

LDPE/EVA B blend의 난연성 및 전기/기계적 특성

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**한국원자력연구원 방사선과학연구소

(2008. 5. 26. 접수 / 2008. 8. 5. 채택)

Flame Retardancy and Electrical/Mechanical Properties of LDPE/EVA Blend

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(Received May 26, 2008 / Accepted August 5, 2008)

Abstract : In this research, magnesium hydroxide as a flame retardant agents and zinc borate as a synergist were mixed with LDPE/EVA blended samples, in order to improve their flame retardancy. We attempted to select the best mixing ratio of the LDPE/EVA blend and the optimum amount of magnesium hydroxide and zinc borate by the comparison and analysis of the flame retardancy, the electrical properties such as the volume resistivity and dielectric loss tangent, and the mechanical properties such as the tensile strength and elongation at break. Particularly, specimen which is the 6phr of zinc borate and 10phr of magnesium hydroxide 70/30phr adding to the LDPE/EVA blended samples has been most excellent in flame retardancy and electrical/mechanical properties.

초 록 : 본 연구에서는 저밀도 폴리에틸렌과 에틸렌 비닐 아세테이트 블렌드(LDPE/EVA)의 난연성을 향상시키기 위해 난연제인 수산화 마그네슘과 난연상승보조제인 zinc borate를 첨가한 후, 난연성과 체적저항률, 유전정접, 교류 절연파괴강도 등의 전기적 특성, 인장강도 및 연신율 등의 기계적 특성을 비교·분석하여 가장 우수한 LDPE/EVA 블렌드의 혼합비 및 적절한 Mg(OH)₂와 zinc borate의 첨가량을 선정하고자 하였다. 혼합비 70/30phr의 LDPE/EVA 블렌드에 10phr의 Mg(OH)₂와 6phr 정도의 zinc borate를 첨가한 시편에서 가장 우수한 난연성 및 전기/기계적 특성을 나타내었다.

Key Words : LDPE/EVA blend, flame retardancy, volume resistivity, tensile strength, elongation at break

1. Introduction

Low density polyethylene(LDPE) is widely used as an insulation material because of its superior insulation, and mechanical flexibility, but it emits a lot of heat and smog when it is fired, because of its being an organic material. Halogenated flame retardant agents were previously used for improving the flame retardancy of materials, but their use is now regulated due to their carcinogenicity which is similar to that of HBr, HCl, corrosive gases, and halide dioxins, furans, etc. This has led to the intensive study of substitutes

offering improved flame retardancy through the addition of metal hydroxides. However, the addition of more than 60wt% of a metal hydroxide results in a decrease in the properties of the material, such as its electrical and mechanical characteristics¹⁾. To solve this problem, the mechanical properties of the material have generally been improved by limiting the amount of metal hydroxide that is added while, at the same time, adding synergists, and blending more than two kinds of high molecular weight polymers. In a previous study in which the dependency of the properties on the amount of magnesium hydroxide added to the LDPE/EVA blend was studied, the best results were obtained in the case where less than 20phr of Mg(OH)₂

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was added to the LDPE/EVA having a compounding ratio of 70/30phr²⁾.

Accordingly, in this study, 10phr of magnesium hydroxide was added to the LDPE/EVA blend having a compounding ratio of 70/30phr. The flame retardancy, electrical and mechanical characteristics of the LDPE/EVA blend were evaluated for various amounts of the added synergist, viz. up to 10phr of zinc borate.

2. Experimental

2.1. Compounding

This study was performed using three types of LDPE/EVA blend. Two types of LDPE/EVA blend at ratio of 100/0, 70/30phr mixtures with Mg(OH)₂ ranging from 10 to 60phr and another type is LDPE/EVA/Mg(OH)₂ blended at ratio of 70/30/10phr, to which 2~10phr of zinc borate were added, and the mixture blended at 60rpm for 5 minutes at 130°C using a Brabender device. After preheating the synthetic resins for 5 minutes at 130°C, they were processed into the form of a sheet using a hot plate press with a pressure of 15MPa for 5 minutes.

2.2. Measurements

2.2.1. Limited Oxygen Index

The limited oxygen index (LOI) was measured by KS(Korean Industrial Standards) M ISO 4589-1-3³⁾. The LOI was measured with a burning sample, while keeping the oxygen-nitrogen compound gases which have voluntary compound rates in the cylinder container. The LOI obtained from the oxygen and nitrogen fluxes using the following formula.

$$\text{LOI}[\%] = \frac{[\text{O}_2]}{[\text{O}_2] + [\text{N}_2]} \times 100 \quad (1)$$

[O₂] : Volumetric flow of oxygen[cm³/min]

[N₂] : Volumetric flow of nitrogen[cm³/min]

2.2.2. Volume resistivity

The volume resistivity was measured using a DC voltage of 400V with an electrometer & high resistance meter(Keithley 6517A) and test fixture(Keithley 8009).

2.2.3. Dielectric loss factor

The dielectric loss factor(tanδ) was measured using a dielectric analyser(TA inst. Model 2970). The dielectric loss factor experiment was carried out in an N₂ gas atmosphere using a frequency of 1Hz, and a temperature ranging from 30°C to 50°C in steps of 2 degrees per every minute.

2.2.4. Tensile strength and Elongation at break

In accordance with ASTM D638, tensile and elongation tests of the specimens were carried out on dumb-bell shaped specimens using an universal testing machine(Zwick Roel Z010) with a cross-head speed of 500mm/min at room temperature⁴⁾.

The number of measurement in each experimental conditions is five times, and an average value of each measured result plotted in the figures.

3. Results and discussions

3.1. Limited oxygen index

Fig. 1 shows the dependence of the LOI of the LDPE/EVA blended samples on the amount of Mg(OH)₂ added the compounding ratio. In the case where less than 30phr of Mg(OH)₂ was added, the LDPE/EVA blend with a compounding ratio of 70/30phr showed a higher LOI than the pure LDPE, and this is considered to be due to the addition of EVA which gives it a slightly higher flame retardancy than the pure LDPE.

The dependency of the LOI of the LDPE/EVA blend on the amount of zinc borate added is shown in Fig. 2. Compared with the specimen to which only 10phr of Mg(OH)₂ was added without adding any zinc borate, an LOI of 18.9~19.3 was obtained in case of the specimen to which up to 4phr of zinc borate was added. In the case of the specimen to which more than 6phr of zinc borate was added, the LOI was sharply increased to 24.1~24.6, and was similar to that observed in the case where more than 40phr of Mg(OH)₂ was added, as shown in Fig. 1. This result is considered to be due to the fact that the flame reatardant effects are improved because of the synergistic effect afforded by Mg(OH)₂ and zinc borate in the form of char, which delayed and controlled the burning by addition of zinc borate more than a certain

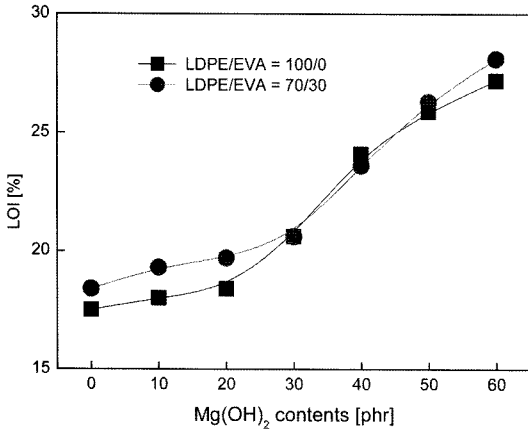


Fig. 1. LOI of the LDPE/EVA blended samples as a function of the Mg(OH)₂ concentration.

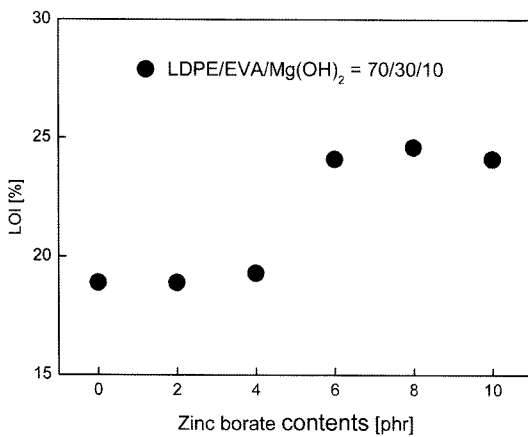


Fig. 2. LOI of LDPE/EVA blend as a function of the zinc borate concentrations.

amount with the flame retardant effect of Mg(OH)₂ in itself⁶⁾.

However, in the case of the specimen to which more than 10phr of zinc borate was added, the LOI was decreased probably due to the increased flame retardancy afforded by the zinc borate, because of the saturation of the residues during the process of burning.

3.2. Volume resistivity

Fig. 3 shows the volume resistivity of the LDPE/EVA as a function of the amount of Mg(OH)₂ added depending on the compounding ratio.

The LDPE/EVA blend with a compounding ratio of 70/30phr had a lower volume resistivity than pure LDPE, probably because EVA contains the polarized VA group.

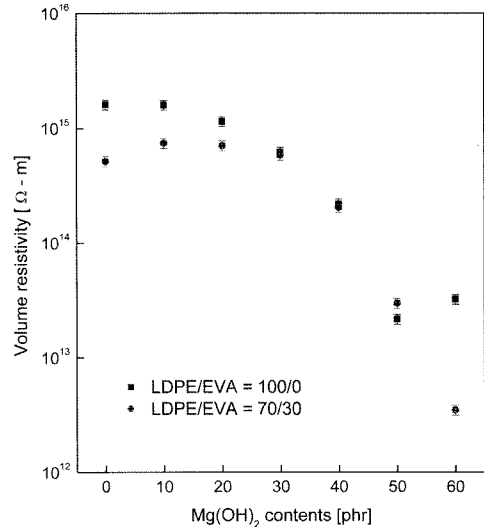


Fig. 3. Volume resistivity of LDPE/EVA blended samples as a function of the Mg(OH)₂ concentrations.

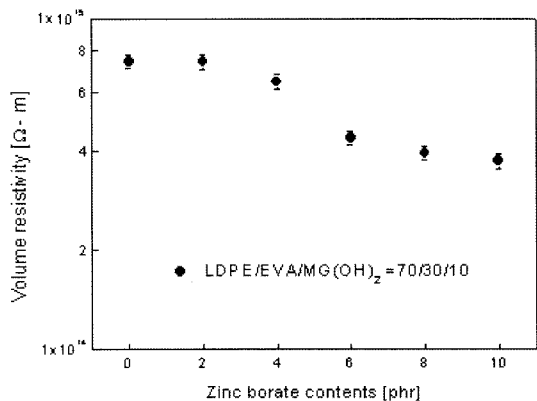


Fig. 4. Volume resistivity of LDPE/EVA blend as a function of the zinc borate concentrations.

Fig. 4 shows the volume resistivity as a function of the amount of zinc borate added. Due to the low volume resistivity by the increase in the added volume of zinc borate, this is caused by the generation of ionic carriers in the inside of the LDPE/EVA blend by added Mg(OH)₂ and zinc borate to improve the flame retardancy of the LDPE/EVA²⁾. In comparing the volume resistivity of the specimen to which 6phr of zinc borate was added and the specimen to which 40phr of Mg(OH)₂ was added with those of the specimens to which a variable amount of Mg(OH)₂ was added in a previous study²⁾, it can be inferred that the volume resistivity of the LDPE/EVA blend was substantially improved by the addition of zinc borate.

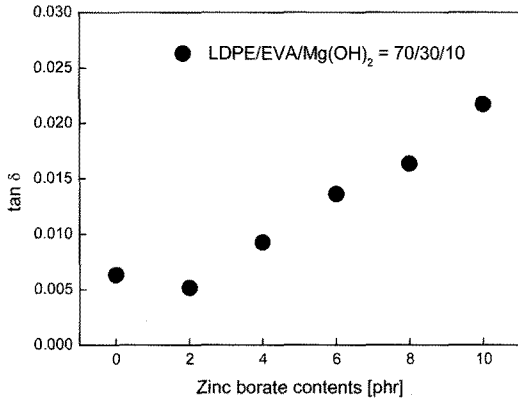


Fig. 5. Dielectric loss factor of LDPE/EVA blend as a function of the zinc borate concentrations.

3.3. Dielectric loss factor

Fig. 5 shows the dielectric loss factor ($\tan\delta$) of the LDPE/EVA blend as a function of the amount of zinc borate that was added. The values of $\tan\delta$ were measured at 1Hz using an alternating current signal showed a tendency to increase after reaching a minimum at a zinc borate content of 2phr.

This phenomenon was due to the decrease in the inner air gap and increase in the free volume that were brought about the addition of a small quantity of zinc borate.

When the amount of zinc borate was more than 4phr, the $\tan\delta$ increased again, because increasing the amount of zinc borate caused an increase in the air gap in the interior of the LDPE/EVA blend with its ionic carriers, which caused the interior of the LDPE/EVA blend to be mixed more irregularly⁶⁾.

3.4. Tensile strength and elongation at break

Fig. 6 shows the tensile strength at break of the LDPE/EVA blend as a function of the amount of $Mg(OH)_2$ added.

Regardless of the ratio of LDPE to EVA in the blend, the results showed a decrease in the tensile strength. In the case of the pure LDPE, the tensile strength of the LDPE containing less than or equal to 40phr of $Mg(OH)_2$ decreased highly and that which contained more than 40phr of $Mg(OH)_2$ showed a tendency to become saturated. This was due to the poor compatibility between LDPE and $Mg(OH)_2$ in accordance with previous studies^{1,2,5)}. In the case of

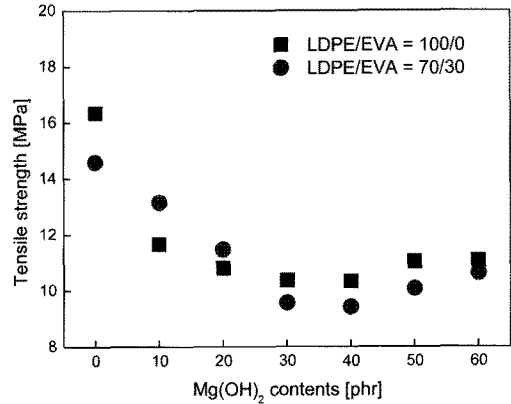


Fig. 6. Tensile strength of the LDPE/EVA blended samples as a function of the $Mg(OH)_2$ concentrations.

the LDPE/EVA blended samples, the tensile strength of the samples contained with $Mg(OH)_2$ ratio of 10, 20phr were higher than that of the pure LDPE, because the EVA improved the compatibility between LDPE and $Mg(OH)_2$ at blending process²⁾.

Fig. 7 shows the elongation at break of the LDPE/EVA blend as a function of the amount of $Mg(OH)_2$.

The results of the elongation were similar to those of the tensile strength, and the greater the amount of $Mg(OH)_2$, that was added, the more the elongation decreased.

In the comparison of the pure LDPE and LDPE/EVA blend containing the same amount of $Mg(OH)_2$, the LDPE/EVA blend showed a higher elongation than the pure LDPE and, as in the case of the tensile strength, this was due to the poor compatibility between LDPE and $Mg(OH)_2$ ^{1,3,7)}.

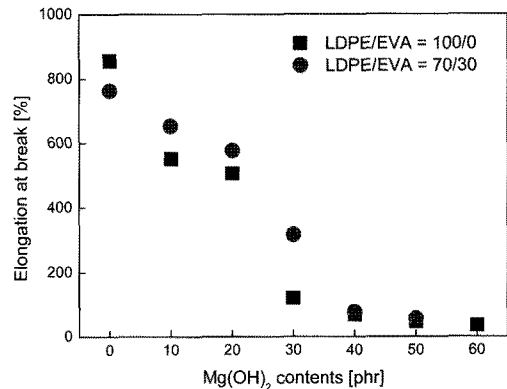


Fig. 7. Elongation at break of the LDPE/EVA blended samples as a function of the $Mg(OH)_2$ concentrations.

Fig. 8 and 9 show the results of the tensile strength and elongation of the LDPE/EVA blend as a function of the amount of zinc borate that was added, respectively. In accordance with the results of the tensile strength, increasing the amount of zinc borate resulted in a small decrease in the tensile strength, but when the amount of zinc borate exceeded 6phr, the flame retardancy of the specimens which contained zinc borate was similar to that of the LDPE which contained up to 40phr of $Mg(OH)_2$.

Therefore we found that the tensile strength was improved. Although the values of the elongation decreased by the addition of zinc borate, there was no decrease of the wide width and, when considering the flame retardancy and elongation together, we found that the addition of more than 6phr of zinc borate limited the amount of $Mg(OH)_2$ to 10phr or less.

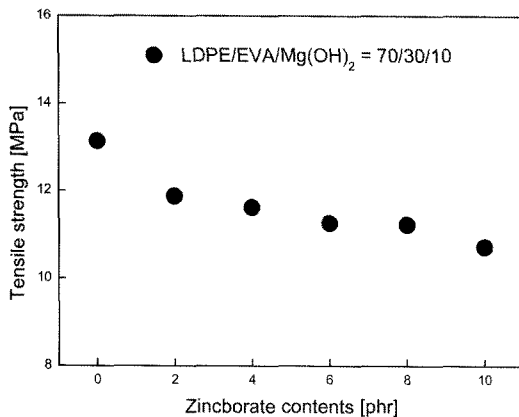


Fig. 8. Tensile strength of the LDPE/EVA blend as a function of zinc borate concentrations.

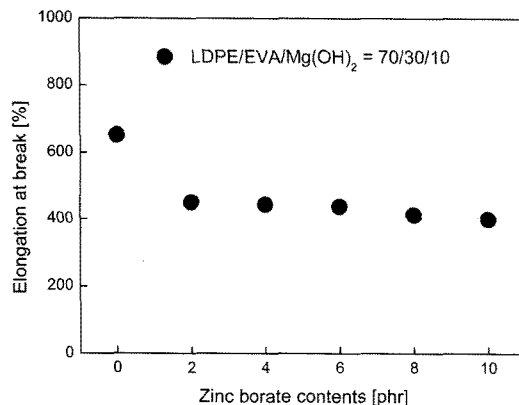


Fig. 9. Elongation at break of the LDPE/EVA blend as a function of the zinc borate concentrations.

4. Conclusions

This study attempts to analyze the changes in the flame retardancy and electrical and mechanical characteristics of the LDPE/EVA blended samples as a function of the mixing ratio and the amounts of magnesium hydroxide and zinc borate added.

In accordance with the synergistic effect between zinc borate and magnesium hydroxide, the addition of zinc borate along with 10phr of magnesium hydroxide to the LDPE/EVA blend having a compounding ratio of 70/30phr was found to improve the properties of the LDPE.

In the analysis of the LDPE/EVA blend depending on the amount of zinc borate added, the specimen to which 6phr of zinc borate was added showed improved flame retardancy, due to the synergistic effect of $Mg(OH)_2$ and zinc borate, without any decrease in the inherent electrical and mechanical characteristics, because only a small amount of zinc borate was added to the LDPE/EVA blend.

Considering that flame retardancy of the LDPE/EVA blend the results for the blend containing 6phr of zinc borate and 10phr of $Mg(OH)_2$ were similar to those of the blend containing 40phr of $Mg(OH)_2$, and in both cases the electrical and mechanical characteristics of the LDPE/EVA blend were remarkably improved by the addition of zinc borate.

Acknowledgements

This work is supported by the Dongguk University Research Fund.

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