Effects of Additives on Thermal Decompositions of Carbon Black/High Density Polyethylene Compounds

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***Abstract*—**In the present work, the effects of additives, including contents of the added antioxidants and type of the selected metallic stearates (either calcium stearate (CaSt) or zinc stearate (ZnSt)), on the thermal stabilities of carbon black (CB)/high density polyethylene (HDPE) compounds were studied. The results showed that the AO contents played a key role in the thermal stabilities of the CB/HDPE compounds — the higher the AO content, the higher the thermal stabilities. Although the CaSt-containing compounds were slightly superior to those with ZnSt in terms of the thermal stabilities, the remaining solid residue of CaSt after heated to the temperature of 600 °C (mainly calcium carbonate ($CaCO_3$) as characterized by the X-ray diffraction (XRD) technique) seemed to catalyze the decomposition of CB in the HDPE-based compounds. Hence, the quantification of CB in the CaSt-containing compounds with a muffle furnace gave an inaccurate CB content — much lower than actual value. However, this phenomenon was negligible in the ZnSt-containing system.

***Keywords*—**Antioxidant, Stearate, Carbon black, Polyethylene.

I. INTRODUCTION

VARIOUS types of additives have been incorporated into the polymeric base resin in order to provide the tailor-made characteristics. Nevertheless, one of the key basic properties of the polymeric materials to properly serve their diverse fields of applications is an acceptable stability at every stage of its life cycle, beginning from during processing to its end-use. Therefore, the suitable stabilization systems are required.

Generally, a combination of hindered phenols with their co-stabilizations like secondary phosphite antioxidants has been used to prevent or inhibit the degradation of the polymeric materials, subsequently leading to the deteriorated properties of the final products [1]-[3]. The co-synergism of the primary and the secondary antioxidants provides processing and long-term stabilizations to the polymer resin via interfering with the oxidation reaction [1]. This co-synergistic effect can be further enhanced with the addition of an acid scavenger, like metallic stearates [1]. In addition to the neutralization of the catalyst residues and the minimization of equipment corrosion, an acid scavenger can act as a slip agent by either reducing shear or decreasing sticking of the molten polymer to the inner wall of the equipment during processing [1]. It is also known that the added acid scavenger is capable of preserving the polymer by preventing acid build-up during processing, or compounding, at high temperature by scavenging the generated acidic species [1], [4].

Regardless of the stabilizing additives, another ingredient generally found in the polymer formulation is pigment. CB, a black powder with extreme fineness, is used in the polymeric compound not only for the coloration but also for various purposes, including enhancing the thermo-oxidative stability [3], improving the ultraviolet (UV) stability [5], providing the weather resistance during the end-use [6], and modifying the mechanical properties [5], [6]. Nevertheless, in the presence of various kinds of additives in the studied system, the additive-additive interaction possibly occurred, sometimes resulting in some undesired effects [7].

The objectives of the present work are: (1) to investigate the effects of the AO contents and the type and amount of the incorporated metallic stearates on the thermal decomposition behavior of the CB/HDPE compounds and; (2) to observe any possible interactions among the additives during the thermal decomposition for a better design of the additive package used for stabilizing the CB/HDPE compounds.

II. EXPERIMENTAL

A. Materials and Chemicals

HDPE produced by Thai Polyethylene Co., Ltd. was used as a polymeric matrix in the compounds. CB was purchased from Birla Carbon. Primary and secondary AOs were supplied by Ciba. Two types of the studied metallic stearates included CaSt (Baerlocher) and ZnSt (Baerlocher).

B. Preparations of CB/HDPE Compounds

The CB/HDPE compounds were prepared at the CB content of 2.25 wt.% by using an intermeshing, co-rotating twin screw extruder (JSW, TEX 30α) with a length-to-diameter (L/D) ratio of 42. Table I shows the formulations of the CB/HDPE compounds used in the present study.

TABLE I
FORMULATIONS OF CB/HDPE COMPOUNDS AT DIFFERENT AO CONTENTS WITH DIFFERENT TYPE OF METALLIC STEARATES

CB/HDPE Compounds	Content (wt.%)			
	Primary AO	Secondary AO	CaSt	ZnSt
1/3	0.20	0.10	0.20	0.00
2/3	0.25	0.15	0.20	0.00
3/3	0.25	0.15	0.00	0.20

C. Analytical Methods and Measurements

Thermal stabilities of the prepared CB/HDPE compounds were analyzed using a thermogravimetric analyzer (Mettler-Toledo, TGA/SDTA 821e) in the temperature ranging from the room temperature to 1000°C under nitrogen (N_2) atmosphere

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at a gas flow rate of 60 ml·min^{-1} at three different heating rates (10, 15, and 20°C·min^{-1}). The thermal decomposition kinetics was calculated based on the Arrhenius equation [8], [9]:

$$\frac{d\alpha}{dt} = \beta\frac{d\alpha}{dT} = Ae^{-\frac{E_a}{RT}}(1-\alpha)^n \qquad (1)$$

where t is time (min), β is a heating rate (°C·min^{-1}), T is an absolute temperature (K), A is a pre-exponential factor (min^{-1}), E_a is an activation energy of the degradation reaction (J·mol^{-1}), R is a gas constant (8.314 J·mol^{-1}·K^{-1}), n is a reaction order, and α, a conversion or a decomposed fraction, is defined as:

$$\alpha = \frac{M_0 - M}{M_0 - M_f} \qquad (2)$$

where M_0 is an initial weight, M is an actual weight at the temperature T, and M_f is a final weight of the test sample at which the weight loss is almost steady.

According to the Kissinger method [8], the temperature T_{max} at which d(dα/dt) is equal to zero was taken into consideration. Equation (1) was differentiated with respect to time t and the expression was set to zero, giving the following equation:

$$\log\left(\frac{\beta}{T_{max}^2}\right) = \{\ln\left(\frac{AR}{E}\right) + \ln\left[n(\alpha - \alpha_{max})^{n-1}\right]\} - \frac{E}{RT_{max}} \qquad (3)$$

Based on (3), the slope of the line in the plot of $\ln(\beta/T_{max}^2)$ against $1/T_{max}$ gave (-E_a/R) while A was calculated from the intercept [ln(AR/E)].

The TGA data was also used for the lifetime prediction at the weight loss percentage of 5, or at α equal to 0.05 [9], by using the following equations:

if n ≠ 1: $$t_f = \frac{(1-0.95^{1-n})}{A(1-n)}exp\frac{E_a}{RT} \qquad (4)$$

if n = 1: $$t_f = \frac{0.0513}{A}exp\frac{E_a}{RT} \qquad (5)$$

where t_f is the predicted lifetime and n is calculated from the symmetrical index of a derivative thermogravimetric (DTG) peak on the basis of the Kissinger method [9]:

$$n = 1.88\frac{\left|\frac{d^2\alpha}{dt^2}\right|_L}{\left|\frac{d^2\alpha}{dt^2}\right|_R} \qquad (6)$$

where the indices L and R are the left and right peak (d$^2\alpha$/dt^2) values on the second derivative thermogravimetric (DDTG) curve of the thermal decomposition process.

Regardless of the TGA analysis under the thermal gradient conditions, the isothermal study was also carried out. Briefly, the test sample was heated from the room temperature to the desired temperature (100, 200, and 600°C) at the heating rate of 10°C·min^{-1} before being held at the desired temperature under N$_2$ atmosphere at a gas flow rate of 60 ml·min^{-1}for 700 min.

The contents of CB in the HDPE-based compounds were analyzed using a muffle furnace. About 1 g of the test sample was put into a crucible before subjected to the CB content analysis in the muffle furnace at the temperature of about 600°C at three different retention times (3, 4, and 5 min). After cooling to the room temperature in a desiccator, the crucible containing the remaining residue, which should be mainly CB, was weighed. The CB content percentage was an average of three independent experiments.

To characterize the solid residues of CaSt and ZnSt, about 10 g of CaSt or ZnSt were put into a crucible and then kept in a muffle furnace at the temperature of about 600°C for 5 min. After cooling to the room temperature in the desiccator, the remaining solid residues were collected and ground to fine powders with a mortar and pestle. The ground sample was pressed into the sample holder before being analyzed by an X-ray diffractometer (PANalytical, X'Pert PRO) operated at a step angle of 0.02° with count time of 0.5 s using CuK$_\alpha$ as an X-ray source. The XRD analysis was carried out at National Metal and Materials Technology Center (MTEC), National Science and Technology Development Agency (NSTDA).

III. RESULTS & DISCUSSION

The present study focused on the two main issues, including (1) the effects of the incorporated additives (the AO contents and/or the type and amount of the selected acid scavenger — metallic stearates) on the thermal stabilities of the CB/HDPE compounds, and (2) the additive-additive interactions and their effects on the thermal decomposition of CB in the investigated HDPE-based compounds.
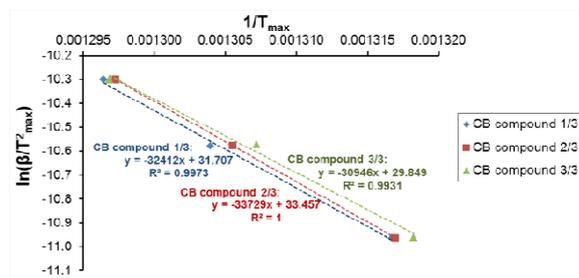

Fig. 1 Kissinger plots of CB/HDPE compounds at different AO contents with different type of metallic stearates under N$_2$ atmosphere

A. Effects of Additives on Thermal Stabilities of CB/HDPE Compounds

To study the thermal stabilities of the formulated CB/HDPE compounds in more details, the Kissinger method was applied. The thermal degradation kinetic parameters were calculated based on the TGA data obtained from several runs operated at different heating rates, β. From the TGA thermograms (data not shown), although all CB/HDPE compounds exhibited only one significant weight loss step at the temperature of about 450°C which should be attributable to the decomposition of the HDPE matrix, the degradation temperature was found to slightly increased with increasing the heating rate, β. From the Kissinger plot of $\ln(\beta/T_{max}^2)$ *vs* $1/T_{max}$ (see Fig. 1), an apparent activation energy, E_a, of CB compounds 1/3, 2/3, and 3/3 was calculated to be 269.5, 280.4, and 257.3 kJ·mol^{-1}, respectively, with a pre-exponential factor A of about 1.9×10^{18}, 1.1×10^{19}, and 2.8×10^{17} min^{-1}, respectively. Therefore, from the thermal

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decomposition kinetic parameters, CB compound 2/3 should have the highest thermal stability among the three developed CB/HDPE compounds. This should be mostly likely due to the synergistic effect between the high enough amount of the AOs and the properly-selected type of the metallic stearate (CaSt) for stabilizing the system.

B. Lifetime Predictions

With the use of (4) in a combination with (6), the lifetimes of the studied three CB/HDPE compounds were theoretically calculated based on the kinetic parameters at the weight loss percentage of 5, or at α equal to 0.05 [9]. Fig. 2 shows the predicted lifetimes of the three CB/HDPE compounds as a function of service temperature. It was obvious that, although the predicted lifetimes of all CB/HDPE compounds decreased with increasing the service temperature, CB compound 2/3 seemed to possess the longest lifetime among the developed formulations.
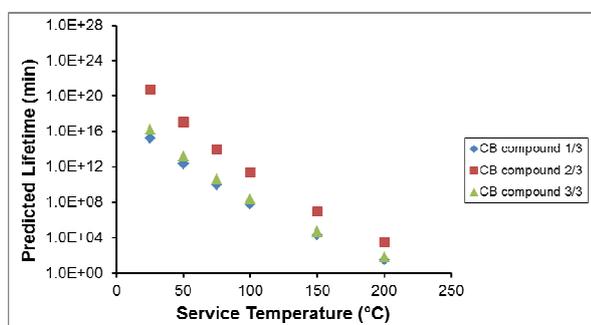

Fig. 2 Predicted lifetimes of CB/HDPE compounds as a function of service temperature at different AO contents with different type of metallic stearates under N_2 atmosphere

The results should be explained in that, when the same type of the metallic stearate was used (CB compound 1/3 *vs* 2/3), higher AO contents should provide a higher thermal stability to the resulting compound. On the other hand, at the same AO contents, a difference in the thermal stabilities between CB compound 2/3 and 3/3 should be caused by the incorporated metallic stearates — either CaSt or ZnSt. Compared between the thermal decomposition of these two metallic stearates, it was observed that CaSt began to degrade at the temperature of about 400°C which was found to be higher than that of ZnSt (started at the temperature of about 300 °C) (data not shown). As a result, a higher thermal stability of CaSt should retard the thermal decomposition of the CB/HDPE compound.

Regardless of the lifetime prediction, the isothermal TGA analysis was also carried out under N_2 atmosphere in order to preliminarily study the thermal decomposition behaviors of the CB/HDPE compounds at different temperatures. Table II shows the isothermal TGA results in terms of the remaining weight percentages after being held at 100, 200, and 600°C for 700 min of the three formulated CB/HDPE compounds.

At the low temperatures (100 and 200°C), it seemed that all CB/HDPE compounds showed comparable thermal stabilities due to their insignificant weight changes throughout the whole experiment, probably, because the 700 min-observation time

was too short to identify any differences in the thermal stabilities among the three formulated compounds. However, when the temperature was increased to 600°C, CB compound 3/3 was found to possess the highest thermal stability because of its highest remaining weight percentage among the three CB/HDPE compounds (see Table II).

TABLE II
REMAINING WEIGHT PERCENTAGES OF CB/HDPE COMPOUNDS AT DIFFERENT AO CONTENTS WITH DIFFERENT TYPE OF METALLIC STEARATES UNDER ISOTHERMAL CONDITIONS AT 100, 200, AND 600°C FOR 700 MIN

CB/HDPE Compounds	Remaining Weight (%) at 700 min		
	100 °C	200 °C	600 °C
1/3	100	100	17
2/3	100	100	17
3/3	100	100	28

From the results of the isothermal TGA analysis, a lower thermal stability of the CaSt-containing CB/HDPE compound at the temperature of 600 °C was hypothesized to be possibly due to the reaction involving the remaining components in the compound at that temperature (the CaSt residue and CB) since the HDPE polymeric matrix should completely decomposed at 600°C. This phenomenon was also observed during the CB content analysis which was generally done at the temperature of about 600°C (see section III-C).

C. Effects of Additives on Thermal Decomposition of CB

One of the easiest methods to determine the amount of the incorporated CB in polyolefin materials, like HDPE, for the purpose of either product quality assurance or product quality control is by heating the CB-containing sample in a 600°C muffle furnace [10]. In the present work, all studied CB/HDPE compounds were subjected to the CB content analysis at three different residence times (3, 4, and 5 min). As shown in Fig. 3, the residual contents of the CaSt-containing system were found to be lower than those of the ZnSt-containing system and tended to rapidly decrease with increasing the residence time from 3 min to 5 min. In addition, it was further observed that CB compound 1/3, which had the lowest AO contents among the CaSt-containing formulations, exhibited the fastest thermal decomposition process due to their lowest residual content at any investigated residence time.
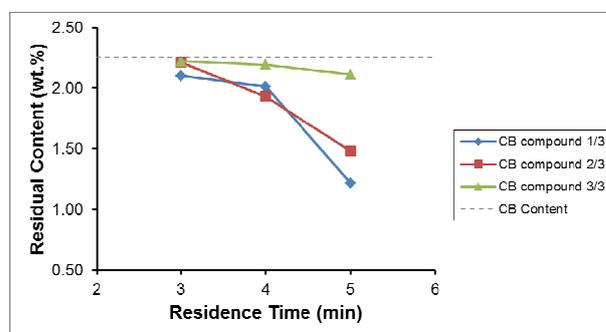

Fig. 3 Residual contents at 600°C of CB/HDPE compounds at different AO contents with different type of metallic stearates as a function of residence time (Dash line indicated CB content of 2.25 wt.%)

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As mentioned above, one major difference in the studied compound formulations at the same AO content was the type of the added metallic stearates (CaSt or ZnSt). Hence, it was hypothesized that a faster thermal decomposition at 600°C of the CaSt-containing system should be probably mainly caused by the reaction involving CB and the remaining solid residue of CaSt while the ZnSt residue should not strongly affect the thermal decomposition of CB.
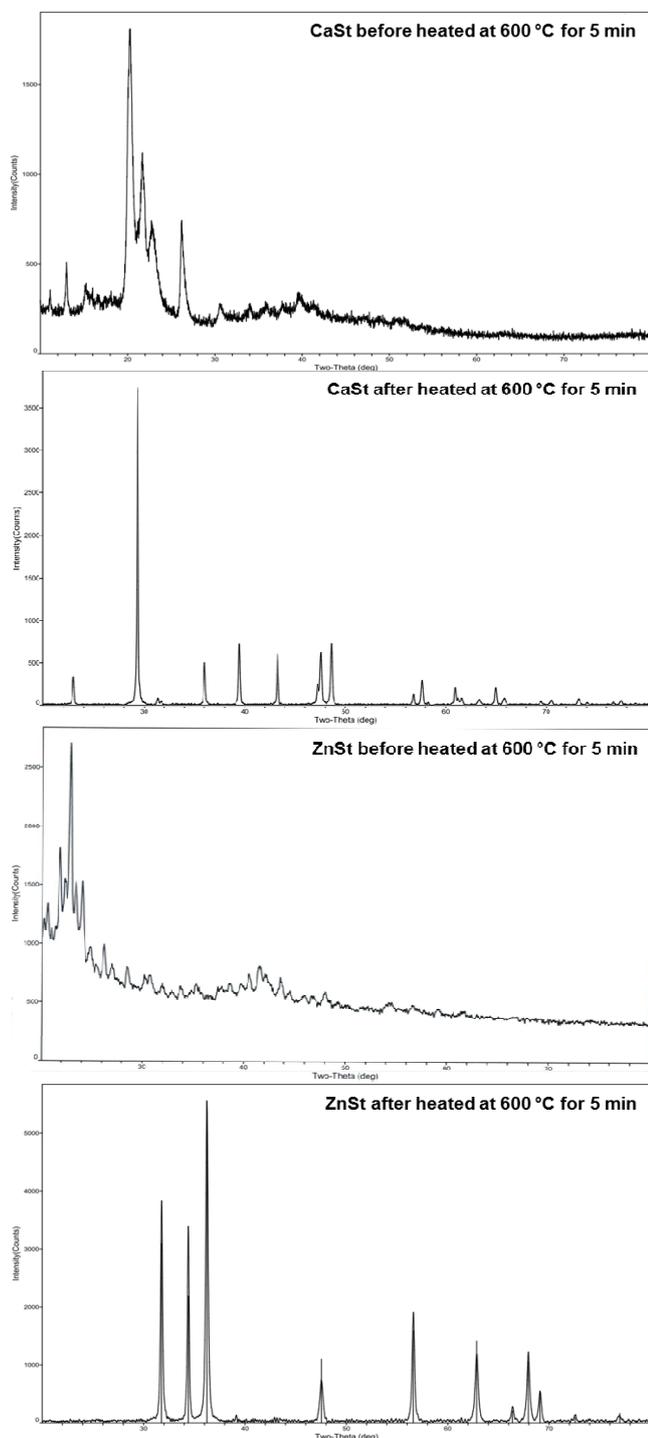

Fig. 4 XRD patterns of CaSt and ZnSt before and after heated at 600°C in muffle furnace for 5 min

To prove the above-mentioned hypothesis, CaSt and ZnSt were analyzed both before and after heated in a muffle furnace at the temperature of about 600°C for 5 min with the use of the XRD technique. As shown in Fig. 4, it was obvious that the XRD patterns of CaSt and ZnSt significantly changed after heated in a 600°C muffle furnace. From the characteristic diffraction peak patterns, the solid residues of CaSt and ZnSt remaining at 600°C were identified as $CaCO_3$ with the calcite crystalline structure and zinc oxide (ZnO) with the hexagonal wurtzite structure, respectively [11], [12]. Our finding agrees well with the decomposition pattern of the metallic stearate, as reported in the literature [8].

One of the possible causes of the CB loss during the CB content analysis should be the combustion of CB itself. It had been reported that $CaCO_3$ could act as a catalyst in the carbon gasification via a two-step mechanism [13]. This phenomenon became more dominant when $CaCO_3$ transformed into calcium oxide (CaO). According to the literature [14], [15], CaO was capable of catalyzing the oxidation reaction and/or combustion of carbonaceous materials, like CB and soot, more effectively than ZnO. Therefore, the results implied that the incorporated additive affected not only the thermal decomposition behavior of the polyolefin-based compounds but their decomposed solid residues also interacted with other type of additives in the system, subsequently resulting in a catalytic decomposition reaction involving both of them.

IV. CONCLUSIONS

Although the incorporation of various kinds of additives into the polymeric base resin was able to provide the tailor-made characteristics to the resulting compounds to suit their diverse applications, the applied additive package should be properly selected to minimize the additive-additive interaction, thus obtaining an acceptable stability at every stage of their life cycles. The results of this present study showed that the thermal stabilities of the formulated CB/HDPE compounds directly depended on the amount of the added AO contents as well as the type and amount of the selected acid scavenger. Although the use of CaSt at an appropriate amount of the AOs acted as an effective stabilizing system for the CB/HDPE compound at the low temperature, the remaining CaSt residue after its decomposition was able to catalyze the oxidation and/or gasification of CB — another key component in the formulated compound. On the contrary, the contradicted result was observed for the ZnSt-containing system. At the low temperatures, ZnSt provide a slightly lower thermal stability to the HDPE-based compound but the ZnSt residue left after its decomposition at the high temperature (600°C) exhibited a much lower catalyzing effect on the CB decomposition.

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