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STUDY OF KINETIC PARAMETERS OF REJECT/ CLAY/COMPOSITES BY THERMAL ANALYSIS

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Abstract

Thermal degradation of granite and marble industry reject (GMIR), a red clay (RC) and their composites were studied by non-isothermal thermogravimetry (TG/DTG) in nitrogen atmosphere, differential thermal analysis (DTA) and derivative thermogravimetry (DTG) in air atmosphere. Measurements were made in the temperature range of 25–1000, 25–1200 and 25–1400°C. The kinetic parameters were determined by Flynn–Wall and Kissinger's methods. The results indicate the absent dominance of one mechanism of reaction, and the composites show smaller values of kinetic parameters than GMIR or RC.

Keywords: clay, composite, kinetic parameters, reject

Introduction

Granite and marble industry reject (GMIR) is a non-degradable, insoluble solid residue and it is obtained when rocks are cut in plates and furbish. X-ray diffraction (XRD) was employed to examine this reject and quartz, plagioclase, orthoclase, calcite, dolomite and mica were found in it [1–2]. This industry has developed over the last years and it has produced around 1 443 000 tons of granite and 578 000 tons of marble a year, and the amount of reject obtained is around 200 000 tons [3]. Today the companies have problems to find safe places to dispose their rejects, owing to environmental restrictions. Previously GMIR was thrown into rivers.

The name clay means a particle size smaller than two microns, a rock or a group of minerals which are known clay minerals. They belong to a group of silicates and their main minerals are kaolin, montmorillonite, chlorite, mica, sepiolite and attapulgite [4]. The first four are sheet silicates (layer lattices) and their structure is formed by layers which are formed by sheets tetrahedron and octahedron [5]. The term composites have been applied to heterophase materials when the dimensions involved approach the macroscopic. Ceramic materials are frequently considered for structural

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applications, due to their high hardness, chemical and wear resistance and good mechanical properties at room and high temperatures [6]. They are used in industries of space, oil, military, electric and others. The objective of this work is to study the reject, red clay and its composites by differential thermal analysis (DTA), thermogravimetry and derivative thermogravimetry (TG/DTG) by applying Flynn and Kissinger's methods.

Experimental

Sample preparation

Granite and marble industry reject (GMIR) and red clay (RC)

This reject is obtained when these rocks are sawed in blocks or slices. It was dried in air oven at 120°C for 24 h and next mechanically ground and sieved. Only the material passed through mesh # 270 was used [1]. Red clay was dried at room temperature for one week and so mechanically set apart and sieved. The small size that mesh # 270 was used.

DTA and TG/DTG measurements

The samples with around 15 mg of reject or clay or composite (reject 70/clay 30% mass/mass) were used to thermal analysis. DTA/DTG of GMIR were measured on a TA Instruments SDT 2960 at a heating rate of 4, 6, 8, 10, 12°C min^{-1} in air atmosphere, in the temperature range of 25 to 1400°C. DTA/DTG of RC were measured on a TA Instruments SDT 2960 at a heating rate of 4, 6, 8, 10 and 15°C min^{-1} in air atmosphere, in the temperature range of 25 to 1200°C. TG/DTG was measured on a TA Instruments TG 2950 at a heating rate of 4, 6, 8, 10, 12 and 14°C min^{-1} in nitrogen atmosphere and flow 100 mL min^{-1}, in the temperature range of 25 to 1000°C.

In order to determine the kinetic parameters of the first degradation step of reject or red clay, the methods based on Flynn and Wall, and Kissinger method were applied. The kinetic parameters of composite samples of the first and second degradation steps were also determined. Both of them derived from the basic kinetic equations for heterogeneous chemical reactions, and as it is not necessary to know the reaction order or the conversional function $g(\alpha)$ to determine the kinetic parameters [7]. Flynn and Wall method is shown by the equation:

$$\log g(\alpha)=\log\frac{AE_a}{R}-\log q-2315-0.4567\frac{E_a}{RT}$$

where: $q(\alpha)$ – conversion function relationship; A – pre-exponential factor; E_a – apparent activation energy; R – general gas constant; q – heating rate and T – absolute temperature.

Apparent activation energy is calculated from the slope of the most probable straight line obtained by drawing the dependence $\log q$ *vs*. $1000/T$ and the pre-exponential factor from the intercept of the straight line the y-axis. The equation of Kissinger's method for calculating the kinetic parameters uses the temperature at which the rate of mass loss is the highest. This is shown below:

$$\frac{qE_a}{RT_m^2}=An(1-\alpha)_m^{n-1}\exp\left(\frac{-E_a}{RT_m}\right)$$

where T_m and n are the temperature of the maximum degradation rate and reaction order, respectively.

Apparent activation energy and pre-exponential factor are determined from straight line obtained by drawing the dependence $\ln(q/T_m^2)$ *vs*. $1/T_m$. The activation energy determined by applying the above methods is the sum value of activation energies of chemical reactions and physical processes in thermal degradation [8].

Results and discussion

Comparison of DTA curves for reject is shown in Fig. 1, which depicts three endothermic events at 570, 610–700 and 1200°C. The first one is a light event which means that α quartz was transformed in β quartz. The second means the degradation of carbonates, in carbonic gas and calcium oxide, and the last one the reject fusion. DTG curves are in Fig. 2, they show one degradation step around 610–700°C, it confirm the degradation of carbonates.

DTA curves of red clay (Fig. 3) show an endothermic event, at around 470–540°C, and an exothermic event at around 950–1000°C. The first one mean the dehydroxylation and the last the mullite prenucleation. Figure 4 shows DTG curves of red clay with two degradation stages at around 100 and 470–540°C. The first one is the loss of water, and the second confirm the dehydroxylation of red clay. TG curves of reject (Fig. 5) show

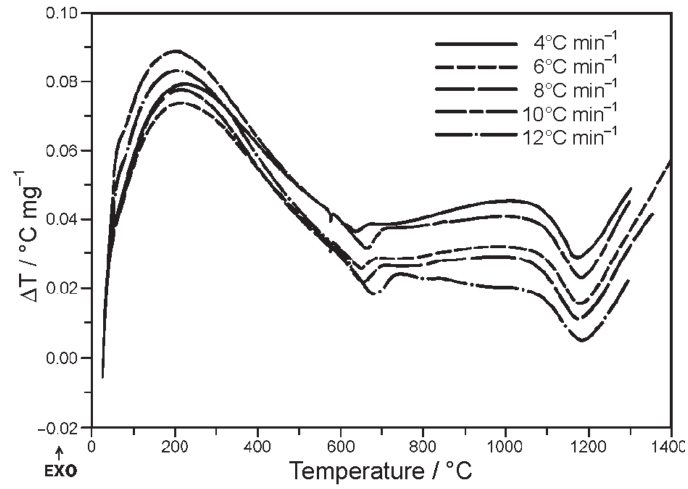

Fig. 1 DTA curves of GMIR

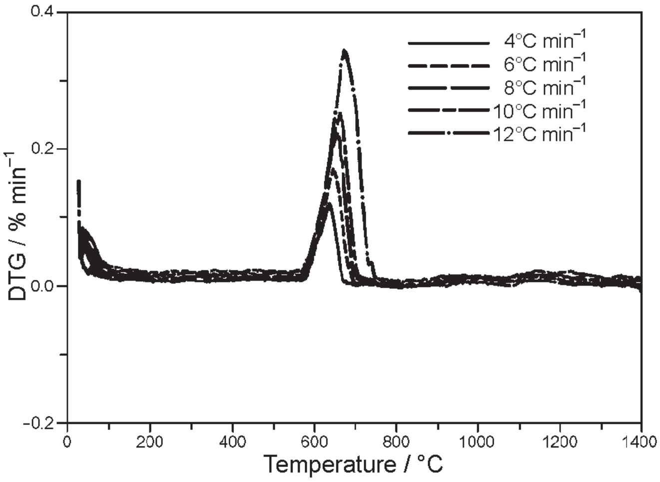

Fig. 2 DTG curves of GMIR

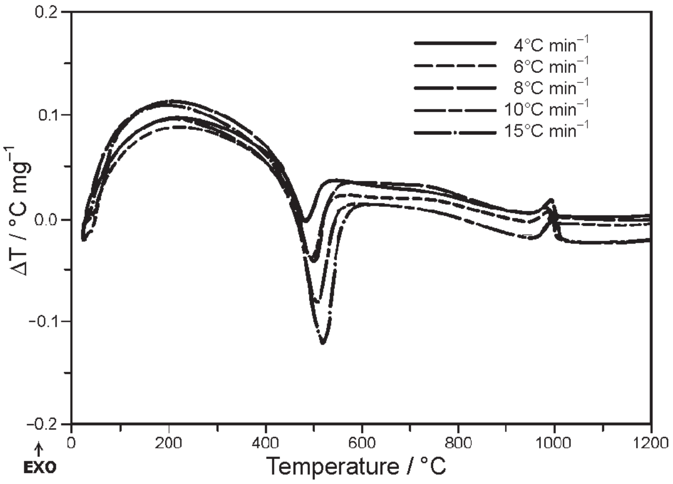

Fig. 3 DTA curves of RC

one degradation stage at 570–640°C, that means the degradation of carbonates. Figure 6 also shows a comparison TG curves of red clay, with one degradation stage, between 400–550°C, and means the dehydroxylation of red clay.

Figure 7 shows TG curves of composite with two degradation steps, that mean the dehydroxylation and the degradation of carbonates. DTG curves of composites are shown in Fig. 8, and they confirm two degradation stages, the first step between 400–550°C ($\Delta m1$), dehydroxylation, the second step at around 570–700°C, loss of carbonate ($\Delta m2$). Thermal degradation temperature interval of all the samples moves to a higher temperature as the heating rate increases. The curves of composites show

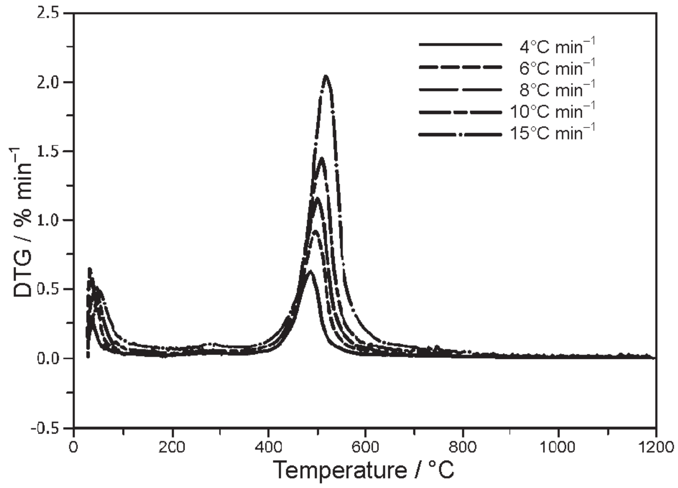

Fig. 4 DTG curves of RC

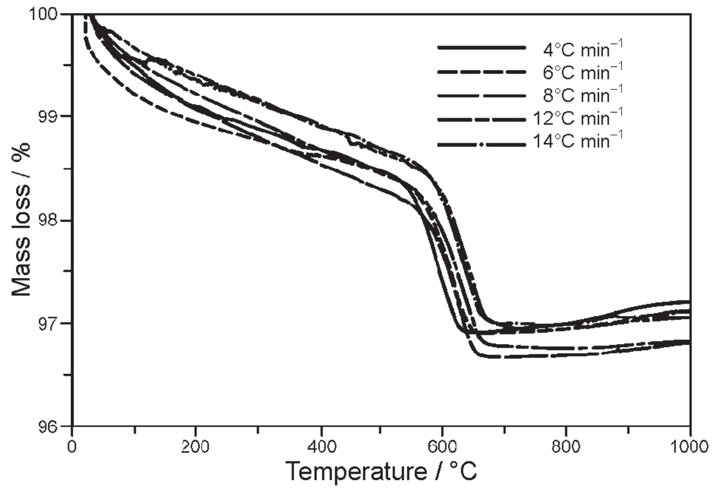

Fig. 5 TG curves of GMIR

the influence of one material over the other, therefore, the second event begins before the first one finishes.

Determination of kinetic parameters by Flynn–Wall method

Applying the analysis after Flynn–Wall method by the linear regression analysis the activation energy and the pre-exponential factor for conversions α=0.20, 0.30, 0.40, 0.50, 0.60, 0.70, 0.80 and 0.90 to reject and red clay, were determined. The obtained

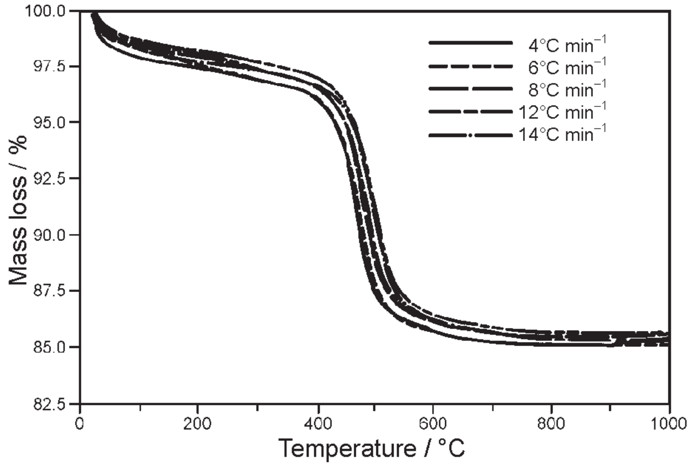

Fig. 6 TG curves of RC

value of E_a (kJ mol^{-1}) and A (min^{-1}) for all the materials is tabulated in Table 1. The change of E_a to a smaller and highest value of conversions denotes absent the dominance of a mechanism. The isoconversional lines for other values are almost parallel, which can indicate a dominance of a reaction mechanism. The isoconversional lines are not parallel, mainly where $\Delta m1$ and $\Delta m2$ meet. The values of E_a of $\Delta m1$ are smaller than those of red clay, just in the same way as $\Delta m2$ is smaller than reject, and the smallest value of parameter generally means the most reactivity in the system.

Table 1 Kinetic parameters of non-isothermal degradation of reject, red clay and composite according to the Flynn. E_a as kJ mol^{-1} and A as min^{-1}

α/%	Red clay		Reject		Composites: $\Delta m1(E_a1, A1)$ $\Delta m2$ $(E_a2, A2)$			
	E_a	A	E_a	A	E_a1	$A1$	E_a2	$A2$
20	253.4	17.29	209.1	11.7	174.7	11.47	126.7	6.49
30	229.6	15.42	199.9	11.1	167.4	10.93	144.8	7.74
40	210.4	13.98	191.0	10.54	166.7	10.88	161.8	8.86
50	199.8	13.20	186.8	10.29	171.8	11.24	170.6	9.43
60	193.1	12.70	184.8	10.19	171.1	11.18	174.4	9.68
70	189.5	10.41	183.4	10.12	161.5	10.49	177.6	9.87
80	188.3	12.26	183.1	10.12	146.6	9.41	172.1	9.56
90	214.5	13.77	176.7	9.78	132.7	8.38	167.7	9.32

Determination of kinetics parameters by Kissinger's method

The kinetic parameters obtained by applying Kissinger's method are presented in Table 2. The previously determined conversions at T_m for all materials increase as the heating rate increase, so that one of the conditions for applying Kissinger's equation

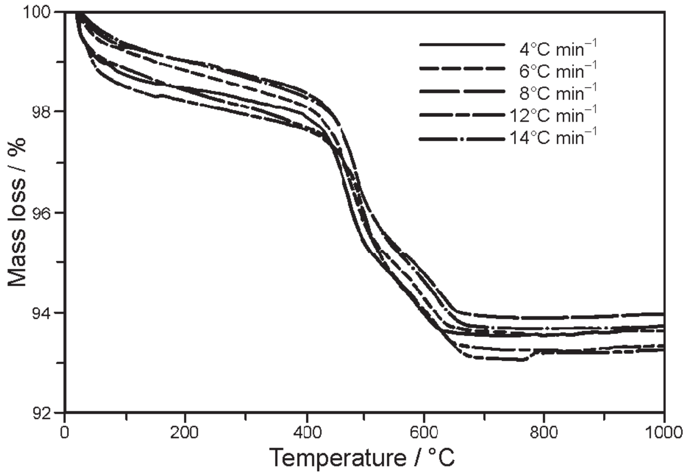

Fig. 7 TG curves of composites

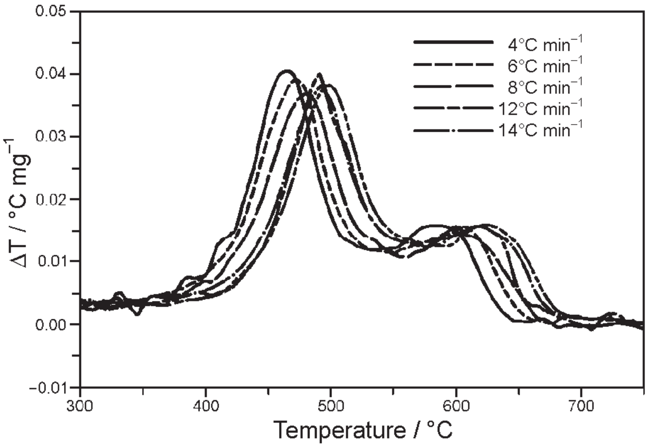

Fig. 8 DTG curves of composites

is fulfilled. The coefficient of regression r is above 0.99 for all the materials (Figs 9, 10, 11 and 12). The activation energy of reject and red clay as determined by DTA or DTG is higher than that of the composite as measured by TG.

Table 2 Kinetic parameters of RC, GMIR and composites, by Kissinger's method, E_a kJ mol^{-1} and A in min^{-1}, of DTA and DTG curves

DTA				DTG							
RC		GMIR		RC		GMIR		Composites			
E_a	A	E_a	A	E_a	A	E_a	A	E_a1	$A1$	E_a2	$A2$
178.0	12.3	180.0	7.5	164.5	10.1	190.4	8.8	159.9	19.2	164.8	19.8

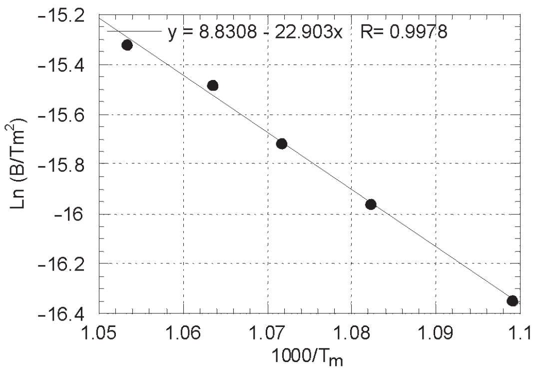

Fig. 9 Kissinger's method plot of GMIR by DTG

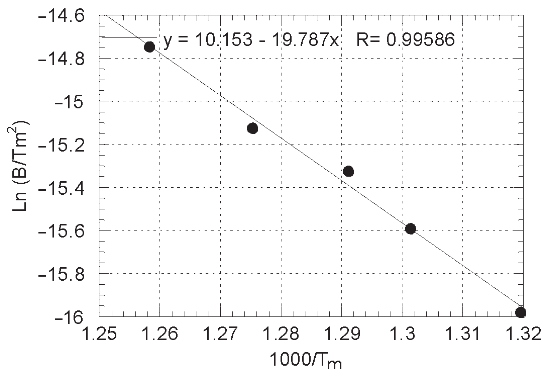

Fig. 10 Kissinger's method plot of RC by DTG

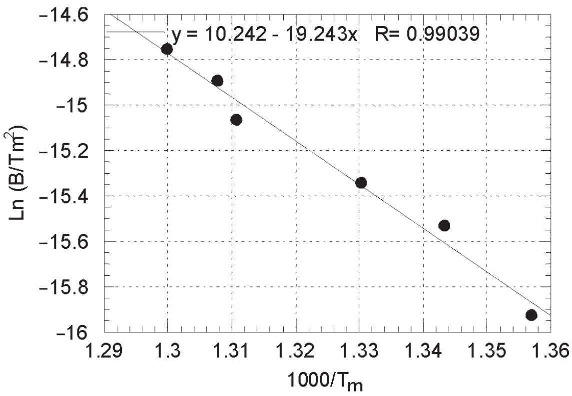

Fig. 11 Kissinger's method plot of first degradation step of composites by DTG

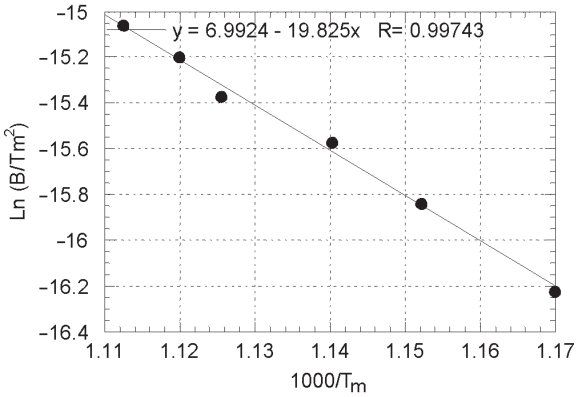

Fig. 12 Kissinger's method plot of second degradation step of composites by DTG

Conclusions

Non-isothermal degradation of granite and marble industry reject (GMIR), red clay (RC) and GMIR/RC composites was studied. GMIR decomposes at one step around 520–700°C, degradation of carbonates. The degradation of RC also occurs at a step between 400–580°C, dehydroxylation, and the composites show two decomposition steps. The first one is between 400–570°C, dehydroxylation and the second step around 570–700°C, loss of carbonates. The apparent activation energy and pre-exponential factor calculated applying Flynn–Wall and Kissinger's methods show smaller values for composites than for GMIR and RC. This indicates the composite exhibited compatibility, so this composite can be used to obtain ceramic material.

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