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DEVELOPMENT OF A UNIVERSAL CONSTANT RATE THERMAL ANALYSIS SYSTEM FOR BEING USED WITH ANY THERMOANALYTICAL INSTRUMENT

J. M. Criado[*], *L. A. Pérez-Maqueda, M. J. Diánez and P. E. Sánchez-Jiménez*

Instituto de Ciencia de Materiales de Sevilla, Centro Mixto Universidad de Sevilla-C.S.I.C.,
Avda. Américo Vespuccio s/n, 41092 Sevilla, Spain

The SCTA method implies to control the temperature in such a way that the reaction rate changes with the time according to a function previously defined by the user. Constant Rate Thermal Analysis (CRTA) is one of the most commonly used SCTA methods and implies achieving a temperature profile at which the reaction rate remains constant all over the process at a value previously selected by the user. This method permits to minimize the influence of heat and mass transfer phenomena on the forward reaction. The scope of this work is to develop a universal CRTA temperature controller that could be adapted to any thermoanalytical device. The thermoanalytical signal is programmed to follow a preset linear trend by means of a conventional controller that at the time controls a second conventional temperature programmer that forces the temperature to change for achieving the trend programmed for the thermoanalytical signal. Examples of the performance of this control system with a Thermobalance and a Thermomechanical Analyser (TMA) are given.

Keywords: *BaTiO$_3$, CRTA, PVC, SCTA, TG, TMA*

Introduction

The study of the kinetics of solid state reactions continues attracting the attention of researchers as shown by the large number of recent articles on the topic [1–24]. Sample controlled thermal analysis (SCTA) methods have proven to be more effective than conventional rising temperature experiments for obtaining reliable kinetic data of thermal decomposition of solids [25–42]. This is because the ability of SCTA for performing a direct or indirect control of both the partial pressure of the gases generated in the reaction and the heat evolution proportional to the reaction rate, minimizing the influence of heat and mass transfer phenomena on the forward reaction. This advantage has been also used for synthesising materials with controlled texture and structure [43–57]. It is noteworthy to point out that the SCTA control systems used all over the world for controlling the reaction temperature in such a way that the reaction rate is maintained constant all over the process are based on the one developed by Rouquerol. This control system implies to use as control signal an analogical output representative of the reaction rate. The scope of the present work is to modify the SCTA control system developed by Rouquerol in order to use a signal representative of the absolute value of the conversion instead if the reaction rate. This new arrangement allows extending the SCTA method for being used with any thermoanalytical instrument, even when an analogical output proportional to the reaction rate is not available.

Experimental

High purity polyvinyl chloride (PVC) and barium titanate samples supplied by Aldrich have been used.

A CI Electronic thermobalance that allows sample masses up to 5 g has been used. The thermobalance can be operated under vacuum or flow of gases. The thermal decomposition of PVC has been carried out using a starting mass of sample of 80 mg and a flow rate of nitrogen of 80 cc min^{-1}.

A thermomechanical analyser (TMA) equipment developed by us has been used. The variation in length of the sample is measured with a LVDT transducer from RDP, model D5 100AG. The LVDT is provided with a guide armature fitted to an alumina pushrod that can be displaced until contacting the sample by means of a micrometric screw. This TMA device can be operated under high vacuum or controlled atmosphere. The shrinkage of BaTiO$_3$ pellets has been followed under air atmosphere. The pellets were prepared from powder samples of 500 mg that were uniaxially pressed into a disc of 13 mm in diameter under a pressure of 660 MPa.

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[*] Author for correspondence: jmcriado@cica.es

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Akadémiai Kiadó, Budapest, Hungary
Springer, Dordrecht, The Netherlands

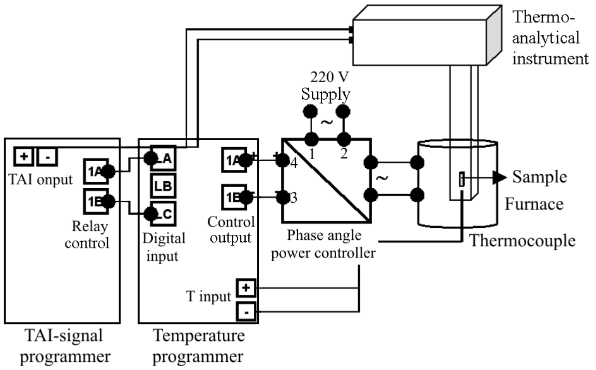

Fig. 1 Scheme of the CRTA system developed for controlling the reaction temperature through the input supplied by any thermoanalytical instrument (TAI)

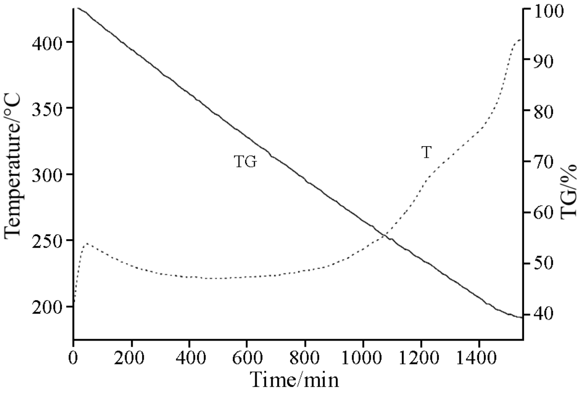

Fig. 2 Plots of mass loss percentage and temperature as a function of the time for the thermal dehydrochlorination of PVC at a constant decomposition rate C=3.10^{-2} mg min^{-1}

Results and discussion

Figure 1 shows the CRTA control system. It is constituted by a conventional Eurotherm programmer, model 2408, which receives the analog output of the thermocouple and controls the temperature of the sample placed in the thermoanalytical instrument (TAI) under either isothermal or rising temperature conditions at a temperature or heating rate previously selected. A second Eurotherm programmer, model 2408, was used for programming the profile of the analog output supplied by the TAI as a function of the time. It is noteworthy to point out that a single programmer cannot control the temperature such that the TAI signal follows a linear profile because the proportional integral differential (PID) control requires the value of the control parameter (the sample mass or the total change in length in our case) to be reversible as a function of the parameter to be controlled (i.e. the temperature). This condition is fulfilled by differential signals, such as decomposition rate or sintering rate, but not by integral signal, such as sample mass (in the case of a TG) or shrinkage (in the case of TMA), because these integral parameters are not reversible. The control of the reaction rate is achieved by connecting the control relay of the TAI programmer to the digital input, LA, of the temperature programmer. CRTA control is performed by selecting from the menu of the digital input a command that allows one to move the temperature program from a preset heating rate when the TAI control relay is closed, to a preset cooling rate when the TAI control relay is open. In other words, the temperature increases if the output signal supplied by the TAI is higher than the programmed setpoint and decreases if it is lower than the setpoint. The Holdback command of the TAI programmer must be activated all over the process in order to stop the program when the TAI signal is lower than the programmed value and to resume again when the input is higher than the setpoint.

Figure 2 shows the percentage of mass loss and the temperature as a function of the time obtained for the thermal dehydrochlorination of PVC under CRTA control. The mass signal schedule was programmed in the TAI programmer outlined in Fig. 1 for a mass decrease rate of 3.10^{-2} mg min^{-1}. The temperature controller was programmed such that either a heating or cooling rate of 2°C min^{-1} was selected depending on whether the mass output of the electrobalance was higher or lower, respectively, than the mass setpoint. The percentage of mass loss *vs.* temperature determined from the CRTA plots of Fig. 2 is shown in Fig. 3 together with a the TG curve obtained at a heating rate of 2°C min^{-1}. It can be observed that CRTA provides a better discrimination of the two steps observed in the thermal degradation of PVC than conventional TG. It is quite clear that the CRTA curve of the first step of the dehydrochlorination of PVC falls back on itself upon achieving the preset constant rate, indicating that this reaction follows

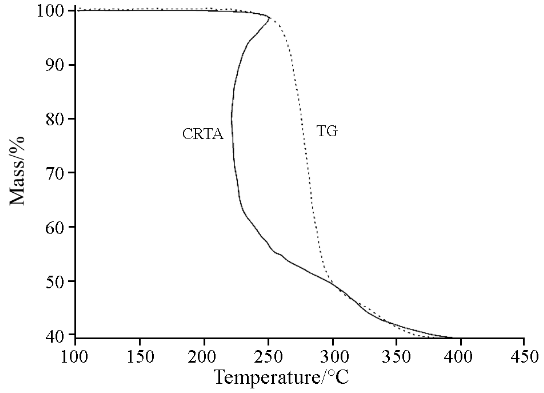

Fig. 3 CRTA and TG plots recorded for the thermal decomposition of PVC under decomposition rate C=3.10^{-2} mg min^{-1} and a heating rate of 2°C min^{-1}, respectively

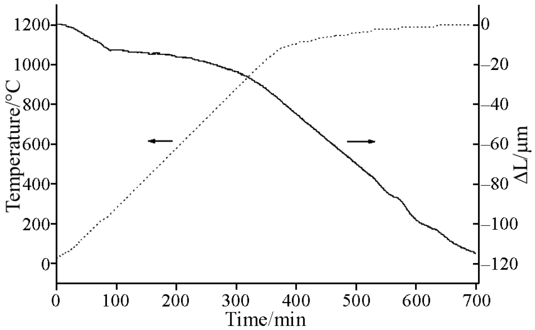

Fig. 4 Rate controlled TMA of a $BaTiO_3$ pellet under a constant shrinkage rate equal to 0.258 µm min^{-1}

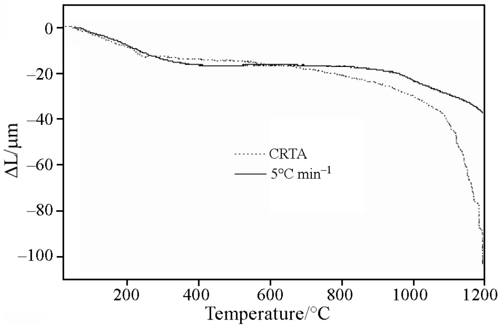

Fig. 5 TMA of $BaTiO_3$ pellets recorded under a linear heating rate of 5°C min^{-1} and under a constant shrinkage rate of 0.258 µm min^{-1}, respectively

either an Avrami–Erofeev kinetics [33], as we suggested in a previous paper [58], or a mechanism controlled by the random scission of the main chain of the polymer (59), instead of obeying a '*n* order' kinetics as commonly proposed in literature [60–65].

Figure 4 shows the change of the dimension and the temperature as a function of the time obtained for $BaTiO_3$ with the TMA developed by us under CRTA control at a constant shrinkage rate C=0.258 µm min^{-1}. In this case the analogical output corresponding to the total change of length supplied by the LVDT transducer was used as input of the TAI signal programmer on the device outlined in Fig. 1 following the procedure previously described for the electrobalance. The shrinkage data taken from Fig. 4 have been plotted as a function of the corresponding temperatures in Fig. 5 together with the shrinkage plot obtained at linear heating of 5°C min^{-1}. These results clearly point out that the densification attained by $BaTiO_3$ under CRTA control of temperature is considerably higher than under linear heating control.

Conclusions

- It has been developed a universal control system that can be easily adapted to any Thermoanalytical Instrument (TG, TMA, Dilatometer, etc.) that supplies to this control system a signal input directly proportional to the total progress of the reaction, without requiring an input representative of the reaction rate.
- The CRTA control system developed here has been successfully applied to the study of a) the thermal decomposition of PVC by means of a conventional electrobalance and b) the sintering of $BaTiO_3$ by means of a TMA equipment developed by us.

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