

Interpenetrating Polymer Networks. I. Photopolymerization of Multiacrylate Systems

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SYNOPSIS

The light-induced polymerization of a triacrylate monomer (TMPTA) has been carried out in a polymer matrix to generate a semi-interpenetrating polymer network (IPN). The reaction kinetics was followed by IR spectroscopy for the various polymer binders studied: poly(vinyl chloride) (PVC), poly(methyl methacrylate), polystyrene, and crosslinked polyurethane. Under intense illumination, crosslinking occurred extensively within a fraction of a second, with formation of a hard and highly resistant polymer material. These semi-IPNs were found to be essentially insoluble in the organic solvents, thus indicating that the acrylate network is grafted onto the polymer matrix, probably because of an efficient chain transfer process. The monomer and photoinitiator concentration, as well as the light intensity were shown to have a great influence on both the rate of polymerization and the final degree of conversion. By using an acylphosphine oxide photoinitiator, PVC-TMPTA blends have been cured within a few minutes in an accelerated QUV-A weatherometer, which emits low-intensity UV radiation similar to sunlight. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

During the past decade, there has been a growing interest in interpenetrating polymer networks (IPN), mainly because of the wide range of properties that, similar to polymer blends, becomes available for organic materials created by this technology.¹ The IPN has indeed the potential for combining the properties of two different types of crosslinked polymers. Light-induced polymerization is one of the most efficient methods for producing rapidly highly crosslinked polymers,^{2,3} as UV radiation permits to generate the initiating species at very high rates. By taking two multifunctional monomers that polymerize by different mechanisms, like acrylate and vinyl ethers, simultaneous IPNs having well contrasted characteristics have been produced within a few seconds under intense illumination.^{4,5} The properties of the UV-cured polymers were

shown to be highly dependent on the monomer composition of the mixture, as well as on the formation of, on one hand, an elastomeric vinyl ether crosslinked polymer and of, on the other hand, a glassy acrylate polymer network.

Interpenetrating polymer networks can also be produced by polymerization of a multifunctional monomer that has been introduced into a preswollen polymer network.⁶ If this monomer is dispersed into a linear polymer, like poly(vinyl chloride) (PVC), polystyrene (PS), or poly(methyl methacrylate) (PMMA), a semi-IPN will be formed. Several studies have been reported recently on the UV curing of multiacrylate monomers in a solid polymer matrix.⁷⁻¹² The compatibility of the two components is essential for ensuring adequate mechanical and optical properties of the final product, since phase separation was found to occur with some systems.^{10,11}

In a recent study,¹² we have followed by infrared spectroscopy the kinetics of such ultrafast polymerizations and shown that the chain reaction can develop extensively, even in a solid polymer matrix, with kinetic chain length values up to 10,000 acrylate double bonds polymerized per initiating radical. Phase separation did not occur in any of the systems

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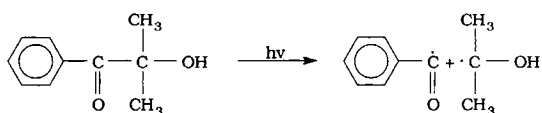
studied, thus making these transparent organic glasses suitable for the fabrication of optical devices. In this article, we present some new results on the UV radiation curing of a triacrylate monomer in different polymer matrixes (PVC, PMMA, and PS), and on the properties of the semi-IPNs thus obtained. In a forthcoming article, the light stability of these UV-cured polymers will be discussed, in view of their possible use as protective coatings in outdoor applications.

EXPERIMENTAL

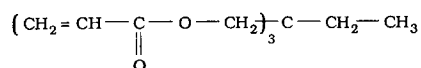
Materials

The photopolymerizable material was made of three basic components:

1. A radical-type photoinitiator (PI) that cleaves readily upon UV exposure to generate free radicals (Darocur 1173 from Ciba):



2. A triacrylate monomer, trimethylolpropanetriacrylate (TMPTA from UCB), known for its great reactivity:



3. A commercial polymer that will constitute the solid matrix, PMMA (Altulite from CDF-Chimie; $M_w = 126,000$), or PVC (Solvic 229 from Solvay; $M_w = 83,000$), or PS (Atochem; $M_w = 130,000$). These polymers were dissolved in toluene, 1-2 dichloroethane, or chloroform, respectively.

The photoinitiator and the monomer were added to the polymer solution (10%) in such amounts as to obtain a dry material containing equal quantities of TMPTA and of polymer, and 5% of Darocur 1173. The solution was cast on a KBr crystal and dried first at room temperature and then at 60°C, up to a constant weight. The film thickness was typically on the order of 10 μm .

Irradiation

Samples were exposed to a 2000-W medium-pressure mercury lamp (IST-M 200 U), which has its main emission lines between 254 and 578 nm. The light emitted was focused by a semi-elliptical reflector on

a conveyor belt. At the sample position, the light intensity was measured by an International Radiometer IL-390 to be 600 mW cm^{-2} in the UV range. Exposures of a given time (between 0.1 and 1 s) were obtained by acting on the belt speed, which could be varied between 6 and 60 m/min.

All the photocuring experiments were performed at ambient. However, the heat evolved by the polymerization makes the sample temperature rise up to a certain value, which depends on both the film thickness and the light intensity. Under the experimental conditions used, the temperature of the sample at the end of the exposure was typically ranging from 30 to 60°C for light intensities between 35 and 600 mW cm^{-2} . Higher temperatures (above 100°C) were reached for thick samples (100 μm) cured under intense illumination.

For the real-time infrared spectroscopy experiments, a 150-W xenon-mercury lamp (Hoya-Schott HLS-210 U) was used, at light intensities ranging from 35 to 350 mW cm^{-2} . Some UV-curing experiments were also performed on a QUV accelerated weatherometer (Q-Panel) equipped with either UV-A 340 or UV-B 313 fluorescent tubes; the light intensity at the sample position was measured to be 1.7 mW cm^{-2} .

The actual rate of polymerization was evaluated by real-time infrared spectroscopy (RTIR), a powerful tool for investigating ultrafast photochemical processes that has already been described at length.¹³⁻¹⁵ The decrease of the IR absorbance at 812 cm^{-1} was monitored continuously as a function of the exposure time. The maximum rate of polymerization was determined from the slope of the linear portion of the recorded curve, which was generally found to extend from 10 to 30% conversion.

The amount of insoluble gel in the UV-cured polymer was evaluated by soaking the irradiated sample in chloroform for 24 h and separation of the insoluble part by filtration.

The hardness of the cured film was measured according to the Persoz method, which consists in monitoring the damping time of the oscillations of a pendulum placed onto the sample coated on a glass plate.¹⁶ The Persoz hardness value, which is expressed in seconds, varies typically from 50 s for a soft elastomeric coating to 350 s for a hard and glassy polymer and reaches a maximum value of 400 s for mineral glass.

RESULTS AND DISCUSSION

When a triacrylate monomer, such as TMPTA, was exposed to intense UV radiation in a solid polymer,

such as PVC, and in the presence of a radical-type photoinitiator, polymerization was found to develop rapidly and extensively with formation of a semi-IPN material. It took less than 1 s to transform the soft elastomeric polymer film, which is plasticized by the monomer, into a hard and tough polymer material.

The crosslinking polymerization (or curing) reaction can be followed quantitatively by monitoring the decrease of the IR absorbance at 812 cm^{-1} , which is characteristic of the acrylate double bond, as a function of the exposure time.¹⁷ Figure 1 shows the IR spectrum of the TMPTA + PVC composition before and after UV exposure during 0.1 s. It can be seen that half of the double bonds have already reacted after such a short irradiation.

In this work we have studied the influence of various factors on the polymerization kinetics, in particular the nature of the polymer binder, and of the photoinitiator, the monomer content of the initial blend, and the radiation wavelength and intensity.

Influence of the Polymer Binder

TMPTA was photopolymerized in three types of polymer binders (PVC, PS, and PMMA), in a 1/1 weight ratio, by using an α -hydroxy phenylketone photoinitiator (Darocur 1173) at a weight concentration of 5%. Typical conversion vs. time curves are shown on Figure 2. It can be seen that the polymerization reaction starts immediately, as soon as the sample is exposed to UV radiation, half of the acrylate double bonds being polymerized after 0.1 s

of exposure. This corresponds to a single pass under the mercury lamp at a speed of 1 m/s or of 4 m/s by using the newly developed high-power Fusion lamp.¹⁸ Further irradiation leads to a much less drastic increase of the degree of conversion, which finally levels up to a constant value upon prolonged exposure, typically between 70 and 85% (Fig. 2), because of severe mobility restrictions of the reactive sites in the tridimensional network formed. The amount of residual acrylate unsaturation can be further reduced by a moderate heating in the dark of the UV-cured sample. For example, a 5-min treatment at 70°C of the PS-acrylate IPN irradiated during 0.5 s makes the degree of conversion increase from 60 to 75%, while at the same time the gel fraction increased from 40 to 80%. This postpolymerization was attributed to trapped polymer radicals, which recover some mobility upon heating the polymer sample above its T_g and can thus continue to grow by reacting with the remaining acrylate double bonds.

The initial rate of polymerization was found to be essentially the same for the three polymers used in this study, whereas the final conversion proved to be strongly dependent on the polymer binder. Indeed, the amount of unreacted monomer in the polymer UV cured during 5 s was found to be twice as large in the PS-based semi-IPN than in the PVC one. Since both polymers are very hard and have high T_g ($> 120^\circ\text{C}$), mobility restrictions are expected to be similar, so that the higher conversion found with PVC and PMMA is likely to result from a better compatibility between the binder and the

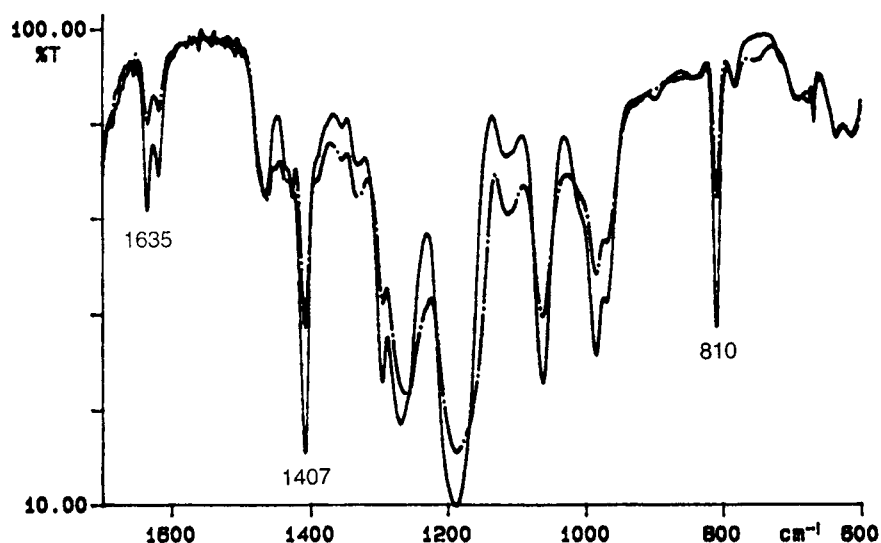


Figure 1 IR transmission spectrum of a 50/50 PVC-TMPTA blend before and after (— · —) UV exposure for 0.1 s.

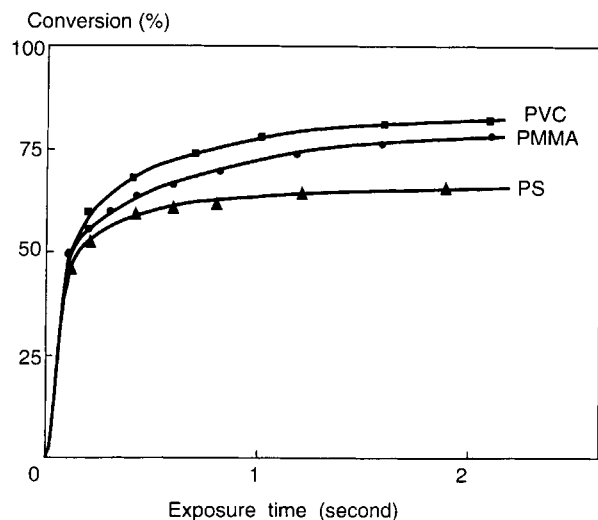


Figure 2 Influence of the polymer binder on the photopolymerization of TMPTA. Monomer-polymer = 50/50 per wt; [Darocur 1173] = 5 wt %; light intensity: 600 mW cm⁻².

acrylic polymer, as well as from a more efficient chain transfer reaction.¹² If the latter process occurs, the acrylate polymer network will be chemically grafted onto the polymer binder, which would thus become partly insoluble.

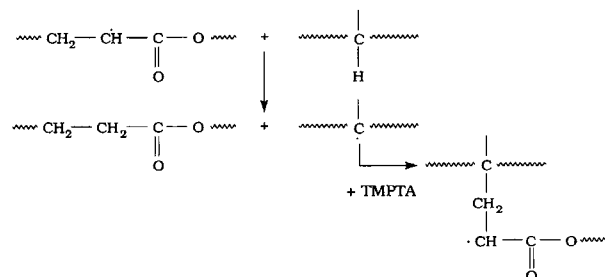


Figure 3 shows how the sol fraction decreases with the exposure time for the three types of binders studied. The fact that more than 50% (the original binder content) of the UV-cured material was found to be insoluble can be considered as a strong argument in favor of a grafting process. After 2 s of exposure a gel fraction of 93% was measured for the PVC and PMMA semi-IPNs, which means that up to 86% of these linear polymers has been incorporated in the acrylate polymer network. The apparent insolubilization of the binder might also result, besides the grafting reaction, from an entanglement in the tight acrylate network of the polymer chains, which would thus become no more extractable by the solvent. However, the fact that the glass transition temperature increased from 80°C for pure

PVC to 130°C for the UV-cured semi-IPN argues in favor of a chemical bonding between the two types of polymers.

It can be seen from Figure 3 that gelation occurs at a much slower pace in PS than in the PMMA or PVC system, even though the polymerization of TMPTA develops almost as efficiently as in PVC.

Exposure Time: 1 s	PS	PMMA	PVC
TMPTA conversion (%)	63	72	75
Gel fraction (%)	60	88	92
Insolubilized binder (%)	20	76	84

The poor compatibility of PS with the acrylate network, which appears from the formation of a translucent UV-cured film, is expected to lead to phase separation and is probably responsible for this difference in behavior.

Essentially the same trend was observed when the pendulum hardness of the coating was monitored as a function of the UV exposure, as shown by Figure 4. The three polymers, which are initially highly flexible and soft (Persoz hardness of 30–70 s) because of the plasticizing effect of the monomer, are rapidly becoming stiff and hard upon UV irradiation, with hardness values up to 350 s for the PVC-acrylate IPN. As expected, the hardness of the cured polymer is highly dependent on the crosslink density, and thus on the monomer concentration. The increase of the hardness with the exposure time is shown in Figure 5 for three PVC-TMPTA systems containing 30, 40, or 50% of monomer. Reducing the TMPTA content from 50 to 30% leads to a con-

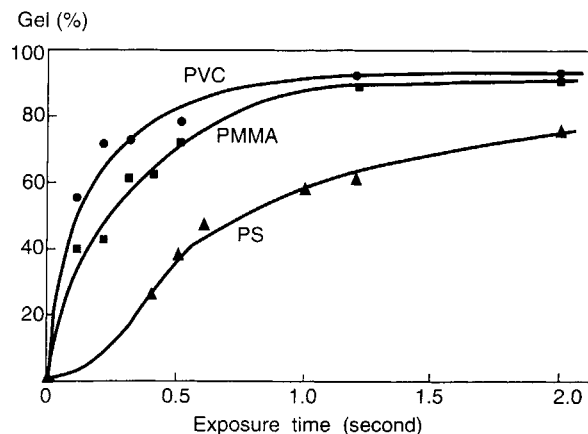


Figure 3 Influence of the polymer binder on the gelation of a 50/50 TMPTA-polymer blend exposed to UV radiation. [Darocur 1173] = 5 wt %.

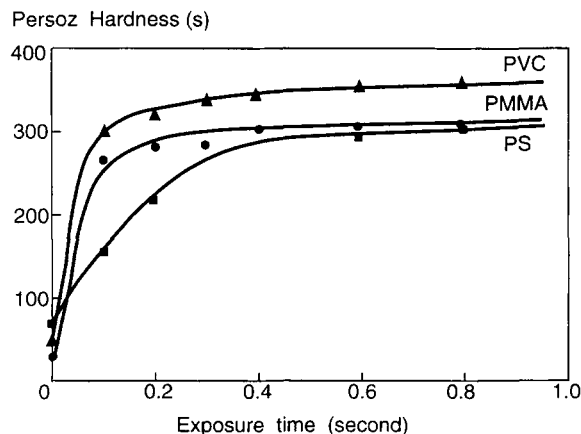


Figure 4 Influence of the polymer binder on the hardness of a 50/50 TMPTA-polymer blend exposed to UV radiation. [Darocur 1173] = 5 wt %.

comittant drop of the Persoz hardness from 350 to 270 s for the fully cured film, a value that is still higher than that of pure PVC.

A most remarkable feature was observed with the PVC- and PMMA-based systems, where an exposure as short as 0.1 s was already sufficient to transform the low modulus elastomer into a high modulus glassy polymer. Reducing the photoinitiator concentration will decrease the polymerization rate (see next section), but it also allows UV radiation to penetrate deeper into the sample, so that a few millimeter thick polymer sheets can be cured extensively by UV irradiation during a few seconds. For such experiments, the mixing of the polymer composition (binder + TMPTA + photoinitiator) must be carried out in the molten state. The solid block

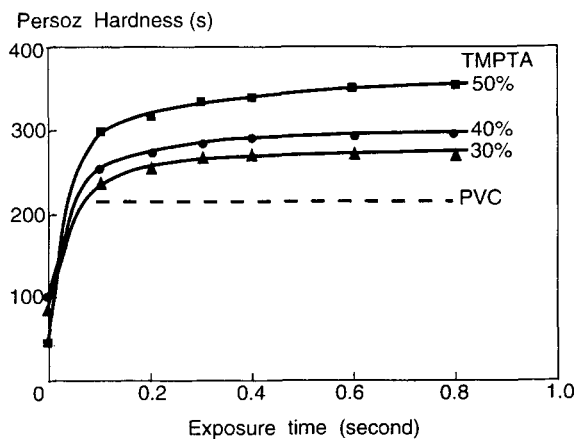


Figure 5 Influence of the monomer concentration on the hardness of a TMPTA-PVC blend exposed to UV radiation. [Darocur 1173] = 5 wt %.

obtained can be either cut into sheets or ground up into granules ready to be extruded. Compared to thermoforming, the UV-curing technology has the great advantage of allowing molding to be performed at ambient temperature in a very short time, by simple exposure to UV light.

Influence of the Photoinitiator Concentration

The photoinitiator plays a key role in light-induced polymerization in that it produces the free radicals (or ions) that, by reacting with the monomer, are initiating the chain process. The rate of initiation (r_i) is proportional to the quantum yield of the radical production (Φ_i) and to the absorbed light intensity (I_a):

$$r_i = \Phi_i I_a$$

The amount of photons absorbed by the sample depends on the photoinitiator concentration:

$$I_a = I_0 \{1 - \exp(-\epsilon l [\text{PI}])\}$$

where I_0 is the incident light intensity and l the film thickness. Figure 6 shows the conversion vs. time profiles obtained for the PVC-acrylate system containing 1, 3, or 5% of photoinitiator. The slower production of initiating radicals at low PI concentration makes the polymerization develop at a slower pace. An additional factor lies in the oxygen inhibition effect, which is due to the scavenging of the initiating radicals by molecular oxygen. The longer

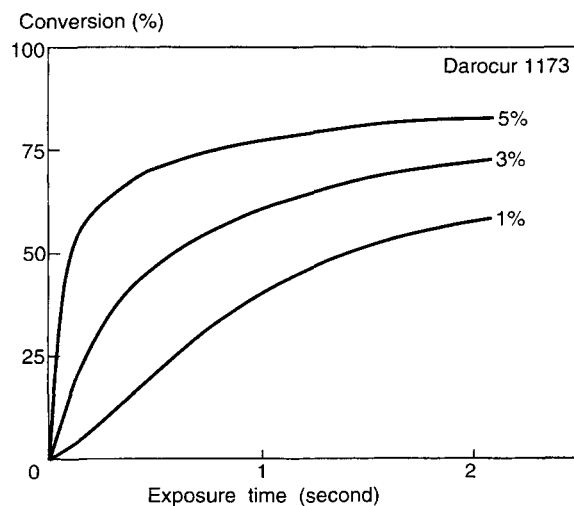


Figure 6 Influence of the photoinitiator concentration on the light-induced polymerization of a TMPTA-PVC blend (50/50 per wt). Light intensity: 600 mW cm⁻².

UV exposure required at low PI concentration will increase the amount of atmospheric oxygen that diffuses into the sample and makes it more difficult to overcome O_2 inhibition.

Essentially the same trend was observed by studying the effect of the photoinitiator concentration on both the gel formation and the hardness increase upon UV irradiation. Figure 7 shows the gel fraction vs. time profiles for the PVC-acrylate system at the three photoinitiator concentrations. Although gelation occurs less rapidly at a 1% PI concentration, over 90% insolubilization was still achieved after 3 s of UV exposure. Figure 8 shows a similar effect of [PI] on the Persoz hardness of the UV-cured IPN film. It can be seen that the sample containing only 1% Darocur 1173 and UV cured for 0.5 s is not as hard as that containing a higher PI concentration (Persoz value: 230 s vs. 350 s), thus requiring prolonged UV exposure to produce hard IPN coatings. A short thermal treatment at moderate temperature (70°C) is another alternative to increase not only the overall conversion but also the hardness of samples polymerized at low PI concentration, and obtain thus a high modulus polymer material.

Influence of the Light Intensity

Real-time infrared spectroscopy was used to study the effect of the light intensity (I) on the polymerization rate of PVC-TMPTA blends. This technique is most useful in that it permits one to monitor continuously the curing reaction while it proceeds upon UV irradiation, simply by following the disappearance of one of the IR absorption bands of the monomer double bond (e.g., the twisting vibration of the

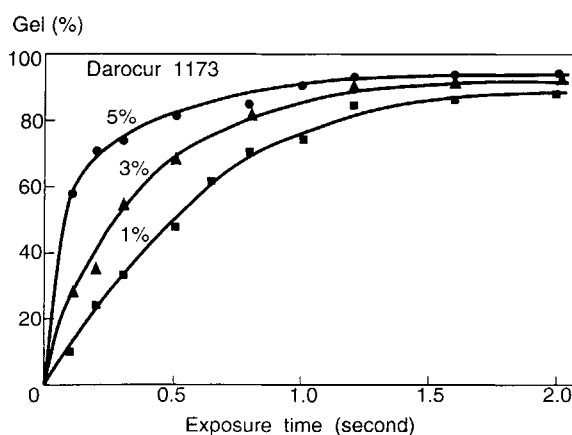


Figure 7 Influence of the photoinitiator concentration on the light-induced gelation of a TMPTA-PVC blend (50/50 per wt). Light intensity: 600 mW cm^{-2} .

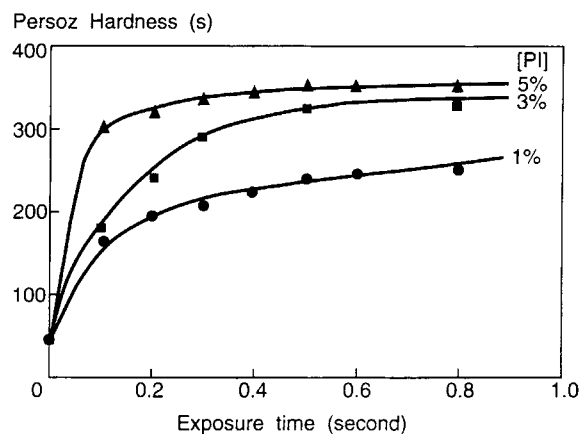


Figure 8 Influence of the photoinitiator concentration on the hardness of a 50/50 TMPTA-PVC blend exposed to UV radiation.

acrylate $\text{CH}_2=\text{CH}$ at 812 cm^{-1}). Conversion vs. time curves can thus be directly recorded for polymerization processes occurring within less than one second upon intense UV or laser irradiation.^{19,20}

Figure 9 shows typical RTIR profiles recorded for a 50/50 PVC-TMPTA blend exposed in the presence of air to UV radiation of different intensities ranging from 35 to 350 mW cm^{-2} . It can be seen that, by contrast to the photopolymerization of liquid monomers,¹⁹ the polymerization starts as soon as the light has been switched on, thus confirming that oxygen inhibition is much less pronounced in solid media because of a slower diffusion of atmospheric oxygen. The chain reaction develops at an apparently constant rate, until crosslinking of TMPTA and its related mobility restrictions make

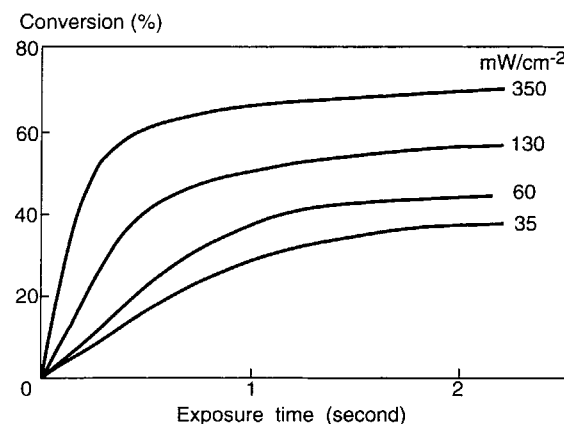


Figure 9 Influence of the light intensity on the polymerization profile, recorded by RTIR spectroscopy, of a 50/50 TMPTA-PVC blend exposed to UV radiation. [Darocur 1173] = 5 wt %.

the process slow down. This slowing down occurs for degrees of conversion ranging between 25 and 50%, depending on the light intensity. The amount of unreacted double bonds in the UV-cured polymer was also found to be strongly dependent on the light intensity, decreasing from 50 to 20% when I_0 was increased from 35 to 350 mW cm^{-2} (Fig. 10). This effect is probably due to a fast rise of the temperature in samples exposed to high light intensities, which allows the polymerization to develop not only faster but also more extensively. Another difference between UV curing in the liquid and in the solid state is that the polymerization of PVC-TMPTA blends was found to stop as soon as the light was switched off, whereas an important postpolymerization was observed in the UV curing of liquid acrylic resins.^{14,15} Here again segmental mobility considerations must be put forward to account for this effect.

A logarithmic plot of the rate of polymerization (R_p) vs. the light intensity gives a straight line, with a slope of 0.9 (Fig. 10), instead of the square root relationship expected if termination would occur by bimolecular radical interaction. This close to first-order kinetics suggests that, in such solid media, most of the polymer radicals undergo a unimolecular termination leading to their trapping in the highly crosslinked network.²¹

Termination Process	Rate Equation
Bimolecular	$R_p = kI^{0.5}$
Monomolecular	$R_p = kI$
Observed	$R_p = kI^{0.9} = k[\alpha I^{0.5} + (1 - \alpha)I]$ (with $\alpha \sim 0.2$)

Note that the above-mentioned temperature effect would also lead to an increase of the rate exponent, so that the calculated fraction of radicals undergoing bimolecular termination ($\alpha = 20\%$) must be a lower limit value.

The rate of polymerization was shown to increase with the TMPTA concentration in the polymer blend, but at a faster pace than the expected linear increase (Fig. 11). This behavior, which is in good agreement with the similar effect observed on the coating hardness (Fig. 5), is probably due to the plasticizing effect of the monomer that favors chain propagation reactions.

The location of the monomer and growing polymer chains in semi-IPN polymerization was recently discussed for PS chains included in a three-dimensional structure.²² Two different diffusion processes

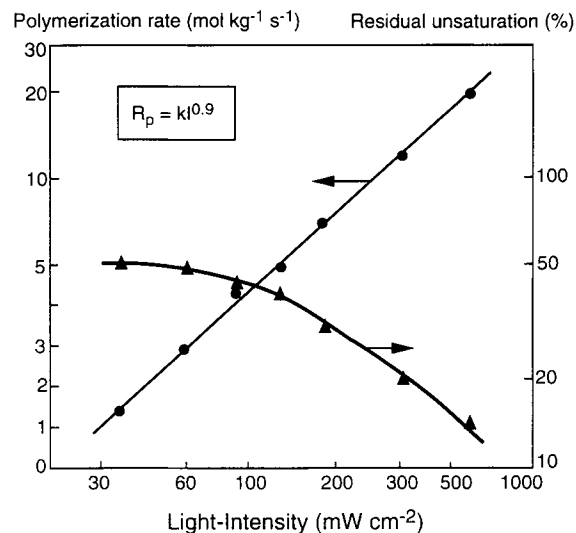


Figure 10 Dependence of the polymerization rate and on the residual unsaturation content of a 50/50 TMPTA-PVC blend exposed to UV radiation.

were characterized, a fast one due to chains free to move inside the network defects and a slow one corresponding to chains effectively entangled in the gel.

UV-Curing in a Weatherometer

In consideration of the high reactivity of these acrylate resins, it was tempting to see whether the UV-curing could be achieved by simple exposure in a typical accelerated weatherometer, like the QUV Tester used to evaluate the light stability of polymer materials.

The much lower intensity of the UV radiation emitted by such a weatherometer (1.7 mW cm^{-2} at the sample position) will, of course, require extending the exposure time accordingly. Moreover, the emission of the fluorescent UV-B lamp, which reaches its maximum at 313 nm, ranges from 280 to 380 nm, compared to 248–578 nm for the medium-pressure mercury lamp. This necessitates using a photoinitiator well suited to the QUV emission range, unlike Darocur 1173, which absorbs weakly above 320 nm and leads to a slow polymerization under those conditions. In addition, the initiator and its photoproducts must not be colored in order to produce clear coatings having a good weathering resistance.

Among the various photoinitiators tested, the best results were obtained with an acylphosphine oxide (Lucirin TPO), which was previously shown to be a very efficient photoinitiator to cure systems exposed to near-UV radiation, like pigmented coatings.^{23,24}

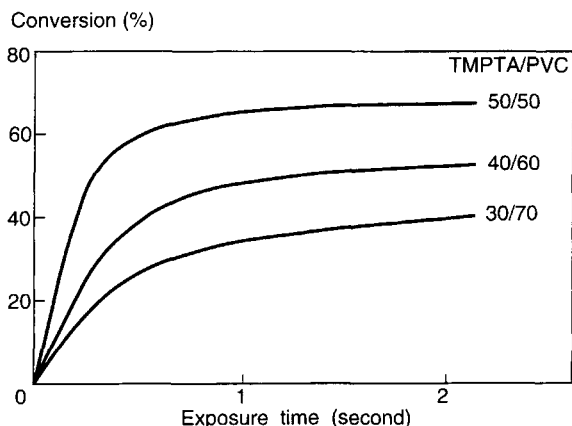


Figure 11 Influence of the monomer concentration on the polymerization profile of a TMPTA-PVC blend exposed to UV radiation. Light intensity: 350 mW cm^{-2} .

Figure 12 shows, for example, the polymerization kinetics of a PVC-TMPTA blend containing 2 or 5 wt % of TPO upon QUV-B exposure. The chain reaction develops quite efficiently to reach 60% conversion after 5 min of exposure, with formation of a hard and highly crosslinked semi-IPN (the crosslink density was calculated to be 3 mol L^{-1}). The polymerization was found to continue slowly upon further exposure up to 75% conversion. Such high values were never obtained in the UV curing of bulk TMPTA, and in particular upon QUV-B exposure where less than 50% of the acrylate double bonds did polymerize after a 30-min exposure (Fig. 12). These results were taken as a strong argument in favor of the participation of the PVC binder in the curing process, probably through a chain transfer

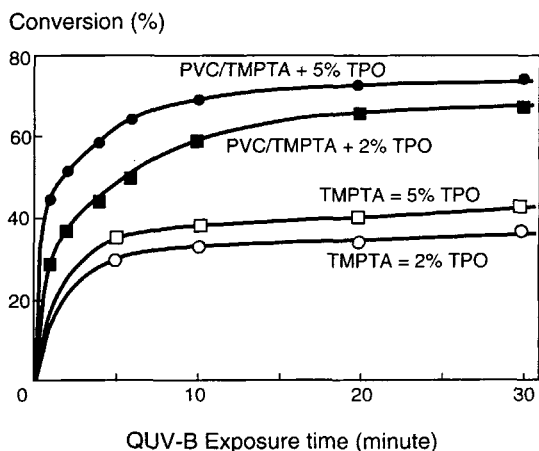


Figure 12 Polymerization kinetics of TMPTA and of a TMPTA-PVC blend upon QUV-B 313 exposure. Light intensity: 1.7 mW cm^{-2} .

reaction. Such a process would indeed allow overcoming the mobility restrictions of the reactive sites brought upon by the formation of the glassy polymer network.

Similar polymerization experiments have been performed by using a UVA-340 fluorescent lamp, which has an emission comparable to terrestrial sunlight in the 300–360 nm region. Here again TMPTA was found to polymerize within minutes, in the PVC blend, especially at a 5% TPO concentration, with formation of a hard and scratch-resistant material (Fig. 13). After 30 min of exposure, the degree of conversion leveled at 70% for the semi-IPN, compared to only 34% for the homopolymer. Since all these experiments have been carried out in the presence of air, one can expect oxygen inhibition to be more pronounced in the liquid TMPTA than in the solid PVC + TMPTA film, and to be thus partly responsible for the slower and less extensive polymerization of TMPTA in bulk. Curing experiments carried out by covering the TMPTA coating with a transparent polyethylene film to prevent atmospheric oxygen diffusion into the sample (laminated) show indeed a faster and more complete homopolymerization (Fig. 13), but the maximum conversion value (50%) was still far below that of the QUV-cured IPN sample (70%). Based on these results, one can expect an efficient photocuring of such binder-acrylate systems to be readily achieved by simple exposure to solar radiation.

Synthesis of IPNs by UV Curing

The objective of this study was to produce rapidly by UV irradiation a true IPN by polymerizing the

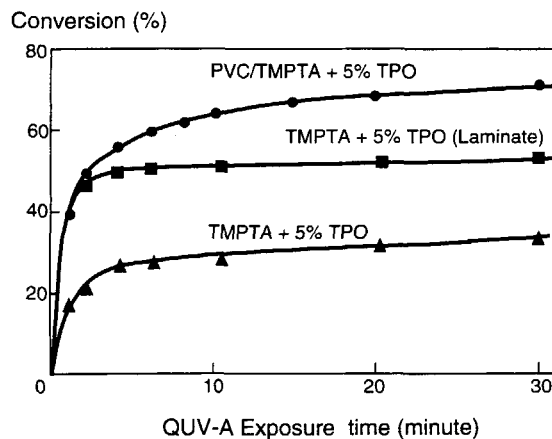
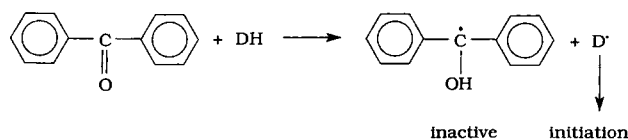


Figure 13 Polymerization kinetics of TMPTA and of a TMPTA-PVC blend upon QUV-A 340 exposure. [Lucirin TPO] = 5 wt %; light intensity: 1.7 mW cm^{-2} .

trifunctional TMPTA monomer in a preformed crosslinked polymer matrix. By building two independent crosslinked polymers having well-contrasted characteristics, one should be able to combine in a single material the properties of the two different types of polymer networks. Because TMPTA generates upon polymerization a hard and glassy polymer, an elastomeric material was used as the preexisting polymer network. It was rapidly produced by UV curing of a liquid polyurethane-diacrylate oligomer (Actilane 27 from HARCROS), in the presence of benzophenone plus a tertiary amine as photoinitiator system. Benzophenone was chosen as photoinitiator here because this compound generates initiating radicals upon photolysis through abstraction of an hydrogen from a H donor molecule (DH):



Initiating sites can thus be generated on the preexisting crosslinked polymer, thus allowing the two networks to be linked together. A highly flexible and impact-resistant material containing only 10% residual unsaturation was obtained within a few seconds of UV exposure, as shown by the polymerization profile of Figure 14 (curve 1).

In a second step, the polymer film was swollen first in chloroform and then in a 1/1 mixture of CHCl_3 and TMPTA containing benzophenone and the tertiary amine. Evaporation of the solvent leaves the TMPTA monomer randomly dispersed within the polyurethane network. A short irradiation of this plasticized film induces the polymerization of TMPTA and generates the second IPN. As expected, the curing reaction develops slower in the solid sample than in the liquid phase (Fig. 14, curve 2), but also because of a lower concentration of TMPTA (30%) and of photoinitiator (3%) in the monomer-swollen network. Nevertheless, more than half of the acrylate double bonds were found to have polymerized after only 0.4 s of exposure.

By pursuing the irradiation during a few seconds, degrees of conversion as high as 85% were obtained, most probably because of an efficient chain transfer reaction that leads to the grafting of the two polymer networks. Experiments carried out by using only benzophenone as photoinitiator have indeed shown that polymerization of TMPTA is still taking place when this monomer is dispersed in the polyurethane

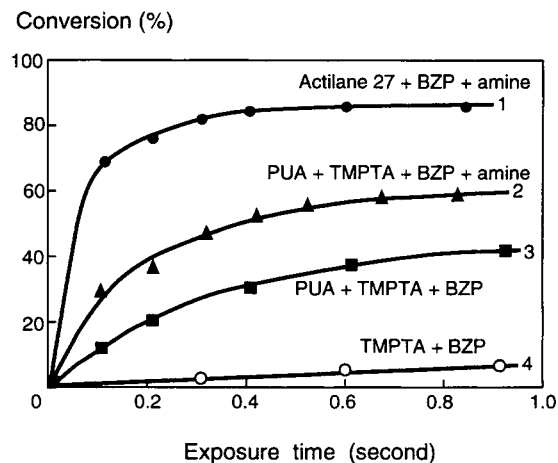
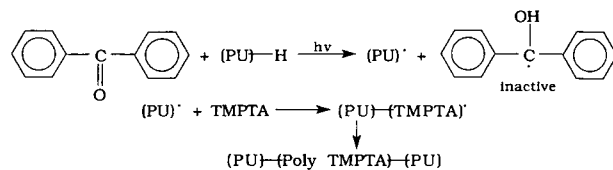


Figure 14 Light-induced polymerization of acrylate systems: (1) polyurethane-diacrylate (Actilane 27); (2 and 3) TMPTA in a UV-cured polyurethane diacrylate (PUA) with and without added tertiary amine (5 wt % methyl-diethanol amine); (4) triacrylate monomer TMPTA without added tertiary amine. Photoinitiator: [benzophenone] = 5 wt %.

network (PU) (curve 3 of Fig. 14), while it hardly occurs in the bulk under those conditions (curve 4 of Fig. 14).



Such additional crosslinks between the two polymer networks are expected to further increase the strength and cohesion of the IPN formed.

Owing to its very method of preparation, the final product consists of an entanglement of two very different polymer networks, one made of the elastomeric polyurethane chains and the other of stiff TMPTA crosslinking segments. As a result, this material was found to be hard and flexible at the same time and to resist quite well to scratching, abrasion, and shocks.

CONCLUSION

One of the distinct advantages of photochemically induced processes lies in the high initiation rates that can easily be reached under intense illumination, thus allowing polymeric materials to be synthesized quasi-instantly by UV curing at ambient

temperature. This technique proved to be particularly well suited to produce IPNs within a few tenths of a second by photopolymerization of a triacrylate monomer dispersed in a linear or crosslinked polymer matrix, with formation of semi-IPN or IPN materials, respectively.

Infrared spectroscopy investigations have shown that the chain reaction can develop both fast and extensively in those solid media where mobility restrictions of the reactive sites become important. This is most probably due to a polymerization mechanism involving a chain transfer process, where the acrylate radical is abstracting a labile hydrogen from the binder chain. The near to complete insolubilization of the semi-IPN formed upon UV irradiation was taken as further evidence of such a process, which leads to the grafting of the acrylate network onto the polymer matrix. Such highly crosslinked polymers exhibit remarkable chemical and physical properties, which make them well suited for industrial applications where toughness, hardness, as well as heat and chemical resistance is required, in particular as binders in composite materials and as protective coatings for a large variety of materials.

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