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.

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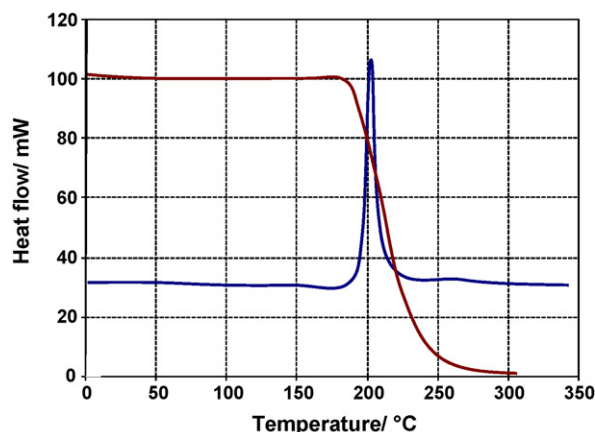
Fig. 1. TG/DTA curves for nitrocellulose with 13.9% nitrate content (sample 1); sample mass 3.0 mg; heating rate 5 °C/min; helium atmosphere.

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.
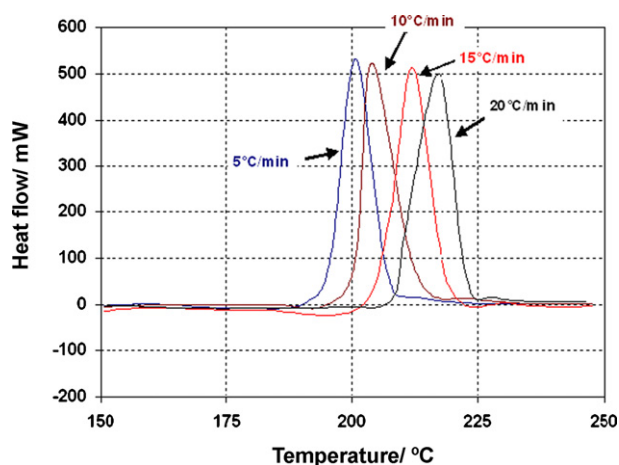

Fig. 2. The effect of heating rate on the DSC results of nitrocellulose with 13.9% nitrate content (sample 1); sample mass 3.0 mg; helium atmosphere.
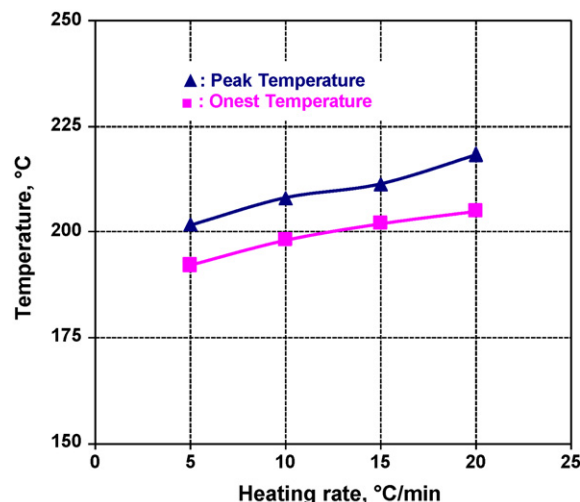

Fig. 3. Variation of onset temperature and peak temperature of nitrocellulose with 13.9% nitrate content (sample 1) by changing heating rate.

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].
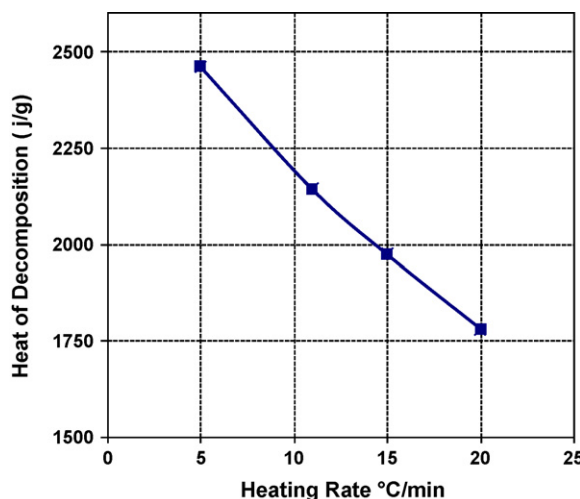

Fig. 4. The effect of various heating rate on heat of decomposition for nitrocellulose with 13.9% nitrate content (sample 1).
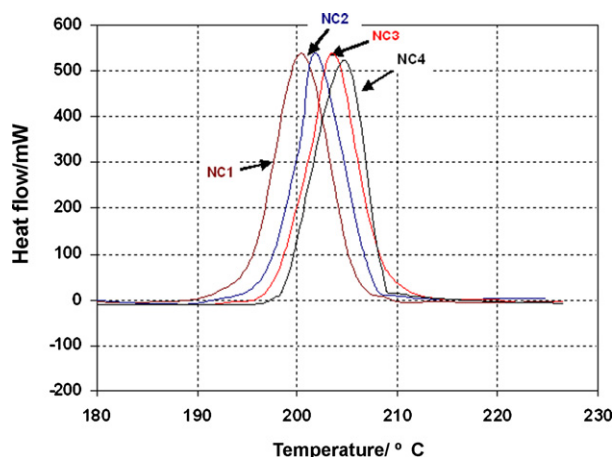
Fig. 5. The effect of nitrate content of nitrocellulose on DSC behaviour (the nitrate content of the samples was—NC1: 13.9, NC2: 13.5, NC3: 12.9 and NC4: 12.5% nitrogen).
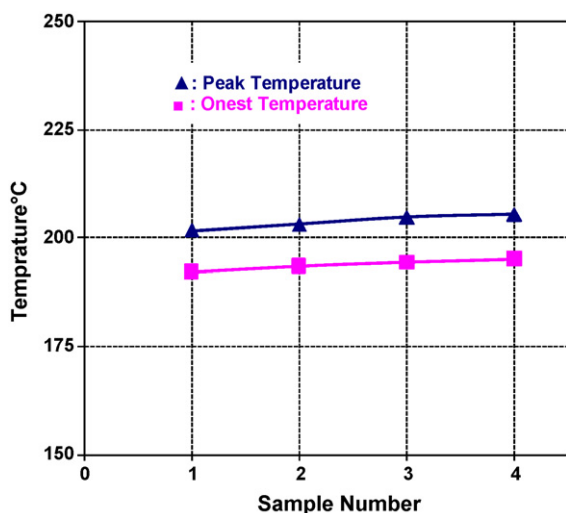

Fig. 6. The effect of nitrate content of nitrocellulose on the onset temperature and peak temperature of decomposition process; sample mass 3.0 mg (the nitrate content of the samples was—sample 1: 13.9, sample 2: 13.5, sample 3: 12.9 and sample 4: 12.5% nitrogen).

The slope of the lines was equal to $-E_a/R$. Therefore, the activation energy (E_a) was obtained from the slope of the graph while the log of the pre-exponential factor, log (Z/S^{-1}) was calculated from the expression given in ASTM E698:

$$Z = \beta \left(\frac{E_a}{RT_m^2} \right) \exp \left(\frac{E_a}{RT_m} \right) \qquad (1)$$

Table 1 contains the calculated values of activation energy and frequency factors for nitrocellulose.

On the other and, activation energy (E_a) for this compound was calculated by Ozawa method. In this method, activation energy could be determined from plots of the logarithm of the heating rate versus the inverse of the temperature at the maximum reaction rate
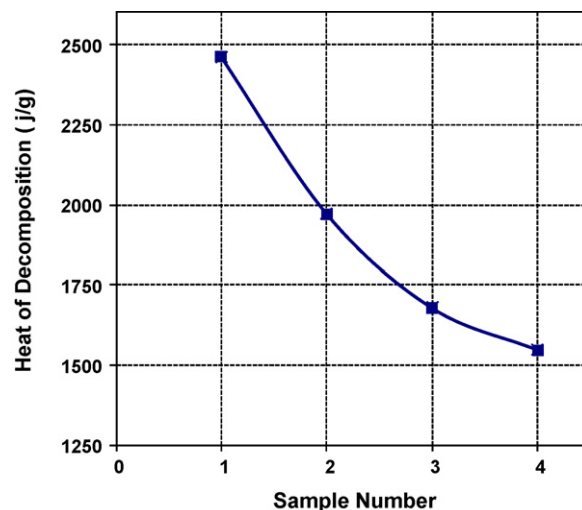

Fig. 7. Effect of nitrate content of nitrocellulose samples on the heat of decomposition.

in constant heating rate experiments. The activation energy can be determined by Ozawa method without a precise knowledge of the reaction mechanism, using the following equation:

$$\log \beta + 0.496 \frac{E_a}{RT_m} = C \qquad (2)$$

The activation energy of degradation of the studied nitrocellulose was estimated using Ozawa method. The plot of logarithm of heating rates versus reciprocal of the absolute peak temperature for sample 1 was straight lines with $r = 0.9917$, which indicated that the mechanism of thermal decomposition of nitrocellulose over this temperature range did not vary [27]. On the other hand, frequency factor (Z) was found for the compound from the Eq. (1).

All resulted data are summarized in Table 1. Comparing the results of the application of the two methods, we observe that values calculated for nitrocellulose (sample 1) by ASTM method are slightly higher than those of Ozawa methods.

After the kinetic parameters (E and A) were obtained, the thermodynamic parameters of activation can be calculated from the following equations [28,29]:

$$A \exp \frac{-E}{RT} = \nu \exp \frac{-\Delta G^{\neq}}{RT} \qquad (3)$$

$$\Delta H^{\neq} = E - RT \qquad (4)$$

$$\Delta G^{\neq} = \Delta H^{\neq} - T\Delta S^{\neq} \qquad (5)$$

where, $\Delta G^{\neq}$, $\Delta H^{\neq}$ and $\Delta S^{\neq}$ are free energy, enthalpy and entropy of the activation, receptivity. ν is the $\nu = K_B T/h$ (where K_B and h are Boltzmann and Plank constant, respectively). Table 1 gives the computed thermodynamic parameters for nitrocellulose.

3.3. Half-life determination

Assuming a first-order decomposition, the equation to determine the half-life is: $t_{1/2} = 0.693/k$. The rate constant (k) for

Table 1
Comparison of kinetic and thermodynamic parameters of the nitrocellulose with 13.9% nitrate content (Sample 1) obtained by ASTM and Ozawa methods

Method	Activation energy (KJ/mol)	Frequency factor $\log Z$ (S^{-1})	r^*	$\Delta G^{\neq}$	$\Delta H^{\neq}$	$\Delta S^{\neq}$	Half-life (Year)	T_b (°C)
ASTM	156.8	16.89	0.9925	121.41	152.88	66	6.7	196.75
Ozawa	154.0	16.58	0.9917	121.38	150.01	60	4.7	196.95

decomposition reaction could be calculated by the following equation [27]:

$$\log k = \log Z - \frac{E_a}{2.3RT} \qquad (6)$$

Which for the temperature of 50 °C and using activation energies (E_a) and frequency factors (Z) obtained in the above; the equation was solved for k. Table 1 listed the half-life for the sample 1. By considering half-lives calculated for nitrocellulose using kinetic parameters obtained by different methods, this compound at 50 °C has a half-life about 5 years.

3.4. Critical explosion temperature

The critical explosion temperature (T_b) an important parameter required to insure safe storage and process operations involving explosives, propellants and pyrotechnics. It is defined as the lowest temperature to which a specific charge may be heated without undergoing thermal runaway [30–32]. T_b may be calculated from inflammation theory and appropriate thermokinetic parameters namely the activation energy, pre-exponential factor, and heat of reaction. In order to obtain the critical temperature of thermal explosion (T_b) for the nitrocellulose, Eqs. (7) and (8) were used [33].

$$T_e = T_{e0} + b\phi_i + c\phi_i^2 \quad , \; i = 1-4 \qquad (7)$$

$$T_b = \frac{E - \sqrt{E^2 - 4ERT_{e0}}}{2R} \qquad (8)$$

where b and c are coefficients, R is the gas constant; E is the value of activation energy obtained by kinetic method.

The value (T_{e0}) of the onset temperature (T_e) corresponding to $\phi \to 0$ obtained by Eq. (7) is 185 °C for nitrocellulose with 13.9% nitrogen content.

The critical temperature of thermal explosion (T_b) obtained from Eq. (8) is 196.75 °C and 196.95 °C for nitrocellulose with 13.9% nitrogen content by using ASTM and Ozawa data, respectively.

4. Conclusion

The thermal stability of nitrocellulose samples was determined by differential scanning calorimetery (DSC) and simultaneous differential thermal analysis and thermogravimetery (TG/DTA). Also, the influence of the different heating rates on the DSC behaviour of this compound was verified. Activation energy and frequency factor for the decomposition were calculated by different methods.

According to the TG/DTA data it was verified that the thermal decomposition of nitrocellulose started at about 192 °C. Based on the kinetic data obtained for the activation energy by ASTM and Ozawa methods, using non-isothermal thermogravimetery experiments, nitrocellulose has approximately 5 years half-life at 50 °C.

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