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KINETIC PARAMETERS OBTAINED FOR THERMAL DECOMPOSITION OF ACRYLIC RESINS PRESENT IN COMMERCIAL PAINT EMULSIONS

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Samples of water based commercial acrylic resin paints were spread in a film form on slides, dried at room temperature and exposed to solar radiation for up to eight months.

The characterization and quantification of resins and charges in the white paint emulsion were carried out for the thermal decomposition. Besides this, X-ray diffractometry was used to identify $CaCO_3$ as charge and TiO_2 (rutile phase) as pigment.

It was observed through thermal techniques similar behavior to the samples even though with varied exposure time.

Kinetic studies of the samples allowed to obtain the activation energy (E_a) and Arrhenius parameters (A) to the thermal decomposition of acrylic resin to three different commercial emulsion (called P_1, P_2, P_3) through non-isothermal procedures. The values of E_a varied regarding the exposition time (eight months) and solar radiation from 173 to 197 kJ mol^{-1} (P_1 sample), from 175 to 226 kJ mol^{-1} (P_2 sample) and 206 to 197 kJ mol^{-1} (P_3 sample).

Kinetic Compensation Effect (KCE) observed for samples P_2 and P_3 indicate acrylic resin *s* present in these may be similar in nature. This aspect could be observed by a small difference in the thermal behavior of the TG curves from P_1 to P_2 and P_3 sample.

The simulated kinetic model to all the samples was the autocatalytic Šesták–Berggreen.

Keywords: *acrylic resin, kinetic parameters, paint emulsions, thermal behavior*

Introduction

Residential paints are used to yield better esthetic and to protect the surfaces. In a general way, resins, pigments, charges, solvents and solid and liquid additives, constitute the paint.

Paint can be defined as a pigmented dispersion in an agglomerate medium that, to be applied to a surface or substrate (a) can form spontaneously a thermoset dry layer without some chemical reactions among its constituents (b) needs a modification of the one constituent element or resin, usually by catalyst actions.

Acrylic resins are known as polyester, and so are macromolecules formed by esterification reaction of a polyacid and a polyalcool modified with fatty acid or oil. They are present around 29–31% in the general formulation of a paint, and are the component in which acting as main function in the formation of the thin layer, resulting in differential properties in relation to the final characteristic of a film depending on its structure. Today, the acrylic paints are the most ones utilized as interior well as exterior coating [1].

The kinetic of acrylic resin thermal degradation has been studied from non-isothermal data. Thermogravimetry analysis (TG) and its first derivative (DTG) have been successfully applied to establish the thermal degradation of a polymer particularly, acrylic resins. X-ray diffractometry has been used to analyze the charges and pigments.

In order to understand and to predict the behavior of the paint in function of temperature or radiation, the kinetic parameters like activation energy (E) and pre-exponential factor (A) have been calculated applying Kissinger or Flynn–Wall–Ozawa (F–W–O) methods. Nevertheless, the kinetic model, ($f(\alpha)$), where α is the fractional reaction of resin decomposition, still remains without a representative function in relation to its specific kinetic exponentials. Resin degradation was studied using TG in order to calculate the kinetic triplet (E, $\log A$ and $f(\alpha)$) from experimental non-isothermal conditions.

Kinetic consideration

By using TG non-isothermal procedures, the thermal decomposition of a material can be mathematically described by the kinetic triplet (E, $\log A$ and $f(\alpha)$).

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A solid state Arrhenius-type reaction can be expressed by the general equation [2–5]:

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

where the fractional degradation (α) is temperature (T) dependent during as increasing constant heating rate (β). Accordingly, the isoconversional F–W–O method, that is the angular and linear coefficient of a plot of log β *vs.* $1/T$ at different and constant α, gives the $E(\alpha)$ and A values, respectively [2–5].

In order to calculate the best kinetic model that represents acrylic resin decomposition, the $y(\alpha)$ and $z(\alpha)$ functions have been defined [6–8]. Koga has used the generalized time introduced by Ozawa to calculate these functions from non-isothermal thermogravimetric data for a solid-state reaction, since the E and log$A$ are known [9–12].

$$y(\alpha)=\frac{\mathrm{d}\alpha}{\mathrm{d}\theta}=Af(\alpha);\ z(\alpha)=y(\alpha)\theta=f(\alpha)g(\alpha) \qquad (2)$$

The maximum of the normalized $y(\alpha)$ and $z(\alpha)$ functions *vs.* α plot is an indicative of the kinetic model function and kinetic exponents that theoretically better represent the studied process [7, 13, 14].

Thus, it is possible to define the kinetic triplet that better represent the resin thermal decomposition mechanism.

Experimental

Acrylic paint samples from three different commercial sources were spread in a film form on slides, dried at room temperature and exposed to the solar radiation in a closed support during eight months in angle of 23° northward.

TG/DTG curves for the kinetic studies were performed using TA Instruments, SDT 2960 module, under dynamic nitrogen atmosphere (100 mL min^{-1}), sample mass around 7 mg and heating rates of 5, 10 and 20°C min^{-1} from 40 up to 900°C.

Results and discussion

Figure 1 shows the representative TG/DTG curves of the P_2 sample recorded at different exposure time. There is no significant mass change in the TG curves indicating similarities in the thermal behavior. It is verified three mass loss steps in TG curves obtained under nitrogen atmosphere at 20°C min^{-1}and mass around 7 mg.The first step is related to the solvent with mass loss of 1.5% (60–230°C), the second one attributed to the thermal decomposition of the acrylic resin with mass loss of 20.5% (300–530°C) and the third one due to the thermal decomposition of $CaCO_3$ with mass loss of 16.5 (550–800°C).

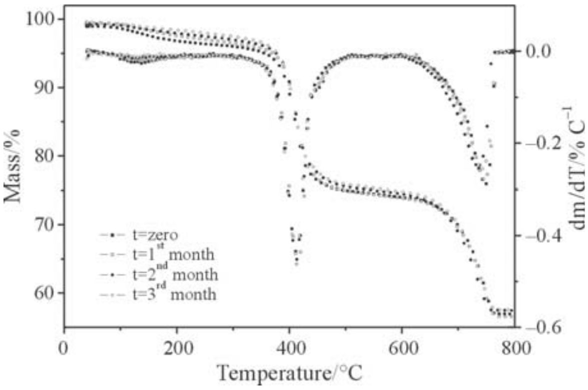

Fig. 1 TG/DTG curves of the P_2 sample at different exposure time, *m*~7 mg, 20°C min^{-1}, nitrogen atmosphere (100 mL min^{-1})

Figure 2 represents TG and DTA to P_2 sample under nitrogen and synthetic air atmospheres. It is verified just a difference in thermal stability through TG curves, that is lower in oxidant atmosphere but with the same final product of thermal decomposition, which was characterized by X-ray diffractometry, as CaO and TiO_2 (rutile phase) from the thermodecomposition of the charge ($CaCO_3$) and of the pigment constituents of the white paint, respectively. Three mass losses are also observed in TG curves and the corresponding endothermic peaks in DTA curves. The only difference observed is the presence of exothermic peaks in the curve obtained under oxidant atmosphere, which is related to the thermal decomposition of the resin.

Thus, kinetic calculations will be presented only for one of the eight-month samples, however they may be extrapoled for the other samples and periods.

The kinetic parameters E and log$A$ of the thermal decomposition were obtained applying the Flynn-Wall isoconversional method [15] to the first step of thermal decomposition. For each fixed fractional con-

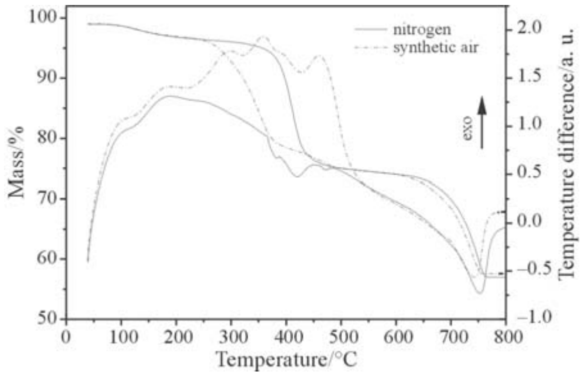

Fig. 2 TG/DTA curves of the P_2 sample at different atmospheres (100 mL min^{-1}), *m*~7 mg, 20°C min^{-1}

Table 1 E and log A (average values), maximum of the functions $y(\alpha)$ and $z(\alpha)$ (α^*_y, and α^*_z) and kinetic exponents (m and n) for three different commercial acrylic paints after eight months of radiation exposition

Samples	E/kJ mol^{-1}	log$A$/min^{-1}	α^*_y	α^*_z	m	n
P_1	197	16.82	0.19	0.50	0.30	1.28
P_2	226	17.39	0.19	0.60	0.26	1.07
P_3	197	15.49	0.28	0.52	0.56	1.46

version, α, the E could be calculated from the slope of lnβ *vs.* 1000/T plot and then the corresponding log$A$. The average values l can be seen in Table 1.

DTA curves show exothermic and endothermic peaks corresponding to the resin decomposition to air and N_2 atmosphere, respectively.

Dollimore's methods [16, 17] could be applied for the DTG curve to obtain the peak temperature, T_p=410°C, at $(d\alpha/dT)_{max}$, (HW=Hi T–Lo T, which is the difference between the high-temperature and low-temperature at half-width of the DTG peak). Through the results it can be obtained F1 (first reaction order, $f(\alpha)=(1-\alpha)$) as the most suitable kinetic model. Once knowing the average E and log$A$, α–T relation and $f(\alpha)$, the corresponding normalized simulated dα/dT *vs.* T plots could be obtained and compared to the normalized experimental DTG curves (Fig. 3).

Applying Koga's procedure [11, 18] for the data taken from DTG curve (Fig. 1) the first thermal decomposition reaction, the kinetic model can be obtained through the $y(\alpha)$ and $z(\alpha)$ functions *vs.* α. The maximum was found at α^*_y=0.19. The behavior which $0<\alpha^*_y<\alpha^*_z$ and α^*_z=0.60 belongs to autocatalytic Šesták–Berggreen model, where $f(\alpha)=\alpha^m(1-\alpha)^n$ [19]. The kinetic exponent n could be obtained through the slope of the linear regression from $\ln[(d\alpha/dt)\exp)E/RT)]$ *vs.* $\ln[\alpha^p(1-\alpha)]$ plot considering that α values are between 340 and 440°C that yields n=1.07. The kinetic exponent m=0.26 could be calculated from the relation m=p.n, where $p=\alpha^*_y/(1-\alpha^*_y)$.

Thus, knowing that $f(\alpha)=\alpha^{0.26}/(1-\alpha)^{1.07}$ for SB model, besides E, log$A$ and α–T relation, the corresponding normalized simulated dα/dT *vs.* T plot can be obtained and compared with the normalized experimental DTG curves (Fig. 3).

Besides E values presented similar to the conversion degree interval studied when it is compared with relation to the exposure time it is verified that the E values increase with the exposition time, that is, it is necessary higher energy to occur the reaction. To P_2 sample the found values are 175 and 226 kJ mol^{-1} to zero and eight months, respectively (Fig. 4).

Similar studies were carried out to commercial alkyd varnish and thermogravimetric data applying Flynn-Wall isoconversional method presented E=176–154 kJ mol^{-1} for different commercial sources at 95% confidence level which F_1, SB and JMA model can be applied taking into account the formal mathematic description to represent the real mechanism of thermal decomposition [20].

Considering the case of heterogeneous reactions in the solid state, the kinetic parameters, E and A, lose their relevance because the concepts of 'order of reaction' and 'concentration' are not applicable. Rising temperature, E and A values have no well-defined meaning, being both treated merely as derived parameters [21, 22].

Through literature, it is known that E values depend heavily on the experimental factors as sample size, particle size and its distribution, heating rate, presence of impurities in the sample, gaseous atmo-

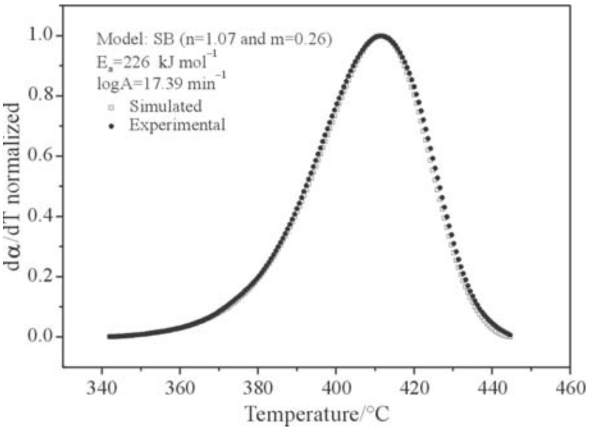

Fig. 3 Normalized simulated and experimental DTG curves of the P_2 sample

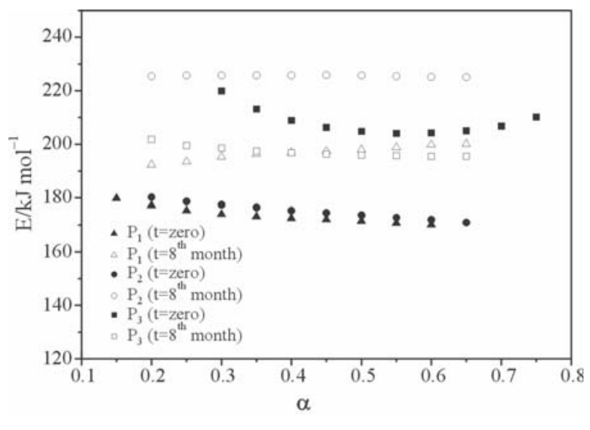

Fig. 4 Activation energy relation with conversion degree to different samples to zero and eight months

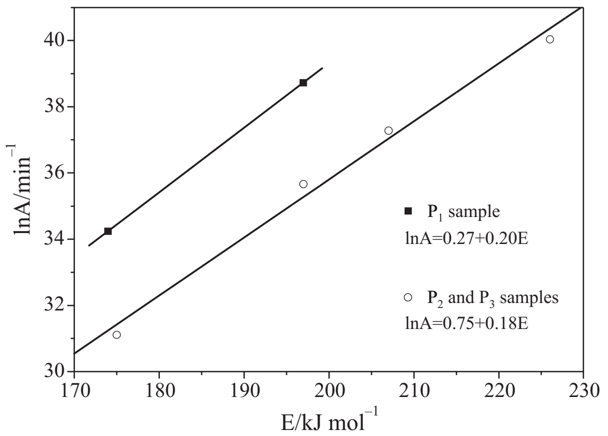

Fig. 5 Kinetic compensation effect to different samples

sphere and that for a reaction under varying experimental conditions, there is a linear relationship between *E* and *A*, generally known as the 'kinetic compensation effect' (KCE), expressed mathematically as $\ln A=a+bE$, where *a* and *b* are characteristic of the system. So, the observation of this reaction can be used to predict the effect of experimental parameters on kinetics, which gives hope for a better utilization of experimental *E* and *A* values in practical applications [21].

Figure 5 shows that the KCE is observed to P_2 and P_3 samples, but with different mathematic expression to P_1 sample.

Conclusions

For the thermal decomposition reaction of acrylic paints, the Šesták–Berggreen model can be applied. The kinetic compensation effect was observed to the samples, with different mathematic expression, which were also realized through the small difference in the thermal behavior in TG curves.

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