-cured material and its good adhesion to various substrates.

One of the main limitations to a greater commercial development of UV-curable epoxy resins lies in their relatively low reactivity, especially when compared to the widely used acrylate-based resins. The photoinitiated cationic polymerization of epoxides has been thoroughly investigated over the past 20 years,^{3–11} in particular by Crivello and co-workers who pioneered this technology by developing appropriate diaryliodonium and triarylsulfonium salts to be used as cationic photoinitiators.⁴ Most of these studies were focused on cycloaliphatic epoxides which proved to be the fastest polymerizing epoxides and which are for this reason

the most utilized in today's industrial photocuring applications. Some successful attempts have recently been made to render these monomers even more reactive by incorporation of other types of cationically polymerizable functional groups, such as vinyl ethers or propenyl ethers in their molecule.^{12–14}

Another way to obtain a faster and more complete polymerization consists of introducing plasticizing agents and reducing the formulation viscosity which has a retarding effect on the curing process.¹⁵ Superior performance was obtained by adding a diacrylate monomer to the diepoxyde, which leads upon UV exposure, to the build-up of two interpenetrating polymer networks.¹⁶ In the present work we have tried to achieve this objective by means of an epoxidized vegetable oil, a cheap compound which should act as reactive diluent and participate in the cationic polymerization of aromatic diglycidylethers or cycloaliphatic diepoxydes, while imparting at the same time some flexibility to the UV-cured coating. The epoxidized soyabean oil (ESO) selected here was shown to be a suitable co-reactant in UV-curable epoxide formulations for improving both the curing performance and some of the properties of the final product.^{17–20} The UV-cured coatings exhibited excellent adhesion, impact resistance, UV-stability, gloss retention and corrosion resistance, while their hardness and tensile strength decreased with increasing oil content.¹⁹ We have studied the photoinitiated cationic polymerization of aromatic and cycloaliphatic epoxy monomers, neat and in blends with ESO, by monitoring both the epoxy group consumption and the insolubilization

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process, together with the hardening of the polymer with irradiation time.

EXPERIMENTAL

Materials

Two types of difunctional epoxy monomers were used in this study: a bis-cycloaliphatic diepoxyde, BCDE (Araldite CY-179 from Ciba Specialty Chemicals) and a diglycidylether derivative of bisphenol A (ADE). Soyabean oil was partly epoxidized by treatment with peracetic acid at 60 °C for 2 h. The two samples of epoxidized soyabean oil (ESO-2 and ESO-3) prepared contained two or three epoxy groups per molecule. The acrylate monomers introduced in the epoxy resin as reactive diluents were hexanediol diacrylate (HDDA) or trimethylolpropane triacrylate (TMPTA) from UCB Chemicals. The cationic-type photoinitiator was a triarylsulfonium salt (TAS) with either PF_6^- or SbF_6^- counterions (Cyracure UVI-6990 or UVI-6974, respectively, from Union Carbide). In the formulations containing acrylate monomers, a radical-type photoinitiator was introduced – Darocur 1173 from Ciba Specialty Chemicals. The chemical formulae of the various compounds used are given in Scheme 1.

Irradiation

The liquid formulation was applied onto a glass plate at a thickness of 36 µm for hardness and insolubilization measurements of the UV-cured sample. For infrared spectroscopic analysis, a film 20 µm thick

was applied onto a KBr crystal. Samples were exposed to the UV radiation of an industrial-type medium pressure mercury lamp (IST) in the presence of air at ambient temperature. They were passed repeatedly under the lamp at a web speed of 1 ms⁻¹, which corresponds to an exposure time of 0.1 s per pass. The intensity of the UV light impinging on the sample was measured by radiometry to be 520 mW cm⁻². Although the sample temperature was initially set at 25 °C, the exothermal polymerization of the epoxy group, which takes place in a short time, makes the sample temperature rise to values as high as 100 °C upon intense illumination.

Analysis

Infrared spectroscopy was used to follow the cross-linking-polymerization reaction, by monitoring the decrease upon UV-exposure of the various bands characteristic of the monomer functional groups: epoxy ring at 790 cm⁻¹ for BCDE, at 865 cm⁻¹ for ADE and at 825 cm⁻¹ for ESO, acrylate double bond at 1410 cm⁻¹. The degree of conversion (x) was calculated from the ratio of the corresponding IR absorbance before and after UV exposure (A_0 and A_t) by using the following equation:

$$x(\%) = 100[1 - (A_t/A_0)]$$

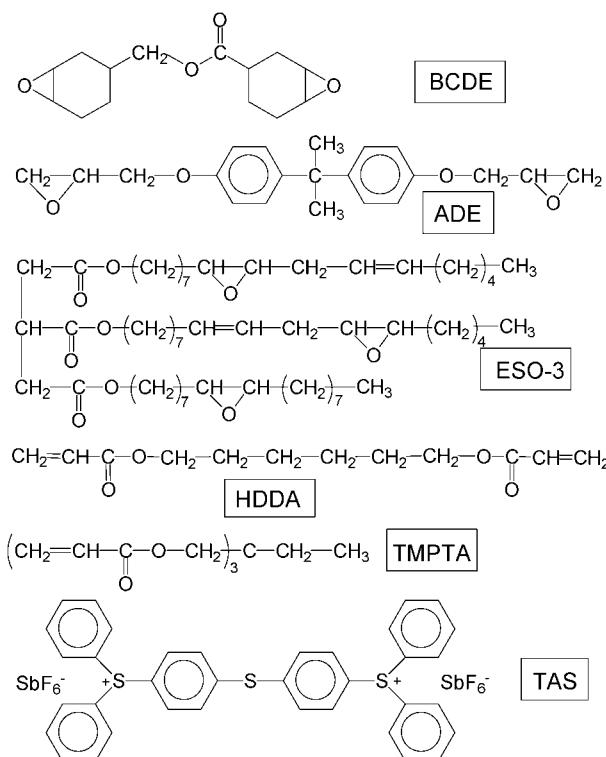
No correction needs to be made for any change of the sample thickness upon UV curing, because shrinkage does not affect the intensity of the IR signal. Indeed, any decrease of the film thickness (l) is compensated by a concomitant increase of the chromophore concentration (c), so that the IR absorbance ($A = \varepsilon lc$) will be unaffected by the liquid-to-solid phase change, assuming a constant absorptivity (ε). We have verified that the ε value of the epoxy group is the same in the liquid formulation and in a solid polymer.

The gel fraction and the degree of swelling (SR) of the irradiated polymer were determined by soaking the sample in chloroform for 1 day at room temperature. The insoluble polymer was recovered by filtration and dried at 70 °C to constant weight. The hardness of the coating was evaluated just after UV irradiation (and for some samples after a given time of storage in the dark) by monitoring the damping time of the oscillations of a pendulum (Persoz hardness). The pendulum hardness was shown to be strongly dependent on the glass transition temperature,²¹ with Persoz values ranging typically from 30 s for soft elastomeric materials, up to 350 s for hard and glassy polymers.

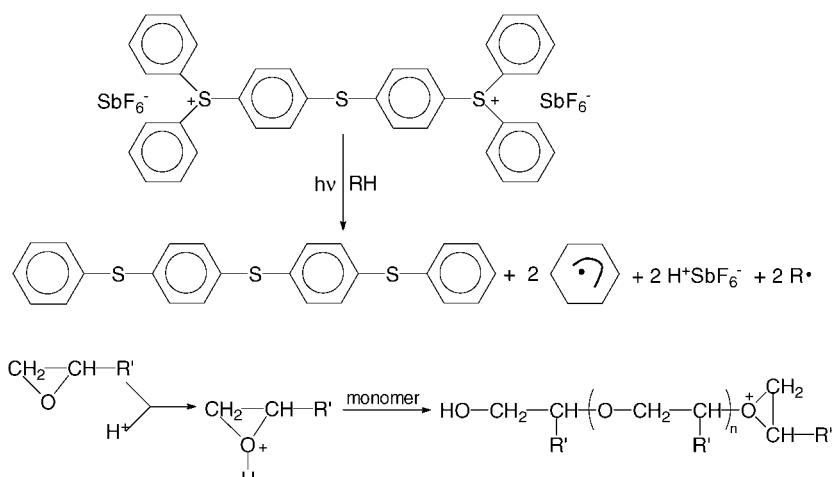
RESULTS

UV radiation curing of aromatic epoxides

Glycidyl ethers are known to be poorly reactive monomers which undergo cationic polymerization at a much lower rate and less extensively than vinyl ether or acrylate monomers. Under intense UV exposure in the presence of an onium salt, the liquid epoxy resin can still be transformed into a hard and insoluble



Scheme 1. Chemical formulae of the compounds used in this study.



Scheme 2. Photoinitiated cationic polymerization of an epoxy monomer.

material within seconds. The crosslinking polymerization process can be formally written as shown in Scheme 2. We have tried to both speed up the chain reaction and increase the extent of cure by the addition of multifunctional monomers such as epoxidized soyabean oil or acrylate monomers which were expected to work as reactive viscosity reducers.

UV curing of a neat aromatic diepoxyde (ADE)

When the ADE liquid resin was exposed to UV radiation in the presence of a triarylsulfonium salt ($[TAS] = 3\text{ wt\%}$), a dry film was obtained after a 0.2 s exposure. At that early stage, the polymer is still totally soluble in chloroform and is very soft. Upon further exposure, the polymer network continues to build up and the UV-cured polymer becomes both harder and increasingly insoluble. Figures 1 and 2 show some typical hardening and insolubilization profiles. The hexafluoroantimonate photoinitiator was found to be

slightly more efficient than the hexafluorophosphate photoinitiator, as expected from its weaker nucleophilic character, and it was therefore selected for our further studies. A TAS concentration of 1 wt% proved to be sufficient to obtain a hard and glassy material after a 5 s UV exposure. At that final stage, about 20 wt% of the UV-cured polymer could still be extracted by chloroform, thus indicating that there existed ADE molecules where neither of the two epoxy groups had reacted and which were trapped in the glassy polymer network, unable to react with the polymeric oxonium ions. The degree of swelling of the insoluble polymer formed is an indication of the crosslink density of the polymer network. Its value decreases steadily with the exposure time (Fig 2), the swelling ratio (SR) dropping from a value of four down to unity for the heavily irradiated sample. Such a low value is a clear indication that a tight polymer network has indeed been formed. For comparison, SR values of the order of 10 have been measured in photocross-linked polybutadiene rubbers.^{22,23}

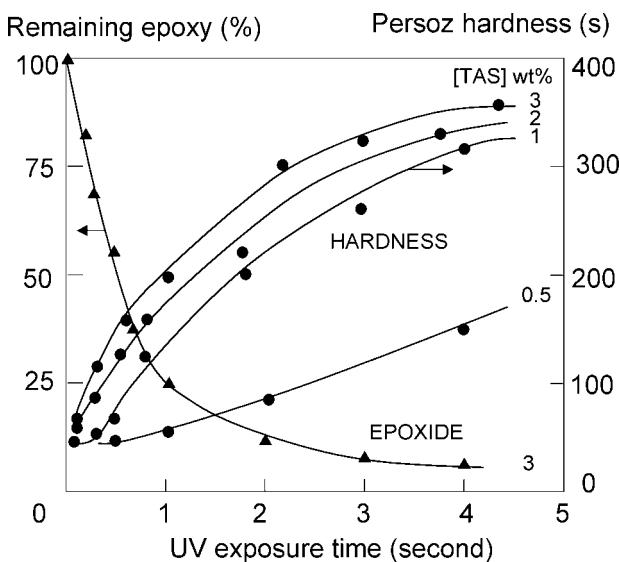


Figure 1. Influence of the photoinitiator concentration (Cyracure UVI-6974) on the polymerization and the hardening of an aromatic diepoxyde upon UV exposure.

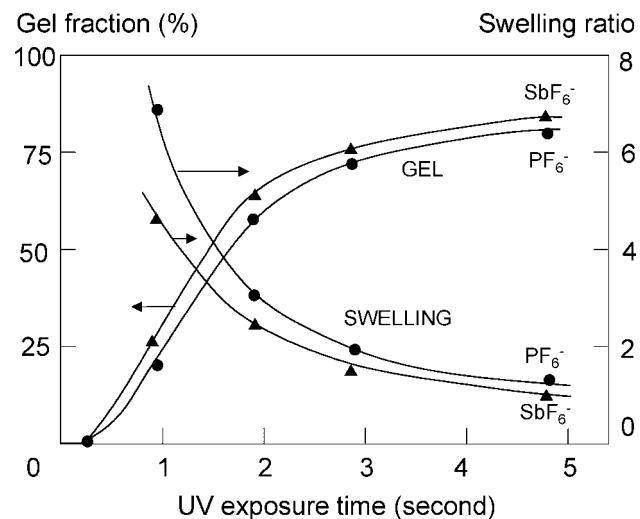


Figure 2. Insolubilization and swelling profiles of an aromatic diepoxyde exposed to UV radiation in the presence of a SbF_6 or PF_6^- triarylsulfonium salt (3wt%).

UV curing of ADE and ESO mixtures

Epoxidized soyabean oil has been used as comonomer to reduce the ADE formulation viscosity and thus speed up the crosslinking reaction. It was previously shown that the kinetics of cationic polymerization is very much dependent on the medium viscosity, a sharp retardation being observed in viscous resins.¹⁵ This behaviour was attributed to the fact that, unlike radical polymerization, the propagation rate constant of cationic polymerization is more strongly affected by the molecular mobility than the termination rate constant.

As expected, the addition of 20wt% ESO-3 was found to accelerate markedly the crosslinking process, as shown by the insolubilization and the swelling profiles represented in Fig 3. After a 1 s UV exposure, a gel fraction of 58% was measured in the ADE/ESO-3 mixture, compared to only 25% for the neat aromatic diepoxyde. It can be seen in Fig 3 that the insolubilization of neat ESO proceeds even faster than that of the blend (62% insoluble polymer by weight after a 0.5 s UV exposure), with final formation of a relatively tight polymer network (swelling ratio of 1.2). The hardening of the resin is slightly less pronounced in the presence of ESO-3, which reduces the polymer brittleness, but Persoz values of up to 340 s were still observed upon prolonged exposure (Fig 4). This quick setting resin is particularly well suited to produce composite materials at ambient temperature, after mixing with glass powder or glass fibres.

The build-up of a hard but still flexible polymer upon UV irradiation of the ADE/ESO-3 mixture indicates that the ESO is not acting as a plasticizer and must therefore be tightly incorporated into the polymer network. Because of its three epoxy groups, ESO-3 is actually working as a crosslinker, thus contributing to strengthen the tridimensional polymer

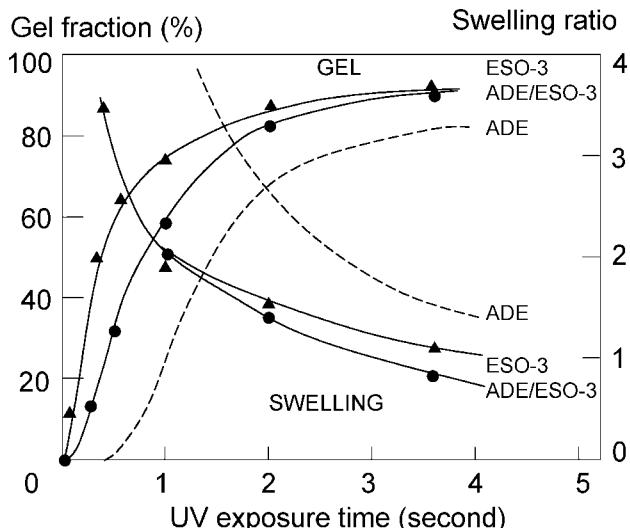


Figure 3. Influence of the addition of an epoxidized soyabean oil (ESO-3) on the insolubilization and swelling profiles of an aromatic diepoxyde (ADE) upon UV exposure: ADE/ESO-3=80/20 by weight; [TAS]=3wt%; ---, neat ADE.

Persoz hardness (s)

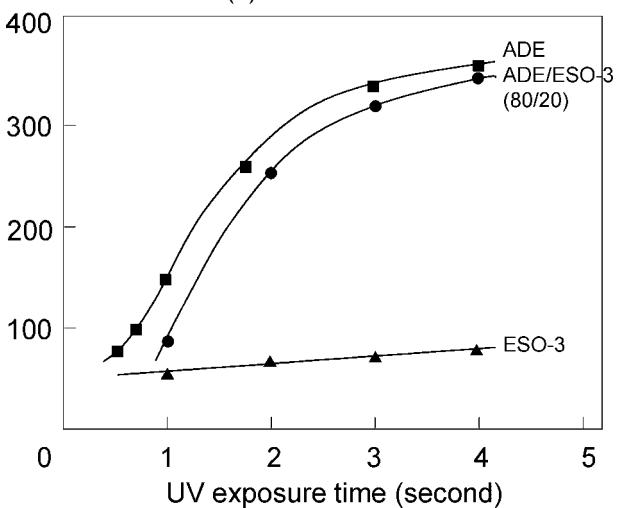


Figure 4. Hardening of various epoxy monomers upon UV curing: [TAS]=3wt%.

network, as shown by the lower degrees of swelling of the UV-cured blend compared to the neat ADE polymer (Fig 3).

The same behaviour was observed by using as reactive diluent the ESO-2 sample, which contains only two epoxy groups, with the expected less pronounced effect on the hardening and insolubilization profiles. A performance analysis of the three formulations (ADE, ADE/ESO-2, ADE/ESO-3) can be inferred from the data reported in Table 1. The formulation containing 20wt% ESO-3 appears to give the best performance with respect to both the reactivity and the properties of the UV-cured polymer.

It should be noted that both samples of ESO undergo efficient crosslinking polymerization when they are UV irradiated neat in the presence of a cationic photoinitiator, as shown in Fig 5 for ESO-3. The epoxy group is rapidly consumed (70% conversion after 0.5 s), with formation of a low-modulus elastomer (Persoz hardness between 50 and 70 s), as shown in Fig 4. Such cheap compounds appear to be particularly well suited for adhesives applications and can be used as quick-setting glues.

The polymerization of the epoxy group of ESO-3 initially proceeds faster than that of the aromatic diepoxyde, most probably because of its lower viscosity, but it levels off at a lower degree of conversion

Table 1. Performance analysis of UV-cured polymers made of an aromatic diepoxyde (ADE) and epoxidized soyabean oil (ESO)^a

| ADE | ESO-2 | ESO-3 | Gel | | | |
|-----|-------|-------|----------------|--------------|----------------|--------------|
| | | | Conversion (%) | fraction (%) | Swelling ratio | Hardness (s) |
| 100 | — | — | 92 | 80 | 1.0 | 350 |
| 80 | 20 | — | 96 | 85 | 0.8 | 300 |
| 80 | — | 20 | 95 | 90 | 0.6 | 340 |
| — | — | 100 | 85 | 90 | 1.2 | 70 |

^a Photoinitiator [Cyracure UVI-6974]=3wt%; UV exposure time, 5s.

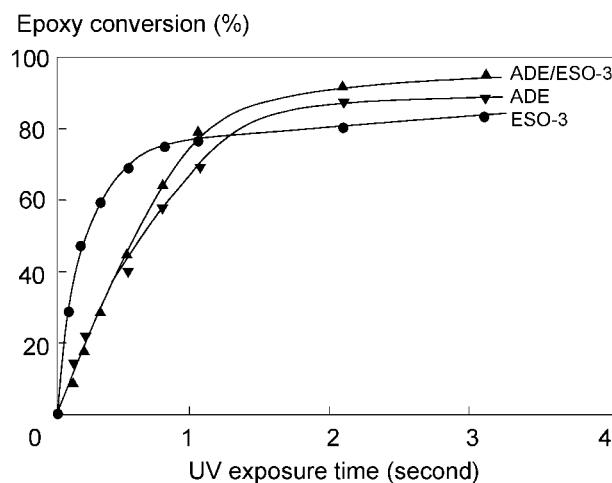


Figure 5. Photoinitiated cationic polymerization of various epoxy monomers, monitored by infrared spectroscopy (ADE epoxy band at 865 cm^{-1} ; ESO epoxy band at 835 cm^{-1}): ADE/ESO-3=80/20 by weight; [TAS]=3wt%.

(85% after a 3 s UV exposure compared to 92% for ADE) as shown in Fig 5. This effect cannot be explained simply by chain mobility considerations, because the UV-cured ESO-3 is a low-modulus polymer. It could be due to some steric hindrance in the ESO molecule which would render the access of the three epoxy groups located on the same molecule more difficult. Indeed, in the case of the diepoxide ESO-2, nearly 100% conversion was reached upon UV exposure. The addition of ESO (20 wt% of ESO-3) has no major effect on the polymerization of the aromatic diepoxide, except for a slightly more complete curing (Fig 5). Unfortunately, it was not possible to follow correctly the polymerization of the epoxy group of ESO in the ADE/ESO-3 mixture, because of its low content (20 wt%) and an overlap with the ADE infrared bands in the 825 cm^{-1} region. Nevertheless, from the almost complete disappearance of these bands it can be concluded that nearly all of the ESO epoxy groups had polymerized after UV exposure of the blend.

A distinct characteristic of cationic initiated polymerization is that the propagating polymer carbocations, or oxonium ions in the case of epoxides, do not react among themselves, as polymer radicals do. Termination reactions are therefore less likely to occur, so that the polymerization, when it has been initiated by a short UV exposure, will continue to proceed in the dark. Such a post-polymerization process has been clearly characterized in the ADE/ESO-3 sample exposed for 1 s to UV radiation in the presence of the sulfonium photoinitiator.

Figure 6 shows how the degree of conversion of the ADE epoxy group increases from an initial value of 68% just after UV exposure up to 95% within 2 h. No residual epoxy groups could be detected by IR spectroscopy in the sample stored for 3 days in the dark. At the same time, the Persoz hardness of the UV-cured coating was found to increase steadily, from an

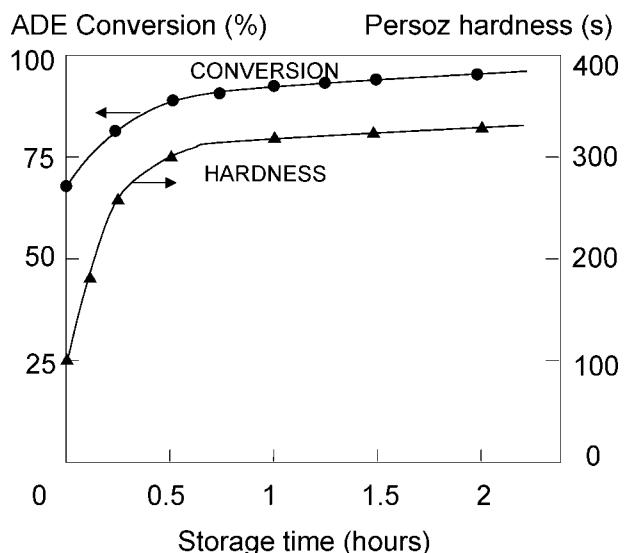


Figure 6. Post-polymerization and hardening in the dark of an ADE/ESO-3 (80/20) coating exposed to UV radiation for 1 s; [TAS]=3wt%.

initial value of 100 s just after the 1 s UV exposure, up to 325 s within 2 h, and 346 s after 3 days. This post-polymerization reaction is beneficial in that it allows one to reduce the exposure time and still achieve full cure of the sample. It is important to take this phenomenon into account when evaluating the final properties of UV-cured epoxy systems. One can take advantage of this dark polymerization process to stick together two non-transparent pieces (such as metallic panels) with a UV-curable epoxy glue. The two pieces were coated with the liquid resin and exposed briefly to UV radiation. Immediately thereafter they were pressed together for about 30 min, during which time the cationic ring-opening polymerization of the epoxide continued to proceed, with formation of a tight assembly.

UV curing of ADE, ESO and acrylate mixtures

Interpenetrating polymer networks (IPN) are typically formed by polymerization of two types of multi-functional monomers that undergo polymerization by different mechanisms, eg radical and cationic types. Highly crosslinked IPNs have recently been produced by UV irradiation for a few seconds of a mixture of diacrylate and diepoxide monomers in the presence of both radical and cationic type photoinitiators.¹⁶ A similar process occurs for mixtures of ESO and hexanediol diacrylate (HDDA).

Figure 7 shows the polymerization profiles of the two monomers upon UV irradiation of a 50/50 mixture by weight of HDDA and ESO-3 in the presence of a triarylsulfonium salt (1 wt%) and a hydroxyphenyl ketone (1 wt%). The polymerization of HDDA proceeds rapidly and is nearly complete after a 1 s UV exposure, by contrast to neat HDDA where the conversion levels off at a value of about 85% because of vitrification. The total polymerization of the acrylate double bonds in the monomer mixture was attributed

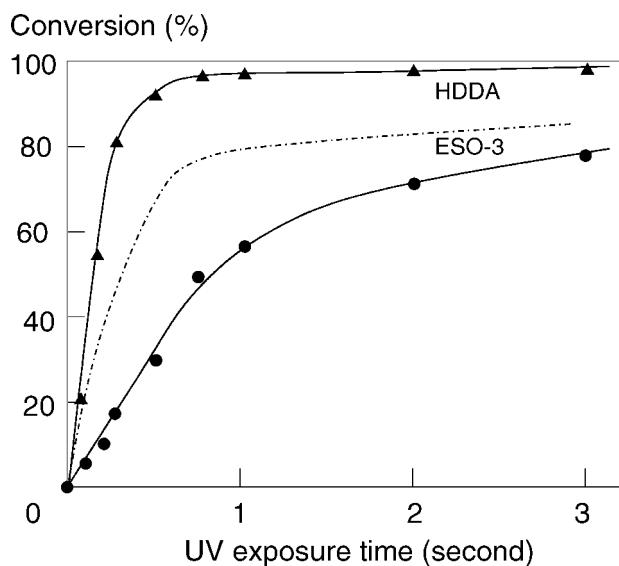


Figure 7. Photoinitiated polymerization of a 50/50 blend of epoxidized soybean oil with a diacrylate monomer: [TAS]=1 wt%; [Darocur 1173]=1 wt%; —, neat ESO-3.

to the plasticizing effect of the less reactive ESO-3 comonomer. As expected, the cationic polymerization of the triepoxide proceeds at a slower pace and it levels off at about 85% conversion, because of the mobility restrictions brought about by the early formation of the acrylate polymer network.

Essentially the same trend was observed when ESO was replaced in the monomer mixture by the aromatic diepoxyde, as indicated by the polymerization profiles of HDDA and ADE shown in Fig 8. The simultaneous build-up of the two IPNs, shown in Scheme 3, produces an insoluble polymer which is tightly cross-linked (SR value of 0.7), as shown in Fig 9.

A similar study was performed with a ternary monomer mixture consisting of the diacrylate (HDDA) and the two epoxides (ADE and ESO-3).

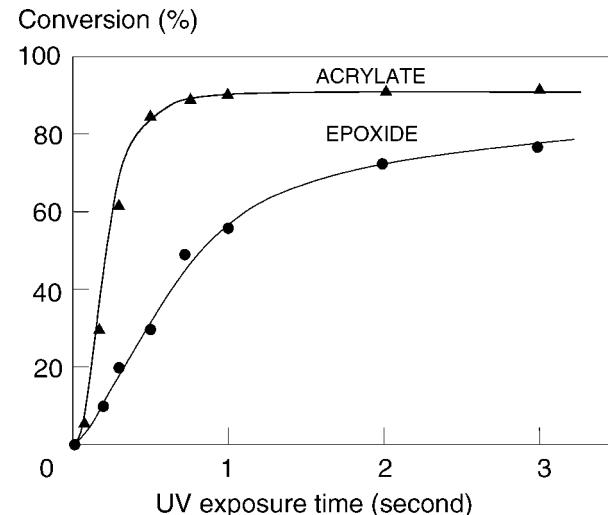
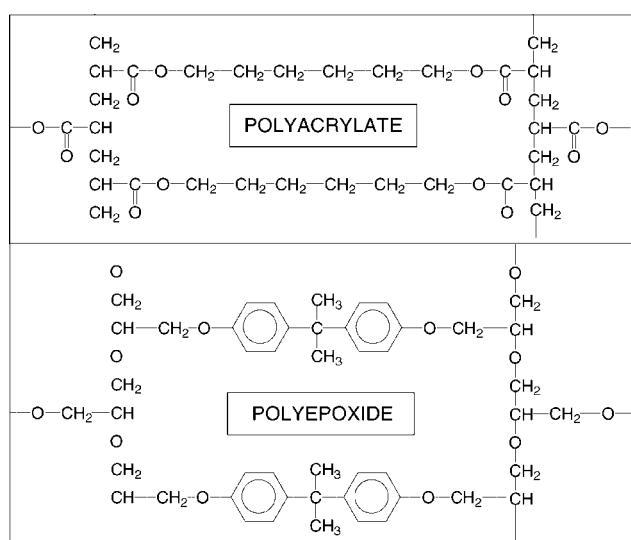


Figure 8. Conversion of the two components during photoinitiated polymerization of a 50/50 blend of an aromatic diepoxyde (ADE) and a diacrylate monomer (HDDA): photoinitiator [TAS]=1 wt%; [Darocur 1173]=1 wt%.



Scheme 3. Diagram of the two interpenetrating polymer networks formed upon UV-curing of a blend of diepoxyde and diacrylate monomers (ADE/HDDA).

Figures 10 and 11 show the polymerization profiles of the HDDA and ADE monomers, respectively, for three mixtures containing various proportions of the acrylate and epoxide compounds. The most complete curing was found for the ADE/HDDA/ESO-3 mixture having the following weight proportions: 40/40/20. It should be mentioned that the polymerization of the ESO epoxide, again, could not be followed by infrared spectroscopy because of an overlap of the various IR bands in the 825 cm⁻¹ region.

The rapid build-up of the acrylate polymer network leads to early insolubilization of the ternary monomer mixture, without the induction period previously observed in the purely epoxide formulation, as shown in Fig 12. A 50% insoluble polymer was obtained after a 0.5 s UV exposure of the ternary monomer mixture,

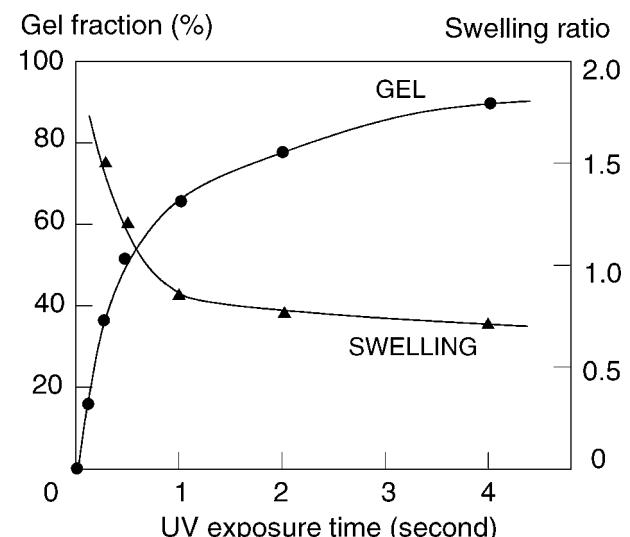


Figure 9. Gel formation and swelling during photoinitiated polymerization of a 50/50 blend of an aromatic diepoxyde (ADE) and a diacrylate monomer (HDDA): photoinitiator [TAS]=1 wt%; [Darocur 1173]=1 wt%.

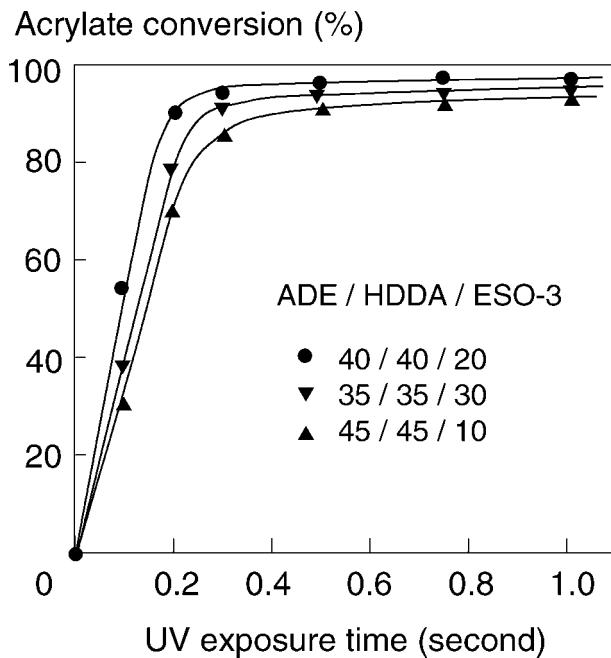


Figure 10. Polymerization of the acrylate double bond upon UV irradiation of various blends of an aromatic diepoxyde, a diacrylate monomer and epoxidized soyabean oil for which weight ratios are given in the figure: [TAS]=1 wt%; [Darocur 1173]=1 wt%.

while this required 1 s for the ADE/ESO-3 mixture and 1.5 s for the neat ADE monomer (Fig 3). The two polymer networks formed are tightly crosslinked, as shown by the low values of the swelling ratio which drops to 0.4 upon extensive irradiation (Fig 12).

The early polymerization of the acrylate monomer transforms the liquid resin within 0.5 s into a soft, low-modulus polymer (Persoz hardness=50 s). The hardening observed upon further UV irradiation (Fig 13)

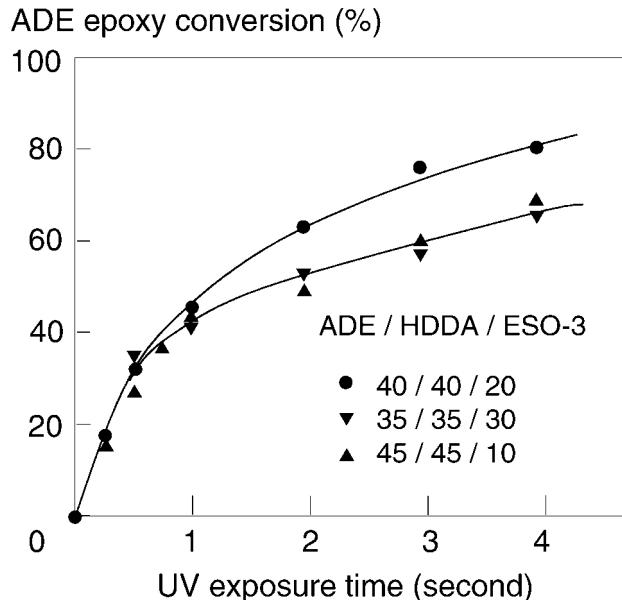


Figure 11. Polymerization of the ADE epoxy group upon UV irradiation of various blends of an aromatic diepoxyde, a diacrylate monomer and epoxidized soyabean oil for which weight ratios are given in the figure: [TAS]=1 wt%; [Darocur 1173]=1 wt%.

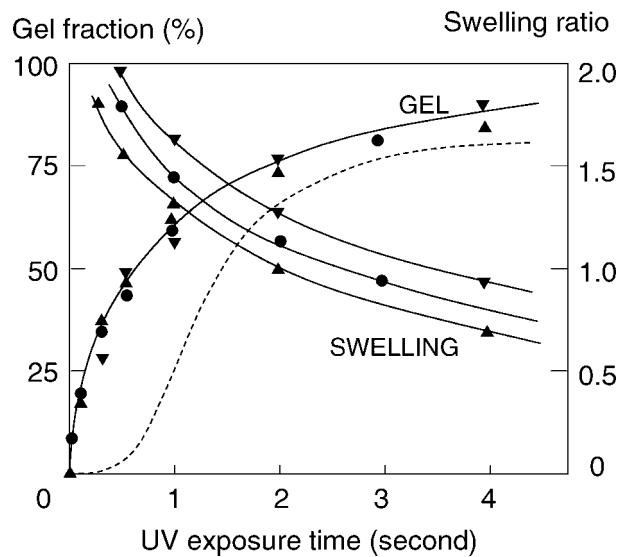


Figure 12. Insolubilization and swelling profiles upon UV irradiation of various blends of an aromatic diepoxyde, a diacrylate monomer and epoxidized soyabean oil having different weight ratios: [TAS]=1 wt%; [Darocur 1173]=1 wt%. ADE/HDDA/ESO-3 weight ratios: 40/40/20 (●); 35/35/30 (▼); 45/45/10 (▲); - - -, neat ADE.

must be due to the polymerization of the epoxy groups of ESO-3 and ADE. It is less pronounced than in the acrylate-free system, so that by adjusting the acrylate content in the formulation one can control the viscoelastic properties of the UV-cured polymer. In particular, the impact resistance, flexibility and abrasion resistance were enhanced in comparison to the glassy and brittle polymer obtained by UV-curing of the neat aromatic diepoxyde. This is of great interest if such UV-cured IPNs are to be used in coating applications.

Similar results were obtained by replacing the diacrylate HDDA monomer by the triacrylate TMPTA monomer, except for a less complete polymerization of the acrylate double bonds (85% conversion) due to

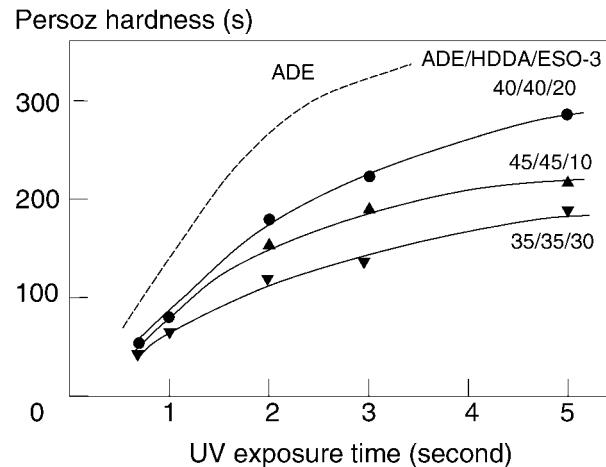


Figure 13. Hardening profiles upon UV-irradiation of various blends of an aromatic diepoxyde, a diacrylate monomer and epoxidized soyabean oil having different weight ratios: [TAS]=1 wt%; [Darocur 1173]=1 wt%. ADE/HDDA/ESO-3 weight ratios: 40/40/20 (●); 35/35/30 (▼); 45/45/10 (▲); - - -, neat ADE.

| Formulation of IPN (wt%) | | | | Conversion (%) | | | | | |
|--------------------------|-------|------|-------|----------------|-----|---------|---------|----------------|--------------|
| ADE | ESO-3 | HDDA | TMPTA | Acrylate | ADE | Epoxide | Gel (%) | Swelling ratio | Hardness (s) |
| 35 | 30 | 35 | — | 99 | 80 | 93 | 0.67 | 190 | |
| 40 | 40 | 20 | — | 99 | 84 | 93 | 0.65 | 220 | |
| 45 | 45 | 10 | — | 98 | 76 | 94 | 0.5 | 290 | |
| | | | | | | | | | |
| 35 | 30 | — | 35 | 82 | 70 | 87 | 0.75 | 320 | |
| 40 | 40 | — | 20 | 85 | 75 | 90 | 0.6 | 280 | |
| 45 | 45 | — | 10 | 81 | 65 | 88 | 0.65 | 350 | |

^a Photoinitiators [Cyracure UVI-6574]=1 wt%, [Darocur 1173]=1 wt%; UV exposure time, 5 s.

Table 2. Performance analysis of UV-cured acrylate/epoxide interpenetrating polymer networks. Mixture of aromatic diepoxyde, triepoxidized soyabean oil and di- or triacrylate monomers^a

greater mobility restrictions in the IPN formed. Indeed Persoz hardness values were found to be significantly higher than in the HDDA-based UV-cured polymers, ranging from 280 to 350 s, depending on the formulation composition.

The curing performance and physicochemical properties of the various epoxy/acrylate IPN systems investigated are summarized in Table 2. It can be seen that the polymerization of both the epoxy groups and the acrylate double bonds proceed less extensively in samples that reach the highest hardness, as expected from molecular mobility considerations. Low-modulus IPNs showing an elastomeric character can be obtained by using an acrylate telechelic oligomer with soft segments, such as polyethylene glycol diacrylate, thus making the UV-cured material well suited for adhesives applications.

UV-radiation curing of a biscycloaliphatic diepoxyde

Biscycloaliphatic diepoxydes (BCDE) are known for being more reactive than glycidylethers, behaviour which was attributed to the strain of the adjacent cyclohexane ring. For this reason, BCDEs are the most widely used epoxy monomers in cationic UV-radiation curing.²⁴ The ring opening polymerization

proceeds rapidly upon UV-exposure of the neat monomer in the presence of a triarylsulfonium salt, as shown in Fig 14. A 0.1 s UV exposure proved to be sufficient to polymerize 60% of the epoxy groups. Upon further exposure, the degree of conversion increased further to finally level off at a value of 83% as a result of gelation and vitrification.

UV curing of BCDE ESO mixtures

The addition of ESO to BCDE has little effect on the cure rate, but it provides a slightly more complete polymerization of the cycloepoxide, especially when using equal amounts by weight of the two monomers (Fig 14). Surprisingly, the presence of the cycloepoxide appears to have a beneficial effect on the polymerization of the ESO which is nearly complete after a 1 s UV exposure (Fig 15), instead of levelling off at 85% conversion as found in neat ESO-3. The similarity between the polymerization profiles of BCDE and ESO-3 argues in favour of a copolymerization reaction taking place between the two types of epoxy groups. The crosslinked copolymer thus formed is shown in Scheme 4.

The incorporation of the ESO structure into the tight cycloepoxide polymer network causes both slower insolubilization and build-up of a looser

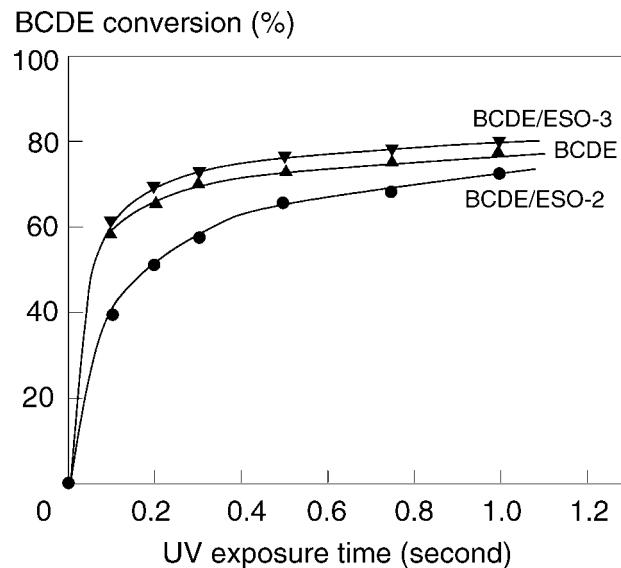


Figure 14. Photoinitiated cationic polymerization of a biscycloaliphatic diepoxyde (BCDE), neat and blended with epoxidized soyabean oil (ESO) in a 80/20 weight ratio; [TAS]=3wt%.

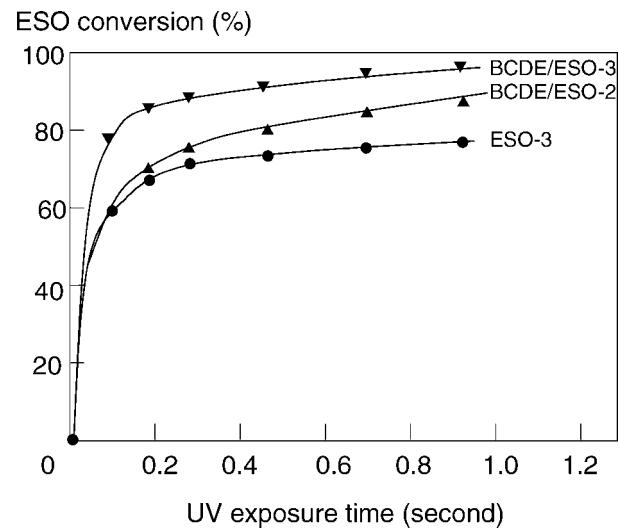
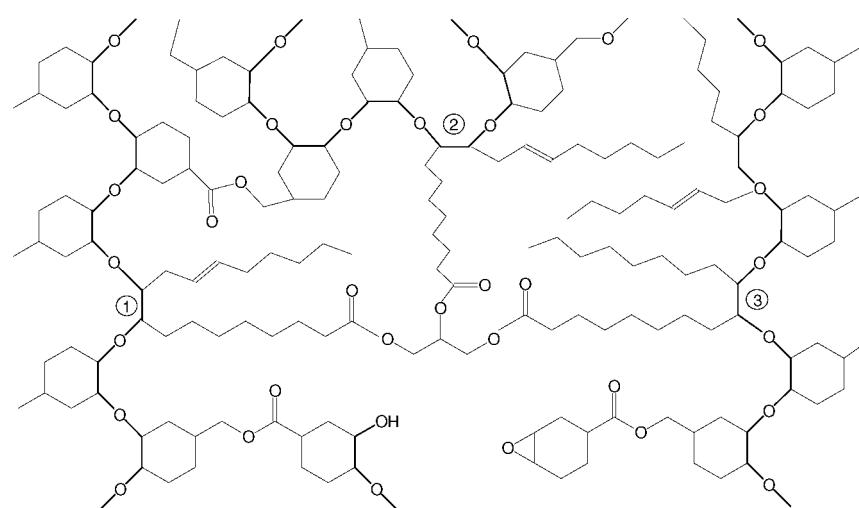


Figure 15. Photoinitiated cationic polymerization of epoxidized soyabean oil, neat and blended with a biscycloaliphatic diepoxyde in a 20/80 weight ratio; [TAS]=3wt%.



Scheme 4. Diagram of the copolymer network formed upon photoinitiated cationic polymerization of a mixture of triepoxidized soybean oil and a biscycloaliphatic diepoxye (1, 2 and 3 are polymerized epoxy groups of ESO-3).

three-dimensional network, as shown in Fig 16. The swelling ratio was found to increase from a value of 0.3 for the UV-cured BCDE polymer up to 1.2 for the crosslinked polymer containing 50 wt% ESO-3. The copolymer BCDE/ESO-3 proved to be hard enough (Persoz hardness of 300 s) to be used as protective coating or to produce composite materials by blending with glass powder. One should note that this polymer is substantially harder than the UV-cured BCDE polymer (Persoz hardness of 240 s), even when the ESO-3 content was increased to 50 wt% (Fig 17). This material combines hardness and flexibility and consequently shows good resistance to abrasion and scratching. It is therefore well suited to improve the surface properties of a large variety of materials, and in particular metals because of its good adhesion on this type of substrate. It should be mentioned that, here again, the sample briefly irradiated continued to harden upon storage in the dark to reach, after 3 days, Persoz values comparable to those attained upon longer UV exposure (250–300 s). This post-cure becomes less important for samples UV irradiated for a few seconds, because the epoxy conversion has

nearly reached its maximum when it emerges from the UV line. In all the systems investigated, the hardness imparted by the ESO was found to be durable.

Similar results have been obtained by using as comonomer the difunctionalized ESO-2 sample which was still found to be somewhat less reactive than ESO-3 (Figs 14 and 15) and to generate less tightly crosslinked and softer polymeric materials. The data obtained in our study of the photoinitiated cationic polymerization of mixtures of a biscycloaliphatic diepoxye and ESO are summarized in Table 3 and illustrated in Fig 18. They clearly show the remarkable performance achieved by incorporating ESO into the BCDE polymer network, and the effect of increasing concentrations of ESO-3 on the epoxy conversion, hardness and swelling of the UV-cured polymer.

The actual reasons for the positive effect of ESO on both the curing of diepoxy monomers and the properties of the cured film are still unclear. One can consider that the copolymerization reaction between the two types of epoxy groups, together with the

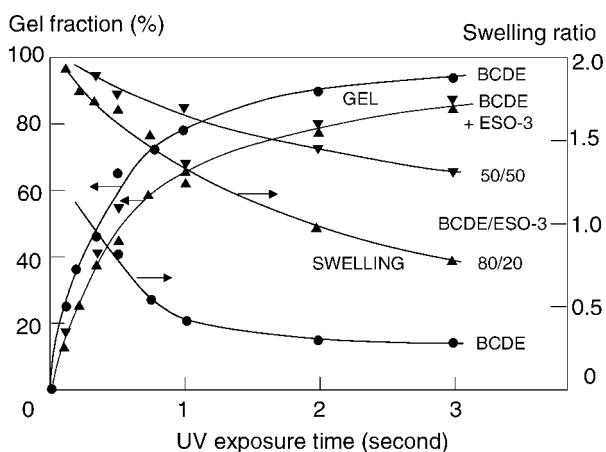


Figure 16. Insolubilization and swelling profiles upon UV curing of BCDE neat and blended with ESO-3 (50/50 and 80/20 weight ratios); [TAS]=3 wt%.

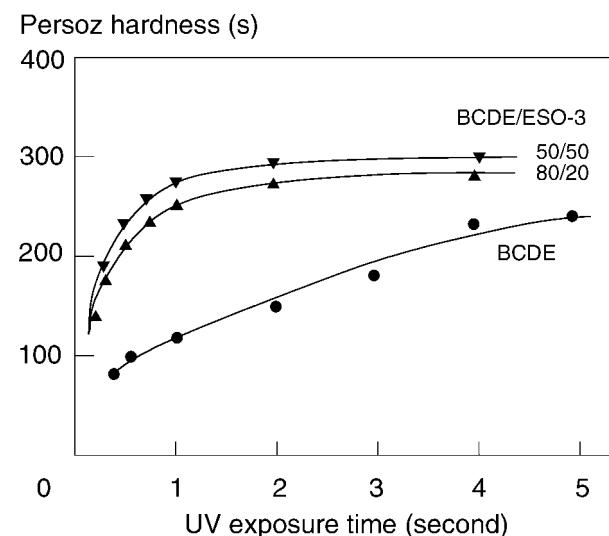


Figure 17. Hardening profiles upon UV curing of BCDE neat and blended with ESO-3 (50/50 and 80/20 weight ratios); [TAS]=3 wt%.

| | | | | | | | | |
|----------------------------------|-----|-----|-----|-----|-----|-----|-----|-----|
| Araldite 179 (wt%) | 100 | 90 | 80 | 70 | 50 | 90 | 80 | 70 |
| ESO-3 (wt%) | 0 | 10 | 20 | 30 | 50 | — | — | — |
| ESO-2 (wt%) | — | — | — | — | — | 10 | 20 | 30 |
| BCDE conversion (%) ^a | 78 | 78 | 79 | 80 | 78 | 80 | 79 | 84 |
| ESO conversion (%) ^a | — | 97 | 98 | 98 | 98 | 81 | 88 | 90 |
| Gel fraction (%) ^b | 97 | 95 | 95 | 92 | 90 | 94 | 90 | 89 |
| Swelling ratio ^b | 0.3 | 0.5 | 0.7 | 1.0 | 1.2 | 0.8 | 1.0 | 1.1 |
| Maximum hardness (s) | 240 | 300 | 280 | 310 | 290 | 270 | 250 | 180 |

Table 3. Performance analysis of UV-cured mixtures of a bicycloaliphatic epoxide and epoxidized soyabean oil

^a After a 1 s UV exposure.
^b After a 3 s UV exposure.

enhanced chain mobility brought upon by ESO, may be helpful in achieving a more complete polymerization. The formation of a copolymer network linking the two monomers tightly together in a complex architecture (Scheme 4) may be responsible for the increased hardness.

UV curing of BCDE and ADE mixtures

We have also studied by FTIR spectroscopy the UV curing of a blend of the cycloaliphatic diepoxyde and the aromatic diepoxyde (50/50 BCDE/ADE mixture by weight). The polymerization of BCDE was found to proceed surprisingly fast and extensively under those conditions (Fig 19). After 0.1 s, as much as 90% of the cycloaliphatic diepoxyde was polymerized, compared to only 16% of the aromatic diepoxyde, and up to 100% after 0.5 s UV irradiation. Because of the great difference in reactivity between the two monomers, the polymerization of BCDE occurs in the liquid ADE monomer, which acts as a plasticizer, and is therefore not limited by molecular mobility. From the clear-cut difference in the kinetic profiles of Fig 19 one can conclude that the two epoxy monomers do not undergo significant copolymerization. By extending the UV exposure up to 6 s, a fully cured polymer was obtained after a 1 day storage at ambient temperature.

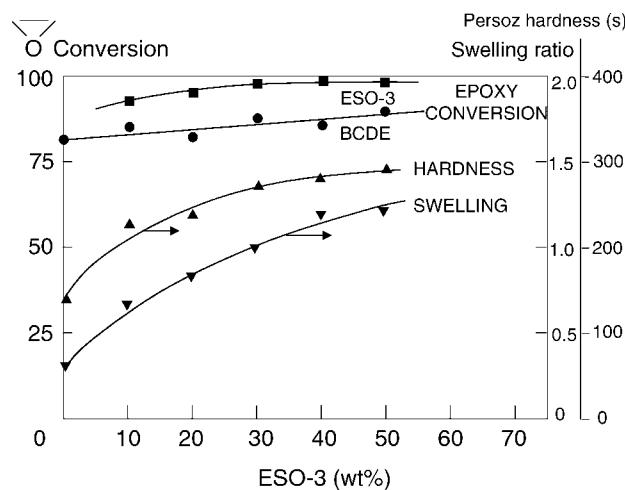


Figure 18. Influence of the epoxidized soyabean oil content on the characteristics of a photocured BCDE/ESO-3 polymer after UV-exposure for 2 s (hardness) or 5 s (epoxy conversion and swelling).

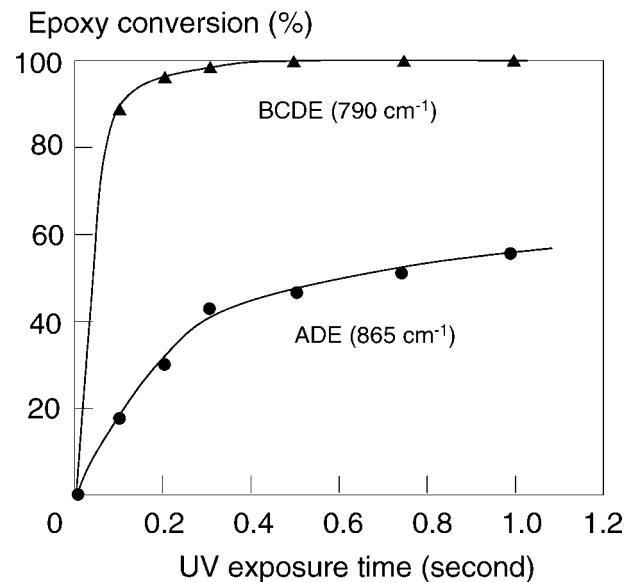
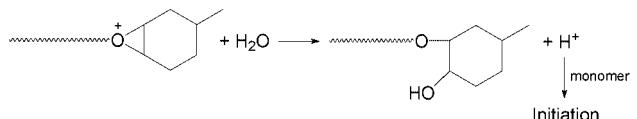


Figure 19. Photoinitiated cationic polymerization of a 50/50 mixture of a bicycloaliphatic diepoxyde and an aromatic diepoxyde; [TAS]=3 wt%.

Influence of humidity on cationic polymerization of BCDE

All the experiments described so far have been carried out in the presence of air at a relative humidity of about 35%. Cationic polymerization of epoxides is known to be sensitive to moisture: on the one hand, the addition of water may stop the polymerization by nucleophilic attack on the oxonium cation, but on the other hand, small amounts of water may enhance the epoxide consumption through a chain transfer reaction leading to re-initiation.



The latter process leads to a more complete polymerization by allowing the polymeric oxonium ions trapped in the polymer network to react further. In the case of the BCDE monomer, moisture was found to have a beneficial effect on the curing process, as shown in Fig 20. When the briefly irradiated sample was placed in a 100% humid atmosphere, the polymerization of the epoxide occurred both faster and more extensively than in a dry atmosphere.

To ensure that the disappearance of the epoxide,

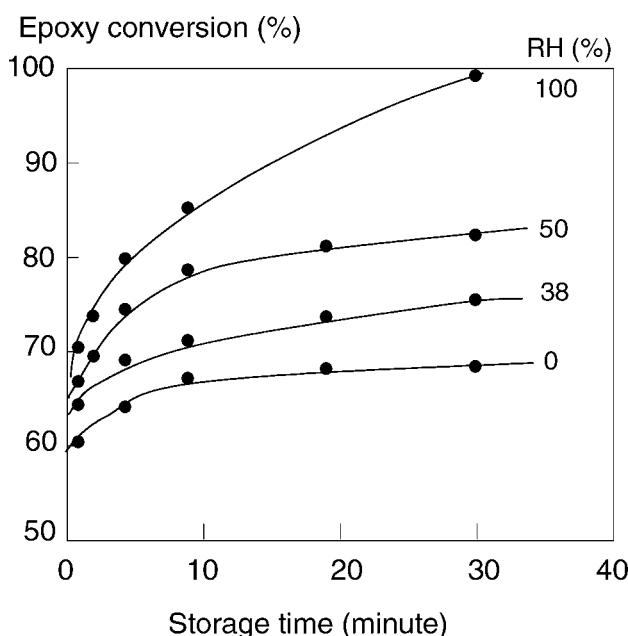


Figure 20. Influence of relative humidity (RH) on the dark polymerization of a biscycloaliphatic diepoxy at ambient temperature; [TAS]=2 wt%; UV dose=70 mJ cm⁻².

monitored by IR spectroscopy, is really due to polymerization and not to a hydrolysis reaction, we studied the influence of humidity on the insolubilization of the UV-irradiated polymer. Gel fraction measurements were made after a given UV exposure, followed by a 4 h storage in the dark at ambient temperature to let post-polymerization proceed. It can be seen in Fig 21 that the sample stored in a 100% humid atmosphere becomes insoluble more rapidly: a gel fraction of 84% is obtained after a 0.1 s UV exposure, compared to only 30% for the sample stored in a drier atmosphere. To obtain a fully insoluble polymer, a UV exposure of 0.2 s was sufficient at 100% relative humidity (RH), while it required 0.5 s at 35% RH. The same trend was observed by measuring the degree of swelling of the insoluble polymer (Fig 21). A tighter polymer network was formed when the sample was stored in a 100% RH atmosphere, a feature which was attributed to more complete curing of the epoxide under those conditions (Fig 20).

It should be mentioned that the polymer cured under high humidity conditions is not as hard as when it was cured in normal conditions. A Persoz value of 180 s was measured for the sample post-cured at 100% RH, compared to 290 s at 35% RH, and as much as 350 s at 0% RH (hardness measurements were made on samples stored subsequently in a dry atmosphere for 1 day to ensure total release of the absorbed water). The formation of a more elastomeric polymer material in humid conditions can be attributed to the moisture-driven chain transfer reaction which reduces the crosslink density. The greater molecular mobility in this softer polymer would also account for the observed total reaction of the epoxy groups. These results clearly show that the conditions under which

the polymerization of the epoxy monomer is conducted have a great influence on the physicochemical properties of the UV-cured polymer.

CONCLUSIONS

Photoinitiated cationic polymerization of multifunctional epoxides is a powerful method to produce rapidly highly crosslinked polymers. This UV-curing technology was successfully applied to aromatic and cycloaliphatic diepoxides to generate within seconds three-dimensional polymer networks well suited for coating and composite applications. The addition of epoxidized soyabean oil to the aromatic diepoxide was found to both accelerate the curing process and generate a more tightly crosslinked polymer showing better chemical resistance.

Interpenetrating polymer networks were readily produced by introducing a di- or triacrylate monomer into the epoxide blend, with the expected increase in the insolubilization rate. By varying the proportions of the different components, one can modulate the physicochemical properties of the UV-cured material. This was also achieved with a mixture of cycloaliphatic diepoxide and epoxidized soyabean oil which undergoes rapid crosslinking copolymerization upon UV exposure in the presence of a triarylsulfonium photoinitiator, with formation of a hard but still flexible material. A fully cured polymer network containing no residual epoxy groups was obtained by UV irradiation of a blend of a cycloaliphatic diepoxide and an aromatic diepoxide. In consideration of the manifold advantages of the UV-curing technology, namely a solvent-free formulation cured within seconds at ambient temperature to give a high quality product, one can expect the epoxy-based resins examined in the present work to find their main applications as protective coatings, composite materials and adhesives.

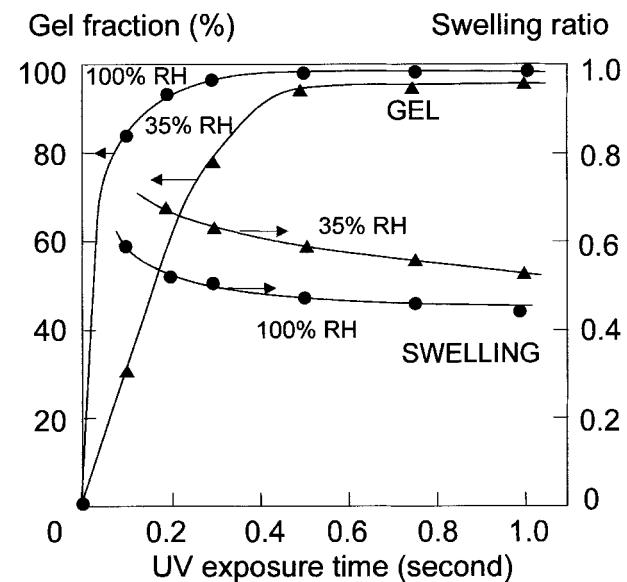


Figure 21. Influence of relative humidity (RH) on the insolubilization of BCDE upon UV exposure and 4 h storage in the dark at 35% or 100% RH.

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