Effects of variation in sample mass, gas flow and lid on chemical reactions during STA measurements

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1 Introduction

Polymer decomposition is such a complex phenomenon because of their intrinsic characteristics and since each polymer has its own characteristics that make its behavior different from the others. Moreover, the chemical reactions that occur during the thermal decomposition are often highly dependent on the conditions of the tests and sample. In fact, thermal analysis tends to be far more sensitive to instrumental parameters than other branches of chemical analysis [1].

Simultaneous Thermal Analysis (STA) is widely used to study polymers decomposition. STA combines Thermogravimetry (TGA) and Differential Scanning Calorimetry (DSC) in a single sample to measure and analyze the sample weight change and the heat flow as a function of temperature. Depending on objectives of the polymer thermal decomposition study, one can find in the bibliography different definitions of the boundary conditions applied to the TGA/DSC tests. Some of the STA definition parameters have been widely studied in the literature and their influence in the decomposition results are well known, such as the heating rate or the atmosphere. However, the influence of the sample mass, the gas flow or the use of lid is not sufficiently studied.

According to the mass, ASTM E1131 – 08 [2] recommends sample mass of 10 to 30 mg for the TGA. Mass sample ranges recommended by ISO standards are between 10 mg and 100 mg for the TGA [3] and between 2 and 40 mg for the DSC [4]. Nevertheless, sample mass under 10 mg are widely used by scientific community to perform TG analysis [5-6]. As far as influence of the gas flow on the STA experimental test is concerned, ASTM E1131 – 08 [2] recommends a flow rate of 50 ml/min for thermoplastic, and ISO 11358-1 [3] allows flow rates between 10 and 150 ml/min. A large amount of works set different values of the gas flow rate like 50 ml•min^{-1} [7], 60 ml•min^{-1} [8-9 and 6], 100 and 80 ml•min^{-1} [10] or 200 ml•min^{-1} [11], although it was not included any explanation of its influence in the results. Furthermore, some studies do not include the gas flow value employed in the STA tests [12-13].

Abu-Bakar and Moinuddin [14] studied the influence of the sample mass and the gas flow in the TGA for PMMA and pine materials. Only a slight difference was obtained in the PMMA sample. The influence of the sample mass and the gas flow in the thermal degradation of the polypropylene was also studied by

Stawski [15]. While it was obtained a clear dependence of the thermal decomposition on the weight of the samples, the influence of the gas flow on the decomposition was not appreciated.

Regarding importance of the study of sample mass effect on STA, that will allow to define if tests should be performed as standards recommendations, or lower mass can be used. Since only two references have been found studying gas flow effect on TGA, therefore it seems necessary a better understanding of its effect in the chemical reactions of decomposition.

The use of lid to cover the samples in the STA test is recommended by the normative ASTM 1269 -01 [16] to determine the specific heat capacity. In addition, the use of lid permits to measure thermal decomposition in self-generated atmosphere and to obtain results in a more homogeneous heat distribution in the pan. The influence of the use of pierced lid in the DSC has been studied by Wolfinger et al. [17]. It was concluded that it is necessary the use of crucibles without a lid when the reaction conditions require a fast gas exchange between the sample and the surroundings. It is remarked the influence of the heat flux rate of radiation when sample and reference have different emissivities. That effect occurs when lid is not used.

We selected poly (vinyl chloride) (PVC) for this study as PVC has a large number of different kinds of chemical reactions, the results could be extrapolated to other materials. In addition, it will allow a better understanding of how each single parameter affects the behavior of that product, and it will facilitate the selection of the different parameters. To sum up, our analysis includes the study of the STA repeatability, sample mass, the gas flow rate and the use of lid in the crucible.

The understanding of the boundary conditions influence in the thermal decomposition during STA analysis is necessary to obtain good results from the experiments and to be able to define appropriate experimental tests. As PVC is a typical representation of thermoplastic, the analysis of combustion and thermal oxidative reactions can extrapolate to other thermoplastic materials.

2 Experimental tests

The Netzsch STA 449 F3 was used to perform the experimental campaign, which allowed to test in a range of temperature between 30 and 1500 ºC in oxidative or inert atmosphere. The temperature and balance resolutions are 0.001 K and 0.1 μg over the entire weighing range, respectively. The DSC enthalpy accuracy is ± 2 % for most materials.

PVC($(C_2H_3Cl)_n$) is a polymer prepared from Vinyl Chloride Monomer (VCM). Thermal decomposition of PVC is substantially a two-stage process. While the first step (227-377°C) mainly involves the progressive dehydrochlorination of the polymer that consists on the elimination of HCl, at temperatures over approximately 377 ºC, a second mass loss can be observed which corresponds to the pyrolysis of the polyene sequences formed during the previous reaction. Some evaporation of plasticizer may be also observed in the first step [5] and the loss of HCl produces a mass loss of approximately 65 %, and the total mass loss in this chemical reaction is slightly higher than the stoichiometric quantity of HCl in the PVC. This may be produced by the formation of some aromatic hydrocarbons, mainly benzene.

A reference test, denoted as Case 1, was considered in air atmosphere without lid with a gas flow rate of 40 ml•min^{-1} and the sample was heated from 30 to 800 ºC with a heating rate of 10 K•min^{-1}. The initial mass considered in that reference case was 12.184 mg. A total of 14 tests were carried out for PVC, varying only one parameter in each experimental test (Table 1).

Table 1 PVC cases for the STA analysis

Test (Case)	Atmosphere	Initial Mass [mg]	Lid	Range T.min (°C)/[K/min]/T.max (°C)	Gas Flow (ml·min-1)
1	Air	12.184	No	30/10.0/800	40
2	Air	12.212	No	30/10.0/800	40
3	Air	12.179	No	30/10.0/800	40
4	Air	*20.736*	No	30/10.0/800	40
5	Air	*4.763*	No	30/10.0/800	40
6	Air	*14.594*	No	30/10.0/800	40
7	Air	*6.576*	No	30/10.0/800	40
8	Air	*18.435*	No	30/10.0/800	40
9	Air	12.251	No	30/10.0/800	*150*
10	Air	12.174	No	30/10.0/800	*50*
11	Air	12.195	No	30/10.0/800	*10*
12	Air	9.349	*Yes*	30/10.0/800	40
13	N_2	13.079	No	30/10.0/800	40
14	N_2	12.639	*Yes*	30/10.0/800	40

The repeatability has been studied to define the uncertainty in same conditions of the test. Cases 1 to 3 have the same boundary conditions with a mass of 12.184 mg ± 0.23%. Figures 1 and 2 show a very good repeatability. The Euclidean Relative Difference (ERD) [18] calculated for the TG for Case 2 and Case 3 are 0.74 % and 0.66 %, respectively. This difference considers the Case 1 as reference.

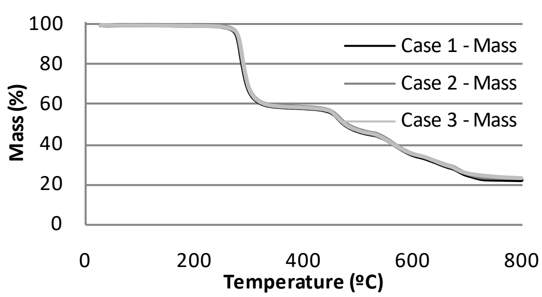

Figure 1. Repeatability on TG curves.

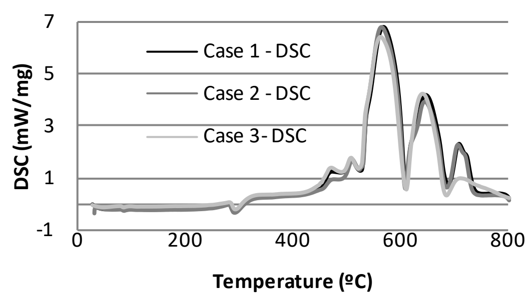

Figure 2. Repeatability on DSC curves.

3 Results analysis

So as to study the sample mass influence in the polymer decomposition, we performed 6 STA tests considering mass variation. Figure 3 includes the mass of the samples used for the repeatability, and for analyze the initial sample mass influence. In addition, it displays the relative error considering Case 1 as reference, and where Case 5 and 7 were tested following standards recommendations.

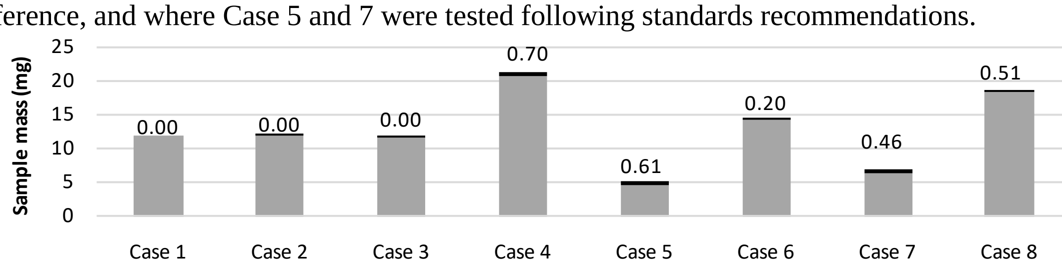

Figure 3. Mass samples variation and relative error.

Figure 4 shows that mass loss tended to be similar in all the cases except in number 5 and 7, which corresponded to the samples with a mass of 4.763 and 6.576 mg. Until oxidation reactions began, the mass loss and DSC curves were the same for all the samples. The heat released in the first oxidative reaction of the PVC, R1, was higher in cases 5 and 7 (Figure 5) and they lost more mass. This oxidative reaction took place between 500 and 600 ºC. We can also observe that oxidative reaction peaks for samples with mass under 10 mg occurred at lower temperatures. While the mass ERD for the cases 5 and 7 was 2 % and 2.1 %, respectively. For the cases 4, 6 and 8 was 1 %, 0.7 % and 0.6 %, respectively.

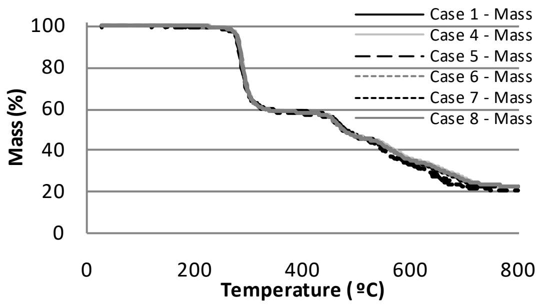

Figure 4. Sample mass influence in TG curve.

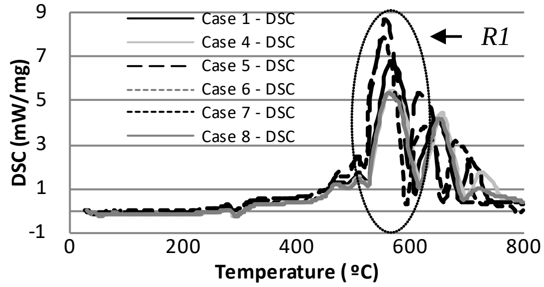

Figure 5. Sample mass influence in DSC curve.

To analyze the gas flow in the thermal decomposition of PVC in STA tests, we analyzed gas flows of 10, 40, 50 and 150 ml•min^{-1}. As it is shown in Figures 6 and 7, the dehydrochlorination reaction of the PVC was not affected by the inlet flow. The differences in the mass loss and in the DSC curves began with the oxidation reactions. On the one hand, the higher the gas flow rate was, the higher first oxidation reaction R1 was (Case 9). On the other hand, the higher air inlet flow was, the faster the mass loss in R1 was considered. In addition, we can observe that for the lower gas flow, case 11, the oxidation reactions are delayed and overlayed, since the oxidative chemical reactions had less air available.

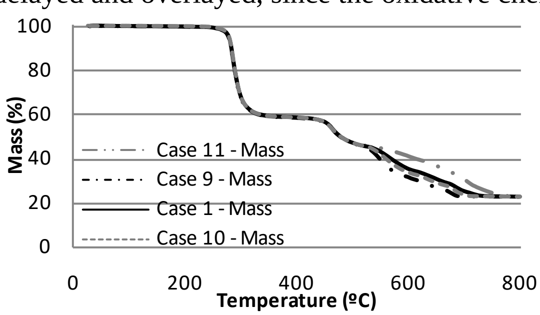

Figure 6. Gas flow influence in TG curve.

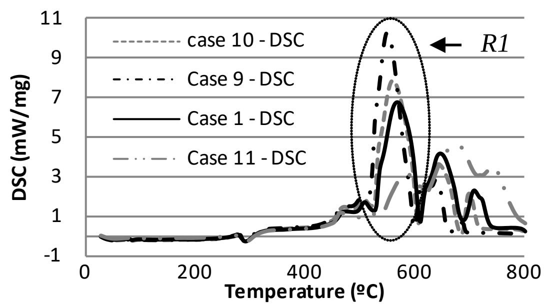

Figure 7. Gas flow influence in DSC curve.

In order to study the effect of the lid in the analysis of the thermal decomposition of PVC in the STA, we performed several tests with and without lid under inert and oxidative atmosphere for the PVC. Figures 8 and 9 show the results for PVC samples with and without lid under an oxidative (air with 21% of oxygen) and inert (nitrogen) atmosphere. Under air atmosphere, the sample without lid releases more heat and it has a higher mass loss rate in the first reaction of oxidation. That is caused by a lower availability of oxygen in the sample with lid. In this case, the gases released during the thermal decomposition pushes the air out of the crucible, decreasing oxygen concentration available to the oxidation of the sample inside it.

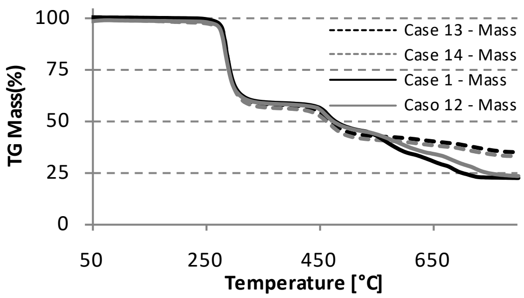

Figure 8. Lid influence in TG curve.

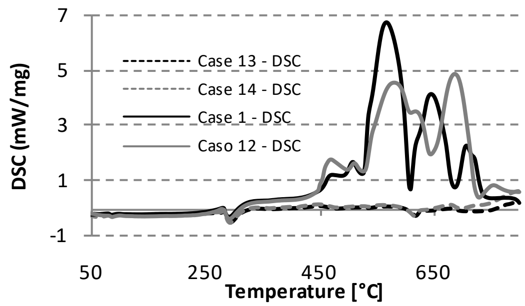

Figure 9. Lid influence in DSC curve.

As we can see, the dehydrochlorination reactions are approximately the same as the atmosphere does not have any influence on this reaction. Under nitrogen atmosphere, there is not influence in the chemical reactions that occur during the decomposition of the polymers and the same reactions at the same temperatures take place. We can observe that DSC curve differences were increased with the temperature which can be related with the radiation effect that affect the sample at high temperatures [17].

4 Conclusions

A sensitivity analysis of the influence of the boundary conditions in the thermal decomposition of PVC under STA experimental tests was performed to demonstrate how each parameter affects the thermal decomposition. We can resume the conclusion in the following sentences:

- Mass samples under 10 mg affect slightly the mass loss rate of the thermal decomposition, although for some specific conditions, following normative [1-3] indications, mass samples up to 10 mg can be recommended.
- Gas flow affects the reaction of the gases released in the thermal decomposition of the sample. Better aeration may well improve the oxidative chemical reactions allowing higher amount of energy release. Chemical reactions that not depend on the atmosphere are not influenced by the gas flow.
- The use of a lid with a pinhole in the holder under an inert atmosphere avoids the influence of the heat flux rate of radiation when sample and reference have different emissivities and improves the heat distribution in the holder. The use of lid in an oxidative atmosphere provides a self-generated atmosphere to the sample.

Although the sensitivity analysis was performed with PVC samples, combustion and thermal oxidative reactions will be affected in the same way by the sample mass, gas flow or lid for other thermoplastic materials. Not specific thermoplastic reaction as dehydrochlorination. All in all, every parameter studied in this analysis have influence in the thermal decomposition of the PVC and they should be well defined to perform the test attending to the desired conditions by the user and an explanation about those parameters has to be always included when tests are defined.

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