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Effect of nitrate content on thermal decomposition of nitrocellulose

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ABSTRACT

Data on the thermal stability of energetic materials such as nitrocellulose was required in order to obtain safety information for handling, storage and use. In the present study, the thermal stability of four nitrocellulose samples containing various amount of nitrate groups was determined by differential scanning calorimetery (DSC) and simultaneous thermogravimetery-differential thermal analysis (TG-DTA) techniques. The results of TG analysis revealed that the main thermal degradation for the nitrocellulose occurs in the temperature ranges of 192–209 °C. On the other hand, the TG-DTA analysis of compounds indicates that nitrate content of nitrocellulose could has affect on its thermal stability and its decomposition temperature decrease by increasing its nitrogen percent. The influence of the heating rate (5, 10, 15 and 20 °C/min) on the DSC behaviour of the nitrocellulose was verified. The results showed that, as the heating rate was increased, decomposition temperature of the compound was increased. Also, the kinetic parameters such as activation energy and frequency factor for the compound was obtained from the DSC data by non-isothermal methods proposed by ASTM E696 and Ozawa.

1. Introduction

Nitrocellulose is a derivative of natural cellulose; it has an outstanding range of properties. The nitrogen content of nitrocellulose for coatings and printing inks is between 10.7 and 12.3%. Nitrocellulose with nitrogen content above 12.6% is classed as an explosive [1–5].

Compatibility studies of different materials by differential scanning calorimetery (DSC), differential thermal analysis (DTA) and thermogravimetery (TG) have been carried out for several years [6–10]. Kinetic studies have become a crucial point in thermal analysis, in which the main purpose is to determine the mechanism of pyrolysis reaction and to calculate the parameters of the Arrhenius equation. These data are required for energetic materials and their related compounds to be qualified for performance and safety in their manufacture, handling, storage and use [11,12].

In this work, the thermal stability of nitrocellulose compounds were investigated by means of differential scanning calorimetery and simultaneous thermogravimetery-differential thermal analysis (TG-DTA). The results allowed us to acquire information concerning these compounds in the solid-state, including their thermal stability and thermal decomposition. Also, this study an attempt has been made to determine kinetic parameters of non-isothermal decomposition of the nitrocellulose. To the best of our knowledge, various data are available on the thermal behaviour and kinetics of decomposition of nitrocellulose compounds [13–21]. Also, in the previous study, the decomposition of nitrocellulose was followed by noting the changes in the infrared spectrum of a thin film as a function of time [22]. But, there is no report on the effect of nitrate content on its thermal behaviour.

2. Experimental

The nitrocellulose compounds with different content of nitrate were synthesized as proposed by ref. [1]. The thermochemical behaviour of nitrocellulose samples with different content of nitrate (12.5, 12.9, 13.5 and 13.9% nitrogen) was characterized. The DSC curves were obtained by Du Pont differential scanning calorimeter model DSC 910S, in temperature rang of 50–400 °C using an aluminum crucible, at different heating rates (5, 10, 15 and 20 °C/min), under helium atmosphere with the flow rate of 50 ml min^{-1}.

Thermal analysis and differential thermal analysis were carried out using a Stanton Redcroft, STA-780 series with an alumina crucible, applying heating rate of 5 °C/min in a temperature range of 50–400 °C, under helium atmosphere with the flow rate of 50 ml min^{-1}. The sample mass used was about 3.0 mg.

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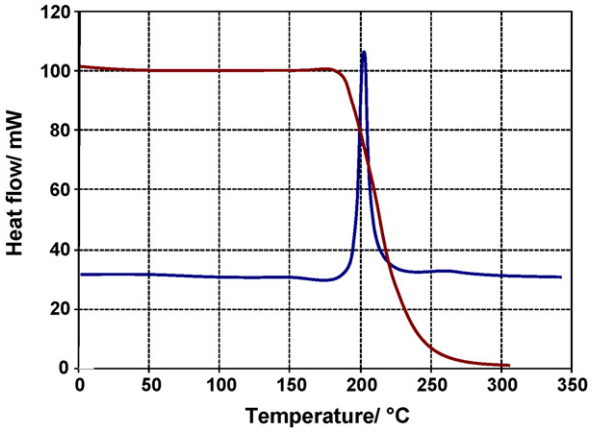

Fig. 1. TG/DTA curves for nitrocellulose with 13.9% nitrate content (sample 1); sample mass 3.0 mg; heating rate 5 °C/min; helium atmosphere.

3. Results and discussion

The thermoanalytical curves of nitrocellulose with 13.9% nitrate content (sample 1) are presented in Fig. 1. The TG/DTA curves showed a single sharp exothermic behaviour with a maximum at 201 °C, accompanied by a sharp weight loss. Previous studies [2,23,24] showed that, the decomposition of nitrocellulose at this temperature produces H_2O, CO, NO and CO_2 as evolved gases and CO is the major decomposition product of nitrocellulose. Also, thermomicroscopy showed [2] that the nitrocellulose melted in the region of 200 °C to give a highly mobile bubbling liquid. There was no indication of melting on the DTA curve, presumably because any endothermic effect was out-weighted by the concurrent exothermic decomposition.

3.1. Effect of heating rate and nitrogen content

Fig. 2 shows DSC curves of the nitrocellulose with 13.9% nitrate content (sample 1) at several heating rates. It was found that, by increasing the heating rate, the decomposition temperature of the nitrocellulose was shifted to higher temperatures. These shifts in onset temperature and peak temperature are shown in Fig. 3. On the other hand, the results of our study show that as the heating rate was increased, the heat of decomposition obtained by peak area was decreased. These reductions in heat of decomposition are shown in Fig. 4.

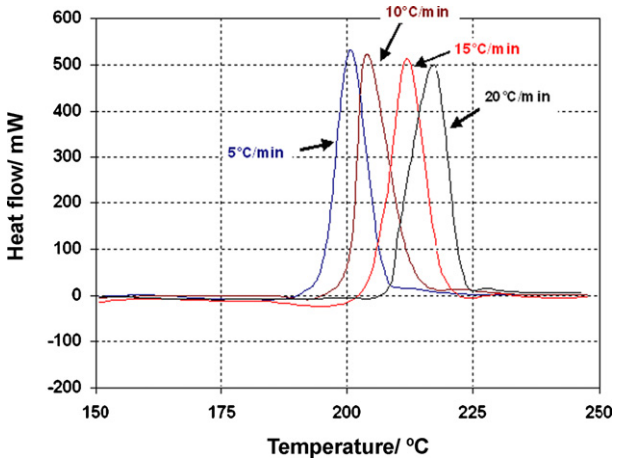

Fig. 2. The effect of heating rate on the DSC results of nitrocellulose with 13.9% nitrate content (sample 1); sample mass 3.0 mg; helium atmosphere.

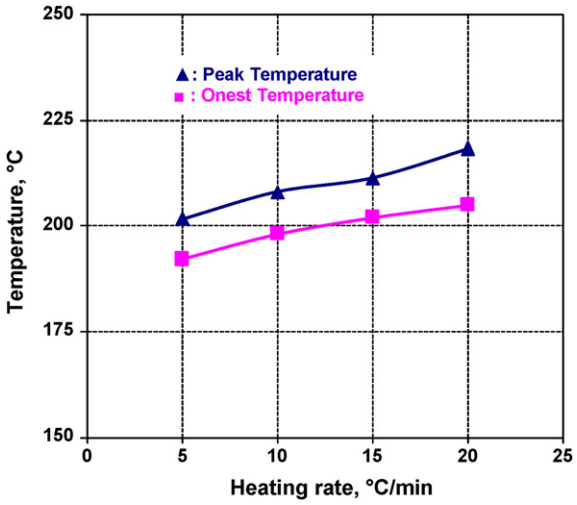

Fig. 3. Variation of onset temperature and peak temperature of nitrocellulose with 13.9% nitrate content (sample 1) by changing heating rate.

Fig. 5 shows DSC curves of different nitrocellulose samples containing various nitrogen contents at 10 °C/min heating rate. The results showed that thermal stability of nitrocellulose decreases with increasing their nitrate content. These shifts in onset temperature and peak temperature for various samples are shown in Fig. 6. Also, the results of this study show that as the nitrate content of nitrocellulose samples was increased, the heat of decomposition obtained by peak area was decreased. These reductions in heat of decomposition are shown in Fig. 7.

3.2. Kinetic methods

The ASTM method E698 [25] was used to determine the Arrhenius parameters for the thermal decomposition of nitrocellulose. In order to calculate the pre-exponential factor (Z), it was assumed that the decomposition followed first-order kinetics. The DSC curves obtained at various heating rates for sample 1 are shown in Fig. 2.

The plot of the ln ($\beta\ T_m^{-2}$) against $1/T_m$ was straight lines for nitrocellulose (sample 1), which indicated that the mechanism of thermal decomposition of these compounds is the first order [26].

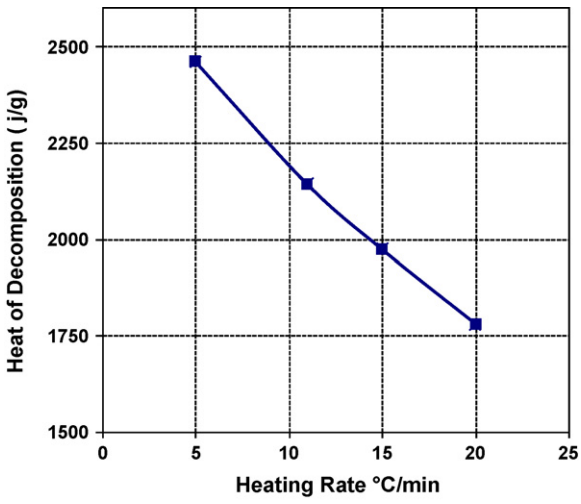

Fig. 4. The effect of various heating rate on heat of decomposition for nitrocellulose with 13.9% nitrate content (sample 1).