

Flammability of Blends of Low-Density Polyethylene and Ethylene Vinyl Acetate Crosslinked by Both Dicumyl Peroxide and Ionizing Radiation for Wire and Cable Applications

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ABSTRACT: Formulations of chemically crosslinked and radiation-crosslinked low-density polyethylene (LDPE) containing an intumescent flame retardant such as ammonium polyphosphate were prepared. The influence of blending LDPE with poly(ethylene vinyl acetate) (EVA) as well as the effects of a coadditive such as talc on flammability was investigated. Chemical crosslinking by dicumyl peroxide and crosslinking by ionizing radiation from an electron-beam accelerator were both used and compared. An increase in the limiting oxygen index (LOI) was found by the partial replacement of LDPE with EVA. The effect of talc on the flammability depended on the amount of

talc in the formulations. The addition of a small amount of talc increased LOI and reduced smoke during cone calorimeter measurements. A higher amount of talc led to a decrease in the LOI values. Formulations crosslinked by ionizing radiation yielded lower LOI values than chemically crosslinked formulations. This could be attributed to the use of trimethylolpropane triacrylate as a crosslinking coagent in formulations crosslinked by ionizing radiation. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 109: 167–173, 2008

Key words: flame retardance; polyethylene (PE); radiation

INTRODUCTION

Low-density polyethylene (LDPE), because of its good mechanical properties, good resistance to chemicals, and easy processing, is used in many applications. However, it has some disadvantages, such as a low melting temperature, low thermal stability, high flammability, and poor compatibility with additives. The compatibility of additives with LDPE can be improved by the addition of some compatibilizers or coupling agents.¹ The thermal properties of polyolefins can be improved by a small addition of stabilizers. A small quantity of processing stabilizers is usually added to prevent the oxidative degradation of polyolefins caused by the combined action of shear, heat, and oxygen during their melt processing. Phenolic antioxidants are widely

used as processing stabilizers for polyolefins.^{2,3} They act as scavengers of oxygen-centered alkoxy and peroxy radicals, but they are not able to provide long-term heat stability.⁴

The flame retardancy of LDPE, on the other hand, can be improved with flame retardants. There are several types of flame retardants that are used to improve the flame retardancy of polyolefins. Recently, there has been a trend to avoid the use of halogenated flame retardants because of environmental and safety concerns. Thus, as nonhalogenated flame retardants, mainly metal hydroxides^{1,5–8} and intumescent flame retardant (IFR) systems^{9–16} are used. Very good efficiency in the flame retardancy of polyolefins can be achieved with IFR systems. However, a higher loading of an IFR additive is needed than that of some halogen-containing flame retardants. This results in lowered mechanical properties of the flame-retardant materials. Thus, the flame-retardant efficiency of IFRs should be further improved. To improve the performance of IFRs in polyolefins, synergistic agents such as boroxosiloxanes (products of the reaction of polysiloxanes with

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TABLE I
Chemically Crosslinked Formulations

Formulation code ^a	LDPE	EVA	APP (phr)	DCP (phr)	TMPTA (phr)	PEgMA (phr)	Talc (phr)
C-1	100	—	30	3	—	3	—
C-2	80	20	30	3	—	3	—
C-3	60	40	30	3	—	3	—
C-4	60	40	30	3	3	3	—
C-5	60	40	35	3	—	3	—
C-6	60	40	30	3	—	3	5
C-7	60	40	30	3	—	3	10
C-8	60	40	35	3	—	3	1
C-9	60	40	35	3	—	3	3
C-10	60	40	35	3	—	3	5

^a Formulations contained 0.3 phr Irganox 1010 and 0.3 phr paraffin wax.

boric acid),^{9,10} clays and nanoclays,^{13,14} or some metal-containing compounds^{15,16} that can enhance the flame-retardant action of IFRs are used. There is no work describing the flammability of chemically or photochemically crosslinked polyolefins with IFR systems. Although IFR systems show higher improvement of flame retardancy in polypropylene than polyethylene resins, the crosslinking of polyethylene has been much better explored. In a recent work,¹⁷ we demonstrated that crosslinking can increase the tensile strength of polyethylene/ammonium polyphosphate (APP) composites and thus, at a reasonable yield of crosslinking, improve their mechanical properties. Moreover, it improves the thermal stability.^{17,18}

In this article, various formulations containing LDPE blended with poly(ethylene vinyl acetate) (EVA) and APP as an IFR were mixed with coadditives, a compatibilizer, a stabilizer, and crosslinking agents and crosslinked chemically (see Table I) or by electron-beam irradiation (see Table II) to achieve improved flame resistance of LDPE/EVA/IFR composites.

EXPERIMENTAL

Materials

LDPE (HP2022J) from Sabic (Jubail, Saudi Arabia) and EVA (Alcudia PA-538) (Madrid, Spain) with 18% vinyl acetate from Gazechim (France) were used as received. Processing stabilizers Irganox 1010 and Irgafos 168 from Ciba Specialty Chemicals (Basel, Switzerland), processing aid paraffin wax from Fluka Chemical Co. (Steinheim, Germany), flame retardant APP (Exolit AP765) from Clariant (Sulzbach, France), compatibilizer PEgMA (12031) from Solvay Co. (Brussels, Belgium), talc (V 3837) from Luzenac (Toulouse, France), crosslinking agent dicumyl peroxide (DCP; Perkadox BC-40K) from Akzo Nobel (Arnhem, The Netherlands), and crosslinking

coagent trimethylolpropane triacrylate (TMPTA; Sartomer 351) from Cray Valley (Rieux, France) were used as received.

Compounding and crosslinking

In the case of chemically crosslinked formulations, all additives except DCP were mixed with the resins for 10 min at 150°C with an internal mixer at a speed of 50 rpm. Then, the mixture was moved into a two-roll mill, and DCP was added at 110°C and mixed for 3–5 min. Crosslinking was performed through the molding of sheets for 30 min at 170°C. Sheets with a thickness of 2 mm were prepared. Formulations are presented in Table I.

In the case of formulations crosslinked by an electron beam, all additives were mixed with the resins with a Brabender DSK 42/6 contrarotating twin-screw extruder (Duisburg, Germany) at a temperature gradient of 150–150–140°C and at a speed of 15 rpm. The residence time of the polymer in the machine at this speed was around 15 min. Sheets with a thickness of 2 mm were prepared through molding for 2 min at 200°C. Crosslinking by an electron beam was performed at Ionisos Co. (Paris, France) with an electron-beam accelerator of 10 MeV. The doses were provided by successive passes of 25 kGy under an air atmosphere. The formulations are presented in Table II.

TABLE II
Formulations Crosslinked by Ionizing Radiation from an Electron Beam

Formulation code ^a	LDPE	EVA	APP (phr)	TMPTA (phr)	PEgMA (phr)
R-1	60	40	30	3	3
R-2	60	40	35	3	3
R-3	60	40	42	3	3

^a Formulations contained 0.3 phr Irganox 1010, 0.3 phr Irgafos 168, and 0.3 phr paraffin wax.

TABLE III
LOI (%) and Cone Calorimeter Results of LDPE/EVA Formulations Containing APP

Formulation code	LOI (%)	Time to ignition (s)	Time to first peak (s)	Time to second peak (s)
Pure LDPE	18 ± 0.5	43	95	—
Pure EVA	19 ± 0.5	33	80	—
C-1 (0% EVA, 30 phr APP)	26.4 ± 0.2	58	~100	210
C-2 (20% EVA, 30 phr APP)	27.4 ± 0.3	52	~100	200
C-3 (40% EVA, 30 phr APP)	27.8 ± 0.2	45	~100	185
C-5 (40% EVA, 35 phr APP)	29.2 ± 0.3	54	~100	195
C-8 (40% EVA, 35 phr APP + 5 phr talc)	28.8 ± 0.3	51	~100	207

Testing methods

The flammability of the prepared formulations was characterized by the limiting oxygen index (LOI) test as well as a cone calorimeter. The LOI tests were performed with an apparatus from Fire Testing Technology, Ltd. (incorporating Stanton Redcroft, UK), in accordance with ISO 4589 (ASTM D 2863). A cone calorimeter from Fire Testing Technology (incorporating Stanton Redcroft) was used to measure heat release, smoke, CO, and CO₂ production in accordance with ASTM 1354-04a under a heat flux of 50 kW/m², which corresponds to the heat that evolves during a fire.

RESULTS AND DISCUSSION

Influence of the EVA content

The addition of 30 phr APP to LDPE for chemical crosslinking leads to an increase in LOI up to 26% versus 18% for pure LDPE (see Table III). It is known that the effect of a flame retardant depends also on its compatibility with the resin. In a previous article,¹⁷ we showed that the compatibility of APP with LDPE can be increased by blending LDPE with EVA. Therefore, the influence of EVA on LOI was studied here. As shown in Table III, an increase in LOI of 1.5% can be observed with an increase in the EVA content from 0 to 40%. This confirms that the good compatibility of a flame retardant with a resin can improve the effect of the flame retardant during burning.

Measurements of heat release can give us more information about the dynamic flammability of prepared formulations. The course of the burning is demonstrated in Figure 1. As shown in Figure 1, the addition of a flame retardant completely changes the course of the burning. First, the time to ignition increases from 43 s for pure LDPE up to 58 s for an LDPE formulation containing 30 phr APP (see Table III). After ignition, there is a high sharp peak of the heat release rate for pure LDPE; however, after the addition of a flame retardant, this peak of the heat release rate decreases, and this is followed by a pla-

teau, which is characteristic of the intumescent layer that forms a short time after ignition. After the destruction of the intumescent layer, the second peak in the heat release rate is observed.

Blending LDPE with EVA in APP formulations produces small changes in the heat release rate. The time to ignition slightly decreases with an increase in the EVA content because of the shorter ignition time of pure EVA in comparison with pure LDPE (see Fig. 1 and Table III). At the same time, the time to the second maximum of the heat release rate decreases from 210 to 185 s as the EVA content is increased from 0 to 40%.

Influence of the flame-retardant content and crosslinking method

Achieving good flame retardancy of IFR compounds and maintaining good mechanical properties of the compound require establishing optimum amounts of flame retardants. It has been found that an increase of APP in LDPE/EVA formulations from 30 to 35 phr gives the same elongation at break and only a slight decrease in the tensile strength.¹⁷ Therefore, the influence of an increase in APP up to 35 phr on

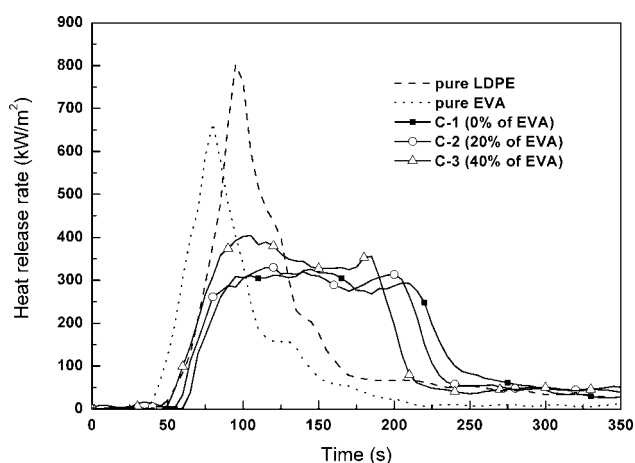


Figure 1 Heat release rate of APP formulations with various EVA contents as a function of the burning time.

the flame retardancy of the developed compounds was studied. Moreover, various types of crosslinking methods, chemical and radiation, at various APP contents were evaluated and compared.

As shown in Figure 2, a slight increase of LOI from 27.8 to 29.2% is observed after an increase in the APP content from 30 to 35 phr in chemically crosslinked formulations. A similar increase of LOI with an increase in the APP content is observed also in radiation-crosslinked formulations (see Fig. 2). However, LOI values decrease by 2% for formulations crosslinked by an electron beam with TMPTA as a crosslinking coagent in comparison with chemically crosslinked formulations with DCP as a crosslinking agent. To find a possible reason, a chemically crosslinked formulation with DCP together with TMPTA was prepared and tested. As shown in Figure 2, a decrease in LOI of 2% was observed after the addition of TMPTA to the chemically crosslinked formulation. The reduction in LOI may be attributed to a reaction between TMPTA and APP and accordingly a smaller amount of APP taking part in imparting flame retardancy to the compounds.

Comparing LOI values of formulations crosslinked by radiation, we see that LOI values decrease after crosslinking. The effect is more significant at higher contents of APP. It is known that an increase in viscosity, which can be achieved also by crosslinking, can reduce the creep of samples and thus stabilize the formation of a carbonized surface layer.¹⁹ For the formation of a foamed (intumescent) layer, it has been reported that bubble nucleation and trapping bubbles formed because of the higher viscosity of the material have a positive effect on the formation of the protective foamed layer and thus on the flame retardancy. On the other hand, it has been observed

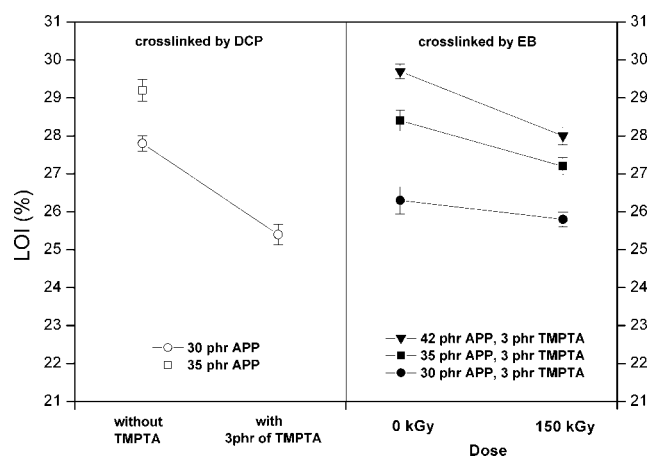


Figure 2 LOI (%) of APP formulations chemically crosslinked without TMPTA (codes C-3 and C-6) and in the presence of TMPTA (code C-5) and crosslinked by radiation as a function of the irradiation dose (codes R-1, R-2, and R-3; EB = electron beam).

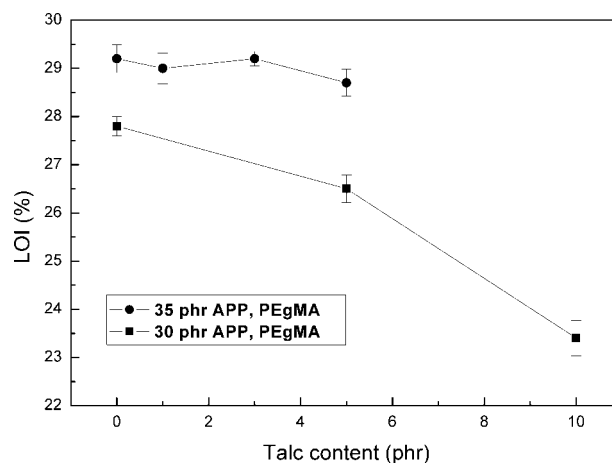


Figure 3 LOI (%) of the APP formulations as a function of the talc content.

that if the viscosity is too high, the trapped bubbles cannot grow, and the foaming effect is reduced.²⁰ Moreover, a crosslinked network may limit the flow of IFR to the surface. Thus, in highly crosslinked polymer composites, the action of a flame retardant and the formation intumescent layer can be depressed.

As shown in Figure 2, better flame retardancy was obtained by chemical crosslinking versus radiation crosslinking. Increasing the APP content to 42 phr in radiation crosslinking formulations was not enough to increase LOI values to be comparable to those for chemically crosslinked formulation containing 35 phr APP.

Influence of talc

The mechanical properties of LDPE/EVA formulations containing APP can be improved by the addition of a small amount of talc. Therefore, the influence of various contents of talc in these formulations on flammability was also investigated.

The addition of a small concentration of talc up to 5 phr to the formulations containing 35 phr APP showed no influence on LOI (see Fig. 3). A slight decrease in LOI was observed when 5 phr talc was added to the formulation containing 30 phr APP, and a dramatic decrease was observed after the addition of 10 phr talc. From Figure 4, it can be seen that although there is no change in the LOI values with an increase in the talc/APP weight ratio up to about 0.1, an additional increase in the ratio up to 0.35 produces an almost linear decrease in LOI. This behavior can be due to a wick effect because mineral fillers can increase the thermal conductivity of the polymer and the effect can be pronounced in high filler loadings.^{19,21} Moreover, although a small amount of talc can improve stability and increase

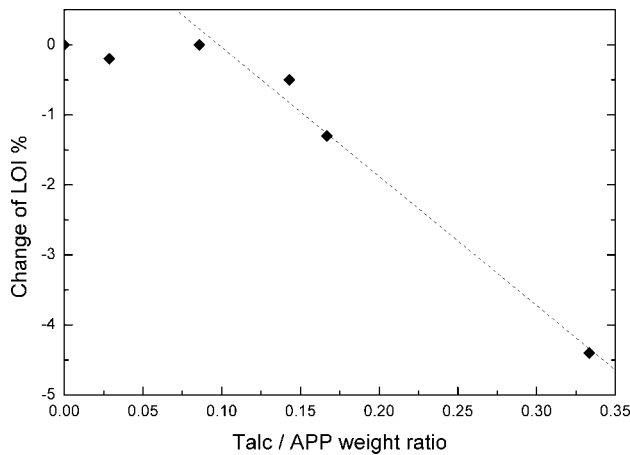


Figure 4 Change of LOI (%) as a function of the talc/APP ratio.

the cohesiveness of the protective intumescent layer during combustion as well as a residual char layer, a higher amount of talc can cause a disturbance in the intumescent layer. The observed differences in char after the burning of formulations with various talc concentrations confirm this assumption. Although the char from formulations containing no talc or 5 phr talc was quite compact, the char from the formulation containing 10 phr talc was more powdery.

The influence of a small content of talc (5 phr) on the flammability of LDPE/EVA/APP compounds was also studied with a cone calorimeter. Thus, a comparison of three formulations containing 30 phr APP, 35 phr APP, or 35 phr APP with 5 phr talc is presented. Heat release measurements (see Figs. 5 and 6) show that although the total heat release is almost the same for all formulations, the course of burning is slightly different. Although an increase in the APP content from 30 to 35 phr delays the time to ignition by about 10 s to start at 54 s, the addition of talc to the formulation containing 35 phr APP has no marked influence on the time to ignition. Moreover,

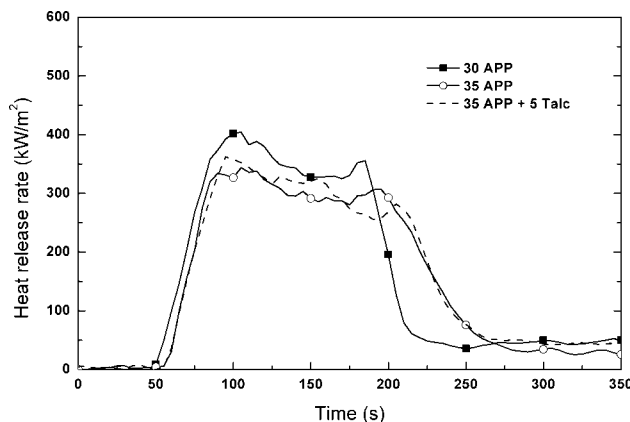


Figure 5 Heat release rate of the APP formulations with and without talc as a function of the burning time.

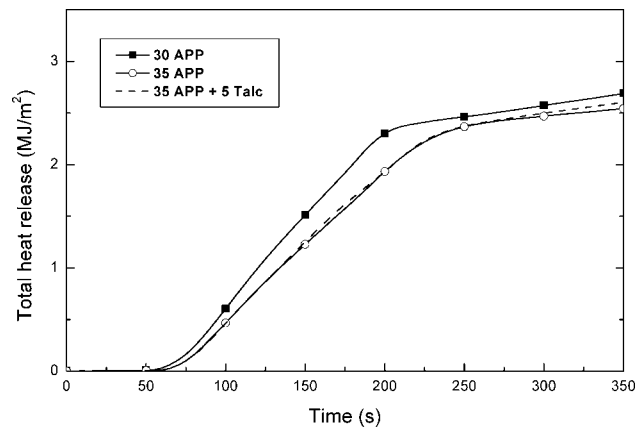


Figure 6 Total heat release of the APP formulations with and without talc as a function of the burning time. The values are normalized to 1 g of tested material.

both the increase in APP and addition of talc delay the second peak and thus increase the time to destruction of the intumescent layer. This means that besides a higher content of a flame retardant such as APP, the addition of a small amount of talc stabilizes the intumescent layer and helps to improve the flame retardancy.

An increase in the APP content up to 35 phr and the addition of 5 phr talc also decrease total smoke production. Moreover, different postburning behaviors were observed for formulations with and without talc as characterized by smoke production measurements (see Figs. 7 and 8). Although postburning production of smoke was present in the formulations without talc, in the case of a formulation containing talc, this postburning smoke was suppressed. Thus, both APP and talc serve as smoke suppressants. Although APP suppresses the total smoke production during the burning, talc improves the postburning smoke suppression. This can be explained by the previously mentioned formation of a very cohesive residue char layer in the presence of a small amount

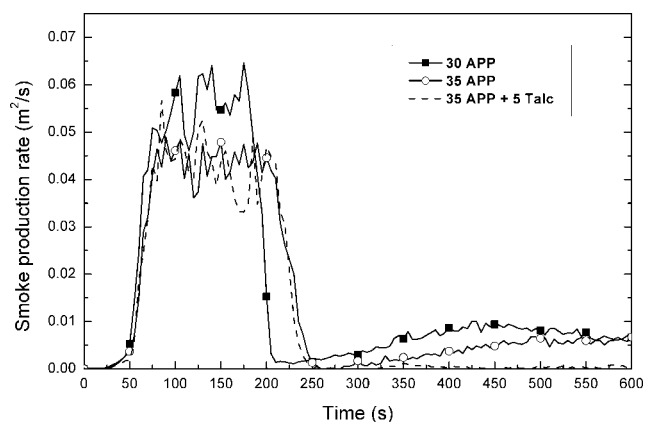


Figure 7 Smoke production rate of the APP formulations with and without talc as a function of the burning time.

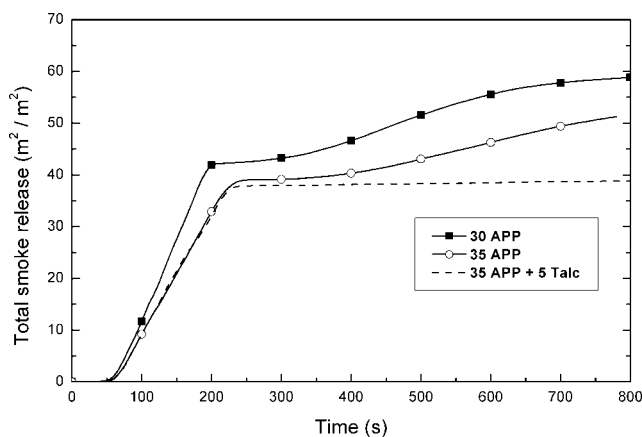


Figure 8 Total smoke production of the APP formulations with and without talc as a function of the burning time. The values are normalized to 1 g of tested formulations.

of talc. Thus, combustion products such as tar and soot particles are limited in making the transition to the gas phase, and so the smoke density can be effectively reduced.

A higher APP content also has an influence on a decrease in the CO production (see Fig. 9). On the other hand, no change in CO production was observed after the addition of 5 phr talc. No influence of either a higher content of APP or an addition of talc on total CO₂ production was observed (see Fig. 10).

CONCLUSIONS

Blends of LDPE/EVA crosslinked by both ionizing radiation and DCP with low flammability were prepared for use in wire and cable applications. LOI values, which considerably increased after the addition of APP, could be further increased through the blending of LDPE with EVA. A marked improvement in heat release results characterizing the course

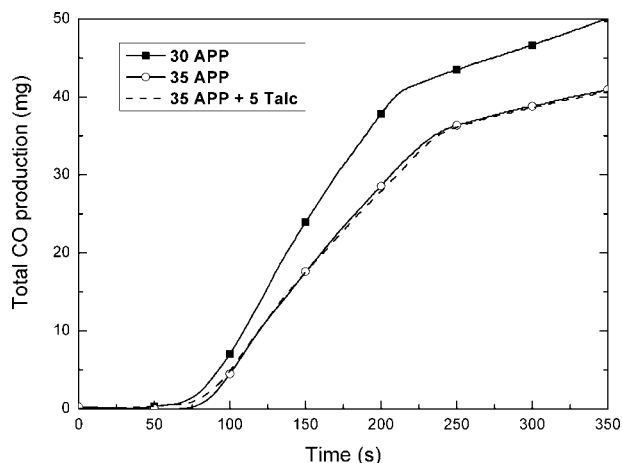


Figure 9 Total CO production of the APP formulations with and without talc as a function of the burning time. The values are normalized to 1 g of tested formulations.

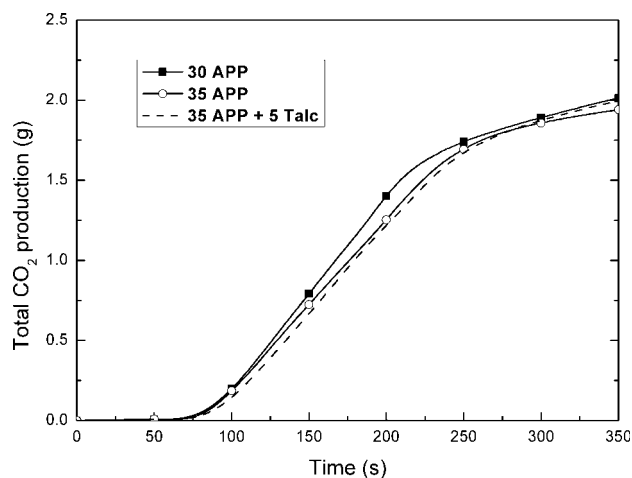


Figure 10 Total CO₂ production of the APP formulations with and without talc as a function of the burning time. The values are normalized to 1 g of tested formulations.

of the burning was achieved after the addition of APP. Although the blending of LDPE with EVA reduced the time to the second peak in heat release because of changes in the properties of the intumescent layer, the stability of the intumescent layer was maintained by the addition of a small concentration of talc. The addition of a small amount of talc, moreover, reduced the smoke emission during cone calorimeter tests by forming a more stable and cohesive char layer. Chemically crosslinked formulations using DCP had higher LOI values than formulations crosslinked by an electron beam. The lower LOI values in formulations crosslinked by an electron beam were caused by the presence of TMPTA, which probably reacted with the main flame retardant by the Michael reaction. Thus, replacing TMPTA with some other crosslinking coagent such as trimethylolpropane trimethacrylate, which is less reactive with a flame retardant, may increase LOI values of radiation-crosslinked formulations. A slight decrease in LOI after the crosslinking of polymer nanocomposites, which was probably due to a too high viscosity reducing the formation of an effective intumescent layer, was observed.

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