eXPRESS Polymer Letters Vol.1, No.6 (2007) 378–384
Available online at www.expresspolymlett.com
DOI: 10.3144/expresspolymlett.2007.53

Silane crosslinking of polyethylene: the effects of EVA, ATH and Sb_2O_3 on properties of the production in continuous grafting of LDPE

*H. Azizi**, *J. Barzin, J. Morshedian*

Iran Polymer and Petrochemical Institute, P.O.Box. 14965/115, Tehran, Iran

Received 31 January 2007; accepted in revised form 14 May 2007

Abstract. In this study, thermal, mechanical and fire retardant properties of silane-crosslinked low-density polyethylene (XLPE) containing ethylene-vinylacetate (EVA) copolymer, alumina trihydrate (ATH) and antimony trioxide (Sb_2O_3) have been studied. Samples were prepared in a single-screw extruder and the silane type was vinyltrimethoxy silane (VTMOS). Incorporation of ATH and Sb_2O_3 into polyethylene at sufficiently high loading introduces good fire retardancy expressed by limiting oxygen index (LOI). However, some tensile properties decreased. These limitations could be overcome by silane crosslinking. By incorporation of EVA into XLPE gel content increased and curing time decreased. Differential scanning calorimetric (DSC) analysis indicated the existence of two distinct melting endothermic peaks corresponding to two different crystalline phases. Results from mechanical properties showed that mechanical properties of XLPE/EVA blends improve by increasing EVA content up to 15 wt%.

Keywords: *material testing, polyethylene, silane croslinking, flame retardant, EVA*

1. Introduction

In many applications there is a need to improve the properties of polyethylene, in particular with respect to heat deformation resistance, but improvement in chemical resistance, stress cracking, etc., may be important as well. Crosslinking is then an obvious alternative and it is used today on large commercial scale in wire and cable and pipe industries [1–4]. In cable jacketing, however, in many occasions especially for low-voltage application (<10 kV) the mechanical and thermal-endurance properties become more important than electrical properties. For example a furnace cable operated at 500 V requires good mechanical properties and stability of mechanical properties at elevated temperature which after ageing is the most important consideration; whereas for oil-resistant and fire retardant cables, the requirements are very different. There are three common methods of crosslinking polyethylene: 1) peroxide 2) irradiation and 3) silane [5–10]. Nowadays, silane crosslinking is becoming increasingly popular as replacement in certain applications for the other methods due to lower capital investment and increased productivity [11, 12].

In addition to polyethylene, today's vinyl acetate modified polyethylenes are also used in the wire and cable industry. The incorporation of small amount of vinyl acetate into polyethylene results in a resin which extrudes much like polyethylene, while providing the ability to accept filler loading e.g carbon black [13–15].

Actually a wide range of properties is possible depending on the vinyl acetate content. Density, crystallinity and toughness can be changed by vinyl acetate. Some researchers have studied the proper-

---

*Corresponding author, e-mail: h.azizi@ippi.ac.ir ties of crosslinked ethylene-vinyl-silane copolymers [16–17]. Another important requirement for cables in some applications is flame resistance. Due to corrosiveness and toxicity of smoke and other emission products generated during the combustion of thermoplastics containing halogen-based fire retardants, extensive works have been carried out to use the alternative halogen free fire retardants. In particular some metallic hydroxide fillers have been studied. These metallic hydroxides are gaining increasing importance in the industry because of the desirable combination of low cost, low smoke and relatively high fire retardant efficiency. However one of the major drawbacks of adding these fillers is that the mechanical properties become much poorer than those of samples without added fillers. Several methods can be used to improve the interaction between polymer and filler [18–23]. Crosslinking can be a suitable method for this purpose [24, 25]. Using of some other new synthetic fire retardants has also been reported [26, 27]. In our previous papers, factors affecting silane grafting and water crosslinking and mechanical and thermal properties of XLPE were investigated [28, 29]. In the present study the effect of EVA and two metallic hydroxides on properties of silane-grafted water-crosslinked polyethylene are investigated. Flammability, mechanical and thermal behaviors of samples are evaluated.

2. Experimental

2.1. Materials

The polyethylene used was low density polyethylene (LDPE) with trade name of poliran-LF0200 (melt index = 1.6 g/10 min, $d = 0.923$ g/cm^3) from Arak Petrochemical Co. Iran. The silane was vinyl trimethoxy silane (VTMOS, $d = 0.97$ g/cm^3, boiling point = 123°C) as tarde name Dynasilan from Silvento, Germany, in the liquid from. Di-cumyl peroxide (DCP) with trade name of Dicup- from Hercules ($d = 1.02$ g/cm^3) was used as initiator. The non-halogenic fire retardants were alumina trihydrate (ATH, $d = 2.42$ g/cm^3) and Antimony trioxide (Sb_2O_3, $d = 5.2$ g/cm^3) in powder form from Merck. Ethylene vinyl acetate copolymer (EVA) prepared by Exxon. (USA. VA% = 18, $d =$ 0.94 g/cm^3). Dibutyltin dilaurate (DBTDL) and Irganox 1010 were used as catalyst and antioxidant, respectively.

2.2. Sample preparation

Compounding was carried out using a single-screw extruder ($L/D = 31$). The screw was modular and designed to achieve best mixing efficiency using different mixing elements such as pineapple, pin-mixers and Maddock along the screw. Two-step Sioplas crosslinking method was selected to prepare XLPE compounds. In this method, catalyst and antioxidant were added to compound as a masterbatch. The amount of EVA was 5, 15 and 25 wt% and for ATH and Sb_2O_3 was 10, 20 and 30 phr. Before blending, the ATH and Sb_2O_3 were pre-mixed with LDPE and fed into the extruder from main hopper. The extrudate was cooled and granulated and resulting granules were compounded with silane and DCP in the extruder to silane-grafted samples. Finally the 95 percent of grafted sample was mixed with 5 percent of catalyst masterbatch and then granulated. The temperature profile was 130, 150, 170, 190, 200, 210, 220°C and screw rotation speed was 40 rpm. The amount of silane and DCP was fixed at 1.5 and 0.15 phr for all samples, respectively.

The granules were compression molded into the sheets. Crosslinking was carried out by exposing the sheets to hot water for 16 hours.

2.3. Characterization

Melting behavior was studied using a differential scanning calorimeter (DSC) model PL 1500 from polymer laboratory. Thermal gravimetric analysis of different samples was carried out by using a STA 625 from Rheometric Scientific in a nitrogen atmosphere at a heating rate of 20°C/min. A mass of about 100 mg of samples was heated at temperatures ranging from 30 to 800°C. Tensile properties were determined using an Instron 6025 according to ASTM D 638.

The gel content of silane crosslinked polyethylene was determined according to ASTM D 2765.The solvent used in the analysis of gel content was Xylene. Flammability behavior was characterized using the limiting oxygen index (LOI) according to ASTM D 2863. The limiting oxygen index was defined as the minimum mole percentage of oxygen in a mixture of oxygen and nitrogen necessary to barely support flaming combustion of a material initially at room temperature under the conditions of test method.

3. Results and discussion

3.1. Effect of ATH and Sb_2O_3 on properties of XLPE

3.1.1. Flammability behavior

Table 1 summarizes the LOI and composition of samples studied. As it can be seen from Table 1, LOI for crosslinked polyethylene is higher than that of original LDPE. This can be explained by increasing the thermal stability of LDPE with crosslinking. Table 1 shows that the limiting oxygen index increases with the amount of alumina trihydrate and antimony trioxide. Generally metallic hydroxides are believed to inhibit the flammability of polymers mainly by diluting the fuel with water vapor, increasing the heat of the material and insulating the substrate from heat source and thus reducing the rate of thermal degradation. It is obvious from Table 1 that the effectiveness of metallic hydroxides is more pronounced at higher loading (>30 phr). Comparison between samples 6 and 10 indicates that crosslinking of filled LDPE increases the LOI.

An important result seen from Table 1 is when using both ATH and Sb_2O_3, for which LOI increases significantly. In other words, there is a synergistic effect by using both ATH and Sb_2O_3. In addition, it is interesting to note that at similar loading – especially at higher loadings – alumina trihydrate inhibits combustion more effectively than antimony trioxide. Some researchers have studied the mechanism of action of ATH and Sb_2O_3. It is believed that Sb_2O_3 is effective in combination with halogen-based fire retardants. Some researchers investigated the interaction and synergism of metallic hydroxides with zinc borate and zinc hydroxystannate [30, 31].

Table 1. LOI of different samples

Sample No.	Sb_20_3 [phr]	ATH [phr]	VTMO [phr]	LOI [%]
1	0	0	0.0	17
2	0	0	1.5	20.4
3	0	30	0.0	22
4	0	10	1.5	19.7
4	0	20	1.5	21
5	0	30	1.5	24
6	30	0	0.0	18
7	10	0	1.5	19
8	20	0	1.5	20
9	30	0	1.5	22
10	15	15	1.5	26

3.1.2. Mechanical properties

Table 2 shows the tensile strength and elongation at break of neat LDPE (sample A), XLPE (sample D), LDPE-ATH (sample B), XLPE-ATH (sample E), LDPE-Sb_2O_3 (sample C) and XLPE-Sb_2O_3 (sample F). It is clearly obvious that by addition of ATH and Sb_2O_3 tensile strength and elongation at break decrease significantly. This is possibly due to insufficient interactions between the polymer and the filler, which result in their inferior properties. In contrast, with crosslinking of LDPE tensile strength improves (samples E, F, G, B, C).

The effect of ATH on tensile strength and elongation at break of XLPE is shown in Figure 1.

Table 2. The effect of ATH and Sb_2O_3 on tensile properties of XLPE

Sample No.	Elongation at break [%]	Tensile Strength [N/mm²]	Sb_2O_3 [phr]	ATH [phr]
A	576	12.2	0	0
B	23	8.4	0	30
C	48	10.5	30	0
D	395	14.5	0	0
E	22	11.7	0	30
F	30	12.7	30	0
G	23	11.7	15	15

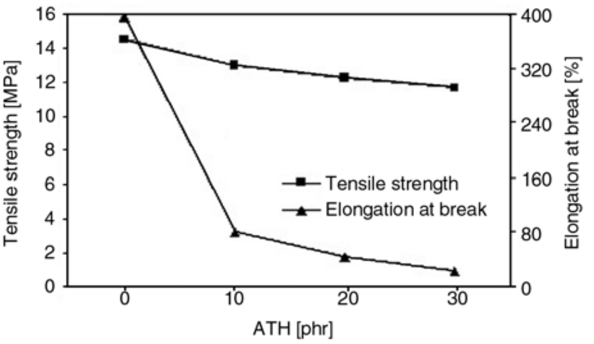

Figure 1. Variation of tensile strength and elongation at break of XLPE with ATH content

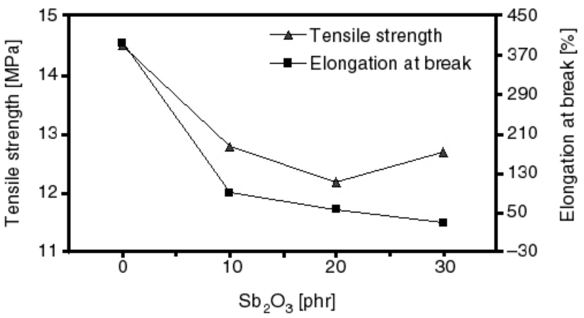

Figure 2. Variation of tensile strength and elongation at break of XLPE with Sb_2O_3 content

Generally, mechanical properties decrease with increasing filler content. Same results were found for XLPE-Sb_2O_3 samples (Figure 2).

3.1.3. Thermal decomposition behavior of XLPE-metallic hydroxide compositions

Polymers, being organic substances, have limited thermal stability. In the event of fire, due to a short circuit or other faults, the temperature of cable system may become very high. The thermal stability of the polymeric material is thus an important consideration in the selection of a cable.

The effect of crosslinking and addition of ATH and Sb_2O_3 (at 30 phr) on thermal decomposition behavior of LDPE is shown in Figures 3 and 4.

As it can be seen the onset decomposition temperature of LDPE-Sb_2O_3 (sample 7) is higher than that of LDPE-ATH (sample 6). However samples containing ATH show two-step decomposition. First at approx. 300°C ATH starts to decompose to yield water. But the temperature for maximum decomposition of ATH is the same as for Sb_2O_3.

With crosslinking thermal decomposition temperature of LDPE- filler samples did not change significantly.

The effect of alumina trihydrate and antimony trioxide on gel content is illustrated in Figure 5. Gel content decreases with increasing filler concentration, but the reduction is not considerable. This can be explained by inhibition effect of ATH and Sb_2O_3 for water permeation into LDPE structure. On the other hand surface of fillers may adsorb the silane component.

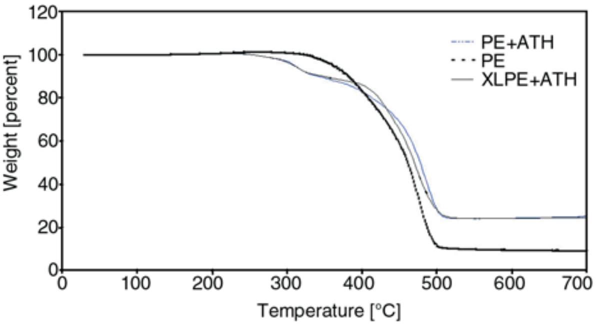

Figure 3. The effect of ATH and crosslinking on TGA thermogram of LDPE

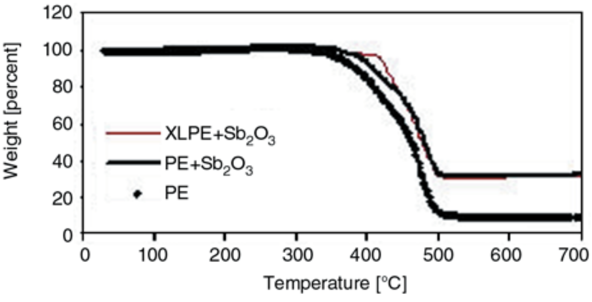

Figure 4. The effect of Sb_2O_3 and crosslinking on TGA thermogram of LDPE

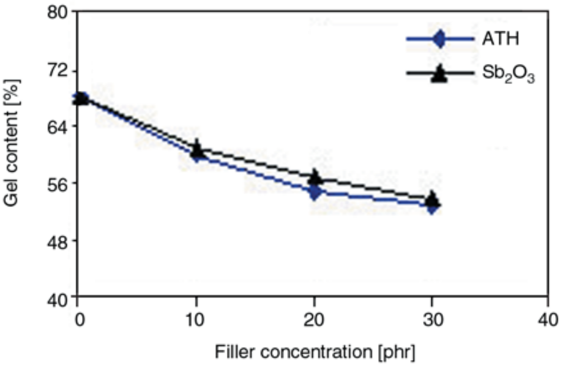

Figure 5. The changes of gel content with ATH and Sb_2O_3 concentration

3.2. Effect of EVA on properties of XLPE

3.2.1. Effect of EVA on gel content

Figure 6 shows the variation of gel content with EVA content. Gel content increases with increasing EVA concentration. By increasing EVA, crystallinity decreases and the amount of side chains increases therefore the permeation of water molecules into polymer structure increases and hence gel content increases. The polar groups of vinyl acetate can also facilitate the permeation of silane component into molecular structure of LDPE. On the other hand the peroxide-generated radicals can easily extract a hydrogen atom from EVA chains. It should be noted that compared to EVA, LDPE is relatively more difficult to crosslink. LDPE is a non-polar molecule with all its hydrogen atoms tightly bound to carbon atoms. The lack of highly reactive hydrogens means fewer sites for radical attack and lower reaction rates. EVA copolymers

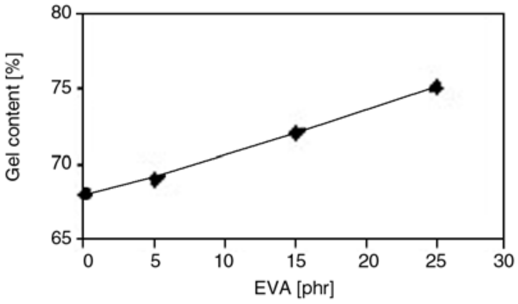

Figure 6. The effect of EVA concentration on gel content

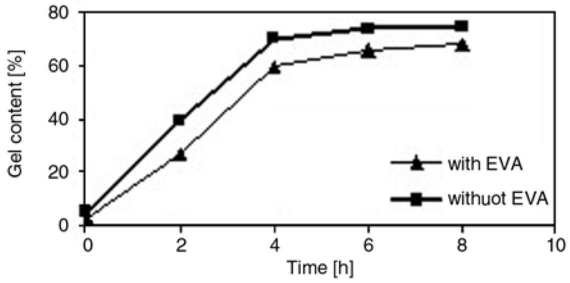

Figure 7. The influence of crosslinking time on gel content with and without EVA

are more readily crosslinked and accept high filler loading. In Figure 7 the influence of crosslinking time on gel content for LDPE/EVA blend is illustrated. The rate of crosslinking increases in presence of EVA.

3.2.2. Effect of EVA on thermal properties

Figure 8 shows the DSC thermogram of neat LDPE, neat EVA, LDPE/EVA and XLPE/EVA blend. As can be seen LDPE shows a sharp endothermic peak at 114.47°C. The effect of EVA and crosslinking on melting behavior of LDPE is shown. Blending of two semicrystalline polymers like LDPE and EVA with much lower crystallinity exhibits two distinct endothermic peaks corresponding to the melting of two different crystallites present in the blend. EVA shows two different peaks in DSC thermogram. In LDPE/EVA blend the melting point of LDPE shifted to lower values compared with that of neat LDPE. In XLPE/EVA blend two distinct endothermic peaks are presented. These peaks correspond to sol and gel fractions of the sample. In general, blending leads to broadening of melting peak.

The existence of two melting peaks for each blend which coincides exactly with peaks corresponding to two pure components eliminates the probability of the intermiscibility of the crystalline phases of two polymers. The polymers may be intimately mixed in the molten state; but as the blends are cooled from the melt, the crystallization of different components occurs separately, leading to two distinctly different crystalline states.

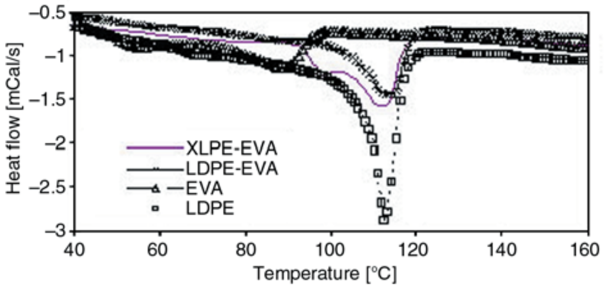

Figure 8. The effect of EVA and crosslinking on DSC thermogram of LDPE

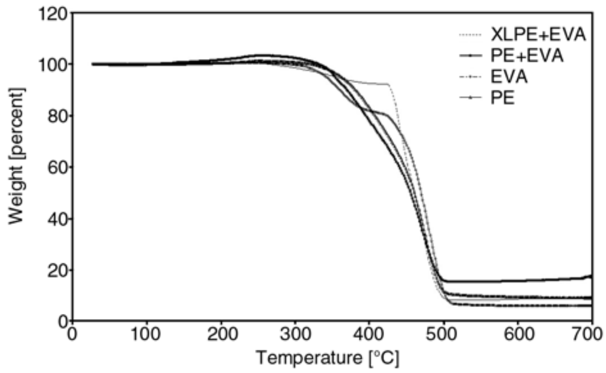

Figure 9. The effect of EVA and crosslinking on TGA thermogram of LDPE

Figure 9 shows the TGA curves of different samples. TGA analysis gives an idea of the thermal decomposition characteristics of different blends at elevated temperature. Two-stage decomposition is characteristics of EVA, whereas LDPE undergoes single-stage decomposition. The temperature at which EVA starts decomposing is about 350°C and the onset temperature of second-stage of decomposition of EVA is about 455°C.

In XLPE/EVA blend decomposition starts at 430°C. It means that decomposition temperature of XLPE/EVA blend is higher than that of LDPE/EVA blend.

3.2.3. Effect of EVA on mechanical properties of XLPE

The variation of tensile strength and elongation at break of XLPE versus EVA content is shown in Figure 10.

Tensile strength increases with increasing EVA concentration up to 15% beyond which it decreases slightly. It is found that for semicrystalline poly-

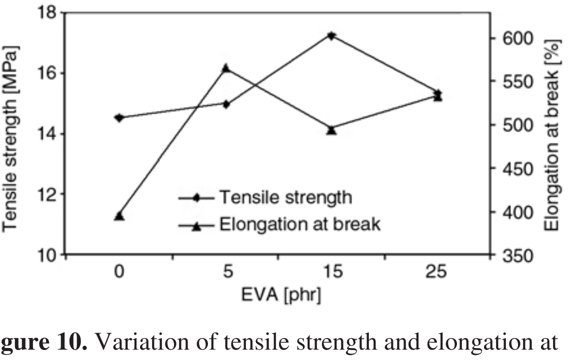

Figure 10. Variation of tensile strength and elongation at break of XLPE with EVA content

mers such as LDPE and EVA, the tensile strength depends not only on the degree of crystallinity but also on the extent of strain induced crystallization (strain-hardening) in the amorphous phase. This phenomenon is more prominent for EVA, which contains a higher ratio of amorphous zones compared to LDPE. Another factor in this study is crosslinking.

The introduction of crosslinking is in favor of the process of strain-induced crystallization by preventing chain slippage. On the other hand crystallinity decreases with crosslinking. As a result the competition between these factors indicates the trend of change of tensile properties. Generally elongation at break of samples containing EVA is higher than that of neat LDPE.

4. Conclusions

A study of the effect of ATH and Sb_2O_3 as non-halogenic flame retardants and EVA on continuous silane-crosslinking of LDPE has revealed the following:

- Flame retardancy is influenced by incorporating of metallic-hydroxide as flame retardant. LOI increases with increasing ATH and Sb_2O_3 content.
- Tensile strength and elongation at break of LDPE decrease by incorporating ATH and Sb_2O_3. With crosslinking the mechanical properties of filled-LDPE improve.
- The results of thermal gravimetric analysis showed that filled-XLPE is more thermally stable than virgin LDPE.
- Gel content decreases with increasing of ATH and Sb_2O_3 concentration while increases with increasing EVA content.
- Melting behavior of LDPE changes with adding EVA and crosslinking. In XLPE/EVA blend two distinct endothermic peaks corresponding to sol and gel fractions of sample are presented.
- Tensile strength and elongation at break of LDPE increase with increasing EVA up to 15 wt% beyond which tensile strength decreases slightly.

References

[1] Rado R., Zelenak P.: Crosslinking of polyethylene. International Polymer Science Technology, **19**, 33–47 (1992).

[2] Dufton P. W.: Recent developments in polymers for wire and cable: an industrial report. Rapra Technology, Shawbury (1995).

[3] Bostrom J-O., Gustafsson B., Lindbom L., Borealis A. B.: XLPE compound for fast cable line speed. IEEE Electrical Insulation Magazine, **13,** 33–36 (1997).

[4] Cameron R., Lien K. Lorigan P.: Advances in silane cross-linkable polyethylene. Wire Journal International, (**12**), 56–58 (1990).

[5] Sirisinha K., Kawko K.: Crosslinkable polypropylene composites made by the introduction of silane moieties. Journal of Applied Polymer Science, **97**, 1476–1483 (2005).

[6] Roberts B. E., Verne S.: Industrial applications of different methods of crosslinking polyethylene. Plastics Rubber and Composites Processing and Applications, **4**, 135–139 (1984).

[7] Vogt H.: Silane crosslined PE-LD for low-voltage cable. Kunststoffe German Plastics, **82**, 830–833 (1992).

[8] Rado R.: Preparation of crosslinkable polyethylene compounds. International Polymer Science Technology, **20**, 78–83 (1993).

[9] Thorburn B.: Crosslinking techniques for electrical jacketing materials. in 'Proceedings of the 52nd Annual Technical Conference, San Francisco, USA', 1379–1385 (1994).

[10] Shieh Y. T., Tsai T. H.: Silane grafting reactions for LDPE. Journal of Applied Polymer Science, **69**, 255–261 (1998).

[11] Kuan H-C., Kuan J-F., Ma C-C., Hung J-M.: Thermal and mechanical properties of silane-grafted water crosslinked polyethylene. Journal of Applied Polymer Science, **96**, 2383–2391 (2005).

[12] Huang H., Lu H. H., Liu N. C.: Influence of grafting formulations and extrusion conditions on properties of silane-grafted polypropylenes. Journal of Applied Polymer Science **78**, 1233–1238 (2000).

[13] Brogly M, Nardin M, Schultz J.: Effect of vinylacetate content on crystallinity and second-order transition in ethylene-vinylacetate copolymers. Journal of Applied Polymer Science, **64**, 1903–1912 (1997).

[14] Ray I, Khastgir D.: Low-density polyethylene (LDPE) and ethylene vinyl acetate (EVA) copolymer blends as cable insulants. Plastics Rubber and Composites Processing and Applications, **22**, 37–45 (1994).

[15] Ray I., Khastgir D.: Correlation between morphology with dynamic mechanical, thermal, physicomechanical properties and electrical conductivity for EVA-LDPE blends. Polymer, **34**, 2030–2037 (1993).

[16] Bolikhova V. D., Gvozdyukevich V. A., Glebko A. S, Drobinin A. N., Morozova L. S., Rumyansev V. D.: Production and properties of a silane-crosslinked ethylene-vinylacetate copolymer. International Polymer Science and Technology, **18**, 44–50 (1991).

[17] Palmlöf M, Hertberg T., Sultan B-A: Crosslinking reactions of ethylene vinyl silane copolymers at processing temperature. Journal of Applied Polymer Science, **42**, 1193–1203 (1991).

[18] Baillet C, Delfosse L.: The combustion of polyolefins filled with metallic hydroxides and antimony trioxide. Polymer Degradation and Stability, **30**, 89–99 (1990).

[19] Doi S., Isaka T.: Ethylene polymer compositions that are flame retardant. US Patent 4397981, USA (1983).

[20] Rychly J., Vesely K., Gál E., Kummer M., Jancar J., Rychlá L.: Use of thermal methods in the characterization of the high-temperature decomposition and ignition of polyolefins and EVA copolymers filled with $Mg(OH)_2$, $Al(OH)_3$ and $CaCO_3$. Polymer Degradation and Stability, **30**, 57–72 (1990).

[21] Vesely K., Rychly J., Kummer M., Jancar J.: Flammability of highly filled polyolefins. Polymer Degradation and Stability, **30**, 101–110 (1990).

[22] Hornsby P. R., Watson C. L.: A study of mechanism of flame retardance and smoke suppression in polymers filled with magnesium hydroxide. Polymer Degradation and Stability, **30**, 73–87 (1990).

[23] Hippi U., Mattila J., Korhonen M., Seppala J.: Compatibilization of polyethylene/aluminium hydroxide and polyethylene/magnesium hydroxide composites with functionalized polyethylenes. Polymer, **44**, 1193–1201 (2003).

[24] Yeh J. T., Yang H. M., Huang S. S.: Combustion of polyethylene filled with metallic hydroxide and crosslinkable polyethylene. Polymer Degradation and Stability, **50**, 229–234 (1995).

[25] Wang Z., Hu Y., Gui Z., Zong R.: Halogen-free flame retardation and silane crosslinking of polyethtylenes. Polymer Testing, **22**, 533–538 (2003).

[26] Haurie L., Fernandez A. I., Velasco J. I., Chimenos J. M., Cuesta J-M. L., Espiell F.: Synthetic hydromagnesite as flame retardant. Evaluation of the flame behaviour in a polyethylene matrix. Polymer Degradation and Stability, **91**, 989–994 (2006).

[27] Cai Y., Hu Y., Song L., Kong Q., Yang R., Zhang Y., Chen Z., Fan W.: Preparation and flammability of high density polyethylene/paraffin/organophilic montmorillonite hybrids as a form stable phase change material. Energy Conversion and Management, **48**, 462–469 (2007).

[28] Barzin J., Azizi H., Morshedian J.: Preparation of silane-grafted and moisture cross-linked low density polyethylene: Part I: Factors affecting performance of grafting and cross-linking. Polymer-Plastics Technology and Engineering, **45**, 979–983 (2006).

[29] Barzin J., Azizi H., Morshedian J.: Preparation of silane-grafted and moisture cross-linked low density polyethylene: Part II: Electrical, thermal and mechanical properties. Polymer-Plastics Technology and Engineering, **46**, 305–310 (2007).

[30] Antonietta G., Shanks R. A.: Structural and thermal interpretation of the synergy and interaction between the fire retardant magnesium hydroxide and zinc borate. Polymer Degradation and Stability, **92**, 2–13 (2007).

[31] Hornsby P. R., Cusack P. A, Cross M., Tóth A., Zelei B., Marosi G.: Zinc hydroxystannate coated metal hydroxide fire retardant. Journal of Materials Science, **38**, 2893–2899 (2003).