

Mechanical and Thermal Properties 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 a poly(ethylene vinyl acetate) copolymer (EVA) and the effects of various coadditives, including polyethylene grafted with maleic anhydride (PEgMA), vinyl silane with boric acid, and talc, on the mechanical and thermal properties were investigated. Chemical crosslinking by dicumyl peroxide and crosslinking by ionizing radiation from an electron-beam accelerator were both used and compared. Improved mechanical properties were

observed by the partial replacement of LDPE with EVA. Similar mechanical or thermal properties were observed with coadditives such as PEgMA and vinyl silane with boric acid. The addition of a small amount of talc improved the tensile strength of the formulations. All crosslinked formulations showed good thermal stability on the basis of the retention of mechanical properties after thermal aging for 168 h at 135°C and a hot-set test. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 107: 642–649, 2008

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

INTRODUCTION

Low-density polyethylene (LDPE) possesses good mechanical properties, good resistance to chemicals, and good processability and has a wide range of applications, including the insulation of wire and cable. 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 flame retardancy of LDPE, on the other hand, can be improved with flame retardants. There are several types of flame retardants used to improve the flame retardancy of polyolefins. At present, there is a trend to avoid the use of halogenated flame retardants because of environmental and safety concerns. Thus, as main nonhalo-

genated flame retardants, mainly metal hydroxides^{1–5} and intumescent flame retardant (IFR) systems^{6–13} are used. Very good efficiency in flame retardancy of polyolefins can be achieved with IFR systems. However, a higher loading of an IFR additive is needed in comparison with that of some halogen-containing flame retardants. This results in lowered mechanical properties of the flame-retarded compounds. Thus, the flame-retardant efficiency of IFR should be further improved. To improve the performance of IFR in polyolefins, synergistic agents such as boroxosiloxanes (products of reactions of polysiloxanes with boric acid),^{6,7} clays and nanoclays,^{10,11} and some metal-containing compounds^{12,13} that can enhance the flame-retardant action of IFR are used.

The thermal properties of polyolefins can be improved by small additions of stabilizers. A small quantity of processing stabilizers is usually added to prevent oxidative degradation of polyolefins caused by combined action of shear, heat, and oxygen during their melt processing. Phenolic antioxidants are widely used as processing stabilizers for polyolefins.^{14,15} They act as scavengers of oxygen-centered

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alkoxy and peroxy radicals, but they are not able to provide long-term thermal stability.¹⁶

The crosslinking of polymers leads to an increase in the melting temperature and an improvement in the thermal stability.¹⁷ Moreover, it can increase the tensile strength of polymers and thus, at a reasonable yield of crosslinking, improve their mechanical properties. There is no work describing the use of chemical or photochemical crosslinking together with IFR systems in polyolefins. Although IFR systems show higher improvement of flame retardancy of polypropylene in comparison with polyethylene resins, the crosslinking of polyethylene is much better developed.

In this work, various formulations containing blends of LDPE and a poly(ethylene vinyl acetate) copolymer (EVA) as a base material and ammonium polyphosphate (APP) as an IFR were mixed with coadditives including compatibilizers, stabilizers, and crosslinking agents and crosslinked chemically by dicumyl peroxide (DCP) or by an electron beam to achieve improved mechanical and thermal properties of LDPE/EVA compounds for wire and cable applications.

EXPERIMENTAL

Materials

LDPE (HP2022J) from Sabic (Jubail, Saudi Arabia) and EVA (Alcudia PA-538) from Repsol YPF (Madrid, Spain) with 18 wt % vinyl acetate from Gazechim (France) were used as received. Antioxidant Irganox 1010 from Ciba Specialty Chemicals (Basel, Switzerland), a processing aid (paraffin wax) from Fluka Chemicals Co., (Steinheim, Germany) APP-based flame retardant Exolit AP765 (~ 21 wt % phosphorus and ~ 18 wt % nitrogen; decomposition temperature > 275°C; density ~ 1.75 kg/L; bulk density ~ 0.6 kg/L) from Clariant (Sulzbach, France), a coupling agent [polyethylene grafted with maleic anhydride (PEgMA); 12031] from Solvay Co. (Brussels, Belgium), a coupling agent (oligomeric vinyl silane; Dynasytan 6498) from Degussa (Hanau, Germany) with boric acid from Brenntag (Mulheim, Germany), talc (V3837) from Luzenac (Toulouse, France), crosslinking agent DCP (Perkadox BC-40K) from Akzo Nobel (Arnhem, The Netherlands), and crosslinking coagent trimethylol propane triacrylate (TMPTA; Sartomer 351) from Cray Valley (Rieux, France) all were used as received.

Compounding and crosslinking

In the case of chemically crosslinked formulations, all additives except DCP were mixed with 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 by the molding of sheets for 30 min at 170°C. Sheets 2 mm thick were prepared.

In the case of formulations crosslinked by an electron beam, all additives were mixed with resins with a Brabender DSK 42/6 counter-rotating twin-screw extruder (Duisburg, Germany) at a temperature gradient of 150–150–140°C at a speed of 15 rpm. The residence time of the polymer in the extruder with a screw length of 25 cm at this speed was around 15 min. Sheets 2 mm thick were prepared by 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. Samples were irradiated at doses of 50, 150, and 200 kGy.

Testing methods

The tensile strength and ultimate elongation before and after aging were measured with a universal testing machine from Instron Co. (Canton, MA) in accordance with ASTM D 638M (at a speed of 50 mm/min).

Thermal aging of the samples was performed at 135°C for 168 h with a heat-aging oven in accordance with IEC 60811-1-2.

Dynamic mechanical analysis was performed with a DMA 2980 from Thermal Analysis, Inc. (New Castle, DE). A temperature scan was performed from the ambient temperature to 180°C at 3°C/min with a frequency of 1 Hz. The shear elastic modulus (G') was taken at 160°C on the rubbery plateau [rubbery plateau modulus (G'_0)]. The standard deviation was lower than 5%.

The oxidation induction temperature (OITP) was performed with a DSC 7 from PerkinElmer Co. (Hartford, CN) according to the specifications of IEC 60544-5. OITP was a temperature scan under oxygen at a rate of 10°C/min. A maximum deviation of $\pm 2^\circ\text{C}$ was obtained.

A hot-set test was performed according to the specifications of IEC 60811. A force of 0.2 MPa/mm² was applied to a dumbbell specimen in an oven at 200°C for 15 min, after which the elongation under load was read. Then, the force was removed, and the samples were kept in the oven for another 5 min before being cooled at the ambient temperature. On the cooled samples, the recovery length was then read. Three samples from each formulation were tested, and the standard deviation was up to $\pm 9\%$.

RESULTS AND DISCUSSION

Mechanical properties

The good compatibility of additives with a resin leads to good mechanical properties. As additives

TABLE I
Chemically Crosslinked Formulations

Formulation code ^a	LDPE	EVA	APP (phr)	DCP (phr)	TMPTA (phr)	Vinyl silane (phr)	Boric acid (phr)	PEgMA (phr)	Talc (phr)
C-1	100	—	30	3	—	1.5	1.5	—	—
C-2	80	20	30	3	—	1.5	1.5	—	—
C-3	60	40	30	3	—	1.5	1.5	—	—
C-4	100	—	30	3	—	—	—	3	—
C-5	80	20	30	3	—	—	—	3	—
C-6	60	40	30	3	—	—	—	3	—
C-7	60	40	30	3	3	1.5	1.5	—	—
C-8	60	40	30	3	3	—	—	3	—
C-9	60	40	35	3	—	—	—	3	—
C-10	60	40	35	3	—	—	—	3	1

^a All formulations contained 0.3 phr Irganox 1010 and 0.3 phr paraffin wax.

usually contain some polar groups, their compatibility with a resin can be achieved with coupling agents or more polar resins. Therefore, formulations including two types of coupling agents, PEgMA and vinyl silane, as well as blends of LDPE with EVA were used in this work. Moreover, because of the higher free volume of EVA in comparison with LDPE, partial replacement of LDPE with EVA can allow higher filler loadings without mechanical properties being hindered. In addition, two crosslinking methods—a chemical method using DCP as a crosslinking agent (see Table I) and an ionizing radiation method using an electron beam and TMPTA as a crosslinking coagent (see Table II)—were used for the investigated formulations. All formulations with vinyl silane as a coupling agent contained boric acid because of the synergism of boroxosiloxanes (generated *in situ* from the reaction of silanes with boric acid) with APP in improving the flame retardancy of polyolefins, as described in the literature.^{6,7}

The tensile strength of blends of LDPE and EVA crosslinked chemically with DCP (Table I, C-1 to C-6) is shown in Figure 1. For both coupling agents, there was no change or a very small change in the tensile strength with an increase in the EVA content up to 20%; however, a further increase of EVA up to 40% increased the tensile strength as EVA had a

higher tensile strength than LDPE (18.5 MPa for EVA vs 12 MPa for LDPE). A comparison of the two coupling agents showed that the tensile strength was almost the same up to 20% EVA. Slightly higher values were achieved with PEgMA as a compatibilizer in the case of 40% EVA compounds. The addition of APP to resins generally leads to a decrease in the tensile strength. Thus, after the mixing of 30 phr APP with LPDE/EVA blends, a decrease in the tensile strength of about 2 MPa was observed.

The addition of additives to a resin generally also decreases the elongation at break. Mixing 30 phr APP with LDPE led to a 250–300% reduction in the elongation at break after chemical crosslinking (see Fig. 2). As shown in Figure 2, for both coupling agents, there was a marked increase in the elongation at break with an increase in the EVA content up to 40%. This was due to the higher elongation at break of EVA in comparison with LDPE as well as the better compatibility of additives with EVA. By comparing the two coupling agents, we observed similar results when 20 and 40% EVA was used. A higher elongation at break was observed in formulations without EVA when PEgMA was used. This may indicate that PEgMA is a better compatibilizer than vinyl silane.

The tensile strength of LDPE formulations crosslinked by an electron beam (see Table II) is shown in

TABLE II
Formulations Crosslinked by Ionizing Radiation from an Electron-Beam Accelerator

Formulation code ^a	LDPE	EVA	APP (phr)	TMPTA (phr)	Vinyl silane (phr)	Boric acid (phr)	PEgMA (phr)
R-1	100	—	30	3	1.5	1.5	—
R-2	80	20	30	3	1.5	1.5	—
R-3	60	40	30	3	1.5	1.5	—
R-4	100	—	30	3	—	—	3
R-5	80	20	30	3	—	—	3
R-6	60	40	30	3	—	—	3

^a All formulations contained 0.3 phr Irganox 1010 and 0.3 phr paraffin wax.

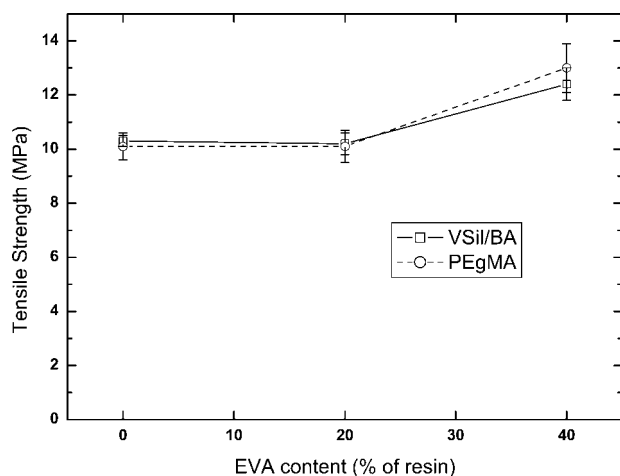


Figure 1 Tensile strength of chemically crosslinked LDPE formulations with various coupling agents [vinyl silane/boric acid (C-1 to C-3) and PEgMA (C-4 to C-6)] as a function of the EVA content.

Figure 3. In the formulations containing vinyl silane, there was almost no difference in the tensile strength with an increase in the EVA content up to 40% for unirradiated samples and samples irradiated with a dose of 50 kGy. An improvement of the tensile strength was achieved only in the sample irradiated at an absorbed dose of 150 kGy in a formulation containing 40% EVA. On the other hand, in the case of formulations containing PEgMA (see Fig. 4), a slight increase in the tensile strength for unirradiated samples and samples irradiated with an absorbed dose of 50 kGy and a marked improvement in the tensile strength for samples irradiated with 150 kGy were observed with an increase in the EVA content.

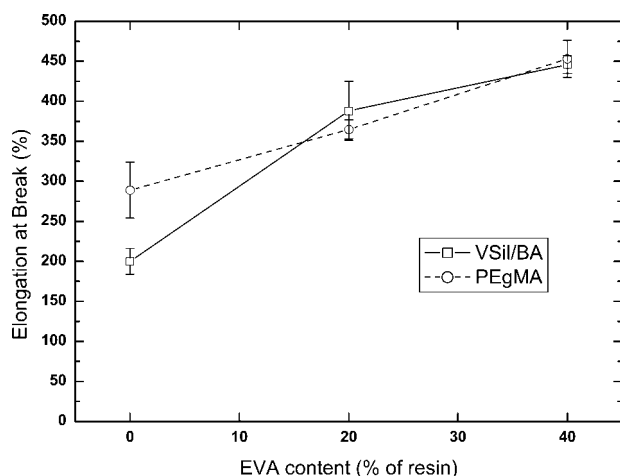


Figure 2 Elongation at break of chemically crosslinked LDPE formulations with various coupling agents [vinyl silane/boric acid (C-1 to C-3) and PEgMA (C-4 to C-6)] as a function of the EVA content.

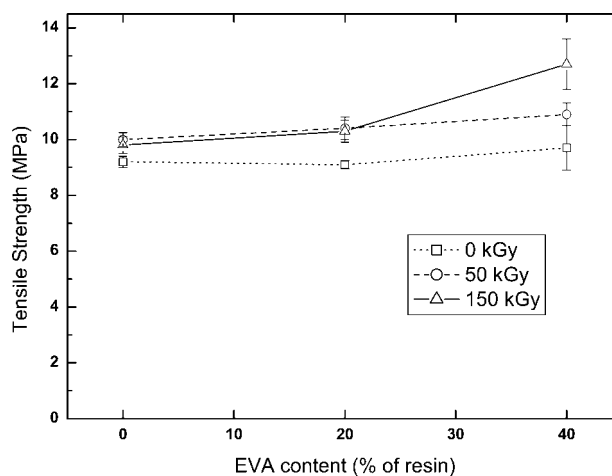


Figure 3 Tensile strength of radiation-crosslinked LDPE formulations with vinyl silane/boric acid (R-1 to R-3) at various radiation doses as a function of the EVA content.

It is well known that the chemical differences between EVA and LDPE make EVA more reactive and therefore more susceptible to crosslinking. A good representation of the crosslink density in polyolefins is G' , which is measured at 160°C on the rubbery plateau (G'_0). In an ideal network, G'_0 is related to the crosslink density by the following equation¹⁸:

$$\text{Crosslink density} = G'_0/2RT$$

where T is the temperature (K) and R is the gas constant.

G' slightly increased after crosslinking with an increase in the EVA content. For example, in the case of radiation-crosslinked formulations containing PEgMA (i.e., R-4 to R-6), G' at an absorbed dose of 150 kGy was 0.36, 0.37, and 0.43 MPa, respectively,

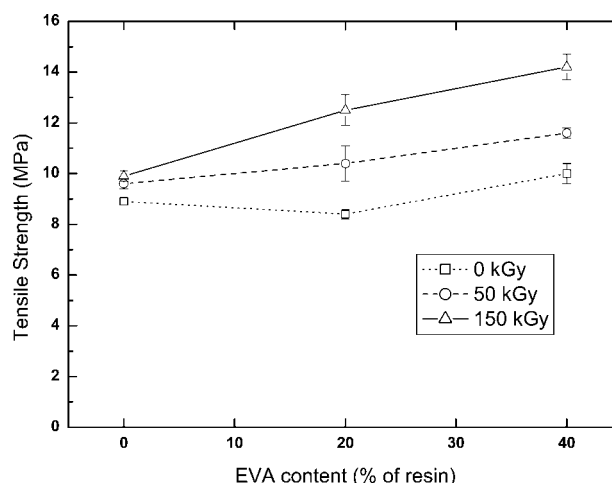


Figure 4 Tensile strength of radiation-crosslinked LDPE formulations with PEgMA (R-4 to R-6) at various radiation doses as a function of the EVA content.

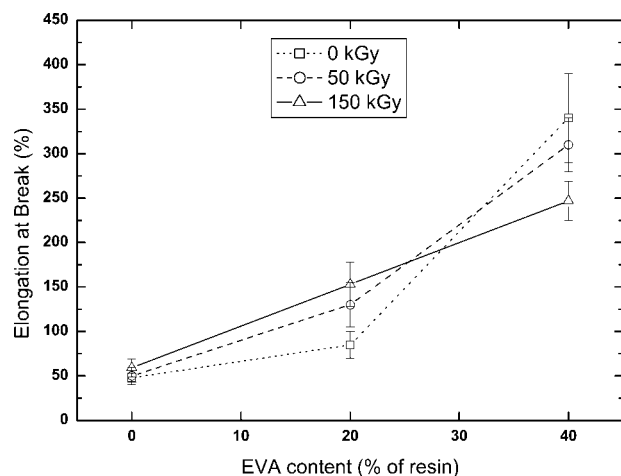


Figure 5 Elongation at break of radiation-crosslinked LDPE formulations with vinyl silane/boric acid (R-1 to R-3) at various radiation doses as a function of the EVA content.

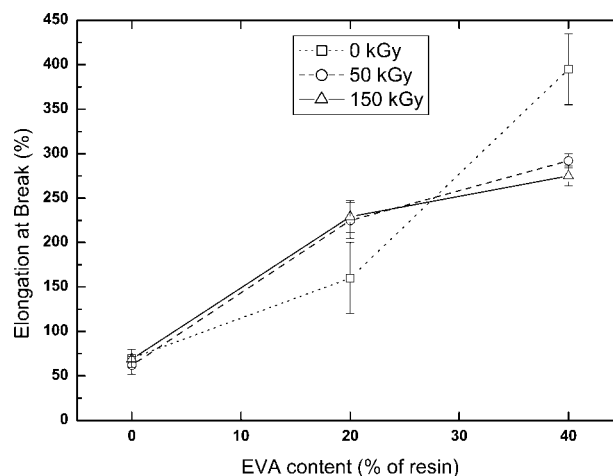


Figure 6 Elongation at break of radiation-crosslinked LDPE formulations with PEGMA (R-4 to R-6) at various radiation doses as a function of the EVA content.

although before irradiation the values were independent of the EVA content in the range of 0.04–0.05 MPa. This can indicate that an increase in the tensile strength with an increase in the EVA content can be caused by both better compatibility and a slightly higher crosslinking yield.

A comparison of the two coupling agents at an irradiation dose of 150 kGy showed that a higher tensile strength was achieved when PEGMA was used in formulations containing 20 or 40% EVA.

An increase in the elongation at break with an increase in the EVA content, because of better compatibility, was observed for both coupling agents at all irradiation doses (see Figs. 5 and 6). A decrease in the elongation at break in formulations containing 40% EVA with an increase in the irradiation dose was expected and perhaps could be attributed to an increase in the crosslink density.

An evaluation of the mechanical properties in this work shows that a blend of LDPE and EVA (60%/40%) gives optimum properties to ensure good compatibility of additives with resins and thus to achieve good tensile strength and elongation at break.

Influence of the crosslinking methods

The best of the chemically crosslinked and radiation-crosslinked formulations were evaluated, and their mechanical and thermal properties were compared (see Table I, C-3 and C-6, and Table II, R-3 and R-6). For a better comparison of the two crosslinking methods, chemically crosslinked formulations containing TMPTA as a crosslinking coagent in addition to DCP were prepared, and the influence of the presence of TMPTA in the flame-retardant compositions was investigated (see Table I, C-7 and C-8).

Table III shows that an increase in the crosslink density after the addition of TMPTA was not observed for chemically crosslinked formulations, whereas G' stayed the same. This shows that 3 phr DCP is enough to achieve a high crosslink density and that the addition of 3 phr TMPTA has no influence or a very small influence on promoting any further crosslinking. This is in agreement with reported literature indicating that crosslinking coagents (i.e., triallyl cyanurate with DCP) are used only when a small amount of DCP in the range of 0.2–1.5 phr is used.^{19,20} No difference in the crosslink density was observed among chemically crosslinked formulations

TABLE III
 G' Values, Retention of Mechanical Properties After Thermal Aging, and Hot-Set Test for Chemically Crosslinked Formulations and Radiation-Crosslinked Formulations

Property	C-3 (DCP + vinyl silane)	C-7 (DCP + TMPTA + vinyl silane)	R-3 (TMPTA + vinyl silane)	C-6 (DCP + PEGMA)	C-8 (DCP + TMPTA + PEGMA)	R-6 (TMPTA + PEGMA)
G' (MPa)	0.49	0.5	0.59 (0.6) ^a	0.5	0.5	0.43 (0.63) ^a
Retention of tensile strength (%)	93	99	91	113	99	77
Retention of elongation at break (%)	74	90	105	97	93	68
Hot-set test (%)	42	35	20	33	40	40

^a After irradiation at 200 kGy.

containing various types of coupling agents, although vinyl silane containing double bonds was expected to give a higher crosslink density. On the other hand, radiation-crosslinked formulations (at 150 kGy) exhibited an increase in the crosslink density in the presence of vinyl silane in comparison with PEGMA as shown by the G' values. This indicates that although vinyl silane was used mainly as a compatibilizer in formulations, it may play a role in radiation crosslinking. However, higher irradiation doses up to 200 kGy led to an increase in the crosslink density of the formulation containing PEGMA (formulation R-6). In the case of the formulation containing vinyl silane (formulation R-3), no further increase in the crosslink density was observed at high irradiation doses. Thus, considering G' for chemically crosslinked and radiation-crosslinked formulations, we believe that a higher crosslink density can be achieved by electron-beam irradiation in comparison with chemical crosslinking using DCP.

As shown in Figure 7, a higher tensile strength was achieved in radiation-crosslinked formulations versus formulations crosslinked by DCP. In the case of formulations containing PEGMA, the tensile strength for a radiation-crosslinked formulation was about 2.5 MPa higher than that of a DCP-crosslinked formulation. No improvement was achieved by the addition of TMPTA to the chemically crosslinked formulations.

The elongation at break, however, was much higher in the case of chemically crosslinked formulations (see Fig. 8); the addition of TMPTA led to an undesirable decrease in the elongation at break.

The thermal properties of the developed formulations were characterized by the retention of mechanical properties after thermal aging, a hot-set test, and OITP with differential scanning calorimetry. It was

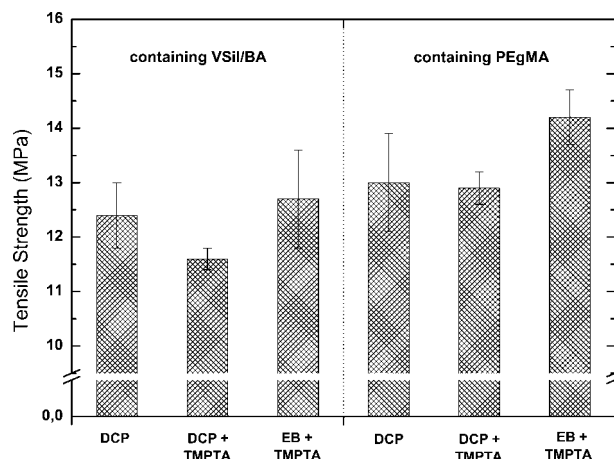


Figure 7 Tensile strength of LDPE/EVA (60/40) formulations containing 30 phr APP with vinyl silane/boric acid or PEGMA crosslinked by DCP or an electron beam (EB).

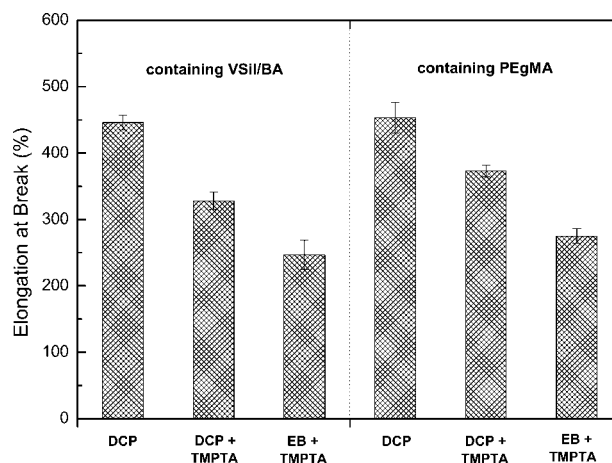


Figure 8 Elongation at break of LDPE/EVA (60/40) formulations containing 30 phr APP with vinyl silane/boric acid or PEGMA crosslinked by DCP or an electron beam (EB).

observed that most of the formulations exhibited very good retention of the tensile strength and elongation at break of about 100% (see Table III). Slightly lower retention was observed only in the case of a chemically crosslinked formulation containing vinyl silane, for which the retention of the elongation at break was 74%, and in the case of a radiation-crosslinked formulation containing PEGMA, for which the retention of the tensile strength and elongation at break was lower than 80%. However, the retention in these two cases was still much better than that of uncrosslinked formulations, the samples of which underwent fatal degradation during thermal aging.

Similarly, hot-set-test results showed very good thermal properties for the prepared formulations. Only about 40% elongation was observed under load

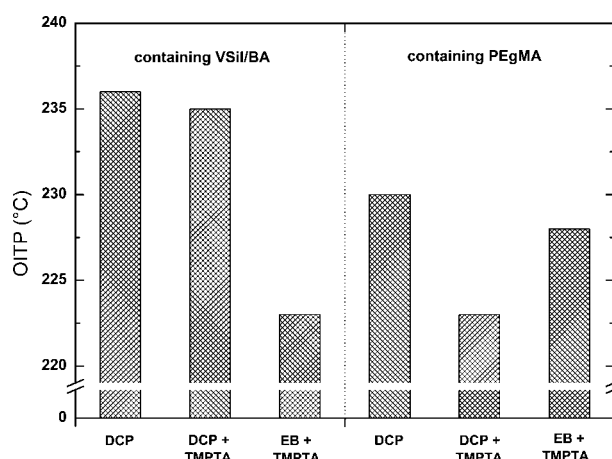


Figure 9 OITP of LDPE/EVA (60/40) formulations containing 30 phr APP with vinyl silane/boric acid or PEGMA crosslinked by DCP or an electron beam (EB).

TABLE IV
Mechanical and Thermal Properties of Chemically Crosslinked Formulations with Two Levels of APP and in the Presence of Talc

Property	C-6 (30 phr APP)	C-9 (35 phr APP)	C-10 (35 phr APP + 1 phr talc)
Tensile strength (MPa)	13.0 ± 0.9	11.9 ± 0.3	15.2 ± 0.8
Elongation at break (%)	453 ± 23	487 ± 18	481 ± 10
Retention of tensile strength (%)	113	104	93
Retention of elongation at break (%)	97	99	97

for all tested crosslinked formulations (see Table III). Moreover, for all crosslinked samples, a permanent elongation of 0% was obtained after cooling, whereas before crosslinking, the samples broke under load.

A good correlation was obtained between OITP and the oxidation induction time for selected formulations. Accordingly, OITP, which was much faster, was used for the evaluation of formulations in this work. OITP for uncrosslinked samples was over 250°C. Figure 9 shows a decrease in OITP after crosslinking for both methods of crosslinking. This may be attributed to the consumption of Irganox 1010 during crosslinking by the reaction of the antioxidant with the produced radicals. Lower oxidation resistance was found for radiation-crosslinked formulations in comparison with formulations crosslinked by DCP. Accordingly, a higher amount of Irganox 1010 in the case of radiation crosslinking may lead to a decrease in the crosslink density and consequently lead to a decrease in other mechanical or thermal properties. For chemically crosslinked samples, vinyl silane gave a higher OITP than formulations with PEGMA with or without TMPTA.

As observed, although a higher tensile strength was achieved by radiation crosslinking, chemically crosslinked formulations using DCP had much higher elongation at break and were more resistant to oxidation.

Influence of the additives

To achieve the required flame-retardant properties of IFR compounds, at least 35 phr APP is required. Therefore, a study of the influence of increasing APP content on the mechanical and thermal properties of chemically crosslinked formulations was performed. Table IV shows that the retention of mechanical properties after thermal aging was not influenced by a larger amount of APP and that the retention of both the tensile strength and elongation at break was still about 100%. On the other hand, an increase in APP from 30 to 35 phr had an influence on the mechanical properties before aging. Although the elongation at break was observed to be practically unchanged after an increase in the APP content, the

tensile strength underwent a slight decrease (see Fig. 10 and Table IV).

It is known that small amounts of some inorganic fillers can improve the mechanical properties of compounds. Therefore, to improve the tensile strength of our crosslinked formulations containing APP, a small amount of talc was added. As shown in Figure 10 and Table IV, the addition of 1 phr talc led to a marked improvement of the tensile strength up to about 15 MPa. At the same time, no decline in the elongation at break was observed (see Table IV), and no decline in the thermal properties was observed either. The retention of the tensile strength and elongation at break was found to be about 100% (see Table IV).

CONCLUSIONS

Blends of LDPE and EVA crosslinked by both radiation and DCP with good mechanical and thermal properties were prepared for use in wire and cable applications. The mechanical properties, which decreased after the addition of APP, could be partially improved by the blending of LDPE with EVA. Good thermal properties were achieved by efficient crosslinking by two methods: a chemical method using

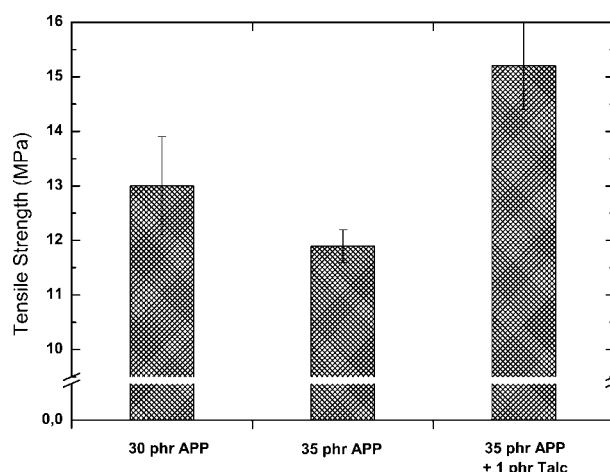


Figure 10 Tensile strength of chemically crosslinked LDPE/EVA (60/40) formulations containing PEGMA and various contents of APP without and with talc.

DCP and an ionizing radiation method using an electron-beam accelerator. Although formulations chemically crosslinked by DCP had lower tensile strength than formulations crosslinked by an electron beam, they had much higher elongation at break and better resistance to thermal oxidation. The improvement of the tensile strength of chemically crosslinked formulations was easily achieved by the addition of a small amount of talc. An evaluation of the flame retardancy and electrical properties of the investigated formulations will be presented in future publications.

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