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MEASUREMENT OF THE RELAXATION TRANSITIONS OF NITROCELLULOSE BASED GUNPOWDER

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In order to be able to perform a complete characterisation of nitrocellulose, as a subject of a surveillance program for the MoD, different techniques (DSC, TMA, DMA) were compared, attempting to measure the different thermal transitions in nitrocellulose gunpowder. The sample preparation in this investigation is fully discussed. With DMA the shear mode was applied, trying to indicate the phase transitions. A clear conclusion could be drawn about the optimal technique to measure the relaxation behaviour. Also some considerations are given about the possibility to use this characterisation in a surveillance program.

Keywords: *nitrocellulose, phase transitions, sample preparation*

Introduction

Nitrocellulose is a well known material which has been studied for a long time [1]. Some of these investigations consider porosity [2, 3], while others inquire parameters as melting enthalpy [4], or decomposition behaviour [5, 6]. Nitrocellulose (NC) has a chain-like structure and therefore it shows behaviour that is similar to (other) more general polymers. This means that NC should exhibit certain relaxation transitions during heating. From literature [7] it is known that NC displays several small relaxation steps, rather than one large relaxation process, known as the glass transition temperature (T_g), like with other polymers. At least two, but possibly three relaxation processes are known to exist in NC, entitled α and β (and possibly γ). These relaxation processes occur approximately around 40, –35 and –80°C, respectively, but are influenced by the presence of plasticizers [8]. The spread in these temperatures can be quite large. Also the existence of the γ process is questionable and sometimes the transition was attributed to residual solvent in the system.

Fig. 1 Several ageing phenomena of NC grains

As a part of a surveillance program for the MoD in the Netherlands it is important to have knowledge of the mechanical behaviour of NC-based gun powders. A change in composition of these materials (like chain scissioning caused by ageing phenomena) can be recognized in an early state by measuring the mechanical properties, and therefore be of great interest during safe storage and use of solid propellants. In Fig. 1 some examples are shown of aged NC grains. A decrease in mechanical integrity of NC grains can result in an increase in fracturing during firing which leads to a significant rise in pressure build-up. A typical example of this fracturing behaviour can be seen in Fig. 2.

Fig. 2 Ageing of NC grains, leading to an increasing grain fracture during firing

The shortening of the chains could result in a change in one of the transitions. However, it is necessary to be able to measure these transitions by a method that is accurate enough to see small changes in these transitions. Several methods are available to measure relaxation processes:

- differential scanning calorimetry (DSC)
- thermal mechanical analysis (TMA)
- dynamic mechanical analysis (DMA)

Each of these techniques has its own characteristic parameters which should be taken into account. In all of these techniques, sample preparation is of great importance for an accurate measurement.

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Experimental

In order to measure the relaxation transitions of single base NC propellant an attempt was made to measure this material with DSC, TMA and DMA. The exact composition of the propellant that was used in these measurements was confidential, but it consisted mainly of pure NC. An overview of the parameters used during these experiments is given in Table 1.

The problem that occurred during this investigation was in all cases the fact that the material was very rigid, so cutting with a knife would be difficult. At the same time, it appeared to be somewhat dangerous to simply saw it as an alternative. The material had to be subjected to a high load in order to be able to machine it, but the load could not be too large because of the energetic nature of the material. Also the amount of heat that would be subjected to the sample during machining could either ignite the material or cause thermal alterations in the molecular structure, prior to testing. Using a remote controlled sawing machine would be too laborious, by reason of the large number of different types of propellants to measure.

In spite of these restrictions in sample preparation, an attempt was made to scrape some material off of a grain with a scalpel. Special care was taken of the graphite layer on the outside of the grain, by taking as much NC material as possible and as little graphite as possible. This amount (3 mg) was measured with DSC. Subsequently an amount of three grains was milled in a grinding machine and sieved to a particle size of less than 500 μm. This fraction was then also measured with DSC after the powder was pressed by hand into an aluminium light cup. Also DSC measurements with a relatively high heating rate (20°C min^{-1}) were performed, as well as measurements with a relatively large quantity of material (18.5 mg), both using the method mentioned above.

For DMA measurements NC grains were milled for a very short time (1 s), which resulted in irregularly shaped samples, approximately 3 mm in size. These kinds of samples are not useful to measure the exact shear modulus of this material, but it should be possible to measure the change in modulus as a function of temperature and therefore to measure relaxation processes. Preliminary to the actual temperature scans, a displacement scan was performed in order to be able to determine the (quasi) linear behaviour of this NC powder.

Using the same method as mentioned above, samples are manufactured for TMA measurements. In these experiments change in geometry was measured as a function of temperature, from which certain transitions could be derived.

Results and discussion

The results of the measurements are summarized in Tables 2 and 3. In these tables several transitions are described, as well as the method of determination of these transitions.

Table 1 Overview of all thermal (mechanical) experiments

	DSC	TMA	DMA
Equipment	Mettler DSC 822[e]	Mettler TMA/SDTA 841[e]	Mettler DMA/SDTA 861[e]
Temperature range/°C	–150→100	–120→100	–120→100
Heating rate/°C min^{-1}	10 and 20	5	2
Atmosphere	N_2	n. a.	n. a.
Flow rate/mL min^{-1}	50	n. a.	n. a.
Cups	aluminium	n. a.	n. a.
Mass/mg	3–19	n. a.	n. a.
Type of load	n. a.	ballpoint probe	shear
Force (amplitude)/N	n. a.	1	6
Displacement amplitude/μm	n. a.	n. a.	1
Frequency/Hz	n. a.	n. a.	1

Table 2 Results of DSC measurements of transitions of NC

Preliminary treatment	Trans./°C	Method	Trans./°C	Method	Trans./°C	Method
Scraping	–	–	–	–	50	peak
Milling and sieving	–	–	14	onset	55	extrap.
High β	–74	inflect.	29	onset	60	peak
Large quantity	–	–	–4	onset	57	peak

extrap. – extrapolated peak, inflect. – inflection point, trans. – transition

Table 3 Results of mechanical measurements of transitions of NC

Applic.	Pretreatment	Trans./°C	Method	Trans./°C	Method	Trans./°C	Method	Trans./°C	Method
DMA	Short milling	–	–	–54	extrap.	–	–	42	peak
TMA	Short milling	–74	onset	–39	onset	–17	onset	56	onset

extrap. – extrapolated peak, trans. – transition

The curves of the DSC measurements are presented in Fig. 3. In these curves, as well as in Table 2 it can be seen that in general the choice of determination of the transition is a peak or an onset temperature. Obviously a relaxation step measured by DSC is represented by a step in the baseline, rather than a peak or an onset temperature. However, in this case the baseline is increasing above 50°C, indicating a (beginning of a) process around these temperatures, which is interfering with the possible relaxation step in this region. For measurements that are a part of a surveillance program it is not a matter of knowing the exact temperature of a relaxation process, but it is necessary to be able to see a change in temperature at which a certain event is taking place (like a glass transition). This is the reason why in this case more distinctive indications like peak and/or onset temperatures are used.

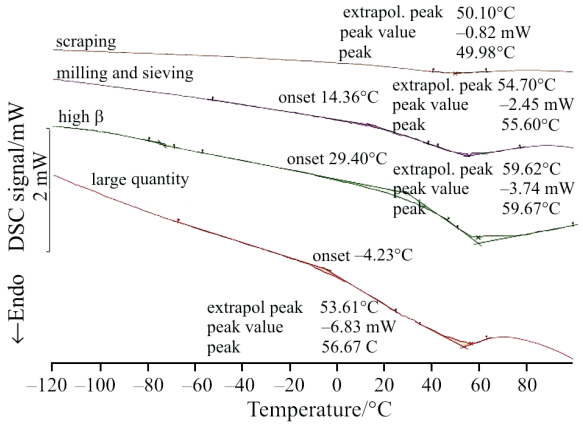

Fig. 3 DSC measurements on NC with different type of sample preparation

In Table 3 the results of the TMA and DMA measurements are summarized. Like stated earlier in this paper, preliminary to the DMA temperature scans, a displacement amplitude scan was performed to determine the (quasi) linear behaviour of this material. The resulting curve is shown in Fig. 4.

From the displacement amplitude scan in Fig. 4 it can be seen that this material shows (quasi) linear behaviour until 1.5 μm. From this result, maximum displacement amplitude of 1 μm was set for the DMA temperature scans (Table 1).

A typical DMA curve is represented in Fig. 5. In this figure the storage modulus (*G*'), loss modulus (*G*'') and tanδ are plotted *vs*. the sample temperature. A relax-

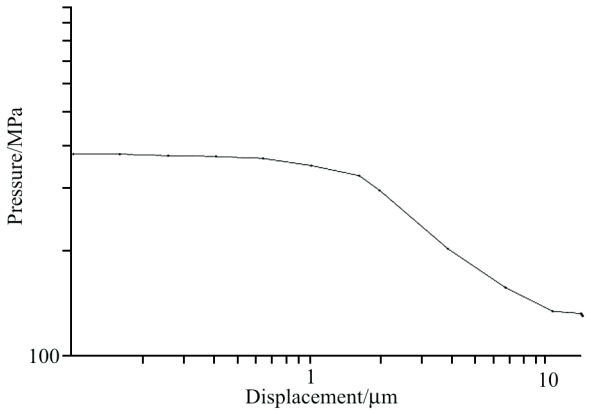

Fig. 4 Displacement amplitude scan of NC powder

ation transition should be visible in these curves as a step in the *G*' curve, accompanied by a peak in the *G*'' curve. Since tanδ is by definition equal to *G*'/*G*'', a peak in the tanδ curve should also indicate a relaxation behaviour. A step in the *G*' curve is only explicitly apparent above 20°C. Still, even this step is only visible as a gradually process over a broad temperature range and the whole step is not completed during the total temperature frame of this experiment. More clearly are the two peaks in the *G*'' curve, however the one at low temperatures is not suitable for an accurate determination, because of the relatively high noise levels. Because the processes are so gradually, also in the tanδ curve, no accurate determination of the temperatures at which the relaxation takes place can be made from this curve.

TMA curve in Fig. 7 is accomplished by taking the original TMA measurement curve and connecting the first and last point of this curve by a 'baseline', as can be seen in Fig. 6. By subtracting this baseline from the original curve a new curve is derived, which shows the behaviour of the material, without the influence of ther-

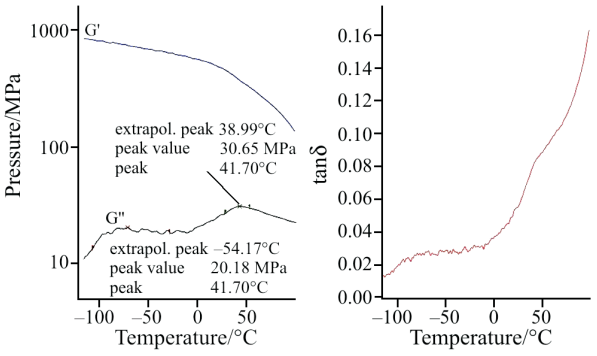

Fig. 5 Typical DMA plot of NC powder

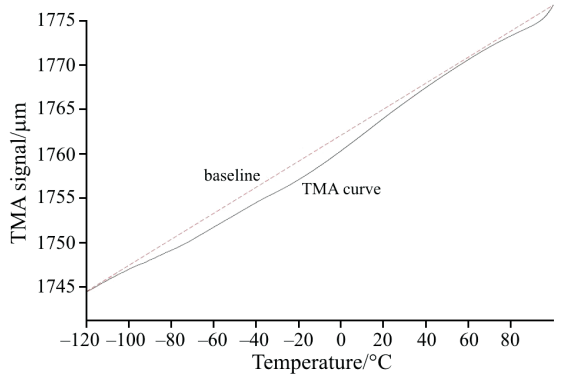

Fig. 6 TMA plot of NC powder and a baseline

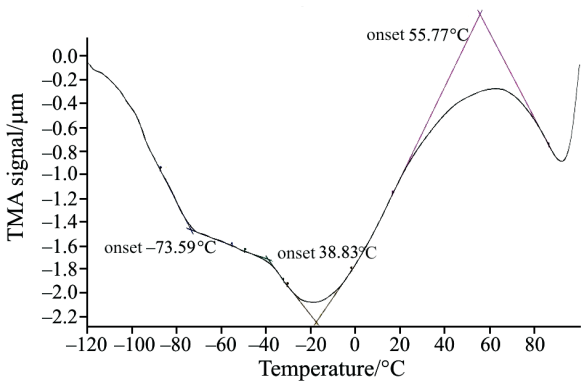

Fig. 7 TMA plot of NC powder, original curve subtracted from baseline

mal expansion. In this way the changes in slope are seen in a much more pronounced way than in the case of a plot of the expansion coefficient as a function of temperature. In such a curve secondary relaxation processes are visible as a variation in slope, determined by the onset temperatures of which the results can be seen in Table 3.

In the low temperature region (Fig. 7) very small undulations of the curve are visible. In fact these undulations are too small to attribute them to relaxation processes, considering the fact that it concerns a curve which shows extreme magnifications of thermal (mechanical) effects. Compared to the values found for the relaxation processes in the literature [7] and to the values presented in this paper, the presence of a transition at –17°C seems to be questionable. Further work is necessary to investigate this effect.

Conclusions

From the tables reporting the found transitions it can be concluded that there is a large spread in the results. Obviously there are also large differences between the methods that are used for sample preparation and measurements. From the curves it appears that the transitions are very weak and difficult to determine. This would result in a relatively inaccurate measurement of these transitions, so it is questionable whether any of these methods is useful for a surveillance program. The worst results seem to come from DSC measurements. These experiments give only very gradually changing curves, making it almost impossible to produce representative values for transition temperatures. This could be explained by the insufficient contact between the hard NC material and the pan. Also the DMA results show no distinct transitions, even while this technique is known to provide information about the smallest of transitions. A reason for this could be that the used measurement mode (shear) is not suitable for these kinds of materials. Possibly three-point-bending or cantilever is a better option. It appears that the TMA measurements give the best results out of these three techniques, although a subtraction of the baseline is necessary to visualize distinct changes in the curve. The found values for the different transitions are only partly in accordance with those found in literature. Still, the supposed transition at low temperatures (around –80°C) is found with two out of three techniques used in this investigation.

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