Ultraviolet-Curable, Abrasion-Resistant, and Weatherable Coatings with Improved Adhesion

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SYNOPSIS

A UV-curable coating for plastics that is abrasion resistant and weatherable is described. The coating consists of colloidal silica functionalized with methacryloxypropyltrimethoxysilane (MAPTMS) in a matrix of acrylic monomers. The formulation employs diethoxyacetophenone (DEAP) as a photoinitiator and a sulfonated benzotriazole as a UV absorber. It has been found that the adhesion of the coating depends greatly on the type of acrylic monomers used and the application parameters. Transmission electron microscopy (TEM) analysis shows that improved adhesion is due to the formation of an interpenetrating layer between coating and substrate.

INTRODUCTION

The range of properties of plastic products such as polycarbonate used in glazing applications is greatly extended by the use of protective coatings.[1] Polycarbonate can be scratched, and it also degrades upon exposure to sunlight.[2] Coatings are desired that are abrasion resistant and minimize the deleterious effects of weathering. Generally, weatherable coatings for these applications are thermally cured via condensation reactions such as that of an alkoxy silicone.[3]

There is currently worldwide interest in UV-curable coatings as a replacement for coatings cured thermally.[4] The UV-curable coatings typically can be applied at higher percentage of solids and have shorter cure times than the thermally cured coatings. Therefore, they minimize solvent emissions and energy requirements.

The lack of adhesion of the coating to the plastic substrate is a commonly encountered problem. Thermally cured coatings often employ a primer to improve adhesion. In the work described here, we utilized UV-cured primerless coatings. While the mechanism of adhesion for our system was not known a priori, the lack of primer and the short contact time between the coating and the substrate due to the fast cure suggested that coating adhesion to the substrate would be an issue.

RESULTS AND DISCUSSION

Over the last several years, a UV-curable and abrasion-resistant coating for polycarbonate has been described.[5] As shown in Scheme 1, the coating contains methacrylate functionalized colloidal silica in a matrix of a 1 : 1 (w/w) ratio of hexanediol diacrylate (HDDA) and trimethylolpropane triacrylate (TMPTA). A photoinitiator such as α,α'-diethoxyacetophenone (DEAP) was also added. The coating formulation was diluted with 50–60% (w/w) of a suitable solvent such as i-BuOH. Sheets of polycarbonate were flow coated with the coating and UV cured under nitrogen.

These cured coatings were abrasion resistant. In Taber abrasion testing after 100 cycles, the uncoated polycarbonate had a percentage of haze value of 36; whereas after 500 cycles, the coated polycarbonate had a percentage of haze value of less than 10.

Upon accelerated weathering (300 h in a QUV weather-o-meter), these coated polycarbonate sheets had yellowness index (YI) values of greater

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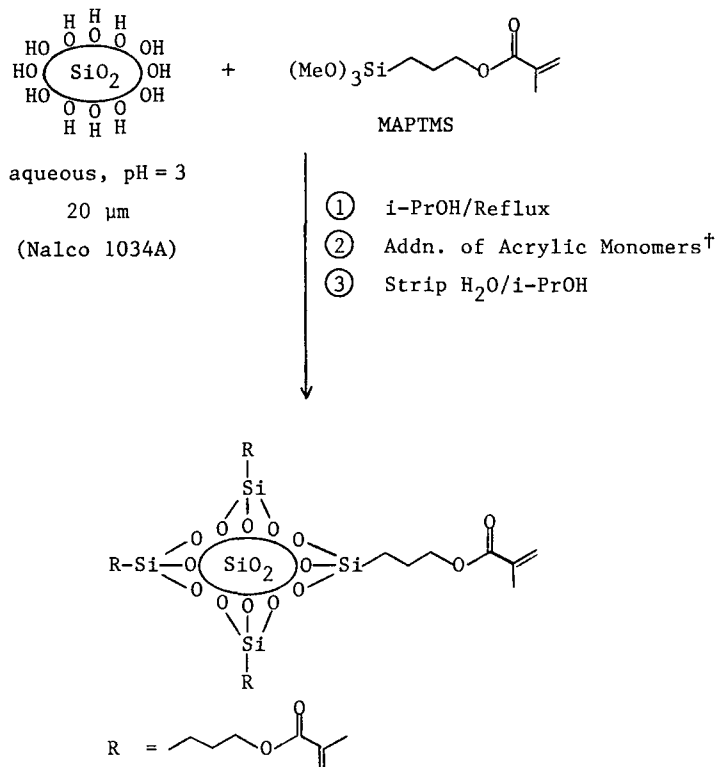
Coating	Acrylic Monomers[†]
1A	Hexanediol Diacrylate (HDDA) + Trimethylol Propane Triacrylate (TMPTA) (1:1 w/w)
1B	HDDA only

**Scheme 1** Preparation of functionalized SiO_2 coating formulation.

than 10. Uncoated polycarbonate also has a YI value of greater than 10 after 300 QUV hours. Yellowness is visibly evident at YI values of 7 and greater.

The use of a UV absorber, such as a benzotriazole, has been shown to improve the resistance of the coatings toward yellowness.[6] However, due to the fact that this was a UV-curable coating, a "latent" UV absorber was required. A latent UV absorber is a molecule whose absorbance does not compete with the photoinitiator absorbance during the cure of the coating. Upon UV exposure (cure lamps and subsequent sunlight exposure), the latent absorber rearranges to a molecule whose absorbance provides protection to the coating and the substrate against yellowing from sunlight (Scheme 2).[7] After 300 h

in QUV, coatings with the latent UV absorber present had a YI value of 3 and were thus more yellow resistant than the coating without UV screen.

Coatings prepared without UV absorber had occasional adhesion failures. Adhesion was measured by the cross-hatch tape test, where a cross-hatch was inscribed into the coating and tape pulled over this area. Removal of any part of the coating by the tape was considered an adhesive failure. The adhesive failures were greatly increased when the UV absorber was added to the coating. The observed increase in adhesive failures may be due to plasticization of the coating by the UV absorber molecule, which may disrupt the coating-to-substrate bonding.

We examined the interface of the coating and the
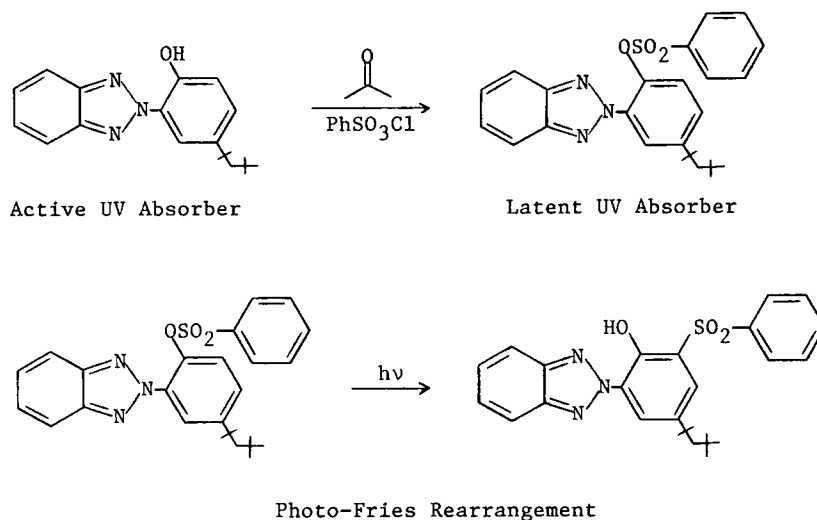
Scheme 2   Latent UV absorber used in the study.[7]

substrate by transmission electron microscopy (TEM). As shown in Figure 1(a), a sharp discontinuity was present between the coating and the plastic. Note that in the higher resolution photograph [Fig. 1(b)] the SiO_2 particles of the coating are clearly visible.

We considered the possibility that penetration of the wet coating to the substrate before cure would improve adhesion. Qualitatively, we found that if the wet contact time was increased, adhesion improved. Several samples of polycarbonate were flow coated and cured after a certain amount of time. The samples cured 1–2 min after flow coating typically failed adhesion, whereas the samples cured 5 min after flow coating typically passed scribed adhesion. When the samples were heated prior to flow coating, the adhesion was also improved. We believe that the effect of contact time and temperature of the samples is related to the diffusion of the wet coating into the polycarbonate. Note that the samples that passed initial scribed adhesion failed scribed adhesion after ca. 450 h of accelerated weathering.

The HDDA alone was an aggressive monomer toward polycarbonate, e.g., application of neat HDDA to the plastic surface resulted in immediate haze formation. A formulation was prepared according to Scheme 1 with HDDA as the only acrylic monomer present (coating 1B). Unlike HDDA alone, which hazed the polycarbonate surface after flow coating, the functionalized colloidal silica formulation in HDDA did not haze the plastic surface. Every coating made in this way passed the initial scribed adhesion. Furthermore, whereas all of the

coatings that contained HDDA/TMPTA failed scribed adhesion after ca. 400 h of accelerated weathering in QUV, no adhesion failures were observed up to 1000 h of QUV accelerated weathering for the silica coating that contained HDDA alone.

Analysis of the coating 1B–substrate interface by TEM is shown in Figure 2. As shown in the figure, a definite interlayer existed between the coating and the substrate. Assignment of the interlayer as an interpenetrating layer between the coating and the substrate was supported by the fact that a lower density of silica particles was present in the interlayer region than in the coating region. This observation was consistent with the interlayer being partially composed of coating and partially composed of polycarbonate.

The 1B coating provided improved adhesion without loss of any of the other properties of the 1A coating. Both coatings had similar Taber abrasion values, less than 10 after 500 cycles, and YI values of 2 after 800 QUV hours. The 1B coating was 8–9 μm thick with a 2-μm interlayer while the 1A coating was 11–12 μm thick.

CONCLUSION

We have described a UV-curable coating for plastics such as polycarbonate that was abrasion resistant and weatherable. We have demonstrated that with the right choice of monomers and application parameters, coatings with excellent adhesion to the polycarbonate can be obtained.
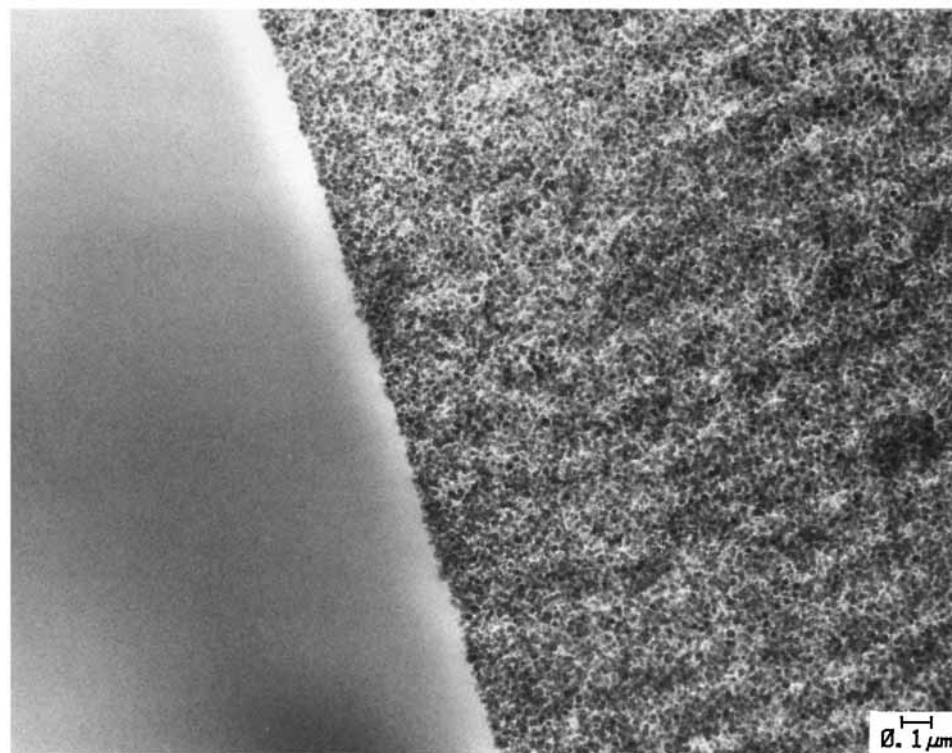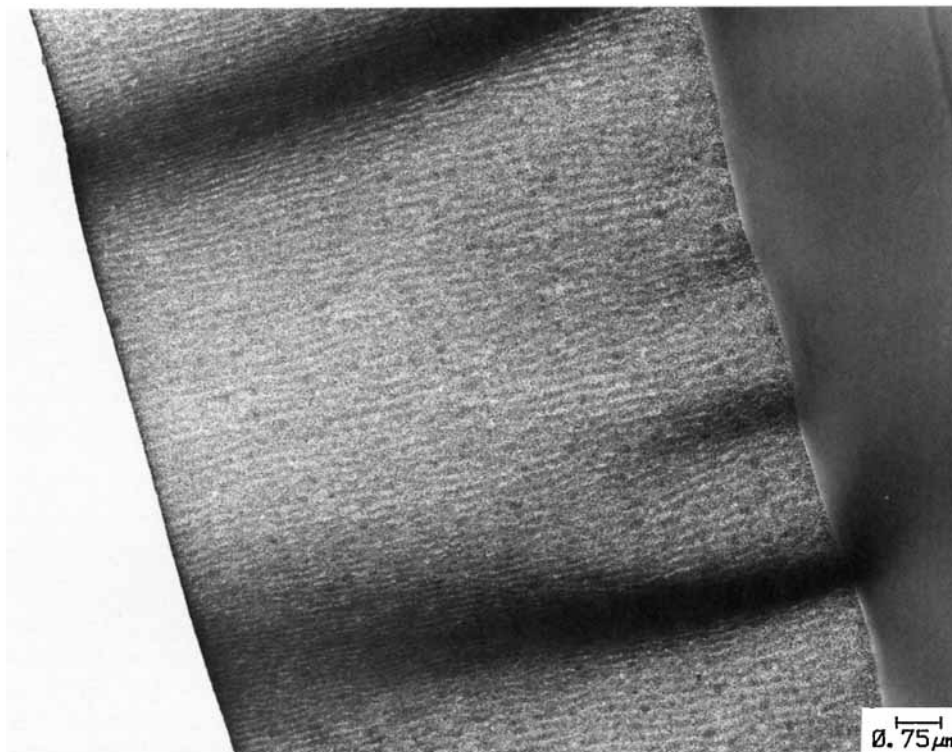
Figure 1   TEM of the interface formed between coating 1A and the polycarbonate substrate. Note the sharp discontinuity between coating and substrate. Part (b) shows higher magnification; note the SiO_2 particles are clearly visible in the coating.
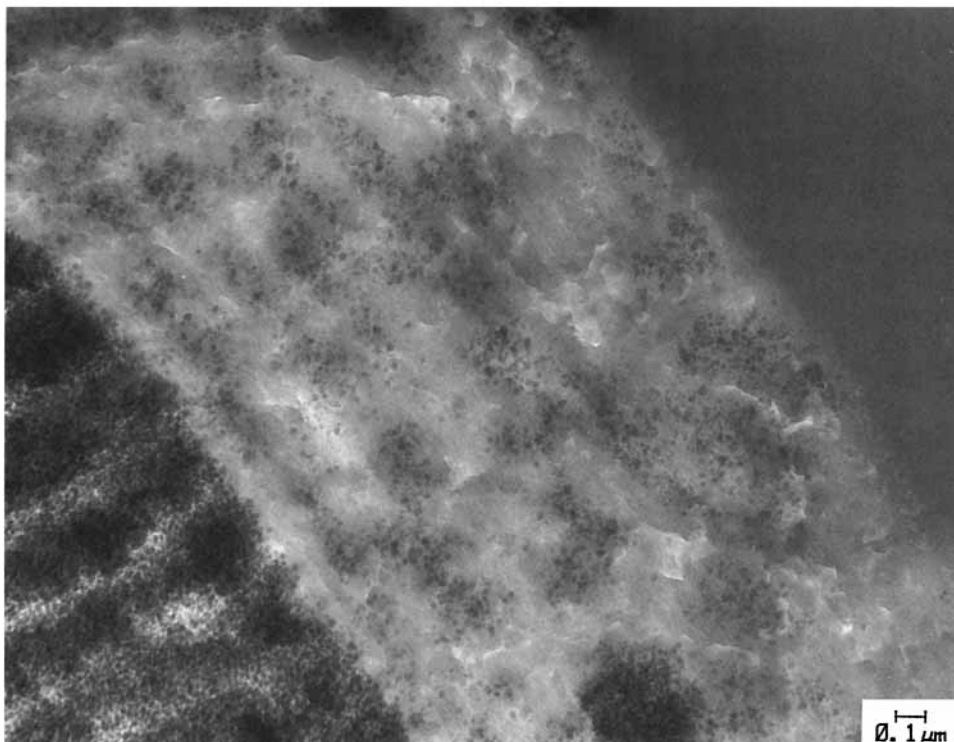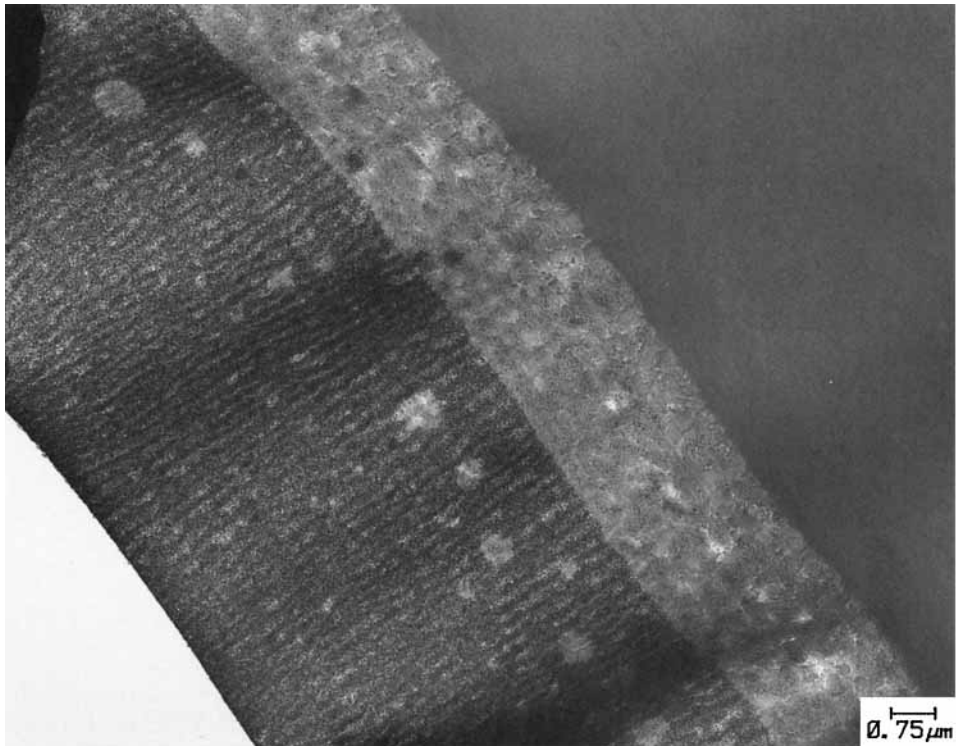
Figure 2   TEM of the interface formed between coating 1B and the polycarbonate substrate. Note the presence of a 2-μm interpenetrating layer. In the higher magnification picture [part (b)] note the lower concentration of SiO₂ particles in the interface region relative to the higher concentration of particles in the coating.

EXPERIMENTAL

Formulation Preparation

A typical preparation of coating formulation 1B follows. To a three-neck, 5-L flask equipped with a thermometer, gas inlet, reflux condenser, and magnetic stir bar was added 2250 g i-PrOH, 70 g methacryloxypropyltrimethoxysilane (MAPTMS), and 468.3 g Nalco 1034A. Nalco 1034A was a product of the Nalco Chemical Co. and contained 34% by weight colloidal silica in water at pH 3.0 with 20-nm particles. The mixture was heated to reflux for 1.5 h, bath temperature not exceeding 100°C. After the heating period, 195.3 g HDDA was added followed by stirring for 5 min. The IPA–H_2O azeotrope was removed via vacuum distillation, with pressure maintained between 70 and 100 mm and a bath temperature of 60°C.

The UV absorber described in Scheme 2 was prepared according to the literature procedure.[7]

Coating Preparation and Curing

A typical formulation that contained 2% DEAP and 7% UV absorber was prepared by combining 45 g coating formulation 1B, 3.5 g UV absorber, and 1 g DEAP; 8 g of this mixture was then combined with 12 g of i-BuOH. The coating solution was used to flow coat a $4 \times 4 \times \frac{1}{4}$-in. Lexan polycarbonate plaque. After standing for 2 min, the plaque was UV cured in a PPG model QC 1202 processor using two water-cooled, 12-in., 300-W/in., medium-pressure mercury lamps at 20 ft/min under nitrogen. The nitrogen blanket was obtained from liquid nitrogen boiled off at a flow rate of 15 scfm.

Testing

Abrasion resistance measurements were made with a model 5150 Teledyne Taber abraser using CS-10F wheels with a 500-g load on each wheel. The abrasion wheels were refaced after each sample using S-11 refacing discs for 25 cycles. The change in the percentage of haze before and after abrasion in each sample was measured on a Gardner model UX10 hazemeter. The values reported were the average of four determinations. Yellowing data, YI values, were recorded on a Gardner model XL-20 colorimeter. Adhesion measurements were made using 3M 610 tape and pulling the tape over a cross-hatched scribe made into the coating. Accelerated weathering of the samples took place in a QUV weather-o-meter using UVB lights. Weathering cycle: 8 h, light, dry at 70°C; 4 h dark, condensation at 50°C. All lights rotated every 400 h and replaced every 1600 h. South Florida testing was carried out by South Florida Test Services where samples were exposed at a 45° angle.

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