Flame Retardancy and Electrical Characteristics of LDPE/EVA Blend Involving $Mg(OH)_2$ and Zinc-borate

Boo Hyung Ryu[a], Gyu Baek Kim, and Sang Ho Jung
Department of Safety Engineering, Dongguk University, Seokjang-dong, Gyeongju-si, Gyeongbuk 780-714, Korea

Youngsuk Cho
Department of Computer Science, Dongguk University, Seokjang-dong, Gyeongju-si, Gyeongbuk 780-714, Korea

[a]E-mail : bhryu@dongguk.ac.kr

(Received December 12 2006, Accepted December 18 2006)

This study shows to blend ethylene vinyl acetate(EVA) and a flame retardant agent, $Mg(OH)_2$, and synergists, zinc borate for improving flame retardancy of low density polyethylene(LDPE). And it studied the property of flame retardancy of LDPE/EVA blend by the amount of addition through LOI and TGA, estimated the electrical characteristics such as volume resistivity and breakdown strength. The flame retardancy of LDPE/EVA blend was much improved in case of adding zinc borate with 6phr degree, and the electrical characteristics were more or less decreased depending on increasing the amount of addition. Zinc borate used for improving the flame retardancy of LDPE/EVA blend let the added amount of a flame retardant agent, $Mg(OH)_2$ limited, and the electrical characteristics decreased extremely by adding a good deal of $Mg(OH)_2$.

Keywords : Electrical characteristics, Flame retardancy, LOI, TGA, Zinc borate

1. INTRODUCTION

Low density polyethylene(LDPE) is widely used as insulation material because of the property of superior insulation, induced electricity, and mechanical pliability, but it emits a lot of heat and smog on fire as organic material. The halogenated flame retardant agents used once for improving flame retardancy appeared to be the superior resistance to flame, but is regulated for the problem of carcinogenic substance like the toxicity of HBr, HCl, corrosion gas, and a halide dioxin, furan etc. Hereby the progressing of the study on substitutes is the improve method of flame retardancy by adding metal hydroxide. However, the addition of metal hydroxide more than 60 wt% results in the drop of matter property such as the electrical and mechanical characteristics of material[1]. To solve this problem, the mechanical property of material has been improved with limiting the added amount of metal hydroxide, at the same time adding synergists, and blending more than 2 high polymers. At the previous study which was measured as the property depending on added magnesium hydroxide of LDPE/EVA blend, when considering the entire property the case adding less than 20 phr $Mg(OH)_2$ at blending LDPE/EVA which have the compounding ratio of 70/30phr showed the excellent property[2].

Accordingly, this study made 10 phr of adding amount of magnesium hydroxide at blending LDPE/EVA which have the compounding ratio of 70/30 phr limit less than 10 phr. It has measured the flame retardancy, the electrical characteristics of LDPE/EVA by adding synergists, zinc borate up to 10 phr.

2. EXPERIMENTAL

2.1 Compounding

This study measured at the ratio of 70/30 phr, LDPE and EVA, changed by the 2 phr of zinc borate after adding 10 phr of $Mg(OH)_2$, and blended with 60 rpm for 5 minutes, 130 ℃ by use of brabender. After preheating synthetic resins for 5 minutes, 130 ℃ by hot plate press, it was processed in the form of sheet with pressing 15 MPa for 5 minutes again.

2.2 Measurements

(1) Limited oxygen index(LOI)

LOI was experimented by KS M ISO 4589-1~3[3]. It was measured with burning sample after keeping oxygen-nitrogen compound gases which have voluntary compound rates in the cylinder container. LOI was given as follow formula on oxygen and nitrogen flux.

$$LOI[\%]=\frac{[O_2]}{[O_2]+[N_2]}\times 100 \quad (1)$$

(2) Thermogravimetric analysis(TGA)

The weight by temperature change of specimens was measured with raising at the speed of 10 ℃/min up to 0~700 ℃ under N_2 gas environment by use of thermogravimetric analyzer(TA instrument com, Model 2950).

(3) Volume resistivity

The volume resistivity was measured by allowing DC 400 V in the indoor with use of electrometer & high resistance meter(Keithley 6517A) or test fixture (Keithley 8009).

(4) Breakdown strength

The AC breakdown strength was measured depending on short-time test method with raising at the speed of 3 kV/sec the allowing AC by using the test device of AC internal pressure(Model YPS-55M) in the trial of the first 100 V, the second 0~50 kV, 60 Hz.

3. RESULTS AND DISCUSSION

3.1 Limited oxygen index(LOI)

Figure 1 appeared depending on the adding the amount of $Mg(OH)_2$ into LOI of LDPE/EVA blend unlike the compounding ratio. In the case of adding less than 30 phr of $Mg(OH)_2$, LDPE/EVA blend with 70/30 phr compounding ratio showed more LOI than pure LDPE, and this is considered as the adding EVA with a little high flame retardancy than pure LDPE.

The LOI of LDPE/EVA blend depending on the added amount of zinc borate appeared on Fig. 2. Compared with specimen adding only 10 phr $Mg(OH)_2$ without adding zinc borate, LOI appeared 18.9~19.3 in case of specimen adding up to 4 phr of zinc borate.

At the specimen of adding more than 6 phr of zinc borate, LOI sharply increased 24.1~24.6, and this showed similar values with the case adding more than 40 phr of $Mg(OH)_2$ on Fig. 1. This result is considered that the flame reatardant effects are improved because of the synergistic effect by $Mg(OH)_2$ and zinc borate with form of char which delayed and controlled burning by addition of zinc borate more than certain amount with the flame retardant effect of $Mg(OH)_2$ in itself[4].

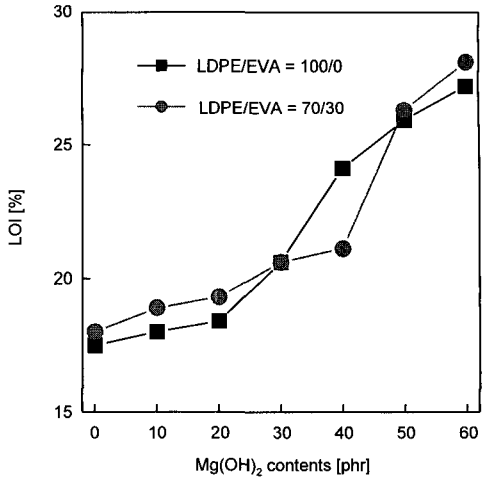

Fig. 1. LOI of LDPE/EVA blends as a function of $Mg(OH)_2$ concentrations.

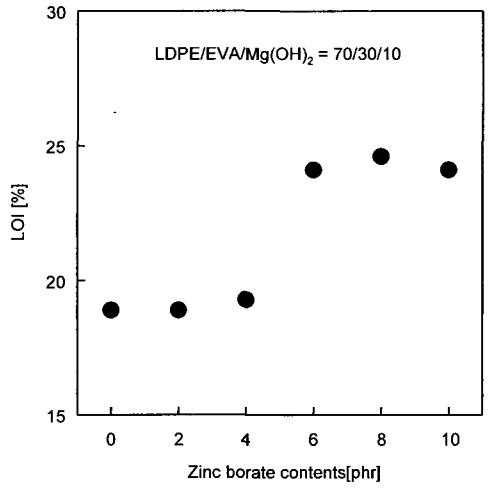

Fig. 2. LOI of LDPE/EVA blends as a function of zinc borate concentrations.

But at the specimen adding more than 10 phr of zinc borate, LOI appeared more or less decreased, and is thought as the raising effects of flame retardancy for zinc borate because of saturation of residues in burning.

3.2 Themogravimetric analysis(TGA)

Figure 3 showed the result of TGA of LDPE/EVA blend by adding $Mg(OH)_2$ and zinc borate. The thermal degradation of LDPE/EVA blend occurs in 3 steps; the first step of 300~360 ℃ happened acetic acid by decomposing vinyl acetate group, the second step of 425~480 ℃ occurred the scission of polyethylene chain, and the third step of more than 480 ℃ was judged as the degradation of residues involving carbon formed during the second step[5].

The case of specimen adding $Mg(OH)_2$ and zinc borate

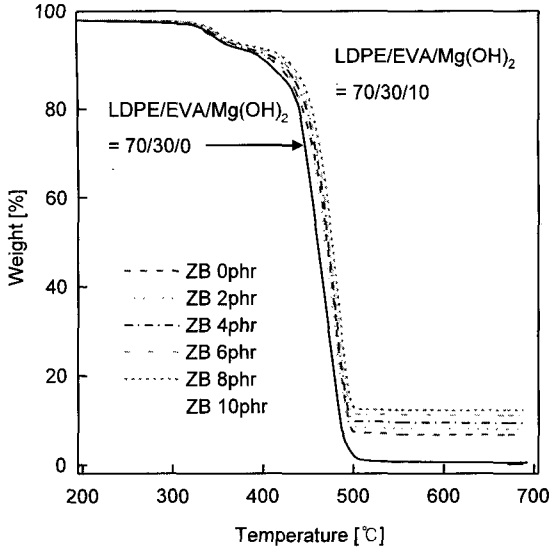

Fig. 3. TG curves of LDPE/EVA blends as a function of zinc borate concentrations.

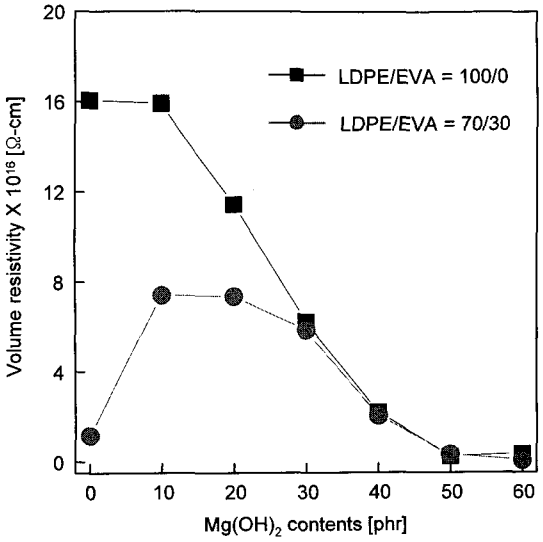

Fig. 4. Volume resistivity of LDPE/EVA blends as a function of $Mg(OH)_2$ concentrations.

showed that it was decomposed at high temperature more than specimen without addition, this can be seen as improving thermal stability of LDPE/EVA blend by addition of $Mg(OH)_2$ and zinc borate.

Viewed in a weight of residues, the specimen without addition were completely decomposed at around 500 ℃, the case of specimen with adding zinc borate increased residue weight more than 10 % depending on added amount of zinc borate against specimen without adding zinc borate appeared 7 %. This is due to the property of pyrolysis for zinc borate increasing the amount residue and promoting the form of char happened in burning[6].

3.3 Volume resistivity

Figure 4 appeared volume resistivity of LDPE/EVA blend adding $Mg(OH)_2$ depending on the compounding ratio. LDPE/EVA blend with 70/30 phr compounding ratio showed less volume resistivity than pure LDPE, this is considered that because EVA contained VA group with polarization.

Figure 5 displayed the volume resistivity depending on the added amount of zinc borate. Due to the low volume resistivity by increase of added volume of zinc borate, this is caused by generation of ionic carrier in the inside of LDPE/EVA blend by $Mg(OH)_2$ and zinc borate added for improving flame retardancy of LDPE/EVA[2].

Comparing specimen adding 6phr of zinc borate and specimen adding 40 phr of $Mg(OH)_2$ with volume resistivity depending on added amount of $Mg(OH)_2$ observed in the previous study[2], the volume resistivity of LDPE/EVA blend by zinc borate addition can have substantially been improved.

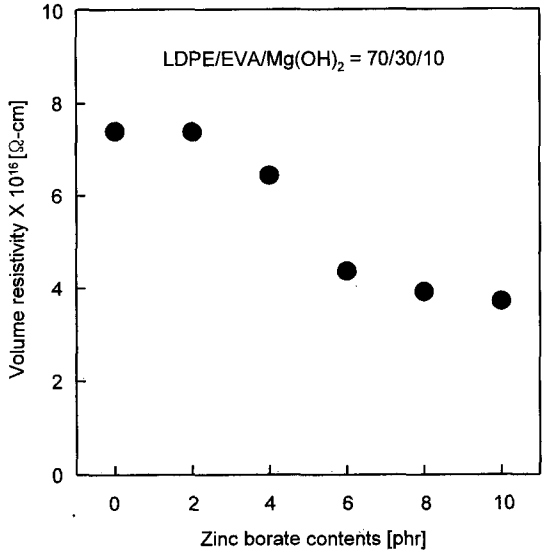

Fig. 5. Volume resistivity of LDPE/EVA blends as a function of zinc borate concentrations.

3.4. Breakdown strength

Figure 6 appeared depending on the adding the amount of $Mg(OH)_2$ into breakdown strength of LDPE/EVA blend unlike the compounding ratio. The case of LDPE/EVA blend with 70/30 phr compounding ratio showed less than pure LDPE, this is considered that because space charge is formed by adding EVA.

In Fig. 7 that showed the breakdown strength that the more increased the added amount of zinc borate is, the more decreased result the breakdown strength displays. This is judged as electron states by colliding electron

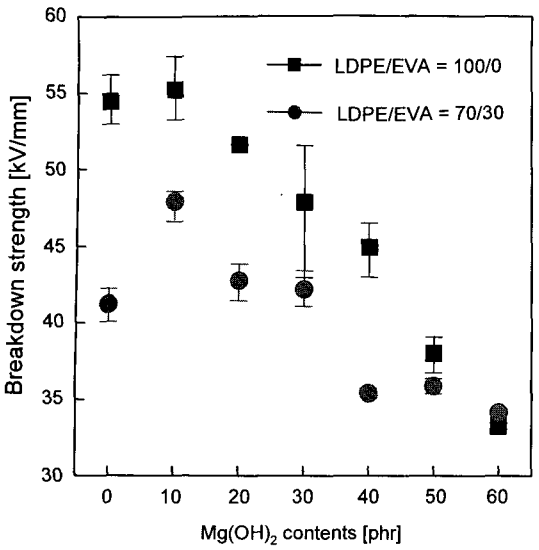

Fig. 6. Breakdown strength of LDPE/EVA blends as a function of $Mg(OH)_2$ concentrations.

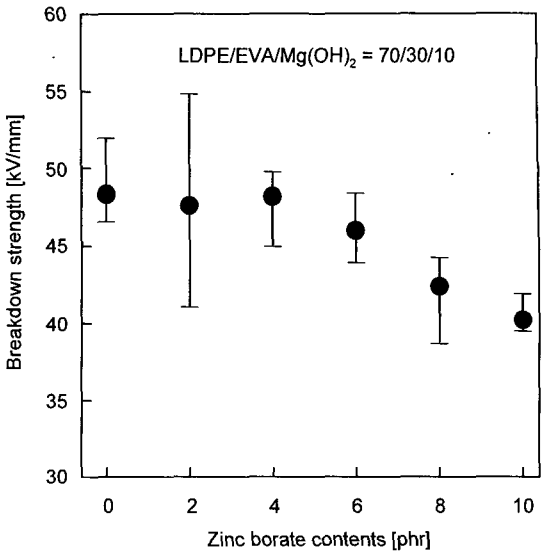

Fig. 7. Breakdown strength of LDPE/EVA blends as a function of zinc borate concentrations.

with ionic carrier of adding $Mg(OH)_2$ and zinc borate[7]. In the case of specimen adding less than zinc borate, it appeared to be similar to breakdown strength without zinc borate, which is due to increase of free volume by adding a small amount of zinc borate

4. CONCLUSION

This study suggests to analyze the change of flame retardancy and electrical characteristics in accordance with adding its synergists, zinc borate with 10 phr of magnesium hydroxide at blending LDPE/EVA which have the compounding ratio of 70/30 phr for improving property of LDPE. As a result of LDPE/EVA blend depending on zinc borate addition, specimen adding 6 phr of zinc borate not only improved flame retardancy due to the synergistic effect for $Mg(OH)_2$ and zinc borate, but also kept without decreasing the inherent electrical characteristics which have LDPE/EVA blend by adding a small amount of zinc borate. Considering that Flame retardancy of LDPE/EVA blend adding 6 phr of zinc borate and 10 phr of $Mg(OH)_2$ is similar to LDPE/EVA blend with 40 phr of $Mg(OH)_2$, electrical characteristics of LDPE/EVA blend by zinc borate addition can have remarkably been improved.

ACKNOWLEDGEMENTS

This work was supported by the research program of Dongguk University.

REFERENCES

[1] R. N. Rothon and P. R. Hornsby, "Flame retardant effects of magnesium hydroxide", Polymer Degradation and Stability, Vol. 54, p. 383, 1996.

[2] S. H. Jung, G. B. Kim, B. H. Ryu, C. Lee, and K. Y. Kim, "Flame retardancy of LDPE/EVA blends containing $Mg(OH)_2$", KOSOS Annual Autumn Conference 2005, p. 379, 2005.

[3] "Plastics-determination of burning behaviour by oxygen index", KS M ISO 4589-1-3, Korean Standards Association, 2002.

[4] Z. Wang, B. Qu, W. Fan, and P. Huang, "Combustion characteristics of halogen-free flame-retarded polyethylene containing magnesium hydroxide and some synergists", Applied Polymer Science, Vol. 81, p. 206, 2001.

[5] Z. Wang, G. Wu, Y. Hu, Y. Ding, K. Hu, and W. Fan, "Thermal degradation of magnesium hydroxide and red phosphrous flame retarded polyethylene composites", Polymer Degradation and Stability, Vol. 77, p. 427, 2002.

[6] S. Bourbigot, M. L. Bras, R. Leeuwendal, K. K. Shen, and D. Schubert, "Recent advances in the use of zinc borates in flame retardancy of EVA", Polymer Degradation and Stability, Vol. 64, p. 419, 1999.

[7] J. Y. Shin, C. H. Lee, and J. W. Hong, "Electrical characteristic of blend with LLDPE/EVA due to mixing ratio", J. of KIEEME(in Korean), Vol. 14, No. 6, p. 525, 2001.