Interpenetrating Polymer Networks. II. Sunlight-Induced Polymerization of Multifunctional Acrylates

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Received 12 January 1998; accepted 29 March 1998

ABSTRACT: Protective coatings and glass laminates have been readily obtained by sunlight-curing of acrylate monomers dispersed in a poly(methyl methacrylate) matrix or in a styrene–butadiene rubber, in the presence of an acylphosphine oxide photoinitiator. The polymerization reaction was followed by infrared spectroscopy and by gel fraction measurements and was shown to proceed extensively within minutes. As expected, the inhibitory effect of atmospheric O_2 on such radical-initiated reactions was less pronounced in solid than in liquid samples. The monomer, photoinitiator, and plasticizer concentrations were found to have a strong influence on the rate of polymerization, the final degree of conversion, and the hardness of the sun-cured polymer. The adhesion of the cured coating on glass was substantially improved by the addition of an acrylate-grafted organosol silica. To produce strongly adhesive glass laminates, a photocurable acrylate resin was poured between two coated glass plates and exposed to sunlight for a few seconds. The same formulation can serve as a light-sensitive quick setting glue to bond glass to a variety of materials [polycarbonates, poly(vinyl chloride), aluminium, and steel]. © 1998 John Wiley & Sons, Inc. J Appl Polym Sci 70: 2269–2282, 1998

Key words: polymerization; curing; acrylates; sunlight; ultraviolet radiation; coatings; adhesives

INTRODUCTION

Photoinduced polymerization is one of the most efficient processes for producing rapidly polymeric materials with well-defined properties.^{1–3} In most ultraviolet (UV) curing applications, powerful medium pressure mercury lamps are employed to generate, by UV irradiation, large quantities of the initiating species. With the widely used multifunctional acrylate systems, the chain reaction was shown to develop extensively within milliseconds, upon UV⁴ or laser⁵ irradiation, with formation of tridimensional polymer networks having the physicochemical characteristics re-

quired for the considered end uses (coatings, adhesives, printing plates, and photoresists). This kind of crosslinking polymerization can also be expected to proceed upon exposure to sunlight of the reactive formulation, provided that the proper photoinitiator has been selected.

It should be reminded that sunlight curing is far from being a recent technology. It was already used 4000 years ago by ancient Egyptians to waterproof papyrus boats by means of an asphalt oil that was undergoing polymerization upon solar exposure. As of today, only scant attention has been directed toward the use of sunlight in polymerization.^{6–8} This green technology combines the advantages of conventional UV radiation curing and solar-assisted processing. It is particularly cost-effective in terms of energy consumption and irradiation device, which are both nil.

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Journal of Applied Polymer Science, Vol. 70, 2269-2282 (1998)

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Moreover, solar curing is unique in that it allows one to polymerize readily large dimension items, up to several square meters, by simple outdoor exposure. A possible application could be found in the field of protective coatings, which would be cured *in situ* after applying a sunlight-sensitive varnish. However, tack-free coatings can not be obtained by solar exposure of liquid UV-curable acrylic resins because of the strong inhibitory effect of atmospheric oxygen in radical-induced polymerization. Indeed, the intensity of terrestrial sunlight is too low for producing enough free radicals to overcome O₂ inhibition in the superficial layer. This issue is not crucial anymore in photoinitiated cationic polymerization, which is not sensitive to oxygen. Crivello et al.⁶ have thus been able to cure 2-mm-thick fiberglass epoxy composites within 25 min under ambient sunlight, using diaryliodonium and triarylsulfonium salts as photoinitiators. Cationic polymerization is yet known to be sensitive to humidity.

The main objective of the present work was to develop acrylate-based resins, which could be readily cured by a short exposure to sunlight in the presence of air. Acrylate monomers are indeed known to be much more reactive than epoxy monomers in photoinitiated polymerization.^{9–11} To reduce the detrimental O_2 inhibition effect, the photocuring of the selected acrylate monomers was performed in a polymer matrix, as in our previous work.¹² Such sunlight-curable systems would be of great interest for some specific applications, in particular, as quick-setting protective coatings of materials used outdoor and as adhesives for glass laminates.

Several reports have already demonstrated the feasibility of the photocuring method to produce safety glasses.^{13–16} Acrylate monomers were usually chosen as bonding materials because of their greater reactivity and their well-suited optical and mechanical properties. We describe here two approaches that have been used to produce, by sunlight curing, protective coatings and glass laminates showing enhanced adhesion. In the first one, a diacrylate monomer was dispersed in a poly(methyl methacrylate) (PMMA) matrix to generate a semi-interpenetrating polymer network having improved chemical resistance. In the second one, an elastomeric functional polymer, a styrene-butadiene-styrene block copolymer (SBS), was selected as matrix to achieve the high adhesive and cohesive strength needed for glass laminates. In both cases, special emphasis has been given to the design of the sunlight-sensitive formulation and to the monitoring of the polymerization kinetics.

EXPERIMENTAL

Materials

The photopolymerizable material was made of three basic constituents.

- 1. A solid polymer, either PMMA (Altulite from CDF Chimie, $M_w = 126,000$) or a linear styrene-butadiene rubber SBR (Kraton 1101 from Shell, with a 31/69 styrene-to-rubber ratio).
- 2. A photoinitiator that cleaves readily upon UV exposure to generate free radicals: 2,4,6-trimethylbenzoyl diphenyl phosphine oxide (Lucirin TPO) was selected because of its high initiation efficiency¹¹ and its significant absorbance in the near UV range (330-400 nm) of the solar emission spectrum.
- 3. An acrylate monomer chosen among the following: hexanediol diacrylate [HDDA from Union Chimique Belge (UCB)], isobornyl acrylate (IBOA from Sartomer), hydroxy propyl acrylate (HPA from UCB), tripropyleneglycol diacrylate (TPGDA from UCB), an amino polyester tetraacrylate (Ebecryl 80 from UCB), and an aliphatic urethane diacrylate (Ebecryl 284 from UCB, which contains 12% HDDA).

All these acrylate monomers were used as delivered without further purification. The chemical formulas of the various compounds used in this study are given in Chart 1. Typical formulations contained 2 wt % of photoinitiator and equal parts by weight of polymer and monomers. In some formulations, Highlink OG-103 from Hoechst was added as an adhesion promoter.¹⁷ This compound consists of nanometric-size silica particles grafted with HDDA chains, which will therefore be incorporated in the polymer network upon polymerization.

Irradiation

Films were cast on glass plates or KBr crystals from chloroform or toluene solutions and dried at 80°C for 1 h. The film thickness was typically on the order of 40 μ m. Thicker samples can be ob-



Lucirin TPO

ACRYLATE MONOMERS AND OLIGOMERS

$$CH_2 = CH - C - O - (CH_2)_6 O - C - CH = CH_2$$

Hexanedioldiacrylate (HDDA)

$$CH_2 = CH - C - O - (CH_2 - CH - O)_3 C - CH = CH_2$$









POLYMER MATRIX



Chart 1 Chemical formulas of the compounds used in sunlight-curable formulations.

tained in a solvent-free process by extrusion at 140°C of the three-component mixture since the photoinitiator used was found to be stable for 20

min at that temperature. Samples were exposed to sunlight in the presence of air, usually between 11 a.m and 3 p.m, at an incident angle of 30°. The intensity of the solar radiation in the UV range (I_o) was measured by radiometry (International Light IL 390) and found to be on the order of 4.3 mW cm⁻² at Mulhouse in June–July, by clear sky at noon. Because the polymerization rate is directly dependent on the light intensity, which controls the initiation rate $(r_i = \phi_i I)$, where ϕ_i is the initiation quantum yield), great care has been taken to carry out all the experiments at essentially the same light intensity $(4.3 \pm 0.2 \text{ mW})$ cm^{-2}). Only the UV radiation of sunlight which is absorbed by the photoinitiator, that is, of a wavelength between 300 and 400 nm, will be effective in generating the initiating free radicals, thus making the polymerization start. Figure 1 shows the UV absorption spectrum of a UV-curable formulation, together with the emission spectrum of terrestrial sunlight. In safety glass experiments, where sunlight is passing through a 3-mm glass plate, the light intensity value dropped to 3.5 mW cm⁻² because UV radiation of a wavelength inferior to 330 nm was cut off by this filter.

Analysis

The polymerization of multifunctional monomers in a polymer matrix leads to partial insolubilization. The gel fraction was evaluated by soaking repeatedly the sun-exposed film in chloroform for 7 days. The insoluble polymer was collected and dried at 60°C to constant weight. The extent of



Figure 1 Absorption spectrum of a UV-curable formulation containing Lucirin TPO (2 wt %) as the photoinitiator and an irradiance spectrum of terrestrial sunlight.

the polymerization process was determined quantitatively by infrared (IR) spectroscopy (Perkin– Elmer spectrophotometer model 1600), by monitoring the decrease upon sunlight exposure of the sharp peak centered at 812 cm⁻¹, which corresponds to the twisting vibration of the acrylate double bond —CH=CH₂. The degree of conversion (x) was calculated from the ratio of the absorbance at 812 cm⁻¹ before and after exposure to sunlight, $(A_{812})_0$ and $(A_{812})_t$, respectively, by using the following equation:

$$x(\%) = [1 - (A_{812})_t/(A_{812})_0] \times 100$$

This value was not corrected for shrinkage, which was found to account for less than 5% of the absorbance decrease at 812 cm^{-1} , based on the variation of the C—H peak at 2960 cm^{-1} . The sunlight sensitivity (S) of a given formulation was determined from the ratio of the incident light intensity to the maximum slope of the conversion versus time profile: $S = I_0 (t_{100} - t_0)$. It is expressed in mJ cm⁻² and corresponds to the energy needed to pass from 0 to 100% conversion at the maximum speed. With this definition, the lower the S value obtained, the more photosensitive the formulation will be. In the SBR-based formulations, the crosslinking was followed though the decrease of the 1-4 trans double bond centered at 970 cm^{-1} . The hardness of the cured film was evaluated 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. Its value is directly related to the hardness of the polymer film and varies between 0 and 400 s for mineral glass. The physical significance of pendulum hardness has been reviewed by Sato,18 who considered it as a reliable parameter for measuring the viscoelastic properties of coating films. The adhesion of the cured coating on glass or other substrates was evaluated by using the standard crosshatch adhesive tape test.

SOLAR POLYMERIZATION OF ACRYLATES IN PMMA

Kinetics of the Polymerization

When a liquid UV-curable acrylate resin was exposed to sunlight, its surface remained tacky, even after several days of exposure. This is due to the inhibitory effect of atmospheric oxygen on



Figure 2 Influence of the photoinitiator concentration (Lucirin TPO) and of the monomer content on the polymerisation kinetics of the PMMA-HDDA system exposed to sunlight.

radical-induced polymerization, which prevents the curing of the top layer of the coating in contact with air. Indeed, the intensity of solar radiation is not large enough to generate an excess of free radicals to scavenge all the oxygen molecules dissolved in the resin and those diffusing through the surface in the liquid film.



This is no more true in a solid polymer in which the diffusion of atmospheric oxygen is strongly reduced. The polymerization of hexanedioldiacrylate (HDDA), dispersed in a 1/1 weight ratio in a PMMA matrix containing 2 wt % of Lucirin TPO (Formulation A), was shown to proceed effectively upon exposure to sunlight in the presence of air. Figure 2 shows how the acrylate conversion, determined by IR spectroscopy, increases steadily with the exposure time (curve 2). Within 1 min, 50% of the acrylate double bonds were found to have reacted, with formation of a semi-interpenetrating polymer network (semi-IPN). As expected, polymerization did not occur in the absence of an added photoinitiator (PI), the PMMA-HDDA system being fully transparent to sunlight (Fig. 2, curve 5). An increase of the PI concentration to 5 wt % is speeding up the crosslinking reaction, as shown in Figure 2 (curve 1), a 75%degree of conversion being reached within 3 min, to give a hard and nearly insoluble coating. On the other hand, the polymerization was slowing





Figure 3 Influence of the plasticizer concentration (dioctyl phtalate) on the polymerization kinetics of HDDA in a PMMA matrix (1/1 weight ratio), upon exposure to sunlight.

down when the monomer content was decreased (Fig. 2, curves 3 and 4) because the reactive sites are becoming less mobile and located further apart from each other. This effect is particularly pronounced when the HDDA concentration is decreased down to 10 wt % (curve 4).

For some applications, flexible and scratch resistance coatings are required. Such coatings can be obtained by sunlight curing of the PMMA–HDDA system, after addition of a plasticizer to increase the molecular mobility. Figure 3 shows the polymerization profiles of a 1/1 mixture of HDDA and PMMA containing 8, 16, and 24 wt % of dioctyl phtalate (DOP). The plasticizer acts both on the polymerization rate and on the final cure extent, which reaches 90% after a 10 min exposure to sunlight for the sample containing 24 wt % DOP. Complete polymerization can be rapidly achieved by rising the photoinitiator concentration to 5 wt %, with formation of a low-modulus and flexible elastomer.

Hardening

Another method to follow the curing reaction, besides IR spectroscopy, is by monitoring the variation of the coating hardness. Figure 4 shows how the Persoz hardness of a PMMA-HDDA coating increases upon exposure to sunlight in the presence of air (curve 1). Hardening occurs mainly after 20 s, when the acrylate conversion rises above 35%, and it is essentially completed after 2 min. The Persoz value was found to level up at about 230 s after a 20 min exposure. This value was reached already within 30 s when the coating was laminated with a transparent polypropylene film to prevent O_2 diffusion (Fig. 4, curve 3). Such a fast increase in hardness results from the enhanced polymerization of the diacrylate monomer under O_2 diffusion-free conditions. Indeed, essentially the same curve was obtained when the Persoz hardness was plotted versus the acrylate conversion, for samples exposed to sunlight either as laminates or in the open air (Fig. 5). The 35 to 55% conversion range appears to be crucial for changes in the viscoelastic properties of the suncured semi-IPN.

The addition of the DOP plasticizer to formulation A causes an early increase of the hardness as a result of the enhanced reactivity (Fig. 4, curve 2). It also leads to a substantial drop of the final hardness value (from 230 to 120 s) because of the plasticizing effect of the 24% DOP dispersed in the crosslinked polymer. The cured coating is expected to retain its flexibility upon outdoor exposure, as the hardness hardly changes in the later stage of the curing when conversion rises from 60 to 85% (Fig. 5).

The HDDA content of PMMA affects both the initial value of the coating hardness through the plasticizing effect of this liquid monomer, and the hardness profile upon exposure to sunlight (Fig. 6). The difference in hardness observed after a



Figure 4 Variation of the pendulum hardness of a sunlight-cured PMMA–HDDA coating with the exposure time.



Figure 5 Acrylate conversion dependence on the hardness of a sunlight-cured PMMA-HDDA coating.

2-min exposure between the 30 and 50% HDDA loaded sample (250 versus 205 s) may be due to the larger amount of unreacted HDDA in the 50% loaded sample (1.9 mol kg⁻¹) than in the 30% loaded sample (1.4 mol kg⁻¹). Upon prolonged exposure to sunlight, the gap tends to narrow, with the Persoz value leveling off at 270 s for both samples, compared to 200 s for neat PMMA.¹⁶

Insolubilization

As the polymerization of the diacrylate monomer generates a tridimensional polymer network





Figure 6 Influence of the HDDA concentration on the hardness of a sunlight-cured PMMA–HDDA coating.





Figure 7 Influence of the HDDA concentration on the insolubilization of a sunlight-cured PMMA-HDDA coating.

within the PMMA matrix, the sun-cured polymer should become partly insoluble. After a 30-s exposure, 62% of the PMMA sample containing 50% HDDA was indeed found to be insoluble in chloroform. The fact that the gel fraction is superior to the initial monomer content indicates that part of PMMA, at least 24%, has been incorporated in the polymer network. The gel fraction continued to increase upon further outdoor exposure, up to 97% after 2 h. A similar behavior was observed with the 20 and 30% HDDA loaded samples. Figure 7 illustrates these results by a plot of the ratio of gel fraction to HDDA content versus the exposure time. The value superior to 1 of this ratio (1.6 after a 10 min exposure) clearly demonstrates the participation of PMMA in the polymer network.

Insolubilization of PMMA is likely to result from the two following processes: (1) the formation of a highly cross-linked polymer network, which traps the PMMA chains and does not allow them to be extracted by the solvent, and (2) a grafting reaction due to hydrogen abstraction from the PMMA chain by the initiator radicals (Scheme 1). It should be mentioned that a PMMA sample exposed to sunlight in the presence of Lucirin TPO, without the acrylic monomer, remains totally soluble in chloroform, even after prolonged outdoor exposure.

Acrylate Monomers and Oligomers

In a previous study, we have shown that various acrylate monomers, other than HDDA, undergo a



Scheme 1 Photografting of HDDA onto PMMA.

fast polymerization in a PMMA matrix when they are exposed to intense UV radiation in the presence of a radical-type photoinitiator.¹⁶ In an attempt to achieve a faster and more complete polymerization, we have evaluated the performance of several acrylate monomers suitable for sunlight curing applications. The most promising results have been obtained by replacing, in formulation (A), 20% of HDDA by an urethane-diacrylate (Ebecryl 284) or by isobornyl-acrylate (IBOA). Figure 8 shows the polymerization profiles of the three following formulations upon sunlight exposure.

Formulation	PMMA	HDDA	Ebecryl 284	IBOA	TPO
A B C	50 50 50	50 30 30	20 10	 10	$2 \\ 2 \\ 2$

With the most reactive formulation C, half of the acrylate double bonds did polymerize within 4 s of exposure to sunlight, in the presence of air, compared to 50 s for formulation A. The polymerization kinetics is very similar to that obtained with the PMMA–HDDA formulation containing 5 wt % Lucirin TPO (Fig. 2, curve 1). The degree of conversion reached 72% after 10 min, instead of only 58% for formulation A, with formation of a hard and more flexible coating. The interest of this monomer combination is to allow one to reduce the photoinitiator concentration and, therefore, to improve the weathering resistance of the sun-cured coatings. The light stability was further increased by the addition of a UV absorber (Tinuvin 400 from Ciba) and a HALS radical scavenger (Tinuvin 292 from Ciba). While HALS was found to have no effect on the polymerization kinetics, the UV absorber, at a concentration of 1 wt %, was causing a 50% drop in the cure speed,





Figure 8 Polymerization profiles of various acrylate monomers exposed to sunlight in a PMMA matrix: (A) HDDA (50%); (B) HDDA (30%), and Ebecryl 284 (20%); (C) HDDA (30%), Ebecryl 284 (10%), and Isobornylacrylate (10%).

		TPO (%)	DOP (%)	E-284	IBOA	Sensitivity (mJ cm ⁻²)	Conversion (%)		Hardness (s)	
1 min	HDDA (%)						1 min	10 min	1 min	10 min
А	50	2	_	_	_	86	50	58	184	225
A^{a}	50	2			_	21	61	72	230	260
	50	5			_	26	66	77		_
	30	2			_	140	36	50	242	270
	46	2	8		_	78	52	60		
	42	2	16		_	47	72	79		
	38	2	24		_	30	87	90	120	
В	50	2		20	_	30	60	72		
С	50	2	—	10	10	21	62	73		

Table I Performance Analysis of Various Sunlight-Cured PMMA-Acrylate Systems

UV light intensity, 4.3 mW cm $^{-2};$ film thickness, \sim 40 $\mu m;$ atmosphere, air. a Laminate.

thus requiring one to double the sunlight exposure. By filtering the harmful UV solar radiation, these stabilized coatings proved to be quite effective in extending the service life of polymeric materials used in outdoor applications.¹⁹

Table I summarizes the results obtained in this study of the sunlight-curing of acrylate monomers in a PMMA matrix by comparing the sensitivity values, that is, the energy needed to pass from 0 to 100% conversion at the maximum speed, usually reached at the beginning of the exposure. Formulation C is 4 times more sensitive than formulation A, which indicates that the chain reaction develops more extensively in this system. One can evaluate the kinetic chain length (kcl) by making the ratio of the number of acrylate double bonds polymerized to the number of initiating radicals generated during a given solar exposure. After a 2-s exposure, 38% of the acrylate groups of formulation C had reacted, which corresponds to a concentration of 1.6 mol kg^{-1} . During that time, the number of initiating radicals (N) formed by photolysis of Lucirin TPO was calculated to be 6 × 10⁻⁴ radical kg⁻¹ ($N = I_a \Phi_i$, where I_a is the absorbed light intensity and Φ_i is the initiation quantum yield). From these values, the kinetic chain length was calculated to be 2600 mol radi cal^{-1} , a value surprisingly high for a chain reaction proceeding in the solid state. This result can be accounted for by considering (1) that there is enough molecular mobility in a PMMA plasticized with 50% monomer, and (2) that kcl has been evaluated in the early stage of the polymerization when the sample is still soft (see Fig. 4). Upon further exposure, kcl was found to drop rapidly as the cured coating was getting harder and mobility restrictions became more severe.

SOLAR POLYMERIZATION OF ACRYLATES IN A STYRENE-BUTADIENE RUBBER

One of the potential applications of sunlight curing is in the production of safety glasses, which could be carried out on large dimension specimens by a fast and cost-efficient process. The organic intercalate must be a low-modulus polymer showing a strong impact resistance and an excellent adhesion on glass. Because the abovestudied PMMA-based coatings do not meet these specifications, we have chosen a styrene-butadiene rubber (SBR) as polymer matrix to perform the polymerization of the acrylate monomers.

A two-step strategy was used to produce safety glasses by sunlight processing of photosensitive polymers. To ensure outstanding adhesion, the glass plates were first covered by a thin and strongly adhering coating made of an acrylate– SBR mixture that was cured by sunlight. A liquid polyurethane-acrylate resin containing a photoinitiator was then poured between the two glass plates and cured by solar exposure to obtain a soft and impact resistant crosslinked polymer. The same technology can be utilized to achieve a fast bonding of glass items by means of a sunlightsetting glue.

Photocrosslinking of SBR-Acrylate

In a previous work, we have shown that acrylate monomers undergo a fast polymerization when they are exposed to intense UV radiation in an SBR matrix, in the presence of a photoinitiator like Lucirin TPO.²⁰ Both the acrylate double bond of the monomer and the 2–3 butene double bond



Figure 9 Polymerization of acrylate monomers in an SBR matrix (formulation D) upon sunlight exposure in the presence of air.

of the polybutadiene chain were found to react rapidly with formation of a tridimensional copolymer network. The same reaction was expected to occur in the sunlight, but at a slower pace. The following formulation (D) was exposed to solar radiation for up to 10 min, as a 30-µm-thick coating: Kraton 1101 (50 p), HDDA (30 p), IBOA (20 p), and Lucirin TPO (2 p).

Figure 9 shows the polymerization profiles of the two reactive functional groups, obtained by plotting the acrylate conversion and the butene disappearance as a function of the exposure time, in the presence of air. Within 20 s, half of the acrylate groups have polymerized and about 12% of the butene double bonds. The chain reaction continues to proceed slowly upon further exposure to reach, after 10 min, a conversion degree of 72% for acrylate and 22% for butene double bonds. It should be noticed that, in the absence of acrylate monomer, the butene did not polymerize at all upon sunlight exposure of a SBR sample containing 2 wt % Lucirin TPO, even after 10 min. This means that the butene double bonds (B) react only with the acrylate radicals (A) by cross-propagation, with formation of a copolymer with isolate butene units, according to the following reaction scheme.



The few vinyl double bonds present in SBR, upon 1-2 polymerization of butadiene, were shown to

copolymerize also with the acrylate double bonds.²⁰ A schematic representation of the polymer network formed is given in Figure 10.

Glass-Filtered Photocrosslinking

If this photosensitive material is to be used for safety glass production, the sample will not be in contact with air anymore, and it will be exposed to sunlight through a glass plate. Curing experiments have therefore been repeated under those experimental conditions. The sample was coated onto a KBr crystal, covered with a thin transparent polypropylene film and exposed to sunlight through a 2-mm-thick glass filter. Figure 11 shows the polymerization profiles of the acrylate and butene double bonds of formulation D under those conditions. The crosslinking reaction was found to proceed much faster than in the presence of air, despite a 25% drop in the UV light intensity. Within 1 s, as many as 40% of the acrylate double bonds had polymerized and 12% of the butene groups. These two values increased steadily to reach 90 and 30% after a 10 min exposure, respectively. From these data, the kinetic chain length of the acrylate polymerization in this elastomer was calculated to be on the order of 6000 mol per radical, under O_2 -free conditions. Because the SBR matrix participates effectively to the crosslinking process, insolubilization occurs faster and more extensively than in the PMMA-based system, with formation of a totally



Figure 10 Schematic representation of the polymer network formed upon sunlight curing of an acrylate monomer in an SBR matrix.

insoluble material within 10 min of outdoor exposure.

Adhesion Improvement

Although the adhesion on glass of the SBR-based coating was better than that of the PMMA-based one, it was still not sufficient to meet the stringent safety glass specifications. Two modifications were made to formulation D to increase the adhesion. The content of the monoacrylate (IBOA) was increased to 30 wt % in order to lower the elastic modulus of the cured polymer, and an acrylate functionalized organosol silica, Highlink OG 103 from Hoechst, was introduced in the formulation (E) which has the following composition: Kraton 1101 (50 p), IBOA (30 p), HDDA (10 p), Highlink OG 103 (10 p), and Lucirin TPO (2 p). Highlink OG 103 consists of a colloidal suspension of amorphous silica particles, modified at their surface by an acrylate-terminated hydrocarbon chain; it was shown to act as an adhesion promoter on glass substrates.¹⁷ A few minute exposure of formulation E to sunlight gives a clear coating showing an excellent adhesion on glass, as evaluated by the severe crosshatch adhesive tape test.

The sunlight-induced polymerization of formulation E was followed by IR spectroscopy, both in the presence of air and on a laminated sample to prevent O_2 diffusion. The polymerization profiles shown in Figure 12 (curves 1 and 3) indicate that formulation E is at least as reactive as formulation D. The increased molecular mobility provided by the monoacrylate component leads to a higher



Figure 11 Polymerization of acrylate monomers in an SBR matrix (formulation D) upon sunlight exposure through a glass filter in the absence of air diffusion.



Figure 12 Polymerization of acrylate monomers in an SBR matrix (formulation E) upon sunlight exposure in the absence (curves 1 and 2) or in the presence (curves 3 and 4) of air. Dashed curves represent exposure through a glass filter.

final degree of conversion: 90% under both types of curing conditions after a 10 min exposure, and nearly complete polymerization upon prolonged outdoor exposure. The crosslinked polymer exhibits a typical elastomeric character, with a high flexibility and break elongation, with the Persoz hardness value leveling off at 120 s. Similar results were obtained by performing the exposure through a glass plate (Fig. 12, dotted curves 2 and 4), with the expected slowing down due to the lower light intensity, but without any affect on the final cure extent.

PRODUCTION OF GLASS LAMINATES BY SOLAR PROCESSING

Experimental Procedure

The main step in the manufacture of glass laminates consists in bonding tightly together two glass plates by means of a structural polymeric adhesive. The bonding reaction can be performed at ambient temperature by using a liquid resin undergoing a fast polymerization upon UV irradiation.²¹ To achieve outstanding adhesion, we used as starting material the glass plates that were previously coated with the sun-cured SBRacrylate film (formulation E). A UV-curable polyurethane acrylate resin was employed to produce the elastomeric intercalate. It had the following formulation (F): Ebecryl 284 (50 p), IBOA (30 p), TPGDA (20 p), and Lucirin TPO (2 p). The liquid



Figure 13 Polymerization of liquid acrylate resins (formulations F and G) upon sunlight exposure through a glass filter in the absence of air diffusion. Dashed curve represent the disappearance of the photoinitiator ([Lucirin TPO]₀ = 2 wt %).

resin was placed between the two glass plates and exposed shortly to sunlight. Within seconds, the two pieces of the assembly were sticking together to form a strongly adhering laminate. To test its cohesion, two 10-cm-long and 2-mm-thick glass plates were stuck together over a 1-cm-wide band by sunlight curing. When opposite pressure was applied to this assembly, it was not possible to separate the two pieces of glass, which ultimately broke apart. A further proof that excellent adhesion has been achieved is that, after smashing the glass laminate with a hammer, all the broken glass pieces remained stuck to the polymeric intercalate. To ensure such outstanding cohesion of the assembly, the SBR-acrylate coating must be exposed for only a short time to sunlight, in order to keep a large enough amount of unreacted acrylate double bonds. During the second exposure, the acrylate groups located at the coating resin interface will copolymerize with the acrylate double bonds of the liquid resin to form a single polymer network, thus bonding tightly together the coating and the intercalate.

Kinetics of Sunlight Curing

The polymerization of the acrylate function was followed by IR spectroscopy on a polypropylene laminated sample exposed to sunlight through a glass filter. Within 2 s, as much as 65% of the acrylate double bonds had reacted, transforming the liquid resin into a sticky polymer (Fig. 13, curve 1). This corresponds to a photosensitivity of 9 mJ cm⁻², a value similar to that of the SBR–acrylate system. Upon further exposure, the crosslinking polymerization continued to proceed at a slower pace in the solid medium to reach over 90% conversion after 2 min. When the same formulation F was exposed to sunlight in the presence of air, polymerization hardly occurred (Fig. 13, curve 3) because of the strong inhibitory effect of atmospheric oxygen on the curing of this liquid resin. After a 3-h direct exposure to sunlight, the film remained still tacky. This is an advantage from a practical point of view because, even in daylight, the glue is not setting as long as the assembly has not been put together.

It should be noticed that the sun-cured polyurethane-acrylate coating shows very poor adhesion on untreated glass, even when 10 wt % of Highlink OG 103 was added to formulation F. To achieve the strong adhesion required for glass laminate, it is therefore necessary to first pretreat the two glass plates with the SBR-acrylate-based coating.

As curing proceeds, the hardness of the coating increases steadily to reach Persoz values above 200 s, as shown in Figure 14 (curve F). By comparing Figures 13 and 14, one can notice that a moderate increase in the acrylate conversion, from 65 to 83% in the 2 to 30 s time range, causes a substantial hardening of the coating. For





Figure 14 Variation of the pendulum hardness of acrylic resins (formulations E, F, and G) upon sunlight exposure through a glass filter in the absence of air diffusion.

	D		Е			
Formulation	Air	Laminate	Air	Laminate	F Laminate	G Laminate
SBS	50	50	50	50		_
HDDA	30	30	10	10	_	
TPGDA	_	_	_	_	20	20
IBOA	20	20	30	30	30	30
OG-103			10	10	_	
Ebecryl-284				_	50	
Ebecryl-80				_	_	50
Sensitivity (mJ cm^{-2})	67	9	40	16	9	10
Conversion (%)						
after 1 min	63	86	83	85	87	82
after 10 min	72	91	89	90	—	_
Hardness (s)						
after 1 min	—	—	100	115	210	120

Table II Performance Analysis of Sunlight-Cured SBS-Acrylate Systems

[Lucirin TPO] = 2 wt %; film thickness, 40 μ m.

safety glass applications, the polymeric intercalate must exhibit a strong elastomeric character to be able to absorb shocks. Replacing the diacrylate TPGDA in Formulation F by a monoacrylate (hydroxypropyl acrylate) yields a softer crosslinked polymer. Another solution is to act on the acrylate functionalized oligomer, which must be as reactive as Ebecryl 284 but show after the cure a lower elastic modulus and a stronger impact resistance. The best performance was obtained by substituting in Formulation F the polyurethane diacrylate by an amino-polyester tetraacrylate (Ebecryl 80). The polymerization profile of this new formulation (G) was very similar to that of Formulation F, as shown in Figure 13 (curve 2), but the sun-cured polymer was much softer, very much like the SBR-based coating. It can be seen in Figure 14 that the Persoz hardness is leveling off at about 130 s, thus making this elastomeric material quite resistant to deformation and impact.

Photocuring of Thick and Large Samples

Table II summarizes the performance of the 4 formulations D to G exposed to sunlight as 40- μ m-thick films. When formulations F or G were used as sun-setting glues, the film thickness was typically in the 30 to 100 μ m range. For safety glass applications, the thickness of the polymeric intercalate must be increased up to a few millimeters to ensure a good absorption of shocks. At the photoinitiator concentration used (2 wt %), sunlight is mainly absorbed in the 200- μ m-thick top layer of the photosensitive polymer, thus leading to a depth-cure gradient and poor polymerization of the 3-mm-deep bottom layer after a 30-s exposure. However, because the photoinitiator is undergoing a fast bleaching reaction upon outdoor exposure (Fig. 13, curve 4), the incident radiation will penetrate progressively deeper into the sample. Thanks to this frontal polymerization, up to a few centimeter thick items have been cured within 15 minutes upon outdoor exposure.

Another approach to achieve a deep-through cure consists in lowering the photoinitiator concentration down to 0.1 wt % to allow, from the outset of the exposure, sunlight to penetrate deeper into the photopolymer. As expected, the resulting decrease in the initiation rate is slowing down the polymerization so that the exposure time had to be extended for up to 15 min, that is, a dose of 3 J cm⁻², to ensure a deep through cure of 3-mm-thick samples. The main interest of this approach, besides lowering the cost in the photoinitiator, is that the cured intercalate remains perfectly clear. A combination of Lucirin TPO and a hydroxy phenylketone (Darocur 1173 from Ciba) proved to also be quite effective to produce noncolored, thick samples by sunlight curing. An additional benefit of this approach is that, by extending the reaction time, one reduces the temperature increase caused by the exothermal polymerization as well.

One of the distinct advantages of solar processing is to allow large dimension items, up to several square meters, to be uniformly insolated. While the width of a conventional UV curing line does not exceed 2 m, such a size limitation does not exist anymore in sunlight curing. In practical applications, the following procedure should be followed to readily produce safety glasses. The two pieces of SBR-coated glass, separated on their edges by a 3-mm-thick rubber spacer, are maintained in a frame, which is tilted at an angle of 30° toward the sun. The UV-curable liquid resin is then injected from the lower side to progressively fill out the void. Curing is simply started by removal of the black curtain protecting the upper piece of glass and exposure to sunlight for 15 min.

As these sun-cured glass laminates might be used in outdoor applications, we have tested their light stability in a QUV weatherometer. After a 2000-h exposure, the sample remained perfectly clear and noncolored.¹⁹ By adding to the liquid resin 1 wt % of a hindered amine light stabilizer (Tinuvin 292 from Ciba), its weathering resistance was increased by a factor of 5, without any slowing down effect on the curing kinetics. It should be noticed that all the sunlight curing operations can be conducted indoor in a rain-free environment by working in a greenhouse-type plant, as the solar UV radiation are filtered anyway by the upper piece of the glass laminate.

A most remarkable feature of this solar technology is that it can be employed to produce laminates in which one of the two parts is an organic glass or a metal. Indeed, excellent adhesion of the sun-cured SBR–acrylate coating (formulation E) was achieved on the following substrates: poly-(methyl methacrylate), poly(vinyl chloride), polycarbonates (PC), aluminium, and stainless steel. The polycarbonate-glass laminate is of particular interest as it exhibits, on one side, the strong impact resistance of polycarbonates and, on the other side, the chemical inertness, scratch resistance, and hardness of mineral glass. By sandwiching the PC plate between two glass plates, one obtains a three-part laminate, which has the same chemical resistance and surface properties as conventional glass laminates, but which exhibits a higher impact resistance due to the presence of the PC core. As polycarbonates are usually stabilized with UV-absorbers, which are filtering the harmful UV solar radiation, both sides of the three-part laminate have to be exposed to sunlight to ensure a strong cohesion of the assembly.

Finally, it should be mentioned that, without changing the formulation of both SBR-acrylate coating and the UV-curable resin, those glass laminates could also be produced by exposure to UV-A-type fluorescent lamps, which emit between 300 and 380 nm and are commonly used in accelerated weathering or artificial suntan devices. As the light intensity is similar to that of sunlight, exposure time values were on the same order as those reported in this article. Such an alternative will prove particularly useful in industrial applications, as it allows the production line to continue to run on cloudy or rainy days. By increasing slightly the photoinitiator concentration, it was even possible to perform the 2 photocuring reactions within less than 1 min by using a conventional overhead projector.

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CONCLUSION

Sunlight curing appears as a promising technology, well-suited to specific applications, particularly in the area of fast-drying protective coatings and adhesives. Its main advantage is that it is a cost-effective process, and easy to implement, which consumes no energy and requires very little investment in equipment, as it needs no lamps. In addition, all the operations are conducted at ambient temperature in the presence of air. They can easily be performed on a very large scale, a feature which makes this technology particularly attractive in the building industry. Moreover, solar curing is based on the well-established UV curing technology and therefore uses conventional photoinitiators and monomers.

By means of IR spectroscopy, we have followed the polymerization of acrylate monomers upon sunlight exposure to determine some of the important kinetic and physical parameters. Highly resistant protective coatings have been obtained within seconds by simple outdoor exposure of acrvlate monomers in a PMMA matrix. A sunlightcurable liquid resin containing an acyl-phosphine oxide photoinitiator has been shown to be quite effective for producing quick setting glues and intercalates for glass laminates. The adhesive strength, which is a crucial issue in the manufacture of glass laminates, has been greatly enhanced by using as polymer matrix a styrenebutadiene rubber, which copolymerizes with the acrylate monomers, and by adding to the formulation silica particles grafted with an acrylate function. This solar curing technology is not restricted to mineral glass laminates and 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.

Further progress in this area should be directed toward the developments of efficient photoinitiators giving noncolored photoproducts and of highly reactive monomers and telechelic oligomers showing the desired physical properties upon cure. For safety glass applications, these photosensitive polymers will have to provide high adhesive strength and impact resistant and to exhibit a great transparency in the visible range as well. In this respect, fluorinated acrylate monomers appear as promising candidates as they were shown to yield highly transparent polymers upon photopolymerization.²²

REFERENCES

- P. R. T. Oldring, Ed., Chemistry and Technology of UV and EB Formulation for Coatings, Inks and paints, Vol. 1–5, SITA Technology, London, 1991.
- J. P. Fouassier and J. F. Rabek, Eds., Radiation Curing in Polymer Science and Technology, Vols. 1-4, Elsevier, London, 1993.
- 3. C. Decker, Prog. Polym. Sci., 21, 593 (1996).
- G. L. Collins and J. R. Costanza, J. Coat. Technol., 51, (648) 57 (1979).
- C. Decker, J. Polym. Sci., Polym. Chem. Ed., 21, 2451 (1983).
- J. V. Crivello, R. Narayan, and S. S. Sternstein, J. Appl. Polym., 64, 2073 (1997).

- C. Decker, T. Nguyen Thi Viet, and H. Le Xuan, Europ. Polym. J., 32, 1319 (1996).
- C. Decker, T. Bendaikha, D. Decker, and K. Zahouily, *Polym. Prepr.*, **38**, 487 (1997).
- 9. J. V. Crivello, Adv. Polym. Sci., 62, 2 (1984).
- C. Decker and K. Moussa, *Macromolecules*, 22, 4455 (1989).
- C. Decker, in *Materials Science and Technology*, Vol. 18, H. E. H. Meijer, Ed., VCH Verlag, Weinheim, 1997, p. 615.
- 12. H. Kaczmarek and C. Decker, J. Appl. Polym. Sci., 54, 2147 (1994).
- 13. T. Ando, Y. Nakarishi and K. U. Rita, Eur. Pat. 119,525 (1984).
- P. Chevreux and C. Chevreux, Eur. Pat. 108,631 (1984).
- 15. J. Pattein and P. Le Roy, U.S. Pat. 4,859,742 (1989).
- K. Moussa and C. Decker, J. Polym. Sci., Polym. Chem. Ed., 31, 2633 (1993).
- 17. A. Eranian and C. Roux, *Inform. Chim.*, **371**, 85 (1995).
- 18. K. Sato, J. Coat. Technol., 56, 47 (1984).
- C. Decker and S. Biry, Progr. Org. Coat., 29, 81 (1996).
- C. Decker and T. Nguyen Thi Viet, *Polym. Mater.* Sci. Eng., 74, 327 (1996).
- C. Decker and K. Moussa, J. Appl. Polym. Sci., 55, 359 (1995).
- C. Decker, Europ. Polym. Paint Colour J., 182, 383 (1992).