

EFFECTS OF ORGANIC COLORANTS ON PHOTO-INITIATED CROSSLINKING AND PHOTO-OXIDATION DEGRADATION OF POLYETHYLENE AND RELATED MECHANISM*

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Abstract The effects of three organic colorants on photo-initiated crosslinking and photo-oxidation degradation of polyethylene (PE) samples irradiated by microwave excited (MWE) UV lamp in the melt and the related mechanism have been studied by gel content and thermal extension rate determinations, X-ray photoelectron spectroscopy (XPS), mechanical property tests, UV spectroscopy, and light microscope. The data from the gel content and thermal extension rate determinations of photo-crosslinked polyethylene (XLPE) samples show that the three colorants can decrease the efficiency of photo-initiated crosslinking of polyethylene to some different degree, in which the effect of red colorant is the largest among the three colorants. The colorized samples of 1 mm thickness are easily to be crosslinked to a satisfactory gel content of about 70% by the MWE lamp and optimized reaction conditions, such as the concentration of colorant, irradiation time, and so on. The XPS results give the evidence that the colorants can accelerate the surface photo-oxidation during the photo-crosslinking of polyethylene. The photo-oxidation products such as $-\text{CH}_2-\text{O}-$ and $-\text{C}(\text{C}=\text{O})-$ groups on the surface of XLPE samples with the colorants apparently increase with increasing the irradiation time. The data from the mechanical tests show that the colorants reduce the tensile strength and improve the elongation at break of XLPE samples. All the above results show that the effects of the three colorants on photo-initiated crosslinking and photo-oxidative degradation decrease with the order of red > blue > green colorants. The light microscope photos show that the colorant can disperse well in PE resin. The mechanism of the colorant effects can be elucidated by comparison of the UV absorption spectra of photo-initiator and colorants. This is because the colorants absorb the same UV wavelength regions as photo-initiator, and thus decrease the photo-crosslinking efficiency of photo-initiator and accelerate the surface photo-oxidation of XLPE materials.

Keywords: Colorant; Photo-initiated crosslinking; Photo-oxidative degradation; UV irradiation; Polyethylene.

INTRODUCTION

In recent years, there have been significant breakthroughs in the photo-initiated crosslinking of bulk polyethylene and industrial application for manufacturing the photo-crosslinked polyethylene (XLPE) insulated cables^[1–9]. The mechanism and cross-link microstructures of the photo-crosslinking of LDPE and its model compounds^[10–12], the surface photo-oxidation of XLPE materials^[13] and the dynamically photo-crosslinking of polypropylene/EPDM thermoplastic elastomer^[14, 15] have been reported in our previous series of work. However, most studies in the past have been focused on photo-crosslinking of the colorless insulated materials, because the colorized materials are very difficult to be photo-crosslinked to a satisfactory crosslinking degree by high pressure mercury (HPM) lamp in a short irradiation time and very easy to produce severely photo- and thermo-oxidative degradation in a long UV irradiation^[13, 16], which can lead the color to disappear. It has been reported that the pigments can absorb the part UV energy^[17, 18] and prevent the UV light from penetrating into thick samples. Therefore, the photo-crosslinking of the colorized materials has become one of the main problems to be solved with developing industrial applications of photo-crosslinking technique.

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It has been found^[9, 19] that the MWE lamp with high light intensity has stronger penetration and higher reaction rate than the HPM lamp in the photo-crosslinking of PE. Usually it takes a few seconds UV irradiation to obtain the cross-linking degrees of practical application. The present work is devoted mainly to study the effects of organic colorants on photo-initiated crosslinking and surface photo-oxidation degradation of PE samples irradiated by the microwave excited UV lamp and the related effect mechanism by gel content and thermal extension rate determinations, X-ray photoelectron spectroscopy (XPS), mechanical properties tests, UV spectroscopy, and light microscope. The main purpose of this work is to develop new colored photo-crosslinked materials that can be used in the industrial application of wire and cable.

EXPERIMENTAL

Materials

Three kinds of polyethylenes were used in this work: HDPE (5000 S) from Yangzi Petrochemical Co. Ltd. China, LDPE (2102TN26) from Qilu Petrochemical Co. Ltd. China, and LLDPE (NTF1840) from Exxonmobile Asia Pacific Pte Ltd. Singapore. Benzophenone (BP) from Shanghai Reagent Factory No.1 (chemical pure) and triallyl isocyanurate (TAIC) from Anhui Institute of Chemical Engineering were used as photoinitiator and crosslinker, respectively. Three kinds of commercial organic colorants were Irgalite Green GLNP, Cromophthal Yellow 3G, and Irgalite Red 2BP supplied by Qingdao Keya Co. Ltd. China. The detailed chemical information of the three colorants can consult from the Ref. [20]. All the above chemicals were used as received without any purification.

Sample Preparation

All the samples (50 g batches of PE with 1 wt% BP and 1 wt% TAIC) were mixed for 10 min at 150°C with an XSS-300 rheomixer (made in China). After being mixed, the samples were hot-pressed into sheets of suitable thickness for 5 min at 150°C for LDPE and LLDPE and at 165°C for HDPE.

UV Irradiation

The samples were UV-irradiated in a UV-CURE device and UV lamp system (F300S/F300SQ) constructed by our laboratory and Fusion Co. USA, respectively. The UV lamps used were high-pressure mercury lamp (Philips HPM-15, 2 kW, light intensity 400 mW/cm²) at a distance of 10 cm and microwave excited (MWE) lamp (Fusion F300, 120 W/cm, light intensity 1800 mW/cm²) at a distance of 5.3 cm from the surface of the sample. The usual irradiation conditions of the samples were BP 1 wt%, TAIC 1 wt%; irradiation temperature $T = 140^{\circ}\text{C}$ for LDPE and LLDPE and 150°C for HDPE under atmosphere; and sample thickness 1 mm unless stated otherwise.

Gel Content

After being irradiated, the sample were cut into thin slices and put into a basket made of 200-mesh stainless steel net. The gel content of samples was determined through the extraction of the irradiated samples (w_1) in the basket for 48 h with boiling xylene stabilized by 0.2% of antioxidant Tinuvin 144 and with N₂ bubbling to prevent oxidation. The solvent was renewed after the first 24 h of extraction. After the extraction, the basket was washed with acetone. After being dried in a vacuum desiccator at about 70°C to constant weight, the insoluble residue (w_2) was weighed. The average gel content (wt%) in the test was calculated as $100 (w_2/w_1)$. Usually, three samples were analyzed to determine the average gel content for a given set of irradiation conditions.

Thermal Extension Rate

The thermal extension rate (TER) measurement was done to measure the extension of samples using a static loading at a fixed temperature. Measurements were carried out in an oven at 200°C with normal air conditions. The sample loading was 20 N/cm². The extension between two marks was determined after 15 min heating of sample in the oven.

XPS Spectroscopy

The XPS spectra were recorded with a VG ESCALAB MK II spectrometer (VG company, UK) using Al K_α excitation radiation ($h\nu = 1253.6 \text{ eV}$).

Mechanical Properties

The mechanical properties were measured with a universal testing machine (DCS500, Shimadzu) at temperatures $(25 \pm 2)^\circ\text{C}$. The crosshead speed was 25 mm/min. Dumbbell-shaped specimens were prepared according to ASTM D412-87. Tensile strength (TS) and elongation at break (EB) were recorded.

Ultraviolet Spectroscopy

The various colorants and photo-initiator BP were dissolved in CHCl_3 . UV absorption spectra were recorded using a Shimadzu UV-240 scanning spectrometer.

Dispersion of Colorants in PE Resin

The dispersion of colorants in PE resin was observed by a light microscope (made in Olympus Co. Ltd., Japan). The film specimens of 0.1 mm thickness were sandwiched between two microscope cover glasses. The proportion between colorant and PE is 1:25.

RESULTS AND DISCUSSION

Effects of UV Light Source on Photo-Crosslinking of Samples with Colorant

The UV lamps of different light intensity have crucial effect on the rates of gel formation for the photo-crosslinked samples. Figure 1 shows the changes of gel contents with the irradiation time for the red colorant samples irradiated by the HPM and MWE lamps. Apparently, the MWE lamp with high light intensity has much higher photo-crosslinking efficiency than the HPM lamp with low light intensity. If we select gel content of about 70% as a compare point, it needs about 40 s irradiation times for the HPM lamp, while it only needs about 3–4 s for MWE lamp at the same conditions. Moreover, the color of sample irradiated by the HPM lamp disappeared after the 20 s irradiation time because of the serious photo- and thermo-oxidative degradation of colorant. On the contrary, the color of the same sample irradiated by MWE lamp still remained after 3–4 s irradiation. So the selection of UV lamp is of key importance for the applications of the colored photo-crosslinked XLPE wire and cable.

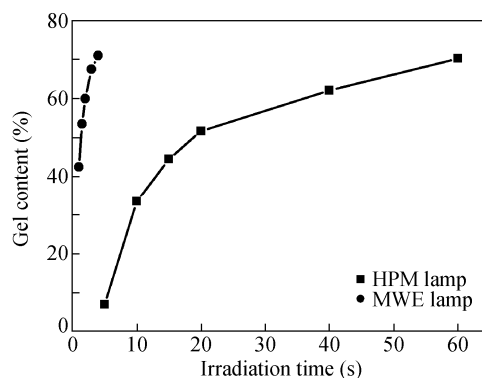


Fig. 1 Effects of UV light source on gel contents of photo-crosslinked HDPE samples with 0.08 wt% red colorant in the presence of 1 wt% BP and 1 wt% TAIC

Effects of Colorants on Photo-Initiated Crosslinking Efficiency

The effects of the colorant concentration on the gel contents of photo-crosslinked HDPE, LDPE and LLDPE samples UV-irradiated by MWE lamp for 4 s are shown in Fig. 2. Apparently the gel contents in the three samples decrease linearly with increasing the colorant concentrations. For example, the gel contents decrease about 8%, 6%, and 6% of HDPE, LDPE, and LLDPE samples with 0.08 wt% red colorant compared with the corresponding samples without colorant, respectively. When the colorant concentration increases to 0.16 wt%, the corresponding gel contents in the above three samples show further decreases of about 16%, 13%, and 14%, respectively. This means that the colorant can decrease the photo-initiated crosslinking efficiency of PE samples because the colorant absorbed the UV light energy and thus decrease the UV light absorption of photo-initiator. The result is similar to the literature^[17, 18], which reported that the UV-curing of pigmented prints remained

difficult due to the high light absorption by pigment. Based on the acceptable degree of photo-crosslinking efficiency and the color vision, 0.08 wt% colorant is chosen as a suitable concentration for the application of XLPE cables.

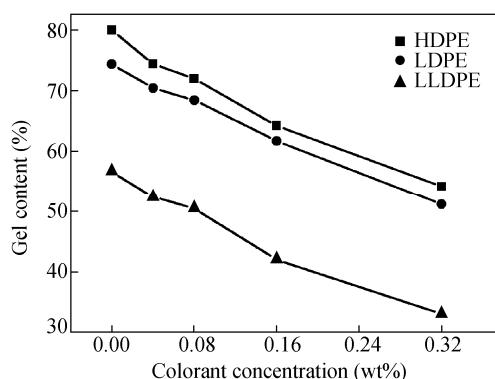


Fig. 2 Effects of red colorant concentration on gel contents of photo-crosslinked HDPE, LDPE and LLDPE samples irradiated by MWE lamp for 4 s in the presence of 1 wt% BP and 1 wt% TAIC

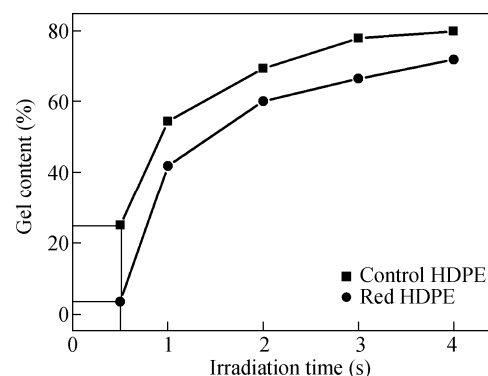


Fig. 3 Changes of gel contents with irradiation time for photo-crosslinked HDPE samples with 0.08 wt% red colorant irradiated by MWE lamp in the presence of 1 wt% BP and 1 wt% TAIC

Figure 3 shows the changes of gel content with the irradiation time for the XLPE samples without and with 0.08 wt% red colorant. It is evident that the gel content of the control XLPE sample without a colorant is higher than that of the sample with red colorant. If 0.5 s irradiation time was selected as a comparison point of the initial step, the gel content of control XLPE sample was 25%, while the gel content from the red XLPE sample was only 3.5% at the same concentrations of BP and TAIC (1 wt% each). However, the gel content from the red XLPE sample rapidly increases to 43% after 1 s irradiation. These results indicate that the effect of colorant on the photo-crosslinking rate mainly occurs in the first initial step.

The effects of different colorants on the photo-crosslinking rates are shown in Fig. 4. It can be seen that the effect of the red colorant on the gel content is the largest among the three samples, while the effect of green colorant is the smallest. However, it has been found that the colorized PE samples of 1 mm thickness with 0.08 wt% colorant are easily crosslinked to a satisfactory gel content of about 70% after 4 s UV-irradiation in the presence of 1 wt% BP and 1 wt% TAIC.

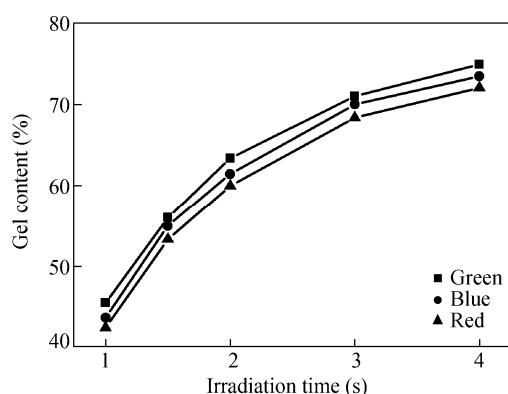


Fig. 4 Effects of different colorants on gel contents of photo-crosslinked HDPE samples irradiated by MWE lamp in the presence of 1 wt% BP and 1 wt% TAIC

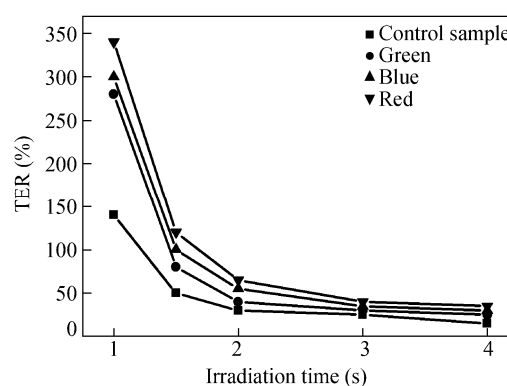


Fig. 5 Effects of different colorant on the heat extension rates of photo-crosslinked HDPE samples with 0.08 wt% colorant irradiated by MWE lamp in the presence of 1 wt% BP and 1 wt% TAIC

The thermal extension rate (TER) data can provide a quick determination for the crosslinking degree of XLPE samples. The TER data of four samples irradiated by MWE lamp are shown in Fig. 5. Apparently the TER values decrease with increasing the irradiation time because of increasing the crosslinking degree. It can be seen that the colorants considerably decrease the crosslinking degree of XLPE samples compared with the control sample without colorant. For example, the TER value of the control sample is 140% after the first 1 s irradiation time whereas the colorant samples have larger TER values of about 280% because of lower crosslinking degree. However, the effect of the colorants becomes small when the irradiation time increases to 2 s. The TER values of all the four samples approach to 50%, in which the TER value of sample with red colorant is the largest, while the TER value of the sample with green colorant is the smallest except for the TER value of control sample. The results give the positive evidence again that the effect of red colorant on the crosslinking efficiency is the largest and the effect of green colorant is the smallest among the three colorants.

Effects of the Colorants on Surface Photo-Oxidation of XLPE

XPS is extensively used to gather information in the outmost few tens of angstroms of the samples, especially for surface photo-oxidation of polymer materials. Figure 6 shows the XPS spectra of C_{1s} for the XLPE samples with and without colorants after 4 s irradiation time at the same reaction conditions. It can be seen from Fig. 6 that the oxidation products B and C marked by the broken lines obtained by the computer separating peaks of C_{1s} bands appear at about 286.5 and 287.5 eV, which have been assigned to $-\text{CH}_2\text{O}-$ and $-\text{C}(=\text{O})-$ groups,

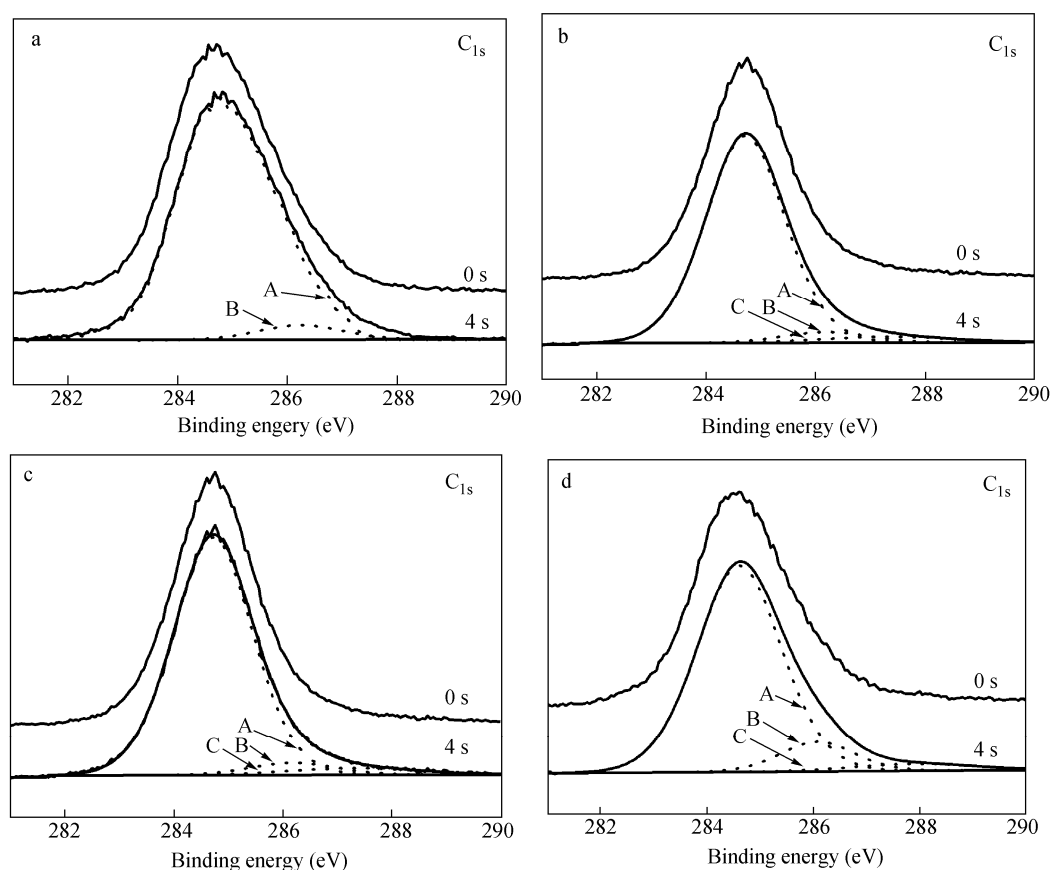


Fig. 6 C_{1s} XPS spectra of photo-crosslinked XLPE samples irradiated by MWE lamp for 4 s in the presence of 1 wt% BP and 1 wt% TAIC: (a) without colorant and with 0.08 wt% colorants, (b) green, (c) blue, and (d) red

respectively. The peak A at about 285.0 eV is due to the $-\text{CH}_x-$ group. All these assigned surface oxidation peaks are in good agreement with those reported in the previous literature^[13, 21]. However, the surface oxidation degree of various XLPE samples with and without colorants is quite different. The control sample without colorant has only B oxidative peak, as shown in Fig. 6(a). But the XLPE samples with colorants have not only B oxidative peak, but also C oxidative peak. Moreover, the areas of B and C oxidation peaks increase with the order of green, blue, and red colorants, respectively. These results show that the colorant can accelerate the surface photo-oxidative of XLPE samples with different degree. Among the three colorant samples, the red sample has the largest area of the surface oxidation peaks at 286–290 eV, which indicates that the XLPE sample with red colorant suffer the most serious surface photo-oxidation.

The stoichiometric O/C atom ratios obtained from the XPS spectra are used to characterize the degree of surface photo-oxidation. The O/C data of XLPE samples without and with colorants are listed in Table 1. It can be seen that the O/C atom ratios increase proportionally with increasing the irradiation time for all the samples. The O/C values of control XLPE sample irradiated for 2 s and 4 s were 0.021 and 0.056, respectively. However, the O/C values of colored XLPE samples with green, blue, and red colorants irradiated for 2 s increase rapidly to 0.035, 0.052 and 0.076, respectively. When the irradiation time further increases to 4 s, the O/C ratio values of the corresponding colorant samples increase doubly to 0.085, 0.110, and 0.157, respectively. These data give positive evidence that the colorants can accelerate the surface photo-oxidation of the XLPE samples. The surface photo-oxidation of the red XLPE sample is the most deteriorative, and the surface photo-oxidation degree of the colorized samples can be ordered as follows: control < green < blue < red.

Table 1. O/C atom ratios of XLPE samples without and with 0.08 wt% colorant irradiated by MWE lamp for different times

Irradiation time (s)	O/C values of XLPE samples			
	Control	Green	Blue	Red
2 s	0.021	0.035	0.052	0.076
4 s	0.056	0.085	0.110	0.157

Effects of the Colorants on Mechanical Properties of XLPE

The tensile strength (TS) and elongation at break (EB) of the XLPE samples with different colorant concentrations UV-irradiated for 4 s are shown in Fig. 7 and Fig. 8, respectively. It can be seen from Fig. 7 that the TS values decrease considerably with increasing the colorant concentration. When the colorant concentration increases to 0.32%, the TS values decrease to about 29 MPa from 34.8 MPa of the control sample without

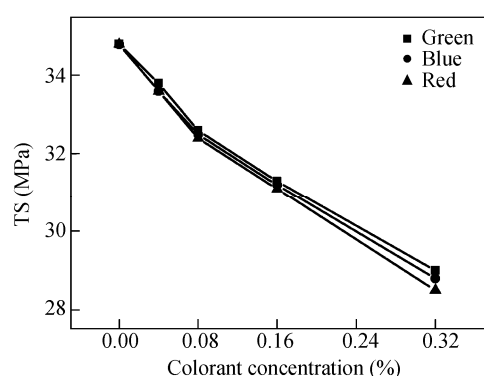


Fig. 7 Effects of colorant concentration on the tensile strength of XLPE samples irradiated by MWE lamp for 4 s in the presence of 1 wt% BP and 1 wt% TAIC

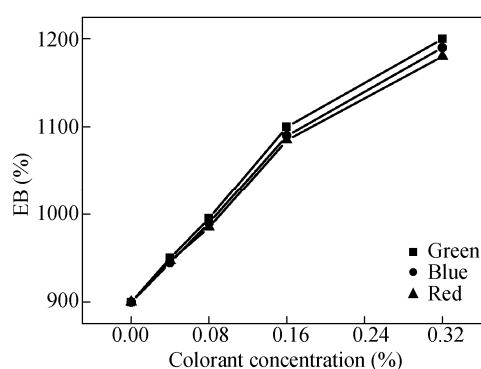


Fig. 8 Effects of colorant concentration on the elongation at break of XLPE samples irradiated by MWE lamp for 4 s in the presence of 1 wt% BP and 1 wt% TAIC

colorant. On the contrary, the EB values greatly increase with increasing the colorant concentration. When the colorant concentration is 0.32%, the EB values of samples increase to 1200% from 900% of the control sample without colorant. The above results show that the colorants can decrease the TS but improve the EB of the XLPE materials. The TS decrease can be due to the decrease of crosslinking degree in the colorant samples, while the EB increase can be due to the colorants acting as plasticizers.

Related Mechanism of Colorants Effects

The light microscopes photos of green, blue and red samples are shown in Fig. 9. It can be observed from Fig. 9 that the colorant in the three samples were well-dispersed and were not obviously agglomerated. The well-dispersed colorants in PE resin are mainly due to the disperser in the colorants^[20].

The UV absorption spectra of the red, blue, green colorants and photo-initiator BP are shown in Fig. 10. The UV spectra of BP show two main characteristic absorptions in the range of 200–400 nm: one strong peak near 260 nm attributed to a singlet (π, π^*) transition of the ketone group, the other peak whose center position is 340 nm attributed to a single (n, π^*) transition of the same group as seen in Fig. 10. It has been proved that the intersystem crossing of singlet (n, π^*) levels to triplet (10^{-12} s) is more efficient than that of singlet (π, π^*) levels to triplet (10^{-10} s)^[22]. The UV spectra of three colorants in the region of 200–400 nm are overlapped with those of photo-initiator BP, as shown in Fig. 10. Their main absorption bands centered at about 250 nm are similar to that of BP. However, the UV absorption peaks of three colorants show different intensities in the region of 300–400 nm. The red colorant has an obvious absorption peak at about 340 nm marked by the asterisks (*). The blue colorant shows a very weak shoulder absorption peak, while the green colorant has no peak at all at 340 nm. This is why the red colorant has the largest effect and the green one has the smallest effect on the gel formation photo-crosslinked XLPE samples among three colorants because the former does decrease the UV absorption of photo-initiator BP whereas the latter effect is much less.

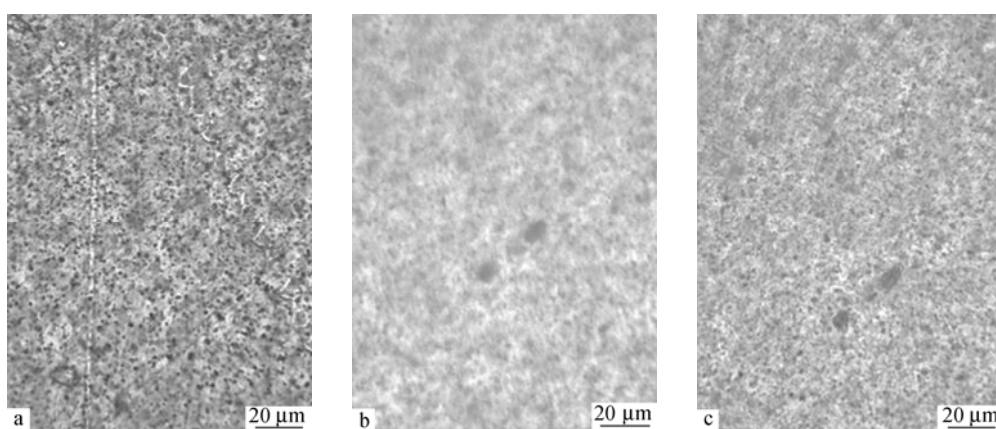


Fig. 9 Photos of light microscopes from the samples: (a) green, (b) blue and (c) red

On the other hand, the colorants absorb the UV light energy; especially on the surface of samples accelerate the surface photo-oxidation degradation during the photo-initiated crosslinking of PE. The degree of surface photo-oxidation degradation depends on the UV absorption intensity of various colorants, in which the UV absorption intensity of red colorant both 200–300 nm and 300–400 nm regions is the largest among three colorants and thus leads the severest surface photo-oxidation degradation of the sample with red colorant.

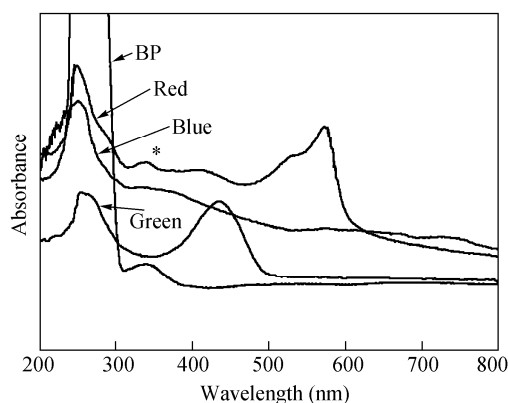


Fig. 10 UV absorption spectra of three colorants (10^{-6} g/mL) and photo-initiator BP (10^{-4} g/mL) in CHCl_3

CONCLUSIONS

The data from the gel content and thermal extension rate of the XLPE samples with the colorants demonstrate that the colorants can decrease the efficiency of photo-initiated crosslinking of PE samples, especially in first photo-initiated stage. The XPS data show that the colorants can accelerate the surface photo-oxidation of XLPE samples. The effect of red colorant on the photo-crosslinking efficiency and surface photo-oxidation are the largest, while the effects of green colorant are the smallest among the three colorants. The mechanism of the above effects can be elucidated by UV absorption spectra that the colorants can absorb the UV light energy in the corresponding UV regions of photo-initiator and thus decrease the photo-initiated crosslinking efficiency and accelerate the surface photo-oxidation of XLPE samples. The colorants have apparent effect on the mechanical properties of XLPE materials. The tensile strength decreases with increasing colorant content while the elongation at break increases with increasing colorant content. However, by optimizing reaction conditions, such as the colorant concentration, UV-irradiation time, and choosing the suitable UV lamp and resin, the colored PE samples as thick as 1 mm are readily to be crosslinked to a gel content of about 70% within 4 s UV-irradiation time. The photo-crosslinking of PE with colorants is promising for the industrial application of color insulated XLPE wires and cables.

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