

# UV-Curable Acrylic Resins for Production of Glass Laminates

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## SYNOPSIS

Glass laminates have been readily obtained by photocuring at ambient temperature of an acrylic adhesive consisting either of a liquid resin or a solid thermoplastic polymer. The light-induced polymerization process was followed by real-time infrared spectroscopy. Close to 100% conversion was reached within a few seconds of exposure, by taking as the photoinitiator an  $\alpha$ -hydroxy alkylphenone or an aryl phosphine oxide. A liquid formulation containing an aliphatic polyurethane-acrylate oligomer, acrylic acid, and butyl acrylate gives the best performance in terms of reactivity, adhesion, impact resistance, and transparency. The impact resistance was further increased by introducing a polycarbonate core between the two glass plates. The solid thermoplastic polymer was obtained either by casting from a solution containing an aliphatic polyurethane, an acrylate oligomer, and the photoinitiator or by mixing these compounds in the molten state and further extrusion. The glass assembly was heated above the softening temperature (80°C) under a 1 MPa pressure and cured by a 1 min exposure to UV radiation to give a strongly adhesive laminate showing good transparency and long term weatherability. © 1995 John Wiley & Sons, Inc.

## INTRODUCTION

Light-induced polymerization of multifunctional monomers is one of the most efficient methods for producing rapid highly cross-linked polymers.<sup>1-3</sup> When compared to conventional methods, UV-curing presents a number of unique advantages, e.g., great cure speed, solvent-free formulations, room-temperature operations, and high-quality products. As a result, this technology has experienced steady growth over the past decade and has found a large variety of applications, mainly in the coating industry,<sup>4</sup> with the development of fast-drying varnishes and printing inks and, more recently, as UV-curable adhesives<sup>5</sup> and as photoresists for imaging applications.<sup>6</sup> In the case of UV-curable structural

adhesives, it is necessary that at least one of the two parts to be assembled exhibits high transparency in the near-ultraviolet region.

The objective of this work was to develop UV-curable resins, best suited for the production of impact-resistant glass laminates, by a process faster and cheaper than the usual thermal cure of poly(vinyl butyral)s under high pressure.<sup>7,8</sup> Several reports have already demonstrated the feasibility of the photocuring method to produce safety glasses.<sup>9-11</sup> Acrylate monomers and oligomers were usually chosen as bonding materials, because of their great reactivity and their remarkable optical and mechanical properties.<sup>12</sup> We describe here two approaches that have been used in order to bond two glass plates together and to achieve rapid high adhesive and cohesive strength: The first is based on the UV-curing of a liquid acrylate resin, performed at room temperature and at normal pressure; the second consists in the photocuring of a solid thermoplastic polymer under an MPa pressure. The first procedure has been applied to both mineral and organic glass laminates, like polycarbonates.

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## EXPERIMENTAL

### Photoinitiator Materials

All the UV-curable formulations contained a radical-type photoinitiator that cleaves readily under UV exposure. Among the many commercial photoinitiators, we selected 1-benzoyl-1-hydroxycyclohexane (Irgacure 184 from CIBA) because of its high initiation quantum yield and the low coloration of its photoproducts. This photoinitiator absorbed weakly above 330 nm, so that the cure speed was significantly reduced when the UV radiation from the mercury lamp was filtered by the glass plate of the laminate. Faster cure was achieved by using 2,4,6-trimethylbenzoyl, diphenyl phosphine oxide (Lucirin TPO from BASF) as the photoinitiator, owing to its greater absorbance in the near-UV region. The photoinitiator concentration was kept low, e.g., at 0.1% for a 2 mm-thick adhesive layer in order to ensure a deep through cure and good adhesion of the polymer to the bottom glass plate. For thinner films, the photoinitiator concentration was increased concomitantly to maintain the overall absorbance constant.

### Liquid UV-curable Resins

Different types of aliphatic polyurethane acrylates, with a molecular weight ranging from 1300 to 5000, were used as functionalized oligomers, in order to obtain after curing low-modulus elastomers showing great impact resistance and good light stability. These compounds (Actilane 9, 19, 23, and 27 from SNPE) are highly viscous and need to be diluted with monomers in order to lower the resin viscosity. Various acrylate monomers were employed as the reactive diluent: ethyldiethyleneglycol acrylate (EDGA), hexanediol diacrylate (HDDA), butyl acrylate (BuA), *N*-vinylpyrrolidone (NVP), acrylic acid (AA), and methacrylic acid (MAA). Small amounts of an organosilane ( $\gamma$ -methacryloxypropyltrimethoxysilane, A 174 from Union Carbide) were added to most formulations to improve the adhesion. A similar effect can be obtained by using silica organosol acrylates (HIGHLINK OG 101 from Hoechst), which will copolymerize with the acrylate resin and act as a polyfunctional cross-linker. A typical liquid UV-curable formulation contained 50–65% oligomer, 35–50% monomer, 1% silane, and 0.1% photoinitiator.

### UV-curable Solid Polymers

A thermoplastic polyurethane (PU), with a molecular weight of 125,000 and a glass transition temperature of  $-30^{\circ}\text{C}$ , was prepared by reacting a diisocyanate with a polyol in the presence of a chain extender (1,4-butanediol). It was dissolved in tetrahydrofuran, and an acrylic oligomer (Actilane 23) was then added, together with the photoinitiator. The solution, with a solid content of 20%, was then evaporated at  $60^{\circ}\text{C}$  to obtain a dry film having the following composition: [PU] = 69.4%, [Actilane 23] = 30%, and [Irgacure 184] = 0.6%. The film thickness was typically 0.3 mm. Thicker films (0.8 mm) were prepared by extrusion at  $150^{\circ}\text{C}$  of a mixture having the following composition: [PU] = 84%, [Actilane 23] = 15.8%, and [Irgacure 184] = 0.2%.

Due to the plasticizing effect of the liquid acrylic oligomer added, the  $T_g$  value of the uncured polymer drops below  $-40^{\circ}\text{C}$ . The softening temperature is ca.  $80^{\circ}\text{C}$  for both cast and extruded films, which become perfectly transparent after keeping them for a few hours at this temperature.

### Irradiation

In the first procedure, the UV-curable liquid resin was poured between two 4 mm-thick glass plates, which were assembled with metal clips and separated on their edges by a 2 mm-thick rubber spacer. Samples were exposed for up to 1 mn to the radiation of a high-intensity mercury lamp (80 W/cm), which has its strongest emission at 365 nm. The incident light intensity at the sample position was measured by radiometry to be  $200 \text{ mW cm}^{-2}$ . Although the irradiation was performed at ambient, the actual temperature of the sample did rise up to  $80^{\circ}\text{C}$  at the end of the exposure, due to both the exothermicity of the polymerization process and the heat produced by the absorbed radiation.

In the second procedure, a sheet of the solid thermoplastic polymer containing the photoinitiator and the cross-linking agent was laminated between two glass plates and maintained at  $80^{\circ}\text{C}$  under a pressure of 10 bar for up to 5 h. The fully transparent sample was then exposed to UV radiation under the same conditions as in the first procedure.

### Analysis

The extent of the polymerization process was determined quantitatively by IR spectroscopy, by

monitoring the decrease upon irradiation of the sharp peak centered at  $810\text{ cm}^{-1}$ , which corresponds to the twisting vibration of the acrylic double bond. In these curing experiments, the resin was laminated between two films of polyethylene, which is transparent to both UV and IR radiation, and exposed to the glass-filtered radiation of the mercury lamp. Infrared analysis has also been used to demonstrate that only a small part of the acrylic group is consumed during the extrusion at  $150^\circ\text{C}$  and none at all when the mixture was heated at  $120^\circ\text{C}$  for several hours.

Upon exposure, the polymer becomes partly insoluble in the organic solvents, due to the cross-linking reaction. Solubility tests were performed in order to evaluate the gel fraction, which can rise up to 100%. The proportion of insoluble material in the UV-cured polymer was measured after repeated extraction in tetrahydrofuran.

The softening temperature ( $t_s$ ) of the thermoplastic polymer was determined by sandwiching the film between two plates of glass and heating the assembly under a pressure on the order of 1 MPa. The temperature at which the film changes in appearance, in particular, by becoming transparent, was taken as the softening or molding temperature. The flow temperature ( $t_f$ ) was determined on the same assembly, by measuring the temperature at which flow starts to take place, enabling the plates of glass to move freely when placed in a vertical position under normal pressure. For the photocross-linked polymer, where flowing is not occurring anymore, we measured the release temperature ( $t_r$ ) at which one of the glass plates suddenly separated from the assembly.

To determine the resistance to shocks of the glass laminate, a 400 g steel ball was dropped on the assembly from a height of 3 m. The process was repeated several times until breakage occurred. To assess the adhesion performance, a 1 kg steel ball was dropped from a height of 5 m, and the type of fracture (cohesive or delaminating) was determined. The adhesion was considered to be good when all of the broken glass pieces remained stuck to the polymeric intercalate.

## PHOTOCURING OF LIQUID RESINS

The most important requirement for the UV-cured polymer is to show strong adhesion to each part of the assembly. In addition, it must be a low modulus material having typical elastomeric behavior in order

to be able to absorb the mechanical and thermal shocks. When used as safety glasses, these laminates must also exhibit excellent optical properties (high transparency, no coloration) and show great resistance to photodegradation upon outdoor weathering. Among the various multifunctional oligomers examined, only aliphatic polyurethane-acrylates (Actilane 9, 19, and 27) were found to fulfill satisfactorily the different specifications. These acrylate-functionalized oligomers differ from one another mainly in the nature and molecular weight of the polyol and in the nature of the isocyanate used for the polycondensation. The reactive diluent was chosen from the following monomers: acrylic acid (AA), *N*-vinylpyrrolidone (NVP), ethyldiethyleneglycol acrylate (EDGA), butyl acrylate (BuA), and hexanediol diacrylate (HDDA). All the formulations contained 0.1% of Irgacure 184 as photoinitiator and up to 1% of the organosilane A 174.

### Kinetic Study of the Photopolymerization

When the liquid acrylic resin was exposed to the radiation of a medium-pressure mercury lamp between two glass plates, polymerization occurred rapidly to give a strongly adherent laminate. A typical formulation contained a polyurethane-diacrylate (65%), BuA (25%), and AA (10%) as the reactive diluent, and a  $\alpha$ -hydroxy alkylphenone photoinitiator (0.1%). The amount of acrylate double bonds polymerized after a 1 min exposure was determined by analyzing each face of the cured adhesive by means of multiple internal reflection (MIR) infrared spectroscopy. To be able to recover the 2 mm-thick polymer intercalate after UV exposure, the glass plates had to be first coated with a thin antiadhesive Teflon film. MIR analyses have shown that all of the acrylate functions located in the top 2  $\mu\text{m}$  layer of the exposed face have been polymerized and as much as 98% for the 2  $\mu\text{m}$  bottom layer. This result clearly indicates that the polymerization process has developed uniformly throughout the 2 mm-thick intercalate, thus ensuring good adhesion on both sides.

Real-time infrared (RTIR) spectroscopy<sup>13</sup> was used to monitor continuously the polymerization reaction in a 50  $\mu\text{m}$ -thick film exposed to unfiltered and glass-filtered radiation. The photoinitiator concentration was increased to 2% in order to have a similar light absorbance to that of the glass laminates. The sample, coated on a KBr crystal, was either in contact with air or covered with a transparent polypropylene film to prevent the diffusion

of oxygen (laminated). The polymerization profiles recorded by RTIR spectroscopy are shown in Figure 1 for a polyurethane-acrylate resin containing 2% Irgacure 184. With the unfiltered radiation, the reaction occurs about twice as slow in the presence of air than for the laminated film, due to the well-known inhibition effect of oxygen on radical-induced polymerization. This trend will become more pronounced as the light intensity or the film thickness is decreased. With the glass-filtered radiation (wavelengths above 330 nm), the polymerization starts after a longer induction and develops at a slower pace than with the unfiltered radiation, as expected from the reduced light intensity. In the presence of air, no significant polymerization was found to occur, because the rate of production of initiating radicals, which are consuming the oxygen dissolved in the sample, is no longer sufficient to compete with the rate of  $O_2$  diffusion. The concentration of oxygen remain too high to allow the monomer to compete successfully with oxygen for the scavenging of the initiating radicals.<sup>14</sup> This is due mainly to the low light absorbance of Irgacure 184 at wavelengths above 330 nm.

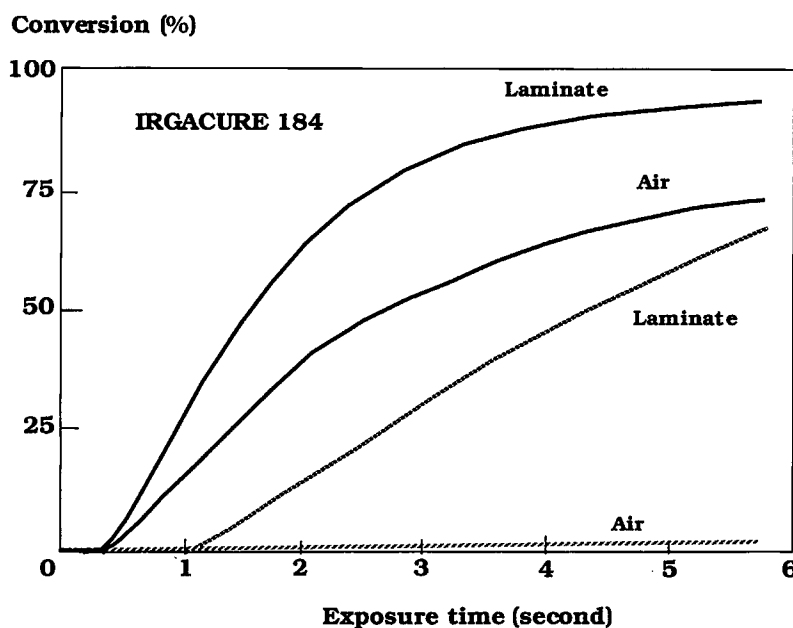
The polymerization rate can be substantially increased by using a photoinitiator that has stronger absorption above 330 nm, like arylphosphine oxides.<sup>15</sup> Figure 2 shows the polymerization profiles

recorded by using Lucirin TPO (2%) as the photoinitiator. The laminated film was found to polymerize four times faster than did the Irgacure 184-based film when exposed to the glass-filtered radiation. The strong light absorbance, together with the high initiation quantum yield, which are characteristic of this photoinitiator, make the rate of radical production great enough to overcome oxygen inhibition, so that the polymerization can develop here even in the presence of air. After 10 s of exposure, close to 100% conversion is reached with the laminated system, which is more relevant for the present study.

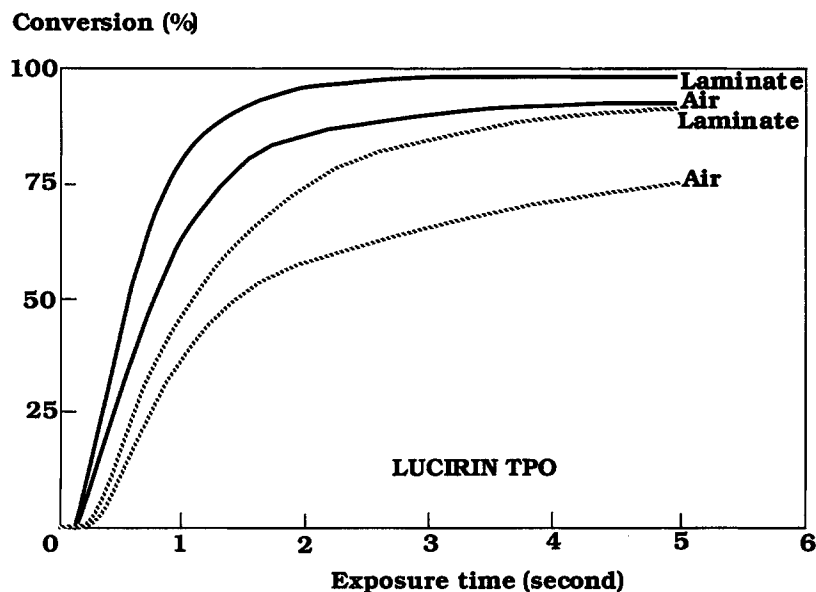
Table I summarizes the results of this kinetic study, with respect to the rate of polymerization, the induction period, and the amount of residual unsaturation in the cured polymer after 10 s exposure. The better performance of Lucirin TPO in terms of reactivity is clearly apparent. Irgacure 184 was still chosen for our further work on the production of highly transparent glass laminates, because it is less likely to give colored photoproducts.

#### Glass-Glass Laminates

The results obtained for the various UV-curable formulations examined are summarized in Table II, with respect to their reactivity, transparency, color,



**Figure 1** Polymerization profiles recorded by RTIR spectroscopy of a liquid PU-acrylate resin irradiated under various conditions: (—) unfiltered light; (---) glass-filtered light. Photoinitiator: [Irgacure 184] = 2%. Actilane 9 (65%), BuA (25%), AA (10%). Light intensity:  $50 \text{ mW cm}^{-2}$ ; film thickness:  $50 \mu\text{m}$ .



**Figure 2** Polymerization profiles recorded by RTIR spectroscopy of a liquid PU-acrylate resin irradiated under various conditions: (—) unfiltered light; (---) glass-filtered light. Photoinitiator: [Lucirin TPO] = 2%. Actilane 9 (65%), BuA (25%), AA (10%). Light intensity:  $50 \text{ mW cm}^{-2}$ ; film thickness:  $50 \mu\text{m}$ .

and adhesion. All the resins containing Actilane 27 (formulations **1**, **3**, and **8**) were found to yield, upon UV exposure, a transparent intercalate showing poor adhesion to glass, as well as low impact resistance. By contrast, both Actilane 9 and Actilane 19 led to a cohesive assembly when associated with an adequate monomer. These two polyurethane acrylate oligomers also impart a strong elastomeric character to the cross-linked polymer, thus making those glass laminates highly resistant to impact.

The monomer used as reactive diluent plays a key role by acting both on the reactivity of the for-

mulation and on the optical and mechanical properties of the cured polymer.<sup>16</sup> The monoacrylate EDGA leads to a low-modulus polymer that has good adhesion to glass in the presence of AA and vinylpyrrolidone. This formulation (**2**) has, however, poor reactivity and requires up to  $60 \text{ J cm}^{-2}$  for a complete cure. The polymerization rate can be increased by introducing a diacrylate such as hexanediol diacrylate (formulations **3**, **4**, and **5**), but at the expense of adhesion and impact resistance. Moreover, the presence of NVP, together with AA, leads to some discoloration of the cured polymer,

**Table I** Light-induced Polymerization of a PU-acrylate Resin; Influence of the Photoinitiator and on the Exposure Conditions; Light Intensity:  $50 \text{ mW cm}^{-2}$ ; Film Thickness:  $50 \mu\text{m}$

Photoinitiator	UV Exposure		Induction Period (s)	Rate of Polymerization ( $\text{mol kg}^{-1} \text{ s}^{-1}$ )	Residual Unsaturation <sup>a</sup> (%)
Irgacure 184 (2%)	Glass-filtered	Air	—	0.01	95
		Laminate	1.2	0.6	5
	Unfiltered	Air	0.4	0.9	15
		Laminate	0.3	1.5	1
Lucirin TPO (2%)	Glass-filtered	Air	0.3	1.5	10
		Laminate	0.3	2.4	0
	Unfiltered	Air	0.2	3.7	2
		Laminate	0.2	4.4	0

<sup>a</sup> In cured polymer after 10 s exposure, i.e., an incident energy of  $0.5 \text{ J cm}^{-2}$ .

**Table II** Performance Analysis of Various UV-curable Resins for Glass-Glass Laminates: Photoinitiator: [Irgacure 184] = 0.1%, [Organosilane A-174] = 1%; Intercalate Thickness: 2 mm; Light-Intensity: 0.2 W cm<sup>-2</sup>

Formulation	Oligomer (%)	EDGA (%)	HDDA (%)	AA (%)	NVP (%)	BuA (%)	Energy <sup>a</sup> (J cm <sup>-2</sup> )	Transmission <sup>b</sup> at 680 nm (%)	Y <sub>f</sub> <sup>c</sup>	Adhesion
1	A-27 (50)	25	—	10	15	—	60	80	15	Poor
2	A-19 (50)	30	—	10	10	—	60	81	14	Good
3	A-27 (50)	25	15	10	—	—	24	78	5	Poor
4	A-19 (50)	35	15	—	—	—	36	82	2	Fair
5	A-9 (40)	—	40	—	20	—	12	75	18	Poor
6	A-19 (50)	—	—	—	15	35	24	72	12	Poor
7	A-19 (60)	—	—	—	10	30	12	80	5	Fair
8	A-27 (65)	—	—	10	—	25	12	80	3	Fair
9	A-19 (65)	—	—	10	—	25	12	82	2	Good
10	A-19 (50)	—	—	30	—	20	12	77	4	Good
11	A-9 (65)	—	—	5	—	30	18	81	3	Poor
12	A-9 (65)	—	—	10 <sup>d</sup>	—	25	18	81	2	Good
13	A-9 (65)	—	—	10	—	25	12	82	2	Good
14	A-9 (60) + Ebecryl 830 (5)	—	—	10	—	25	9	82	2	Good
15	A-9 (65) <sup>e</sup>	—	—	10	—	25	5	78	5	Good

<sup>a</sup> Energy required for the curing.

<sup>b</sup> Transmission at 680 nm of the reference water-filled glass laminate: 85%.

<sup>c</sup> Yellow index of the cured laminate.

<sup>d</sup> Methacrylic acid.

<sup>e</sup> [Lucirin TPO] = 0.1%.

with yellow index values rising up to 18 for the 2 mm-thick intercalate.

A significant improvement was achieved by using BuA as the reactive diluent, in association with AA (formulations 8–14). The cure speed was markedly increased, while at the same time a highly transparent noncolored polymer was formed that showed good adhesion to glass and excellent impact resistance. The AA content had to be maintained to at least 10% in order to ensure high adhesion to glass and cohesive fracture upon impact. The AA can be partly or totally replaced by methacrylic acid (formulation 12), without significant changes in the laminate characteristics, except for the expected decrease in the resin reactivity. The best overall performance was achieved with a resin containing 65% Actilane 9, 25% BuA, and 10% AA (formulation 13). This glass laminate was found to withstand, without breaking, 10 consecutive impacts of a 400 g steel bead dropped from an height of 3 m. The addition of small amounts (5%) of a polyester hexaacrylate (Ebecryl 830 from UCB), formulation 14, leads to further improvement of the impact strength and reactivity without detrimental effect on the other characteristics. With the acylphosphine oxide photoinitiator (formulation 15), the polymerization reaction proceeded twice as fast, but the optical properties of the glass laminate were not as good as with the hydroxyphenyl ketone photoinitiator (Table I).

For all these systems, it is important to keep the organosilane content to at least 1% in order to ensure good adhesion to the glass substrate. In this respect, one should mention that similar performance can be obtained by using the acrylate-grafted organosol (HIGHLINK OG 101) newly developed by Hoechst. It consists of a colloidal suspension of amorphous silica particles modified at their surface by an acrylate-terminated hydrocarbon chain, which makes them compatible with organic media. Such silicon acrylate grafts can be used as reactive diluents in UV-curable resins, in particular, for coatings and adhesives applications, where they were shown to improve the properties of the cured product.<sup>17</sup>

The light stability of these UV-cured glass laminates was tested on formulation 13 in a QUV accelerated weatherometer. After 2000 h of continuous exposure at 40°C, the laminate stayed perfectly transparent and noncolored, with a yellow index value of less than 2, while the adhesive strength remained essentially unaffected. A 10-fold increase of the weathering resistance of such cross-linked polyurethane-acrylate polymers was achieved by adding to the liquid resin small amounts (1%) of a hindered

amine light stabilizer, like Tinuvin 292.<sup>18</sup> This efficient radical scavenger was shown to have no adverse effect on the cure speed, probably because the polymerization occurs in an O<sub>2</sub>-depleted medium where the active nitroxy radical cannot be formed.

### Glass-Polycarbonate Laminates

The UV-curing technology was also applied to produce polycarbonate-glass laminates by a fast and inexpensive process. Such safety glasses should present some distinct advantages, as they are expected to exhibit on one side the strong impact resistance that is characteristic of polycarbonates (PC) and, on the other side, the chemical inertness, scratch resistance, and hardness of mineral glass.

A major difficulty was encountered in this study when we tried to use as adhesives the various UV-curable resins developed previously for the glass-glass laminates. Indeed, all the formulations containing 10% or more of AA were found to react with the PC plate, with a total loss of adhesion. Moreover, as a result of this chemical attack, such laminates rapidly lost their transparency, making them useless for safety glass applications. This detrimental effect can be suppressed by lowering the AA content, down to less than 5%. The UV-cured intercalate then shows good adhesion to the PC plate, which remains transparent, but at the same time, it loses its adherence to the mineral glass plate (Table III).

To overcome this difficulty, we first protected the surface of the PC plate in contact with the adhesive resin by a thin UV-cured coating having less than 5% AA in its formulation. Under those conditions, a resin containing 10% or more of AA was found to have good adhesion after UV-curing to both the glass plate and the coated PC plate. Such laminates are highly transparent and have excellent impact resistance. Their weak point lies in the sensitivity of PC to sunlight, moisture, and acidic pollutants, to which they will be exposed in outdoor applications. The degradation of the PC can be prevented to a large extent by sandwiching the PC plate, coated on both sides, between two glass plates (Fig. 3). These three-part laminates, glass-PC-glass, have the same chemical resistance and surface properties as those of glass-glass laminates, but they exhibit higher impact resistance due to the presence of the PC core and also because of the related thickness increase (16 mm instead of 10 mm).

It should be noted that the PC used in this study contained some light-stabilizers and that it is therefore not transparent in the near-UV where the photoinitiator absorbs. The photocuring of the acrylate

**Table III Performance Analysis of UV-curable Resins for Glass-PC Laminates<sup>a</sup>; Photoinitiator: [Irgacure 184] = 0.1%; Thickness: 2 mm**

Formulation	Actilane 19	HDDA	EDGA	AA	Adhesion on	
					PC	Glass
16	50	20	20	10	Poor	Good
17	60	10	20	10	Poor	Good
18	70	10	20	0	Good	Poor
19	65	6	25	4	Good	Poor
PC coated with formulation 19, and formulation 17 as intercalate					Good	Good

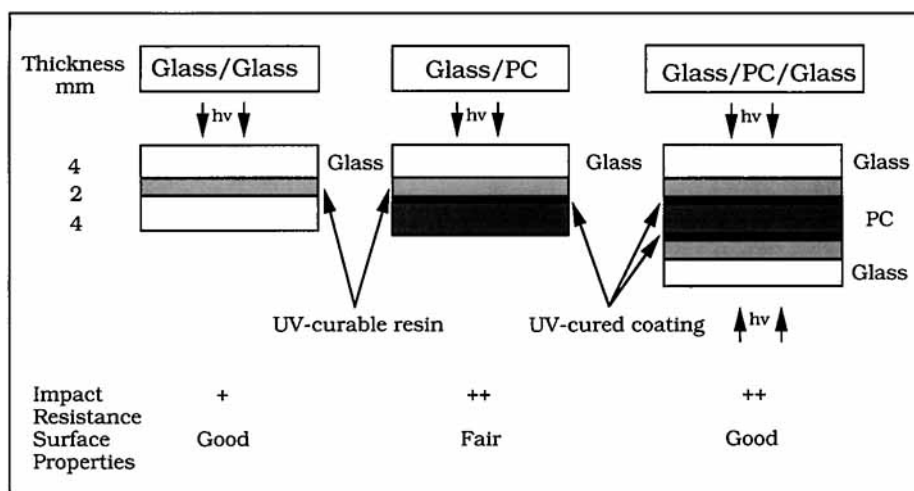
<sup>a</sup> The UV exposure was performed through the glass plate.

adhesive had thus to be always performed by exposing the laminate to UV radiation through its glass side. Consequently, the three-part laminate cannot be cured in a single step and requires two successive exposures through each of the glass plates. This is also the reason why previous attempts to produce PMMA-PC laminates by means of UV-curable adhesives have been unsuccessful. Both parts of the assembly are indeed strongly stabilized by UV absorbers, which, by their great UV filter effect, prevent the photoinitiated polymerization of the intercalate to proceed efficiently.

### UV-CURING OF THERMOPLASTIC SOLID POLYMERS

Although the UV-curing process described above appears as a very promising technology to produce high-performance glass laminates at a low cost, some

practical problems may arise upon industrial implementation, due to the use of a liquid resin, which requires special handling and storage conditions, as well as the fabrication by casting in a mold. We have therefore attempted to produce safety glasses by a dry process based on the photocross-linking of a solid polymer plasticized with a reactive monomer. Previous work<sup>19</sup> has indeed shown that multifunctional acrylic monomers and oligomers can be polymerized readily in a polyurethane matrix, by simple exposure to UV radiation in the presence of an adequate photoinitiator. If applicable to the fabrication of safety glasses, such a process will have the great advantage of being faster, cheaper, and easier to work out than the usual high-pressure thermal cure, which is carried out at 150°C for 2 h in an autoclave. In addition, the plasticizing effect of the acrylic monomer introduced is expected to lower the softening temperature of the uncured polymer. The products could thus be



**Figure 3** Fabrication of glass laminates by UV-curing of PU-acrylate adhesives.

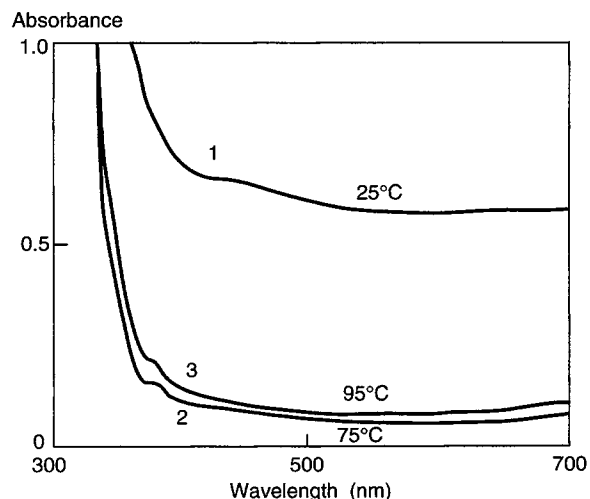


formed to the desired shape, before being cured and hardened by exposure to UV radiation.

The thermoplastic polymer used in this study was an aliphatic polyurethane (PU) prepared by reaction of dicyclohexylmethylenediisocyanate with a polyol in the presence of a chain extender. Its molecular weight was measured to be 125,000, and its glass transition temperature was on the order of  $-30^{\circ}\text{C}$ . As the acrylic oligomer, we selected an aliphatic PU-diacrylate (Actilane 23), because of its high reactivity<sup>19</sup> and its very high viscosity (210 Pa-s at  $50^{\circ}\text{C}$ ). The thermoplastic PU was found to remain tack-free and easy to handle after incorporation of as much as 30% Actilane 23. Irgacure 184 was again used as the photoinitiator at concentrations between 0.2 and 2%, depending on the film thickness. The photocurable thermoplastic film, which served as adhesive for the fabrication of glass laminates, was obtained either by casting from a solution or by extrusion at  $150^{\circ}\text{C}$  of the polymer composition. The main characteristics and performance of the various photosensitive polymers used to produce glass laminates by UV-curing of acrylate-PU films are reported in Table IV.

### Cast Films

The three components of the formulation (PU, Actilane 23, and Irgacure 184) were dissolved in tetrahydrofuran at room temperature. The solution, with a solid content of 20%, was cast on a Teflon plate and dried at  $50^{\circ}\text{C}$ . The  $300\text{ }\mu\text{m}$ -thick polymer film was peeled off and placed as intercalate between two glass plates. The elastomeric and easy deformable film is translucent at room temperature, but becomes transparent upon heating, as shown by the UV-visible absorption spectra of Figure 4. The thermal behavior of the sample was studied by pressing the film between two glass plates under a pressure of 1 MPa. The softening temperature was measured to be  $85$  and  $75^{\circ}\text{C}$  for the PU film plasticized with 18 and 30% of Actilane 23, respectively, compared to  $125^{\circ}\text{C}$  for the pure thermoplastic PU. Such an important drop in the softening temperature is of great interest for the manufacture of glass laminates, as it allows one to operate at lower temperature than in the usual thermal process. After UV-curing, the film remains noncolored and perfectly transparent upon storage at ambient. It also shows good thermal stability, its UV-visible absorption spectrum being hardly affected after 24 h of heating at  $95^{\circ}\text{C}$  (Fig. 4). Flowing of the polymer adhesive was found to



**Figure 4** UV-visible absorption spectrum of a  $500\text{ }\mu\text{m}$ -thick acrylate plasticized PU, laminated between two glass plates: (1) initial laminate at  $25^{\circ}\text{C}$ ; (2) after 2 h heating at  $75^{\circ}\text{C}$ ; (3) after UV-curing and 24 h heating at  $95^{\circ}\text{C}$ .

occur above  $140^{\circ}\text{C}$  for the original PU and above  $110^{\circ}\text{C}$  for the uncured plasticized PU. After UV exposure, the cross-linked polymer can no longer flow, and the assembly holds strongly together up to  $160^{\circ}\text{C}$ , above which one observes the sudden release of one of the glass plates.

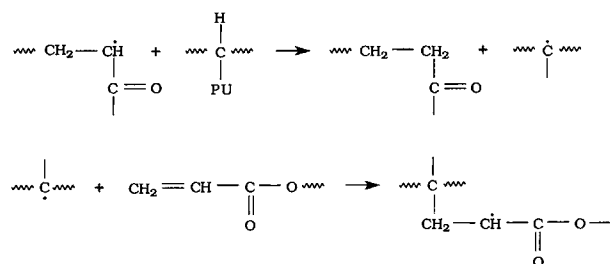
The polymerization rate can be markedly accelerated by increasing the light intensity and the photoinitiator concentration, as shown on Table IV. The optimum photoinitiator concentration needed to achieve a fast deep through cure depends on the film thickness and corresponds to an absorbance of 0.43 at the maximum emission wavelength of the UV lamp ( $365.5\text{ nm}$ ). IR spectroscopy analysis of a polyethylene laminate, cured under the same conditions, shows that more than 90% of the acrylate double bonds have been polymerized after 5 s of exposure at room temperature and up to 100% when the irradiation was performed on the hot sample ( $85^{\circ}\text{C}$ ). At the same time, the polymer becomes partially insoluble, due to the cross-linking reaction of the difunctional monomer. The gel fraction was found to vary between 50 and 80% in tetrahydrofuran, and to increase up to 100% for samples photocured at  $85^{\circ}\text{C}$ . Because the thermoplastic polymer composition contained only 16% cross-linking agent, this result strongly suggests that the acrylate network formed is grafted to the PU matrix, which is thus rendered insoluble. This could occur by a chain-transfer reaction proceeding through the abstraction of a labile hydrogen from the PU chains by the

**Table IV Photocuring of Thermoplastic Acrylate PU Films in Glass-Glass Laminates**

PU	Composition		Light Intensity (W cm <sup>-2</sup> )	Exposure Time (s)	Gel Fraction (%)	Softening Temperature <sup>a</sup> (°C)	Release Temperature <sup>b</sup> (°C)
	Actilane 23	Irgacure 184					
<u>Cast films</u>							
70	30	0.6	0.2	40	50	75	140
70	30	2	0.6	5	60	75	140
84	16	2	0.6	6	80	85	> 160
<u>Extruded Films</u>							
84	16	0.2	0.2	60	55	80	> 160

<sup>a</sup> Uncured sample.<sup>b</sup> Cured sample.

propagating acrylate radical, according to the following scheme:



### Extruded Films

In these experiments, the mixing of the polymer composition (84% PU, 16% acrylic monomer, 0.2% photoinitiator) was carried out in the molten state at 125°C and not in a solvent medium. A solid block was obtained after cooling, which can be either cut into sheets or ground up into granules ready to be extruded. The 0.8 mm-thick photosensitive polymer film was laminated between two glass plates and maintained at 80°C under a pressure of 1 MPa until it became transparent. The photoinitiator concentration was kept low (0.2%) in order to ensure a deep through cure of the adhesive, thus leading to a relatively slow cure, which can be accelerated by increasing the light intensity or by using an arylphosphine oxide photoinitiator. The main characteristics of the product obtained after UV exposure are shown in Table IV. Here, again, a release temperature above 160°C was observed for the cured laminate, while the molding temperature of the uncured plasticized polymer dropped by 45°C, compared to the original thermoplastic PU film. The photocured polymer exhibits the strong elastomeric character required to ensure high-impact resistance, as shown by its tensile mechanical properties.

Breaking of the test sample was found to occur at 300% elongation and a 22 MPa stress.

All the glass-glass laminates obtained by UV-curing of cast or extruded films have good impact resistance and excellent adhesion, showing always a cohesive fracture. In addition to their good optical properties, these safety glasses appear to be very resistant to photodegradation. No yellowing or loss of transparency could be noticed after 2000 h of accelerated QUV aging at 40°C under continuous illumination.

### CONCLUSION

The photoinitiated polymerization of multiacrylate monomers has been utilized to produce rapidly low-modulus cross-linked polymers suitable for adhesives applications. Highly resistant safety glasses have thus been obtained by a process that is faster, cheaper, and easier to work out than the usual thermal cure carried out under high pressure. The photosensitive system can be either a liquid resin to be poured into a glass mold and UV-cured at ambient or a plasticized polymer film to be squeezed between two glass plates under moderate pressure. In both cases, acrylate monomers, associated with an aliphatic PU, functionalized or not, give the best performance in terms of reactivity, adhesion, impact resistance, transparency, and weathering.

This UV-curing technology is not restricted to mineral glass laminates and can be applied to any assembly made of organic glasses, provided that at least one of the elements be transparent to near UV radiation. In this respect, one should mention the remarkable properties of the three-component laminate glass/PC/glass that combines the chemical

inertness, scratch resistance, and hardness of mineral glass, with strong impact resistance due to the PC core, which is sandwiched between two sheets of the UV-cured PU-acrylate elastomer.

Further progress in this area should be directed toward the development of more reactive monomers and of highly efficient photoinitiators giving non-colored photoproducts, in order to further reduce the exposure time and be able to operate the curing line on a continuous mode. Those photosensitive polymers must not only provide high adhesive strength and impact resistance, but also exhibit transparency in the visible range. In this regard, very promising results have been obtained recently with fluorinated acrylate monomers that yield highly transparent polymers, well suited for safety glass applications.<sup>20</sup>

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