INFLUENCE OF THE PARTICLE SIZE IN KINETICS OF PYROLYSIS OF UNSATURATED POLYESTER

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Abstract. *The disposal of unsaturated polyester in landfill sites or their incineration creates a number of environmental problems because they contain some additives and halogenated flame retardant, which are hazardous for environment. In this paper, a kinetic study of pyrolysis of unsaturated polyester with glass fibre reinforced was studied under non-isothermal heating in nitrogen as carrier gas. Thermalgravimetric (TG/DTG) experiments were performed from ambient temperature to 1000 ºC at heating rate 20 ºCmin-1 with four different particle size ranges, 0.433, 0.79, 3.90 and 5.66 mm. Based on TGA/DTG curves the kinetics parameters, activation energy and frequency factor, were calculated using the method of Coats ─ Redfern, assuming a first-order reaction. The results discussed that activation energies increases as the particle size increases.*

Keywords*: pyrolysis; unsaturated polyester; particle size*

1. INTRODUCTION

The unsaturated polyesters are very popular because of their low cost, easy processing, low densities, good corrosion resistance and high strength-to-weigh ratios. However, the disposal of used unsaturated polyesters is an increasing economical and environmental problem for most of the developed countries. Unsaturated polyester are among the commonly use matrices with a world consumption of approximately 1 million tones per year, (Abdel-azim et. al., 2004). The problem of unsaturated polyester is not only one of quantity, but also of the hazardous impacts associated with final disposal. Because, unsaturated polyesters containing various flame-retardants, and epoxy/ unsaturated polyester based polymer interpenetrating networks (IPNs) were developed, (Shih et al., 2004) and (Shizu et al., 1997).

The disposal of unsaturated polyester in landfill sites or their incineration creates a number of environmental problems, because they contain some additives and halogenated flame retardants which are hazardous for environment.

The generation of solids plastic residues has been motivating many researchers to investigate the treatment of those residues through the pyrolysis process to generate combustible gases or new chemical products. Therefore, they have been extensive the theoretical and experimental studies on pyrolysis of plastics. Pyrolysis is one of the best alternatives to treat polymeric materials because the majority of the macromolecular organic substances are decomposing to volatile compounds at elevated temperatures while metals, inorganic fillers and supports generally remain unchanged and accumulate in the residue. Thermogravimetric analysis (TGA) is one of the most common techniques used to investigate thermal events and kinetics during pyrolysis of solid raw materials such as coal, unsaturated polyester biomass, plastic and municipal solid waste, (Budrugeac and Segal, 1996a), . (Budrugeac and Segal, 1996a), (Budrugeac, Petre and Segal, 1996b), (Budrugeac and Segal, 1997) and (Budrugeac and, 2001)

The aim of the present work is to find the values of the kinetic parameters characterizing the pyrolysis of unsaturated polyester in inert medium using data from non-isothermal thermogravimetric four different particle size ranges, 0.433, 0.79, 3.90 and 5.66 mm and the calculation procedure of Coats ─ Redfern method, (Coats and Rredfern, 1964).

2. Experimental

2.1 Thermobalance

The experiments were carried out on a RB-thermobalance model 3000-20 (Brazil) controlled by a PC AT compatible system. The atmosphere used was nitrogen with a flow rate of 60 ml min^{-1}. Modulate of service: amplifier, plate of acquisition of data and controllers PI and PID. The thermobalance incorporates a servo-operated system in which an electrical signal from an optical null detector is applied directly to control the current in a torque motor. The balance has provision for digital mass readout using four digit thumbwheels and two digit verniers with three full-scale ranges: 100, 1000 and 10000 mg.

2.2 Materials and operating conditions

In all the experiments the material used was unsaturated polyester (Fibralit Industrial e Commercial Ltda). Experiments in dynamic conditions were carried out over a range of temperatures that included the entire range of solid decomposition, with heating rate of 5, 10, 15 and 20 ℃ min-1. The experiments were repeated three times to determine their reproducibility, which was found to be good. Average data obtained at each heating rate were considered for computer purposes. The mass of the sample used was 5000 mg. The values of temperature considered were those recorded by the thermocouple. The sample were heated at 1000 ℃. The physical characteristics and ultimate analysis of unsaturated polyester were given in Table 1 and 2, respectively.

Table 1 ─ Proximate analysis and physical characteristics of unsaturated polyester.

Parameter	Unsaturated polyester
Ash (%)	13.9
Volatile matter (%)	79.5
Fixed carbon (%)	5.5
Moisture (%)	1.1
Heating Value (kcal/kg^{-1})	5292.08
Apparent density (kg/m^3)	1043

Table 2 ─ Elemental analysis of unsaturated polyester

Parameter	Unsaturated polyester
Carbon	13.9
Nitrogen	79.5
Hydrogen	5.5
Oxygen	1.1

2.1. Theoretical considerations

The kinetic equation applied pyrolysis of unsaturated polyester can be written as follows:

$$\frac{d\alpha}{dt} = k(T)f(\alpha) \tag{1}$$

where k(T) the temperature dependent rate constant; T the absolute temperature, t the time and α the degree of transformation. The temperature dependence of the rate constant usually described by the Arrhenius equation:

$$k = A\exp\left(-\frac{E}{RT}\right) \tag{2}$$

where A is pre-exponential or frequency factor, E the activation energy, R the universal gas constant (8.314 J mol^{-1} K^{-1}). Under constant heating rate:

$$\frac{dT}{dt} = b = cons\tan t \tag{3}$$

where b is heating rate.

The kinetic function: f(α) is related to the reaction mechanism, although some authors prefer to consider empirical kinetic laws of the type . In this work, is fractional pyrolysis of the unsaturated polyester used, which is calculated from the corresponding TG curve by the formula: Table 3 shows the most common kinetic models and their algebraic expressions, (Conesa et al., 2001).

Table 3 ─ Algebraic expression of and for kinetic models commonly used.

Kinetic model	$f(\alpha)$	$g(\alpha)$
First-order	$1-\alpha$	$-\ln(1-\alpha)$
First-order	$(1-\alpha)^2$	$\dfrac{1}{(1-\alpha)}$
Third-order	$(1-\alpha)^3$	$\left[\dfrac{1}{(1-\alpha)}\right]^2$
One-dimensional	$\dfrac{1}{2\alpha}$	α^2
Two- dimensional	$(-\ln(1-\alpha))^{-1}$	$(1-\alpha)\ln(1-\alpha)+\alpha$
Three- dimensional	$\dfrac{3}{2}(1-\alpha)^{\frac{2}{3}}\left(1-(1-\alpha)^{\frac{1}{3}}\right)^{-1}$	$\left[1-(1-\alpha)^{\frac{1}{3}}\right]^2$
Contracting area	$2(1-\alpha)^{\frac{1}{2}}$	$1-(1-\alpha)^{\frac{1}{2}}$
Contracting volume	$3(1-\alpha)^{\frac{1}{3}}$	$1-(1-\alpha)^{\frac{1}{3}}$
Avrami-Erofeev	$2(1-\alpha)(-\ln(1-\alpha))^{\frac{1}{2}}$	$[-\ln(1-\alpha)]^{\frac{1}{2}}$
Avrami-Erofeev	$3(1-\alpha)(-\ln(1-\alpha))^{\frac{2}{3}}$	$[-\ln(1-\alpha)]^{\frac{1}{3}}$
Avrami-Erofeev	$4(1-\alpha)(-\ln(1-\alpha))^{\frac{3}{4}}$	$[-\ln(1-\alpha)]^{\frac{1}{4}}$

$$\alpha = \frac{W_i - W_t}{W_i - W_f} \tag{4}$$

Therefore,

$$\frac{d\alpha}{dt} = A\exp\left(-\frac{E}{RT}\right)f(\alpha) \tag{5}$$

When the reaction is carried out under a linear temperature programmed ($T = T_0 + bt$), Eq. (5) may be written as:

$$\frac{d\alpha}{dT} = \frac{A}{b}\exp\left(-\frac{E}{RT}\right)f(\alpha) \tag{6}$$

After substitution in Eq (1) and some transformations:

$$\int_0^\alpha \frac{d\alpha}{f(\alpha)} = \frac{A}{b}\int \exp\left(-\frac{E}{RT}\right)dT \tag{7}$$

The right hand side of Eq. (7) has no exact analytical solution, but making some variable substitutions and applying Cauchy's rule the expression can be solved to give:

$$\frac{A}{b}\int_0^T \exp\left(-\frac{E}{RT}\right)dT \cong \frac{ART^2}{bE}\left(1-\frac{2RT}{E}\right)\exp\left(-\frac{E}{RT}\right) \tag{8}$$

If the solution of the integral on the left-hand-side of Eq. (7) is denoted with:

$$g(\alpha) = \int_0^\alpha \frac{d\alpha}{f(\alpha)} \tag{9}$$

then, after division by T 2 taking logarithms, Eq. (8) is transformed to:

$$\ln\frac{g(\alpha)}{T^2} = \ln\frac{AR}{bE}\left(1-\frac{2RT}{E}\right) - \frac{E}{RT} \tag{10}$$

If $\dfrac{2RT}{E} << 1$ is assumed, Eq (10) become:

$$\ln\frac{g(\alpha)}{T^2} = \ln\frac{AR}{bE} - \frac{E}{RT} \tag{11}$$

A first-order $(-\ln(1-\alpha))$ reaction model was proposed to describe the main pyrolysis process of unsaturated polyester and activation energies and frequency factors were determined. Thus, a plot of $\ln[g(\alpha)/T\,2]$ against $1/T$ should be a straight line with a slope $-E/R$ since $\ln(AR/qE)$ is nearly constant nearly constant, for a fixed heating rate b, and a chosen degradation function $f(\alpha)$, the apparent activation energy E and the apparent pre-exponential factor A may be obtained. In this study, models First-order (as indexed in Table 3) was chosen as the degradation function f(a) to investigate the reaction order of the degradation process.

3. Results and Discussions

Fig 1 shows TG typical weight loss against temperature curves the pyrolysis for unsaturated polyester grain in inert atmosphere under non-isothermal conditions for the four different particle size ranges, 0.433, 0.79, 3.90 and 5.66 mm and heating rate of 20 ºC min-1. It could be seen that there was a lateral shift in the thermograms for different particle size. Besides, there was an effect of particle size on the total weight loss. As the particle size was increased, a slower pyrolytic reaction occurred, resulting in lower pyrolytic conversion.

Fig 2 shows DTG curves for unsaturated polyester for the four experiments out 0.433, 0.79, 3.90 and 5.66 mm and heating rate of 20 ºC min-1. The temperature between 30 and 150ºC, for all the curves, in this zone the drying. However, as the moisture content of unsaturated polyester is very low, it is not appreciable the corresponding weight-loss. Following the particles drying, it is observed that the unsaturated polyester decomposition begins. Low reaction rates are observed specially between 150 and 200ºC. In this stage of the pyrolysis reaction, probably the additives are slowly decomposed and incorporated to the flow rate. During their decomposition, it is not observed a sharp peak. It is observed that for each heating rate there are peaks temperatures different in DTG curve.

It is observed that for each diameter particle there are peaks temperatures different in DTG curve. The temperature of the peaks in the DTG curve depends on the heating regime. Therefore, the kinetics parameters characterizing the different processes were expected to be different. Table 4 compiles the kinetic parameters obtained from the experimental results by fitting the reaction rate versus temperature curves. It could be seen that heating rate played an important role in both the first and second stages of the pyrolysis of unsaturated polyester. With an increase in the diameter particle, both the starting and ending temperatures of the intermediate decreased. It was also noted that the weight fraction of the intermediate started to decrease above a certain temperature. The higher the diameter particle, the higher would be the temperature at which the intermediate started to diminish. Consequently, the second-stage reaction occurred at a higher diameter.
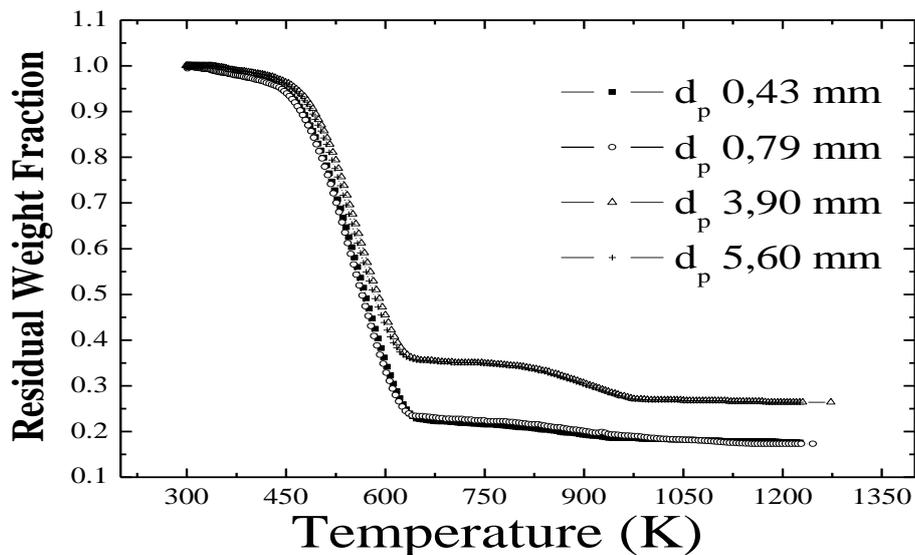
Figure 1. Residual weight fraction for pyrolysis of unsaturated polyester of for several particle diameter.
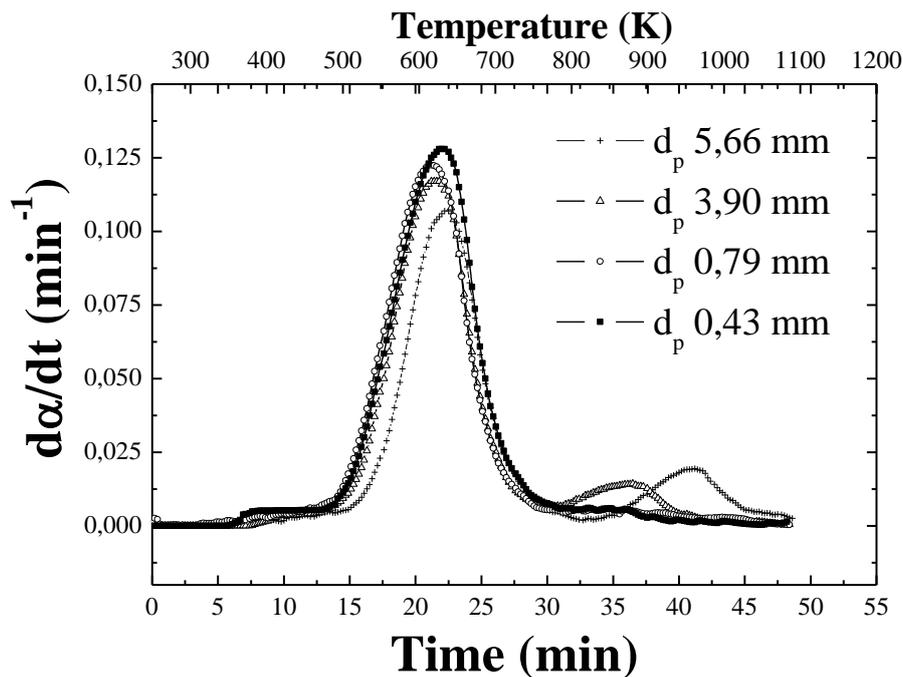
Figure 2. Derivative Thermograms (DTG) for pyrolysis of unsaturated polyester.

Using data from the pyrolysis thermograms (Fig. 1), the kinetic parameters including the order of reaction (n), the activation energy (E) and the frequency factor (A), were estimated with high correlation coefficients (all above 0.99) and listed in Table 4.

In Table 4, the activation energies of degradation for unsaturated polyesters were 79.07, 88.09, 117.77and 131.24 kJ/mol for diameter particle 0.43, 0.79, 3.90, 5.66 and heating rate 20 ºC min-1, respectively. One would note that the regression factor (R^2) calculated by heating rate 0.43 min-1 (0.997) , 0.79 (0.998), 3.90 (0.988) and 5.66 (0.999) are not different from each other. As seen from Table 4, diameter particle have effects on the activation energy and the

frequency factor. However, as the diameter increasing, the activation energy increasing while the frequency factor increasing significantly.

Fig. 3 presents graphically the dependence described by Eq (11) for the four heating rate studied and shows the typical plots of $\ln[-\ln(1-\alpha)]/T^2$ versus 1/T, indicating that for unsaturated polyester pyrolysis, single first order reaction should be used to describe the pyrolysis process.

Table 4 ─ kinetics parameters for the pyrolysis unsaturated polyester.

Diameter particle (mm)	$d\alpha/dt$	Peaks temperature (ºC)	Activation energy (kJ/mol)	Frequency factor (min^{-1})	Correlation coefficient (R^2)
0.43	0.034	278	79,07,	1.54×10^6	0.997
0.79	0.074	300.5	88,09	2.68×10^6	0.998
3.90	0.088	310.7	117,77	1.98×10^{10}	0.988
5.66	0.124	380.6	131,24	1.69×10^{11}	0.999
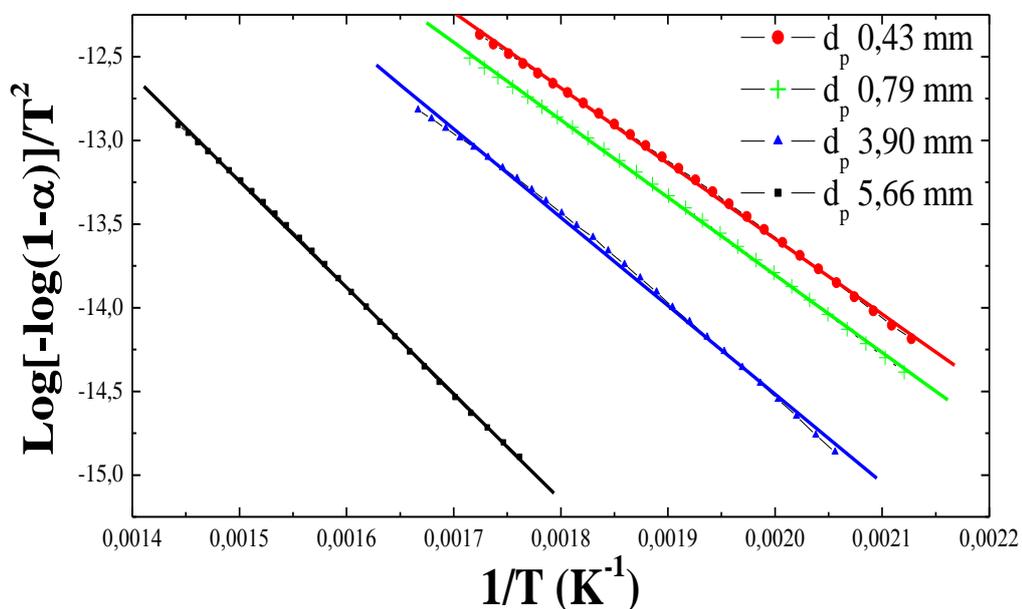
Figure 3. Plot of $\ln[-\ln(1-\alpha)]/T^2$ versus $1/T^2$ for pyrolysis unsaturated polyester.

4. Conclusions

Based on the kinetic study by the CoatseRedfern method, kinetics parameters for unsaturated polyester at 0.433, 0.79, 3.90 and 5.66 mm for heating rate 20 ºC/min. Kinetic parameters (activation energy, frequency factor and reaction order) were obtained by curve-fitting the experimental data. The values of the activation energy were the following: 79.07, 88.09, 117.77 and 131.24 kJ/mol, for diameter of particle 0.433, 0.79, 3.90 and 5.66 mm, respectively. Based on the thermogravimetric analysis particle size were found to have significant influences on the pyrolysis of unsaturated polyester, a cheap and abundantly available solid waste. The temperature of the peaks in the DTG curve depends on the heating regime. The values the temperature of the peaks were 278, 300.5, 310.7 and 380.6 ºC, for particle size of the order of 0.433, 0.79, 3.90 and 5.66 mm, respectively. Using these kinetic parameters, a First-order model was used to predict the best rate heating. This model could fit the experimental data very well and the best of the heating rate was 20 20 ºC/min.

5. ACKNOWLEDGEMENTS

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