

Surface Protection of Poly(vinyl Chloride) by Photografting of Epoxy–Acrylate Coatings

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Synopsis

UV-curable epoxy–acrylate coatings were used to protect poly(vinyl chloride) against superficial degradation. With α -hydroxy–acetophenone photoinitiators, the crosslinking polymerization develops in the ms time scale; 50% degree conversion is reached after irradiation times of 2.5 ms in a nitrogen atmosphere and 17 ms in air. The adhesion of the coating on to the PVC substrate can be greatly improved by inducing a photochemical grafting process. The best results are obtained by incorporating the photoinitiator into the top layer of the PVC sheet. Highly crosslinked epoxy–acrylate coatings are very stable toward UV radiations and chemical agents like organic solvents and strong acids. By their light-screening effect they provide an excellent protection against photodegradation for light-sensitive polymeric materials.

INTRODUCTION

Most of the industrial polymers used for outdoor applications undergo degradation when they are exposed to the combined action of sunlight, oxygen of air, humidity, and acidic pollutants. This process develops primarily at the surface of the polymer and leads to a substantial modification of the aspect (color, gloss) as well as of the mechanical properties (hardness, elasticity, impact resistance) of the irradiated material. One of the possible methods of protecting polymers against natural weathering consists of applying organic coatings that offer a good resistance to both UV light and chemical attack. These coatings are usually highly crosslinked polymers which can be conveniently obtained by photopolymerization of multifunctional monomers or oligomers. Besides improving the surface properties of the coated material, this treatment may provide, by its light-screening effect, a good protection for polymers which are very susceptible to photodegradation, as, for instance, poly(vinyl chloride) (PVC), one of the leading thermoplastics.

UV curable systems used as varnishes, printing inks, or plastics and paper coatings often contain urethane–acrylate oligomers,^{1–3} which, after cure, remain flexible enough to ensure a good adhesion to the support. However, the light-stability of aromatic polyurethanes is rather low⁴ so that, for outdoor systems that demand long-term stability, UV absorbers must be introduced into the coating to prevent its yellowing.⁵ This leads to an undesirable decrease of the speed of cure since light-absorbing stabilizers will reduce the rate of initiation. The other main type of UV coatings are based on epoxy–acrylates which are less sensitive to weathering⁶ and exhibit excellent surface hardness and impact resistance characteristics. Unfortunately, the adhesion of these epoxy resins onto polymeric materials, and on PVC in particular, is often poor, thus reducing their

effectiveness as protective coatings. The objective of this work was to improve the adhesion of epoxy-acrylate resins onto PVC by inducing a superficial photografting process.

Photografting of vinyl monomers onto synthetic polymer substrates has often been used to modify their surface properties. For a recent survey of the considerable work published on this subject, see the comprehensive review of Arthur.⁷ In the specific case of PVC, photografting has been mostly carried out in order to either increase the glass transition temperature⁸ or to obtain hydrophilic⁹ or anticoagulant surfaces,¹⁰ but no study has been reported so far on the surface grafting of multifunctional acrylates onto PVC as a way to improve its resistance to natural weathering. The basic idea was to create polymeric radicals by photolysis of the PVC substrate, which was at first impregnated superficially with an efficient photoinitiator. In the presence of a difunctional monomer or oligomer, these macroradicals should then be able to initiate the polymerization process with formation of a highly crosslinked coating grafted on to the polymer surface.

EXPERIMENTAL

Polymer Substrate

PVC was used under the form either of rigid sheets of 0.5 cm thickness from a commercial material, or of transparent films, 100 μ thick, casted from 1% dichloroethane solutions of Solvic 229 from Solvay. Remaining traces of solvent were removed by vacuum treatment for 5 h at 70°C.

Resin

The UV-curable resin consists of a mixture of three components: (i) an epoxy-diacrylate oligomer (Ebecryl 605 A from UCB) derived from the glycidyl ether of bisphenol A, (II) a monomer, tripropylene-glycol diacrylate (TPGDA from UCB) which acts as a reactive diluent, and (iii) a photoinitiator, 1-benzoylcyclohexanol (Irgacure 184 from Ciba Geigy) which revealed as efficient as the more commonly used Irgacure 651 but yielded less colored photoproducts. For the coating of transparent PVC films, the optical properties of the grafted system can be improved by using a liquid photoinitiator, 2,2-dimethyl-2-hydroxyacetophenone (Darocure 1173 from Merck), which shows a better compatibility with PVC.

Sample Preparation

Two types of samples were prepared for both PVC sheets and films.

Sample A: the resin was formulated to the composition: monomer 48%, oligomer 48%, initiator 4%. The formulation was applied as a layer of 30- μ thickness on the PVC substrate using a wire-wound applicator. The coated polymer was then irradiated for different times up to 1 s.

Sample B: the photoinitiator was at first incorporated into the top layer of the PVC film or sheet by applying a 1,2-dichloroethane solution of the photoinitiator (5% weight by weight). This poor solvent of PVC diffuses slowly into the polymer substrate, thus allowing the initiator to penetrate into the upper layer

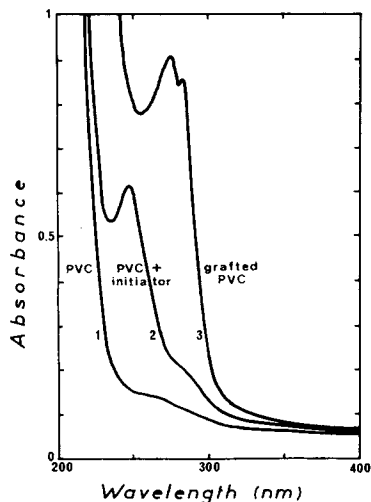


Fig. 1. UV absorption spectra of a 100- μ PVC film, initially (1), after impregnating with Darocure 173 (2), and after photografting of a 5- μ -thick epoxy-acrylate coating (3).

of the support. After complete evaporation of the solvent at room temperature, the PVC film was washed several times with methanol to eliminate the fraction of initiator that was adsorbed at the surface only. The amount of initiator incorporated into the polymer was estimated by ultraviolet spectroscopy to be about 0.2 g/m². Figure 1 shows the UV absorption spectrum of the PVC film before and after impregnation with the photoinitiator. From the comparison of transmission and MIR infrared spectra, the penetration of the initiator molecules into the support was calculated to be $\sim 3 \mu$, which corresponds to an average concentration of the initiator in this superficial layer of 0.3 mol/L, i.e., 1 initiator molecule for 66 monomer units. Finally, a mixture of Ebecryl 605 A and TPGDA, in the ratio 1:1, was applied on the PVC film or sheet impregnated with the photoinitiator, and then exposed to UV radiations for a short period of time.

Irradiation

A medium-pressure mercury lamp (MAZDA—UV 8200) with a nominal input of 80 W/cm and equipped with a semielliptical reflector was used to initiate the photopolymerization. At the focus point, the incident light intensity was measured by ferrioxalate actinometry¹¹ to be 1.5×10^{-6} einstein \cdot s⁻¹ \cdot cm⁻² (1 einstein = 1 mol of photons; energy $\approx 4 \times 10^5$ J \cdot mol⁻¹). Samples A and B were irradiated at room temperature in the presence of air; very short exposure durations, between 1/400 and 1/10 of a second, were obtained by using a camera shutter.

In order to evaluate the light resistance of these epoxy-acrylate coatings and their ability to protect PVC from photodegradation, UV-coated films of PVC were exposed to the radiations of a medium-pressure mercury lamp (Philips HPK—125 W) at an intensity comparable to the sunlight (5×10^{-8} einstein \cdot s⁻¹ \cdot cm⁻²). The change in the UV-visible absorbance, which reflects the discoloration of the irradiated PVC film, was followed by using a Cary 15 spectrophotometer.

Analysis

Infrared spectroscopy was used for quantitative analysis of the polymerization process over the full range of conversion from 0% to 100%. The resin was applied as a thin film to the surface of a polished sodium chloride disc. The infrared spectrum exhibits a sharp peak at 810 cm^{-1} , which corresponds to the $\text{CH}_2=\text{CH}$ out of the plane vibration of the acrylate function. The decrease of this peak after exposure to light was used to calculate the percentage of residual unsaturations. In order to take into account the apparent thickness increase due to shrinkage and the accompanying increase in density as the polymerization proceeds, values of the residual unsaturations were corrected by using the absorption at 2960 cm^{-1} as a criterium of thickness.

Grafted epoxy-acrylate coatings were analyzed by multiple internal reflection (MIR) infrared spectroscopy in order to evaluate the percentage of original double bonds that remain after the cure in the top layer of the coating. MIR spectra were recorded on a Perkin-Elmer 580 B Spectrophotometer by using a multiple internal reflection accessory with a KRS-5 crystal. The single incident angle used was 45° . The penetration depth d , which depends upon the wavelength considered, λ , can be calculated from the equation¹²

$$d = (\lambda \cdot) / 2\pi(\sin^2 \theta - n^2)^{1/2}$$

where θ is the angle of incidence and n the ratio of the refractive index of the reflecting KRS-5 crystal to the refractive index of the polymer (~ 1.54). For the 810 cm^{-1} band, the penetration depth, i.e., the distance at which the electric field amplitude is reduced to $1/e$ of the boundary surface value, was calculated to be $6.4\ \mu$.

Tests of Coating Films

(1) The adhesion of the coating on to the PVC support was measured according to the standard crosscut method followed by a tape test (DIN 53 151). The indication GT 5 means that, after an incision has been made with a knife, the coating can be removed completely with an adhesive tape, whereas GT 0 means that 100% of the coating remains on the substrate.

(2) The surface hardness of the UV-cured coatings was measured according to DIN 53 157 using the pendulum hardness rocker made by Erichsen.

(3) Contact angles of a drop of liquid on PVC and coated PVC films were determined by using a goniometer from Rame Hart (Model 104).

PHOTOINITIATED CROSSLINKING POLYMERIZATION AND GRAFTING

Kinetics

When PVC films, coated with the epoxy-acrylate resin containing the photoinitiator (sample A), are exposed to UV radiations, the polymerization process develops rapidly, a 50% degree of conversion being observed after 17 ms of irradiation in the presence of air. Figure 2 shows the kinetics of disappearance of the acrylate double bond as a function of the irradiation time. The rate of cure can be greatly increased by performing the reaction in an inert atmosphere since

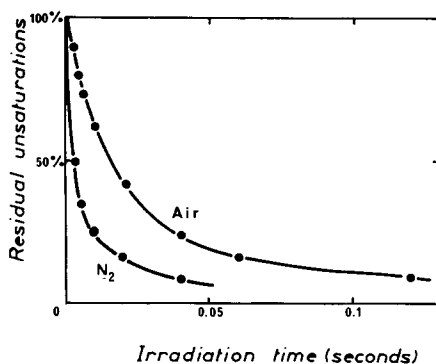


Fig. 2. Kinetics of the crosslinking photopolymerization of the epoxy-acrylate resin (sample A) in air and in pure nitrogen.

oxygen is well known to inhibit strongly the surface curing of resins which polymerize by a free-radical mechanism. As shown by Figure 2, the photopolymerization proceeds about seven times faster in the presence of pure nitrogen than in air; a 50% degree of conversion was reached after an exposure time of only 2.5 ms. The quantum yield of polymerization, i.e., the number of reacting unsaturations per photon absorbed, was calculated to be 7000 in nitrogen, compared to 1100 in air.¹³ The amount of residual unsaturations can be reduced to less than 3% by extending the irradiation time in air over 1 s. The surface hardness of the coating is then very high and comparable to glass (~330 Persoz).

For the sample B, where the photoinitiator is incorporated into the top layer of the PVC film or sheet but not in the resin, the polymerization occurs at a lower rate than in sample A, since the initiating radicals are located only at the PVC-resin interface. The drying time of the resin, which corresponds to a degree of conversion of about 75%, is two to four times longer than for sample A, depending on the coating thickness.

MIR investigations on the cured coatings as well as surface hardness measurements indicate that, for a given overall degree of monomer-to-polymer conversion, for instance, 85%, measured by infrared transmission, the 6 μ thick top layer of coating A is more crosslinked (91%) than the bottom layer (~82%), while the reverse is true for coating B. This seems quite feasible if one considers the spatial distribution of the initiating sites: in sample A, more radicals are created in the upper layers of the coating than beneath due an internal light-screening effect by the photoinitiator; in sample B, on the contrary, the polymerization starts from the deep layers of the coating, in close contact with the polymer substrate which sole contains the initiator, and grows progressively towards the surface.

Adhesion

Measurements of the adhesion of the epoxy-acrylate coating on to the PVC support reveal a very different behavior between samples A and B. In coating A, the adhesion which starts initially at 100% for the liquid resin drops rapidly as the polymerization proceeds, as shown by curve A of Figure 3. After 0.1 s of irradiation and a degree of conversion of about 85%, the coating does not adhere

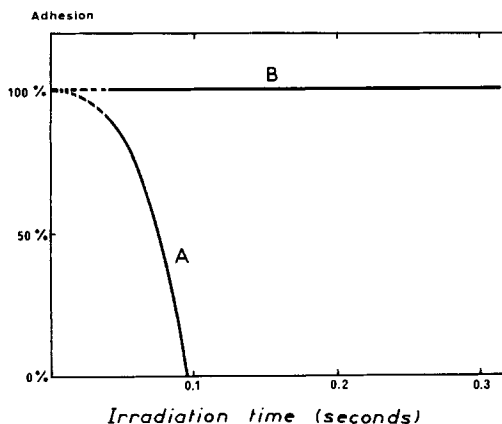


Fig. 3. Influence of the irradiation time on the adhesion of the epoxy-acrylate-resin-coated (A) or grafted (B) onto a PVC sheet.

anymore to the support (GT 5) and can just be peeled off from the PVC sheet. In coating B, on the other hand, the adhesion remains excellent (GT 0), even after exposure times greatly exceeding the duration of drying (curve B of Fig. 3). This result strongly suggests that, when the PVC sheet is superficially impregnated with the photoinitiator, the epoxy-acrylate coating is grafted on to the polymer substrate.

In order to demonstrate that a chemical grafting has indeed taken place in sample B, the following experiment was carried out. The PVC sheet, impregnated with Irgacure 184 or Darocure 1173, was exposed to UV radiations for a short period of time (0.1–0.3 s) and then coated with the epoxy-acrylate resin. The benzoyl and alcohol radicals which were shown to be formed by photocleavage of this type of initiators¹⁴ are highly reactive short-lived species. They are expected to react rapidly with surrounding PVC by hydrogen abstraction to yield mostly α -chloro alkyl radicals on the polymer chain.¹⁵ These macro-radicals have a longer lifetime¹⁶ and should thus be able to initiate the graft polymerization by reacting with the epoxy-acrylate resin, which is applied on the substrate immediately after the UV irradiation. After treatment with tetrahydrofuran to eliminate the unreacted monomer, we observed indeed the presence of a grafted polymer on the surface of the PVC sheet or film (Fig. 1). This epoxy-acrylate coating was characterized by determination of the superficial free energy and by MIR spectroscopy.

—Measurements of the wettability of the sample-treated according to the above-mentioned procedure indicate that the PVC sheet is coated with an epoxy-acrylate network. The contact angle between the coated polymer and a drop of water was 55° compared to 65° for the PVC film. From this value and the 25° contact angle observed with tricresylphosphate, the interfacial free energy of the epoxy-acrylate coating was calculated¹⁷ to be $39 \text{ mJ}\cdot\text{m}^{-1}$ for the dispersive component (γ_S^D) and $15 \text{ mJ}\cdot\text{m}^{-1}$ for the polar component (γ_S^P).

—The MIR infrared spectrum of the coating grafted on PVC (Fig. 4) is characteristic of the epoxy-acrylate resin used and exhibits major bands centered at 3520 cm^{-1} (O—H), 2960 cm^{-1} (C—H of CH_3 and CH_2 groups), 1730 cm^{-1} (O—C=O), 1610 cm^{-1} ($\text{CH}=\text{CH}_2$), 1510 and 1450 cm^{-1} (benzene ring), 1370

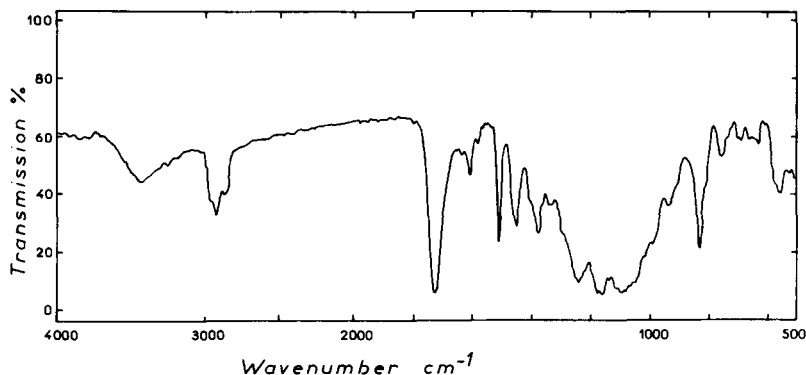


Fig. 4. MIR infrared spectrum of the epoxy-acrylate coating grafted onto a PVC sheet.

cm^{-1} (CH_3), 1240 cm^{-1} (aromatic ether), 1160 and 1090 cm^{-1} (aromatic C—H) and 810 cm^{-1} ($\text{CH}=\text{CH}_2$). From the intensity of the peak at 810 cm^{-1} , the degree of conversion was evaluated to be $\sim 80\%$ for the top layer of the coating that can be investigated by this technique.

—There is a final and strong argument which demonstrates that the epoxy coating is chemically grafted on to the PVC substrate. When the experiment described above is carried out on a glass plate instead of a PVC sheet, the resin does not polymerize at all and can be completely removed by treatment with THF. No epoxy-acrylate coating could be detected by surface analyses of the treated glass plate. This result clearly indicates that the polymer substrate plays the major role by initiating the crosslinking polymerization process through the macroradicals which are formed by photolysis of the photoinitiator incorporated into the PVC film.

Another advantage of this grafting process, which takes place only in sample B, lies in the fact that the surface hardness of the cured coating B is lower than for coating A, where the photoinitiator is incorporated into the resin formulation. This will improve the adhesion of the top coat that is usually required in order to ensure an efficient protection of the polymeric material. After this second coating, carried out this time with the photoinitiator dissolved in the resin, the surface properties of samples A and B appear finally to be identical, but the adhesion of the grafted network B is much better (GT 0 or 1) than for the conventionally cured sample A (GT 5).

If a one-step coating process is still required, it is possible to improve the surface hardness of the grafted coating B, without significant loss in the adhesion, by introducing small amounts of photoinitiator ($\sim 0.5\%$) into the resin formulation. The photopolymerization, which develops then slightly more rapidly, will be initiated by both the PVC macroradicals and the benzoyl and alcohol radicals formed within the coating.

Reaction Scheme

The photografting of epoxy-acrylate coatings on to the PVC substrate is assumed to involve the following steps (see Fig. 5):

(1) radical formation by intramolecular bond cleavage of the photoinitiator under UV irradiation (reaction 1);

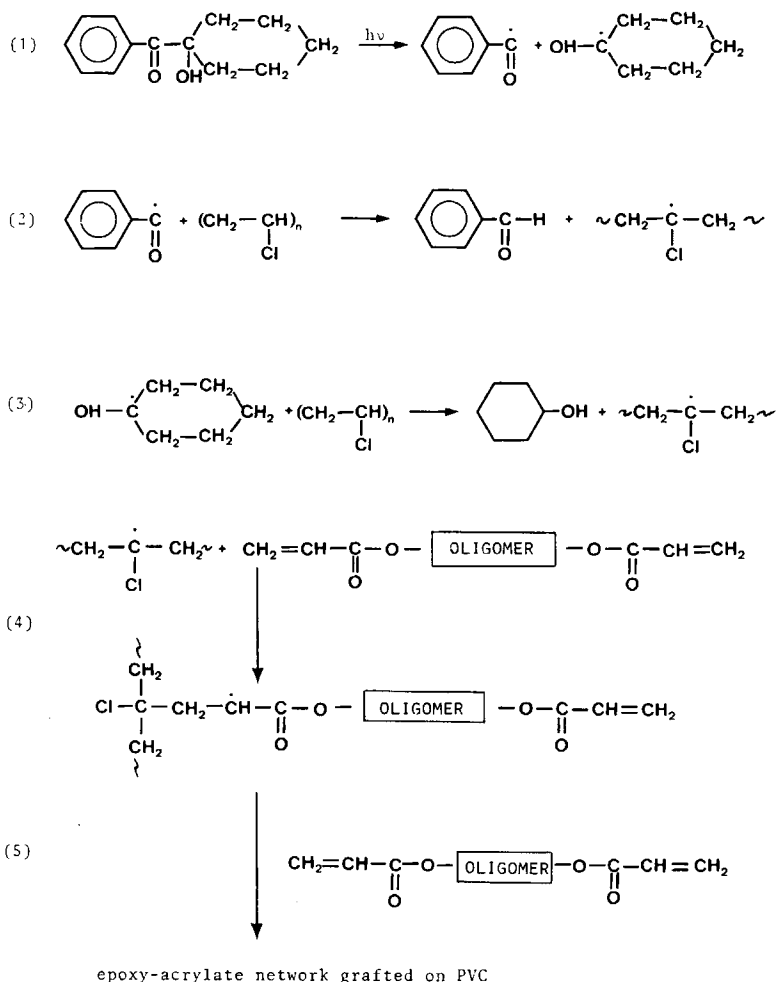


Fig. 5. Photografting of epoxy-acrylate coatings on PVC.

(2) hydrogen abstraction from the PVC chain by the initiator radicals with formation of benzaldehyde and hexanol (reactions 2 and 3);

(3) initiation of the crosslinking polymerization of the diacrylate oligomer by the PVC radicals (reaction 4);

(4) chain propagation and termination leading to an epoxy-acrylate network grafted on to the PVC backbone (reaction 5).

In the absence of free-radical scavenging O_2 molecules, the propagation process develops extensively leading to a highly crosslinked polymer with infinite molecular weight. From the values of the quantum yields of initiation and of polymerization,¹³ we were able to evaluate the kinetic chain length of the crosslinking polymerization; it appeared to be very large, of the order of 10^5 unsaturations consumed per initiating radical. For photopolymerizations carried out in the presence of air, it was not possible to evaluate the kinetic chain length because, although we know the extent to which oxygen reduces the rate of polymerization (a factor of about 7), we were not yet able to estimate the extent

to which it reduces the rate of initiation. More work is now in progress in order to answer this important question.

STABILITY OF THE EPOXY-ACRYLATE COATING

Chemical Stability

Crosslinked epoxy-acrylate coatings were found to be completely insoluble in all the organic solvents tested. They exhibit also a high stability towards corrosive chemical agents and pollutants. Consequently, PVC sheets which have been coated with this UV curable resin become resistant to solvents like THF, DMF, or DMSO, as well as to strong acids like H_2SO_4 , HCl , or HNO_3 . Coated PVC thus behaves as a chemically inert material, comparable to high-density polyethylene or polytetrafluoroethylene.

Light Stability

When epoxy-acrylate coatings are exposed to UV radiations of wavelength above 250 nm and at a light intensity of $\sim 30 \text{ mW}\cdot\text{cm}^{-2}$, they remain remarkably stable, no apparent degradation being observed, even for extended irradiation times up to 100 h. After a small increase of the absorbance in the 300–350 nm wavelength region due to the photodecomposition of the initiator during the first hour of exposure to light, the epoxy-acrylate coating remains clear and completely transparent to visible light. This is one of the main advantages of using Irgacure 184 as photoinitiator rather than Irgacure 651 which shows a comparable initiation efficiency¹⁸ but yields slightly colored photoproducts upon further irradiation or photochemical aging.

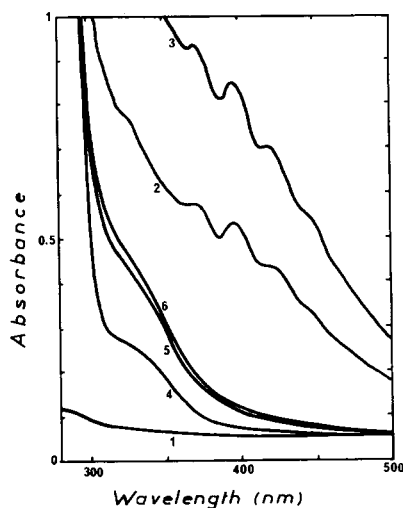


Fig. 6. UV absorption spectra of a 100- μ PVC film (1,2,3) and of an epoxy-acrylate-coated PVC film (4,5,6), initially (1 and 4) and after exposure to UV light for 60 min (2 and 5) and 90 min (3 and 6).

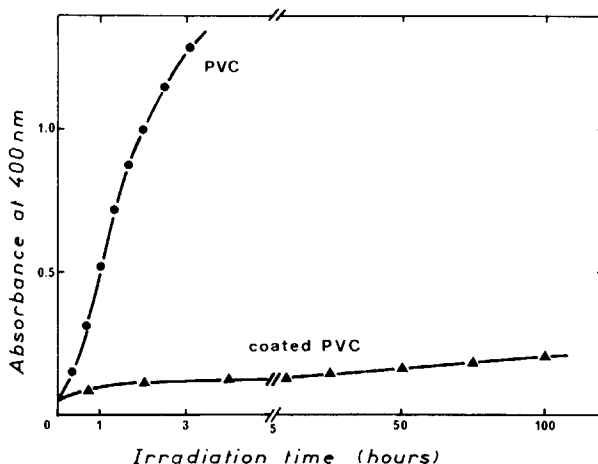


Fig. 7. Kinetics of the discoloration of a 100- μ PVC film (●) and of an epoxy-acrylate-coated PVC film (▲) upon exposure to UV light.

Photostabilization of PVC

Since epoxy-acrylate coatings absorb ultraviolet radiations of wavelength below 300 nm which were shown to be very harmful to PVC,¹⁶ they are expected to act as an effective UV filter, thus preventing the photodegradation of PVC to proceed. This protective action of the coating is clearly apparent on Figure 6, which shows the UV absorption spectra of a PVC film and an epoxy-acrylate-coated PVC film, initially and after 60 and 90 min of exposure to light. While the unprotected PVC film becomes rapidly colored and exhibits the UV absorption spectrum characteristic of polyene structures (spectra 2 and 3), the coated PVC film is not affected at all by the UV radiations (spectra 5 and 6). The kinetics of the discoloration process is shown by Figure 7, where the film absorbance at 400 nm has been plotted against the duration of the exposure to UV light. After 100 h of irradiation, the coated film remains quite transparent and uncolored and exhibits the same absorbance at 400 nm that the uncoated PVC film irradiated during only 20 min. Polyene structures were not detected on the substrate, thus indicating that PVC has been effectively photostabilized by the light-screening epoxy-acrylate coating. The addition of adequate UV absorbers, like benzotriazoles or cyano compounds, into the resin formulation permits further improvement of the light stability of the coating and enhancement of its filter effect, without substantial reduction of the rate of curing.¹⁹

CONCLUSIONS

From the present work it can be concluded that the photografting of multifunctional acrylate resins onto polymer substrates is an efficient method of protecting the surface of polymer-formed materials against photodegradation and weathering since it greatly improves the adhesion of the coating which, in addition, acts as an effective UV screen. The main advantage of using the very reactive α -hydroxy-acetophenone photoinitiators lies in their ability to give clear, nonyellowing epoxy coatings which exhibit a remarkably high photostability.

The grafting method that we developed for epoxy-acrylate coatings on PVC is now being extended to other types of UV curable oligomers like polyester and polyurethane acrylates as well as to other polymeric materials like polyolefins and cellulosic substrates.

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