

Evaluation by thermogravimetry of the interaction of the poly(ethylene terephthalate) with oil-based paint

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Abstract: The recycling of post-consumer soft-drink bottles poly (ethylene terephthalate) (PET) has been used as an additive in paint containing alkyd resin. Samples of paint containing PET (PPET) were applied in a film form on slides, and its thermal properties were evaluated for thermogravimetry (TG). The thermal behavior of PPET, it was possible to identify that the maximum of PET added to the paint without a change in the film properties was 1%. The kinetic parameters such as activation energy (E_a) and pre-exponential factor (A) were calculated using the isoconversional Flynn – Wall - Ozawa method for samples containing 0.5 to 1.0% of PET. The kinetic analysis indicates that there was a variation in E_a values. The kinetic compensation effect (KCE), represented by the equation $\ln A = 0.105E - 0.21$ for the first stage of thermal decomposition.

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Keywords: PET, paint oil-based, paint and PET, Non-Isothermal Kinetic

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INTRODUCTION

Paint have been used to several numbers of finishes, as makes the protection of walls, steel corrosion, concrete, improve aesthetic, among another one. Today, there are two principal types of paint, which are known as acrylic latex paint and oil-based (alkyd paint) [1]. The latex paint is made with water and acrylic resin which are called of binders. It can include the synthetic or natural resins such as acrylics, polyurethanes, polyesters, melamines, among others. While the oil-based are made of different oil, such as linseed oil, castor oil or alkyd resins are the primary binders for oil-based paints 100% acrylic or vinyl are binders for water based paint like latex or acrylic [2-4]. The oil-based contain a higher level of organic solvents, as hydrocarbon-based solvent as the vehicle and several alkyd resins, which are responsible for intense and characteristic odor, but both, oil-based and latex paints, use binders to solidify the paint and form a thin layer [4,5]. Oil paint was originally made with linseed oil as a binder, which has a high content of di- and tri-unsaturated esters, which are especially susceptible to polymerization reactions upon exposure to oxygen in the air. In fact, the polymerization occurs due the non-saturated molecules in the oil and are called *drying*, and results in the solidification of the paint [6]. The linseed oil, soybean, castor oil and coconut, and others are widely used in several paint types, especially for inferring different drying times. Moreover, the drying of these paints can be attributed in part by solvent evaporation and also in part by oxidation of the oil, allowing a plasticizing function [7,8].

The paints from alkyd resins, improved physicochemical properties, because oil based paints have a slow drying time and also exhibit poor weather ability and are also subject to yellowing. As a result, many properties have been improved because the alkyd resins allow combining different kinds of raw materials, given the reactions between polyalcohols (glycerine, pentaerythritol) and polyacid (phthalic acid). The process of drying alkyd paints takes place by evaporation of the solvent and also by oil oxidation. Upon this, the use of different polymers

added in these alkyd paints can improve the curing process [9-11].

Due to the 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. Furthermore, different sectors of society have been pushing for the reduction or recycling of polymeric materials. 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, or PET) from soft-drink bottles, which is used in the production a variety of goods such as fibers and films, or is incorporated into other types of plastics as an additive [12-14]. In Brazil, several polymers are amongst the most environmentally damaging waste products due to their slow degradation, as the post-consumer PET bottles were recycled [15].

As the PET is usually transparent and has excellent resistance to oxygen and carbon dioxide present in the atmosphere, it becomes a material of choice for bottling beverages, but when disposed of improperly, it becomes harmful to the environmental. Since recycled PET is a polycondensation polymer polyester formed from ethylene glycol (EG) and terephthalic acid (t-PA), it can be used in the synthesis of coating materials where alkyd resins are used. Many researchers tried to employ several techniques to modify the molecular structure of PET and prepare PET with high performance. These coating polyesters synthesized from PET, EG and t-PA have characteristics and structure similar to 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 random distributions in the polymer. The properties of the films formed from PET, EG and t-PA are comparable to those of conventional film coatings [16]. TG/DTG curves have been used to establish the thermal decomposition reaction and kinetic parameters of alkyd resin from commercial paint [17,18].

The aim of this work is to evaluate the decomposition reaction for TG curves of the film obtained from the post-consumer soft-drink bottles (PET) used as an additive in commercial alkyd paint (paint oil-based). Besides, the present study also improves the knowledge on the kinetic behavior of isoconversional method that was used as a way of obtaining reliable and consistent kinetic information and also to avoid the use of explicit kinetic models [16,19]. Thus, the activation energy ($E_a/kJ mol^{-1}$) data were obtained applying the method proposed by Flynn-Wall-Ozawa [19-21].

Kinetic considerations

The mathematical description of the data from a single-step solid-state decomposition is usually defined in terms of a kinetic triplet, as activation energy E_a , 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 [19].

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

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

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

The activation energy from the dynamic data can be obtained from the Flynn-Wall isoconversional method [20,21] using the Doyle's approximation [22] for $p(x)$, 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. $1/T$:

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

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 $E_a = E_a(\alpha)$ independent of the kinetic model. The pre-exponential factor is evaluated taking into account that this is a first-order reaction and can be defined as [23]:

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

EXPERIMENTAL PROCEDURES

Post-consumer soft-drink bottles were washed, dried at room temperature, cut into pieces of approximately $2 mm^2$ and for each gram of PET solubilized, were used 10 g of the phenol and 5 mL of the tetrachloromethane at $60^\circ C$. 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, surfactant and drying organometallic compound agents.

The soluble paint oil-based was also obtained in trichloromethane once it is used to avoid the precipitation of PET in the mixture.

After the solutions had been separately heated to $60^\circ C$, the PET solution was added drop by drop to the paint solution, under vigorous stirring. The mass relationships of PET to paint solutions are presented in Table 1. Also, the mass adopted were necessary to avoid the precipitation of PET in paint oil-based.

The paint/PET mixtures (PPET) 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 hours to analyze their thermal behavior by TG curves. Also, after prepare of the compound mixture was observed that the visual properties of the film obtained have similar characteristics of paint oil-based.

Table 1: PET and paint mass relationships for samples 1-3

Sample	1	2	3
Paint (g)	10.044	9.998	10.087
PET (g)	0.051	0.084	0.101

TG/DTG curves for the kinetic studies were performed using an SDT module from TA Instruments under a dynamic nitrogen atmosphere (50 mL min⁻¹), with initial sample mass around 9 mg. The heating rates of 10, 15 and 20°C min⁻¹ were used from 40 up to 800°C.

RESULTS AND DISCUSSION

The TG-DTA and DTG curves under synthetic air and nitrogen gas purge with the rate of 10°C min⁻¹, of this samples, are showed in Figures 1 and 2, respectively.

For analysis under nitrogen, the PET sample show to be stable until 378°C. The mass loss occurs one only stage up to 500°C, with the loss of 77.24%., while between 500 and 900°C this sample also exhibits a loss of 7.73%. This fact was attributed to the partial thermal decomposition of the sample, and therefore, this mass was converted to residue carbonaceous slowly during the heating. The TG/DTG curves of paint oil-based indicate that the thermal decomposition occurs three times between initial temperature and 500°C, while until 700°C occur other mass loss. After 700°C, the sample shows that is another mass loss, which was attributed to the inorganic filler of the paint. These values of mass losses are showed in Table 2. From Figure 1, also, it is possible to observe that PPET1, which has thermal behavior similar to the paint, with little weight variation difference between one and another (Table 2). However, the major difference can be seen from 700°C, which shall not be regarded mass loss only occurs in the ink. It was attributed to the interaction between pet and ink, which changed the thermal behavior of inorganic filler paint. For the other

samples, PPET2 and PPET3, the thermal behavior shows a similar profile, but have little variation in the mass loss, more intensely in the fourth stage of thermal decomposition. It demonstrates that the used amount of PET is suitable for use, taking into account that larger quantities of PET mixture cause the precipitation of material in the paint.

In addition to this work, we showed the TG and DTA curves in Figures 2 and 3, respectively, which were carried out in the synthetic air only for sample PPET1, which is intended only to show a comparison of thermal behavior in other gas. The TG/DTG curves of PET in the synthetic air indicate that the thermal stability is low about analysis under nitrogen gas purge, as see in Table 3. This analysis also shows that there are two main stages of thermal decomposition, where the first stage occurs between 328 – 468°C and the second mass loss in the interval of 468 – 540°C, without formation of carbonaceous residue to the final analysis. The analysis of paint, the DTG curve show that the thermal decomposition occurs three stages, between initial temperature and 390°C, 390 – 490°C and 490 – 570°C, where the losses can be seen in Table 3. So, also, it is important to observe that the paint shows 12.66% of residue mass in the final of the analysis, which was attributed to the inorganic filler of the paint, as was seen in nitrogen analysis. The TG analysis of mass loss PPET1 sample shows that the thermal behavior is similar to the paint, but the mass loss is lower (Table 3) in this case, indicating that the interaction the paint and PET favor the thermal stability of the compound. Besides, the amount of residues, in the final analysis, was 26.41%, which is higher that the paint.

Table 2: TG data of the mass loss observed in a nitrogen atmosphere (50 mL min^{-1}) with a heating rate of $10^\circ\text{C min}^{-1}$ for PET, paint, and PPET1.

Sample	Stage	$\Delta T / ^\circ\text{C}$	mass loss/%
PET	1	30 – 378	1.82
	2	378 – 500	77.24
	3	500 – 900	7.73
Paint	1	30 – 120	1.55
	2	120 – 250	6.45
	3	250 – 369	21.7
	4	369 – 500	36.17
	5	500 – 700	2.86
	6	700 – 900	13.20
PPET 1	1	30 – 120	1.11
	2	120 – 250	4.63
	3	250 – 369	20.51
	4	369 – 500	39.29
	5	500 – 700	2.87
	6	700 – 900	2.41
PPET 2	1	30 – 120	1.01
	2	120 – 250	4.64
	3	250 – 365	19.90
	4	369 – 500	34.81
	5	500 – 700	3.03
	6	700 – 900	2.10
PPET 3	1	30 – 120	1.17
	2	120 – 250	5.04
	3	250 – 364	19.95
	4	369 – 500	38.42
	5	500 – 700	3.18
	6	700 – 900	2.10

Now, when we see the analysis of synthetic air, the mass loss of the paint it is different from that observed in nitrogen. Note that the mass loss between the initial temperature and 570°C for both samples is greater in paint pure, which is attributed to the interaction between the material and oxygen. However, under a nitrogen atmosphere, there is an additional loss at the end of the analysis. Furthermore, it is also possible to see that the paint sample with PET has a smaller mass loss of the paint, indicating that this interaction favors the thermal stability. As an additional analysis, the DTA curve, Figure 3, for PET sample exhibit an exothermic reaction for second thermal decomposition stage. This fact also is seen to paint and PPET1 sample, where both reactions show

similarity, and therefore without significant thermal event in the interval of 400 to 600°C .

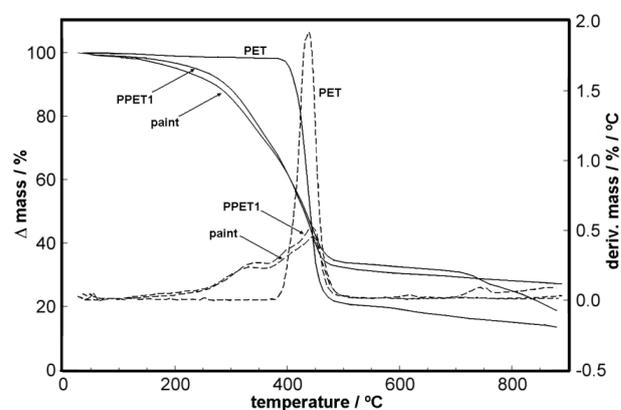


Figure 1: TG/DTG curves for the decomposition of the PET, paint and PPET 1 in nitrogen atmosphere with a heating rate of 10°Cmin^{-1} .

Table 3– TG data for the mass loss observed in a synthetic air atmosphere (50 mL min^{-1}) with a heating rate of $10^\circ\text{C min}^{-1}$ for a sample of PET, paint and PPET 1

Sample	Stage	ΔT ($^\circ\text{C}$)	Weight loss (%)
PET	1	30 – 328	1.30
	2	328 – 468	77.63
	3	468 – 540	21.01
Paint	1	30 – 390	31.30
	2	390 – 490	40.56
	3	490 – 570	15.48
PPET 1	1	30 – 392	24.75
	2	392 – 501	38.02
	3	501 – 575	10.82

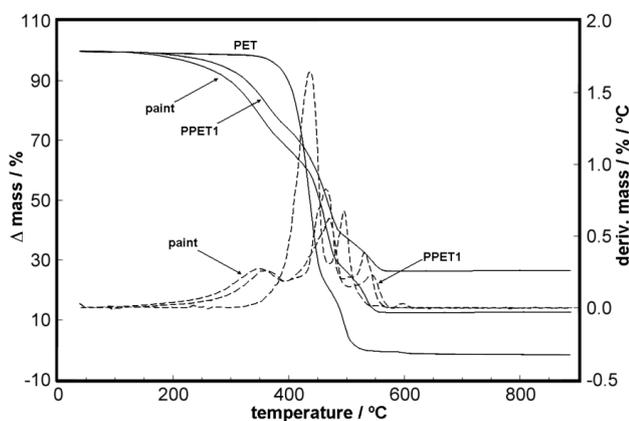


Figure 2: TG/DTG curves for the decomposition of the PET, paint and PPET 1 in a synthetic air atmosphere with a heating rate of $10^\circ\text{C min}^{-1}$.

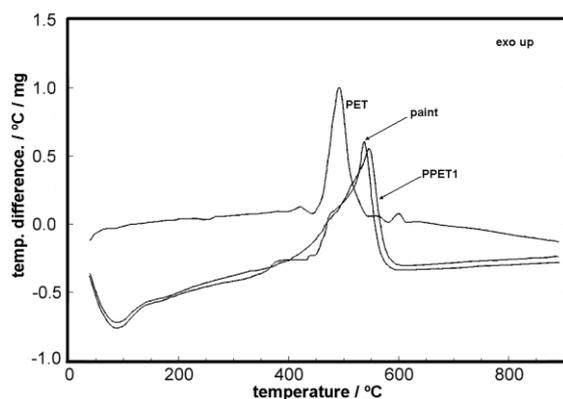


Figure 3: DTA curves for the decomposition of the PET, paint and PPET 1 in a synthetic air atmosphere with a heating rate of $10^\circ\text{C min}^{-1}$.

Kinetic parameters

To establish the kinetic model for the decomposition reaction, the kinetic parameters, the activation energy, E_a , and the pre-exponential factor,

$\log A$, TG/DTG curves of sample 1 (PPET 1), Figure 4, were obtained at three different heating rates (10 , 15 and 20°Cmin^{-1}) within the temperature range used in this study such as to apply the Ozawa isoconversational method [15].

The activation energy (E_a) versus conversion degree (α) values for the decomposition stage is shown in Figure 5. The nearly constant E_a values were obtained within the range of $0.05 \leq \alpha \leq 0.95$ with average values for the first stage of 78.0 kJ mol^{-1} , 69.5 kJ mol^{-1} and 70.8 kJ mol^{-1} for PPET1, PPET2, and PPET3, respectively while the mean value of PET was $170.6 \text{ kJ mol}^{-1}$ [15].

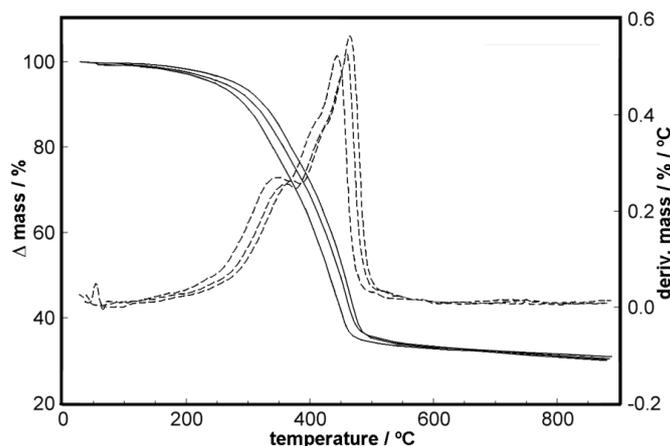


Figure 4: TG/DTG curves for the decomposition of PPET 1 in nitrogen gas purge with a heating rate of 10 , 15 and $20^\circ\text{C min}^{-1}$.

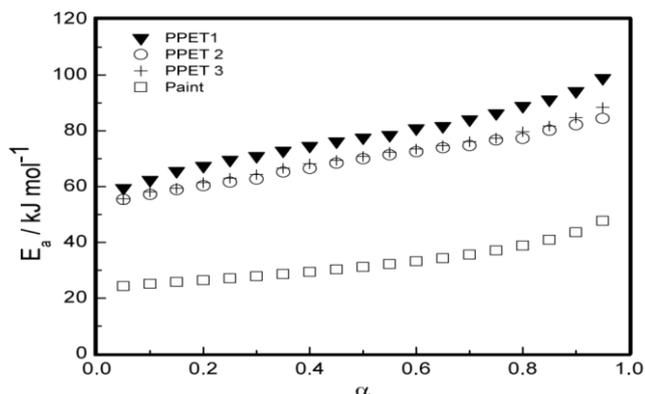


Figure 5: The values of E_a at various α calculated using the Flynn-Wall-Ozawa method for the thermal decomposition of PPET samples 1-3 and paint oil-based.

The analysis show that it is evident that the apparent activation energy is more high that paint evaluation and also show that there weren't appreciable variation on the conversion degree (α). Moreover, when TG/DTG curves are evaluated, we can see that there is an overlapping reaction at the beginning of thermal decomposition, which would explain the kinetic behavior at the beginning. Furthermore, It could be associated with the non-complex superficial reaction. Besides, the linearity observed in conversion degree indicates that the samples have the same decomposition reaction, as seen in TG/DTG curves. Moreover, in another studies previously published by Kobelnik *et al.* about vegetable oils, the kinetic behavior is often not similar to the observed thermal behavior [24, 25].

Also, the behavior observed can be used to the evaluation of the kinetic compensation effect (KCE). This parameter 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 without modification in the reaction velocity and with the rate of the reaction remaining constant. As an explanation, it was suggested that the pre-exponential factor A varied with the activation energy by Equation 5.

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

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

This effect has been observed in many reactions, where the kinetic parameters (A and E_a) vary with the

experimental conditions even if the mechanism does not change. However, it is important to note that the presence of a certain set of variables, such as impurities, size, the sample size, particle size and distribution of the particles, the heating rate, in the sample, or the presence of gaseous atmosphere surrounding the sample can cause influence in activation energy. Thereby, the thermal reaction of a polymer is a complex solid-gas reaction, and its mechanism remains largely unclear since it may take place via either radical chain depolymerization or disproportions of the end chain scission reactions. Each group of process rates that constitutes compensation set, an identified fit of A and E_a values, contains common chemical characteristics.

For decomposition of PPET mixtures 1-3, $\ln A$ was plotted against E_a , as shown in Figure 6. To calculate the activation energy, a conversion degree of α between 0.05 and 0.95 were used for each sample. The existence of kinetic compensation for the three sample is observed from the scattering of the points such that a straight line does not occur, thus suggesting that the equation for this step corresponds to $\ln A = 0.1706E - 6,949$ with $r^2 = 0.99987$. The linear depending confirms that the analyzed samples have a similar degradation mechanism in two stages, the line slope being 0.005 about [26]. Therefore, in this study, it was verified that the amount of mass of PET in the increased up to a limit of 1% limit. The decomposition reaction mechanism for all the samples was the same, as is observed from the sloped straight line for the relationship between $\ln A$ and E_a [27-33].

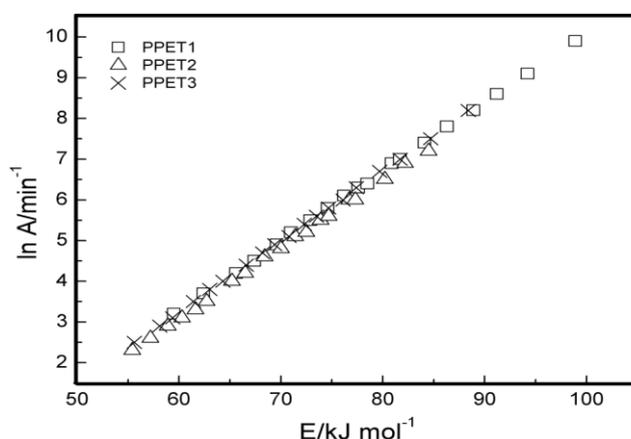


Figure 6: Arrhenius plots of $\ln (A)$ vs. E_a of the decomposition reaction PPET, with mixtures 1-3.

CONCLUSION

After preparing the compound, the mixture was observed that the visual properties of the film obtained have similar characteristics of paint oil-based. The TG/DTG curves were carried out in non-isothermal conditions. It became closer to the real conditions existing in industrial practice. So, the experimental data obtained from the decomposition process of TG/DTG curves, under the non-isothermal condition, allowed getting the Arrhenius parameters and calculating the activation energy (E_a). It was found that activation energy values linearly increased and while the paint oil-base has a low activation energy, which was attributed to the mixture of PET sample in paint oil-based.

The kinetic behavior of the thermal decomposition of PPET mixtures 1-3 can be correlated with the kinetic compensation effect (KCE) because there was a linear relationship between $\ln A$ and E_a , which reveals phenomena attributed to the similar thermal decomposition. Besides, this fact indicates that there was a well homogenized sample during the preparation of paint oil-base and PET sample.

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