Thermal Decomposition Kinetic of CaCO₃ Filled Recycled PET/PP Blend

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Abstract— *An environmental friendly thermoplastic of recycle polyethylene terephthalate (RPET) and recycle polypropylene (RPP) blend filled with calcium carbonate (CaCO₃) was prepared. Cockleshell-derived CaCO₃ (CS) was ground and prepared for using as renewable filler in the recycled blends. The effects of filler type and content on thermal stability, mechanical performance and flame retardant properties of the blends were investigated. The iso-conversion of the Flynn-Wall-Ozawa was developed by the second order polynomial function for thermal oxidative degradation of the blends while peak derivative temperature from the Kissinger method was able to verify the mechanism of degradation in these blends. The results indicated that both CS and commercial grade CaCO₃ improved thermal stability and enhanced the stiffness as well as impact performance of the blends. However, flame retardant could not achieve when low filler content was present in the RPET/RPP blends.*

Keywords— **Thermal decomposition kinetic, polyethylene terephthalate, recycled blend, CaCO₃, cockleshell**

1. INTRODUCTION

Polyethylene terephthalate (PET) is an engineering thermoplastic, which has been widely used as packaging for beverage, food and other liquids, which constitutes a large portion of postconsumer wastes. In the present day, the volume of the PET bottle products greatly increased. Therefore, recycling of PET bottle is one of the solutions to prevent environmental problems due to lack of landfill space. Blending of recycled waste PET drinking bottles (RPET) and its polypropylene based cap (RPP) is a viable solution for reducing the cost of separation of these components. Blending of RPET and RPP to yield a tough material is possible with proper compatibilization. However, this would lead to a reduction in modulus as well as strength. The incorporation of calcium carbonate (CaCO₃), which is a kind of mineral that is non-toxic and colorless, as filler for RPET/RPP blends in order to improve its rigidity, dimensional stability and thermal degradation resistance. It is especially important to ensure high thermal degradation resistance of recycled materials since these materials are usually prone to degradation due to the presence of moisture and impurities. Moreover, it is thought that CO₂ could be produced during decomposition of CaCO₃ can function as a flame retardant by preventing the access of oxygen. CaCO₃ filled RPET/RPP blends will be especially useful for manufacturing products such as electrical housing, construction materials and automotive parts that require high flame retardancy.

The aim of this research is to investigate the effect of CaCO₃ from renewable resource and commercial grade on thermal degradation stability, mechanical performance and flame retardancy of filled RPET/RPP blends. The effect of particle size on thermal decomposition kinetic of cockleshell filled RPET/RPP blend was elucidated.

2. EXPERIMENTAL

Materials and Sample Preparation

RPET and RPP from crushed waste bottle were provided by Yasuda Sangyo Co., Ltd. SEBS base copolymer supplied by JSR Corporation was used as compatibilizer. A finely ground CaCO₃ with an average particle size of 1.8 μm was purchased from Bihoku Funka Kogyo, Co., Ltd, which referred as "Softon". Waste cockleshell were taken from Thailand and used as original without purification. The shells were washed, dried, ground and sieved at 400 mesh size, which averaged particle size was 25 μm. Cockleshell-derived CaCO₃ is referred as "CS". The ratio of RPET/RPP was 95/5, which RPET was 95 wt% and RPP was 5 wt% filled with 10wt% filler at 5 phr (part per hundred resin by weight) compatibilizer. All compositions were melted blending in a single screw extruder before subjecting to dumbbell specimens by injection molding machine.

Characterization

Thermal stability and decomposition kinetic were carried out by thermogravimetric analyzer (TGA2950, TA Instruments) at heating rate of 2, 5, 10 and 20 °C/min under nitrogen (N₂) and air. Thermal stability of the blends was elucidated according to thermal decomposition kinetic of iso-conversion model of Flynn-Wall-Ozawa (FWO) and Kissinger models [1], which are based on the Arrhenius equation

$$\frac{d\alpha}{dT} = \frac{A}{\beta}\exp\left(\frac{E_a}{RT}\right)(1-\alpha)^n \qquad (1)$$

where α is the fraction of weight loss, t is time (s), T is degradation temperature (K), A is the pre-exponential factor, β is heating rate (K/min), E_a is activation energy (J/mol), n is reaction order and R is a universal gas constant (8.314 J/mol K).

Flame retardant property of the blends was characterized by using limiting oxygen index (LOI) (ONI, oxygen index meter, Suga Test Instruments Co., Ltd.,

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Japan) according to JIS K 7201-2, specimen type IV.

Tensile test was performed by an Instron 4206 universal testing machine according to ASTM D638. The gauge length was 115 mm at an extension rate of 20 mm/min.

Impact testing was conducted by a Toyo Seiki Izod impact tester according to ASTM D256 with a pendulum of 5.5 J.

3.   RESULTS AND DISCUSSIONS

Fig.1. presents FWO plots of log heating rate (β) as a function of inverse temperatures of the blends under N_2 and air. It can see that FWO plots shows linear relationship of the plots under N_2 whereas FWO plots under air atmosphere exhibited non-fitting data of the plots. Therefore, in this study the non-fitting data was successfully developed by using polynomial function.
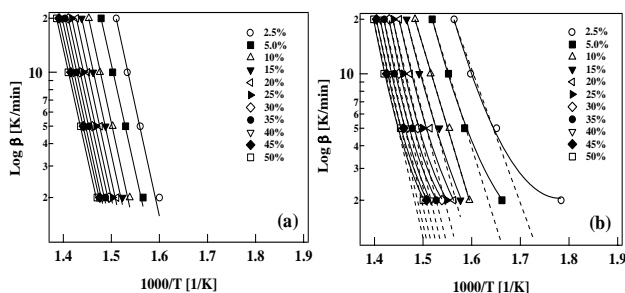

Fig.1. FWO plots of Softon filled blend (a) N_2 (b) air.

These results are considered that E_a of thermal oxidative degradation was dependent on the slow heating rate, size of filler, RPP dispersed particles and complex degradation mechanism.

Fig.2. presents the activation energy (E_a) values of the blends from FWO and polynomial fitting data under decomposition in N_2 and air, respectively. The incorporation of Softon and CS yielded higher E_a values indicating that filler improved thermal oxidative degradation of the blends, especially at the initial stage of the degradation. However, smaller size of Softon exhibited higher E_a values than CS filled blend.
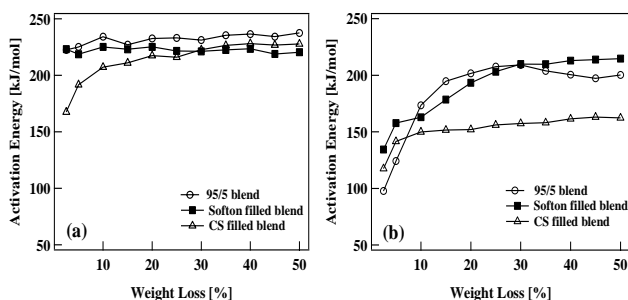

Fig.2. E_a of unfilled and filled blend (a) N_2 (b) air.

Fig.3. illustrated the compensation effect from kinetic parameter of E_a and pre-exponential factor (A) from Kissinger model. This linear relationship indicates that an iso-kinetic relationship was established whereby the thermal decomposition mechanisms of unfilled and filled RPET/RPP blends were similar [2].

Table 1. summarized mechanical properties and LOI values of the blends. Softon and CS enhanced tensile modulus (E) and impact performance of the blend, which

due to stiffness of fillers and good interaction between fillers and the blend matrix. However, reduction in yield strength (σ) was probably due to poor adhesion between fillers and the blend matrix.
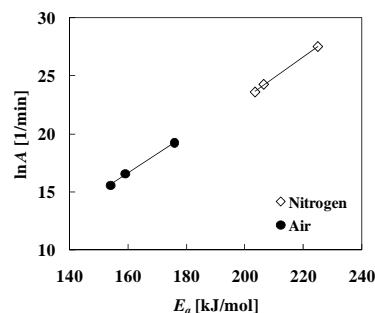

Fig.3. Compensation effect of unfilled and filled blend.

The LOI values of RPET/RPP blends decreased indicating higher flammability with adding low filler content as shown in Table 1. It was probably due to char formation of filler could not effective at low filler content. The incorporation of $CaCO_3$, however, prevented the dripping thus causing the specimens to continue burning.

Table 1. Mechanical properties and LOI values of unfilled and $CaCO_3$ filled RPET/RPP blends.

Blend	Filler	E (GPa)	σ (MPa)	Impact strength (kJ/m²)	LOI (%)
95/5	-	1.54	46.5	1.54	23.2
	Softon	1.78	43.0	1.77	20.3
	CS	1.99	42.6	1.09	20.4

4.   CONCLUSION

The incorporation of CS and SOFTON improve thermal stability of RPET/RPP, which exhibited higher E_a. Thermal decomposition in N_2 of the blend was fitted by FWO model whereas thermal oxidative degradation in air of the blends was fitted by the second order of polynomial function, which influenced by filler particle size. The kinetic results from Kissinger method suggested similar decomposition mechanisms would occur in these blends due to the linearity of the compensation plot. However, both fillers could not act as effective flame retardant for the blend. Furthermore, it is interesting to note that fillers enhance stiffness and impact performance of the blends.

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