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APPLICATION OF NON-ISOTHERMAL CURE KINETICS ON THE INTERACTION OF POLY(ETHYLENE TEREPHTHALATE) - ALKYD RESIN PAINTS

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Samples of paint (P), reused PET (PET-R) and paint/PET-R mixtures (PPET-R) were evaluated using DSC to verify their physical-chemical properties and thermal behavior. Films from paints and PPET-R are visually similar. It was possible to establish that the maximum amount of PET-R that can be added to paint without significantly altering its filming properties is 2%. The cure process (80–203°C) was identified through DSC curves. The kinetic parameters, activation energy (E_a) and Arrhenius parameters (A) for the samples containing 0.5 to 1% of PET-R, were calculated using the Flynn–Wall–Ozawa isoconversional method. It was observed that for greater amounts of PET-R added, there is a decrease in the E_a values for the cure process. A Kinetic compensation effect (KCE), represented by the equation $\ln A=-2.70+0.31E_a$ was observed for all the samples. The most suitable kinetic model to describe this cure process is the autocatalytic Šesták–Berggreen, model applied to heterogeneous systems.

Keywords: *paint, paint/PET-R mixture, PET*

Introduction

Industrial activity and household consumption generate an ever-growing amount of waste products that pose environmental risks and are a matter of concern for public environmental agencies. Thermosets are amongst the most environmentally 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 to those concerned with the protection of the environment. Currently, one of the polymers present in large quantities in urban solid waste is poly(ethylene terephthalate) from recycled PET bottles, which is used in the production of a variety of goods such as fibers and films, or incorporated to other types of plastics as an additive [1].

Since the 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 the coating materials where alkyd resins are used. These coating polyesters synthesized from PET, EG and t-PA present the structure and characteristics of a polyester synthesized from EG and phthalic anhydride (PA). The polycondensation that takes place during the reaction, causes the depolymerization of PET, EG and t-PA, with unpredictable distributions in the polymer. The properties of the films formed from PET-R, EG and t-PA are comparable to those of conventional film coatings [2]. The TG/DTG curves have been used to establish the thermal decomposition reaction and kinetic parameters of alkyd resin from commercial varnish [3].

The aim of this work is to evaluate the cure reaction, by DSC curve, of the film obtained through the reutilization of PET bottles used as an additive in commercial alkyd resin paints.

Kinetic aspects

Using DSC non-isothermal procedures, the thermal decomposition of a material can be mathematically described by the kinetic triplet (E_a, $\log A$ and $f(\alpha)$). A solid-state Arrhenius-type reaction can be expressed by the general equation [4–7]:

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

where the fractional process of cure (α) is temperature (T) dependent during an increasing constant heating rate (β). Accordingly, the isoconversional Flynn–Wall–Ozawa method, that is the angular and linear coefficient of a plot of $\log\beta$ *vs.* $1/T$ at different and constant α, gives the $E_a(\alpha)$ and A values, respectively [4–7].

In order to calculate the best-fit kinetic model that represents reaction of cure, the $y(\alpha)$ and $z(\alpha)$ functions have been defined [8–10].

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The test to find the kinetic model proposed by Malek [11–13] is based on this equation and on the normalized $y(\alpha)$ and $z(\alpha)$ functions that, under non-isothermal conditions, are given by:

$$y(\alpha)=\phi\exp\left(\frac{E_a}{RT}\right) \tag{2}$$

$$z(\alpha)=\phi T^2 \tag{3}$$

It is possible to determine the kinetic models for each step in study by using $y(\alpha)$ and $z(\alpha)$ maximum functions, that is, α_m and α_p, respectively. Once the kinetic model is known, the corresponding functions can be verified [9, 10].

Experimental

Recycled PET bottles were washed, dried at room temperature, cut in pieces of approximately 2 mm^2 and solubilized using phenol/tetrachloromethane (1:1) at 60°C. Trichloromethane was used as the solution's stabilizing agent.

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

After the solutions had been separately heated to 60°C, the PET-R solution was added drop by drop to the paint solution, under strong stirring. The mass relations of the paint and PET-R solutions are presented in Table 1.

The paint/PET-R mixtures (PPET-R) were then spread in a film form on slides and wood 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 through DSC curves.

DSC recording was obtained using a DSC 2910 module from TA Instruments in a dynamic atmosphere of nitrogen (50 mL min^{-1}) covered with an aluminum crucible of 10 μL with a sample mass of around 2 mg, with the aluminum crucible as reference material and heating rates of 10, 15 and 20°C min^{-1} from 40 up to 300°C. The E_a and log$A$ kinetic parameters were calculated using a DSC ASTMK software running in a V4.08 from TA Instruments.

Table 1 PET-R and paint mass relations in samples 1–3

Sample	PET-R/g	Paint/g
1	0.0505	10.0442
2	0.0835	9.9985
3	0.1014	10.0872

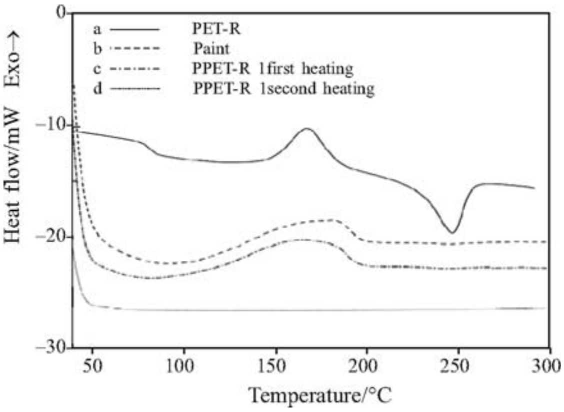

Fig. 1 DSC curves to PET-R, paint, PPET-R 1 first heating and second heating, nitrogen atmosphere, heating rate 10°C min^{-1}

Results and discussion

The DSC curve for PET-R, for the second heating, Fig. 1a, presents three characteristic events comparable with data reported in the literature [2]: *Tg* (vitreous transition temperature) at ~65°C, *Tc* (crystallization temperature) at 150°C and *Tm* (melting temperature) at 250°C.

The DSC curve for paint (Fig. 1b) shows the thermal event in the temperature interval 90–205°C due to the curing reaction. The DSC curve for PPET-R 1, (Fig. 1c) presents an exothermic peak (80–203°C) on the first heating caused by the curing reaction of the sample, while in the second heating curve, (Fig. 1d) that peak has disappeared, indicating a complete reaction that is, the material had already been completely cured.

To establish the kinetic model for the curing reaction, the kinetic parameters, the activation energy, E_a, and the pre-exponential factor, log$A$, were obtained from the DSC curve of sample 1 (PPET-R 1) at three different heating rates (10, 15 and 20°C min^{-1}) within the temperature range used in this study applying the Ozawa isoconversional method [5, 6, 15].

Figure 2 shows the α dependence of the apparent values of E_a. The nearly constant E_a values were obtained at a range of $0.1\leq\alpha\leq0.8$ with mean values of 94.34, 86.07 and 71.40 kJ mol^{-1} respectively for PPET-R 1, 2 and 3. The E_a values being similar at different α is a prerequisite for the application of the general Eq. (4). The results in Fig. 2 indicate that the present reaction can be treated within the restricted range of $0.1\leq\alpha\leq0.8$ [15].

$$\left(\frac{d\alpha}{dt}\right)=A\exp\left(-\frac{E_a}{RT}\right)f(\alpha) \tag{4}$$

The observed linearity of several fractional conversions indicates that the proposed kinetic model can be used to evaluate the curing reaction of PPET-R. It

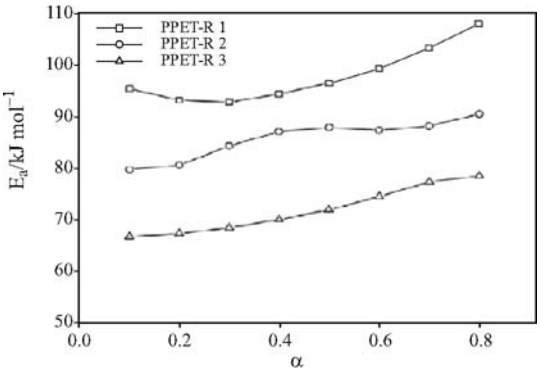

Fig. 2 The values of E_a at various α calculated by the Flynn–Wall–Ozawa method, to PPET-R 1, 2 and 3

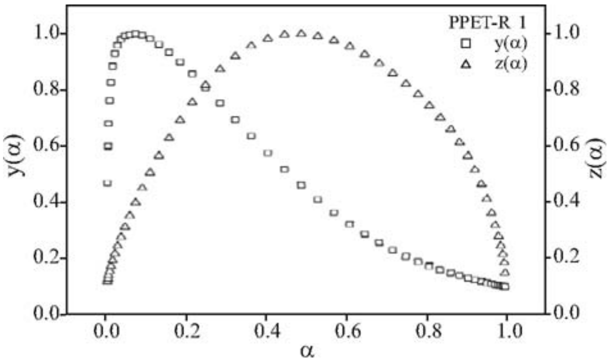

Fig. 3 The $y(\alpha)$ and $z(\alpha)$ functions calculated from DSC data to PPET-R 1

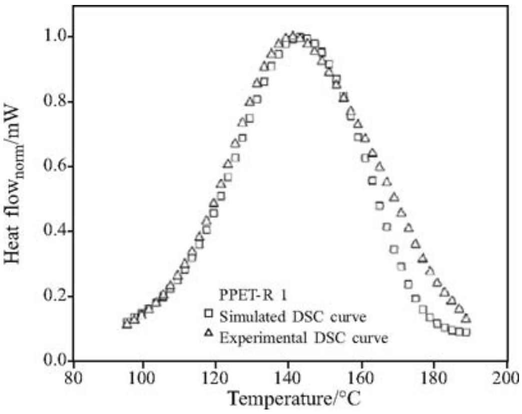

Fig. 4 Experimental and simulated DSC curves at 20°C min^{-1} to PPET-R 1

was observed that, as the amount of PET-R decreases, E_a increases, although not linearly.

Once the E_a values had been defined, it was possible to establish the best kinetic model to describe that set of measures obtained through DSC curves.

To that end, the $y(\alpha)$ and $z(\alpha)$ functions were used, for they can be easily obtained by transformations of the experimental data expressed by Eqs (2) and (3), respectively.

The $y(\alpha)$ function is proportional to the $f(\alpha)$ function, which must be invariable in relation to the experimental parameters, such as mass sample 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 a range of <0–1>, which is the 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_m between 0 and α_p^∞, which is the case in the JMA (n>1) and SB (m,n) models [9]. The α values between 0.1 and 0.9 and the respective temperatures were obtained through non-isothermal DSC curves (10, 15 and 20°C min^{-1}), while the heating flow, ϕ, was obtained by subtracting the baseline values from those of the cure process curves.

DSC curves obtained using Eqs (2) and (3) show that the $y(\alpha)$ function yields a maximum when α_m=0.064 and $z(\alpha)$, α_p^∞=0.47 for the PPET-R 1 (Fig. 3). These results confirm that the Šesták–Berggren (SB) model is the most appropriate to represent the cure process for these samples, which is represented by the function $f(\alpha)=\alpha^m(1-\alpha)^n$.

The n kinetic exponent can be obtained from the angular coefficient of $\ln[\mathrm{d}\alpha/\mathrm{d}t)\exp(E_a/RT)]$ *vs.* $\ln[\alpha_p(1-\alpha)$ at $0.2<\alpha<0.8$. In sample 1, n=1.78 and, therefore, m=0.12, considering the relation $m=pn$, where $p=\alpha_m/(1-\alpha_m)$.

Figure 4 presents the DSC curves for simulated and experimental data, which show that the Šesták–Berggren model describes the cure mechanism for sample 1, and that it can also be applied to the other samples.

Table 2 presents the α_m, α_p^∞, n, m, E_a and log$A$, values for the cure reactions.

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 velocity the rate of the reaction remaining constant. To explain this, it was suggested that the pre-exponential factor A varied with the activation energy in accordance with Eq. (5).

$$\ln A = a + bE_a \quad (5)$$

where constants a and b are referred to as compensation parameters.

This effect has been observed in many types of reactions. The kinetic parameters (A and E_a) vary with the experimental conditions even if the mechanism does not change.

The thermal reaction of a polymer is a complex solid-gas. For the reaction of the cure of PPET-R 1,

Table 2 $y(\alpha)$ and $z(\alpha)$ maximum functions, kinetic exponents calculated through the SB model, and values of the kinetic parameters for the samples

Sample	α_m	α_p	n	m	E_a	log$A$
PPET-R 1	0.064	0.47	1.78	0.12	97.9	11.91
PPET-R 2	0.021	0.71	1.15	0.02	85.7	9.93
PPET-R 3	0.16	0.66	0.95	0.11	71.8	8.41

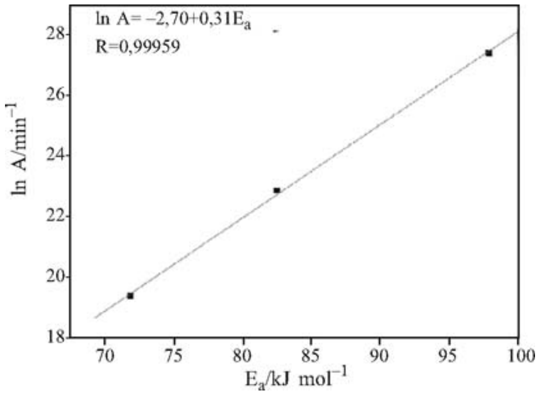

Fig. 5 Arrhenius plots of ln(A) *vs.* E_a for the cure reactions to PPET-R 1

ln$A$ was plotted *vs.* E_a, as shown in Fig. 5. Such relation indicates that

$$\ln A = -2.70 + 0.31E_a$$

In this study, it was verified that the amount of mass of PET-R in the paint increased until the 1% limit and the cure reaction mechanism, in all the samples is the same, as observed through the inclination of the straight line for the relation between ln$A$ and E_a [16–20].

Conclusions

Experimental data from the cure process in non-isothermal conditions allowed the kinetic triplet (E_a, log$A$ and $f(\alpha)$) to be calculated. The kinetic procedures applied in this work were consistent in order to obtain the kinetic parameters and a mathematical kinetic model function. Based on the best fit between normalized simulated data with the SB kinetic model function and experimental data, it was evident that the cure process presents an initial step explained by an induction characteristic applied to heterogeneous systems.

If was found activation energy values decreased from 97.9 to 71.8 kJ mol^{-1}, while the physical chemical properties of the film obtained were similar to those commercial alkyd paint, making the process proposed here, technologically viable.

Acknowledgements

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References

1 E. B. Mano and L. C. Mendes, Introdução a polímeros, Edgard Blucher Ltda, São Paulo 1999.
2 C. Kawamura; K. Ito, R. Nishida, I. Yoshihara and N. Numa, Prog. Org. Coat, 45 (2002) 185.
3 G. C. A. Amaral, M. S. Crespi, C. A. Ribeiro, M. Y. Hikosaka, L. S. Guinese and A. F. Santos, J. Therm. Anal. Cal., 79 (2005) 375.
4 J. H. Flynn and J. Wall, Polym. Lett., 4 (1966) 323.
5 T. Ozawa, Bull. Chem. Soc. Jpn., 38 (1965) 1881.
6 T. Ozawa, J. Thermal Anal., 2 (1970) 301.
7 T. Ozawa, Polymer, 12 (1971) 150.
8 J. Málek, J. M. Criado, J. Šesták and J. Militký, Thermochim. Acta, 153 (1989) 429.
9 J. Málek, J. Šesták, F. Rouquerol, J. Rouquerol, J. M. Criado and A. Ortega, J. Thermal Anal., 38 (1992) 71.
10 J. Málek, E. Cernesková, J. Svejka and G. Van der Plaats, Thermochim. Acta, 280/281 (1996) 353.
11 J. Malek, J. Therm. Anal. Cal., 56 (1999) 763.
12 J. Malek, Thermochim. Acta, 355 (2000) 239.
13 J. Málek, T. Mitisuhash and J. M. Criado, J. Mater. Res., 16 (2001) 1862.
14 A. R. Silva, M. S. Crespi, C. A. Ribeiro, S. C. Oliveira and M. R. S. Silva, J. Therm. Anal. Cal., 75 (2004) 401.
15 N. Koga, Thermochim. Acta, 258 (1995) 145.
16 R. MacCallun and M. V. Munro, Thermochim. Acta, 203 (1992) 457.
17 C. Gupta and S. G. Viswanath, J. Thermal Anal., 47 (1996) 1081.
18 T. P. Prasad, S. B. Kanungo and H. S. Ray, Thermochim. Acta, 203 (1992) 503.
19 M. E. Brown and A. K. Galwey, Thermochim. Acta, 387 (2002) 173.
20 A. K. Galwey, Thermochim. Acta, 413 (2004) 139.

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