

Thermogravimetric Investigation of the Composite based of Unsaturated Polyester Resin and Porcelaine Powder

Mohamed Farsane, Abdellah Anouar, Souad Chah, Miloud Bouzziri.

Laboratory of Applied Chemistry and Environment,
Faculty of Science and Technologies,
University Hassan 1, Km 3, B.P. 577,
Settat, Morocco.

Abstract - The kinetic parameters for the degradation of composite based on unsaturated polyester resin and porcelain powder were determined by using thermal gravimetric analysis (TGA). The Flynn-Wall-Ozawa (FWO) method using the integral procedure was applied to the non-isothermal TGA results. The mean values of the activation energies in the range of conversion 0.05-0.95 are 59.29-164.22kJ mol⁻¹ for resin and 36.74-193.20 kJ mol⁻¹ for composite.

Key words: Activation energy, composite, UPR, Flynn-Wall - Ozawa method.

1. INTRODUCTION

The thermal stability of an unsaturated polyester resin has been studied in numerous researches in the past by different authors, and has demonstrated that the stability depends on the structure of the UP resin in particular with the constituent monomers [1].

The authors Anderson and Freeman [2] used the TG-ATD method to demonstrate that a resin made from propylene glycol, maleic anhydride, phthalic anhydride and crosslinked with styrene at 30 °/° had begun to decompose in air at a temperature of 200°C and had lost 87% of its initial weight at 418°C and 97 °/° at 550°C. In argon, the decomposition is similar leaving a residue of 6°/° at 450°C.

The Flynn-Wall-Ozawa [3-4] method uses an approximate evaluation of the integral formulation in a simplified version of Doyle (1961).

As described above, the fundamental relation of the kinetics of degradation of solids can be written as follows:

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

The simple transformation of the terms of this formula gives us the following expression:

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

By setting the integration limits, we obtain:

$$\int_0^\alpha \frac{d\alpha}{f(\alpha)} = \frac{A}{\beta} \int_{T_0}^T \exp\left(-\frac{E}{RT}\right) dT \quad (3)$$

Or T₀ is the value of T at t = t₀. Considering the hypothesis or the rate of reaction is low at low temperature, it is possible to write:

$$\int_{T_0}^T \exp\left(-\frac{E}{RT}\right) dT \approx \int_0^T \exp\left(-\frac{E}{RT}\right) dT \quad (4)$$

Let x = E / RT and p(x) = $\int_0^x \frac{\exp(-x)}{x^2} dx$ (5), we are getting

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

The value of p (X = E / RT) can be approximated by the following formula if 20 < X = E / RT < 60 [5]:

$$\text{Log}(p(x)) = -2.315 - 0.4567 \frac{E}{RT} \left(x = \frac{E}{RT}\right) \quad (7)$$

$$\log \beta = \log \frac{AE}{R} - \log g(\alpha) - 2.315 - 0.4567 \frac{E}{RT} \quad (8)$$

This relation (Equa.8) defines a set of linear relationships between log (β) and the reciprocal of the temperature 1/T for a certain degree of conversion (α), so we can easily calculate the activation energy from the slopes of the lines. This equation leads to the linear representation of log (β) as a function of 1/T. Which allows us to determine the activation energy for each conversion rate α. Where β is the heating rate (°C min⁻¹), A is the pre-exponential factor (min⁻¹), R is the gas constant (8.314Jmol⁻¹K⁻¹) and α: In thermogravimetric analysis, the degree of progress (degree of transformation) defines the evolution of the reaction and can be expressed according to the following formula:

$$\alpha = \frac{m_i - m_t}{m_i - m_f} \quad (9)$$

Where m_i is the initial mass of the sample, m_t is the mass of the sample at temperature t and m_f is the final mass at a temperature at which the mass loss is approximately unchanged.

In this method, plots of $\log \beta$ versus $1/T$ give parallel lines for each value. The slope of these lines gives the activation energy, as seen from equation 10,

$$\text{Slope} = -0.4567(E/R) \quad (10)$$

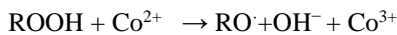
Tibielli et al. [6] obtained different values activation energy (38.7-50.7-74.2-107.6-114.7-133-153.2-164.5-166.1-206.4) as a function of conversion (0.01-0.05-0.1-0.2-0.3-0.5-0.6-0.75-0.8-0.98).

2. EXPERIMENTAL

2.1 Materials

The material developed in this work is the unsaturated ortho-phthalic porcelain powder polyester containing increasing load 50g of porcelain powder introduced in 50 g of resin (UPR).

This resin is particularly adapted to the preparation of the thermosetting composite by its kind. This liquid is a resin which contains styrene and bidimensionnels chains. In the presence of a catalytic system consisting of benzoyl peroxide (diacyl peroxides) and cobalt salt, the resulting reaction between the two using equation (11) [7], there are cross-linking by formation of bridges and the cured resin.



The resin is characterized by a viscosity of 8 poises, it contain almost 34% of styrene, density 1.13, an acid value of 25-30mgKOHg

The reactivity characteristics are a gel time (4-6 min), curing (8-15 min) and the exothermic peak at 190 °C.

2.2 Method

All thermal analysis work was done using a TA instruments (labsys TM Evo TGA-DTA 1600°C) thermal analyzer at various heating rates in a argon atmosphere (30ml/min). Thermal analysis of UPR and composite were carried in computer –controlled from Labsys TM Evo TGA-DTA 1600°C thermal analyzer (Fig.1)

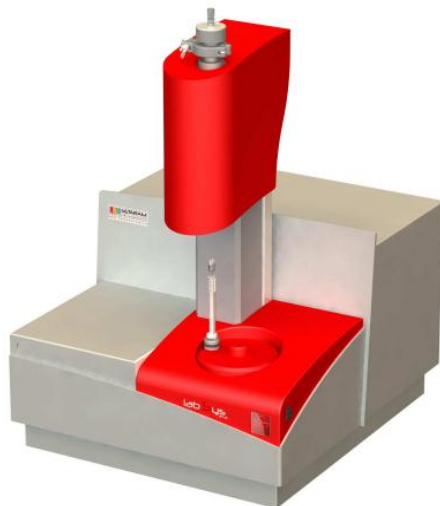


Figure.1: LABSYSTMEVO

The continuous records of weight loss and weight loss rate with temperature were obtained. In this device, a weight of 25 mg was placed in platinum pans for each test.

3. RESULTS AND DISCUSSIONS

Thermogravimetry of Samples

The thermograms were obtained at three different heating rates: 10, 15 and 20°Cmin⁻¹. TG and DTG thermograms resin and composite at a heating rate of 10 Cmin⁻¹ are given in Figure 2 and 3. Analysis of these curves estimates the mass loss associated with the processes of degradation. The former is estimated from mass loss up to 200 °C and the later between 200 and 440 °C.

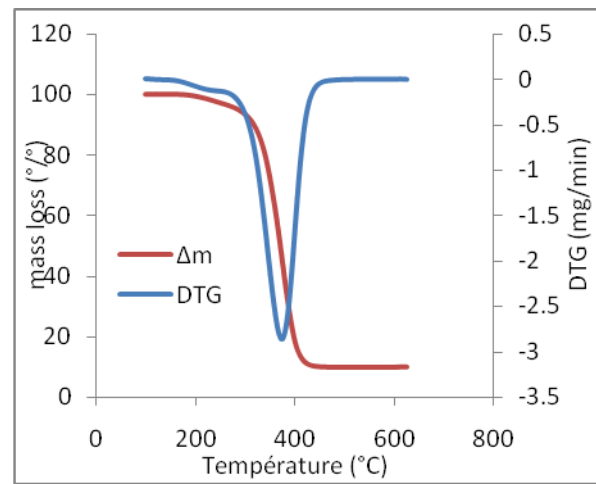


Figure 2.TG and DTG thermograms of resin.

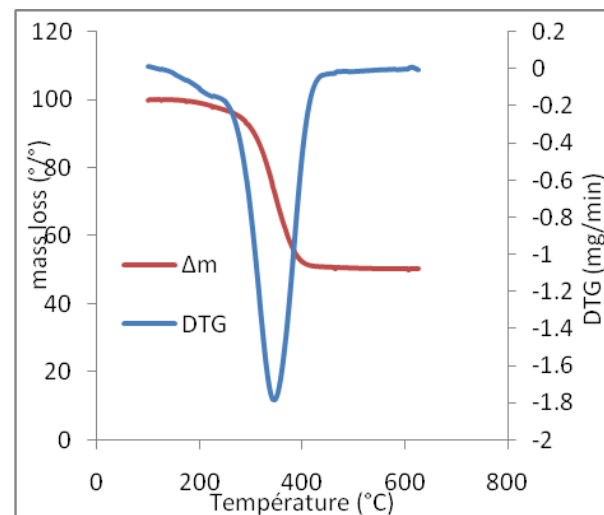


Figure 3. TG and DTG thermograms of composite

The TG curves (Fig.2 and Fig.3) shows that in argon UP resin began to decompose at about 200°C. with Loss of mass of 0.7%, and had lost 94% of its initial weight leaving a residue of 4% at 420°C. For the composite this loss reached 0.35% at 200°C and a residue of 48% at 420°C. The TG curves were divided into two parts: the first covering the range up to 200 C and the second covering the

range from 200°C to 440°C. These results are similar to those obtained by the authors [1-2].

The Ozawa Method

The activation energies (E) determined from the slope of each line is listed in Table 3. At low conversion rates the activation energy is low and increases gradually to reach stable values in the 0.2-0.8 conversion range and finally they achieve maximum values at high conversions.

These results are in good agreement with those mentioned in the literature [6].

Table 1. Activation Energies from Flynn-Wall-Ozawa Method.

conversion	E (Kj/mol)	
	Resin UPR	Composite
0.05	59.29	36.7
0.1	99.60	74.57
0.15	103.63	93.65
0.2	111.06	102.97
0.25	116.27	109.14
0.3	123.07	112.69
0.35	123.14	116.25
0.4	126.30	118.78
0.45	122.91	120.28
0.5	125.12	118.62
0.55	121.56	123.20
0.6	120.70	130.47
0.65	123.62	131.98
0.7	129.54	135.53
0.75	134.12	139.72
0.8	140.21	146.44
0.85	136.81	154.66
0.9	128.83	169.83
0.95	164.22	193.30

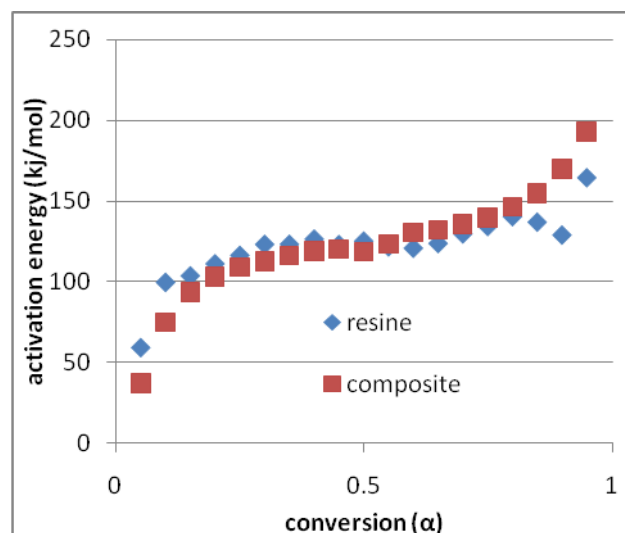


Figure 4. Evolution of the activation energy as a function of the conversion rate (α) for the resin and composite calculated by the method FWO.

From the figure 4, it can be concluded that the activation energy evolves in the same way with the conversion rate for the two materials.

4. CONCLUSIONS

In this study, the non 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 FWO method change as a function of conversion for two materials in the same way, Activation energies of thermal degradation are in the order of 36.7 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 193KJmol⁻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).

1. The mean values of the activation energies in the range 0.05-0.95 are 121.58 kJ mol⁻¹ for resin⁻¹ and 122.56 for composite in the case of the Ozawa method.
2. The evolution of the values of the energies of activation shows that the mechanism of degradation is complex indicating the course of different reactions. The estimated mean values of E in the Ozawa method are not very different from the published values 338.
3. It is difficult to compare these results obtained in the context of our study with those of the literature because it is a mechanism of degradation very complex and very different from one resin and another and also the mode of manufacture.

5. REFERENCES

- [1] D.A. Anderson and E.S. Freeman, J. Appl. Polym. Sci., 1 (1959) 192.
- [2] S.J. Evans 1, P.J. Haines, G.A. Skinner * The effects of structure on the thermal
- [3] Ozawa T. A new method of analyzing thermogravimetric data. Bull Chem Soc Jpn 1965;38:1881e6.
- [4] Flynn JH, Wall LA. A quick, direct method for the determination of activation energy from thermogravimetric data. J Polym Sci Polym Lett 1966;4:323e8.
- [5] Doyle CD. Kinetic analysis of thermogravimetric data. J Appl Polym Sci 1961;5(15):285-92.
- [6] L. Tibiletti, C. Longuet, L. Fertty, P. Coutelen, A. Mas, J-J Robin, J-M Lopez-Cuesta., Polym. Degrad. Stab., 96(2011) 67-75.
- [7] Johannes Karl Fink, Reactive Polymers Fundamentals and Applications, 2005.