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Photo-Oxidation of PVC-Coated Membrane Material Under Different Light Sources†

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The effects of accelerated weathering tests on PVC-coated membrane material are studied to establish the possible correlation between different light sources and ultraviolet radiation intensities. Two light sources and three UV radiation intensities were provided in accelerated weathering tests, they are 1 UVB-313 lamp, 4 UVB-313 lamps and 4 UVA-340 lamps, respectively, to study the influences of different UV irradiation intensities and light sources on photo-oxidation of the PVC-coated membrane material. The tensile properties of the PVC-coated samples under different accelerated weathering conditions were then measured. In addition, FTIR (Fourier Transform Infrared) and UV-visible (ultraviolet visable range) were used to analyze the samples. The study shows that the photo-oxidation mechanism of PVC weathering samples does not change under the two different light sources and different UV radiation intensities. However, the study indicates that the weathering degree of PVC samples is incongruous when accepted equivalent radiation energy. The difference between the luminescence spectra of the two light sources is the main reason. Therefore, the Reciprocity law does not apply to predict the performance of PVC-coated membrane material used outdoors. However, according to the different luminescent spectrum of the two light sources, the effective UV radiation was introduced in the Schwarzschild's law. Eventually, the correlation of different weathering results under different UV radiation intensities and light sources could be better established.

Keywords: PVC-coated membrane, Photo-oxidation, Accelerated weathering, Correlation, Schwarzschild's law.

INTRODUCTION

PVC-coated membrane material is a new flexible textile composite material which coated with PVC on the surface and uses high power fiber fabric as substrate[1]. The use of PVC-coated membrane material has expanded to such an extent that nowadays they are almost certain to be included in any construction work. However, the PVC material has poor resistance to photo-oxidation. Ultraviolet (UV) radiation will cause serious degradation of the material and consequently weaken its power when it is exposed directly in the open air. Therefore, it is necessary to evaluate the weathering performance of PVC-coated membrane material and predict its service life before we put it into use.

At present, accelerated weathering process, which is more efficient by intensifying UV radiation, has commonly been used for measuring the weathering performance of the PVC-coated membrane material. The design includes Carbon-Arc weathering, Fluorescent UV weathering, Xenon-Arc weathering, which are classified by the different lamp types. Different light sources have different luminescent spectra and UV radiation intensities. Consequently, the photo-oxidation rate of samples will be various, when they are exposure under different light sources. Therefore, it is necessary to study the effects of light sources and UV radiation intensity on photo-oxidation performance of PVC-coated membrane material in order to predict the service life of the PVC material. Formerly, the correlation was found on the basis of Reciprocity law[2], which shows that the material's chemical reaction is only related to the cumulative UV radiation energy, but has nothing to do with the intensity of UV radiation and weathering time. However, some researchers held contrary opinions, after the Reciprocity law was provided[3-5]. The Schwarzschild law was given on the basis of the Reciprocity law, which shows that the aging level of the material should be same when the product of the p square of the UV radiation intensity (weathering time) and weathering time (the UV radiation intensity) is constant (I^p t = constant or I t^p = constant). The p is not constant, it changes with the different test conditions and materials. Better correlation between weathering effects under different UV

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radiation intensities of the same light source was found with the Schwarzschild law. Whether or not the Schwarzschild law applies between different light sources, from existing studies it is difficult to reach a definite conclusion.

Therefore, different intensities of UV radiation and light sources were selected in the present study to conduct accelerated weathering tests. The objective of the present study is to examine the influence of different UV irradiation intensities and light sources on the photo-oxidation kinetics of the PVC material. Then the correlation of different light sources could be found by using the results from the accelerated weathering tests.

EXPERIMENTAL

Test sample: To concentrate the study on the degradation of PVC- coated membrane material due to UV radiation and to avoid system errors, the same material without anti-weathering agents was chosen in the experiments. The membrane material is made from pure PVC coated with plasticizer. The specimen thickness is 300 µm and its size is 25 mm × 100 mm.

Photo-oxidation tests: Following the standard ASTM G154-00, an accelerated weathering apparatus (Model UV-II by Changzhou Puke Co., China) with uorescent lamps (UVB-313 and UVA-340) was performed to conduct accelerated weathering test. Fig. 1 shows the relative spectral power distribution of the light in the wavelength between 300 and 400 nm from both lamps.

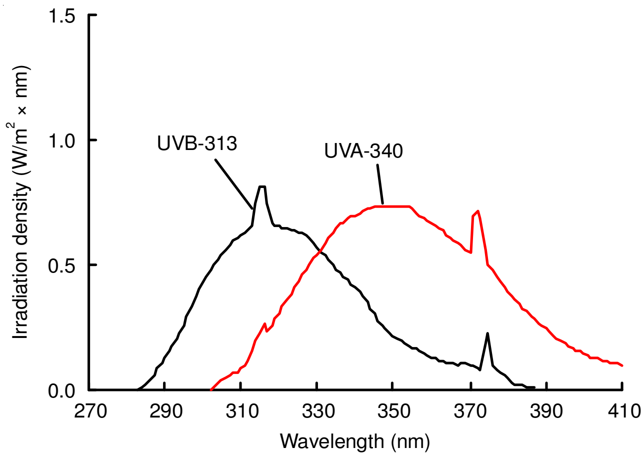

Fig. 1. Comparison of spectra between UVB313 lamp and UVA340 lamp

The maximum UV intensity of the UV-II apparatus is provided by totally eight uorescent lamps. For the purpose of this study, 4 UVA-340 lamps and 4 UVB-313 lamps were used, respectively to begin. Then, to study the effects of different UV intensities, 1 UVB-313 lamp was selected in the experiment.

In the experiments, the accelerated weathering tester was performed at a working cycle of 22 h continuously light exposure followed by 2 h water spray. To guarantee the cumulative UV radiation energy was the same and to compare the weathering behaviours under different UV intensities and light sources, sampling time is shown in Table-1. UV radiation intensity was measured by ultraviolet radiation detector (TN 340) as shown in Table-2.

Characterization: The tensile properties of the PVC-coated samples were measured on a universal tester (Hualong microcomputer control electron universal tester) at an elongation rate 50 mm/min according to the standard ASTM D 5035-2006[6].

The reduction of mechanical properties of PVC-coated membrane material under accelerated weathering conditions is mainly due to the chemical reactions during photo-oxidation. The new products were formed after the reaction, such as carbonyl and double bonds[7,8]. They were measured by the FTIR (Nicolet 670) and UV-visible spectrometer (Lambda35) separately.

RESULTS AND DISCUSSION

Influence of UV intensity on tensile strength of sample: The tensile strength retention of the samples from both 1 UVB-313 lamp and 4 UVB-313 lamps tests is in inverse proportion to cumulative UV radiation power (the product of UV radiation intensity and exposure time), shown in Fig. 2. From the results, it is seen that the tensile strength of samples decreases to 48.2 % of the original value after 864 h of UVB313-1 weathering test. The power of the samples in the UVB313-4 weathering test is reduced to 45.3 % (4-lamp-test, 216 h) of the original value. It indicates that the higher the UV intensity is, the faster the deterioration of the material in tensile strength, when accepted equal UV radiation energy.

Influence of different light sources on tensile strength of sample: The tensile strength retention of the samples from both UVB313-4 tests and UVA340-4 tests are curved with the cumulative UV radiation energy (the product of UV radiation

TABLE-1
SAMPLING TIME

Test type	Aging time (h)									
UVB313-1	1	96	192	288	384	480	576	672	768	864
UVB313-4	0	24	48	72	96	120	144	168	192	216
UVA340-4	0	24	48	72	96	120	144	168	192	216

TABLE-2
MONITORING DATA OF UV RADIATION INTENSITY

Test type	UV radiation intensity (mW/cm^2)										
	0	1	2	3	4	5	6	7	8	9	Average
UVB313-1	0.57	0.57	0.57	0.56	0.56	0.56	0.56	0.56	0.55	0.55	0.56
UVB313-4	2.25	2.25	2.24	2.24	2.23	2.24	2.24	2.24	2.23	2.23	2.24
UVA340-4	3.42	3.42	3.41	3.40	3.39	3.40	3.40	3.38	3.38	3.39	3.40

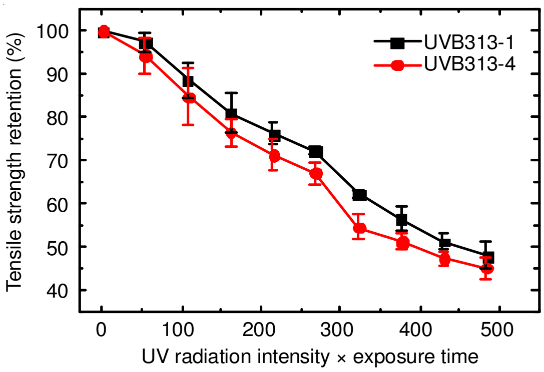

Fig. 2. Tensile strength of samples under different UV intensities

intensity and exposure time) as shown in Fig. 3. From the curve, it is seen that the tensile strength of samples reduces to 45.3 % of the original value after 216 h of UVB313-4 aging test. The power of the samples in the UVA340-4 weathering test reduce down to 69.1 % (4-lamp-test, 216 h) of the original value. It obviously indicates that when accepted equal UV radiation energy, the deterioration of samples under UVB313 tests is faster than under UVA340 tests. That is to say, the acceleration coefficient of UVB313 fluorescent lamp is higher than that of UVA340 fluorescent lamp.

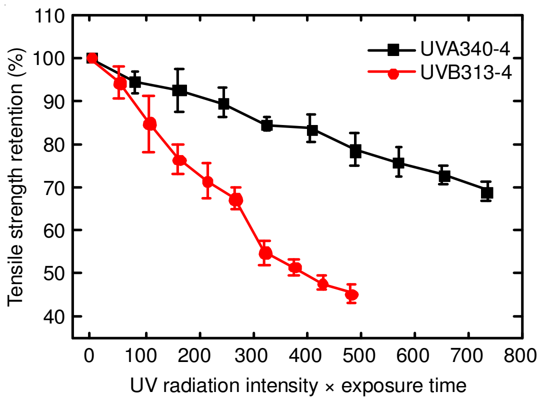

Fig. 3. Tensile strength of samples under different light sources

As shown in Fig. 1, UV radiation energy of UVB-313 fluorescent lamp is mainly at 313 nm and UVA-340 fluorescent lamp is at 340 nm. However, PVC material's sensitive wavelength is between 310-320 nm, close to 313 nm. Therefore, when accepted the same UV radiation energy, effective UV radiation energy accepted by samples is more under UVB-313 fluorescent lamp. So photo-oxidation rate under UVB-313 fluorescent lamp is quicker than that under UVA-340 fluorescent lamp.

In conclusion from Figs. 2 and 3, When accepted equal UV radiation energy, weathering level of sample is incongruous under different light sources. Further spectral analysis is needed to find out the cause, so as to analyze photo-oxidation kinetics under different UV radiation intensities and different light sources.

Infrared spectroscopic analysis: FTIR spectrum of original PVC sample is shown in Fig. 4. The peak at 1720 cm^{-1} indicates that plasticizers exist in samples.

Photo-oxidation mechanism of PVC material has been quite clear. It is known from the mechanism that carbonyl and

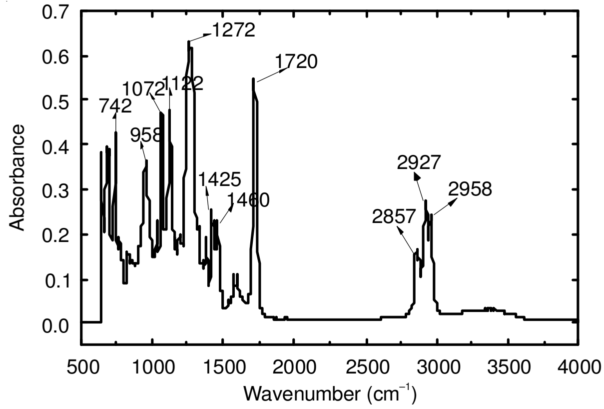

Fig. 4. FTIR spectrum of original PVC sample

double bonds are the main products of the photo-oxidation of PVC material[7]. Carbonyl can be examined by FTIR spectrometry technique[9].

Fig. 5 is the character absorption range (1700-1750 cm^{-1}) of carbonyl in FTIR spectrum. As it is seen from Fig. 5, the maximum absorption position shifts to1720 cm^{-1} under these three group tests. So they have the same change tendency: at the early stage of weathering, the absorbance increases gradually, but the absorbance decreases at the mid-later stage of weathering. The main cause of this change tendency is the produced carbonyl and the movement of plasticizers[10]. At the early stage, the carbonyls begin to be generated and the plasticizers move to the surface of samples, so the absorbance increases gradually. With the weathering time going on, the concentration of plasticizers decreases with its evaporation[11] and the rate of evaporation is greater than the carbonyls' and then absorbance reduces at the mid-later weathering stage. Because of the existence of plasticizers, the generation rate of carbonyl can not be compared under these three group tests, but it can conclude that same products are produced under three group tests.

UV-visible analysis: To further examine the photo-oxidation kinetics under different UV radiation intensities and different light sources and to compare the rate of photo-oxidation weathering of PVC material under two light sources, UV spectrum was tested on the samples[12] (Fig. 6).

As shown in Fig. 6, the longer the exposure time is, the higher the absorbance of samples rises and the absorbed wavelength is between 300 and 700 nm. Original sample has an apparent absorption peak at 350 nm. That is because degradation happens and shorter polyene structures with three to five conjugated double bonds are formed during the samples' manufacture. However, the samples' absorbance curve does not exist apparently absorption peak hereinafter weathering. The longer polyene structure is immediately created in the UV radiation process of PVC material. Therefore, the curves become relatively smooth.

Exposed to UV radiation, PVC molecular would carry out the reaction of the dehydrochlorination and then different lengths of conjugated double bonds are made in the main chain. So the weathering degree of PVC-coated material has familiar relationship with the length of conjugated double bonds (n). In the UV spectrum, the greater value of the n, the longer of the absorption wavelength is. Previous workers[6-8] found that

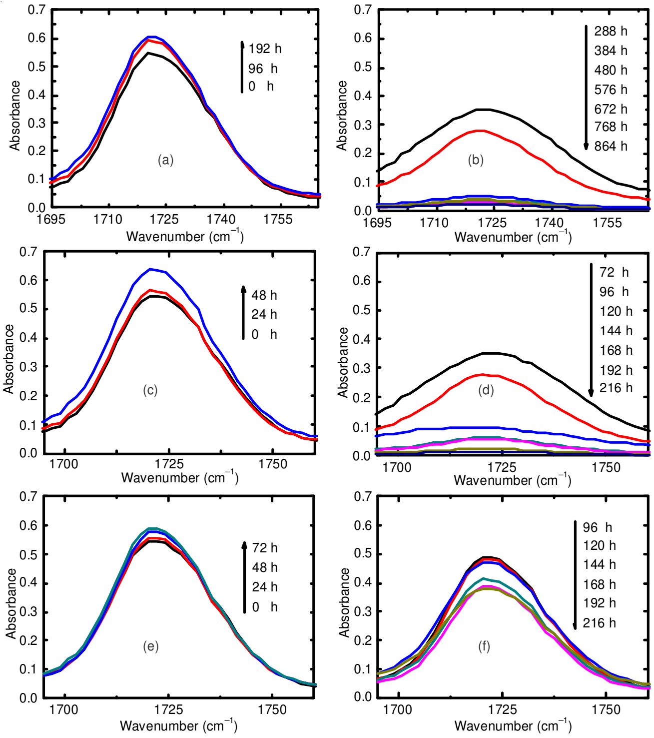

Fig. 5. FTIR spectrum of different samples in the carbonyl domain (a) Early stage of aging under UVB313-1; (b) Later stage of aging under UVB313-1; (c) Early stage of aging under UVB313-4; (d) Later stage of aging under UVB313-4; (e) Early stage of aging under UVA340-4; (f) Later stage of aging under UVA340-4

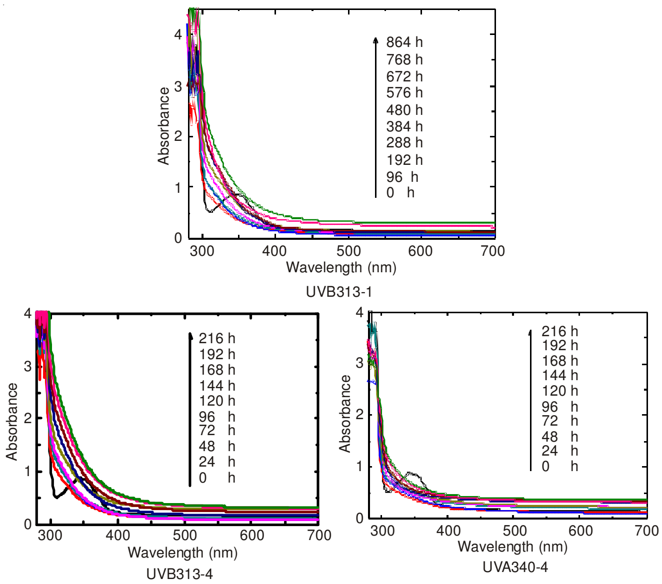

Fig. 6. UV-visible spectra of samples

when n is from 4 to 10, the corresponding UV absorption wavelengths for the conjugated double bonds structure are, respectively near at 304, 334, 364, 390, 410, 428 and 447 nm[11,13]. Fig. 7 is the absorbance of different lengths of conjugated double bonds against cumulative UV radiation energy.

From Fig. 7, it can be found that the absorbance of different lengths of conjugated double bonds increases with the increase of cumulative UV radiation energy, but their rates of increase are not consistent. The rates are faster at early stage

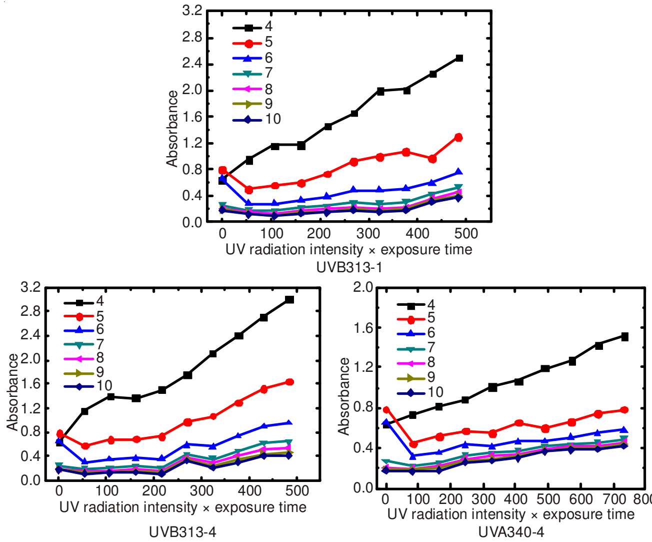

Fig. 7. Absorbance of conjugated double bonds with different chain lengths *versus* cumulative UV radiation energy

and slower at later stage. It indicates that at the beginning of the exposure, dehydrochlorination reaction rate is very fast. When n (the length of conjugated double bonds) is 4, the variation rate of polyene structure's absorbance is faster than others. The absorbance of different lengths of conjugated double bonds structure changes following the same law. It shows that the photo-oxidation mechanism does not change under different radiation intensities.

To compare the rate of photo-oxidation under different UV intensities and light sources, UV absorbance of conjugated double bonds structure (n = 4) is used to describe the rate of photo-oxidation in Fig. 8.

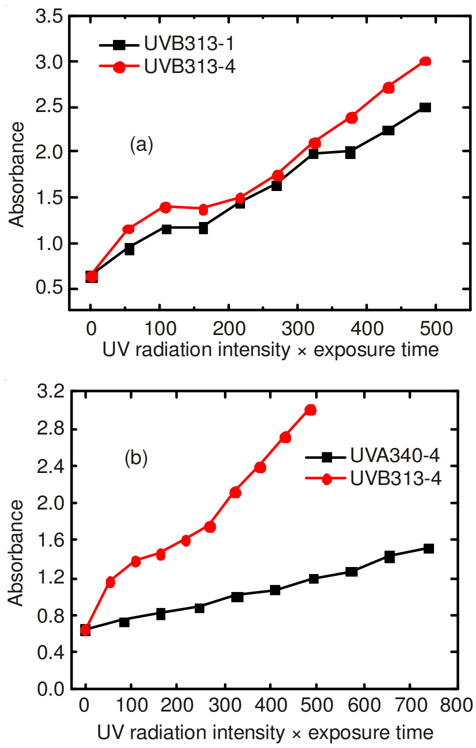

Fig. 8. Absorbance of conjugated double bonds (n = 4) *versus* cumulative UV radiation energy (a) comparison under different UV radiation intensities; (b) comparison under different light sources

As shown in Fig. 8, when the cumulative UV radiation energies are equal, the UV absorbance of conjugated double bonds (n = 4) is not same. Comparing the UV absorbance of UVB313-1 test and UVB313-4 test, it concludes that aging level is greater under high UV radiation intensity. Then comparing UV absorbance of UVB313-4 test and UVA340-4 test, it concludes that aging level is greater under UVB-313 fluorescent lamp. In addition, as UVB-313 lamp's radiation intensity is lower than UVA-340 lamp's radiation intensity, it estimates that the difference of photo-oxidation rate is caused by the light sources.

Correlation between different weathering tests

Influence of UV radiation intensity on the correlation: As photo-oxidation reaction is not proportional to UV radiation intensity, the original Reciprocity law[2] doesn't precisely apply to predict PVC material's working life. According to Schwarzschild's law ($I^p t$ = constant), when the product of the UV radiation intensity of the p th square by the weathering time is constant, the weathering level of the PVC material should be equal and the p depends on experiment conditions or materials.

When p is 1.112, absorbance of conjugated double bonds (n = 4) under different UV intensities and tensile strength retention are curved with the value of the UV radiation intensity of the p th power by exposure time in Figs. 9 and 10, respectively. As shown in Figs. 9 and 10, photo-oxidation results have better correlation under different UV radiation intensities.

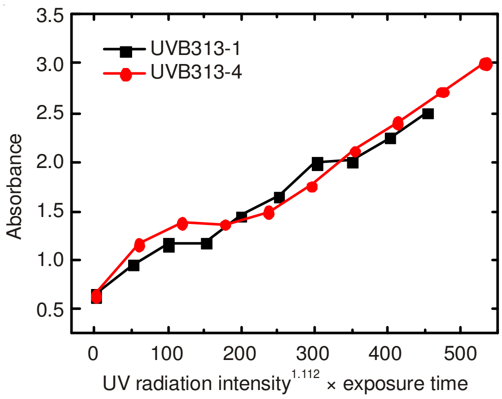

Fig. 9. Photo-oxidation reaction rates after revised under different UV intensities

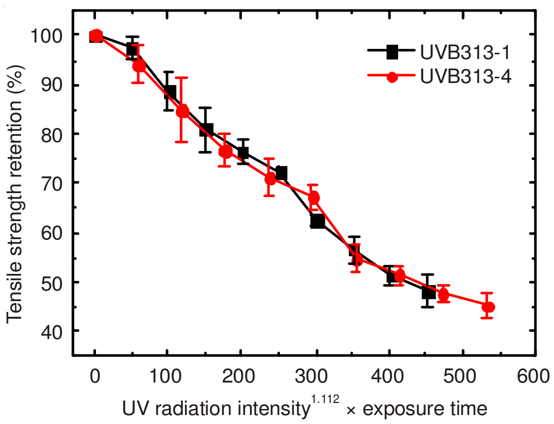

Fig. 10. Tensile strength retention after revised under different UV intensities

To get the correlation under different UV radiation intensities, a better fitting curve is obtained by using the updated data of tensile strength retention (Fig. 11). And the curve's equation is:

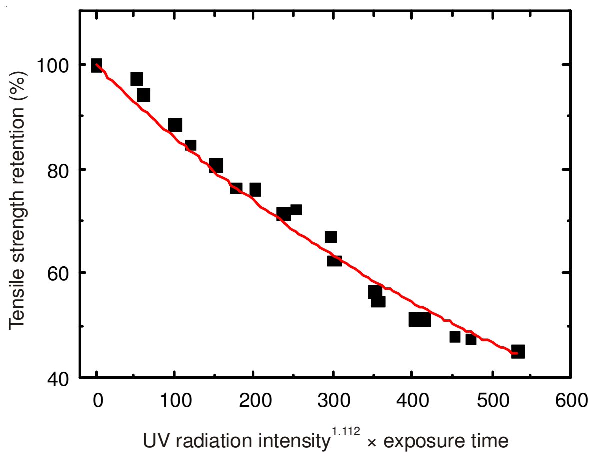

Fig. 11. Fitting curve of tensile strength retention

$$Y = 100e^{-0.00152X} \quad (1)$$

where, Y means the tensile strength retention, X equal to $I^{1.112} \times t$, I means the UV radiation intensity, t (h) is the exposure time.

Via eqn. 1, exposure time that reaching a certain level of aging need under some UV radiation intensity can be estimated. The equation form is:

$$t = \frac{\ln 100 - \ln Y}{0.00152 I^{1.112}} \quad (2)$$

Influence of different light sources on the correlation: The correlation among different UV radiation intensities has been successfully established according to Schwarzschild's law. So it is tried to establish the weathering correlation between different light sources by using Schwarzschild' law, but it failed.

Effective UV radiation intensity is introduced by combining the luminescent spectrums of UVB-313 fluorescent lamp and UVA-340 fluorescent lamp[14]. Effective UV radiation is the radiation that plays a key role on photo-oxidation of PVC material. The ratio of effective UV radiation to total UV radiation is marked as effective UV radiation coefficient α. Putting α into Schwarzschild's law, a new body is obtained: $(\alpha I)^p t$ = constant.

In this study, the ratio of UV radiation of the part below 340 nm among total UV radiation is the effective radiation coefficient α. Through integration, α is separately 0.76 and 0.26 for UVB-313 fluorescent lamp and UVA-340 fluorescent lamp. So when p is 1.22, tensile strength retention is curved with the value of the effective UV radiation intensity of the p to the power by exposure time in Fig. 12. As shown in Fig. 12, photo-oxidation results have better correlation between UVB-313 lamp and UVA-340 lamp.

To get the correlation between UVB-313 lamp and UVA-340 lamp, a better fitting curve is obtained by using the updated data of tensile strength retention as shown in Fig. 13. And the curve's equation is:

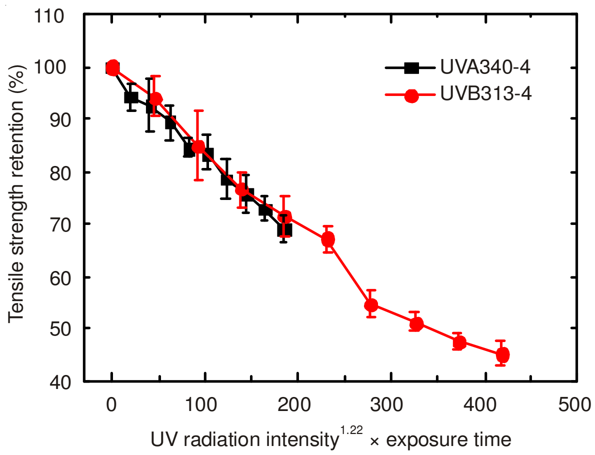

Fig. 12. Tensile strength of samples after revised under different lamps

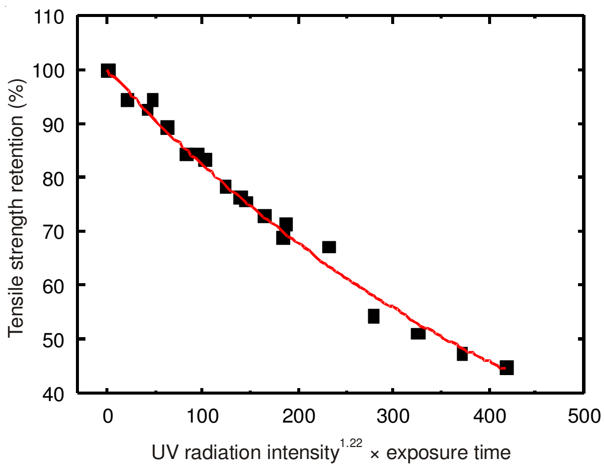

Fig. 13. Fitting curve of tensile strength retention

$$Y = 100e^{-0.00194X} \quad (3)$$

where, Y means the tensile strength retention, X equal to $(\alpha I)^{1.22} \times t$, α means effective UV radiation coefficient, I is the UV radiation intensity, t (h) is the exposure time.

Via eqn. 3, exposure time that reaching a certain level of aging need under some light sources can be estimated. The equation form is:

$$t = \frac{\ln 100 - \ln Y}{0.00194(\alpha I)^{1.22}} \quad (4)$$

Conclusion

Accelerated weathering tests of PVC-coated samples with two intensities of UV radiation (1 UVB-313 lamp and 4 UVB-313 lamps) and two light sources (UVB-313 lamp and UVA-340 lamp), respectively, were carried out in the present study. The tensile strength under different weathering conditions was measured. In the meantime, FTIR spectrometry technique and UV-visible spectrometry technique were applied to examine the existence of carbonyl and conjugated double bonds of the samples. According to the analysis of test results, some conclusions are obtained:

• The photo-oxidation mechanism of PVC-coated material does not change under different UV radiation intensities and different light sources.

• When accepted equal cumulative UV radiation energy, weathering level of samples is not equal. The higher the UV radiation intensity is, the greater the weathering level of material is. So it indicates that the photo-oxidation reaction rate is not proportional to UV radiation intensity.

• When accepted equal cumulative UV radiation energy, samples under 4 UVB-313 fluorescent lamps have larger weathering level than under 4 UVA-340 fluorescent lamps. So this is caused by their difference of luminescent spectrum.

• With Schwarzschild's law, the correlation equation between different UV radiation intensities (1 UVB-313 lamp and 4 UVB-313 lamps) is found. So according to the new Schwarzschild's law, the correlation equation between different fluorescent lamps (UVA-340 lamp and UVB-313 lamp) is also found. Through these equations, material's service life can be predicted.

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