RESEARCH ARTICLE

Photocrosslinking of ethylene-vinyl acetate (EVA)–polyethylene-octene (POE) copolymer containing halogen-free flame retardants

Giacomo Morselli[1] | Marco Villa[1] | Paola Ceroni[1] | Luca Medici[2] |
Fabio Tarlazzi[2] | Stefano Dossi[2] | Pietro Matteucci[2] | Andrea Galanti[2] |
Andrea Magrì[2]

[1]Department of Chemistry "Giacomo Ciamician", University of Bologna, Bologna, Italy

[2]Mixer S.p.A., Ravenna, Italy

Correspondence
Marco Villa, Department of Chemistry "Giacomo Ciamician," University of Bologna, Via Selmi 2, 40126, Bologna, Italy.
Email: marco.villa11@unibo.it

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Abstract

Photocrosslinking of polymers for industrial applications show undoubted advantages related to the mild conditions needed and the economical equipment. However, some issues include: the use of (i) mercury lamps as light sources, which poses concerns about safety and energy consumption, (ii) typical additives, such as halogen-free flame-retardant fillers (HFFR) are powdered materials, which can scatter UV photons and avoid a deep penetration of the light. In this study, we explore the UV-curing of an innovative EVA-POE blend containing hydrotalcite and aluminum hydroxide as HFFR in the presence of a 370-nm UV LED, namely Ekopren® XI1321, a plastic used as coverage for electric cables. Two commercially available photoinitiators (benzophenone and ethyl Michler's ketone) were analyzed as well as two crosslinking coagents widely used in industry, that is, triallyl cyanurate and trimethylolpropane trimethacrylate. A comparison with pure EVA and LDPE was performed to show a higher cross-linked content of the proposed blend, even in the presence of light scattering mineral fillers at high concentration.

KEYWORDS
crosslinking, curing of polymers, flame retardance, initiators, irradiation

1 | INTRODUCTION

Polymers are probably the most versatile materials available nowadays. By engineering both the nature of the monomers and the structure in which the monomers are linked together, it is possible to obtain a virtually infinite set of combinations leading to the most diverse properties. In particular, three of the most used polymers for industrial applications are: low density polyethylene (LDPE), ethylene-vinyl acetate copolymer (EVA), and ethylene-octene copolymer or polyolefin elastomer (POE), whose structure is reported in Scheme 1.

The above-mentioned polymers are rarely used in their pure form; to obtain the desired properties, also in terms of cost and safety, they are commonly mixed with other substances to form a so-called plastic. A typical recipe of a plastic contains several chemicals like antioxidants,[1,2] plasticizers,[3,4] fillers,[5] activators,[6,7] modifiers,[8] vulcanization
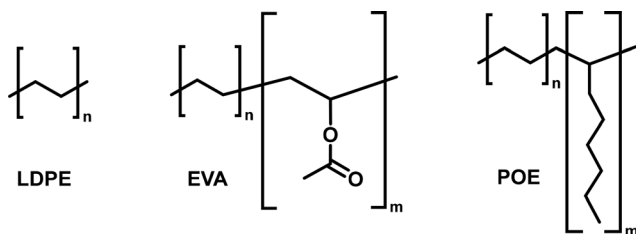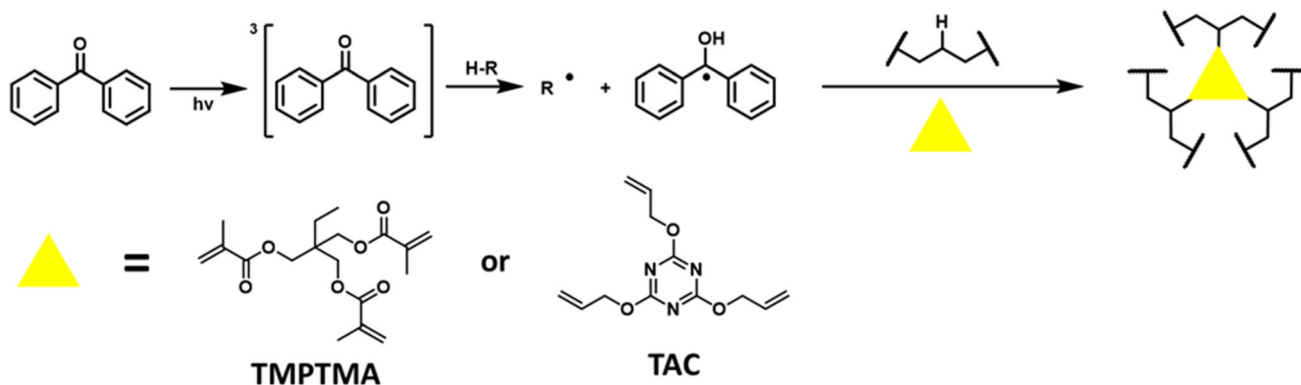
SCHEME 1 Chemical structure of the investigated polymers low density polyethylene (LDPE), ethylene-vinyl acetate (EVA), and polyethylene-octene (POE).

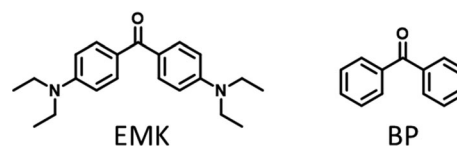**SCHEME 3** Structural formulas of ethyl Michler's ketone (EMK) and benzophenone (BP).

agents,[9,10] etc. Among them, halogen-free flame retardants (HFFR) are used as additives to avoid combustion and flame propagation in case of exposure to fire.[11] They find their main application in buildings, cables, furniture, vehicles, and in all the situations where fires can occur.[12]

Besides the formulation of compounds, to improve the mechanical and thermal properties of the polymers and of their compounds, crosslinking (also named curing) is required.[13,14] This process creates chemical bonds between the polymer chains donating further strength to the structure and fixing the shape of a manufacturing. Resistance to aging, chemicals, and environmental stress is greatly improved together with an enhancement of the mechanical response and resistance to stress and fatigue. The first method of curing, using sulfur and natural rubber, was invented by Charles Goodyear and Thomas Hancock in 1839[15] and found the first mass application in the tire industry.

Crosslinking can be accomplished by various methods that involve ionizing radiation (^{60}Co γ-rays or electron beam), organosilanes, or peroxides. The above listed curing strategies, however, can display numerous disadvantages, including the use of sophisticated equipment, hazardous materials, and elevated temperatures.[16–18] A valid alternative is represented by photoinduced crosslinking (or photocrosslinking).[19–21] The principal types of photocrosslinking follow a cationic or a radical mechanism.[22–25] In particular, radical photocrosslinking

consists in the absorption of light by a photoinitiator which generates radicals upon bond cleavage (type I photoinitiators) or by hydrogen abstraction or electron transfer to a coinitiator molecule (type II).[26] An example of type-II photoinduced crosslinking in the presence of a crosslinking agent is collected in Scheme 2.

So far, the most common light sources that have been used to activate the photoinitiators are mercury UV lamps[27–30]; however, due to the high costs, reduced depth of penetration and environmental concerns, the research is focusing on their replacement with near-UV emitting LEDs.[31]

In this work, we propose the photoinduced crosslinking of Ekopren® XI1321, a blend composed of EVA and POE containing HFFR useful as insulating coverage of electrical cable. A comparison with pure EVA and LDPE was performed in the presence of different photoinitiators, namely ethyl Michler's ketone (EMK) and benzophenone (BP, Scheme 3)[32] and different crosslinking agents (trimethylolpropane trimethacrylate, TMPTMA and triallyl cyanurate, TAC).

2 | EXPERIMENTAL SECTION

2.1 | Materials and methods

Polymers and additives were purchased by suppliers of Mixer SpA and are commercially available grades. All the materials were used without purification.

SCHEME 2 Radical mechanism of photoinduced crosslinking in the presence of a type II initiator and crosslinking agent (represented by the yellow triangle, i.e., trimethylolpropane trimethacrylate [TMPTMA] or triallyl cyanurate [TAC], the reagents used in this work).

Low-density polyethylene polymer (LDPE) with melt flow index (at 190°C/2.16 kg) of 2.2 g/10 min, density 0.924 g/cm^3 was purchased from Sabic®. Vinyl acetate polyethylene (EVA), with a vinyl acetate content of 28%, melt flow index (at 190°C/2.16 kg) of 3–4.5 g/10 min, density 0.95 g/cm^3 was obtained from Arkema. Furthermore, a POE polymer, melt flow index (at 190°C/2.16 kg) of 5.0 g/10 min, density 0.870 g/cm^3·was obtained from LG Chem. Aluminum trihydroxide filler (ATH, Al(OH)$_3$, 99.5%) was provided by Nabaltec. The additive triethoxy(vinyl)silane (VTEO, CAS-No. 78–08-0) was obtained from Evonik. The crosslinking agent trimethylolpropane trimethacrylate (TMPTMA, CAS-No. 3290-92-4, >85%) was purchased from Lehmann&Voss&Co®. The crosslinking agent triallyl-cyanurate (70% on silica carrier, 30%, TAC, CAS-No. 101–37-1) was obtained from Kettlitz-Chemie GmbH & Co. The photoinitiator 4,4′-bis(diethylamino)benzophenone (EMK, CAS-No. 90–93-7, >99%) was provided by IGM resins. Benzophenone (BP, CAS-No. 119–61-9) was obtained from Sigma Aldrich.

The antioxidants Irganox® 1035 (thiodiethylene bis [3-(3,5-di-tert-butyl-4-hydroxy-phenyl)propionate], CAS-No. 41484–35-9), Irganox® PS 802 (dioctadecyl, 3,3′-thiodipropionate, CAS-No. 693–36-7), Irgafos® 168 (tris(2,4-ditert-butylphenyl) phosphite, CAS-No. 31570–04-4) were provided by BASF.

Other additives such as zinc sulfide (ZnS, content >96%) was obtained from Sachleben, Mg-Al Hydrotalcite (molar ratio MgO/Al$_2$O$_3$ 4.3, specific surface area 11 m^2/g) was purchased from Kisuma.

2.2 | Photophysical measurements

Photophysical measurements were performed in anhydrous and degassed acetonitrile or chloroform at room temperature or in a mixture dichloromethane: methanol (1:1, v/v) at 77 K. UV–visible absorbance spectra were recorded with a Perkin Elmer λ650 spectrophotometer, using quartz cells with 1.0 cm path length. Phosphorescence spectra and lifetime measurements in the microseconds–seconds range were obtained either with a Perkin Elmer LS-50 spectrofluorometer, equipped with a Hamamatsu R928 phototube, or an Edinburgh FS5 with a PMT980 detector.

2.3 | Sample preparation

The measurements were carried out on blends of polymers (LDPE, POE, and EVA), photoinitiators (EMK, benzophenone), and crosslinking coagents (TMPTMA, TAC).

Other measurements were performed on Mixer's prototype compound called Ekopren® XI1321. The formulation of this compound is shown in Table 1.

The blends were obtained by mixing all the components in a two-roll mill according with the procedure described in ASTM D3182. The mill rotors were set at 120°C so that photoinitiators and crosslinking coagents are liquid. Plaques of 0.7 mm thick were obtained by pressing at 180°C for 5 min in a pressing molding machine.

Specimens for irradiation and mechanical tests were die cut in the milling direction. The compound Ekopren® XI1321 was industrially prepared in an internal mixer (Banbury) with two counter-rotating rotors. The typical procedure to prepare a compound in a Banbury consists of four steps. The first step is the loading all the ingredients while the rotors are rotating at the minimum speed of 28 rpm.

Once the loading is completed the rotors speed increase to 33 rpm, this step lasts 99 s and the speed is increased until 45 rpm, after 60 s this third step is finished. Varying the relative speed of the rotors and through a piston which push the material in the chamber. Shear and friction are applied to the ingredients to mix all of them. In the final step the speed is set up to 60 rpm and the compounding cycle is completed when the molten mass reaches 160°C.

The mass is then transferred into an extruder, which forces the material through a screen pack to remove any impurities and then pelletized under a constant spray of cooling water. Afterwards, the pellets are transported to a rotating drum for drying and eventually packed in an industrial big bag.

As described above, the pellets previously obtained were mixed in a two-roll mill to obtain a homogenous material, and according with ASTM D3182, the

TABLE 1 Formulation of Ekopren® XI1321.

Products	Composition w/w
EVA 28.3	30.00%
POE	10.00%
ATH	58.24%
VTEO	0.30%
IRGANOX 1035	0.03%
IRGAFOS 168	0.01%
IRGANOX PS 802	0.02%
ZnS	0.50%
Mg-Al hydrotalcite	0.90%

Abbreviations: ATH, aluminum trihydroxide; EVA, ethylene-vinyl acetate; POE, polyethylene-octene; VTEO, triethoxy(vinyl)silane; ZnS, zinc sulfide.

Samples	Polymer or compound	Photoinitiator	Crosslinking agent
L1	LDPE	BP	TAC
L2	LDPE	BP	TMPTMA
L3	LDPE	EMK	TAC
L4	LDPE	EMK	TMPTMA
E1	EVA	BP	TAC
E2	EVA	BP	TMPTMA
E3	EVA	EMK	TAC
E4	EVA	EMK	TMPTMA
X1	XI1321	BP	TAC
X2	XI1321	BP	TMPTMA
X3	XI1321	EMK	TAC
X4	XI1321	EMK	TMPTMA

TABLE 2 Samples under investigation.

Note: The concentration of the photoinitiators and crosslinking agents are 1% (w/w).

Abbreviations: BP, benzophenone; EMK, ethyl Michler's ketone; EVA, ethylene-vinyl acetate; LDPE, low density polyethylene; TAC, triallyl cyanurate; TMPTMA, trimethylolpropane trimethacrylate.

photoinitiators and co-crosslinking agents were added at 120°C. Plaques of 0.7 mm thick were obtained by pressing at 180°C for 5 min in a pressing molding machine. Specimens for irradiation and mechanical tests were die cut in the milling direction.

The samples for the study were prepared as reported in Table 1, where the concentration of photoinitiator and crosslinking agent was 1% w/w. All the sample are reported here below in Table 2.

2.4 | Sample irradiation

Sample irradiation was performed with a PR160L Kessil 370 nm LED (estimated irradiation intensity of ca. 137 mW/cm^2 at 6 cm) at a distance of 5 cm, at different exposure time (10′, 5′, 1′, 30″). Furthermore, the samples were heated at 150°C and then at 180°C, with a hotplate. In alternative, a medium-pressure mercury lamp (ca. 11 mW/cm^2 at 30 cm) was used.

2.5 | Mechanical and physical measurements

To evaluate the crosslinking density of the irradiated samples the hot set test was performed. According to the method CEI EN 60811–507, this test consists of suspending a sample in an oven for 10 min under a tensile force applied with a counterweight, after this period the distance between two mark-lines is measured for evaluating the percentage of elongation under loading. The counterweight

is then removed, and the sample is left to recover in the oven for further 5 min.

The test ends letting the samples cool down at room temperature, after which the distance of the mark-lines is measured again for evaluating the percentage of the retained elongation. For this study the temperature of the oven was settled at 200°C and the force applied to the sample was 20 N/cm^2.

The mechanical properties (stress–strain curves) were measured with a Gibitre Tensor Check Profile according with the method ASTM D412. This instrument allows to measure the mechanical properties, like the tensile strength and the elongation at break, by stretching a sample with a rate of 50 mm/min at 23°C and detect the applied force using a dynamometer.

Solubility tests were performed in xylenes at 130°C for 1 h on sample strips of about 100 mg irradiated at different times at 5 cm at 150 or 180°C. The cross-linked content was obtained for the samples by dividing the mass of the dry non-solubilized sample and the mass recorded before the solubility test.

3 | RESULTS AND DISCUSSION

3.1 | Photophysical characterization

Photophysical characterization of the two considered photoinitiators, namely BP and EMK, was performed to assess the best choice for the irradiation-induced curing and to evaluate the effect of the typical additives present in the polymeric blend.
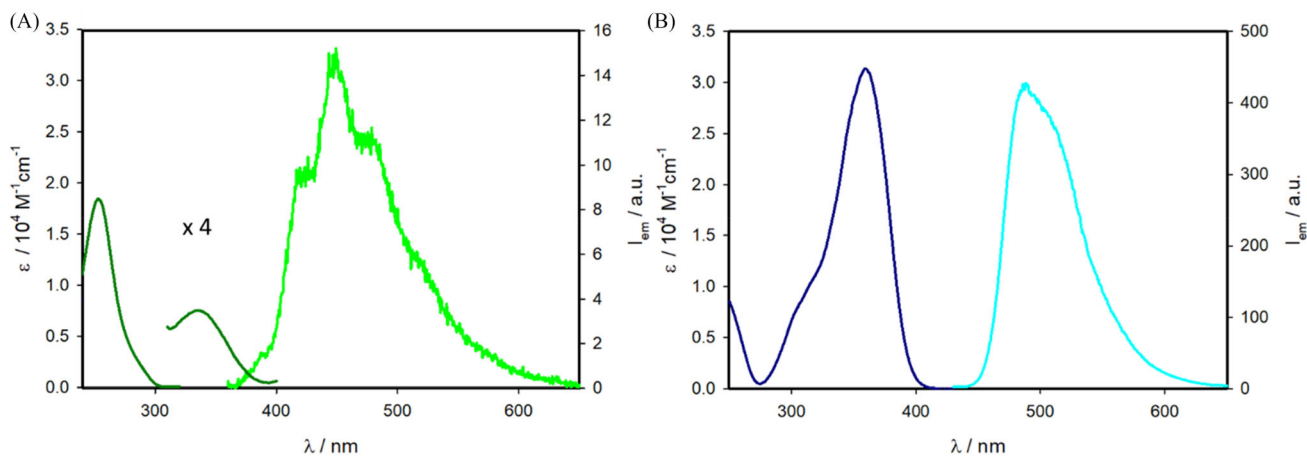
FIGURE 1 Absorption spectra (darker lines) of (A) BP and (B) EMK in acetonitrile and phosphorescence spectra (lighter lines) of (A) BP in degassed acetonitrile solution at room temperature and (B) EMK in dichloromethane: methanol 1:1 (v/v) rigid matrix at 77 K. BP, benzophenone; EMK, ethyl Michler's ketone.

TABLE 3 Lifetimes of the lowest triplet excited state of BP in degassed dichloromethane solution in the absence (first row) or in the presence of 1 mM of different quenchers, corresponding quenching constants and relative quenching efficiency (RQE) at the concentrations of the additives in the Ekopren® XI1321 blend.

	τ (T_1) (μs)[a]	k_q $(10^8 \, M^{-1} \, s^{-1})$	RQE[b]
Pure	2.3		
TMPTMA	0.91	6.64	76%
TAC	2.0	0.652	0%
IRGANOX 1035	1.1	4.74	18%
IRGANOX PS802	1.1	4.74	3%
IRGAFOS 168	0.90	6.76	3%

[a]$\lambda_{exc} = 250$ nm; $\lambda_{em} = 460$ nm.
[b]Contributions of the additives to the BP quenching in a polymeric blend containing each component at the same concentration of the Ekopren® XI1321.
Abbreviations: TAC, triallyl cyanurate; TMPTMA, trimethylolpropane trimethacrylate.

The absorption spectrum of benzophenone (Figure 1A) shows a low-intensity band associated to the symmetry-forbidden $n \rightarrow \pi^*$ electronic transition with maximum at 334 nm ($\varepsilon = 190 \, M^{-1} \, cm^{-1}$) and a stronger absorption band peaked at 252 nm ($\varepsilon = 18,500 \, M^{-1} \, cm^{-1}$), associated to the $\pi \rightarrow \pi^*$ transition localized in the aromatic rings.[33] In the case of EMK (Figure 1B), the lowest-energy band centered at 360 nm has a high molar absorption coefficient ($\varepsilon = 31,400 \, M^{-1} \, cm^{-1}$) and it is associated to an intramolecular charge transfer electronic transition from arylamine donor to ketone,[34–36] while the shoulder at about 300 nm is associated to the $n \rightarrow \pi^*$ transition.[34] It is worth noting that the presence of the anilines strongly affects the absorption spectrum, so that the lowest energy band is red-shifted

and characterized by a much higher value of the molar absorption coefficient with respect to the pristine compound: this makes EMK a more promising candidate as photoinitiator in terms of light-absorption in the investigated spectral range (vide infra). Figure 1 also displays the phosphorescence spectra of the photoinitiators, which are both related to the radiative relaxation from the lowest triplet excited state (T_1) to the ground state. From the emission spectra it is also possible to evaluate the T_1 energy, which is 2.98 eV for BP and 2.68 eV for EMK.

The lifetime of the phosphorescent T_1 excited state of BP is 2.3 μs in degassed dichloromethane solution and 7.7 μs in degassed acetonitrile solution, in good accordance with the data reported in literature.[37] Since the T_1 excited state is known to be responsible of the generation of radicals on the coinitiating compound, we investigated the change of T_1 lifetime of BP in the presence of typical additives (1.0 mM concentration), namely TMPTMA and the antioxidants IRGANOX 1035, IRGANOX PS802, and IRGAFOS 168. The lifetime of BP in degassed dichloromethane solution decreases after the addition of each component. Knowing the lifetime values before (τ_0) and after (τ) the addition of the additive and the molar concentrations of the compounds ($[Q]$), it is possible to estimate the quenching constants k_q, as reported in Table 3, based on the Stern-Volmer equation (Equation 1)[33].

$$\frac{\tau_0}{\tau} = 1 + k_q \tau_0 [Q] \qquad (1)$$

It is worth noting that in a polymeric blend, the different viscosity affects the quenching constant. Therefore, a value which is independent from the diffusion rate, that is, the relative quenching efficiency, was evaluated.
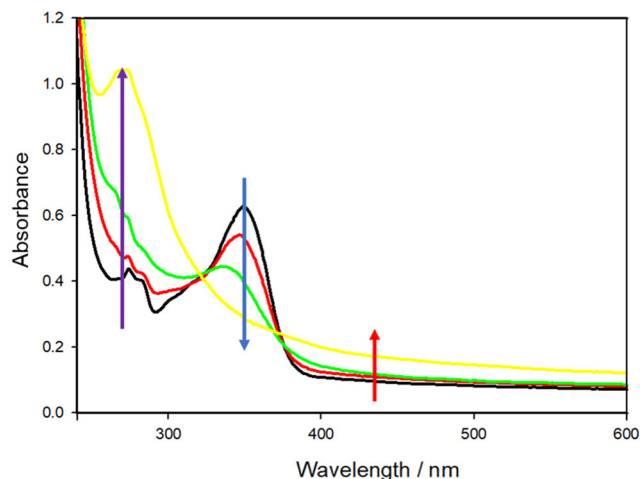
FIGURE 2 Absorption spectra of an ethylene-vinyl acetate blend mixture containing ethyl Michler's ketone before (black line) and after irradiation for 20 s (red line), 2 min (green line), and 10 min (yellow line) at 370 nm.

FIGURE 3 Cross-linked content of low density polyethylene blends (black dots) and ethylene-vinyl acetate blends (red triangles) containing benzophenone (1%) after different irradiation times. Both the samples contained 1% in weight of crosslinking agent.

Assuming a mixture with all the additives at the concentrations described in Table 1 for the Ekopren® XI1321, the relative quenching efficiencies (RQE) of the photoinitiator (Table 3) can be estimated by the following equation (Equation 2):

$$\text{RQE} = \frac{k_{qi}[Q_i]}{(1/\tau_0) + \sum_{i=1}^{n} k_{qi}[Q_i]} \cdot 100 \qquad (2)$$

where k_{qi} is the quenching constant of a component of the mixture and $[Q_i]$ its concentration expressed in molarity.

Although the antioxidants can quench the triplet state of BP, which poses some concerns on the effectiveness of crosslinking in the polymeric blend, an elevated quenching constant is calculated for the crosslinking agent TMPTMA, which is crucial to promote the reticulation of the polymer. The quenching of BP triplet state was associated to a hydrogen abstraction or electron transfer, which yields the radicals responsible of the crosslinking (see Scheme 2).

The same study could not be performed in the case of the EMK as photoinitiator since it is not phosphorescent in degassed fluid solution: phosphorescence is observed only in rigid matrix at 77 K, where bimolecular quenching processes are prevented.

The first proof of the activity of the photoinitiator inside the polymeric mixture was assessed by monitoring the absorption spectrum of the sample before and after different irradiation times at 370 nm at 100°C. In particular, 0.6-mm thick film of EVA blend containing EMK (0.012% in weight), TMPTMA (0.004%) and a mixture of
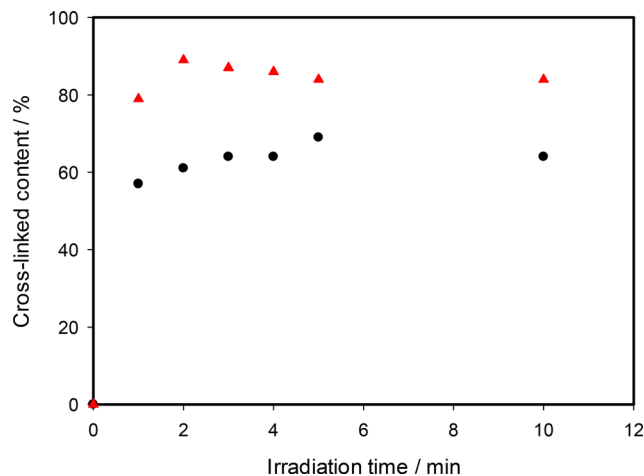
IRGANOX compounds was irradiated for 20 s, 2 min and 10 min. The absorption spectrum (Figure 2) showed a decrease in the EMK band at 360 nm and the appearance of a band peaked at about 280 nm. Concomitantly, the baseline shifted towards higher values, accompanied by a yellowing of the sample.

The blue shift of the absorption band at lower energy and the change in color was attributed to the formation of the products generated by the reactions between the radical species derived from the photoinitiator, which are less conjugated than EMK, as reported in literature.[38]

Another important parameter for the photocrosslinking is the viscosity, that can be modulated by changing the temperature of the polymeric sample.[39] The first experiment on the EVA mixture containing EMK at 90°C does not show significative crosslinking, failing both solubility and dynamic mechanical tests, while increasing the temperature (superior to 150°C), diffusion of the generated radicals is increased and results in a better reticulation of the polymeric chains. After the irradiation at 180°C for up to 5 min at a distance of 5 cm from the UV source, a solubility test in hot xylene was performed to assess the cross-linked content (which was obtained from the ratio between the mass of the polymeric component after and before the solubilization in xylene, Figure 3) of LDPE and EVA samples containing EMK (0.05% w/w or 1% w/w) or BP (1%) in the presence of 1% TMPTMA or TAC as crosslinking agents. Analyzing the experimental results, we can draw the following conclusions: polymers containing EMK at concentration >1% shows a limited crosslinked content (inferior to 5%, while no significant crosslinking was observed for concentration of EMK <1%; the LDPE samples containing benzophenone

reached a yield of crosslinking up to 65% over an irradiation period of 5 min (Figure 3, black dots); the EVA samples containing benzophenone reached a yield of crosslinking up to 89% over an irradiation period of 2 min (Figure 3, red triangles), which slightly decreased over time.

Inspired by the great results obtained for EVA polymer, the same experiments were performed for Ekopren® XI1321, a polymeric blend of EVA/POE containing HFFR based on hydrotalcite and aluminum trihydroxide, and antioxidant agents. As reported for the polymeric components described above, EMK did not provide an acceptable crosslinking, while insolubility of the samples containing BP, if irradiated for more than 1 min, was observed, suggesting that even in the presence of mineral additives, photoinduced curing was successful. We believe that the scarce results provided by EMK are due to the formation of colored compounds that hinder the penetration of the light in the sample. Control experiments in the dark (at 180°C) or at room temperature (upon irradiation) failed the test, implying a necessity of a source of light and a low viscosity of the medium.

Photocrosslinking was evaluated also upon irradiation with a medium-pressure mercury lamp, to assess the differences with the LED-induced irradiation. This is assumed to a be better choice for BP-containing mixtures, since its emission profile presents various peaks also at wavelengths inferior to 260 nm, where the molar absorption coefficient of the photoinitiator is higher.[40] The irradiation was conducted at 150°C at a distance of 30 cm from the lamp for different temperatures ranging from 1 min to 1 h. The irradiated samples, however, completely failed the solubility test in xylenes. This experiment suggested the superiority of the results obtained with the LED over the conventional mercury lamp, especially due to the lower irradiation intensity of the light source at low wavelengths.[40]

3.2 | Mechanical characterization

To mechanically evaluate the crosslinking density of the samples a hot set test was performed starting with an irradiation time of 10 min and decreasing it progressively till 30 s. Samples reported in the following tables as failed did not withstand the applied force in the test conditions. In the first series of experiments, the samples were heated at 150°C during the irradiations.

All the results are summarized in the tables and graphs shown below. Surprisingly, the first outcome is that all the LDPE specimens, that is, L1-L4, failed the hot set test, therefore are not listed. Another observation that can be drawn is that, even with a long exposure time, the

TABLE 4 Hot elongation values of samples irradiated at 150°C for different times.

Irradiation time	E1	E2	X1	X2
10 min	20%	50%	10%	20%
5 min	20%	50%	15%	30%
3 min	35%	50%	20%	45%
90 s	Failed	100%	30%	75%
60 s	Failed	Failed	35%	Failed
30 s	Failed	Failed	Failed	Failed

TABLE 5 Cold relaxation values of samples irradiated at 150°C for different times.

Irradiation time	E1	E2	X1	X2
10 min	0	5%	0	5%
5 min	0	5%	0	5%
3 min	10%	5%	5%	5%
90 s	Failed	5%	5%	10%
60 s	Failed	Failed	5%	Failed
30 s	Failed	Failed	Failed	Failed

TABLE 6 Hot elongation values of samples irradiated at 180°C for different times.

Irradiation time	E1	E2	X1	X2
10 min	20%	50%	5%	20%
5 min	25%	50%	10%	25%
3 min	25%	115%	15%	30%
90 s	Failed	Failed	25%	65%
60 s	Failed	Failed	35%	70%
30 s	Failed	Failed	75%	90%

samples containing EMK fail the hot set test due to a poor crosslinking density, that is, E3, E4, X3, and X4. On the contrary, a sufficient crosslinking density was obtained with BP in the specimens E1, E2, X1, and X2, which all passed the hot set test. Looking closely, the combination of BP with TAC leads to less deformation when compared to BP and TMPTMA, that is a clear indication of a tighter crosslinking.

The results clearly display that a 3-min irradiation is still generating satisfactory results for the four samples. Compared to a 5-min irradiation, the difference between the values is minimal, although a slight trend of increasing of both hot elongation and cold relaxation is noticeable. At 90 s of irradiation, while E1 fails, the other samples still comply with the test. A further increase is clearly observable, however remarkably, X1 exhibits a

very low deformation, indicating that a tight crosslinking was generated even with these conditions. Further, X1 is the only specimen successfully passing the hot set test at 60 s of irradiation time. All the other failed. At 30 s, all the samples failed the hot set test.

Once more it is affirmed that BP and TAC induce a faster and tighter crosslinking when compared to BP and TMPTMA. Notably, XI1321 with BP and TAC, passed the hot set test at a 60-s irradiation, which is close to reasonable conditions for real industrial applications.

The results concerning the hot and cold relaxation values are reported in the Tables 4 and 5, respectively. At last, to simulate real industrial conditions, the tests were repeated with the samples heated at 180°C, the results are shown in Tables 6 and 7.

For comparison with the previous data, samples E1 and E2 were examined also in these conditions. The mechanical properties of X1 and X2 were measured to demonstrate the feasibility of a future application in manufacturing.

This series of experiments was carried out starting with an exposure time of 10 min and reducing it stepwise till 30 s. The results reported in Tables 6 and 7

demonstrate the effect of the temperature, which impacts on the mobility of the radicals resulting in a more effective crosslinking. That is verified by a comparison of hot elongation and cold relaxation obtained at the same irradiation time and at different temperatures. Besides few scattered points, the trend is a reduction of both properties by increasing the temperature.

Interestingly, via an increment of the temperature both the samples X1 and X2 were able to pass the hot set tests at 30 s of exposure time. In addition, also at 180°C the higher crosslinking efficiency of the combination BP/TAC is confirmed.

As aforementioned, the mechanical properties of the samples X1 and X2 were measured. That is fundamental to estimate a reasonable trade-off between irradiation time, crosslinking density, and mechanical properties for a real-life application.

Stress–strain curves were recorded by applying an elongation rate of 50 mm/min at 23°C, and the findings are listed in Tables 8 and 9 for X1 and X2 samples, respectively. In addition, the curves are plotted in Figures 4 and 5.

Coherently with the observations drawn for the hot set test, at long exposure times the tensile strength is maximized while the elongation is minimized. Further to this, the modules are the highest, which indicates a stiffening of the material. That is completely consistent with a tight crosslinking between the polymer chains. Decreasing the irradiation time, therefore producing a less dense crosslinking, the tensile and the modules are lowering and conversely the elongation is increasing.

Likewise, when comparing the properties of X1 and X2 obtained in the same conditions, the tensile strength, and modules of X1 are higher than those of X2. Conversely, the elongation of X1 is shorter compared to that of X2.

The changes observed in both graphs referring to the samples X1 and X2 are consistent with an

TABLE 7 Cold relaxation values of samples irradiated at 180°C for different times.

Irradiation time	E1	E2	X1	X2
10 min	0	0	0	0
5 min	0	0	0	5%
3 min	5%	5%	5%	5%
90 s	Failed	Failed	5%	5%
60 s	Failed	Failed	5%	10%
30 s	Failed	Failed	10%	10%

TABLE 8 Mechanical properties obtained from X1 irradiated samples.

Irradiation time	TS[a] (N/mm²)	EB[b] (%)	Mod 50%[c] (N/mm²)	Mod 100%[d] (N/mm²)
10 min	11.7	105	8.9	11.6
5 min	11.6	135	8.6	10.7
3 min	10.7	140	8.2	10.0
90 s	9.8	177	7.7	9.3
60 s	9.0	181	7.4	8.7
30 s	7.8	232	6.7	7.8
Pristine	6.9	322	7.4	8.4

[a]Tensile strength (TS).
[b]Elongation at break (EB).
[c]Modulus at 50% of elongation.
[d]Modulus at 100% of elongation.

TABLE 9 Mechanical properties obtained from X2 irradiated samples.

Irradiation time	TS[a] (N/mm^2)	EB[b] (%)	Mod 50%[c] (N/mm^2)	Mod 100%[d] (N/mm^2)
10 min	10.8	178	8.1	9.7
5 min	9.6	189	7.5	8.9
3 min	8.7	202	7.0	8.3
90 s	8.4	258	7.0	8.2
60 s	8.2	245	7.1	8.1
30 s	7.4	248	6.7	7.7
Pristine	6.9	322	7.4	8.4

[a]Tensile strength (TS).
[b]Elongation at break (EB).
[c]Modulus at 50% of elongation.
[d]Modulus at 100% of elongation.

FIGURE 4 Strain curves of X1 samples irradiated at different times at 180°C.
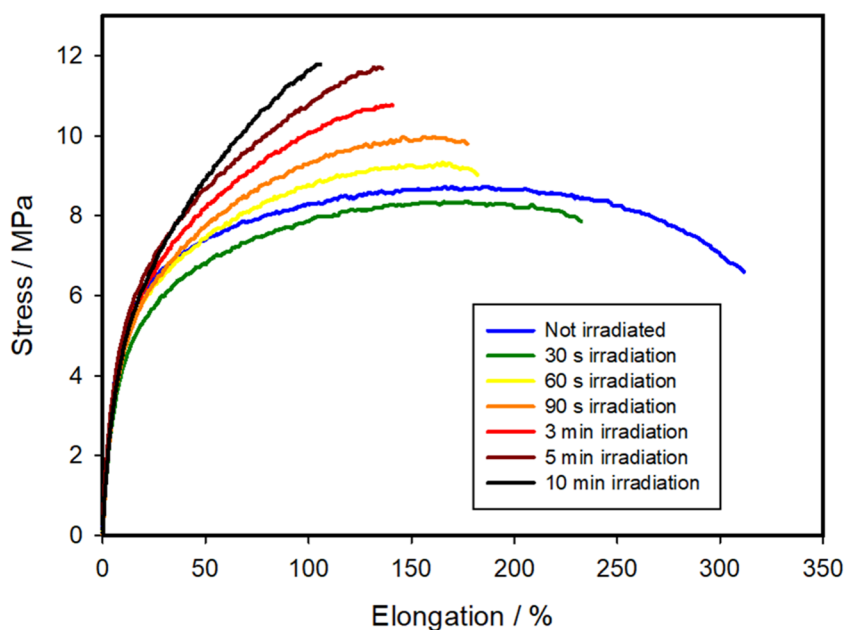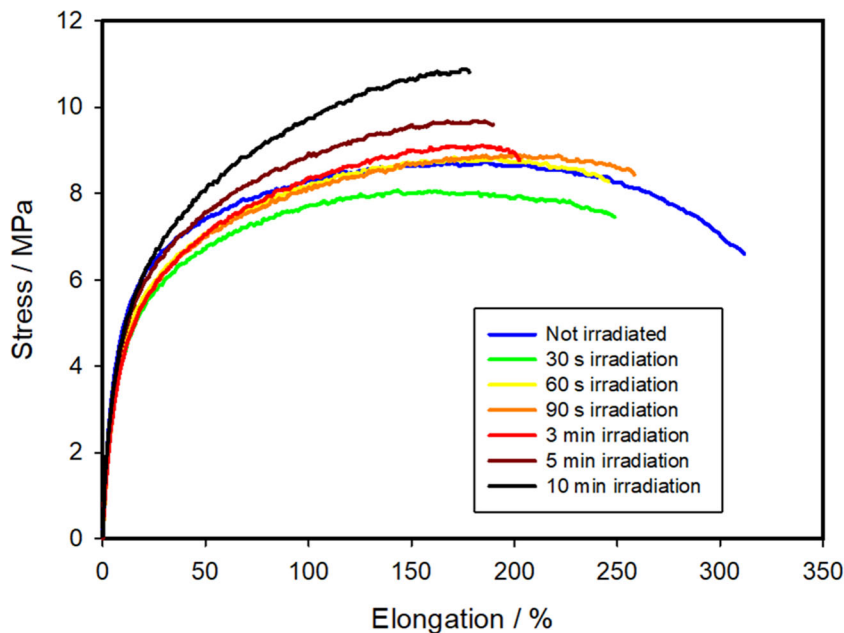

FIGURE 5 Strain curves of X2 samples irradiated at different times at 180°C.

increasing crosslinking density. The non-irradiated sample shows an initial increase of the stress as a result of the crystallinity of the EVA polymer and a subsequent yielding which is characteristic of a dominant plastic behavior of a thermoplastic EVA/POE blend. By heating and irradiating the samples for 30 s there is a partial destruction of the crystallinity of the polymers and a beginning of crosslinking leading to a shorter yielding but also a lower tensile strength. Increasing the irradiation time, the plastic behavior of the blend decreases and disappears above 90 s of exposure. From 3 min of exposure the dominant behavior of the deformation is elastic, with a strong response to the stress applied to the sample, conversely, the elongation at break is considerably reduced. The changes in the curves are coherent with the increase of the bonds between the polymer chains generated by longer irradiation time.

Ultimately, from these results it is clear that by selecting the right conditions in terms of chemicals, time of irradiation and temperature of the material will be possible to obtain a sufficient crosslinking and the desired mechanical properties for the target application. Remarkably, photoinduced crosslinking was obtained for the formulation in the presence of mineral fillers, which are known to scatter the incident light and reduce the photons absorbed by the photoinitiator.

4 | CONCLUSION

We successfully conducted the photoinduced crosslinking of Ekopren® XI1321, a polymer blend composed of EVA and POE in the presence of mineral HFFR and antioxidant agents. Curing was performed upon irradiation with a 370-nm LED, a more sustainable alternative to conventionally used mercury lamps.

Crosslinking was evaluated in the presence of different photoinitiators (BP or EMK) and reticulation agents (TAC or TMPTMA) at 180°C at different times. From the obtained results, BP resulted to yield a high degree of cross-linked content, while EMK does not provide sufficient reticulation: we attribute the scarce reticulation to the formation of a colored coproduct that hampers the penetration of the light in the sample. TAC-containing blends induced better mechanical responses analyses if compared to TMPTMA containing compounds.

To complete the study and to evaluate possible industrial applications, the hot set test of the pure polymers and of the Ekopren® XI1321 compound were investigated. At last, the mechanical properties of the compound XI1321 were measured.

The first observation is that EVA is more prone to crosslink when compared to LDPE. All the samples containing LDPE failed the hot set test for all the conditions of the study. Nevertheless, the results of the remaining samples indicate clearly that combination of BP and TAC yields the higher crosslinking density, leading to best results in terms of hot set test.

Most remarkably, the samples X1 and X2 passed the hot set test with an irradiation time as short as 30 s when preheated at 180°C. Moreover, it is clearly observed how at long irradiation time the mechanical properties increase substantially when compared to the pristine material.

All these results allow a foreseeable industrial application where, by a careful choice of photoinitiator, coagent, and exposure time, it will be possible to determine the final properties of an HFFR compound.

Future studies will be aimed to expand the knowledge on photoinitiators with improved absorption in the UV-A spectral region and good photo reactivity in the compound. As Mixer SpA is involved in the field of wire and cables, industrial trials will be carried out to evaluate possible solutions for real-life applications.

DATA AVAILABILITY STATEMENT
Data available on request from the Authors

ORCID
Giacomo Morselli https://orcid.org/0000-0001-9113-6381
Marco Villa https://orcid.org/0000-0001-5300-1590
Paola Ceroni https://orcid.org/0000-0001-8916-1473

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