Fire Retardance Mechanism of Magnesium Hydroxide for Ethylene–Ethylacrylate Copolymers

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ABSTRACT
The fire retardance mechanisms of magnesium hydroxide and magnesium oxide for ethylene-ethylacrylate copolymers were studied experimentally, using polyethylene as a reference polymer, utilizing a high radiant furnace, thermogravimetry-differential scanning calorimeter (TG-DSC) and Fourier-transform infrared spectroscopy (FT-IR). The results show that both magnesium compounds have little fire retardance on polyethylene, but have remarkable one on the copolymers. The difference in these fire retardancy is due to the thermal stability of char layer formed on the sample surface, where char formation is due to certain intermolecular and/or intramolecular reactions resulting in cross-linking or aromatization between acrylates and magnesium compounds. A set of IR absorption bands obtained from the heated copolymer sample system indicates formation of double bond or metallic salt, supporting char formation mechanism.

KEYWORDS : non-halogen, fire retardant, magnesium hydroxide,
           ethylene-ethylacrylate, polyethylene, TG-DSC, FT-IR

1. INTRODUCTION

The communication cables play very important role in the modern society through the information exchange. On November 1984, a cable fire, which occurred underground at Setagaya Tokyo, paralyzed the city functions for several days and revealed the weak point of the communication system. When such fire occurs, cable sheath and insulator, which are generally made from organic polymers, may behave as fuels and a great amount of heat and smoke will be released [1]. For example, the amount of heat released from burning polyethylene (PE) and polyvinylchrolide (PVC) used for cable materials is equal to or greater than that from coal (11,200 kcal/kg for PE, 5,370 kcal/kg for PVC, and 5,500 kcal/kg for coal)[2]. In a narrow tunnel such as an underground pass, it is known that fire propagate rapidly [1]. Combustion products from burning PE give simple suffocating gases (CO_2 and lack of the O_2) as well as chemical suffocating gas (CO). PVC and polymers retarded with halogen agent generate not only these suffocating gases but also stimulating gases

(e.g. HCl, HBr, etc.). It is difficult to extinguish and fight against such cable fire because of vigorous flame, heavy smoke and toxic gases in a limited space. Fire products affect not only on lives but also on function of precision instruments such as computer, and telecommunication exchanges due to smoke and corrosive damages. Thus, the cables for information exchange must be retarded by the agents which produces no stimulating gases. Since materials for cable sheath and insulator are made from organic compounds, it is quite hard to reduce the generation of CO, CO_2 and smoke as they are burning. Recently, interest has been shown on metal hydroxides such as $Mg(OH)_2$, $Al(OH)_3$, and etc. as non-harogen fire retardant system for polymers. The endothermic effect due to dehydration is suggested to be the primary retardant mechanism of these metal hydroxide. For example, endothermic reaction (184 kcal/g) of $Mg(OH)_2$ occurs between 340 to 490°C [3]. It is suggested that the chemical reaction between magnesium compound and polymer, and particularly, char layer formation on the surface of the polymer system may be responsible for fire retardancy [4,5]. In order to understand the fire retardant mechanism of $Mg(OH)_2$, we have examined the fire retardant mechanism of copolymer-$Mg(OH)_2$ and copolymer-MgO systems using high radiant furnace, TG-DSC, and FT-IR.
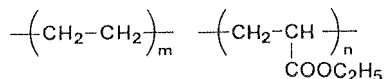
Table 1   Samples used in the experiments.

Amount of EA (wt.%)	Amount of Additives	
	$Mg(OH)_2$ (parts)	MgO (parts)
0 *)	0	0
0 *)	50	0
0 *)	100	0
0 *)	150	0
0 *)	0	100
20	0	0
20	50	0
20	100	0
20	150	0
20	0	100
25	0	0
25	50	0
25	100	0
25	150	0
25	0	100
50	0	0
50	50	0
50	100	0

*)polyethylene

2. EXPERIMENT

Samples

Samples used in this study are polyethylene (PE) as a reference polymer, and ethylene-ethylacrylate copolymers (EEA), and the composition of EEA which is given as,

$$-\left(CH_2-CH_2\right)_m \quad -\left(CH_2-CH\right)_n$$
$$\quad\quad\quad\quad\quad\quad\quad\quad\quad | $$
$$\quad\quad\quad\quad\quad\quad\quad\quad COOC_2H_5$$

Samples with EA percents of 0, 20, 25 and 50% by weight, were used for both high radiant furnace tests and TG-DSC analysis. Molecular weight of polymers used in the experiment are; Number average molecular weight: Mn=840 and Weight average molecular weight: Mw=5250 for PE, and Mn=1510 and Mw=3980 for EEA copolymer, respectively. Magnesium hydroxide, $Mg(OH)_2$, and magnesium oxide, MgO, were added to the base polymers. Table 1 shows the composition of the sample systems. The size of a sample used for high radiant furnace tests was 100mm diameter and 5mm thick.

Apparatus for high radiant furnace tests

An apparatus of the high heat radiation furnace which was designed to simulate the high temperature with low oxygen concentration atmosphere was used in the study. The function and basic design of the furnace, similar to Tewarson's flammability apparatus [6], is outlined in Figure 1. A sample was horizontally located on the sample platform (B), which was connected to an electric balance (A). Quartz tube (C), 700mm high and 170mm diameter, was set to control the oxygen concentration in the tube. Air or mixed gases of N_2/O_2 was supplied at 30 l/min from the bottom of the furnace through the glass beads bed. The combustion gas was sampled at point E and sent to the gas analyzer (Beckman 864 for CO and CO_2, Beckman 755 for O_2) to measure CO, CO_2 and O_2 gas concentrations simultaneously. External radiant heat flux was applied to the sample by using 24 high density infrared heaters (F: General Electric, 9H2MT3-1CL-5S). These heaters were set in four holders and which located in square configuration surrounded the quartz tube in order to give the uniform external radiant heat flux on the sample surface. Radiative heat flux
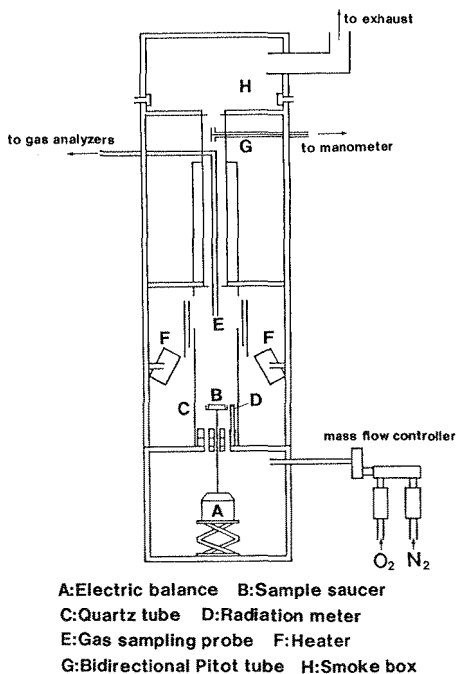
A:Electric balance   B:Sample saucer
C:Quartz tube   D:Radiation meter
E:Gas sampling probe   F:Heater
G:Bidirectional Pitot tube   H:Smoke box

Figure 1
Outline of the high radiant furnace.

applied to the sample was monitored during tests by a radiation meter (D:
Hy-cal Res., C-1301-A). Flow velocity in the duct was measured by a manome-
ter (Shibata Instrument IPS-3-5S) by monitoring the differential pressure,
using a bidirectional Pitot tube (G). Smoke concentration in the smoke box
(H) was also measured optically. Temperatures were measured, using K-type
thermocouples, at several locations. Char formation behavior of the sample
was observed visually and recorded by a video system. In the experiments,
external radiant heat flux of 4 W/cm^2 with O_2 concentrations of 10 % (non-
flaming condition) or 21 % (air) by volume were used.

TG-DSC Analysis

TG-DSC analysis, (using Rigaku Instrument, TG8110), were also per-
formed on the samples. A heating rate of 10°C/min in air or N_2 atmosphere
condition was used in the experiments.

FT-IR Measurement

The sample used for the FT-IR measurement were EEA, EEA-Mg(OH)$_2$, and
PE-Mg(OH)$_2$ (both systems included with 3 parts of Mg(OH)$_2$) after they were
altered to film. These samples were heated at 300 and 400°C respectively
under the ambient air, and absorption of IR were measured (Nihon-Denshi,
JIR-3510). As a reference, the film sample without heating, was also meas-
ured at 300 and 400°C.

3. RESULTS AND DISCUSSION
Ignition Time

Figure 2 shows the ignition time of samples, applied external radiant
heat flux of 4 W/cm^2 in air, as a function of amount of Mg(OH)$_2$ and MgO
additives. From this figure it is clear that as the amounts of EA and
Mg(OH)$_2$ increased, time to ignition increased rapidly. Addition of MgO,
however, appears to have little effect of fire retardancy, irrespective of
amount of EA. The increase in the time to ignition in the Mg(OH)$_2$-polymer
system, as amounts of EA and Mg(OH)$_2$ are increased.

When Mg(OH)$_2$ or MgO was added to the polymers, melting and boiling
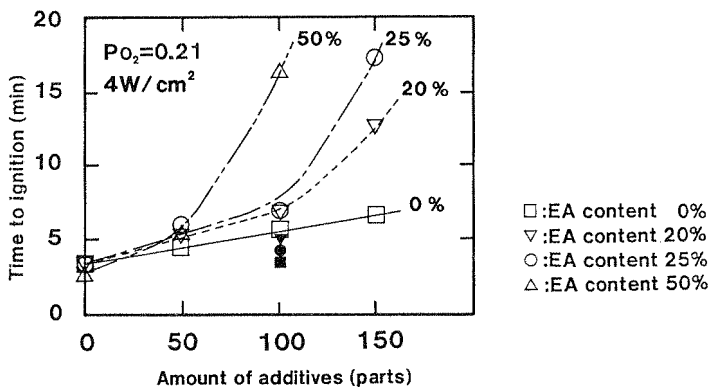behaviors were not observed for heating period. These samples formed char

Figure 2
Time to ignition as a function of amount of additives at 4W/cm^2
of external heat flux, open symbols : Mg(OH)$_2$, and dark symbols :
MgO.

layer on its surface. Especially, the samples, which showed remarkable delay in the time to ignition, formed the char layer with fine foams inside before ignition occurred.

Weight Loss

Figure 3 shows the typical time variation of weight loss rate of $Mg(OH)_2$ and MgO-polymer systems as a function of amount of additives under non-flaming condition. It can be noted that weight loss rate decreases by adding MgO and $Mg(OH)_2$ to polymer system. The increase in $Mg(OH)_2$ amount decreases the peak value of weight loss rate and increases the time to peak value of the weight loss rate curve.

Figure 4 shows the typical time variation of weight loss rate of $Mg(OH)_2$-polymer systems as a function of EA amount under non-flaming condition. Although the peak value of weight loss rate does not change with amount of EA, the time to peak value increases with increase of EA amount.

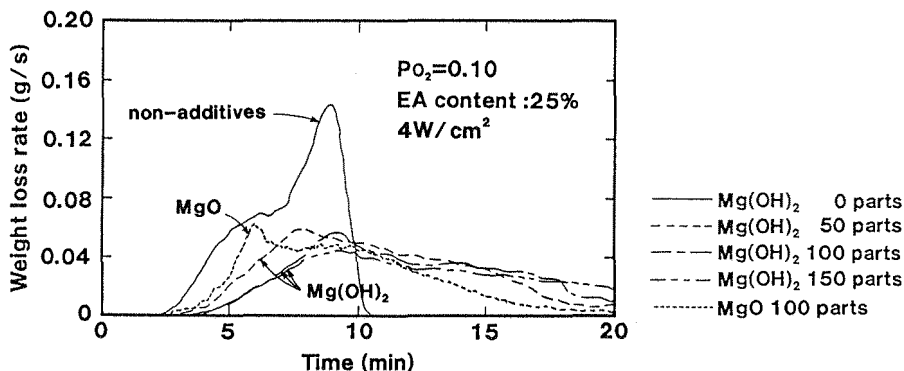Figure 3
Effect of amount of EA on weight loss rate as a function of time at 4W/cm² of external heat flux under non-flaming condition.
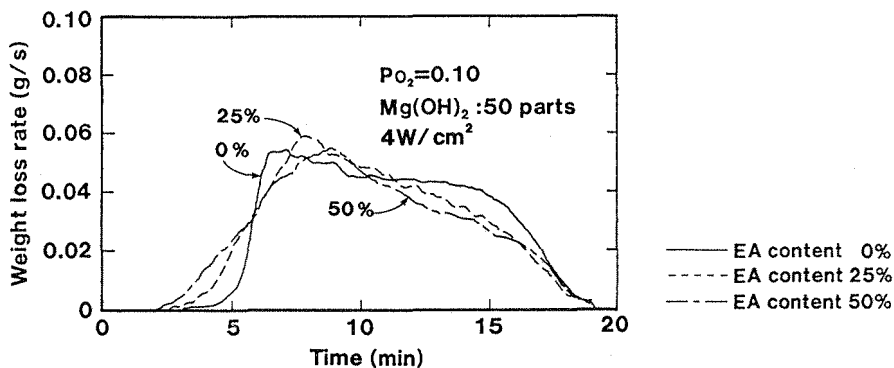
Figure 4
Effect of amount of $Mg(OH)_2$ on weight loss rate as a function of time at 4W/cm² of external heat flux under non-flaming condition.

The previous discussion on the difference in the time to ignition suggest that the fire growth becomes slower with increase in amounts of EA and Mg(OH)$_2$. The changes in the weight loss rate with variation of the amounts of EA, Mg(OH)$_2$, and MgO relate to char layer formation on the surface as well as indepth interactions between additives and polymers. The fire retardancy, i.e. time to ignition here, is classified as effective (long) or weak (short) depending on whether the char layer has fine independent foams or not.

TG-DSC Analysis

Derivative thermogravimetry (DTG) curves, i.e., weight loss rate of each sample were calculated from TG. Figure 5(a) shows DTG curves of non-additive polymer systems under N$_2$ atmosphere. DTG curves obtained from PE-non-additives and EEA-non-additives systems have clear single peak, respectively.

Figure 5(b) shows DTG curves of PE-Mg(OH)$_2$ and EEA-Mg(OH)$_2$ (both systems have 150 parts of Mg(OH)$_2$) under N$_2$ atmosphere illustrating two peaks respectively. Comparing the figures 5(a) and 5(b) and considering that the decomposition temperature range of Mg(OH)$_2$ is 350-400°C, peaks in lower temperature region for both systems are assigned as the reaction which relate mainly to the decomposition of Mg(OH)$_2$ in each system. It should be noted that the weight loss starts around 380°C for both systems indicating little higher temperature than the decomposition of Mg(OH)$_2$. Further, the temperature difference of about 10°C between two peaks in the lower temperature region for PE-Mg(OH)$_2$ and EEA-Mg(OH)$_2$ systems is observed. The temperature shifts to higher region in these weight loss rates suggest that Mg(OH)$_2$ in the polymer system make some reaction with polymer indicating the physical and/or chemical interactions. The peaks in higher temperature region of around 450°C are also observed in no-additives systems, as shown Figure 5(a), therefore, those peaks are assigned to the weight loss due to the decomposition of main polymer chains.

Figure 5(c) shows DTG curves of PE-Mg(OH)$_2$ and EEA-Mg(OH)$_2$ systems (both have 150 parts of Mg(OH)$_2$) under air atmosphere. It is very significant that EEA-Mg(OH)$_2$ system shows only single peak around 410°C and second peak around 460°C in Figure 5(b) is not observed. This single peak in weight loss rate corresponds to the evolution of heat which is estimated by DSC data of another experiment. Comparing Figures 5(b) and 5(c), which implies whether the oxygen exist in the atmosphere or not, it indicates the presence of interactions between Mg(OH)$_2$ and polymer under oxygen. Remembering that the increases of EA amounts and Mg(OH)$_2$ increased the time to ignition, it is expected that interaction between Mg(OH)$_2$ and polymer with presence of oxygen relates to the char layer formation.

FT-IR Measurement

Figure 6(a) and 6(b) show the results of FT-IR measurements, which illustrate the spectrum of EEA copolymer with 3 parts of Mg(OH)$_2$: (a) without thermal treatments and (b) heated at 400°C under air atmosphere, respectively. The absorption bands of 470 cm^{-1} and 3695 cm^{-1} observed in Figure 6(a) indicate the presence of Mg(OH)$_2$. Figure 6(b) shows that these two bands disappear when the system is heated at 400°C. The sample heated at 400°C shows the absorption band around 1600 cm^{-1}. This may due to the formation of double bonds in the main chain or to the formation of metallic salt on the surface of crystallized MgO.
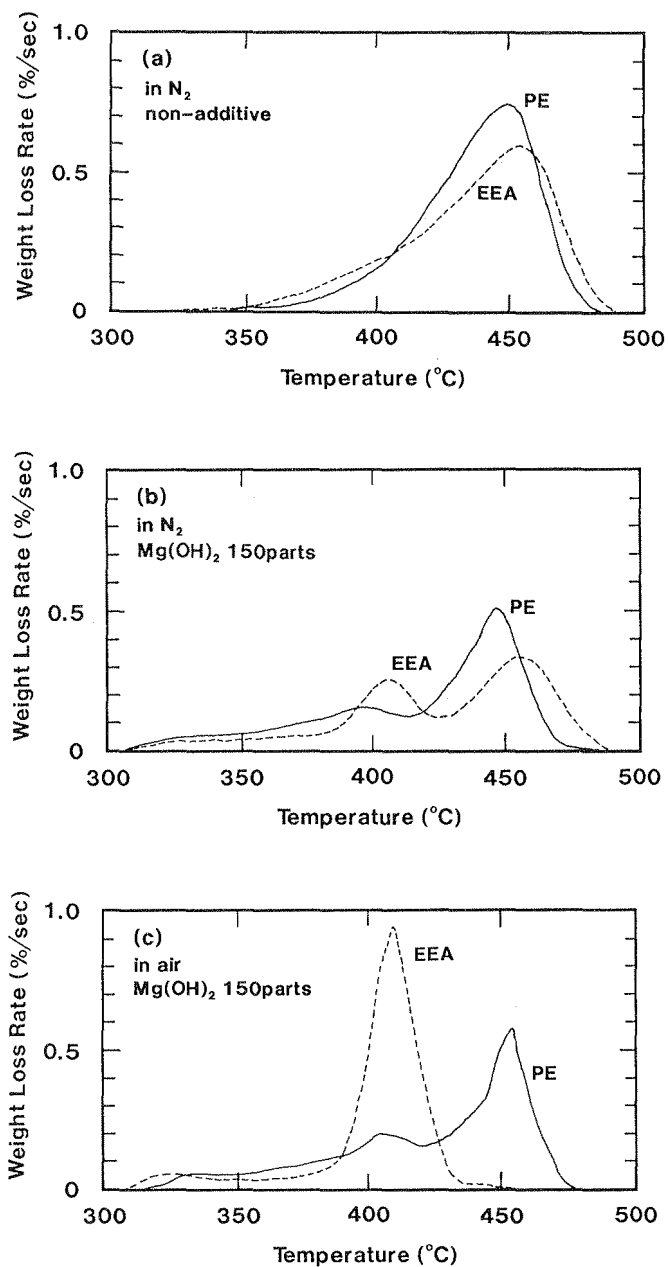
Figure 5
Comparisons of DTG curves between PE system and EEA system,
(a) polymer-non-additives systems in N_2 atmosphere,
(b) polymer-Mg(OH)$_2$ (150parts) systems in N_2 atmosphere, and
(c) polymer-Mg(OH)$_2$ (150parts) systems in air atmosphere.
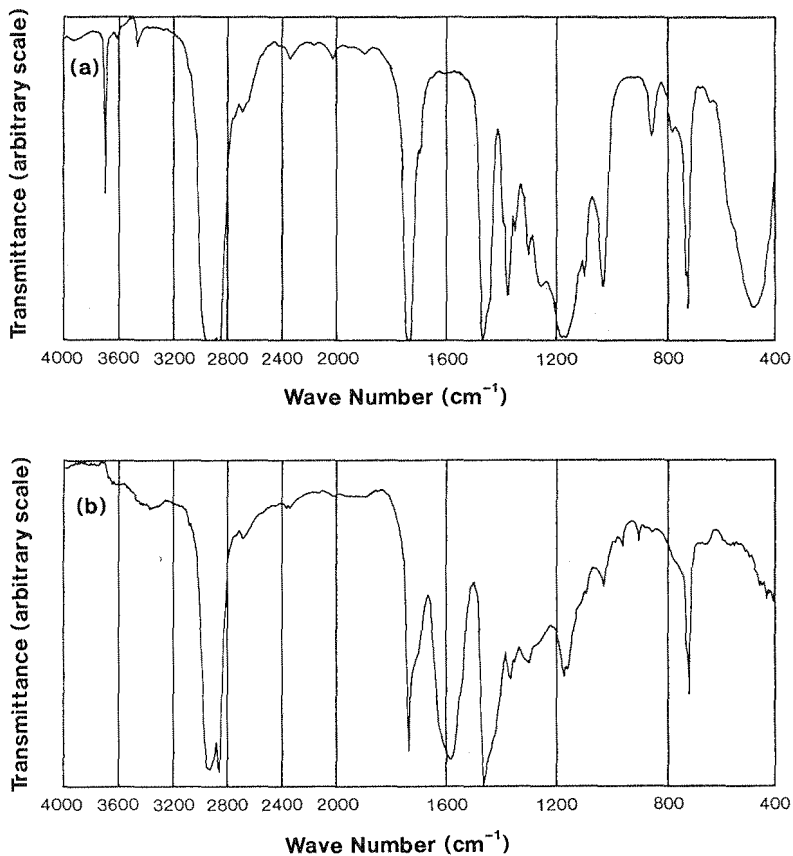
Figure 6
Absorption bands of EEA-Mg(OH)$_2$ (3 parts) system,
(a) without thermal treatment, and (b) heated at 400°C.

Fire Retardance Mechanism
    From the above results and discussion, the catalysis models of Mg(OH)$_2$
and MgO are proposed as follows:

(1) The catalysis of MgO, produced from dehydration of Mg(OH)$_2$, enhances
the subtraction of hydrogen form main chain by radicals.

$$\underset{\underset{COOC_2H_5}{|}}{-CH_2-CH-} \ + \ R\cdot \ \longrightarrow \ \underset{\underset{COOC_2H_5}{|}}{-CH_2-\overset{\cdot}{C}-} \ + \ RH \ \longrightarrow \ \underset{\underset{COOC_2H_5}{|}}{-CH=C-} \ + \ H\cdot$$
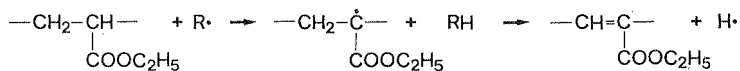
Such double bond formation leads cross-linking or aromatization.

(2) On the crystal surface of MgO (or Mg(OH)$_2$), the intermediates, as follows, are formed, which leads cross-linking and/or aromatization promoted with intermolecular and/or intramolecular.

$$
\begin{array}{c}
-CH_2-CH- \\
| \\
C=O \\
| \\
O \\
| \\
Mg \\
| \\
O \\
| \\
C=O \\
| \\
-CH_2-CH-
\end{array}
\qquad \text{or} \qquad
\begin{array}{c}
-CH_2-CH-CH_2-CH- \\
| \qquad\qquad\quad | \\
O=C \qquad\quad C=O \\
\diagdown \qquad\; \diagup \\
O \qquad O \\
\diagdown \diagup \\
Mg
\end{array}
$$

4. SUMMARY

The increases of amounts of EA and Mg(OH)$_2$ in the system decrease the rate of weight loss and increase the time to ignition, both of which are useful for fire retardancy.

The char layer formed on the surface of the system plays important role for fire retardancy. The char layer formation relates to interactions between polymer and Mg(OH)$_2$ or MgO under the presence of oxygen atmosphere.

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