

Compositional Thermal Analysis of Polymer Plastic Mixtures

Xiayang Diao¹ and Hern Kim²

¹Department of Environmental Engineering and Biotechnology, Myongji University, Yongin, Korea, Email: diao.xiayang@gmail.com

²Department of Environmental Engineering and Biotechnology, Myongji University, Yongin, Korea, Email: hernkim@mju.ac.kr

ABSTRACT: Thermal analysis by TGA is used as a tool to investigate the inter-relationships between thermal degradation properties of pure polymer plastics and those of their mixtures. Thermal decomposition of plastic mixtures comprising high density polyethylene, polystyrene and polypropylene were examined under nitrogen atmosphere. The results show that if mixed, the individual components are more clearly recognised from the differential mass loss curves. Weighed sum method was applied to evaluate the share of the constituents. Inaccuracy in determining the composition could be caused by interaction between constituents. To illuminate the effect of interaction, an equation describing the difference of weight loss between experimental and theoretical ones is defined. In addition, activation energy was calculated by model free method and the dependencies of activation energy on conversion were studied.

Keywords: thermal property, plastic, kinetic, composition

1. INTRODUCTION

Nowadays plastic materials have been widely applied in our daily life and industrial production not only because of their outstanding characteristics but also because of their economics and durability. Along with the conveniences, environmental problems caused by waste plastics are also brought into our sight. The disposal of waste plastics has become a major environment problem all over the world. Large amount of post consumer plastic waste material are generated every year. General method of disposing waste plastics is landfilling. But since plastics are durable and degrade very slowly and place available for landfilling decreases it's very necessary to find an

alternative method to landfill disposal of plastic wastes. One method comes into researchers' consideration is incineration not only because it is high efficient but also because plastic refuses represent an alternative source of energy and chemical raw materials. In order to dispose plastic wastes properly by pyrolysis we have to face and solve some problems. First, since plastic is a wide range of synthetic or semi-synthetic polymerization products, their mechanism of pyrolysis is quite different. Second, sorting of plastic refuses is a crucial problem. Though beverage bottles, water pipes, plastic bags and so on are always made of a single type of plastic material it is difficult to sort them automatically. In case like waste cellular phone, refrigerator etc.

the situations become more complicated because they may consist of over a dozen of different types of plastics.

In order to recover high yields of useful products from waste plastic pyrolysis and in order to control any potentially harmful products released during the pyrolysis reactions, the decomposition behaviours of the waste plastics must be known. And when sorting is very difficult a practical method to identify the composition of a plastic mixture is quite useful.

In this study thermogravimetric analysis (TGA) was used as a tool to study the thermal decomposition behaviours of individual and blended plastics. Weighed sum method was applied to evaluate the shares of constituents in the binary mixtures. Inaccuracy in determine the shares could be caused by interaction between constituents. To illuminate the effect of interaction, an equation describing the difference of weight loss between experimental and theoretical ones is defined. In addition, activation energy was calculated by model free method and the dependencies of activation energy on conversion were studied.

2. EXPERIMENTAL

2.1 Sample and Instrument

The materials investigated were pure polymers without fillers, stabilizers and colorants including high density polyethylene (HDPE), polypropylene (PP) and polystyrene (PS). The plastic samples used in this study were commercial grade materials representative of plastics commonly found in municipal solid waste (MSW). Thermal Gravimetric (TG) instrument (SETARAM TG92) was used in this research. This apparatus uses a horizontal differential balance and platinum crucibles.

The samples of this study could be divided into two categories: individual plastics including HDPE, PP and PS and binary mixtures composed by them. For a binary mixture with certain constituents four

kinds of share were prepared: 20%, 40%, 60% and 80%. Thus there were fifteen groups of samples totally.

To improve the miscibility of the components, the granules were shredded into very small pieces with size less than 2mm. Total mass of sample taken was 9-10mg for each run of the experiments.

2.2 Operation of experiments

The experiments were repeated thrice at heating rate of 10K/min to confirm the repeatability and authenticity of the generated data. Experiments were carried out under nitrogen atmosphere for a range of temperature 273-823K. Nitrogen flow rate was maintained at 60-80 ml/min according to the specification of the equipment. Experiments were conducted in dynamic condition at different heating rates of 5, 10, 15 and 25K/min.

3. RESULTS AND DISCUSSION

3.1 Examination and selecting of experiment conditions

Various experiment conditions such as sample weight, nitrogen flow rate and heating rate were taken to examine their effect on results firstly. The sample weight was recorded over a large temperature range in the test runs using powder and pellet materials. The influence of the sample form and weight on the reaction extent was found to be negligible. According to the requirement of instrument, nitrogen flow rates at 60, 70 and 80ml/min were adopted. The result showed that its influence also could be negligible.

But heating rate was found having great influence on curve pattern. From Fig 1 it could be seen that for TG curve, increasing of heating rate led to shifting to the right but seemingly didn't change the trend much. High heating rates seemed to make the DTG curves ambiguous. At high heating rates some adjacent peaks or shoulders were overlapped. Based on observation, different components are easier to be distinguished

from DTG curves than from TG curves, and low heating rates are necessary.

Therefore, in the following, DTG curves at heating rate of 5K/min were taken to present the thermal decomposition behaviours of the samples.

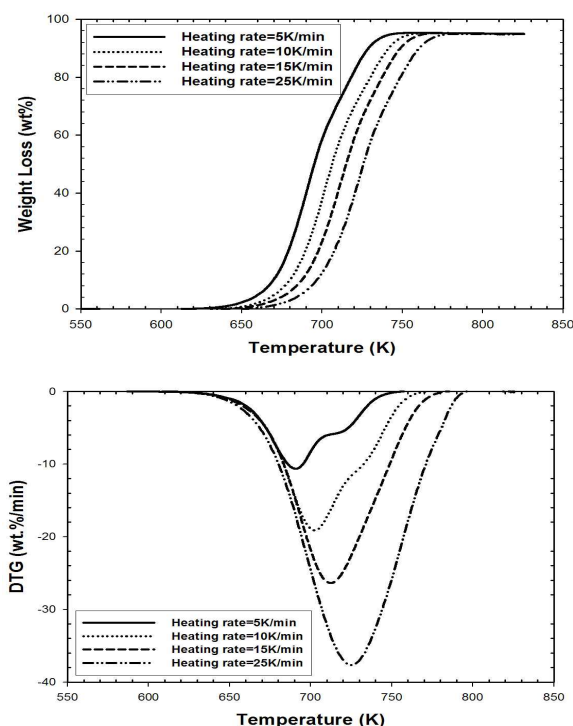


Figure 1: TG and DTG curves of PP/PS mixtures at various heating rates (60PP/40PS)

3.2 Pyrolysis of individual plastics and their binary blends

Fig 2 showed the experimental results obtained at 5°C/min under nitrogen atmosphere condition for all the individual polymers investigated in this study. It was obvious that the order of thermal stability of the studied polymers was HDPE>PP>PS. The weight loss of all samples increased with temperature increasing for all samples. For PP and PS, the pyrolysis started at the temperature above 630K and ended at around 730K and 690K, respectively. For HDPE, the pyrolysis started above 710K and ended around 760K. The DTG curves indicated that there should be at least one reaction during the decomposition process for these three plastics. For PS and HDPE, the decomposition rates were faster than PP.

The peak temperatures are 680, 725, and 750K for PS, PP and HDPE respectively. These peak temperatures indicate the maximum decomposition rates.

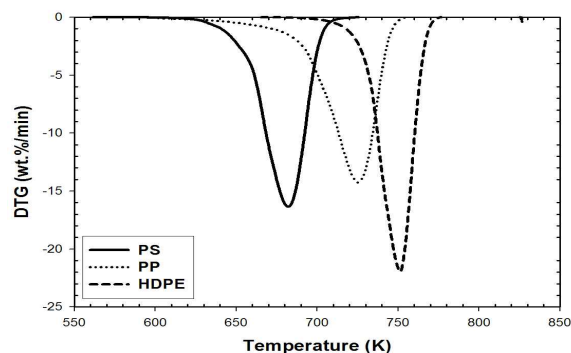


Figure 2: DTG curves of individual plastics at heating rate of 5K/min

Compare with individual plastics thermograms of their mixtures appeared to be very different, even the pyrolysis behaviours of HDPE, PP and PS were similar. Fig 3 showed the DTG curves of the three binary mixtures and compared them with the single plastics.

It could be seen that in the case of HDPE/PP mixtures there was only one peak on each curve. This meant that PP decomposition was retarded and HDPE was destabilized. The destabilization could be explained by an intermolecular transfer of a hydrogen atom from the less stable polymer to a free radical depropagating chain of the second component during decomposition. For the mixtures of PS and PP, shoulder became clearer when increase the share of PP. On the DTG curves of mixtures blended by HDPE and PS there were obvious two peaks. The peak positions were similar as the ones of individual plastics.

3.3 Composition of mixtures evaluated by weighed sum method

In order to determine the composition of a binary plastic mixture, the superposition principle was assumed: the thermal degradation curve of a mixture was calculated as a sum of the contributions of the corresponding individual components.

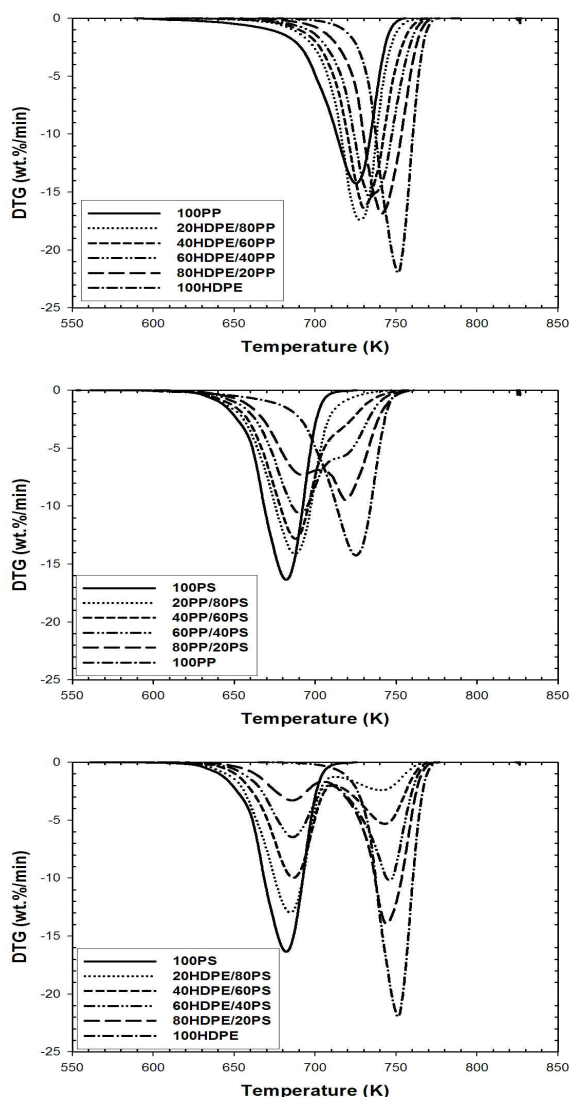


Figure 3: DTG curves of plastic mixtures at heating rate of 5K/min

This approach has been widely applied to express the pyrolysis of biomass as a sum of its major components i.e. cellulose, hemicelluloses and lignin [1-3]. In this work, the weighed sum method was applied on binary plastic mixtures. Mathematically, the weighed sum method was formulated, e.g., by Cozzani et al. [4]:

$$Y_{mix} = x_1 y_1 + \dots + x_n y_n = \sum_{i=1}^n x_i y_i \quad (1)$$

where Y_{mix} is the calculated value of the DTG mixture curve and y_i is the measured value of DTG curve of component i . The coefficients x_i are the unknowns i.e. the mass fractions of each component i in the

mixture. n is the number of components taken into account. For the x_i in Eq. (1), the least squares method was used to minimize the difference between the measured and calculated values. The object function S_R is defined as:

$$S_R = \sum_{N_{data}} [y_{mix} - Y_{mix}]^2 = \sum_{N_{data}} \left[y_{mix} - \sum_{i=1}^n x_i y_i \right]^2 \quad (2)$$

where y_{mix} is the measured value of DTG mixture curve and N_{data} is the number of data points taken into account. The weighed sum method was applied considering the measurement data between 550 and 830K with an increment of 1K.

The share of each constituent was calculated and shown in Table 1. It was obvious that the calculated shares in the case of HDPE/PS mixtures were much closer to the real value than in the case of HDPE/PP and PP/PS mixtures. This could be explained by that the effect of interaction between components was different.

Table 1: Calculated share of each constituent in the mixtures

	20/80	40/60	60/40	80/20
PE/PP	4/96	22/78	41/59	65/35
PP/PS	14/86	26/74	45/55	67/33
PE/PS	15/85	32/68	52/48	71/29

3.4 Interaction between two components

To further illuminate the interaction between the components, the following equation was defined:

$$\Delta W = W_{mixture} - (x_1 W_1 + x_2 W_2) \quad (3)$$

where $W_{mixture}$ is the weight loss of mixture, x_i is the weight fraction of each component in the mixture, W_i is the weight loss of each component in the same operational conditions and ΔW is the difference of weight loss. ΔW describes the ‘extent’ of interaction effect during co-pyrolysis. Theoretically ΔW should be zero without interaction. Positive value of ΔW indicates the destabilization of the mixture while

negative value indicates an increasing of thermal stability of the mixture.

Fig 4 showed the variation of ΔW with temperature for the different binary plastic mixtures. And Table 2 summarized the ΔW range. It could be seen that, for the three mixtures, ΔW was less than 3% before 650K. Because at this temperature plastic was still not decomposed, obviously there was no interaction between two constituents. The curve patterns for all the mixtures were similar. ΔW first increased with temperature from zero to a positive peak value and then sharply declined to a negative value. After this ΔW increased again and went back close to zero. This implied that the mixture was destabilized first by the less stable single plastic. After the more stable one started to pyrolysis the stability of the mixture increased. Base on ΔW range it was found that the extent of interaction of the three binary mixtures was HDPE/PP > PP/PS > HDPE/PS and the closer the amounts of two constituents were the larger the interaction effect was.

Table 2: ΔW range for the mixtures

		ΔW (wt %)
HDPE/PP	20%+80%	9.5 ~ (-11.2)
	40%+60%	7.3 ~ (-16.1)
	60%+40%	4.5 ~ (-19.8)
	80%+20%	2.8 ~ (-18.2)
PP/PS	20%+80%	6.0 ~ (-10.2)
	40%+60%	2.9 ~ (-14.7)
	60%+40%	3.3 ~ (-16.2)
	80%+20%	1.2 ~ (-12.9)
HDPE/PS	20%+80%	4.5 ~ (-8.7)
	40%+60%	7.3 ~ (-14.0)
	60%+40%	4.9 ~ (-16.5)
	80%+20%	1.6 ~ (-18.0)

3.5 Kinetic analysis

Kinetic studies of thermally stimulated reaction in solids are ordinarily performed under isothermal (temperature is a constant) or linear nonisothermal (temperature is a linear function of the time) heating. The kinetic equation of thermal decomposition

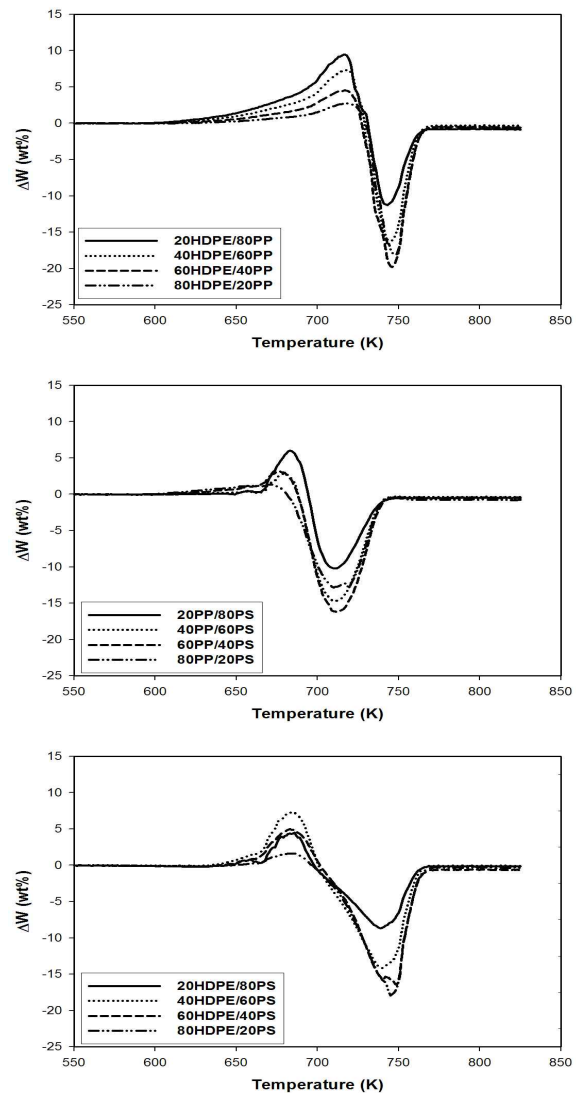


Figure 4: DTG curves of plastic mixtures at heating rate of 5K/min

can be expressed as

$$\frac{d\alpha}{dt} = k(T)f(\alpha) = A \exp\left(\frac{-E}{RT}\right)f(\alpha) \quad (4)$$

which is used to describe the kinetics of these reactions under both isothermal and non-isothermal conditions, where t is the time, T the temperature (K), α the conversion of reaction $(W_0 - W)/(W_0 - W_\infty)$, W_0 the initial weight of the sample (mg), W the sample weight (mg) at any temperature T , W_∞ the final sample weight (mg), $d\alpha/dt$ the rate of reaction, and $f(\alpha)$ is the reaction mode. $k(T)$ is the Arrhenius rate constant.

A is the pre-exponential factor (K^{-1}) and E is the activation energy ($kJmol^{-1}$). A and E are called Arrhenius parameters. R is the gas constant. The reaction model may take various forms based on nucleation and nucleus growth, phase boundary reaction, diffusion, and chemical reaction [5, 6]. However, the present investigation does not require any information of reaction model since we report here thermal decomposition kinetics of samples using model-free approach.

For non-isothermal conditions, when the temperature varies with time at a constant heating rate, $\beta = dT/dt$, Eq. (4) is represented as following:

$$\frac{d\alpha}{dT} = \frac{A}{\beta} \exp\left(\frac{-E}{RT}\right) f(\alpha) \quad (5)$$

For a set of four experiments carried out at four different heating rates (5, 10, 15 and 25K/min) the E can be determined at any particular value of α by finding the value of E for which the objective function Ω is minimized [6], where:

$$\Omega = \sum_{i=1}^n \sum_{j \neq i}^n \frac{I(E_{\alpha}, T_{\alpha,i}) \beta_j}{I(E_{\alpha}, T_{\alpha,j}) \beta_i} \quad (6)$$

and

$$I(E_{\alpha}, T_{\alpha,i}) = \int_0^{T_{\alpha,i}} \exp\left(\frac{-E}{RT}\right) dT \quad (7)$$

The temperature integral can be evaluated by several popular approximations. Approximation of Cai [7], a temperature integral approximation superior to other approximations, is as under:

$$\int_0^T \exp\left(\frac{-E_{\alpha}}{RT_{\alpha i}}\right) dT = \frac{RT_{\alpha i}^2}{E} \left(\frac{\frac{E_{\alpha}}{RT_{\alpha i}} + 0.66691}{\frac{E_{\alpha}}{RT_{\alpha i}} + 2.64943} \right) \exp\left(\frac{-E_{\alpha}}{RT_{\alpha i}}\right) \quad (8)$$

The minimization of Eq. (6) was done by numerical method in FORTRAN using the “Brent” function. Plots for E dependency on conversion obtained for non-isothermal decomposition for individual plastics and their binary mixtures were shown in Fig 5 and 6. It is observed that the activation

energy of thermal degradation varied throughout the process.

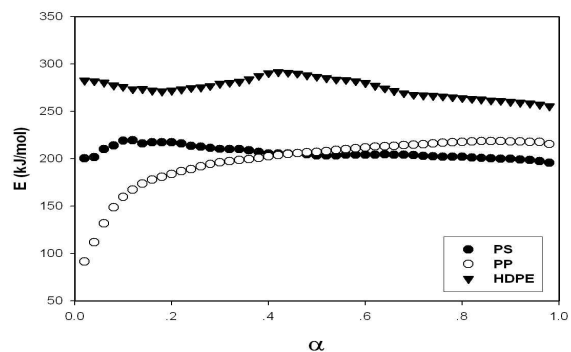


Figure 5: Activation energy dependencies of thermal degradation of PS, PP and HDPE

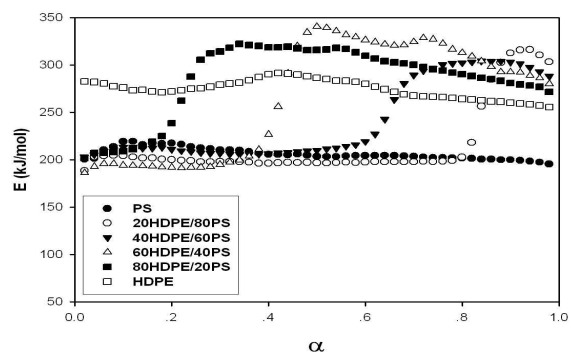
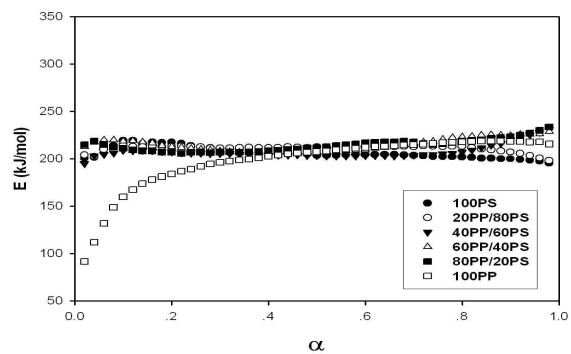
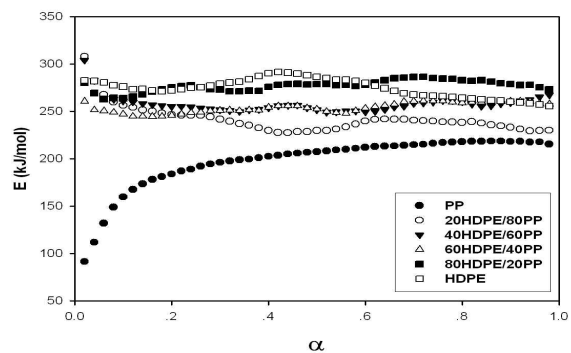


Figure 6: Activation energy dependencies of thermal degradation of binary mixtures

It was observed from Fig 5 that the dependencies on conversion for three individual plastics had different patterns. For HDPE and PS, the activation energy varying ranges were 250-300kJ/mol and 180-300kJ/mol respectively. The activation energy was weak but decreasing function of conversion, though there were some fluctuations. For PP, the activation energy kept increasing from around 80kJ/mol to 200kJ/mol. The difference of activation energy changing pattern between HDPE, PS and PP might be due to different side groups and end groups.

As being shown in Fig 6, for binary mixtures, E-dependencies in the case of HDPE/PP and PP/PS mixtures only weakly changed throughout the whole conversion. And compare the value of the mixtures with the individual plastics it could be estimated that the activation energy of a constituent didn't change much. In the case of HDPE/PS mixtures, one step could be found on the E- α curve. The α value of starting point of the step well corresponded to the share of PS. This could be explained by that the temperature ranges of thermal decomposition of PS and HDPE were separated. HDPE began to decompose after PS almost all decomposed. The E value in the two steps related to PS and HDPE, respectively. The E of PS was slightly reduced and the E of HDPE was increased.

5. CONCLUSION

The order of thermal stability of the studied plastics is HDPE>PP>PS. Results of experiments taken under various conditions showed that heating rate affected much on the data. It was easier to distinguish between materials based on DTG curve at low heating rate (around 5K/min). Thermograms of binary mixtures with different components were quite different. Peaks and shoulders intensively overlapped in case of HDPE/PP and PP/PS mixtures. The share of constituent also affected on the curve pattern.

In order to determine the composition of an unknown component in the mixture,

weighed sum method was applied. This method was more accurate for HDPE/PS mixture than the others.

Activation energy varies with conversion. This variation for HDPE and PS is less than PP. The side groups of PP and PS have strong influence on the thermal property of the polymers. For binary mixtures, significant activation energy change was found in the mixture of HDPE/PS. And the conversion extent well corresponds to the share of PS. The results show that when the pyrolysis temperature ranges of the components in a mixture are well separated, the activation energy dependency is a good tool to determine the shares of the components.

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