

Effect of artificial weathering on surface properties of unsaturated polyester (UP) resin

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ABSTRACT

Unsaturated polyester resin samples were exposed to artificial weathering environment for different time intervals. The change of appearance, morphology, chemical structure and contact angle on unsaturated polyester resin surface before and after exposure in this environment was monitored by spectrophotometer, gloss meter, microscope, Specular Reflection Fourier Transform Infrared (SR-FTIR) spectroscopy and optical contact angle measuring device. The results showed that the surface of unsaturated polyester resin turned darker and yellower in the first stage and then remained nearly unchanged during further ageing. Gloss reached maximum when the sample was aged for 12 days and then decreased. With increasing aging time, small cracks appeared and developed on the unsaturated polyester resin surface. Hydroxyl and carbonyl groups produced in aging process increased the wettability of unsaturated polyester resin surface.

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1. Introduction

Unsaturated polyester (UP) resin is an important kind of thermosetting material on the market today. It can be widely used in many fields [1–4] due to its low cost, easy processing and good mechanical properties. In outdoor applications, the weathering conditions such as ultraviolet (UV) radiation [5], heat [6,7] and water [8,9], etc., deteriorate its surface properties and reduce the service lifetime. So it is essential to investigate the surface properties of UP resin in such conditions.

Natural weathering tests are often used to evaluate the durability of materials, but they are time-consuming and the environmental factors are not easily controlled. In the laboratory, artificial weathering test is often adopted to study the materials durability. Carrasco et al. [10] studied the aging of high-density polyethylene in artificial weathering environment and found that UV radiation was the main environmental factor affected its behavior. Jakubowicz [11] studied the effect of artificial weathering test on the impact strength of poly(vinyl chloride), where a xenon arc was used as the light source. However, there are few

reports focused on surface properties of unsaturated polyester resin in artificial weathering environment, where UV fluorescent lamp was used as light source and condensation equipment was adopted.

The objective of the present work was to investigate the surface properties of unsaturated polyester resin upon exposure to an artificial weathering environment produced by fluorescent UV/condensation weathering equipment. The change of appearance, morphology, chemical structure and contact angle on UP surface before and after exposure in this environment was monitored by spectrophotometer, gloss meter, microscope, Specular Reflection Fourier Transform Infrared (SR-FTIR) spectroscopy and optical contact angle measuring device.

2. Experimental

2.1. Material

The material used in this study was a commercially available unsaturated polyester resin with the trade name of J-108 supplied by Beijing Beianhe Glass Reinforced Plastic Factory, China. The chemical structure is shown in Fig. 1. Methyl ethyl ketone peroxide was used as initiator and cobalt naphthenate was used as accelerator. The acid number is 18 mg KOH g⁻¹ and the viscosity is 0.45 Pa s (25 °C). The mixture composed of a measured quantity of UP resin, 1.96 wt.% of initiator and 0.45 wt.% of accelerator, was degassed in a vacuum chamber for 5 min at 0.1 MPa. Polymerization was completed under ambient environment for 12 h in a specially prepared mold to yield rectangle sheets with dimensions of 135 mm × 40 mm × 5 mm.

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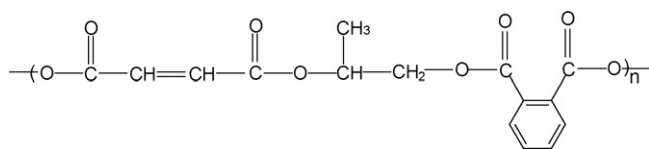


Fig. 1. Molecular structure of unsaturated polyester.

2.2. Artificial weathering test

Artificial weathering test was carried out in fluorescent UV/condensation weathering equipment (UV 2000TM, USA). The samples were exposed for different time intervals up to 48 days. The cycle consisted of 4 h of UV ($\lambda = 313$ nm) radiation at 50 °C and 4 h of condensation at 50 °C. The irradiance intensity was 0.55 W m⁻².

2.3. Color changes

Surface color changes were measured using a spectrophotometer (GretagMacbeth COLOREYE XTH, USA). The change of color ΔE was calculated by the equation $\Delta E = \sqrt{(\Delta L)^2 + (\Delta a)^2 + (\Delta b)^2}$, where ΔL represents the brightness relationship between light and dark, Δa represents the relationship between green and red and Δb represents the relationship between blue and yellow. The symbol Δ implies the difference between the samples before and after being aged. Yellow index (YI) was calculated from the equation $YI = (100(1.28X - 1.06Z))/Y$, where YI represents yellow index, X, Y and Z represent tristimulus values.

2.4. Gloss measurement

The specular gloss is given by the ratio of the two fluxes reflected in a selected specular direction, one on the sample and the other on the standard. The calibration was performed on the black gloss standard. Surface gloss measurements were recorded through a portable gloss meter (XGP, China) using a 60° incidence angle.

2.5. Morphology observation

The surface morphology of UP surface was observed by a three-dimensional digital microscope (VHX-100K, Keyence Corporation, Japan). The magnification ratio was 500.

2.6. Specular Reflection Fourier Transform Infrared (SR-FTIR) analysis

The surface chemistry was monitored by SR-FTIR spectroscopy analysis conducted on the exposed side of the samples using a Spectrum GX spectrometer (PerkinElmer, England) with 32 scans and a resolution of 4 cm⁻¹.

2.7. Contact angle and surface energy measurement

The contact angles were measured by using an OCA15 plus optical contact angle measuring device (Data Physics Instruments GmbH Corporation, Germany). Water and formamide were used as the probe liquids. For each liquid, three measurements were performed and the average was recorded. A standard deviation of $\pm 3\%$ could be obtained.

To calculate the surface energy from contact angles, the Fowkes' theory is one of the most recognized methods. The surface energy is split into a dispersive and a polar component: $\gamma = \gamma^d + \gamma^p$, where γ is the surface energy, γ^d and γ^p represent the polar and the dispersive component, respectively. The work of adhesion W^a can be expressed as: $W^a = 2(\gamma_s^d \gamma_l^d)^{0.5} + 2(\gamma_s^p \gamma_l^p)^{0.5} = \gamma_l(1 + \cos \theta)$, where indices s and l represent solid and liquid, respectively, and θ is the contact angle. According to the contact angles of water and formamide, the dispersive and the polar component can be calculated, and then the surface energy can be obtained. The parameters of the liquids used in this measurement are given in Table 1 [12].

3. Results and discussion

3.1. Change in surface color

The change in surface color of UP sample exposed in artificial weathering environment was evaluated by the ΔE and YI measurement.

Table 1
Parameters of water and formamide.

Liquid	γ (mJ m ⁻²)	γ^d (mJ m ⁻²)	γ^p (mJ m ⁻²)
Water	72.8	21.8	51.0
Formamide	58.2	39.5	18.7

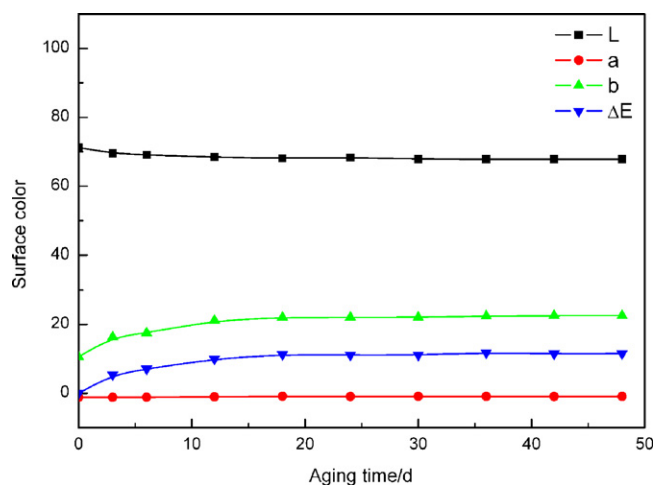


Fig. 2. Effect of aging time on surface color.

Fig. 2 illustrates the effect of aging time on the surface color. It can be seen that the lightness index L decreased slowly from 71.25 to 69.10 after 6 days of aging and then kept almost unchanged. Color index a changed little in the whole aging process. Color index b increased in the first 12 days from 10.59 to 21.14, which means the surface changed from blue to yellow, and then subsequently remained stable. ΔE changed in nearly the same way as b , it rose sharply in the first 18 days from 0 to 11.28 and then leveled off in the range of 11.09–11.52. YI measurement was also conducted to get detailed information about the surface color change. Fig. 3 presents the effect of aging time on UP surface YI. It can be seen that the change of YI is similar to that of ΔE . It increased in the first 18 days from 24.16 to 47.32 and then leveled off in the following days.

From the above results it can be concluded that compared with the unaged sample, the surface of the aged UP resin turns yellower and darker in the first stage of artificial weathering test and then remains almost unchanged in the following days.

3.2. Specular gloss

Gloss is an important parameter to characterize the surface optical properties, defined as the specular reflection ability of a material surface under a particular standard source and using a particular incidence angle. Effect of aging time on surface specular gloss of a

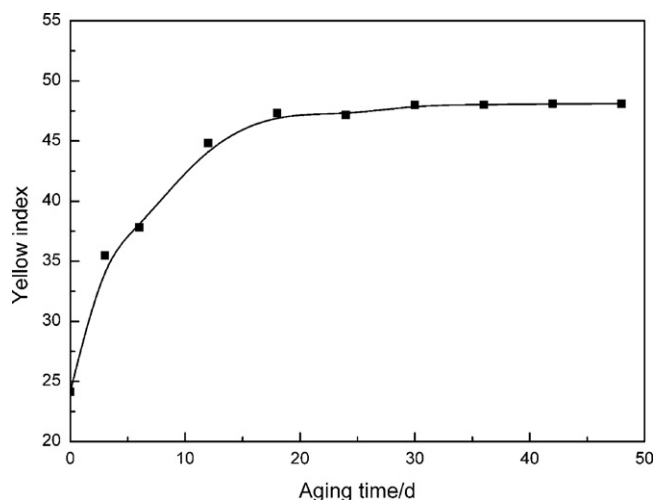


Fig. 3. Effect of aging time on surface yellow index.

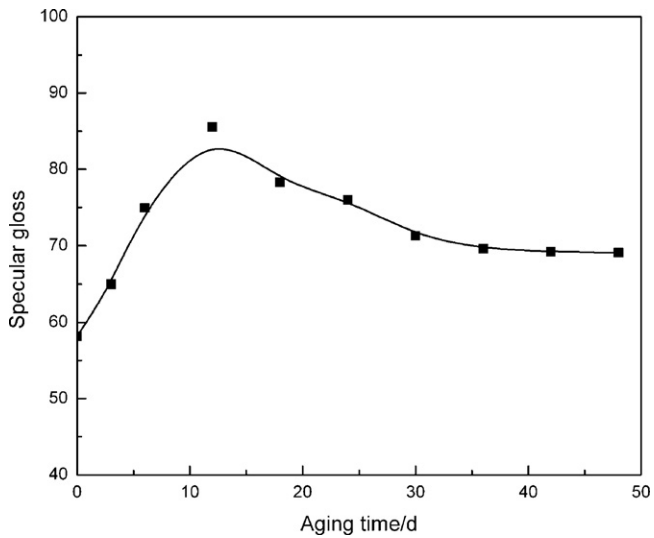


Fig. 4. Effect of aging time on surface specular gloss.

specimen is presented in Fig. 4. It can be observed that with increasing aging time, the specular gloss increased at the initial stage and reached a maximum at 12 days of aging, then began to decrease.

3.3. Morphological observation

Fig. 5 shows micrographs of UP samples before and after aging for different times in the artificial weathering environ-

ment. No cracks were observed on the unaged UP sample surface. After 12 days of aging, small cracks appeared. With increasing aging time, the size and number of small cracks increased. When the aging time reached 48 days, the cracks became deeper and wider.

In the artificial environment, the cycle consisted of 4 h of UV ($\lambda = 313 \text{ nm}$) radiation at 50°C and 4 h of condensation at 50°C . During the aging process, the absorbed water in the condensation phase would have occupied the voids resulted from the break of the bond caused by photo-degradation and hydrolysis of the polymer. With increasing aging time, the water in the voids would cause the accumulation of hygroscopic stress which could crack the resin when it gets a finite value [13].

3.4. SR-FTIR analysis

The chemical changes of UP surface in artificial weathering environment were detected by SR-FTIR. Fig. 6 shows the FTIR spectra of UP specimens before and after exposure for different times. Ten characteristic absorption peaks can be observed in the spectrum of the unaged UP resin. The peaks at 2950 cm^{-1} and 1377 cm^{-1} are assigned to asymmetric C–H stretching vibration and symmetric C–H deforming vibration of methyl, respectively, while the peak at 1453 cm^{-1} is assigned to $-\text{CH}_2-$ scissoring vibration. The peak at 1728 cm^{-1} is assigned to C=O stretching vibration of ester. The peaks at 1287 cm^{-1} and 1134 cm^{-1} are assigned to asymmetric and symmetric C–O–C stretching vibration of aromatic ester, respectively, while the peaks at 1160 cm^{-1} and 1072 cm^{-1} are assigned to asymmetric and symmetric C–O–C stretching vibration of aliphatic ester, respectively. The peaks at 764 cm^{-1} and 703 cm^{-1}

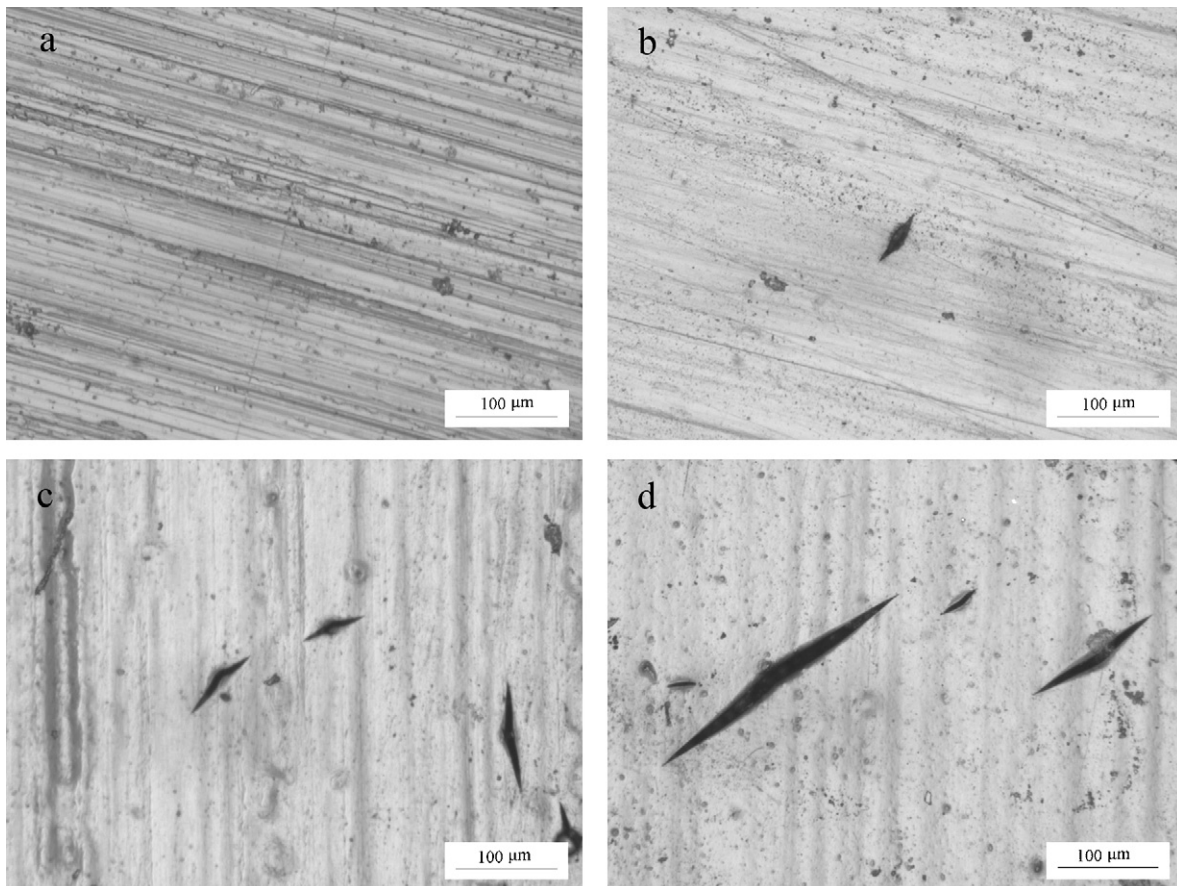


Fig. 5. Micrographs of UP specimens exposed to artificial weathering environment for different times: (a) 0 day (500 \times), (b) 12 day (500 \times), (c) 30 day (500 \times), and (d) 48 day (500 \times).

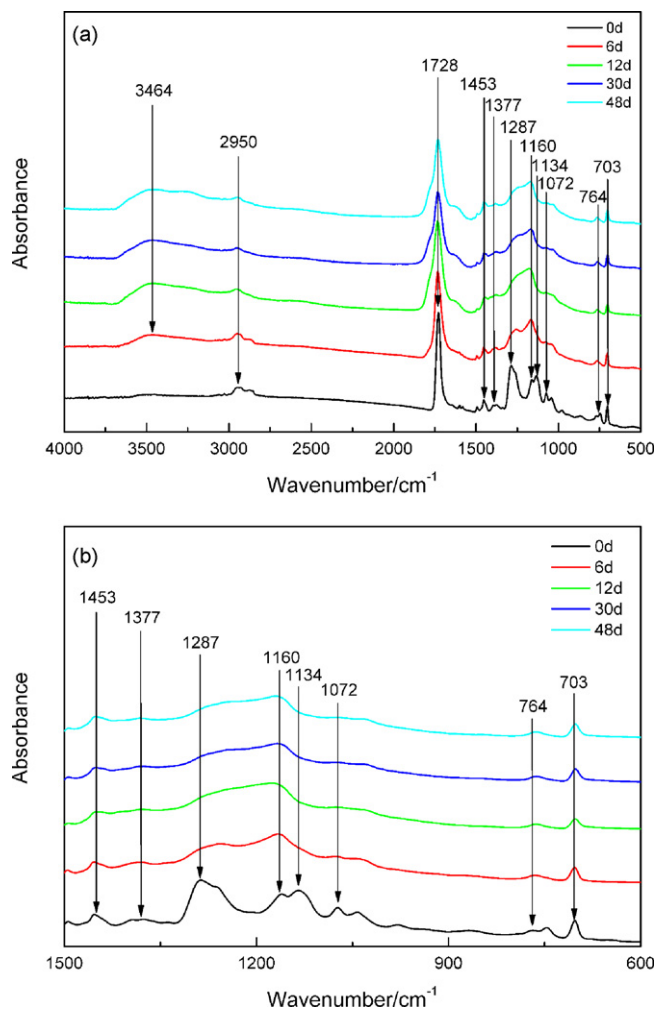


Fig. 6. SR-FTIR spectra of an UP specimen before and after aging for different times: (a) 4000–500 cm^{-1} and (b) 1500–600 cm^{-1} .

are assigned to C–H out-of-plane bending wagging vibration of aromatic ring.

It can be seen that with increasing aging time, the bands assigned to asymmetric and symmetric C–O–C stretching vibration of aromatic ester decreased in intensity, while that of aliphatic ester kept almost unchanged, which could suggest that the polymer chain was broken at aromatic ester position rather than aliphatic position. After 6 days of exposure, a new broad peak assigned to O–H stretching vibration appeared at about 3464 cm^{-1} , which was probably caused by hydrolysis of UP resin. The intensity of the peak at 1728 cm^{-1} attributed to C=O stretching vibration increased with increasing aging time. By the analysis of the FTIR, the relationship between the content of carbonyl group and the aging time can be expressed as Fig. 7. The concentration of carbonyl group increased with the aging time, which confirmed the form of new carbonyl groups caused by photo-oxidation. The form of carbonyl group can cause increase of YI. Fig. 7 presents the dependence of YI on content of carbonyl group. It can be seen that YI increases with increasing content of carbonyl group. The relationship between YI and content of carbonyl group can be expressed as: $\text{YI} = -0.0695 + 1.0972C$, where the correlation coefficient R is 0.9961.

3.5. Contact angle measurement

The effect of aging time on the contact angles of water and formamide is shown in Fig. 8. It can be seen that the contact angle

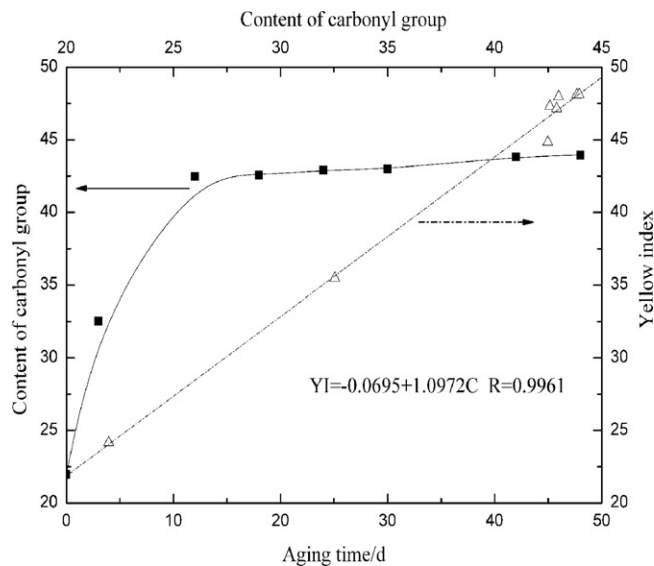


Fig. 7. Dependence of yellow index on content of carbonyl group.

of water decreased from 66.15° to 35.90° during 30 days of exposure and then began to increase slowly. The formation of polar groups such as hydroxyl and carbonyl resulted in the decrease of contact angle. The increase of contact angle after 30 days of exposure was probably caused by the loss of small molecule product containing polar groups. For the unaged UP resin, the contact angle of formamide was 41.29°, which was lower than that of water. It decreased quickly to 7.06 after 30 days of aging and then leveled off.

The total surface energy and its polar and dispersive component were calculated from the contact angles and plotted against aging time in Fig. 9. The polar component of surface energy increased from 15.65 mJ m^{-2} to 35.68 mJ m^{-2} in 30 days of exposure and then decreased slowly. The total surface energy increased from 46.99 mJ m^{-2} to 61.91 mJ m^{-2} and then kept stable at about 61 mJ m^{-2} . Fig. 10 presents the variation of γ_s^p/γ_s^d ratio on aging time. It can be seen that γ_s^p/γ_s^d increased up to a maximum at 30 days of aging and began to decrease in the following days. From the above results it can be concluded that polar species such as hydroxyl and carbonyl groups are generated on the surface during

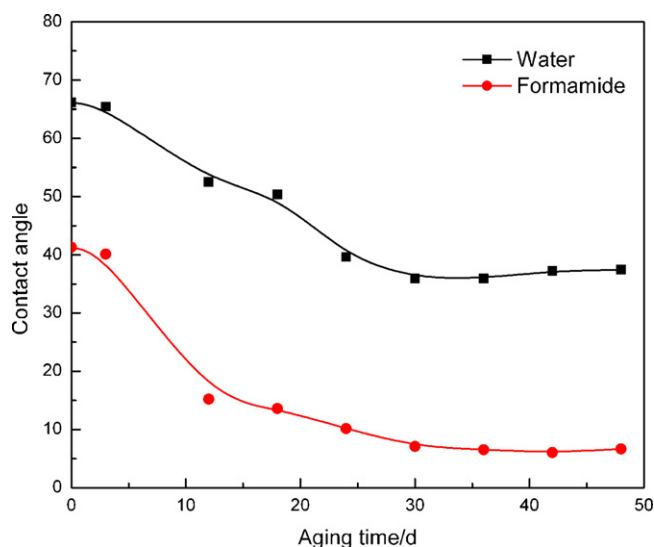


Fig. 8. Effect of aging time on the contact angles of water and formamide.

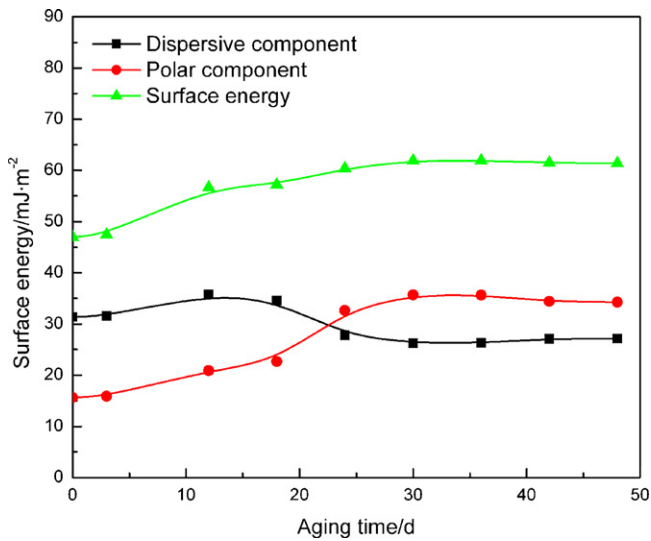


Fig. 9. Variation of surface energy on exposure time.

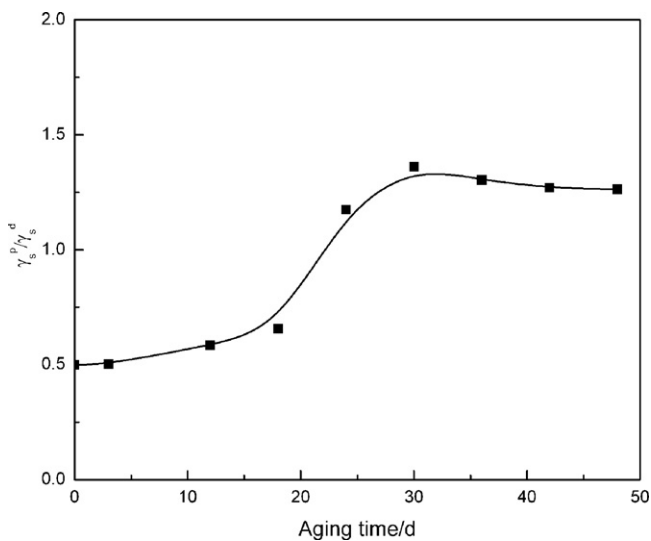


Fig. 10. Variation of γ_s^p/γ_s^d ratio on exposure time.

aging. The decrease of γ_s^p/γ_s^d ratio maybe resulted from the loss of small molecule product from the surface.

4. Conclusion

In the artificial weathering environment produced by fluorescent UV/condensation weathering equipment, the surface of UP resin turned darker and yellow in the first stage and then remained nearly unchanged during further aging. Gloss reached maximum when the sample was aged for 12 days and then decreased. With increasing aging time, cracks appeared and developed on the UP surface. Hydroxyl and carbonyl groups produced in aging process increased the wettability of UP resin surface.

Acknowledgements

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