NON-ISOTHERMAL DECOMPOSITION KINETICS OF THE INTERACTION OF POLY(ETHYLENE TEREPHTHALATE) WITH ALKYD VARNISH

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The recycling of soft drink bottles poly(ethylene terephthalate) (PET) has been used as an additive in varnish containing alkyd resin. The PET, called to recycled PET (PET-R), was added to the varnish in increasing amounts. Samples of varnish containing PET-R (VPET-R) were used as a film onto slides and its thermal properties were evaluated using thermogravimetry (TG). Throughout the visual analysis and thermal behavior of VPET-R it is possible to identify that the maximum amount of PET-R added to the varnish without changing in the film properties was 2%.

The kinetic parameters, such as activation energy (E) and the pre-exponential factor (A) were calculated by the isoconversional Flynn–Wall–Ozawa method for the samples containing 0.5 to 2.0% PET-R. A decrease in the values of E was verified for lower amounts of PET-R for the thermal decomposition reaction. A kinetic compensation effect (KCE) represented by the $\ln A = -13.42 + 0.23E$ equation was observed for all samples. The most suitable kinetic model to describe this decomposition process is the autocatalytic Šesták–Berggren, being the model applied to heterogeneous systems.

Introduction

Industrial activity and household consumption generate continuously increasing amount of waste products that cause environmental troubles. Thermosets are amongst the environmentally most damaging waste products due to their low degradation. Thus, the recycling of those polymeric materials has become of great interest, not only to researchers and users but also in the aspect of environment protection. Currently one of the polymers present in large quantities in urban solid waste is poly(ethylene terephthalate) from recycled PET bottles, which can be used to produce a variety of goods such as fibers and films or incorporated as an additive to other types of plastics [1, 2].

Since recycled PET-R is a polycondensation polymer polyester formed by ethylene glycol (EG) and terephthalic acid (t-PA) it can be used in the synthesis of coating materials where alkyd resins are used. These coating polyesters are synthesized from PET, EG and t-PA present the structure and characteristics for a polyester synthesized from EG and phthalic anhydride (PA). Polycondensation, which takes place during the reaction causes the depolymerization of PET, EG and t-PA with unpredictable distribution in the polymer. The properties of the films formed from PET-R, EG and t-PA are comparable to those of conventional film coatings [3].

TG/DTG curves were used to obtain the thermal decomposition reaction and kinetic parameters of the alkyd resin of commercial varnish [4, 5].

The aim of this work is to study the decomposition reaction on the base of the TG curve of the film obtained from the reutilization of PET bottles which was used as an additive in commercial alkyd varnish.

Kinetic considerations

The mathematical description of the data from a single step solid-state decomposition is usually defined in term of a kinetic triplet, as activation energy, E, Arrhenius parameters, A and a mathematical expression of the kinetic model as a function of the fractional conversion α, $f(\alpha)$, which can be related to the experimental data as follows [6]:

$$\frac{d\alpha}{dt} = A\exp\left(-\frac{E}{RT}\right)f(\alpha) \qquad (1)$$

For dynamic data obtained at a constant heating rate, $\beta = dT/dt$, this new term is inserted in Eq. (1) which can be simplified as:

$$\frac{d\alpha}{dt} = \frac{A}{\beta}\exp\left(-\frac{E}{RT}\right)f(\alpha) \qquad (2)$$

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The activation energy from the dynamic data can be obtained from the Flynn–Wall isoconversional method [7, 8] using Doyle's approximation of $p(x)$ [9], which involves the measurement of temperature corresponding to fixed values of $p(x)$ obtained from experiments at different heating rates and plotting $\ln\beta$ *vs.* $1/T$:

$$\ln\beta = \left[\frac{AE}{Rg(\alpha)}\right] - 5.331 - 1.052\frac{E}{RT} \qquad (3)$$

where R=gas constant ($8.31432 \ K^{-1} \ J^{-1}$) and $g(\alpha)$=integral of $d\alpha/f(\alpha)$ from 0 to α.

This method allows us to obtain the apparent $E=E(\alpha)$ independently from the kinetic model. The pre-exponential factor is evaluated taking into account a first-order reaction and can be defined as [10]:

$$A = \frac{\beta E}{RT_m^2}\exp\left(\frac{E}{RT_m}\right) \qquad (4)$$

where T_m is the temperature of the sample and this is where the peak deflection occurs in the DTG curves.

An accurate procedure to predict the kinetic model described by Koga [11, 12] using data obtained from DTG curves, the activation energy and $\log A$ has been widely used. The selection of the kinetic model is based on the maximum value of the normalized $y(\alpha)$ and $z(\alpha)$ functions under non-isothermal conditions as follows:

$$y(\alpha) = \frac{d\alpha}{d\theta} = \frac{d\alpha}{dT}\exp\left(\frac{E}{RT}\right) \qquad (5)$$

and

$$z(\alpha) = h(\alpha)g(\alpha) = \frac{d\alpha}{d\theta}\theta \qquad (6)$$

where $d\alpha/d\theta$ is the reaction rate at infinite temperature at the corresponding α, and where β is the heating rate, $h(\alpha)$ is the empirical kinetic model function in its differential form and $g(\alpha)$ is the integral form. θ is the generalized time introduced by Ozawa [13, 14] for an Arrhenius-type rate constant and is given as:

$$\theta = \int_0^T \exp\left(-\frac{E}{RT}\right)\frac{1}{\beta}dT \qquad (7)$$

Experimental

Recycled PET bottles were washed, dried at room temperature, cut into pieces of approximately 2 mm² and dissolved using phenol/tetrachloromethane (1:1) at 60°C. Trichloromethane was used as solution stabilizing agent.

The commercial varnish studied was constituted of modified alkyd resin, vegetal oil, aromatic and aliphatic hydrocarbons, tensoactive and drying organomethalic compound agents. The varnish was solubilized using the same method as was applied to the PET-R solution.

Trichloromethane was added to the varnish to avoid the precipitation of PET-R in the mixture. Then the solutions were heated to 60°C separately. The PET-R solution was added drop by drop to the varnish solution under vigorous stirring. The mass-to-mass ratios of the varnish and PET-R solutions are presented in Table 1.

The varnish/PET-R mixtures (VPET-R) were then sprayed to form a film and dried at room temperature to verify that their visual appearance was effectively similar. The samples were collected after 48 h to analyze their physical-chemical behavior using TG method.

TG/DTG curves for the kinetic studies were performed using a TA Instruments SDT module under dynamic nitrogen atmosphere (50 mL min⁻¹) with an initial sample mass of around 9 mg. Heating rates of 10, 15 and 20°C min⁻¹ from 40 to 300°C were applied.

Results and discussion

Figure 1 presents TG curves of PET-R, varnish and VPET-R recorded in nitrogen atmosphere. It can be seen that PET-R decomposes in one step of mass loss only as does the varnish sample but it exhibits a lower thermal stability. VPET-R 1 presents a two-step thermal decomposition in the same temperature interval as the varnish sample with intermediate residue compared to PET-R and the varnish sample, as is shown in Table 2.

Figure 2 presents TG curves of PET-R, varnish and VPET-R 1 in synthetic air.

From Fig. 2 one can see that PET-R decomposes in two mass-loss steps while the varnish and the PET-R 1 samples decompose in three mass-loss steps as is presented in Table 3.

Both in an inert atmosphere and at air the mixture samples present similar thermal behavior to that of the varnish sample.

To establish the kinetic model for the decomposition reaction the kinetic parameters, the activation energy, E, and the pre-exponential factor, $\log A$, the

Table 1 PET-R and varnish mass-to-mass ratios in samples 1–5

Sample	1	2	3	4	5
Varnish (g)	10.0128	10.0046	10.0000	10.0053	10.0000
PET-R (g)	0.2003	0.1500	0.1006	0.0801	0.0503

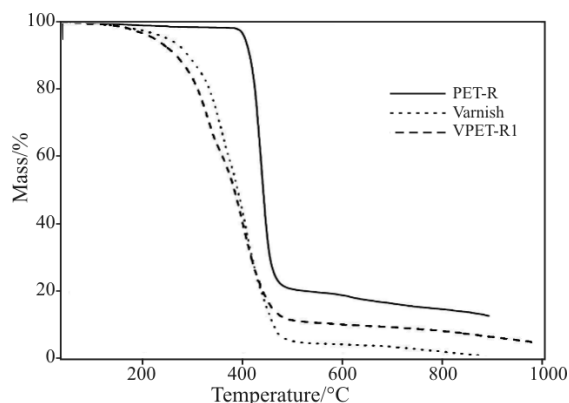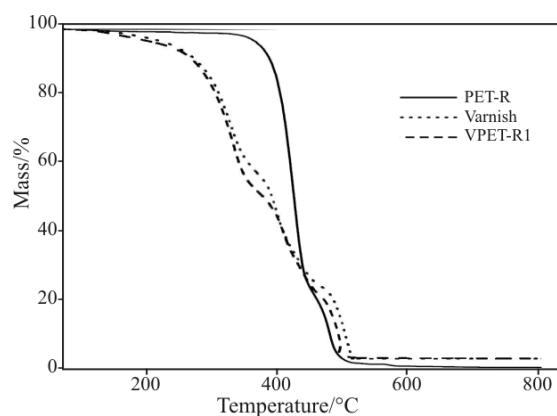**Fig. 1** TG curves of the decomposition of the PET-R, varnish and VPET-R 1 in nitrogen atmosphere at a heating rate of 10°C min⁻¹

Fig. 2 TG curves of the decomposition of the PET-R, varnish and VPET-R 1 in synthetic air atmosphere at a heating rate of 10°C min⁻¹

TG curves of sample 1 (VPET-R 1) were recorded at three different heating rates (5, 10 and 20°C min⁻¹) within the temperature range used in this study applying the Ozawa isoconversional method [6].

Figure 2 shows the α dependence of the apparent values of E. Nearly constant E values were obtained within the range of $0.1 \leq \alpha \leq 0.8$ with mean values of 357.0, 170.0, 199.6, 135.1 and 143.4 kJ mol⁻¹ for VPET-R 1–5, respectively. The constancy of the E value at different α is a prerequisite of the application of the general kinetic equation, i.e., Eq. (1) [11, 15].

Table 2 TG mass loss data for PET-R, varnish and VPET-R 1 in nitrogen

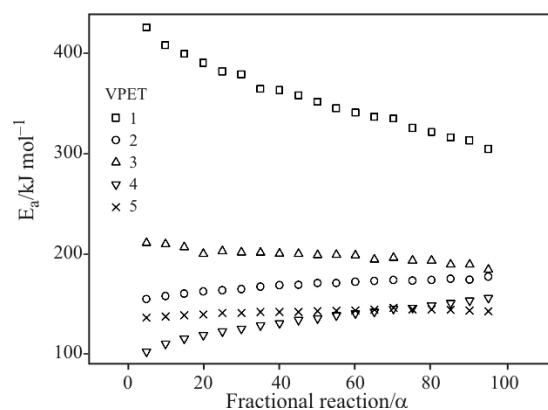| Sample	Step	ΔT/°C	Mass loss/%
PET-R	1	375–513	77.7
Varnish	1	214–519	86.6
VPET-R 1	1	195–360	37.6
	2	360–534	47.6

Fig. 3 The values of E at various α calculated using the Flynn–Wall–Ozawa method for the thermal decomposition VPET-R 1

Table 3 Mass loss for PET-R, varnish and VPET-R 1 in synthetic air

Sample	Step	DT/°C	Mass loss/%
PET-R	1	328–468	78.0
	2	468–540	20.6
Varnish	1	192–377	44.6
	2	377–476	30.7
	3	476–546	19.1
VPET-R 1	1	175–376	41.4
	2	376–479	33.5
	3	479–539	22.0

Table 4 presents E and log$A$ values for thermal decomposition reaction PET-R, varnish [4] and VPET R-1 to VPET R-5 samples.

The E and log$A$ of PET-R and varnish have similar values but with the addition of increasing amount of PET-R to the varnish the value of E shifted to higher values (from 143.4 to 357.0 kJ mol⁻¹). Increasing the amount of PET-R in the mixture should form products requiring larger activation energy for thermal decomposition.

The observed linearity of several fractional conversions indicates that the proposed kinetic model can be used to evaluate the decomposition reaction of VPET-R. It was observed that as the amount of PET-R decreases, E decreases, although not linearly.

When the E values were calculated it was possible to establish the best kinetic model to describe that set of measurements obtained from the TG curves.

To this end, the $y(\alpha)$ and $z(\alpha)$ functions were used since they can be easily obtained by transforming the experimental data expressed by Eqs (5) and (6), respectively.

The $y(\alpha)$ function is proportional to the $f(\alpha)$ function, which must be invariable in relation to the experi-

Table 4 Average E and log$A$ for PET, varnish [4] and PPET 1–5

Sample	Average E/ kJ mol^{-1}	Average log$A$/ min^{-1}
PET-R	170.6±6.8	20.16±0.69
Varnish	161.4±2.1	13.31±0.23
VPET 1	357.0±34.2	68.08±7.59
VPET 2	170.0±6.3	24.80±0.80
VPET 3	199.6±6.8	30.84±1.84
VPET 4	135.1±15.2	17.83±2.68
VPET 5	143.4±2.5	17.78±0.26

mental parameters, such as sample mass and heating rate (non-isothermal conditions) or temperature (isothermal conditions). Thus, the form of the $f(\alpha)$ function is obtained by plotting the normalized $y(\alpha)$ in the $0<y(\alpha)<1$ range, which is characteristic of a specific kinetic model. The $f(\alpha)$ function can be used to determine the model in which the $y(\alpha)$ function presents an α_y^* between 0 and α_z^*, which is the case in the JMA ($n>1$) and SB (m,n) models [16]. The α values between 0.1 and 0.9 and the respective temperatures were obtained from non-isothermal TG curves (recorded at 5, 10 and 20°C min^{-1} heating rates).

For the data obtained from the TG curves using Eqs (5) and (6) show that the $y(\alpha)$ function reaches a maximum when α_y^*=0.09 and $z(\alpha)$, α_z^*=0.61 for
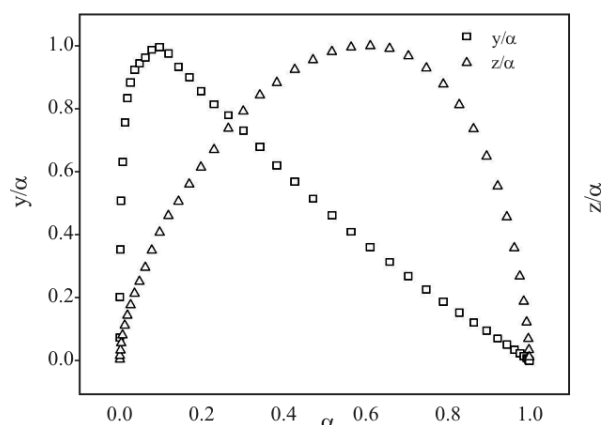

Fig. 4 The $y(\alpha)$ and $z(\alpha)$ functions calculated from the first step of the thermal decomposition of the VPET-R 1

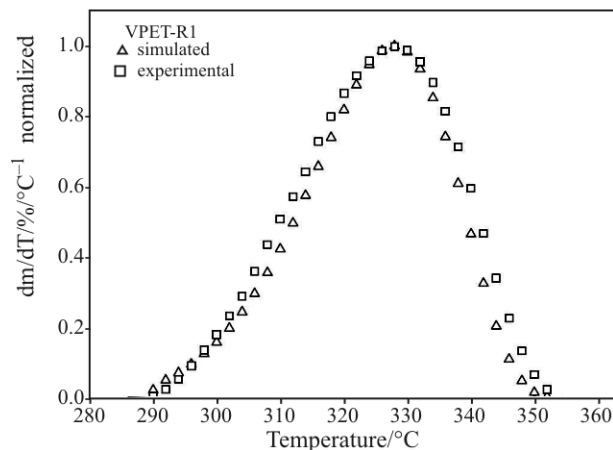**Fig. 5** Experimental and simulated DTG curves at 10°C min^{-1} for VPET-R 1

VPET-R 1 (Fig. 4). These results confirm that the Šesták–Berggren (SB) model is the most appropriate one to represent the curing process for these samples, which is represented by the $f(\alpha)=\alpha^m(1-\alpha)^n$ function [17].

The n kinetic exponent can be obtained from the angular coefficient of $\ln[d\alpha/dt)\exp(E/RT)]$ *vs.* $\ln[\alpha^p(1-\alpha)]$ at $0.2<\alpha<0.8$. In sample 1, n=1.23 and, therefore, m= 0.12, considering the $m=pn$ relationship where $p=\alpha_y^*/(1-\alpha_y^*)$.

Figure 5 presents the DTG curves for simulated and experimental data, which show that the Šesták–Berggren model describes the decomposition mechanism for sample 1 and that it can also be applied to the other samples.

The kinetic compensation effect

The kinetic compensation effect (KCE) was first developed in catalysis studies to account for the fact that different treatments of a catalyst resulted in a change in the calculated activation energy, but with no corresponding change in the reaction rate, which remains constant. To explain this it was suggested that the pre-exponential factor A varied with the activation energy according to Eq. (8).

$$\ln A = a + bE \tag{8}$$

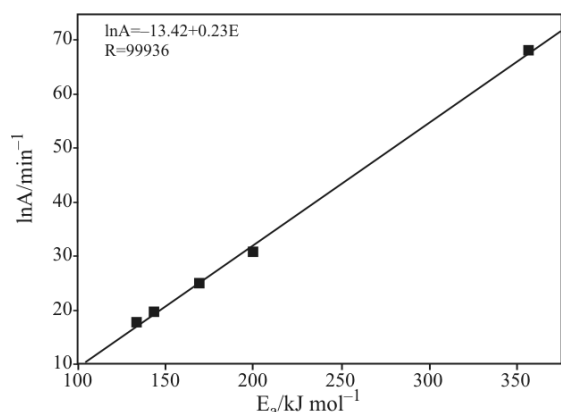where a and b are constants and act as compensation parameters.

Table 5 $y(\alpha)$ and $z(\alpha)$ maximum functions, kinetic exponents calculated from the SB model and the values of the kinetic parameters for the samples

Sample	α_y^*	α_z^*	n	m	E/kJ mol^{-1}	log$A$/min^{-1}
1	0.09	0.61	1.23	0.12	357.0	68.08
2	0.03	0.66	0.75	0.02	170.0	24.80
3	0.16	0.63	0.93	0.18	199.6	30.84
4	0.03	0.72	0.72	0.02	135.1	17.83
5	0.39	0.82	0.82	0.52	143.4	17.78

Fig. 6 Arrhenius plots of ln$A$ *vs.* E for the decomposition reaction of VPET-R 1

This effect can be observed in several types of reactions. The kinetic parameters (A and E) vary with the experimental conditions even if the mechanism does not change.

The thermal reaction of a polymer is a complex solid–gas reaction process. For the reaction of the decomposition of VPET-R 1, ln$A$ was plotted *vs.* E as it is shown in Fig. 6. Such a relationship indicates that

$$\ln A = -13.42 + 0.23E$$

In this study, it was verified that the amount of PET-R mass in the varnish increased up to 2% limit and the decomposition reaction mechanism in all the samples is the same, as observed from the sloping for the ln$A$ and E relationship [18–24].

Conclusions

Experimental data from the decomposition process under non-isothermal conditions allowed to determine the kinetic triplet (E, log$A$ and $f(\alpha)$). The kinetic analysis procedures applied in this work were consistent in order to obtain the kinetic parameters and a mathematical kinetic model function. The best fit between normalized simulated data and experimental data for the decomposition process was the autocatalytic SB kinetic model applied to heterogeneous systems.

The activation energy values were found to increase from 143.4 to 357.0 kJ mol^{-1} while the physical chemical properties of the film obtained such as its adherence, color and flexibility were similar to those of the commercial alkyd varnish making the process proposed here technologically viable.

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