

# Synergistic Effect of Hindered Amine Light Stabilizers/Ultraviolet Absorbers on the Plasticized PVC during Photo-Irradiation

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**ABSTRACT:** Two kinds of piperidine derivatives including a low-molecular weight (Wt. 481, T770) and a high-molecular weight (Wt. 2000–3100, C944) hindered amine light stabilizers (HALS) are added singly or with ultraviolet absorbers (UVA) in combination to plasticized poly(vinyl chloride) (PVC) samples. Digital photos, color changes, attenuated total reflection-Fourier transform infrared spectra (ATR-FTIR), and mechanical properties are obtained to investigate the photostable effect of the light stabilizers on the plasticized PVC after artificial aging. PVC samples with HALS perform well at the first 400 h of irradiation in color change, FTIR, and mechanical properties, but at the last 400 h the photostability decreases. Besides, C944 performs better than T770, because C944 is a

high-molecular weight UV stabilizer and has good extraction resistance. Plasticized PVC samples with UVA resist discoloring and photooxidation from the photo-irradiation. Excellent synergism is observed between the combination of HALS and UVA. PVC with HALS/UVA performs better than PVC with HALS and PVC with UVA in color differences, FTIR, and mechanical properties. The synergism is due to the different stages of functions between HALS and UVA. © 2012 Wiley Periodicals, Inc. *J Appl Polym Sci* 000: 000–000, 2012

**Key words:** poly(vinyl chloride); hindered amine light stabilizers; ultraviolet absorbers; artificial accelerated weathering; mechanical properties

## INTRODUCTION

Plasticized poly(vinyl chloride) (PVC) is widely used in the world to prepare hoses, cables, wires, toys, auto accessories, sporting goods, and so on.<sup>1–3</sup> However, these materials easily absorb sunlight and suffer photolysis and photooxidation.<sup>4–6</sup> The reactions may influence the applications of materials, ranging from yellowing of outward appearance to loss of elasticity and mechanical properties.<sup>7</sup>

Benzophenone and benzotriazole derivatives are efficient ultraviolet absorbers (UVA) for PVC products.<sup>8</sup> Xiang et al.<sup>9,10</sup> find both benzophenone type UVA and benzotriazole type UVA show good behavior in inhibiting the photochromism and photooxidation of casted PVC films. Xu et al.<sup>11</sup> synthesize a bisbenzotriazole derivative which is particularly effective in preventing the discoloration of both rigid and flexible PVC.

In contrast, little positive description in literatures has been seen on the photostability of hindered amine light stabilizers (HALS) for PVC products, since the hindered amines are recognized as effective light stabilizers. The phenomenon may be ascribed to the deactivating influence of the volatilized hydrogen chloride (HCl) on the basic amine groups in the early HALS. On the other hand, the base–acid neutralization decelerates the generation of HCl. For example, Adeniyi and Scott<sup>12</sup> introduced the HALS in PVC as effective light stabilizers with the existence of an effective HCl scavenger. What's more, Martine et al.<sup>13</sup> find that the flexible PVC sheets containing single HALS and single UVA maintain good residual elongation, when exposed to both natural and artificial light. It is found that the non-basic HALS protects plasticized PVC from color change and decrease of elongation retention and the effect is much better than benzophenone and benzotriazole type UVA.<sup>14</sup>

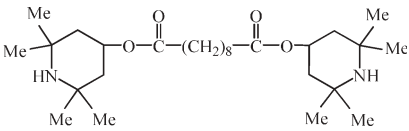
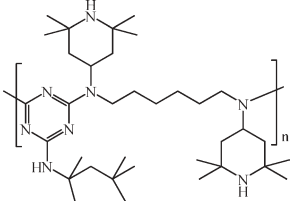
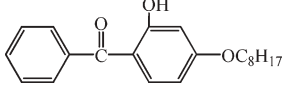
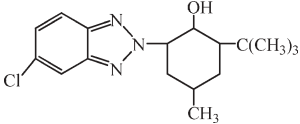
The combination of HALS and UVA is commonly and efficiently applied in many polymer systems such as plastics,<sup>15</sup> coatings,<sup>16</sup> composite materials,<sup>17</sup> and so on. But since the HALS is seldom used to protect PVC materials from UV radiation, the photostability of HALS and UVA in combination on PVC is almost unknown. It is only reported that the

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TABLE I  
Detailed Information of Additives Used in This Study

Commercial name	Formula	Molecular structure
Tinuvin 770 <sup>a</sup> (T770)	Bis(2,2,6,6-tetramethyl-4-piperidine) sebacate	
Chimassorb 944 (C944)	Poly[[6-[(1,1,3,3-tetramethylbutyl)amino]-1,3,5-triazine-2,4-diyl][(2,2,6,6-tetramethyl-4-piperidiny)imino]-1,6-hexanediyl[(2,2,6,6-tetramethyl-4-piperidiny)imino]]	
Chimassorb 81 (UV531)	2-hydroxy-4-(octyloxy) benzophenone	
UV326	2-(2-hydroxy-3-tert-butyl-5-methylphenyl)-5-chlorobenzotriazole	

<sup>a</sup> The four kinds of additives are obtained from Ciba Specialty Chemicals China Ltd., China.

elongation of plasticized PVC with HALS/UVA (benzophenone type) decreases more slowly than PVC with HALS, but more quickly than PVC with UVA.<sup>13</sup>

In the previous work,<sup>18</sup> we investigated the photostability of singly used and combined used HALS and UVA in casted PVC films and found that the basic HALS accelerate the photodegradation of PVC films, but UVA and HALS/UVA protect PVC films from degradation. In the practical applications, various substances have to be added into the PVC, due to the instability of it to sunlight, heat, etc., and the need of modification.<sup>19</sup> For example, plasticizers like phthalate are introduced into PVC formulations to obtain elasticity. But the photodegradation and migration of plasticizers also influence the stability of PVC materials.<sup>13</sup> So the study of the stable effect of HALS and UVA in plasticized PVC is much more complex than in the casted PVC films.

In this study, a low-molecular weight (Wt. 481) and a high-molecular weight (Wt. 2000–3100) HALS are added singly or with UVA in combination to dioctyl phthalate (DOP)—plasticized PVC samples. Digital photos, color changes, attenuated total reflection-Fourier transform infrared spectra (ATR-FTIR), and mechanical properties are obtained to investigate the photostable effect of light stabilizers on the plasticized PVC after artificial aging.

## EXPERIMENTAL

### Materials

PVC resin (SG-3,  $\overline{DP} = 1300$ ,  $K = 71-72$ ) is supplied by Jiangdong Chemical Co., Ltd., China. The liquid plasticizer DOP is obtained from No. 1 Chemical Plant of Jinling Petrochemical Co., China. Calcium stearate ( $\text{CaSt}_2$ ) and zinc stearate ( $\text{ZnSt}_2$ ) are supplied by Nanjing Jinling Chemical Plant Ltd., China.

Detailed information of additives used in this study is listed in Table I.

### Preparation of PVC samples

The PVC resin, DOP, and thermal stabilizers (complex of  $\text{CaSt}_2$  and  $\text{ZnSt}_2$ ) are put in a high-speed mixing machine and mixed at 80°C for 10 min to make the materials pre-plasticized. The pre-plasticized PVC (167.5 phr) and photostabilizers in Table II are mixed by a two roll mixing mill (Shanghai Rubber Machinery Works, China) at  $(145 \pm 5)^\circ\text{C}$  for 5 min. Then the materials are pressed (at 155°C for 15 min and at room temperature for 5 min) into thin pieces of 1 mm thickness and cut into dumb-bell samples.

### Artificial photo-irradiation of samples

The dumb-bell samples are photo-irradiated in a Q-SUN1000 Xenon Test Chamber (Q-Panel Ltd., USA)

**TABLE II**  
**Nine Formulations of PVC Samples with Various Photostabilizers**

Sample name	Composition (phr <sup>a</sup> )				
	Pre-plasticized PVC	T770	C944	UV531	UV326
Control	167.8	–	–	–	–
T770	167.8	0.5	–	–	–
C944	167.8	–	0.5	–	–
UV531	167.8	–	–	0.5	–
UV326	167.8	–	–	–	0.5
T770/UV531	167.8	0.25	–	0.25	–
T770/UV326	167.8	0.25	–	–	0.25
C944/UV531	167.8	–	0.25	0.25	–
C944/UV326	167.8	–	0.25	–	0.25

<sup>a</sup> phr = parts by weight per hundred parts of resin. The basic formulation of PVC without additives is as follows: PVC resin 100 phr, DOP 65 phr, CaSt<sub>2</sub> 2.5 phr, and ZnSt<sub>2</sub> 0.3 phr.

in the atmosphere of air at (65 ± 3)°C, according to ISO 4892-2:2006. The intensity of the light inside the chamber is 0.51 W/m<sup>2</sup> at 340 nm and its distribution is consistent with sunlight. The total irradiation time is 800 h and the samples are taken out at the interval of 200 h. A black standard thermometer is used to assure the temperature of circulating air at 65°C during irradiation.

### Characterization and analysis

Digital photos of photo-irradiated and unirradiated samples are taken by a camera (Canon Power Shot A720 IS, Japan).

According to ASTM D2244-89, the changes of color of irradiated PVC samples compared to the unirradiated samples are recorded by a colorimeter of Konica Minolta model CR-300 (Konica Minolta,

USA.). The total change ( $\Delta E$ ) is influenced by three parameters ( $\Delta L$ ,  $\Delta a$ ,  $\Delta b$ ) and calculated by the following equation:

$$\Delta E = \sqrt{(\Delta L)^2 + (\Delta a)^2 + (\Delta b)^2} \quad (1)$$

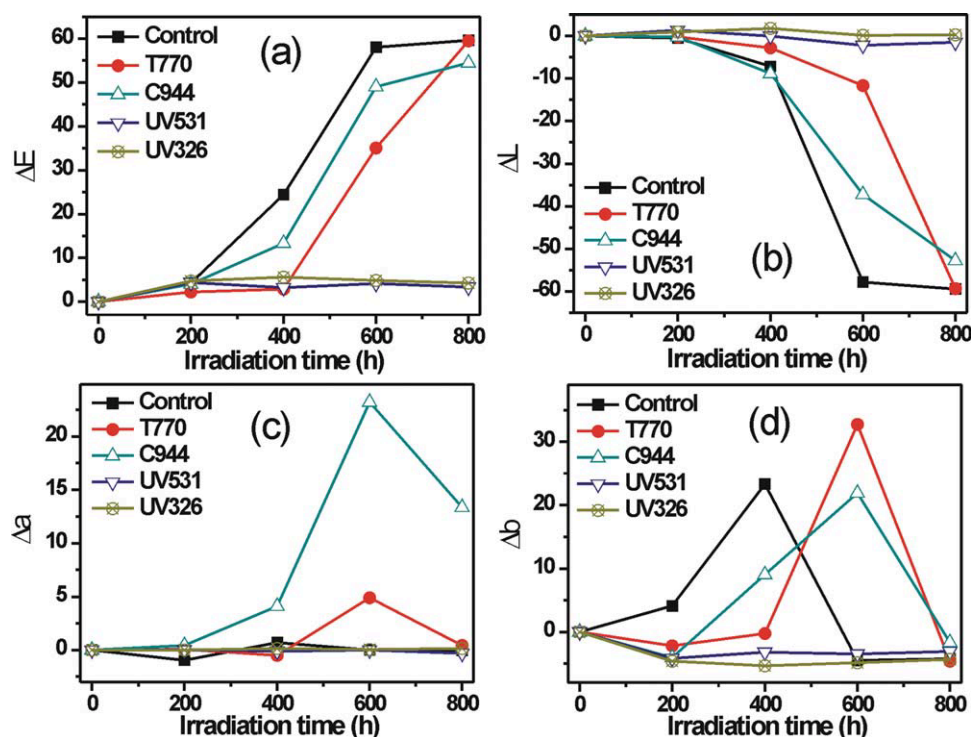
in which + $\Delta L$  = lighter, – $\Delta L$  = darker; + $\Delta a$  = red, – $\Delta a$  = green; + $\Delta b$  = yellow, – $\Delta b$  = blue.

In order to remove the influence of plasticizers, DOP in the irradiated and unirradiated PVC samples is extracted by a Soxhlet apparatus for 48 h in the solvent of ether. Then the samples are determined by ATR-FTIR technology with a resolution of 4 cm<sup>–1</sup> in the range of 580–4000 cm<sup>–1</sup> in IFS 66/S infrared spectrometer (Bruker Optics, German).

The tensile properties of the dumb-bell samples before and after irradiation are obtained by a CMT 5254 type electromechanical universal testing

**TABLE III**  
**Digital Photo of Plasticized PVC Samples Before and After Irradiation [Color table can be viewed in the online issue, which is available at wileyonlinelibrary.com.]**

Sample	Irradiation time (h)					Sample	Irradiation time (h)				
	0	200	400	600	800		0	200	400	600	800
Control						Control					
T770						T770/UV531					
C944						T770/UV326					
UV531						C944/UV531					
UV326						C944/UV326					



**Figure 1** Changes of color parameters of plasticized PVC with single additive during irradiation. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

machine (Shenzhen SANS Testing Machine Co., Ltd., China) at the rate of 200 mm/min, according to ISO 527. The hardness of the samples before and after irradiation is obtained by a LX-A Shore A hardness degree tester (Jiangdu Mingzhu Testing Machinery Co., Ltd., China).

## RESULTS AND DISCUSSION

### Digital photos

The digital photos of the plasticized PVC samples before and after photo-irradiation are presented in Table III. The color of PVC control develops quickly, from light yellow (unirradiated) to deep yellow (200–400 h) and then to dark (600–800 h).<sup>20</sup> The discoloring of PVC samples with T770 and PVC with C944, turning to yellow after 400 h of irradiation, is less obvious than that of PVC control. Besides, the better photostable effect of C944 than that of T770 may be because C944 has higher molecular weight and good extraction resistance.<sup>21,22</sup> So the more physical loss of T770 makes the less amount that left to participate in the photostable reactions, resulting in the quicker discoloring of PVC with T770 than that of PVC with C944.

The color of PVC with UV531 and PVC with UV326 almost does not change after irradiation for 800 h. The results indicate that HALS can provide some protection to plasticized PVC from UV rays,

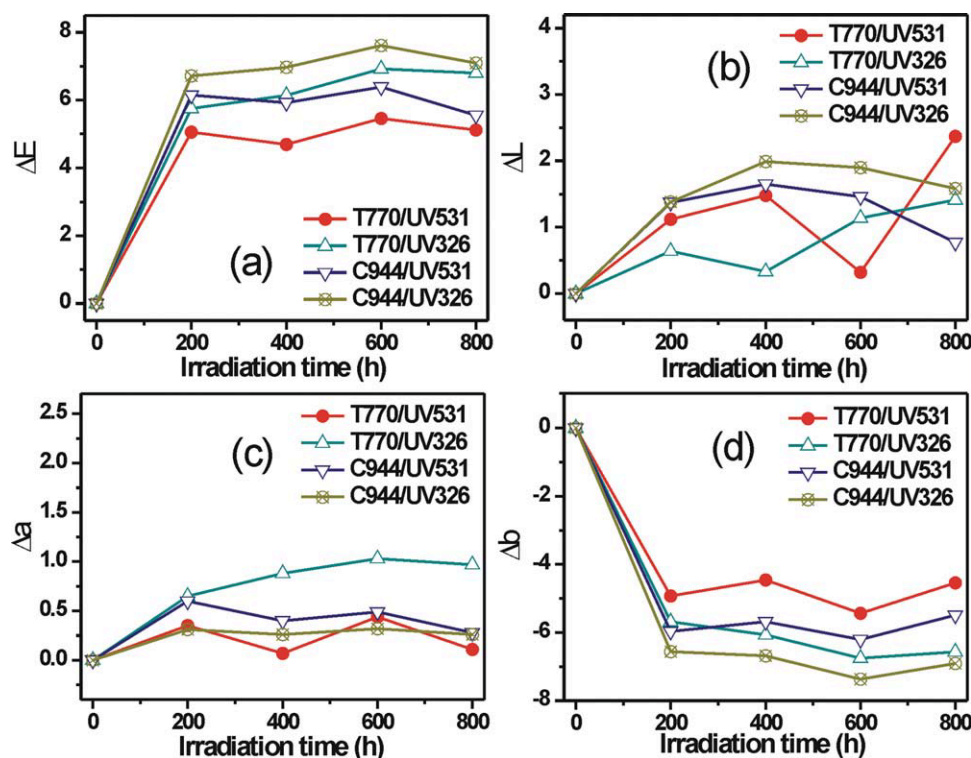
but the effect of UVA is much better. This is consistent with the effect of HALS and UVA in the casted PVC films,<sup>18</sup> since the UVA takes effect before the UV rays can damage the covalent bond of the samples but HALS cannot absorb UV rays and only takes effect after oxyradicals are generated.

PVC samples with 0.25 phr HALS plus 0.25 phr UVA are as colorless and transparent as PVC samples with 0.5 phr UVA. This indicates that effect of the combination of HALS and UVA on the color change during degradation color is as good as the effect of the single use of UVA.

### Color differences

The quantified changes of color of the plasticized PVC samples are divided into four parameters (called  $\Delta E$ ,  $\Delta L$ ,  $\Delta a$ , and  $\Delta b$ ) and shown in Figures 1 and 2. The total color change [ $\Delta E$ , Fig. 1(a)] of PVC control develops quickly from 200 h (24.41) to 600 h (58.03), and then keeps constant until 800 h (59.6).  $\Delta E$  of PVC with T770 is low in the first 400 h (2.85) but it increases to 35.07 at 600 h and 59.52 at 800 h, respectively. For PVC with C944, the value of  $\Delta E$  increases to 49.04 at 600 h.

According to eq. (1),  $\Delta E$  of PVC control, PVC with T770, and PVC with C944 was first depended on yellowness [ $\Delta b$ , Fig. 1(d)], and then on darkness [ $\Delta L$ , Fig. 1(b)]. The phenomena suggest that during photo-irradiation the three kinds of samples change



**Figure 2** Changes of color parameters of plasticized PVC with combined additives during irradiation. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

from colorless to yellow and dark at last, which is consistent with the results of digital photos.

The fact that the lower value of  $\Delta E$  of PVC with HALS than that of the control sample during the first 600 h means that T770 and C944 prohibit the formation of long conjugated polyenes in the plasticized PVC to some degree. This may be explained by the fact that the acid–base neutralization reaction<sup>23</sup> between basic HALS and acidic HCl decelerates the dehydrochlorination of plasticized PVC, because the zip dehydrochlorination and expansion of polyenes is autocatalyzed by HCl.

When irradiated for 800 h, the control sample and plasticized PVC with HALS thoroughly change into darkness. This is because the polyene structures absorb UV rays due to their very high extinction coefficients,<sup>20</sup> and they may obtain longer polyene sequences or be oxidized. So the color of samples changes into dark.<sup>24,25</sup>

The values of  $\Delta E$  of PVC with UV531 and PVC with UV326 are low (about 4–5) after irradiated for 800 h. However, it is highly depended on the change of blueness [ $\Delta b$ , Fig. 1(d)] The minus value of  $\Delta b$  reflects that a trace of original yellowness fades away. This is because the color of the UVA is yellow. As the UVA consumes or transforms in the photostable reactions, the original color also goes to colorless.

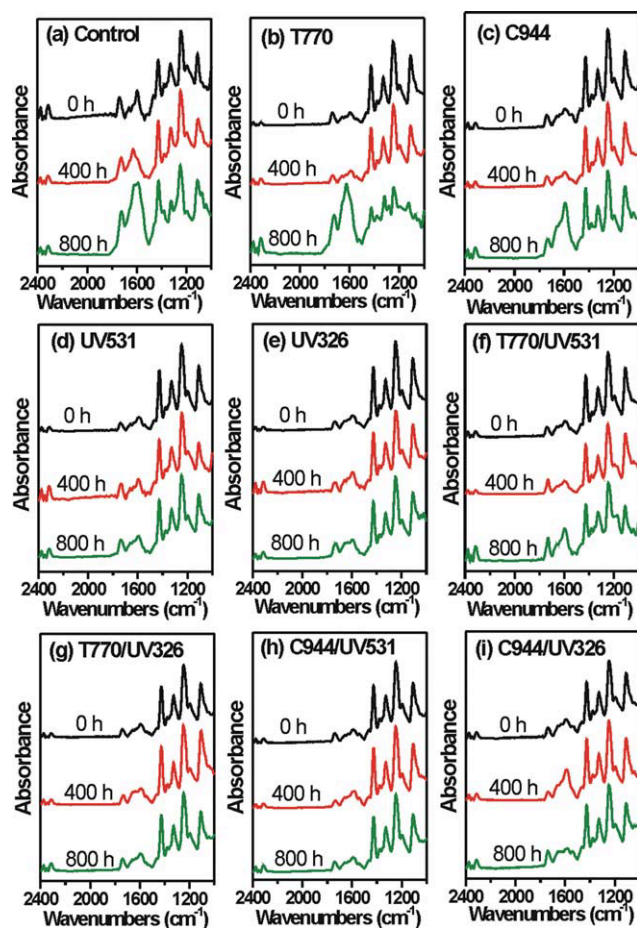
It is shown in Figure 2(a) that  $\Delta E$  of PVC with HALS/UVA is quite low (about 5–7) when irradiated from 200 h to 800 h. Compared with  $\Delta E$  of PVC

control and PVC with HALS, it can be seen that the combined HALS and UVA prohibit the discoloring of PVC samples due to photodegradation.<sup>17</sup>

According to eq. (1), the  $\Delta E$  of PVC with HALS/UVA is decided by the yellowness [ $\Delta b$ , in Fig. 2(d)], like PVC with UVA. The sequence of the anti-discoloring effect of this combination is C944/UV326 > T770/UV326 > C944/UV531 > T770/UV531. This order indicates that the efficacy of HALS is C944 > T770 and efficacy of UVA is UV326 > UV531. This also proves that the synergistic effect of HALS and UVA does not mean there is an intramolecular reaction between them and the products have the ability of anti-degradation, but means that they act at different stages—not only prevent the samples from harmful UV rays but also trap free radicals.

#### Fourier transformation infrared spectroscopy analysis

When the PVC samples are irradiated in the atmosphere of oxygen or air, photooxidation will occur. An efficient approach for the molecular level of the photooxidation of PVC samples is supplied by infrared spectroscopy. The FTIR spectra of unirradiated PVC and irradiated for 400 h and 800 h are presented in Figure 3. Obvious absorption bands appear at about  $1730\text{ cm}^{-1}$  and  $1590\text{ cm}^{-1}$ . It indicates that photooxidation occurs and some oxidative products



**Figure 3** FTIR spectra of plasticized PVC samples during irradiation. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

containing carbonyl groups appear in PVC materials during aging.<sup>4,26</sup>

Carbonyl index (CI) is introduced to quantify the photooxidation products. Since the photooxidation

of PVC materials is a surface reaction and the distributions of the photooxidation products are correlated with the thickness of samples. Now that the methylene ( $-\text{CH}_2-$ ) is not influenced during irradiation, the absorption band of its C—H bond is selected as internal reference. So the standardized absorbance of carbonyl groups around  $1730\text{ cm}^{-1}$  is calculated by eq. (2)<sup>1,27,28</sup>:

$$\text{Carbonyl index} = \left( \frac{A_{1730}}{A_{1427}} \right) \times 100\% \quad (2)$$

where  $A_{1730}$  is the integrated surface area of the absorption bands from  $1500$  to  $1850\text{ cm}^{-1}$ ,  $A_{1426}$  is the integrated surface area of the absorption band from  $1400$  to  $1500\text{ cm}^{-1}$ . The calculated results are listed in Table IV.

The CI reflects the content of carbonyl groups and represents the degree of the photooxidation of PVC samples that undergo weathering. It is shown in Table IV that CI of PVC control arises from 106% at 0 h to 303% at 400 h and quickly grows to 832% at 800 h, meaning that the photooxidation of PVC is an autocatalytic reaction and is accelerated at the latter stage of irradiation. PVC with T770 and PVC with C944 have low values of CI at 400 h, but CI of them rapidly increases to 884% and 418% at 800 h, respectively. This indicates that the basic hindered amines have good initial antioxidative efficiency, but at the latter stage of irradiation T770 cannot prohibit the oxidation of samples and C944 retains its ability for photostabilization of PVC samples.

Though the basic HALS may lose its ability of trapping radicals by HCl,<sup>14</sup> it easily reacts with other acidic groups such as ROOH [eqs. (3) and (4)], to form hydroxylamines which participate the Denisov cycle [eqs. (5) and (6)]<sup>23,29</sup> and prohibit the photooxidation of PVC samples.

**TABLE IV**  
Carbonyl Index of PVC Samples Before and After Irradiation

Sample	Irradiation time (h)	CI = $A_t$ (%)	$A_t - A_0$ (%)	Sample	Irradiation time (h)	CI = $A_t$ (%)	$A_t - A_0$ (%)
Control	0	106	0	Control	0	106	0
	400	303	197		400	303	197
	800	832	726		800	832	726
T770	0	99	0	T770/UV531	0	115	0
	400	97	-2		400	147	33
	800	884	785		800	292	177
C944	0	117	0	T770/UV326	0	108	0
	400	114	-3		400	149	40
	800	418	301		800	151	43
UV531	0	92	0	C944/UV531	0	98	0
	400	106	14		400	130	32
	800	213	121		800	125	26
UV326	0	105	0	C944/UV326	0	134	0
	400	141	36		400	220	86
	800	203	98		800	152	18

**TABLE V**  
**Tensile Properties of Plasticized PVC with Single Additives Before and After Irradiation**

Sample	Irradiation time (h)	Tensile strength (MPa)	Change rate of tensile strength (%)	Elongation at break (%)	Change rate of elongation at break (%)
Control	0	16.3	0	367	0
	200	4.8	-71	96	-74
	400	4.5	-72	76	-79
	600	6.7	-59	36	-90
	800	4.3	-74	21	-94
T770	0	16.5	0	365	0
	200	12.1	-27	239	-35
	400	6.4	-61	125	-66
	600	6.6	-60	103	-72
	800	5.5	-67	40	-89
C944	0	16.4	0	350	0
	200	10.4	-37	218	-38
	400	5.7	-65	93	-73
	600	6.3	-62	81	-77
	800	6.1	-63	68	-81
UV531	0	16.7	0	376	0
	200	12.6	-25	271	-28
	400	10.1	-40	202	-46
	600	8.6	-49	126	-66
	800	5.4	-68	74	-80
UV326	0	17.0	0	370	0
	200	14.8	-13	303	-18
	400	14.9	-12	285	-23
	600	13.2	-22	224	-39
	800	11.2	-34	190	-49



CI of PVC with UV531 and PVC with UV326 increases just to 213% and 203% after 800 h of irradiation, respectively. The result implies that UV531 and UV326 can efficiently prohibit the photooxidation of PVC samples.

The CI of PVC with T770/UV531 at 800 h (292%) is higher than that of PVC with UV531 (213%), but

**TABLE VI**  
**Tensile Properties of Plasticized PVC With Combined Additives Before and After Irradiation**

Sample	Irradiation time (h)	Tensile strength (MPa)	Change rate of tensile strength (%)	Elongation at break (%)	Change rate of elongation at break (%)
T770/UV531	0	16.2	0	351	0
	200	16.8	4	336	-4
	400	14.3	-12	301	-14
	600	11.9	-27	195	-44
	800	8.0	-51	127	-64
T770/UV326	0	16.3	0	316	0
	200	16.4	1	356	13
	400	15.2	-7	306	-3
	600	14.4	-12	247	-22
	800	11.7	-28	190	-40
C944/UV531	0	16.6	0	349	0
	200	13.9	-16	267	-23
	400	12.5	-25	236	-32
	600	12.9	-22	228	-35
	800	11.0	-34	196	-44
C944/UV326	0	16.2	0	330	0
	200	16.7	3	346	5
	400	14.1	-13	230	-30
	600	13.4	-17	226	-32
	800	13.0	-20	216	-35

TABLE VII  
Hardness (Shore A) of Plasticized PVC Before and After Irradiation

Irradiation time (h)	Control	T770	C944	UV531	UV326	T770/UV531	T770/UV326	C944/UV531	C944/UV326
0	75	77	76	77	76	75	78	77	75
200	78	78	76	74	75	75	75	74	74
400	73	76	76	73	72	75	76	76	75
600	81	78	77	74	75	74	75	76	76
800	85	84	81	74	77	78	77	76	76

much lower than that of PVC with T770 (884%). Besides, in other three formulations, PVC with HALS/UVA has lower value of CI than that of PVC with single HALS or UVA at 800 h. It can be seen that obvious synergistic effect is observed in the combined samples.

The excellent long-term performance of HALS/UVA in plasticized PVC is also due to the different stages of functions of HALS and UVA. The UVA absorbs most UV rays that reach the surface of samples. Then the left UV rays participate into the dehydrochlorination and oxidation reactions, but the generated products like HCl and free radicals are reacted or transformed by HALS. As a result, the combined HALS and UVA protect plasticized PVC efficiently than the singly used additives.

Similar to the results in the color difference part, the oxidative degree of PVC with T770/UV531 is the most obvious among the combined samples.

### Mechanical properties

An important parameter of the plasticized PVC is the mechanical property, which determines the practical value of the products. Tables V and VI show the tensile properties of PVC samples with single or combined additives, respectively.

In Table V, the tensile strength of PVC control apparently decreases from 16.3 MPa to 4.8 MPa, with 71% lost, after 200 h of photo-irradiation. Then it almost does not change from 200 h to 800 h. Tensile strength of PVC with T770 and PVC with C944 falls by 27% and 37%, respectively, at 200 h and by about 60% from 400 h to 800 h. This is because the basic HALS traps the oxyradicals in polymer matrix and prohibits the photooxidative degradation of PVC samples to some degree.

Though the performance of UV531 and UV326 is excellent in protecting PVC samples from color change and photooxidation, after 800 h tensile strength of PVC with UV531 and PVC with UV326 decreases by 68% and 34%, respectively. This is because the efficiency of absorbing harmful radiation of UV531 is a little lower than that of UV326, so less radiation reaches the surface of PVC sample with UV326 and induces photodegradation to a less content. On the other hand, the continuous drop of

tensile strength of PVC with UV326 was because the UVA cannot prohibit the degradation by trapping radicals or scavenging excited structures. As a result, the degree of degradation continually grows and the photostability of UVA drops to some content.

The elongation at break of PVC control rapidly decreases from 367% at 0 h to 96% at 200 h, losing most of its elasticity. The drop of elongation at break of PVC with T770 and PVC with C944 changes more slowly at 200 h, by 35% and 38%, then gradually to 89% and 81% at 800 h, respectively.

The order of the decreasing rate of elongation at break of PVC with singly added additives is Control > T770  $\approx$  C944 > UV531 > UV326.

The data of the tensile properties in Table V indicate that the singly added HALS and UVA prohibit the drop of tensile strength and elongation at break of PVC samples. Besides, the effect of UVA on the samples is better than HALS and UV326 performs better than UV531.

When HALS and UVA are used in combination (Table VI), tensile strength and elongation at break of PVC samples decrease much more slowly than that of PVC control and PVC with the single additives. This is opposite to the observation in literature.<sup>13</sup> Martine et al. report that the elongation of plasticized PVC with HALS/UVA (The UVA is also called UV531) decreases more quickly than PVC with UVA. The inconsistency can be explained by the fact that the light source used in the literature emits in 280–390 nm region but in this study ranging from 300 to 800 nm. Because of the two absorptive peaks at 290 and 330 nm,<sup>30</sup> UV531 in the literature protects plasticized PVC more efficiently than that in this study. Besides, the formulations, method of sample preparation, and data processing are also different.

At the first 400 h, PVC samples with T770/UVA have better initial retention of tensile strength and elongation at break than that of C944/UVA. But at the last stage of irradiation, the situation is opposite.

The hardness of PVC samples before and after photo-irradiation is determined and shown in Table VII. For PVC control, the hardness changes a little in the first 400 h, but gradually increases by 6 and 10 Shore A at 600 and 800 h, respectively. In plasticized PVC samples, degradation causes the chain-scission



of macromolecules and so the hardness drops. What's more, the scission of the molecules makes the migration of plasticizer from the inside of polymer to the surface more easily and results into the increase of hardness.<sup>31</sup> For PVC control, the hardness increases in the latter stage of photo-irradiation, because large amount of plasticizer emigrates from the matrix.

The increase of hardness of PVC with T770 and PVC with C944 at 800 h indicates that the migration of DOP in the two samples is put off by T770 and C944. The drop of hardness of PVC with UVA means that only a low degree of degradation occurs.

PVC samples with HALS/UVA have a slightly changed hardness, which is because the combination of HALS and UVA protects PVC from photodegradation and crosslinking.

### CONCLUSIONS

Two kinds of HALS with different molecular weight (T770 and C944) and two kinds of UVA are added singly or in combination into plasticized PVC to investigate their photostable effect of light stabilizers during photo-irradiation. Excellent synergism is observed between the combination of HALS and UVA. PVC samples with HALS/UVA perform better than PVC with HALS and PVC with UVA in color, FTIR, and mechanical properties. The excellent long-term performance of HALS/UVA in plasticized PVC is also due to the different stages of functions of HALS and UVA. The UVA absorbs most UV rays that reach the surface of samples. Then the left UV rays participate into the dehydrochlorination and oxidation reactions, but the generated products like HCl and free radicals are reacted or transformed with HALS. As a result, the chemical reactions induced by harmful lights and the generated defect structures are reduced to a large extent.

UVA takes effect before the UV rays can damage the molecule bond of PVC matrix but HALS cannot absorb UV rays and only takes effect after oxyradicals are generated.

The basic HALS may lose parts of its ability of trapping radicals by reacting with HCl. Besides, it reacts with other acidic groups such as ROOH, to form hydroxylamines which participate in the Denisov cycle and prohibit the photooxidation of PVC samples. The better effect of C944 than T770 may be because C944 is a high-molecular weight UV stabilizer and has good extraction resistance.

The photodegradation and migration loss of DOP induce decrease of elasticity and mechanical properties. So another polymeric plasticizer, powder of butadiene acrylonitrile rubber, will be selected in the following study.

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