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Pyrolysis of Low and High Density Polyethylene. Part I: Non-isothermal Pyrolysis Kinetics

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Abstract *Thermal decomposition kinetics of low- and high-density polyethylene (LDPE, HDPE) were investigated. Thermal degradation of raw and waste LDPE and HDPE was performed using a thermogravimetric analyzer (TGA) in nitrogen atmosphere under non-isothermal conditions. Heating rates between 5 and 50 K/min were employed in TGA experiments. First-order decomposition reaction was assumed, and for the kinetic analysis an integral method was used. The apparent activation energy (E_a) and the pre-exponential factor (k_o) were evaluated. It was found that value of the kinetic parameters and apparent activation energy of HDPE were larger than the LDPE.*

Keywords kinetic analysis, polyethylene, TGA, thermal degradation

1. Introduction

The considerable increase on energy demand, consumption of fossil fuels, and growth of world population has caused a great amount of wastes. Plastics are one of the wastes and are being used in many fields as a part of modern life nowadays. They have an important part in municipal solid waste (MSW). Appreciable increase in the production of plastics has been realized in the last decades due to the increasing demand of plastics. To prevent environmental pollution and to reduce damage of plastic wastes, they must be recycled and recovered.

Thermal behavior of plastics can be improved by knowing thermal degradation kinetics. Many studies on pyrolysis kinetics of plastic wastes have been carried out, and also various reaction kinetic models are available to estimate plastic degradation, including integral method (Kayacan et al., 2002a, 2000b, 2004; Doğan and Uysal, 1996; Coats and Redfern, 1964; Petrovic and Zavargo, 1986; Ceamanos et al., 2002; Westerhout et al., 1997). A thermogravimetric analysis (TGA) technique is an excellent way for studying the kinetics of thermal degradation. It provides information on pre-exponential factor and activation energy.

One of the materials in significant quantities in MSW is polyethylene wastes which consist of LDPE and HDPE. Thus, the objective of this work was just to study the thermal decomposition kinetics of these two kinds of plastic wastes which have the highest portion (∼50%) of municipal and industrial plastic wastes in Turkey.

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In this work, the study of the thermal decomposition behavior and determination of the kinetic parameters of the LDPE and HDPE were involved. The apparent activation energy (E_a) and the pre-exponential factor (k_o) for the decomposition reaction of raw and waste LDPE and HDPE have been determined by using thermogravimetric analysis (TGA) and integral method. Heating rates of 5, 10, 20, and 50 K/min were employed in TGA experiments.

2. Experimental

2.1. *Plastics Investigated*

Two plastic types (LDPE and HDPE) were used in this work. Raw plastics have been produced by PETKIM Petrochemical Holding Co., Izmir, Turkey. The properties of raw plastics are presented in Table 1. Waste LDPE and HDPE samples were obtained from the municipal wastes in Ankara and ground in the laboratory.

2.2. *TGA Procedure*

The thermal decomposition behavior was studied by thermogravimetric (TGA) analyzer. Kinetic data were obtained using a Linseis-L81 TGA apparatus. The LDPE and HDPE samples of about 500 mg were placed on the sample holder and pyrolyzed in nitrogen atmosphere in each experiment. The nitrogen flow rate was kept constant at 12 L h^{-1}. Pyrolysis was carried out at non-isothermal conditions (Kayacan et al., 2002a, 2002b, 2004; Doğan and Uysal, 1996). TGA data were taken at different heating rates as 5, 10, 20, and 50 K/min in the temperature range of 300–973 K. The weight loss data were recorded as a function of time and temperature using special software in computer.

2.3. *Analysis of Weight Loss Data*

Thermogravimetric analysis (TGA) has been widely used in studying pyrolytic processes. Methods for evaluation of mass loss curves obtained by this means have been studied by many other investigators. Weight loss data were used in the analysis of the decomposition reaction kinetics of HDPE and LDPE. Assuming first-order decomposition reaction, the integral method was used to evaluate the kinetic parameters. Details of the mathematical procedure used in this analysis of TGA data can be found elsewhere (Gersten et al., 2000; Kayacan et al., 2002a, 2002b, 2004; Kıran et al., 2000; Doğan and Uysal, 1996; Petrovic and Zavargo, 1986; Bockhorn et al., 1999).

Table 1
Properties of raw LDPE and HDPE sample used

Property	LDPE	HDPE
Manufacturer	PETKIM	PETKIM
Appearance	Pellet	Pellet
Density, kg/m^3 at 296 K	918–922	950–956
Melt flow rate, g/10 min	1.7–3.0	0.3–0.5
Melting point	383	399–405

The extent of conversion, or fraction of material pyrolyzed, x, was defined by the expression:

$$x = \frac{w_o - w_t}{w_o - w_\infty} \tag{1}$$

where w_o is the initial weight (mg), w_t is the weight after "t" minutes (mg), and w_∞ is the weight after pyrolysis (mg). Assuming that the reaction order is close to unity, it would be advantageous to simplify the kinetics to first-order. The well-known rate expression can then be written:

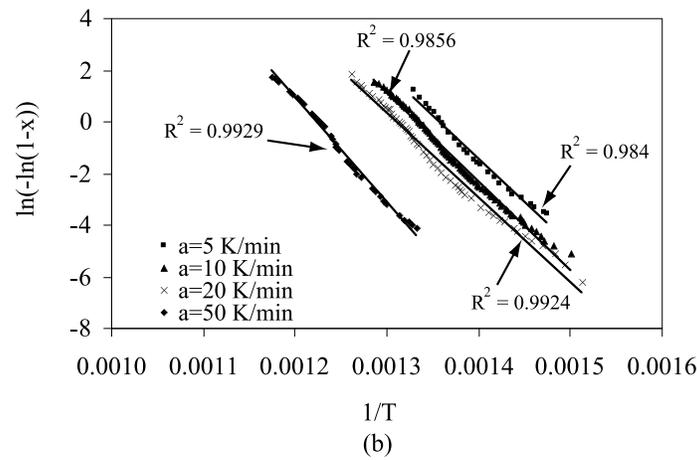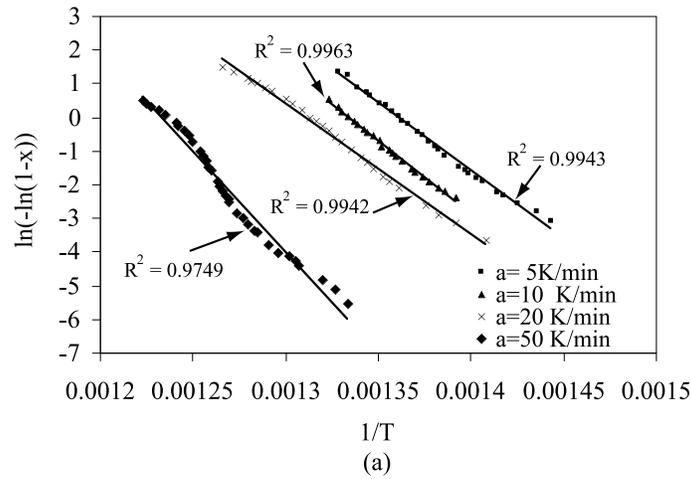$$\frac{dx}{dt} = k(1 - x) \tag{2}$$

$$k = k_o \exp(-E_a/RT) \tag{3}$$

Figure 1. $\ln(-\ln(1 - x))$ as a function of $1/T$: (a) raw LDPE and (b) waste LDPE.

where R is the universal gas constant (8.314 J K^{-1} mol^{-1}), k_o is the pre-exponential factor (min^{-1}), and E_a (kJ mol^{-1}) is the activation energy. With a linear heating rate of a, K min^{-1},

$$a = \frac{dT}{dt} \tag{4}$$

The integration of Eq. (2) results in

$$\ln[-\ln(1-x)] = \ln\left[\frac{k_o R T^2}{a E_a}\left(1 - \frac{2RT}{E_a}\right)\right] - \frac{E_a}{RT} \tag{5}$$

The plot of $\ln[-\ln(1-x)]$ against $1/T$ should correspond to a straight line with a slope of $(-E_a/R)$ giving the activation energy. The pre-exponential factor can be calculated by using activation energy and the intercept. Figures 1 and 2 show these results for LDPE and HDPE.
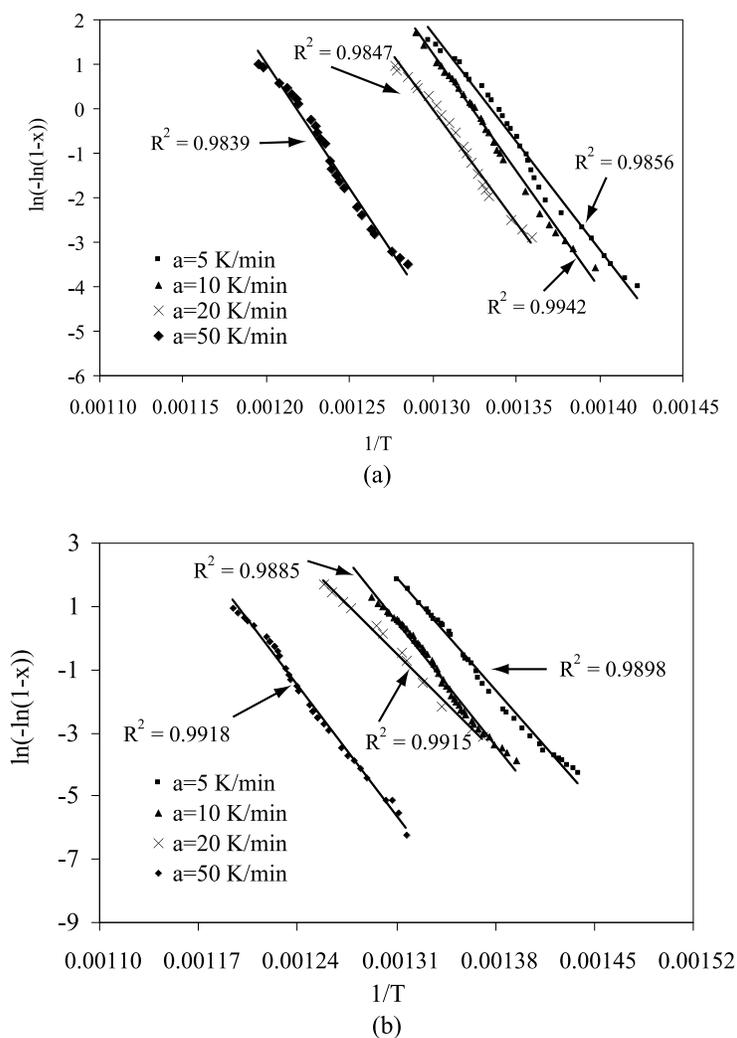

Figure 2. $\ln(-\ln(1-x))$ as a function of $1/T$: (a) raw HDPE and (b) waste HDPE.

3. Results and Discussion

The thermogravimetric weight-loss kinetics of raw and waste LDPE and HDPE are discussed below. Figures 3a, 3b, 3c, and 3d show typical TG curves for polyethylene samples in nitrogen atmosphere at different heating rates. Each weight loss curve is smooth, with one inflection point during reaction under nitrogen atmosphere. In all experiments, final temperature was 900 K. Although the decomposition curves of LDPE and HDPE are very close to each other at the heating rate range of 5–20 K/min, the decomposition curve for the heating rate of 50 K/min is far from the others. At high heating rate, fast pyrolysis was observed.

Figures 1 and 2 show the plots of the integral method for raw and waste LDPE and HDPE under non-isothermal conditions. In these figures, as the entire range of $\ln(-\ln(1-x))$ as a function of $1/T$, data could be represented by a single straight line ($R^2 = 0.99$) for all heating rates. Decomposition reactions for all heating rates occurred at the temperature range from 660 K ($x = 0.002$) to 850 K ($x = 0.99$) for LDPE, 695 K ($x = 0.0014$) to 840 K ($x = 0.99$) for HDPE. As it can be seen, HDPE samples decomposed later than the LDPE samples. Reasonable fits of data to straight lines in these figures indicate that the assumption of first-order kinetics for thermal decomposition of raw and waste LDPE and HDPE over the indicated ranges is acceptable. On the overall,
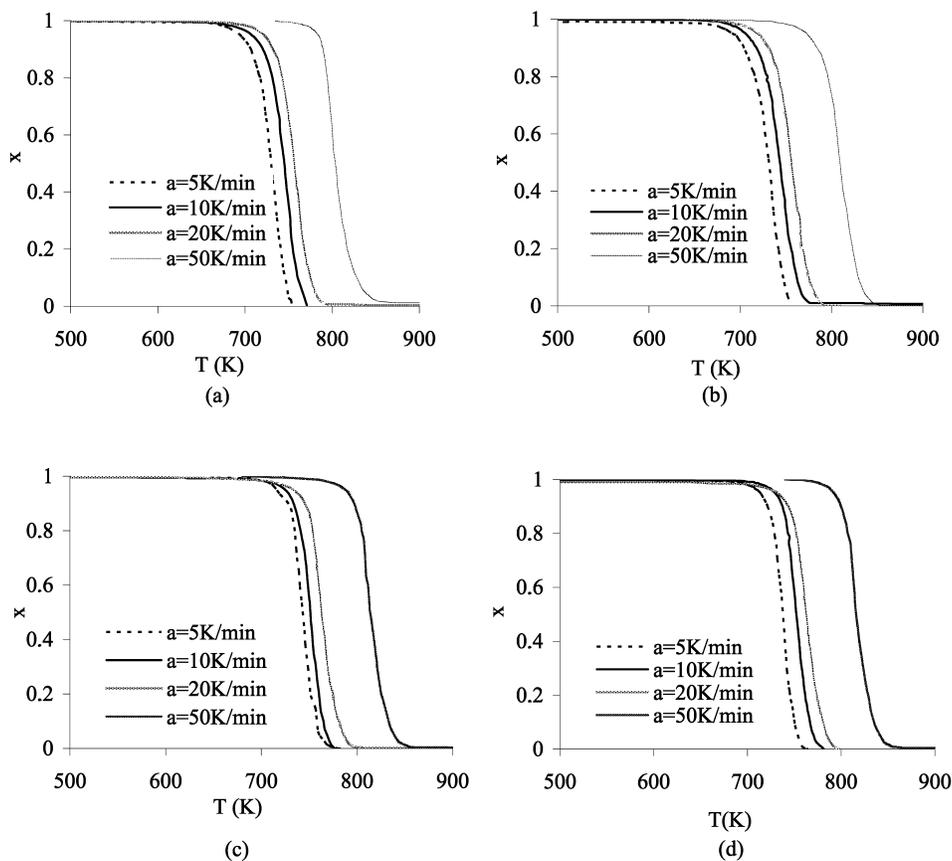

Figure 3. TG curves for polyethylene samples at a different heating rates: (a) raw LDPE, (b) waste LDPE, (c) raw HDPE, and (d) waste HDPE.

Table 2
Apparent kinetic parameters determined by integral
method for LDPE and HDPE

Material	a, K/min	E_a kJ/mol	k_o min^{-1}
Raw LDPE	5	335.14	2.63×10^{23}
	10	360.47	1.08×10^{25}
	20	324.08	2.19×10^{22}
	50	497.88	5.84×10^{32}
Waste LDPE	5	278.74	2.02×10^{19}
	10	285.21	4.42×10^{19}
	20	271.09	4.53×10^{18}
	50	333.43	6.52×10^{21}
Raw HDPE	5	401.92	9.64×10^{26}
	10	437.23	1.60×10^{30}
	20	422.07	8.22×10^{28}
	50	470.71	4.02×10^{30}
Waste HDPE	5	420.86	2.05×10^{29}
	10	464.73	1.11×10^{32}
	20	396.05	1.77×10^{25}
	50	493.43	1.47×10^{32}

the analysis presented above reveals that the thermal decomposition of LDPE and HDPE can be described by a first-order reaction.

The apparent kinetic parameters, thus obtained, are shown in Table 2. The activation energy values have been found for raw LDPE between 324–497 kJ/mol and 271–333 kJ/mol for the waste LDPE, respectively. Similarly, the activation energy for raw HDPE has been calculated between 401–470 kJ/mol and for the waste HDPE 396–493 kJ/mol. Bockhorn et al. (1999) found about 268 kJ/mol for polyethylene. The calculated activation energy values agree reasonably well with the results reported by some other studies (Park et al., 2000; Kıran et al., 2000; Ceamanos et al., 2002; Westerhout et al., 1997; Bockhorn et al., 1999).

4.   Conclusion

Conclusions obtained from examinations of thermal degradation of LDPE and HDPE are summarized as follows:

- The TGA experiment showed that the heating rate has an important role on the decomposition reaction. When the heating rate increases, the decomposition temperature of the plastics samples also increases.
- The kinetics of the degradation of the LDPE and HDPE for non-isothermal conditions can be considered as a first-order reaction.

Acknowledgment

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Nomenclature

a	linear heating rate (K min^{-1})
E_a	activation energy (J mol^{-1})
k	reaction rate constant (min^{-1})
k_o	per-exponential factor (min^{-1})
R	universal gas constant (8.31451 J K^{-1} mol^{-1})
t	time (min)
T	temperature (K)
x	fraction of plastic sample decomposed
w	weight (mg)

Subscripts

o	initial
t	t minutes after
∞	final or infinite