

Thermal Degradation of Unsaturated Polyester-Porcelain Powder Composite Material

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Abstract:- The objective of this study was to investigate the thermal degradation of composite based on unsaturated polyester resin. The degradation of UPR and composite were studied by thermal gravimetric analysis (TGA). Several non-isothermal experiments at different heating rates were performed. The isoconversional kinetic analyzing using the integral procedure was applied to the non-isothermal TGA results. Energy of activation of degradation for the composite, as well as for the unmodified UPR, was calculated by the isoconversional Kissinger-Akahira-Sunose method, and was found to be different for the composite than for the UPR system. The degradation process was described by n-th reaction order. The results indicated that presence of inorganic network influences the mechanism of degradation of organic phase.

Keywords:- KAS method, Composite material (PP), UPR-unsaturated polyester resin, degradation kinetics, Thermogravimetric analysis

1. INTRODUCTION

For many years, unsaturated polyester resin composites have been used in very varied technologies, like manufacture article for sanitary furniture, panels, pipes, boats [1], The UP comes from their low cost and easy processing and has good thermal properties.....

Their processing consist of two polymer, a short chain polyester containing polymerisable double bonds and a vinyl monomer that serves as solvent for unsaturated polyesters and reduces its viscosity, such as styrene which is most commonly used [1],

Due to their widespread use, many of the investigation of thermal degradation of different kinds of resins have been carried out using thermal methods, especially thermogravimetry [2-5].

2. EXPERIMENTAL

2.1 Materials

The resin composition containing propylene glycol, phthalic anhydride, maleic anhydride and styrene at 34% as cross linking agent. The original porcelain powder of ceramic industry waste is used in the formulation of unsaturated polyester resin composite material with a size particle of 180µm. The content of this filler is 50(w/w) dispersed in polymeric matrix with the respect a better homogenization and dispersion.

2.2 Method

Thermogravimetric analysis (TGA) was carried using a TA instruments (labsys TM Evo TGA-DTA 1600°C) at different heating rates 10, 15 and 20°C from 25 to 650°C in argon atmosphere (30ml/min).

A quantity of 25mg of samples was placed in platinum pans for each test.

Thermal analysis of UPR and composite were carried in computer –controlled from Labsys TM Evo TGA-DTA 1600°C thermal analyzer. Prior to the experiment runs, the instrument was calibrated for precise temperature and weight reading. Non isothermal experimental runs were performed at three different heating rate of 10,15 and 20°Cmin⁻¹ under argon atmosphere. The continuous records of weight loss and weight loss rate with temperature were obtained. Thermal degradation behavior was shown as TG and DTG profiles. They were also used as data for kinetics modeling.

3. RESULTS AND DISCUSSIONS

3.1. Kinetic procedure

Model-free Kinetic

The specific reaction rate is defined as [2-4].:

$$\frac{d\alpha}{dt} = K(T)f(\alpha) \quad (1)$$

Where $\frac{d\alpha}{dt}$ is the reaction rate (s⁻¹), t is the time, α the conversion ($\alpha = \frac{m-m_0}{m-m_f}$: where m_0 , m_t and m_f are initial mass, mass at time t and mass at the end of reaction, respectively), $f(\alpha)$ is the kinetic model reaction, and $K(T)$ describes the effect of temperature.

The function $K(T)$ is always described by the Arrhenius equation

$$K(T) = A \cdot \exp\left(-\frac{E\alpha}{RT}\right) \quad (2)$$

Where: A is the pre-exponential factor (s⁻¹),
R is the constant gaz = 8.314 Jmol⁻¹K⁻¹,
E is the activation energy (kJ/mol).

Moreover, taking into account that under non-isothermal conditions the heating rate β can be described by:

$$\beta = \frac{dT}{dt} \quad (3)$$

Combining eq (1), (2) and (3) yields.

$$\frac{d\alpha}{dT} = \frac{d\alpha}{dt} \cdot \frac{dt}{dT} = \frac{A}{\beta} \cdot \exp\left(-\frac{E}{RT}\right) \cdot f(\alpha) \quad (4)$$

Most the methods that describe the kinetics of reactions in solids use eq.4 as well as several approximations of its integral form

$$g(\alpha) = \int_0^\alpha \frac{d\alpha}{f(\alpha)} = \frac{A}{\beta} \int_{T_0}^T \exp\left(-\frac{E}{RT}\right) dT \quad (5)$$

if we set, $x = \frac{E}{RT}$ and $p(x) = \int_{x_0}^\infty \frac{e^{-x}}{x^2} dx$ we obtain the equation

$$g(\alpha) = \int_0^\alpha \frac{d\alpha}{f(\alpha)} = \frac{AE}{R\beta} p(x) \quad (6)$$

For the kinetic of reactions in the solid-state, there are several methods that can be used: isoconventional (model-free) method and model-fitting. In this work we chose the isoconversional methods, these methods do not assume a kinetic model [6,7]. The isoconversional methods yield the value of activation energy as a function of conversion, which can indicate the complexity of reaction mechanism. The rate of reaction for a constant extent of conversion, α , depends only on the temperature is the basic assumption of these method mathematic [8,9]

Several non-isothermal experiment at different heating rates were performed, for to use the methods [10]. For this work we chosen the of kisinger -Akahira-Sunose method [11,12] applied without any assumption concerning the kinetic model and was shown to be correct in interval of activation energy [13] This method uses the approximation presented in Eq. (6) :

$$P(x) \approx \frac{e^{-x}}{x^2} \quad (7)$$

We use this approximation; the logarithm of Equation 5 gives the following formula:

$$\ln\left(\frac{\beta}{T^2(\alpha)}\right) = \ln\left(\frac{AR}{Eg(\alpha)}\right) - \frac{E(\alpha)}{RT(\alpha)} \quad (8)$$

This is defined as a dynamic equation, which is used for the determination of the activation energy as a function of different values of conversion (α) for two materials.

For each conversion value (α), the $\ln\left(\frac{\beta}{T^2(\alpha)}\right)$ vs. $1/T$ plot will give a straight line with an $-E(\alpha)/R$ slope from which E is obtained as a function of the conversion. (α)

Table.1: linear regression equation according to conversion degree by application of KAS method for UPR and Composite

$$\left(\ln\left(\frac{\beta}{T^2(\alpha)}\right) = Y \text{ and } \ln\left(\frac{AR}{Eg(\alpha)}\right) - \frac{E(\alpha)}{RT(\alpha)} = b + ax.\right)$$

α	UPR		Composite	
	$Y = ax + b$	R^2	$Y = ax + b$	R^2
0.05	$y = -6.381x + 1.252$	0.783	$y = -3.568x - 3.230$	0.573
0.1	$y = -11.43x + 1.252$	0.895	$y = -8.298x + 4.625$	0.884
0.15	$y = -11.90x + 9.341$	0.858	$y = -10.68x + 8.268$	0.986
0.2	$y = -12.83x + 10.54$	0.897	$y = -11.84x + 9.898$	1
0.25	$y = -13.15x + 10.82$	0.918	$y = -12.62x + 10.89$	0.996
0.3	$y = -14.32x + 12.5$	0.909	$y = -13.05x + 11.37$	0.988
0.35	$y = -14.32x + 12.30$	0.940	$y = -13.49x + 11.87$	0.981
0.4	$y = -14.72x + 12.77$	0.972	$y = -13.80x + 12.17$	0.976
0.45	$y = -14.27x + 11.91$	0.951	$y = -13.98x + 12.27$	0.968
0.5	$y = -14.55x + 12.19$	0.960	$y = -13.76x + 11.76$	0.959
0.55	$y = -14.09x + 11.34$	0.961	$y = -14.33x + 12.49$	0.957
0.6	$y = -13.97x + 11.01$	0.973	$y = -15.25x + 13.79$	0.919
0.65	$y = -14.33x + 11.42$	0.983	$y = -15.42x + 13.87$	0.929
0.7	$y = -15.07x + 12.39$	0.980	$y = -15.86x + 14.36$	0.921
0.75	$y = -15.65x + 13.10$	0.975	$y = -16.39x + 14.95$	0.932
0.8	$y = -16.41x + 14.05$	0.968	$y = -17.22x + 16.01$	0.904
0.85	$y = -15.97x + 13.20$	0.956	$y = -18.25x + 17.32$	0.869
0.9	$y = -14.95x + 11.47$	0.935	$y = -20.16x + 19.86$	0.810
0.95	$y = -19.41x + 17.53$	0.916	$y = -23.11x + 23.68$	0.552

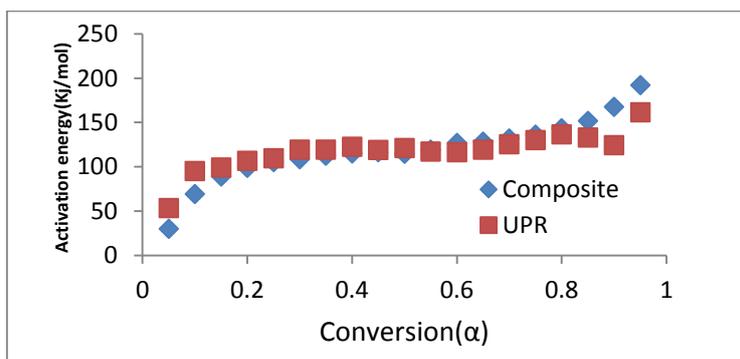


Fig. 1.: Dependence of activation energy on conversion as obtained by Kissinger-Akahira-Sunose method, for all investigated systems.

Table.2 Values of activation energy for UPR and composite as a function of conversion.

α	Activation energy(Kj/mol)		α	Activation energy(Kj/mol)	
	UPR	Composite(PP)		UPR	Composite(PP)
0.05	53.051	29.66	0.55	117.14	119.14
0.1	95.03	68.99	0.6	116.15	126.79
0.15	98.94	88.79	0.65	119.14	128.20
0.2	106.67	98.44	0.7	125.29	131.86
0.25	109.33	104.92	0.75	130.11	136.27
0.30	119.056	108.50	0.80	136.43	143.17
0.35	119.056	112.16	0.85	132.77	151.73
0.4	122.38	114.73	0.90	124.29	167.61
0.45	118.64	116.23	0.95	161.37	192.14
0.5	120.97	114.40			

The results obtained from ATG were elaborated according to model-free method calculus (KAS) the activation energy. The activation energy was obtained using KAS method. By applying this method, the relationship between $\ln(\beta/T^2\alpha)$ versus $1000/T$ of decomposition for UPR and composite is shown in table 1 for different values of (α) . The regression equations and the square of the correlation coefficient (R^2) is also presented for different values of conversion (α) . The activation energy can be obtained from the slope of the straight line. Figure. 1 shows the evolution of the activation energy (E) as a function of conversion (α) . In Figure. 1 we can observe that the thermal degradation of resin and composite was not similar for all conversion indicates the existence of the complex multistep mechanism that occurs in solid state. It was evident that the value of activation energy for two materials increased as a function of conversion and takes different values. For the resin the value is about 53 -161Kj/mole for the value of conversion is about 0.05-0.95, and for the composite a small difference exists (the detail information in Table 2). The activation energy for resin found in literature was calculated from different methods and different conditions. Mortaigne et al. [5] delaminated the thermal degradation for two kinds of UP resin by ATG in air at five different heating rates and obtained activation energy values: 118 and 138 Kj/mole computed in the temperature range 200-400°C). Tibielli et al. [14] obtained different values of activation energy (38.7-50.7-74.2-107.6-114.7-133-153.2-164.5-166.1-206.4) as a

function of conversion (0.01-0.05-0.1-0.2-0.3-0.5-0.6-0.75-0.8-0.98).

On the other hand, it is difficult to compare the activation energy obtained in our study with that obtained in the literature. Vyazovkin [15] reported the differences in the values of activation energy for the same solid state process of two parameters (the differences in experimental conditions, sample characteristics).

3.2. Modeling of degradation kinetics.

In this section, we are interested in the model of the degradation of UPR and the composite based on UPR.

The degradation of UPR is a complex mechanism as previously described, the same complexity was supposed in the degradation process of composite based on UPR.

Considering degradation as a one-stage chemical reaction, the overall rate of this process is given by Eq. (9)

$$\frac{d\alpha}{dt} = A \cdot e^{-E/RT} \cdot f(\alpha) \tag{9}$$

The function $f(\alpha)$ has usually the form

$$f(\alpha) = (1 - \alpha)^n \tag{10}$$

Where n is the reaction order, and Equation (9) can be written

$$\frac{d\alpha}{dt} = A \cdot e^{-E/RT} \cdot (1 - \alpha)^n \tag{11}$$

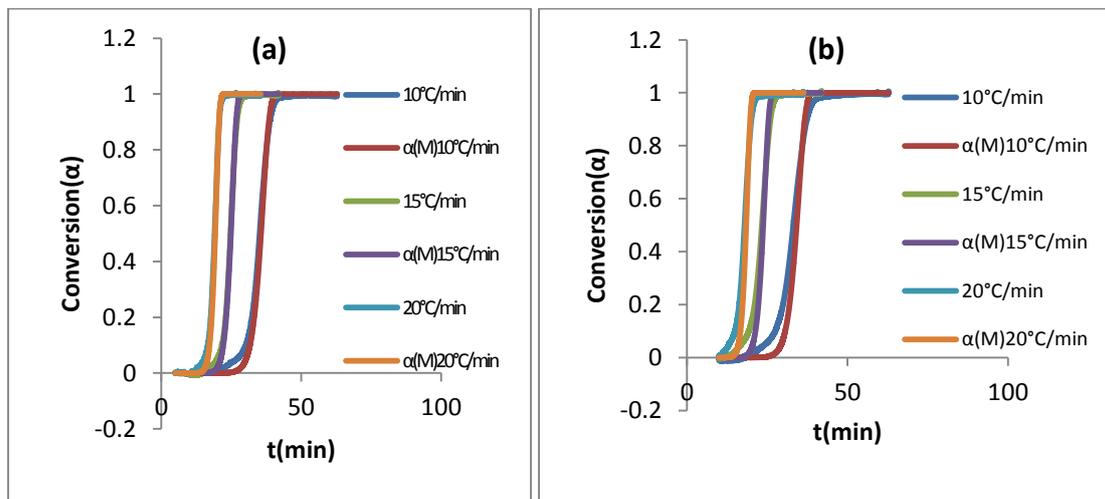


Fig. 2.: Comparison of experimental data with kinetic model obtained for investigated systems for all heating rates : (UPR) unsaturated polyester resin system(a); (PP) composite system(b).

We assumed according to the method described in previous publication (16), it is possible to select the range of conversion 0.2 - 0.8, the mean value of E was calculated

for two samples of this work. The kinetic parameter values (computed in the conversion range 0.2 - 0.8) are presented in Table 3.

Table: 3 Activation energy (E), pre-exponential factor (A) and reaction order (n) for two materials.

Material	E (KJ/mol)	Ln A (s ⁻¹)	n
UPR	134.22	23.82	0.90
Composite	146	26.94	1.128

As shown in Table 3, the activation energy, E, for the composite is about 146KJ/mol, while the ln(A) take 26.94. The reaction order, n, is estimated to be 1.128.

More or less variance could be found in the calculations of these kinetic parameters for the UP resin (see Table 3).

Fig. 2 shows the comparison between the three theoretical curves at a different heating rates of 10, 15 and 20°C/min and the experimental curve at the same heating rate for two materials (kinetic parameters were selected from Table 3, the conversion range 0.2-0.8). Although the kinetic parameters differ significantly for two materials, all calculated curves show tendencies more or less similar to the experimental curve.

The composite material is composed of two phases: the organic phase and inorganic phase, but the resin consist one phase. Obviously, the higher value of E for the composite is due to the effect of the inorganic phase. In addition, the dispersion values of E for the resin is low for different values of the conversion rate than for the composite is greater. This results show probably that the inorganic network influences the degradation mechanism.

4. CONCLUSION

In this study, the no isothermal TG analysis of UP resin and composite based on UP resin under argon were investigated at three different heating rates, up to 650°C. It Was observed that the activation energy calculated by KAS method change as a function of conversion for two materials in the same way, Activation energies of thermal degradation are in the order of 53 KJmol⁻¹ at the beginning of thermal degradation and of the order 130 during the main degradation step and in the end it increased up to

161KJmol⁻¹ for Unsaturated polyester resin. The small differences take place for composite. Moreover, the composite contains the fraction of UP resin (decomposed phase) and the mineral filler (undecomposed phase).

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