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THERMODESORPTION STUDIES OF AMMONIUM NITRATE PRILLS BY HIGH-RESOLUTION THERMOGRAVIMETRY

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Abstract

High-resolution thermogravimetry was used to study the thermodesorption of octane from ammonium nitrate (AN) prills with different porosities. The samples were wetted by immersion in octane. Multiple steps were obtained from the measured mass-loss curves, which reflect the evaporation of the excess liquid, as well as the thermodesorption of octane from the pores and the surface of the AN prills. The quantity of octane desorbed in these steps was correlated with the volume in the pores and the amount adsorbed on the surface, and used to estimate the adsorption capacity, porosity and surface area of AN prills. The results were also compared to observations from scanning electron microscopy.

Keywords: ammonium nitrate, high-resolution TG, thermodesorption

Introduction

ANFO, an admixture of ammonium nitrate (AN) prills with fuel oil, is widely used as a commercial explosive. The wettability of AN prills is one of the primary factors determining the physical stability and detonation behaviour of ANFO. The wettability of AN has been found to be affected by several factors, including porosity and surface area of the prills.

In terms of the porous structure of AN prills, there is scarce information available in the literature. At present, there are various methods for characterizing porous materials; however, among these methods, only electron microscopy and mercury penetration are suitable for describing the pore size range of AN prills (>1 μm). Mercury porosimetry has been shown to incorrectly assess the overall pore geometry and the distribution of pores in AN prills [1]. Scanning electron microscopy (SEM) has been used to obtain a two-dimensional view of pores [2–3]. However, SEM is only able to sample surface pores and a small fraction of the area of the sample. Although SEM is insufficient for evaluating the percentage of the pore structure in the entire sample, it is a very important tool and gives valuable insight into the porosity of the area sampled. 3-D nuclear magnetic resonance (NMR) microscopy has also been ap-

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plied to evaluate the porous structure of AN [1]. However, the NMR technique involves a relatively elaborate and time-consuming procedure.

High-resolution thermogravimetry (HR-TG) is useful in monitoring the stepwise thermodesorption of adsorbed molecules from porous solids [4–5]. The technique can be used to characterize surface and structural properties of various materials [6–15]. The HR-TG results agree with those obtained from nitrogen adsorption measurements [8–14] and differential scanning calorimetry (DSC) [15]. In contrast to adsorption measurements, TG is more flexible with respect to the adsorbate used, and the reagents are inexpensive and easier to handle than mercury. Given these advantages, TG becomes a valuable alternative for the routine measurement of the porosity of various materials.

There is considerable interest in finding new methods to evaluate surface and structural properties of AN prills. This research explores the possible application of HR-TG as a simple alternative to study the adsorption capacity, the porosity and surface area of AN prills. The results obtained from HR-TG were compared with those derived from SEM.

Experimental

Sample preparation

Three samples of ammonium nitrate prills of different categories (Table 1) were used in this study. They are identified as Prills A–C. The samples were kindly donated by Orica Canada Inc., ETI Canada Inc. and Agrium. The categories, single prill mass, average prill diameter, and apparent volume are summarized in Table 1. Samples have a wide distribution in prill size. Only prills within the diameter range specified in Table 1 were used in TG experiments. The apparent volume (V_a), which was calculated using this average prill diameter, refers to the total volume occupied by 1 g of prill sample, excluding inter-prill spaces. Wetted AN prills were prepared by immersing them in octane (reagent grade, purity >98%) for at least 1 day.

Table 1 Characteristics of various AN prills

Prill	Category	Mass per prill/mg	Diameter/mm	V_a/cm^3 g^{-1}
A	Porous	6.3±0.6	2.0±0.2	0.66±0.06
B	Mini	1.0±0.2	1.0±0.1	0.52±0.05
C	Dense	7.0±1.0	2.0±0.1	0.59±0.03

Thermogravimetry measurements

A TA Instruments 2950 High-Resolution Thermogravimetric Analyzer (HR-TG) was used for the thermodesorption measurements on various AN prills. The dynamic rate high resolution technique was used. This technique allows the heating rate to be varied between a fixed minimum and a maximum specified, in this case 5°C $\min^{-1}$. The resolution (*R*) and sensitivity (*S*) parameters were 4 and 6, respectively. These parameters were established experimentally to provide the optimal heating rate for thermodesorption.

Thermodesorption of octane from the AN prills was monitored over a temperature range from 25 to 120°C. The samples were purged with dry nitrogen at flow rates of 60 mL $\min^{-1}$ in the furnace and 40 mL $\min^{-1}$ in the balance chamber. An open platinum pan was used for all measurements. For each run, 3 (Sample A and C) or 15 (Sample B) wetted prills were removed from the octane and placed in an unsealed DSC aluminium pan. This pan was used to minimize the evaporation of octane prior to the experiments. For experiments with no excess octane, the prills were placed in the pan using tweezers, instead of a spatula. The mass of the sample varied between 20–30 mg depending on the prill density and the amount of octane adsorbed. To confirm the baseline of the TG, an experiment using the same heating profile was performed on an empty pan. The TG drift was ~5 μg, which represents 0.02 mass% for 20–30 mg of sample.

Results and discussion

The HR-TG mass loss curves were measured for various AN prills, which had been immersed in octane. Figure 1, where the ratio of sample mass to the mass of neat AN prills, m/m_{AN}, is plotted *vs*. temperature, shows the typical mass loss behaviour for AN Sample A. Figure 2 shows the derivative of mass with respect to temperature. The TG results show that octane desorbs from the AN samples via a multi-step process. In order to identify each step, experiments were conducted using different conditions. In Figs 1 and 2, the three TG (or DTG) curves represent the results obtained for: (*a*) as-received prills, (*b*) prills wetted with octane, (*c*) prills wetted with excess octane.

Comparison of the various TG curves suggests that the initial step is the mass loss due to the evaporation of the bulk liquid. The subsequent step represents the thermodesorption of adsorbed octane on the surface of AN remote from the monolayer, which is

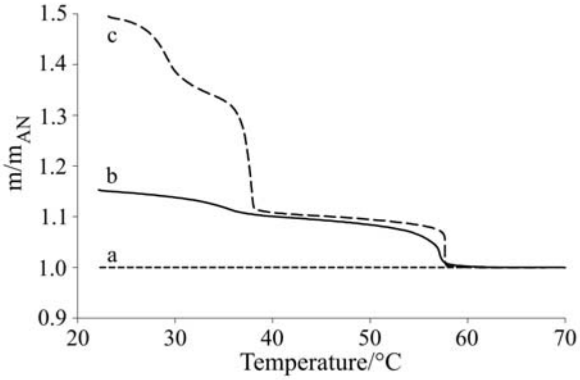

Fig. 1 TG curves for desorption of octane from AN (*R*=4; *S*=6). a – as-received prills; b – prills wetted with octane; c – prills wetted with excess octane

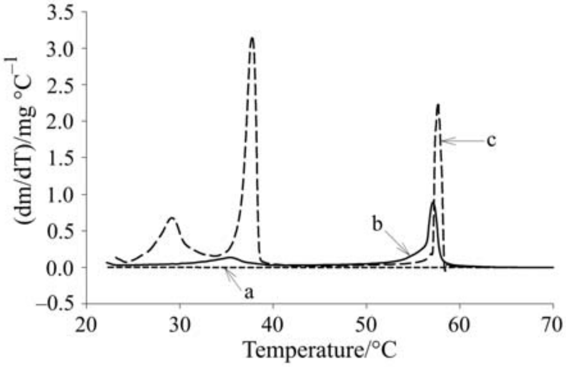

Fig. 2 DTG curves for desorption of octane from AN (R=4; S=6). a – as-received prills; b – prills wetted with octane; c – prills wetted with excess octane

in direct contact with the AN surface. The last step reflects a gradual thermodesorption of adsorbate in the pores and of the monolayer of octane on the AN surface.

The properties of surface liquid differ significantly from those observed for bulk liquid because adsorbate molecules interact with the solid surface. The adsorbate requires higher energies to thermodesorb from the solid surface and the pores. These properties change with distance and approach those of bulk liquid at relatively long range.

From the TG results for various AN prills, the total adsorption capacity (n_t) was estimated from the total mass loss of the wetted samples. The values of n_t for the various AN prills are summarized in Table 2.

To evaluate the pore volume and the specific surface area of the various AN prills, a higher HR-TG setting (R=5 and S=8) was applied to further study the thermodesorption of octane from wetted AN prills.

Table 2 TG results for porosity analysis of AN prills

Prill	n_t/mass%	n_p/mmol g^{-1}	V_p/cm^3 g^{-1}	ε	n_m/mmol g^{-1}	a/m^2 g^{-1}
A	15.7±0.3	0.83±0.06	0.14±0.01	0.21±0.01	0.14±0.03	39±9
B	9.1±0.5	0.29±0.05	0.05±0.01	0.09±0.02	0.02±0.01	4±2
C	7.7±0.5	0.31±0.03	0.05±0.004	0.08±0.01	0.08±0.02	23±5

As shown in Fig. 3, the TG curve has a sharp initial step (reflecting the thermodesorption of surface liquid) and two subsequent steps for the thermodesorptions of the pore liquid and of the monolayer. However, the transition between thermodesorption of the pore liquid and monolayer is not easily distinguished. The minimum of the derivative of the time-dependent TG curve (Fig. 4) can be used to localize the characteristic point on the mass loss curve [10].

As illustrated in Fig. 4, the differential DTG curve plotted vs. time shows two local minima (denoted by I and II). The mass loss estimated between the projection of the points I and II on the TG curve represents the thermodesorption of octane inside

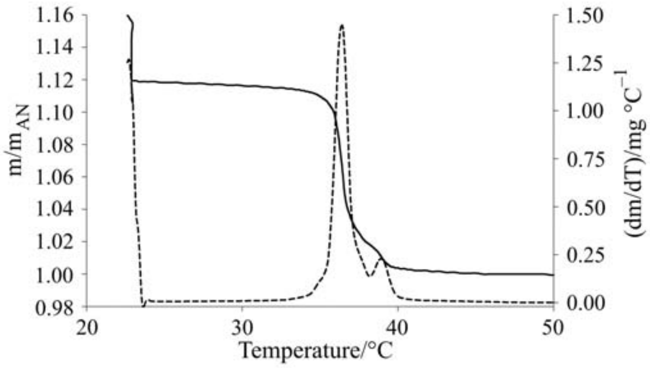

Fig. 3 TG results for AN prills wetted with octane (*R*=5; *S*=8). Solid line – mass ratio (*m* to mass of AN); dashed line – derivative of mass with temperature

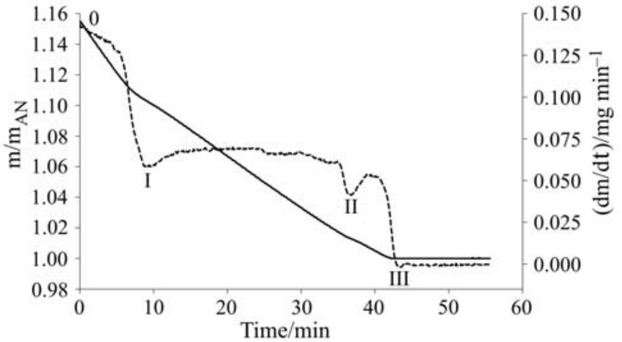

Fig. 4 TG results for AN prills wetted octane (*R*=5; *S*=8). Solid line – mass ratio (*m* to mass of AN); dashed line – derivative of mass with time

the pore. In Table 2, the results are expressed as pore capacity (n_p), in millimoles of thermodesorbed octane per gram of the dried AN sample.

The total volume of pores (V_p) is the product of pore capacity and the molar volume of liquid octane. The porosity (ε), which is defined as the ratio of the total pore volume (V_p) to the apparent volume (V_a) for 1 g of AN prills, is also included in Table 2.

The projection of the point II and the residue point III on the TG curve gives the monolayer capacity (n_m), which can be converted to the specific surface area (a) of the sample assuming that the cross-sectional area (σ) of the octane molecule is known:

$$a=n_m L\sigma$$

where L is Avogadro's constant and σ is the average area occupied by each molecule in the monolayer.

A molar volume of 163.6 cm^3 mol^{-1} and a cross-sectional area (σ) of $4.2\cdot10^{-19}$ m^2 molecule^{-1} were used for octane to calculate the volume and specific surface area of the various AN prills. The molecular cross-sectional area (σ) was calculated using the equation proposed by Emmett and Brunauer [16]:

$$\sigma = f\left(\frac{M}{\rho L}\right)^{2/3}$$

where f is a packing factor, which for hexagonal close-packing becomes 1.091, ρ is the density of the liquid, and M is the molar mass of the adsorbate.

Prior to comparing the surface and structure of the various AN prills, it is essential to consider the reproducibility of the HR-TG results. The results in Table 2 are the average value of at least two replicates. The uncertainty of the values represents one standard deviation of the repeated measurements. For prills A and C, the adsorption capacity and porosity data (error ±10%) are more reproducible than the surface area data (error ±23%). For prill B, there is a large uncertainty in the values of n_m and a because the specific surface area of the prill B is smaller than that for prills A and C. Therefore the mass loss resulting from the thermodesorption of the monolayer (~0.15 mass%) is affected significantly by the baseline drift (0.02 mass%, see the experimental section). Variations in the TG and subsequently the derived data are believed to be caused by variations in the structure of the prills. AN prills are highly irregular [2, 3], the differences in the surface roughness and pore structure among the prills significantly affect the reproducibility of the results.

Note that for the specific surface area of AN prills, the values were obtained by assuming the mass loss of the last step was due to the monolayer of octane adsorbed on AN. However, the mass loss may be due to adsorbed octane extending beyond the monolayer and consequently, the surface area may be overestimated. On the other hand, the monolayer capacity (n_m) in Table 2 may still be able to provide information about the relative surface area of each sample.

In comparison with prills B and C, AN prill A has significantly higher values of adsorption capacity (n_t), porosity (ε) and specific surface area (a), as shown in Table 2. Thus, the porosity and surface roughness, which increase the surface area, could be the main factors affecting the adsorption of octane.

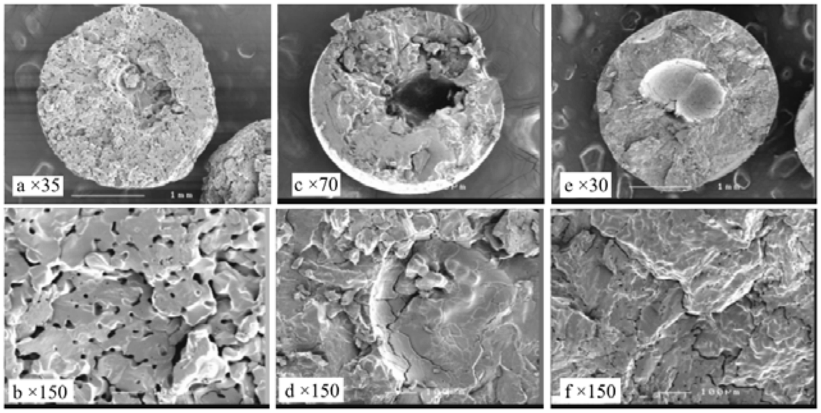

Fig. 5 SEM micrographs on: a – b – Prill A; c – d – Prill B; e– f – Prill C

For AN prills B and C, there are no significant differences in the porosity. The HR-TG results suggest that the structural properties of these two samples are similar. However, prill B has a higher adsorption capacity than prill C, while its surface area is lower. Their differences in adsorption capacity may be due to other factors such as their moisture content and surface impurity.

The porosity of the various AN prills obtained from HR-TG results agrees with the general observations from SEM, but the latter technique does not give any quantitative information about the pore parameters. The SEM micrographs for prills A, B and C are illustrated in Fig. 5. The SEM micrographs suggest that the pore sizes of various AN prills range from 10 to 80 μm. The relatively high porosity and surface area of prill A contribute to enhanced wettability with fuel oil, which leads to its effective application in making ANFO.

Conclusions

High-resolution thermogravimetry (HR-TG) was applied to study the thermodesorption of octane from ammonium nitrate (AN) prills. The adsorption capacity, porosity and specific surface area of three different AN samples were evaluated from the resulting HR-TG curves. The estimated porosity of the AN prills agree with scanning electron microscopy observations. It appears that HR-TG is a simple and valuable technique to characterize AN porosity and adsorption capacity.

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