Preparation and Characterization of Spironaphthooxazine/Polyacrylate Photochromic Hard Coatings on Plastic Substrates

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Abstract

Optical coatings exhibiting photochromic effects were prepared by UV-curing of a coating formulation that incorporates a hexa-functional monomer, DPHA, and an organic dye, spironaphthooxazine. Spectroscopic studies of the coatings indicated efficient photochromic activities in response to UV irradiation. The depth of color and the rate of bleaching at 610 nm were found to depend on the UV dosage and the dye content; specifically, the transmittance returned from 42 to 82\% and from 38 to 67\% in 60 s. for the coating containing 3.7 wt\% dye that received 0.45 and 3.6 of J/cm\textsuperscript{2} of UV exposure, respectively. Furthermore, the coatings were very hard (7H, pencil hardness) and adhered perfectly (100\%, peel test) on poly (methyl methacrylate) substrates.

Key Words: Photochromic, Coatings, Spirooxazine, Polyacrylate

1. Introduction

Organic dyestuffs exhibiting reversible photochromic properties are used in a wide variety of commercial products, e.g., eye glasses, building windows, clothes, etc. When exposed to UV/Vis irradiation, the dye molecules undergo molecular structure change or electron transfer, e.g., cis-trans isomerization, to give a different color. And when the light source is removed, the reaction reverses and the molecules regain their original state and color. Such extraordinary non-contact mode of reversible structural/property alteration (via photo energy conversion) has made the photochromic dye a target of extensive research in recent years [1–23].

To realize practical applications, the dyestuffs are generally required to disperse in a matrix, which can be shaped into films, wires, tubes, etc. to meet specific needs. Preparation of photochromic hard coatings on plastic substrates is of our major concern in the present investigation [18]. In addition to photochromic response, these coatings also serve as a protective layer for the plastic substrates that are susceptible to mechanical damages. Photochromic coatings have frequently been reported in the literature [11–14,17–21]. For example, Hou and Schmidt used the sol-gel method to prepare silica-based Ormocer coatings, which incorporated the silylated spiroooxazine dyestuff [20]. The de-coloration study indicated that silylation would not affect the photochromic intensity, yet would give rise to a reduction of bleaching rate and a significant deviation from first-order kinetics. Yamano and Kozuka prepared poly (methyl methacrylate) (PMMA)-silica hybrid coatings heavily loaded with 20 wt\% spiropyran on silica glass plates [21]. The coatings showed visual color changes in response to UV/Vis illumination. While employment of PMMA was found to improve the chemical durability of the coatings against xylene leaching, excess amount of PMMA caused photo-degradation due to formation of
spiropyran aggregates. Gao et al. synthesized acrylate-functional viologen (dye) and then UV-cured it with polyester urethane diacrylate and acrylic monomers to form films that exhibited both photo- and electro-chromic properties [22,23].

Although many kinds of photochromic films have been successfully prepared and well documented, most of them were coated on glass surfaces. To form films on plastic substrates, adherence and mechanical strength of the coatings have to be considered in addition to the photochromic response. In this research, spironaphtho-oxazine was employed to prepare photochromic hard coatings on PMMA substrates. The compound is derived from spiropyran with the C=C bond of the latter being replaced by the C=N bond. As shown in Figure 1, the mechanism for photochromism is associated with reversible transformation between the spiro and merocyanine forms (termed S-form and M-form, hereinafter) of the compound, which involves heterolytic cleavage of the C-O bond and cis-trans conversion with respect to the C=N bond [12,13,20]. Coatings were prepared by UV-curing of a multi-functional acrylic monomer along with the dye compound on PMMA substrates. Their hardness, adhesiveness, and photochromism were examined and the results are discussed in this report.

2. Experimental

2.1 Materials

Spironaphthooxazine was purchased from Aldrich. Methyl ethyl ketone (MEK, > 99.5%) was purchased from J. T. Baker and was used as the solvent for preparing coating sols. The crosslinking agent, dipentaerythritol hexaacrylate (DPHA, regent grade), was purchased from Aldrich. The photoinitiator, 2-hydroxy-2-methyl-1-phenyl propan-1-one, (Darocure 1173) was supplied by Ciba-Geigy. All materials were used as received.

2.2 Preparation of Photochromic Coatings

The sample codes and compositions for all coating sols are summarized in Table 1. As an example, the preparation procedure of the sample D4 is described below. 0.03 g of spironaphthooxazine and 0.72 g of DPHA were dissolved in 1.125 g of MEK to form a homogeneous solution. This solution appeared reddish-purple initially and it changed gradually to pale yellow upon standing over the period of ~24 h. To the solution, 0.0375 g Darocure 1173 was added to give a coating sol that has a theoretical solid content of 41 wt%. The sol was spin-coated (500 rpm, 15 s) on PMMA substrate, prebaked at 80 °C for 1 min, and then UV irradiated (1000 mJ/cm², broadband) to yield a cured film on the substrate. The thickness of the film was measured to be ~5.5 μm by means of a surface profilometer, and the dye content is 3.8 wt%.

2.3 Characterization

The following methods were employed to characterize the synthesized materials:

(1) Infrared absorption spectra of the coating sol and cured films were obtained using a Fourier transform infrared (FTIR) spectrophotometer (Nicolet spec-
trometer 550, USA). Samples were prepared on KBr discs, and the spectra were collected over the wavenumber range of 400–4000 cm\(^{-1}\) with resolution set at 4 cm\(^{-1}\).

(2) The photochromic performances of the prepared hard coatings were studied by a UV/visible spectrometer (UV500, Unicam) over the wavelength range of 400–800 nm. The photochromic coating was UV-irradiated (350–450 nm) at 15 mW/cm\(^2\) for a short period of time (typically, 30, 50, 100, or 240 s) and then the bleaching spectra of the coating were recorded at different times until color changes become visually undetectable.

(3) Morphology of the cured films was observed using a field emission scanning electron microscope (FE-SEM, S4800, Hitachi). The samples were vacuum-dried and then fractured in liquid nitrogen to expose the cross section. The lateral sides of the samples were wrapped with conductive copper tape and clamped in a sample holder. Silver paste was applied at the edges of the sample to enhance electronic conductivity. It was then sputtered with a thin layer (ca. 1.0 nm) of a Pt–Pd alloy and imaged at high magnifications (e.g. 100 KX) under the acceleration voltage of 15 kV via an in-lens detector.

(4) Surface profile and thickness of the coatings were obtained by a surface profilometer, EZSTEP, Force Precision Instrument Co. The force exerts on the sample surface was 4.9 × 10\(^{-5}\) N, the scanning rate was 4 mm/s, and the length of each scan was 0.9 mm.

(5) Tape test (ASTM D3359), also called peel test, was carried out to evaluate the adhesion strength of cured coatings on the PMMA substrate. The degree of adhesion was recorded as the percentage of the residual film on the substrate after peeling by standard tapes (3M-610). The hardness (ASTM D3363) of the cured coatings was examined by the widely used pencil hardness test, using pencils of different hardness at the load of 750 g.

3. Results and Discussion

The FTIR spectra of spirooxazine, DPHA, and cured film (D4) are shown in Figure 2. The absorption band at 1607 cm\(^{-1}\) in Figure 2(a) is assigned to the vibration of C=C stretching in benzene ring of spironaphthooxazine, which is absent from the spectrum of pure DPHA, Figure 2(b). The C=O of DPHA is located at 1727 cm\(^{-1}\). The absorption bands at 1619 and 1635 cm\(^{-1}\) correspond to the stretching vibration of the aliphatic C = C in DPHA. After receiving 1400 mJ/cm\(^2\) of UV-irradiation, the intensities of these bands decreased by ~40% (with reference to

Figure 2. FTIR spectra of (a) spirooxazine; (b) DPHA; (c) coating DD4.
C=O), as shown in Figure 2(c). As each DPHA molecule has 6 vinyl groups available for free radical polymerization, it is expected that the crosslinking degree would approach 100%; thereby a strong polymeric network was formed with dyes dispersed in it. Also, the C=O and the aromatic C=C bands in the coating shift slightly compared with those in unreacted DHPA and spironaphthooxazine.

Figure 3 shows the bleaching spectra of the coating, D4, which has been UV-irradiated for 30s. A major absorption band at 610 nm and a small less significant one at 525 nm can be identified. These two bands correspond to the absorption by the M-form and S-form of spirooxazine in the DPHA matrix, respectively. In other words, the coating appears pale-red with a 70% transmittance at 525 nm at ambient condition, while upon UV-exposure for 30 s., its color changes to blue with a transmittance as low as ~42% at 610 nm. After removed from the UV source, the transmittance of the coating increases very rapidly initially, then the increment rate turns slow, and finally after 20 min of free standing, the coating recovers nearly to its original pale-red color. This de-coloration behavior is thought to be associated with the relative population of the S-form and M-form of the dye. Right after removing from UV irradiation, the population of M-form is high while that of S-form is low, which favors a fast conversion of M-form to S-form. However, at the late stage of the bleaching process, population of the M-form molecule falls, resulting in a smaller concentration driving force for M-to-S conversion, and thus a sluggish increment of transmittance is observed. The evolution of color during a typical bleaching process for the sample D4 is manifested in Figure 4. The blue color changes quickly to light-purple in 20 s, yet it takes another 20 min to change from light-purple to pale-red.

The effect of exposure time on photochromic performance is shown in Figure 5. As is expected, the longer the exposure time, the lower the transmittance, which is due to the fact that larger amount of M-form molecules are generated for coating receiving higher amount of UV-dosage. However, it is also noted that the depth of color approaches saturation at exposure time of ~4 min; longer irradiation deepened the color only limitedly. The bleaching rate also varies with the exposure time. For illustration, Figure 5(b) compares the transmittance (614 nm) versus bleaching time of the coating D4 that has been subjected to 30 and 240 s of irradiation. For both cases, the transmittance changes very sharply for the first 20 s, which corresponds to the fast color recovering period indicated in Figure 4. After ~5 min, the curves flatten-out, and the transmittance increases so slowly that variation in color is almost undetectable by bare eyes. Although both cases demonstrate efficient photochromic response, there is still difference in their bleaching rates. For example, at 1 min. after removing from the UV source, the transmittance of the coating with 30 s of exposure changes back to 82%; yet

![Figure 3. Bleaching spectra for the coating D4. UV exposure time = 30 s.](image)

![Figure 4. Change of color for sample D4 during a typical bleaching process. (a) before UV-irradiation, (b) 1 s, (c) 20 s, (d) 1 min, (e) 5 min, (f) 20 min, after UV exposure for 4 min.](image)
it is only 67% for the coating that has been shined for 240 s. Obviously, this is because there is larger amount of M-form molecules that need to be transformed to S-form in the latter UV-irradiation case.

The effect of dye-content in the coating on bleaching behavior is demonstrated in Figure 6. The coatings contain, 1.9, 3.8, and 5.7 wt% of dye, and all of them have received 240 s. of UV irradiation beforehand. As is expected, the coating with lower dye content has higher transmittance (i.e., lighter color) and it took shorter time to retrieve its original color than that with higher dye content. For example, after 20 s. of bleaching, the transmittance of D2 already reaches 87% (close to the transmittance before UV exposure, 92%) while that of D6 is 54%, much lower than the initial coating. This phenomenon is associated with the fact that population of M-form after UV-exposure is much higher for coatings with higher dye contents. As a result, even with a higher initial bleaching rate, it still takes much longer time for D6 to regain its original color than D2. Since darker color takes longer time to recover, a compromise between depth of color and recovering time has to be made in practical cases.

Morphologies of the coatings were observed by FESEM. Figure 7 shows the cross sectional view of the sample D4. It is dense and uniform without any evidence of aggregated domains or particulate objects under the resolvable length scale of 20 nm (cf. the high magnification image in the inset), which suggests that DPHA and spironaphthoxazine have certain compatibility so that after UV-cured, a homogeneous film can be formed free of nano-scale phase separation. This result echoes the bleaching photographs shown in Figure 4, for which uniform colors are seen across the entire surface (except for the thicker edges). The surface roughness of various coatings was determined by profilometry. As an example, Figure 7(b) shows the surface profile of the sample D4. It is very smooth with a maximum peak-to-trough height of ~24 nm over the scanning range of 120 μm. The average roughness ($R_a$) is as small as 1.6 nm. Surface

**Figure 5.** (a) Spectra of the coating D4 at 1 min. after turning off the UV; exposure times being 30, 60, 120, and 240 s, respectively. (b) Transmittance (614 nm) during bleaching of the coating D4 subjected to 30 and 240 s of irradiation.

**Figure 6.** Transmittance (614 nm) during bleaching of coatings containing different amounts of dye. The coatings have been UV-irradiated for 240 s.
roughness of other samples is listed in Table 2. D6 has a slightly higher surface roughness than both D2 and D4, which may be caused by compatibility (between DPHA and spironaphthooxazine) reduction at higher dye contents — as is evident from the fact that some localized haziness and uneven color distribution is already seen on D8. Thickness of the coating layer of D4, also measured by the surface profilometer cf. Figure 7(c), is found to be ~5.5 μm, which is in agreement with the value determined from SEM imaging. As the solid content for all coating sols was kept at 40%, it is expected that thicknesses of all coatings should be close.

The hardness of various coatings was tested using the industrial pencil-test method. The tested results are listed in Table 2. All of the samples are very hard, ~6–7 H, except for D8. Such high hardness stems from the strong cross-linked network provided by the hexa-functional monomer, DPHA, as is also evident from the thermogravimetric analysis (TGA) data of cross-linked DPHA, where decomposition temperature higher than 435 °C has been reported [24]. In contrast, if a mono-functional monomer such as 2-HEMA was employed rather than DPHA as the precursor of the polymeric matrix, the cured film would have hardness of only ~1H, which appeared to be too low for practical usage. The coatings D8 has lower hardness, 5H, because phase separation due to over-saturation of dye in the polymer matrix has occurred. The aggregated dye-rich domains are expected to be weaker than the polymer bulk. Phase separation also gives rise to poorer adherence to the PMMA substrate; as is seen from the peel test results shown in Table 2, the coating D8 only has 90% adherence, while D2, D4, and D6 adhere perfectly (100%) to the PMMA substrates.

4. Conclusions

High hardness photochromic coatings were successfully prepared via UV-curing of the cross-linking agent DPHA together with the organic dye, spironaphthooxazine. The hardness, adherence and surface roughness of the coatings are listed in Table 2. D4 has the highest hardness, 7H, while D8 has the lowest, 5H. D4 also has the highest adherence, 100%, while D8 has the lowest, 90%. The surface roughness of D4 is the lowest, 1.3 nm, while D8 has the highest, 5.5 nm.

Table 2. Hardness, adherence and surface roughness of the coatings

<table>
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<th>Code</th>
<th>Hardness</th>
<th>Adherence (%)</th>
<th>(R_a) (nm)</th>
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<tr>
<td>D2</td>
<td>7H</td>
<td>100</td>
<td>1.7</td>
</tr>
<tr>
<td>D4</td>
<td>7H</td>
<td>100</td>
<td>1.3</td>
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<tr>
<td>D6</td>
<td>6H</td>
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<td>2.6</td>
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<tr>
<td>D8</td>
<td>5H</td>
<td>90</td>
<td>5.5</td>
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Figure 7. (a) SEM micrographs of the cross section of the coating D4; on the upper-left corner is the high magnification image; (b) Surface profile of the coating D4 measured by surface profilometer; (c) Thickness of the coating measured by surface profilometer.
oxazine. Upon UV irradiation, the coatings changed their colors from pale red to blue, and they bleached rapidly when the irradiation was turned off. The bleaching time was found to depend on the UV dosage and the dye-content in the coating; the higher the latter two factors, the darker the color and the longer it takes to bleach. Furthermore, the coatings were robust (hardness up to 7H), and adhere strongly to the PMMA surface.

Reference


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