

Low-Temperature UV Irradiation Induced the Color Change Kinetics and the Corresponding Structure Development of PVC Film

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ABSTRACT: The low-temperature ultraviolet (UV) irradiation equipment, developed in our Lab, was used to study the photo-aging of poly (vinyl chloride) (PVC) films at low temperature. The color change kinetics and corresponding structure development of PVC film during low-temperature UV aging were studied through $L^*a^*b^*$ coordinates Commission International d' Eclau-age (CIE 1976 color space) and Ultraviolet spectrophotometer (UV-vis) and Fourier transform infrared spectroscopy (FTIR). It was found that the yellowness difference (Δb^*) and color difference (ΔE^*) of the PVC film increased almost linearly with the aging time. Their values had a slower change at lower temperature. The kinetic study showed that the relationship between the velocity of coloration of the PVC film and the temperature agreed well with

Arrhenius equation at low temperature. The activation energy of coloration of the PVC film was calculated. The FTIR spectra indicated that photo-dehydrochloration, resulting in the generation of conjugated carbon-carbon double bonds, was the main reaction for PVC during photo-aging at low temperature. Meanwhile, the photo-oxidation was also obvious and could not be neglected. It clearly confirmed that the absorption peaks of conjugated carbon-carbon double bond increased and shifted to longer wavelength during photo-aging in the UV-abs analysis. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 122: 2588–2593, 2011

Key words: PVC; photo-aging; UV irradiation; $L^*a^*b^*$; coloration; kinetic; chromatics

INTRODUCTION

Poly (vinyl chloride) (PVC) would undergo photo-dehydrochloration(I), photo-oxidation(II), crosslinking, and cleavage of molecular chain(III) as shown in Figure 1.^{1–9} As a results of that, many properties of PVC, such as appearance, mechanic properties, electrical properties, and so on, would be deteriorated. Among these, discoloration leading to esthetic damage was the most notable phenomenon.^{8–15}

$L^*a^*b^*$ coordinates according to Commission International d' Eclau-age (CIE 1976 color space) is a classical and efficient method to measure the chromatic aberration of PVC during photo-aging. Pi showed that the chromatic aberration of PVC was obvious no matter what kind of thermo stabilizer was used, especially when lead salt stabilizer was used.⁸ It also showed that the addition of acrylonitrile-butadiene-styrene copolymer (ABS) would accelerate this reaction. Reversed phenomenon was observed when PVC was blended with chloride polyethylene (CPE) or acrylic

resin (ACR).⁹ Ye et al.¹⁶ found that the chromatic aberration was inevitable even though a high ultraviolet (UV) resistance coating was covered on the PVC sheet. Matuana found that the ΔL^* , Δa^* , Δb^* , and ΔE^* values of PVC and PVC/wood composite changed notably after photo-aging. And the $L^*a^*b^*$ coordinates of the PVC/wood composite were larger than those of the neat PVC.¹⁷ Bacaloglu studied the relationship between the color indexes and the structure of PVC. It was found that the chromatic aberration had high sensitivity to the degraded monomer, and the b^* value and Yellow index were proportional to the concentration of the carbon-carbon double bonds.¹⁸

To the best of our knowledge, the most reports were focused on the photo-aging of PVC above room temperature. The photo-aging of PVC at low temperature (subzero temperature) was hardly reported, because the UV lamp would not light up in such a low temperature without special treatment. In our low temperature environmental experiment, UV irradiation caused the visible sacrifice of the PVC properties especially the esthetic properties was found. Therefore, it is important to understand the photo-aging process of PVC caused by low-temperature UV irradiation. In our Lab, the low-temperature UV irradiation equipment was developed. In this work, the photo-aging process of PVC film at

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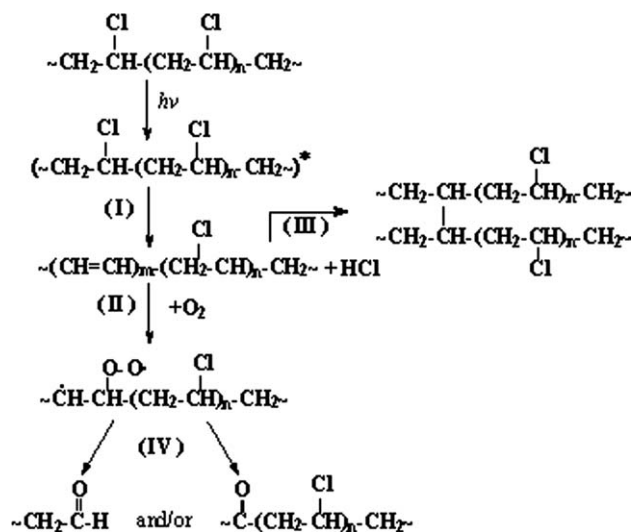


Figure 1 The main reaction of PVC during photo-aging.

low-temperature UV irradiation was carried out in the temperature range from 0°C to −30°C in this equipment. The surface color of the film after irradiation was measured with the color in $L^*a^*b^*$ coordinates at three locations by X-rite Color Difference Meter. The color change kinetics of PVC film during irradiation and the activation energy for the discoloration as well as the color change induced the structure development of PVC film were also studied.

EXPERIMENTAL

Materials

PVC (SG-8) with a number-average molecular weight of 5.0×10^4 was purchased from Jinlu Group (Sichuan, China). Tetrahydrofuran (THF, A. R. degree) was purchased from Haihong reagent company (Chengdu, Sichuan, China), and it was used without further purification.

Preparation of samples

A 50 g PVC was dissolved in 250 mL THF and stirred at a rotation of 120 r/min at 25°C for 48 h to get a uniform solution. Aluminum sheet (17 mm × 17 mm × 1 mm) was fixed in the Spin Coater (KW-4A, Institute of Microelectronics, CAS) as a substrate. A 5 mL of the PVC solution was injected in the middle of the substrate. The spin coating was conducted by two steps, the substrate rotated at 330 r/min for 9 s to make the sheet be full covered by PVC solution at step 1, and then the sheet was rotated at 880 r/min for 30 s to get a uniform film at step 2. The substrate was then vacuum dried (10^{-4} Torr) for 24 h to remove the solvent and the PVC film was formed. The PVC film was separate from the sheet for later use. The thickness of the film was 13–14 μm.

Low temperature UV irradiation

Equipment

A UV lamp was made by setting a 500 W high pressure mercury lamp inside a special quartz tube, both ends of which were closed to reduce the heat transition. The gap between the lamp surface and the tube was 5 mm which was designed to guarantee the heat insulation. The UV lamp was set in a high- and low-temperature humidity test chamber, which used to provide the low-temperature atmosphere. The average irradiation intensities at different temperature were checked by irradiatometer. It was found that the subzero temperature had few influence on it after special treatment.

UV irradiation of samples

The average irradiation intensity was 5 W/m² at 340 nm. And the test temperature was controlled at −30°C/−20°C/−15°C/−10°C/0°C, respectively. The temperature variation was strictly controlled in ±1°C.

Characterization

Color evaluation

The surface color of samples were determined by measuring the color in $L^*a^*b^*$ coordinates at three locations on each sample by X-rite Color Difference Meter. As defined by the CIE (CIE 1976 color space), L^* axis represents the lightness, a^* and b^* are the chromaticity coordinates. L^* , a^* , and b^* color coordinates were calculated base on a D65 light source as established by the CIE 1976.¹⁰ The color difference (ΔE^*) was obtained according to the follow formula:

$$\Delta E_i^* = \sqrt{\Delta L_i^{*2} + \Delta a_i^{*2} + \Delta b_i^{*2}}$$

The un-aged sample having color difference $\Delta E^*_0 = 0$ was used as a reference.

UV-vis analysis

A U-3010 UV spectrophotometer (Hitachi, Tokyo, Japan) in the wavelength range of 200–600 nm was used to obtain UV spectra of samples. The sample was vacuum dried for 2 h at room temperature, and it was cut into 1 cm × 4 cm ribbons before test.

FTIR analysis

The infrared (IR) spectra of the samples were obtained on a Nicolet 560 Fourier transform infrared spectroscopy (FTIR) spectrometer (Thermo Fisher Scientific, Waltham, MA) at a resolution of 4 cm^{−1}.

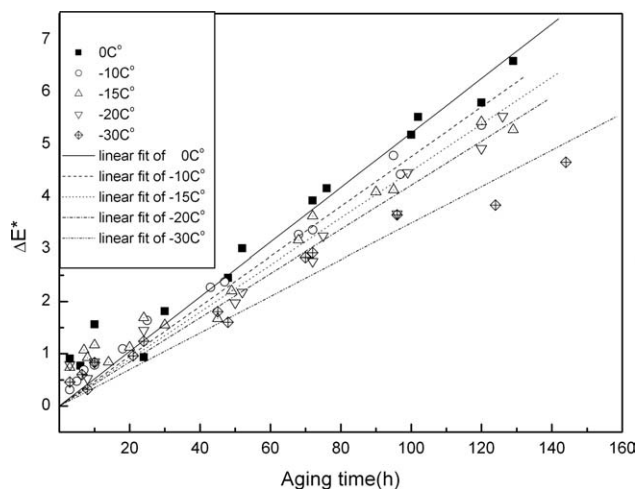


Figure 2 The effect of aging time on ΔE^* value of PVC at different temperature.

A total of 64 scans were used for each spectrum. IR absorbance spectra were measured over the range of $4000\text{--}500\text{ cm}^{-1}$.

RESULTS AND DISCUSSION

Color change analysis

ΔE^* analysis

Color is one of the principal parameters of the quality of PVC materials, since it is the first characteristic to be perceived. The color also gives information about possible defects during photo-aging. Color difference (ΔE^*) is the summary of redness, yellowness, and lightness differences of the chromatic aberration. It is a comprehensive index to evaluate the chromatic aberration. Figure 2 represented the color difference (ΔE^*) of samples during photo-aging from 0°C to -30°C . It was found that the ΔE^* of all samples increased quickly with the aging time. And the values were 5–7 after 120 h's aging, even at -30°C . That meant photo-aged phenomenon, especially the chromatic aberration was still obvious even though in such a low temperature. Another interesting finding was that the rate of the ΔE^* changing was correlative with the test temperature. The lower the test temperature was, the slower the increasing of ΔE^* was. Low temperature decreased the activity of molecules and abated the photo-aging of PVC. It could be found that the ΔE^* almost got a linear growth during UV irradiation, no matter what the temperature was.

Kinetic analysis

The chromatic aberration of PVC during UV irradiation at low temperature could be expressed as the following formulas:

$$E_i^* = E_0^* + \Delta E_i^* \quad (1)$$

Here, E_i^* was the color value of the sample at i hour, E_0^* was the origin color value, and ΔE_i^* was the chromatic aberration.

To calculate kinetic parameters according to Arrhenius equation, the basis rate equation was used:

$$\frac{d(\Delta E^*)}{dt} = A e^{-E/RT} \quad (2)$$

The logarithmic form of eq. (2) was that:

$$\ln\left(\frac{d(\Delta E^*)}{dt}\right) = -\frac{E}{R}\left(\frac{1}{T}\right) + \ln A \quad (3)$$

The minus form of eq. (3) was that:

$$\Delta \ln\left(\frac{d(\Delta E^*)}{dt}\right) = -\frac{E}{R}\Delta\left(\frac{1}{T}\right) \quad (4)$$

By plotting $\Delta \ln\left(\frac{d(\Delta E^*)}{dt}\right)$ against $\Delta\left(\frac{1}{T}\right)$, the slope of the line was $-\frac{E}{R}$ (shown in Fig. 3), where E was the apparent activation energy (kJ mol^{-1}), A was pre-exponential factor (h^{-1}), R was gas constant ($8.3136\text{ J mol}^{-1}\text{ K}^{-1}$), T was test temperature (K), and t was aging time (h).

The apparent activation energies (E) of the ΔE^* change was calculated as 7.4 kJ/mol . This value was so low that the reaction of discoloration of PVC could easily take place. That is why photo-aged phenomenon of sample was still notable even at such a low temperature.

$L^*a^*b^*$ analysis

Color difference (ΔE^*) is the summary of L^* (lightness), a^* (redness), and b^* (yellowness) differences of the color change. To find the key influence factor,

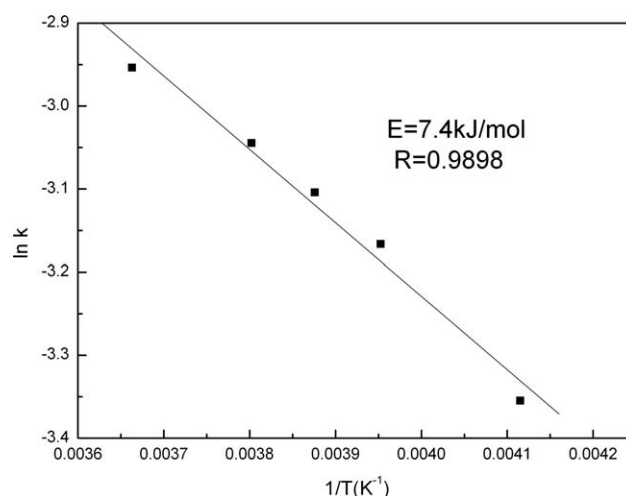


Figure 3 The relationship between $\ln k$ of ΔE^* and $1/T$.

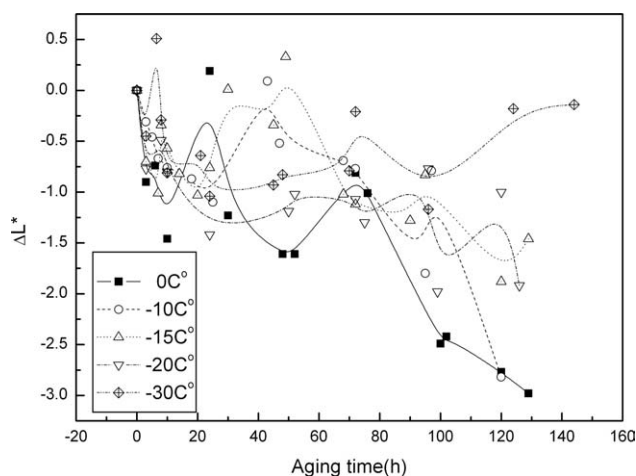


Figure 4 The effect of aging time on ΔL^* value of PVC at different temperature.

the change of L^* , a^* , and b^* of the samples were also analyzed. The L^* coordinate serves as the psychometric correlate of perceived lightness and covers a range from white (100) to black (0) along a gray scale. The values of ΔL^* versus exposure time were represented in Figure 4. It could be found that the L^* value slightly decreased as the exposure time changed. The lower the temperature was, the smaller the ΔL^* showed. Meanwhile, it almost kept constant when aged at -30°C . This indicated that the samples got dark during the process, and the low temperature could delay this process.

The a^* value represents the chromaticity coordinates in the definition of CIE 1976 color space. It was directly relevant to the structure of the sample.¹⁰ From Figure 5, it could be seen that the a^* decreased with photo-aging time slightly. And Δa^* of all samples were small, which were not higher than 0.4. Besides, the a^* value of all samples reached to the bottom of curve when it had been aged for 70 h. And

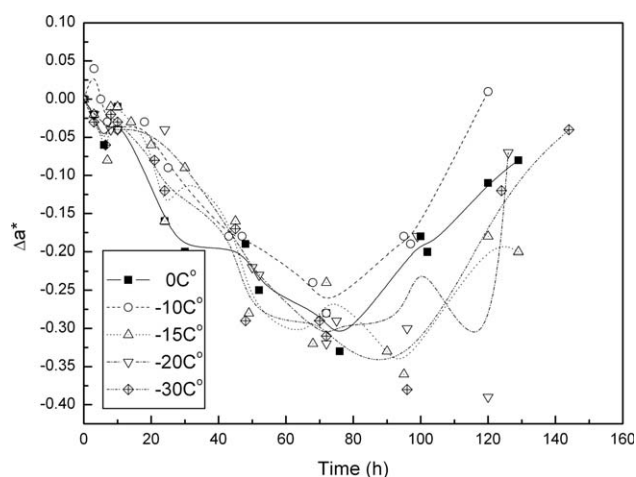


Figure 5 The effect of aging time on Δa^* value of PVC at different temperature.

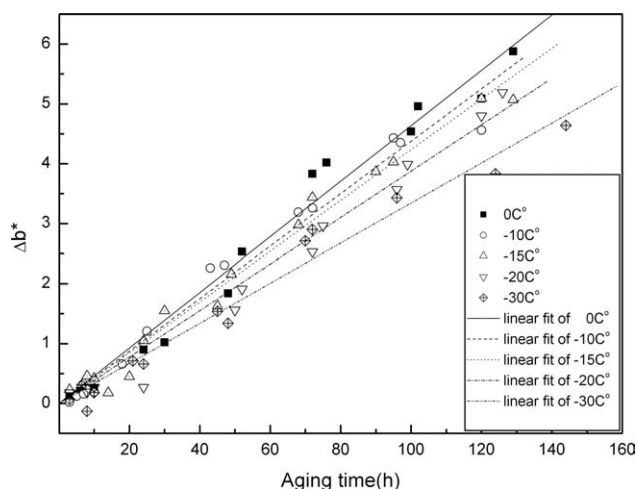


Figure 6 The effect of aging time on Δb^* value of PVC at different temperature.

then the a^* value increased. That meant there were green chromospheres accumulated in the samples in the first period of the photo-aging. It reached to a maximum after 70-hs' irradiation. And then, the red chromospheres generated which induced the Δa^* value increased. The total extent of this change was so tiny and had little effect on discoloration of samples.

From above analysis, we could conclude that the influence of ΔL^* and Δa^* on ΔE^* was small. The variable Δb^* was also studied. Figure 6 showed the Δb^* changes of samples during photo-aging. It could be found that the Δb^* almost got a linear growth during UV irradiation, no matter what the temperature was. The linear fitting of Δb^* value was conducted, and the Δb^* change ratio (k) was calculated. It clearly indicated that the Δb^* changed more slowly at a lower temperature, and the change ratio (k) was proportional to the photo-aging temperature. The natural logarithm of the ratio versus reciprocal of the temperature ($1/T$) was represented in Figure 7. It could be

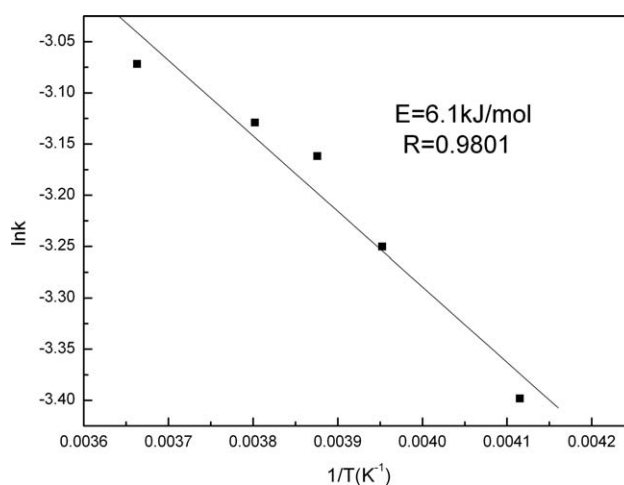


Figure 7 The relationship between $\ln k$ of Δb^* and $1/T$.

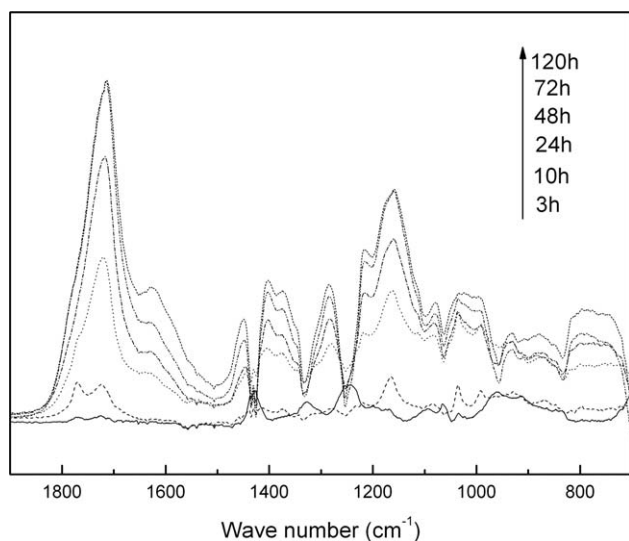


Figure 8 FTIR spectra of PVC aged at 0°C.

seen that the $\ln k$ was linear with $1/T$. According to Arrhenius equation, the activation energy of the yellowness change was calculated as 6.1 kJ/mol. Now, conclusion could be certainly made that Δb^* gave the largest contribution to ΔE^* . That meant the color change of the samples focused on yellowness.

Microstructure analysis

FTIR analysis

To find the correlation between microstructures' profiling and CIE $L^*a^*b^*$ parameters, FTIR was used to examine PVC during photo-aging at low temperature. The differential IR spectra of PVC photo-aged at 0°C was illustrated in Figure 8. It was chosen as an example to study the structure change. It could be seen that new absorption bands mainly emerged in the region of 1650–1450 cm^{-1} (C=C stretching model) and 950–850 cm^{-1} (=CH₂ bending model). The strength of the absorption peaks lied in above regions increased and showed "red shift" with the aging time. That meant the reaction of dehydrochlorination leading to generation of the conjugated C=C bonds was dominating when PVC undergoing photo-aging no matter how low the temperature was. Moreover, the absorption bands at 1720 cm^{-1} (C=O stretching model) and at 1300–1050 cm^{-1} (C—O—C stretching model) distinctly increased with the aging time. This indicated that oxygenated structures resulting from photo-oxidation reaction of PVC

TABLE I
The Relationship Between UV-vis Absorption Wavelength and the Conjugated Chain Length

Length of conjugated chain	3	4	5	6	7	8	9	10
λ (nm)	287	311	326	342	361	390	420	450

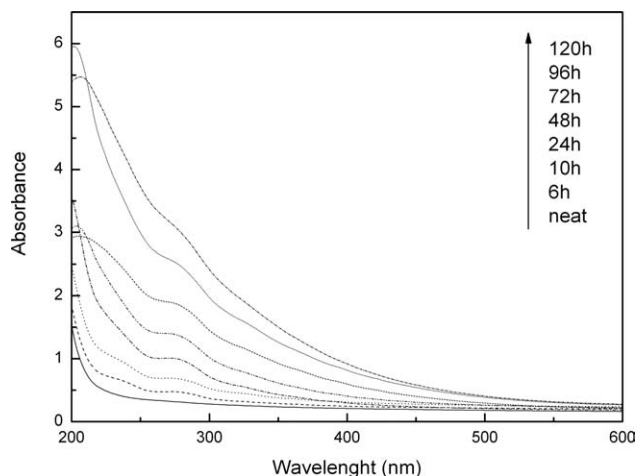


Figure 9 The UV-absorbance curves of PVC aged at 0°C.

under UV irradiation could not be neglected even at such a low temperature.

UV-vis analysis

In fact, the structures of conjugated C=C bones could absorb part of the visible light, which was the basic reason for the color change of PVC. So it is important to specifically determinate these structures. Here, a UV-vis spectrophotometer was used. As shown in Table I, the conjugated chain length was closely corresponded to UV-vis absorption wavelength (here, the absorption of C=O group was neglected because of its low ϵ_{max} comparing with that of C=C). Figure 9 showed the UV-vis spectra of PVC photo-aged at 0°C in different time. It was found that the change of the curves could be divided into two parts, one was below 400 nm which increased obviously during UV irradiation, and the other was above 400 nm which raised slightly

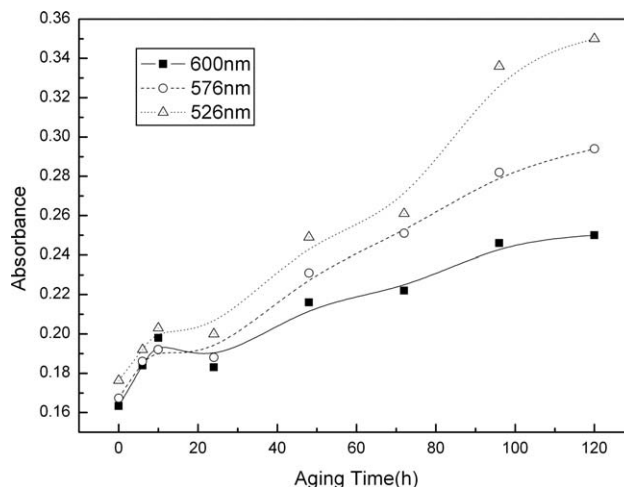


Figure 10 The UV-vis absorbance of photo-aged PVC at 0°C.

during the process, especially in the first 24 h. Besides that, the absorption ranges were shift to long wavelengths with the aging time. According to Table I, we could easily know that there were conjugated C=C bonds with chain length ranging from 3 to 12 carbon atoms in the samples. And the most of them were 3–8 carbon atoms. The amount of the conjugated C=C bonds increased with the aging time. On the base of chromatics, inevitably, the color of the sample changed primarily from yellow to red same as other previous reports.¹⁸

To accurately characterize and differentiate of the buildup of color, the value of the absorption at 600/576/526 nm of the samples photo-aged at 0°C, which represented the absorption of orange/yellow/green light, were recorded correspondingly and list in Figure 10. It could be found that each curve increased with the aging time, the rising velocity and extent of 576 nm and 526 nm were higher than that of 600 nm. That is why the color of the sample mainly showed yellow. Yellowness (Δb^*) was the decisive factor for color difference (ΔE^*).

CONCLUSIONS

Accelerated photo-aging of PVC at low temperature which was conducted in our own design equipment was studied in this article. $L^*a^*b^*$ coordinates were used to study the color change of samples. It was found that the Δb^* and ΔE^* changed almost linearly with the aging time, and both of the values were changed more slowly at lower temperature. According to the Arrhenius equation, the activation energy were calculated as 6.1 kJ/mol for Δb^* and 7.4 kJ/mol for ΔE^* . The color changes of PVC mostly focus on the yellowness and the reaction of coloration was easily generated. The FTIR spectra validated that the C=O (1770cm^{-1} – 1720cm^{-1}) and C–O (1300 – 1100cm^{-1}) generated and they increased

with the aging time, which indicated that the photo-oxidation was also took placed. However, the C=O and C–O groups contributed little to the color change of PVC. The UV–vis curves confirmed clearly that the absorption peaks of conjugated C=C bond increased and shifted to longer wavelength during the UV irradiation. And we have found that there is a good correlation between microstructures' profiling and CIE $L^*a^*b^*$ parameters.

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