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Performance analysis of acylphosphine oxides in photoinitiated polymerization

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Abstract

The initiation efficiency of acylphosphine-oxides has been evaluated in different types of UV-curable resins. Real-time infrared spectroscopy was used to monitor in situ the polymerization process in thin coatings exposed to UV-radiation. When compared to typical radical photoinitiators, acylphosphine oxides proved to be the most efficient ones with respect to both the polymerization rate and the cure extent, mainly because of their fast photolysis. Frontal polymerization proceeds readily with such photobleachable initiators, thus allowing thick specimens to be deep-through cured by simple exposure to sunlight. Because they absorb in the region of 350–400 nm, acylphosphine oxides proved particularly well suited to induce the photopolymerization of both pigmented systems and protective coatings used in exterior applications, which contain UV-absorber-type light stabilizers. Superior performance was also achieved with these photoinitiators in the photocrosslinking of functionalized polymers, such as acrylated polyisoprene and polybutadiene with pendent vinyl groups. The addition of small amounts of a trifunctional thiol was shown to drastically speed up the crosslinking polymerization, insolubilization being achieved within a 0.3 s UV-exposure, even for initiator concentrations as low as 0.1 wt%. © 2001 Elsevier Science Ltd. All rights reserved.

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1. Introduction

The photoinitiator plays a key role in UV-curable systems by generating the reactive species, free radicals or ions, which will initiate the polymerization of the multifunctional monomers and oligomers. Through its concentration, it controls directly both the polymerization rate and the penetration of the incident light, and therefore the cure depth. To be efficient, a radical-type photoinitiator must fulfil a number of requirements [1], namely:

- a strong absorbance of the UV-radiation emitted by mercury lamps,
- a short lifetime of the excited states to avoid quenching by atmospheric oxygen,
- a fast photolysis and bleaching which generate the free radicals,
- a high reactivity of the free radicals evolved toward the monomer function,
- a good solubility of the photoinitiator in the formulation,
- the formation of non-colored and odorless photoproducts.

With the steady growth of the UV-radiation curing technology in manifold applications, a large variety of photoinitiators has been developed to meet at best these requirements. Among the radical-type photoinitiators currently used in UV-curable systems, acylphosphine oxides were found to give superior overall performance [2–10]. These compounds have the distinct advantage of absorbing in the near UV-range to undergo a fast photolysis which generates benzoyl and phosphinoyl radicals. Both of these free radicals proved to be very reactive [5] and capable to initiate the polymerization of a large variety of monomers such as acrylates, styrene, thiol-ene systems and maleimides. These compounds show a low volatility, as required for UV-curable water-based systems and UV-powders, and a good solubility in acrylate monomers, in particular the monoacylphosphine oxides [10]. Bisacylphosphine oxides have been shown to be particularly effective to photopolymerize pigmented coatings [8] and composite materials [11]. The process by which they initiate the polymerization upon UV exposure has been thoroughly investigated by TR-ESR and CIDNP spectroscopy [12].

In this article we review some recent results showing the great efficiency of acylphosphine oxides for initiating

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the photopolymerization of acrylate-based resins to produce rapidly clear and pigmented coatings. Special emphasis has been given to the kinetic aspect of such ultrafast reactions which were monitored in real time by infrared spectroscopy. We have examined the initiating efficiency of both monoacylphosphine oxides (MAPO) and bisacylphosphine oxides (BAPO), in comparison to some commercial photoinitiators.

2. Experimental

2.1. Materials

The two following acylphosphine oxide photoinitiators were used in this study: Lucirin TPO (MAPO) from BASF and Irgacure 819 (BAPO) from Ciba Specialty Chemicals. Their efficiencies were compared to those of typical photocleavable initiators, e.g. Irgacure 651 (DMPA), Irgacure 369 (MoK) or Darocur 1173 (HPK), all from Ciba Specialty Chemicals, benzophenone (BZP) from Aldrich and Quantacure CPTX from Octel Chemicals. They were introduced in the formulation at a typical concentration of 2 wt%. The chemical formulas of the various photoinitiators used are given in Chart 1.

The acrylate resin consisted of a polyurethane diacrylate (Ebecryl 284) or an aminopolyester tetraacrylate (Ebecryl 80), with hexanediol diacrylate (HDDA) as reactive diluent, the three compounds from UCB Chemicals being used without further purification. The performances of MAPO and BAPO photoinitiators were also evaluated in a UV-curable vinyl ether/maleate resin (Uralac XP-1400 UV from DSM Resins). In another series of experiments, acylphosphines oxides were used as photoinitiators to crosslink rapidly by UV irradiation some functionalized polymers, such as acrylated polyisoprene (synthesized in the laboratory) or a thermoplastic elastomer (Kraton SBS-1101 from Shell) in combination with a thiol crosslinker (TRIS from Evans Chemical).

2.2. Irradiation

The liquid resin was applied onto a transparent polypropylene film or on a silicon wafer by means of a calibrated wire-wound applicator. In some experiments a second polypropylene film was laminated on top of the sample to prevent oxygen diffusion. The thickness of the UV-curable film was set typically between 5 and 25 μm, as determined by IR spectroscopy by means of a calibration curve. The sample was placed in the compartment of an IR spectrophotometer where it was exposed for a few seconds to the UV-radiation of a medium pressure mercury lamp. The light intensity at the sample position could be set between 5 and 200 mW cm^{-2}, as measured by radiometry (International Light IL-390). Some curing experiments were performed on an industrial-type UV-line (IST-80 W/cm) which was operated at belt speeds between 5 and 60 m/min, i.e. UV-dose of 780 and 65 mJ cm^{-2} per pass, respectively.

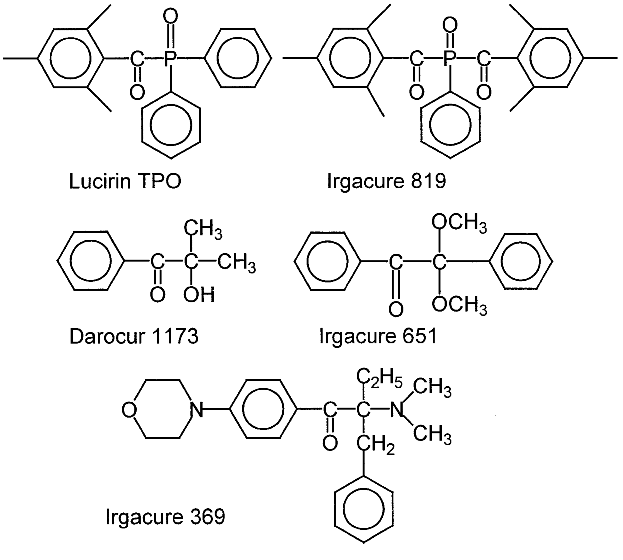

Chart 1. Chemical formulas of some radical-type photoinitiators.

2.3. Analysis

The polymerization of acrylate resins was followed in real time by monitoring the decrease upon UV exposure of the infrared band at 812 cm^{-1} of the acrylate double bond [13]. Conversion vs. times curves were directly recorded by this technique (RTIR spectroscopy) for high-speed polymerizations. The disappearance of the photoinitiators upon UV irradiation was followed in real time by UV spectroscopy [14], by setting the detection wavelength at their maximum absorbance. Chloroform was used as solvent to measure the insoluble fraction of the crosslinked polymer. The hardness of the UV-cured coatings was determined by means of a Persoz pendulum.

3. UV-curing of acrylate-based clearcoats

The initiation efficiency of acylphosphine oxides has been evaluated in a polyurethane-acrylate (PUA) resin which was exposed to the UV radiation of different types of light sources: a medium pressure mercury lamp, sunlight and an argon ion laser. The photoinitiated crosslinking polymerization reaction is represented schematically in Chart 2.

3.1. Performance analysis of photoinitiators

Fig. 1 shows the polymerization profiles recorded by RTIR spectroscopy for a clear PUA resin exposed to the UV radiation of a mercury lamp in the presence of different photoinitiators. Very similar results have been obtained in a vinyl ether/maleate system UV-irradiated under similar

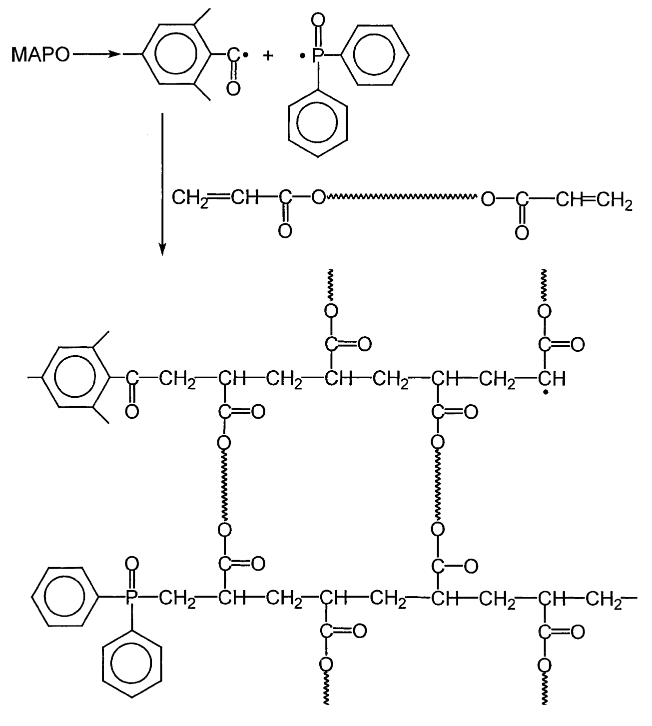

Chart 2. Photoinitiated crosslinking polymerization of a diacrylate oligomer.

conditions (Fig. 2). The superior efficiency of the acylphosphine oxides (MAPO and BAPO) is clearly apparent. It can be attributed to several factors:

- a greater absorptivity in the near UV range, where the mercury lamp has its strongest emission,
- a large quantum yield of free radical production,
- a high reactivity of benzoyl and phosphinoyl radicals,
- a fast photolysis upon UV exposure.

The last factor appears to play a major role in the better performance of acylphosphine oxides, as the rate of initiation is directly related to the rate of the photoinitiator photolysis. Fig. 3 shows the decay profiles of three photoinitiators recorded by real-time UV spectroscopy for a PUA clearcoat exposed to UV radiation. The faster destruction of the acylphosphine oxides accounts for most of the increase in the cure speed observed with these photoinitiators (Figs. 2 and 3). Eventhough each BAPO molecule can generate upon photolysis 4 initiating radicals by cleavage of the two carbon-phosphor bonds, instead of only two radicals for MAPO, this will not increase the initiation quantum yield because it requires the absorption of two photons.

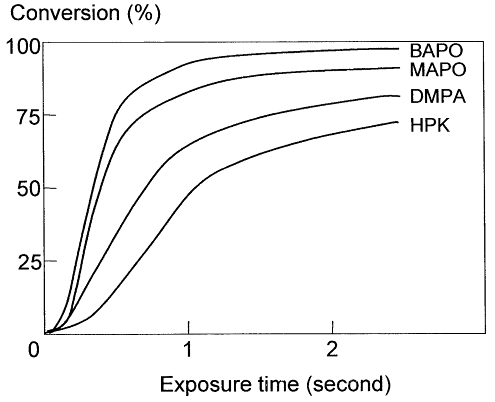

Fig. 1. Influence of the photoinitiator (2 wt%) on the polymerization of a polyurethane-acrylate coating. Light intensity: 12 mW cm^{-2}.

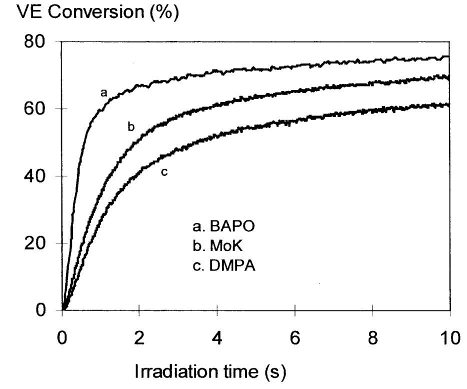

Fig. 2. Influence of the photoinitiator (2 wt%) on the polymerization of a vinyl-ether/maleate coating. Light intensity: 60 mW cm^{-2}.

3.2. Sunlight curing

Acylphosphine oxides are ideal candidates to perform photoinduced frontal polymerization as they fulfil the two main requirements: high light absorbance and fast photobleaching [15]. At the beginning of the exposure, the initiating radicals are mainly generated in the top layer because of the limited penetration of UV radiation. As the absorbing photoinitiator is being destroyed upon UV exposure, the incident light penetrates deeper into the sample and the polymerization front moves progressively from the surface to the bulk of the sample. By using BAPO as photoinitiator, a deep-through cure of a few centimeter thick PUA sample

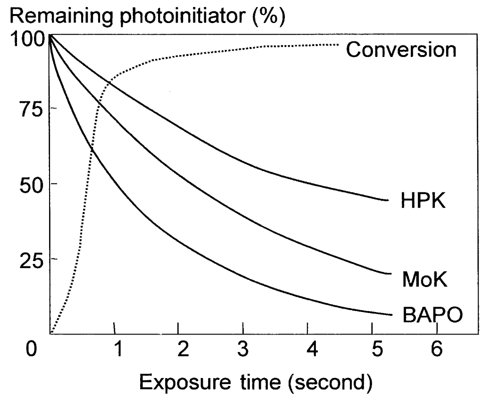

Fig. 3. Photoinitiator loss profiles recorded by RTUV spectroscopy upon UV exposure of a polyurethane-acrylate coating.

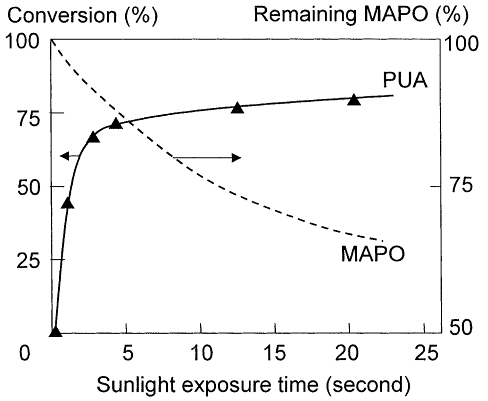

Fig. 4. Polymerization of a polyurethane-acrylate resin upon sunlight exposure through a glass filter. – – –: loss of the MAPO photoinitiator.

was achieved within less than 1 min of UV irradiation to give a transparent glass.

Such frontal polymerization was also carried out in a very economical way by simple exposure to sunlight. This solar technology was successfully applied to produce glass laminates, as acylphosphine oxides have the distinct advantage of absorbing effectively the UV sunlight filtered by mineral glass [16]. Fig. 4 shows the polymerization profile of an aliphatic polyurethane-acrylate resin exposed to sunlight between two glass plates, with Lucirin TPO (2 wt%) as photoinitiator. After 1 min, 90% of the acrylate double bonds were found to have polymerized, and up to 98% when the diacrylate reactive diluent (HDDA) was replaced by a monoacrylate monomer (isobornyl acrylate). The sun-cured polymer is a low-modulus elastomer which shows a high impact resistance, as required for safety glass applications. This intercalate is transparent and non-colored, and it remains so upon prolonged outdoor exposure if a HALS radical scavenger ([Tinuvin 292] = 1 wt%) has been introduced in the formulation.

The adhesive strength, which is a crucial issue in the manufacturing of glass laminates, has been greatly enhanced by coating firstly the two glass plates with a sun-cured styrene-butadiene rubber/acrylate film, acylphosphine oxides being also used here as photoinitiators [16]. The acrylate monomer was shown to copolymerize with the SBS unsaturation to form a tight polymer network showing excellent adhesion to glass, and to other materials as well (PMMA, PVC, polycarbonates, aluminium, stainless steel). Upon the second exposure to sunlight, the unreacted acrylate double bonds copolymerize with the PUA resin, thus creating covalent bonds between the coating and the intercalate to ensure the required cohesion.

This solar curing technology is not restricted to mineral glass laminates; it can be applied to a large variety of materials to be assembled, provided that at least one of the elements is transparent to near UV-radiation. Different types of laminates (glass/metal, glass/plastic, glass/composites, plastic/metal) have thus been produced by this 'green' technology which requires no special equipment, consumes no energy, emits no volatile organic compounds and is easy to implement (fast curing at ambient temperature in the presence of air). Acylphosphine oxides were recently shown to be also very effective photoinitiators to achieve the daylight curing of waterborne acrylate formulations for outdoor applications [17].

3.3. Laser curing

Similar results have been obtained by replacing sunlight by an argon ion laser tuned to its UV emission line at 363.8 nm, a wavelength at which acylphosphine oxides show a distinct absorption [7]. Because of the high photon flux which is concentrated in the narrow laser beam, the liquid to solid phase change occurs here within milliseconds, in tiny well-defined areas.

High resolution relief images have been obtained by a fast scanning (up to 1000 m/s) of the photoresist layer with a modulated laser beam, followed by aqueous development [18]. Fig. 5 shows some typical insolubilization profiles obtained upon laser irradiation of a PUA resin in the presence of air or in an inert atmosphere. The Laser Direct Imaging (LDI) technology eliminates the manufacture of the expensive mask and makes image transfer obsolete, thus reducing the overall production time. In consideration of today's requirements for process flexibility and a fast turnaround in design, LDI appears as an ideal tool for in-line and small batch production [19].

Another advantage of using lasers to initiate the polymerization, besides the rapidity of the process, is that the solidification of a given area can be performed at a great distance because of the high directivity of the coherent laser beam. For instance, two pieces of an assembly located on a satellite can be instantly bound together, on order, by simply firing a guided laser.

3.4. Photopolymerization in the presence of a UV absorber

Although UV-cured coatings are generally considered to have a poor light stability, we have shown that aliphatic

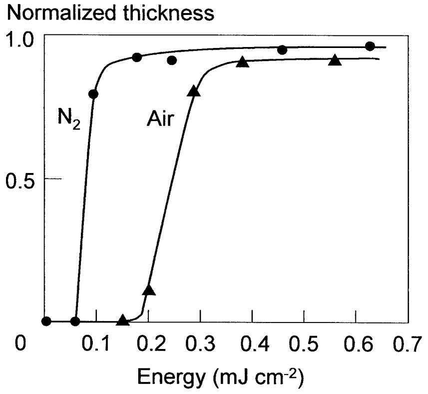

Fig. 5. Influence of atmospheric oxygen on the photosensitivity of an acrylic photoresist.

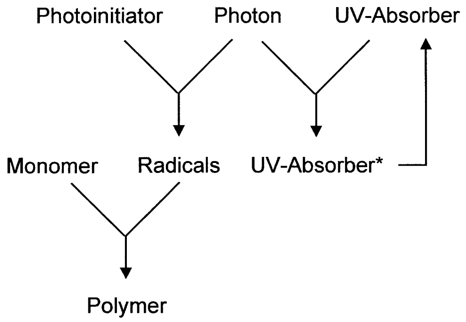

Chart 3. Photopolymerization in the presence of a UV-absorber.

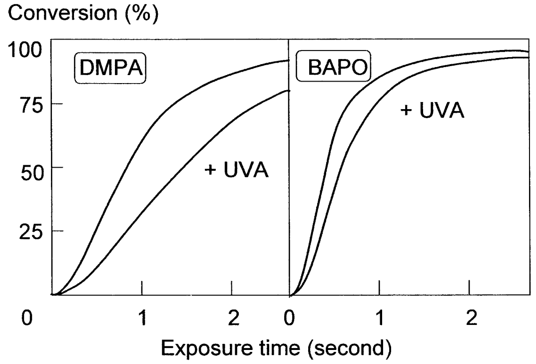

Fig. 6. Influence of a UV-absorber ([Tinuvin 400] = 2 wt%) on the UV-curing of a polyurethane-acrylate containing DMPA or BAPO as photoinitiator (2 wt%).

polyurethane-acrylate networks are quite resistant to photoageing if HALS radical scavengers are present [20]. They proved quite effective in improving the weathering resistance of different types of polymeric materials used in outdoor applications [21–23]. To achieve such performance, it was necessary to introduce in the resin formulation a UV-absorber (UVA) which will screen the harmful UV radiation of sunlight and thus prevent the photodegradation of the polymeric substrate.

The UV absorber has yet a detrimental effect on the UV-curing process by competing with the photoinitiator for the incident photons (inner filter effect), as shown in Chart 3.

Besides reducing the cure speed, the UVA is also causing a sharp top to bottom cure depth gradient within the coating, due to the decreased penetration of light. At a UVA concentration of 2 wt%, the absorbance at 340 nm of a 30 μm thick film is typically on the order of 2, i.e. only 1% of the incident photons is reaching the bottom layer of the coating. The resulting insufficient cure at the coating/substrate interface is responsible for the reduced adhesion often observed in UVA loaded photocured coatings.

A possible way to overcome these two detrimental effects (slower cure and poor adhesion) is by selecting a photoinitiator which absorbs in the near UV range (370–400 nm) where the UV absorber is essentially transparent (at 380 nm the UVA absorbance is only 0.1, i.e. a 90% light transmission). In this respect, acylphosphine oxides appear as choice photoinitiators because they show a distinct absorption in the UVA transmission window. Consequently, the slowing down effect on the polymerization will be less pronounced than with the other photoinitiators, such as the widely used dimethoxyacetophenone (DMPA), as shown in Fig. 6.

The greater penetration of UV-radiation in the samples containing an acylphosphine oxide photoinitiator leads also to a more uniform through cure. Fig. 7 shows for example the depth cure profiles obtained for two 40 μm thick stabilized polyurethane-acrylate coatings, which contained either a BAPO or a HPK photoinitiator. After a UV-dose of 100 mJ cm^{-2}, 60% of the acrylate double bonds located in the bottom layer were found to have polymerized for the BAPO-based coating, compared to only 12% for the HPK-based coating. These values are rising upon further UV-irradiation. As a result of the greater deep-through cure, in particular at the coating/substrate interface, better adhesion was achieved with the sample containing the BAPO photoinitiator, as shown in Fig. 8.

If necessary, the adhesion can be further enhanced by promoting a grafting reaction [24]. The polymer material has first to be coated with a layer of a benzophenone solution in a diacrylate monomer (HDDA), and exposed briefly to UV radiation. Polymer radicals, generated by hydrogen abstraction from the substrate by the excited benzophenone molecules, effectively initiate the polymerization of the acrylate double bonds. This reaction will therefore produce a chemical bonding between the coating and the substrate. In a second step, the treated substrate is coated with the UV-curable PUA resin containing the light stabilizers, and then exposed to UV light. Excellent adhesion was achieved by this two-step UV-curing process because of the copolymerization reaction which occurs between the PUA double bonds and the unreacted acrylate double bonds of the base coat (Fig. 8).

An additional advantage of acylphosphine oxides is that,

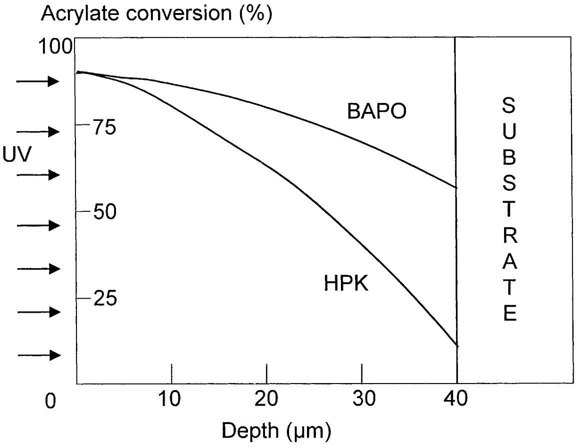

Fig. 7. Cure depth profile in a photocured coating containing a UV-absorber-type light stabilizer. [Tinuvin 400] = 2 wt%. UV-dose: 100 mJ cm^{-2}.

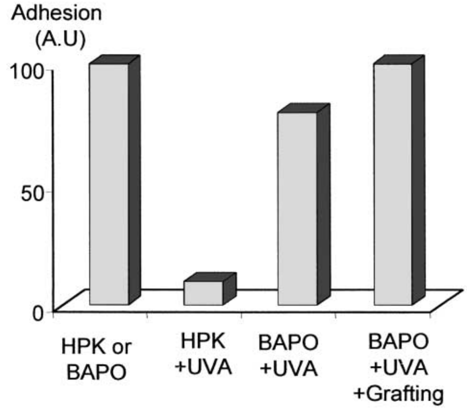

Fig. 8. Influence of the UV absorber (2 wt% Tinuvin 400) on the adhesion of a UV-cured PUA coating.

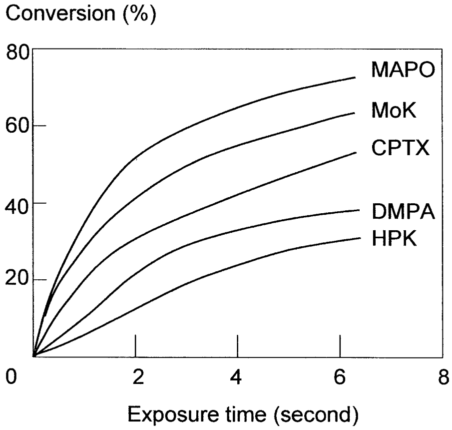

Fig. 9. Influence of the photoinitiator (2 wt%) on the UV-curing of a white polyester-acrylate lacquer. Film thickness: 23 μm. Light intensity: 50 mW cm^{-2}.

owing to their fast photolysis, the amount of residual photoinitiator in the UV-cured coating will be low, dropping to zero within minutes upon exposure to sunlight (Fig. 4). This will prevent unwanted photoinitiated degradation reactions to occur in UV-cured coatings used in exterior applications. The weathering resistance of well-stabilized photoset urethane acrylate coatings was shown to be superior to that of the thermoset melamine/acrylate coatings currently used as automotive finishes [25,26].

4. UV-curing of pigmented systems

Achieving a fast deep-through cure of thick pigmented coatings by UV-radiation remains one of the greatest challenges in photocuring, as the light screening by the pigment particles prevents the penetration of photons in the deep-lying layers. An efficient cure can be obtained only by achieving the best overlap between the absorption spectrum of the photoinitiator, the transmission spectrum of the pigment and the emission spectrum of the light-source.

Among the numerous photoinitiators developed for UV-curable printing inks or lacquers, the most promising ones appear to belong to three major classes of radical-type photoinitiators:

- morpholino-ketones [6], such as Irgacure 369,
- acylphosphine oxides [4,8], such as Lucirin TPO or Irgacure 819,
- propoxy-substituted thioxanthones [27], such as Quantacure CPTX.

The marked increase in the cure speed provided by these photoinitiators is illustrated by the polymerization profiles shown in Fig. 9 for a polyester-acrylate white lacquer. It is due mainly to a larger absorption of the photoinitiator in the near UV range, where the mercury lamp has its strongest emission and where the pigment becomes more transparent. In addition, these photoinitiators undergo a photo-bleaching process, thus allowing UV-radiation to penetrate progressively deeper into the sample. Up to 50 μm thick pigmented coatings have thus been photocured within a few seconds by using either one of these photoinitiators. By contrast to morpholino-ketone and thioxanthone derivatives, which yield slightly yellow photoproducts, acylphosphine oxides undergo a fast photolysis that generates essentially non-colored products, a distinct advantage for the curing of white lacquers where any color change is redhibitory.

In UV-curable printing inks and paints, the polymerization rate and the final conversion are highly dependent on the color of the pigment used, and more precisely on its light absorbance in the UV range. Like in the case of the UV absorber examined previously, the screen effect of the pigment particles will reduce the initiation process. The great efficiency of BAPO photoinitiators, in combination with hydroxyphenyl ketones, has been recently demonstrated in the UV-curing of colored pigmented acrylate coatings [28].

Fig. 10 shows some typical polymerization profiles recorded by RTIR spectroscopy for various acrylate-based paints, by using BAPO as photoinitiator. As expected, the black sample was the most difficult to cure by UV irradiation, because of the strong light absorbance of carbon black over the whole UV-visible range. By using acylphosphine oxides as photoinitiators (2 wt%), it was still possible to achieve a deep-through cure of a 30 μm thick coating within seconds on an industrial-type UV-line. This black resin could also be rapidly hardened by means of a focused laser beam (emission line at 363.7 nm of the Ar + laser) to generate a high resolution black image after solvent development. It is an easy way to produce by LDI the well-contrasted masks which are needed in photolithography, in particular for the manufacture of printed circuit boards.

In clear coats, UV light is absorbed mainly by the photoinitiator and it is progressively attenuated as it passes through the sample. The penetration of the incident photons

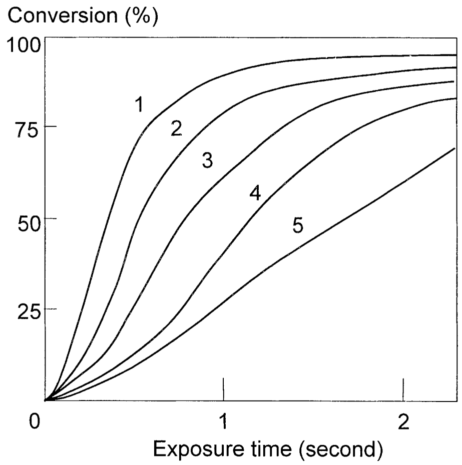

Fig. 10. Influence of the colored pigment on the UV-curing of various acrylic paints. [BAPO] = 2 wt%. Light intensity: 100 mW cm^{-2}. **1**: red; **2**: blue; **3**: green; **4**: blue; **5**: black. Film thickness: 24 μm. Pigment load: 5 wt%.

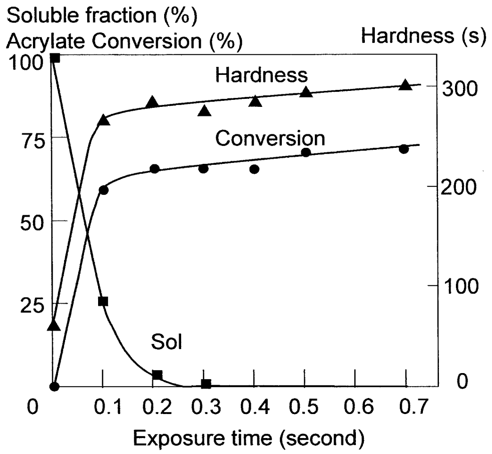

Fig. 12. Photocrosslinking of an acrylated polyisoprene film plasticized with a triacrylate monomer ([TMPTA] = 20 wt%) upon exposure to UV-radiation (600 mW cm^{-2}). Film thickness: 10 μm; Photoinitiator: [MAPO] = 2 wt%.

is directly dependent on the photoinitiator concentration, on its absorptivity and on the film thickness. With photobleachable initiators, like acylphosphine oxides, the sample becomes increasingly transparent to UV radiation upon exposure, which leads to a quasi-uniform deep-through cure of the coating [29]. The situation is quite different in pigmented coatings, where the screen effect leads to a pronounced through cure differential which persists upon irradiation. This is clearly illustrated in Fig. 11 which shows how the cure distribution profile varies with the exposure time in a 25 μm thick white lacquer film. Prolonged irradiation is required here in order to obtain sufficient curing at the coating/substrate interface to ensure a good adhesion. Increasing the light intensity by means of more powerful lamps and using doped mercury lamps which emit in the near UV range (D and V bulbs) proved to be an efficient way to achieve a deep-through cure of thick pigmented coatings [30], which are then showing a long-lasting adhesion to the substrate.

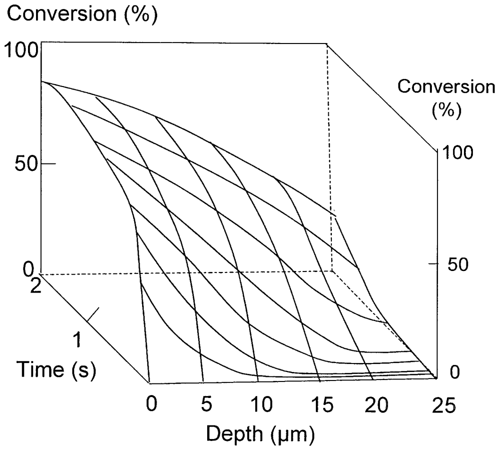

Fig. 11. Cure depth profiles of a white polyester-acrylate lacquer exposed to UV-radiation in the absence of air. Photoinitiator: [MAPO] = 2 wt%. Light intensity: 50 mW cm^{-2}.

5. Photocrosslinking of functionalized polymers

Besides transforming a liquid resin into a solid material, UV-radiation can also be used to induce the polymerization of the reactive groups of a solid polymer to achieve its insolubilization and to modify its physical properties. Photoinitiated radical polymerization has proved to be a very effective process to crosslink readily functionalized polymers, in particular acrylated polyisoprene [31] and styrene-butadiene thermoplastic elastomers [32,33]. In both cases, superior performance was obtained by using acylphosphine oxides as photoinitiators.

5.1. Acrylate functionalized polyisoprene (API)

In the presence of a radical-type photoinitiator, like

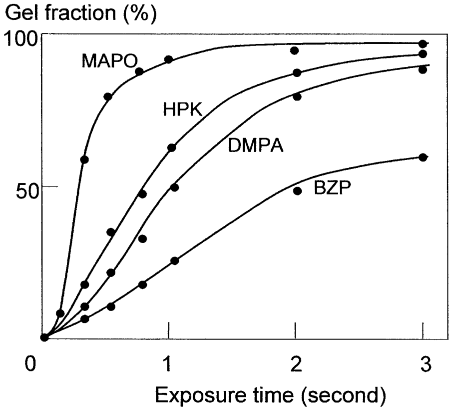

Fig. 13. Influence of the photoinitiator (3 wt%) on the insolubilization profile of a 20 μm thick SBS film exposed to UV radiation (600 mW cm^{-2}).

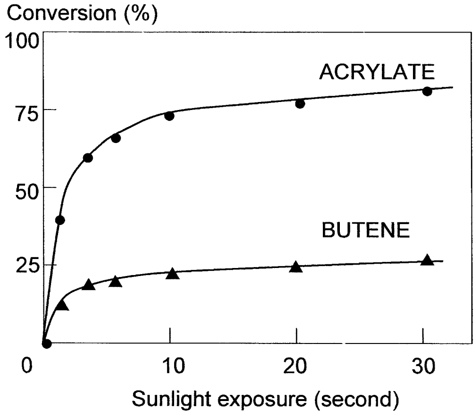

Fig. 14. Polymerization of an acrylate monomer ([HDDA] = 30 wt%) in a SBS matrix upon sunlight exposure through a glass filter. Film thickness: 40 μm; Photoinitiator: [MAPO] = 2 wt%.

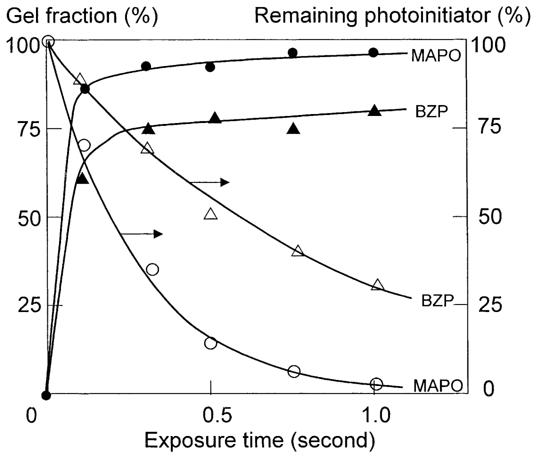

Fig. 15. Influence of the photoinitiator (2 wt% of MAPO or BZP) on the UV-curing of the SBS/TRIS system. Loss profile of the photoinitiator. Light intensity: 600 mW cm^{-2}.

Lucirin TPO, the polymerization of the pendent acrylate double bonds of API proceeds within seconds upon UV exposure to give a totally insoluble crosslinked polymer. The addition of a multifunctional monomer, like trimethylolpropane triacrylate (TMPTA), leads to a marked increase of the crosslinking rate and cure extent, because of the greater molecular mobility imparted by this monomer which acts as a reactive plasticizer. A 0.2 s exposure to intense UV radiation or to a laser beam proved to be sufficient to polymerize more than half of the acrylate functions and transform the low-modulus elastomer into a hard and insoluble material. Fig. 12 shows some typical kinetic profiles obtained by monitoring the acrylate conversion, the insolubilization and the hardness increase of the API/TMPTA blend upon UV exposure. The great photosensitivity of this system allows crosslinking of the rubber to be achieved by a simple exposure to sunlight for a few minutes [31].

5.2. Vinyl functionalized polybutadiene

By contrast to polyisoprene which does not undergo crosslinking upon UV exposure in the presence of a photoinitiator, polybutadiene can be 'photovulcanized' through its pendent vinyl double bonds. Thermoplastic elastomers, like polystyrene-*block*-polybutadiene-*block*-polystyrene (Kraton® SBS) have thus been made more resistant to organic solvents and heat, while improving their adhesive strength [34]. In the presence of MAPO, insolubilization was achieved after a 2 s UV exposure when about 17 crosslinks have been formed per polybutadiene chain [32], while crosslinking occurred at a slower pace with the other types of photoinitiator tested (Fig. 13).

The addition of a diacrylate monomer (HDDA) was found here again to accelerate markedly the crosslinking process, insolubilization occurring within 0.5 s. Both the vinyl and the 2-butene double bonds were found to undergo copolymerization with the acrylate double bonds. The MAPO-based resin proved to be reactive enough to be cured by glass-filtered sunlight within 20 s, as illustrated in Fig. 14. The crosslinked polymer showed excellent adhesion on glass and was used in our two-step process of manufacturing of safety glasses [16].

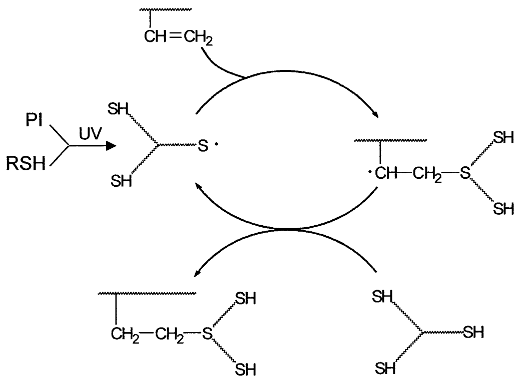

Chart 4. Reaction scheme of the thiol-ene polymerization of the SBS/TRIS system.

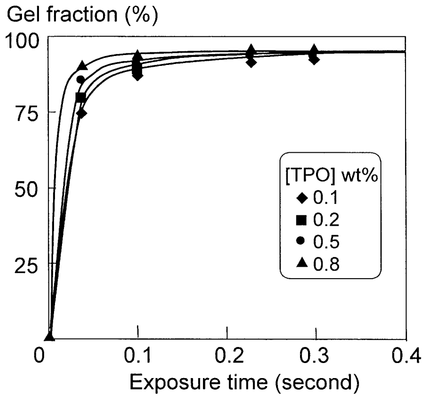

Fig. 16. Influence of the photoinitiator concentration (MAPO) on the insolubilization of the SBS/TRIS system upon UV exposure. [TRIS] = 1 wt%.

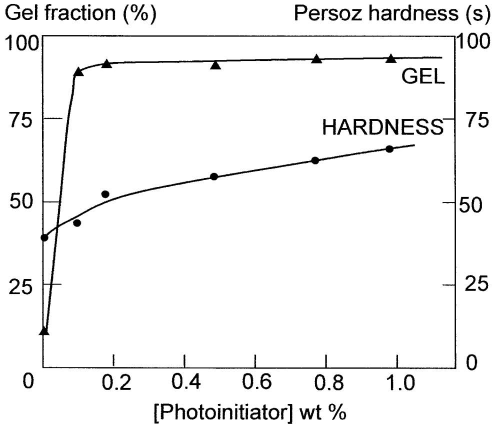

Fig. 17. Influence of the photoinitiator concentration (MAPO) on the photocrosslinking of the SBS/TRIS system. [TRIS] = 1 wt%; light intensity: 600 mW cm^{-2}. UV exposure: 0.3 s.

An even more effective photocuring of the SBS rubber was achieved by using a trifunctional thiol as crosslinking agent [33], at a concentration as low as 1 wt% [35]. Under intense illumination, the thiol/ene polymerization proceeds within a fraction of a second by a step growth addition mechanism to yield an insoluble and tight polymer network, as represented in Chart 4.

A hydrogen abstraction-type photoinitiator, like benzophenone, is typically used in the thiol/ene polymerization to generate the chain carrier thiyl radicals. Unlike the other photocleavable initiators, acylphosphine oxides were found to be even more efficient than benzophenone to initiate the crosslinking of the SBS/TRIS system, as shown in Fig. 15. This is due here again to the faster photolysis of the acylphosphine oxide photoinitiator which was essentially consumed after a 1 s UV-exposure (Fig. 15). The thiol/ene polymerization was shown to be a much more efficient process to crosslink polybutadiene and polyisoprene-based thermoplastic elastomers than was the copolymerization of the rubber double bond with a diacrylate monomer [36].

A quite remarkable feature observed in the SBS/TRIS system is that the photoinitiator concentration (MAPO) can be reduced down to 0.1 wt% without much effect on the insolubilization profile, as shown in Fig. 16. The influence of the photoinitiator concentration on the curing of a sample exposed for 0.3 s to UV light is illustrated in Fig. 17. Hardening is hardly taking place upon UV-curing, so that the thermoplastic elastomer retains its viscoelastic properties, as required for hot-melt adhesive applications, while it becomes more resistant to heat and chemicals. As the photoinitiator concentration can be lowered down to 0.1 wt%, relatively thick samples, up to 1 mm thickness, can be rapidly crosslinked by this UV technology owing to the increased penetration of the incident light.

6. Conclusion

UV-radiation curing has now become a field of recognized importance in various industrial sectors because of its unique advantages regarding both process facility and product quality. The high initiation rates that can be reached under intense illumination allow highly crosslinked polymeric materials to be synthetized quasi-instantly by photopolymerization of multifunctional monomers and oligomers. Significant progress has been recently achieved in UV-curable systems with the development of acylphosphine oxide photoinitiators. The superior efficiency of these compounds is best assessed by real-time infrared spectroscopy, a technique that allows one to monitor continuously the rapid formation of the polymer upon UV-exposure.

Acylphosphine oxides have the distinct advantage of undergoing a fast photolysis which generates very reactive free radicals. They proved to be particularly efficient in a number of systems where conventional photoinitiators are lagging behind, such as for the photocuring of pigmented coatings and of UV-absorber loaded clearcoats, the curing by laser and sunlight and the solid state polyene/thiol polymerization. In consideration of their superior performance, illustrated in Chart 5, it is anticipated that acylphosphine

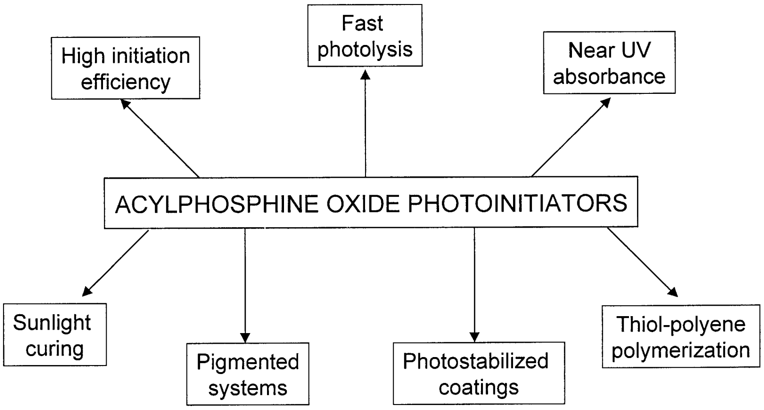

Chart 5. Performance of acylphosphine oxide photoinitiators in UV-radiation curing.

oxides will be increasingly used in UV-curable formulations, attracting attention in an ever growing number of industrial applications of this advanced technology.

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