Transitions and relaxations in plasticised nitrocellulose

R. C. Warren
Defence Science and Technology Organisation, Weapons Systems Research Laboratory, Defence Research Centre, Salisbury, South Australia
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Mixtures of nitrocellulose (NC) and various plasticisers were studied by dynamic mechanical analysis (d.m.a.) and differential scanning calorimetry (d.s.c.). The plasticisers were nitroglycerine, triacetin, diethylene glycol dinitrate and dimethylacetamide. At high plasticiser concentrations a single glass transition was observed. However, at lower plasticiser concentrations the glass transition split into two processes: a low temperature transition associated with the glass transition of the plasticiser, and a higher temperature loss process associated with the NC. The splitting of the glass transition was attributed to a breakdown in the cooperativity of motion of the plasticiser and NC molecules. An additional transition of a different type occurred at about 50°C. This transition temperature was independent of plasticiser type and concentration, and of the d.m.a. measuring frequency. It was accompanied by an endothermic peak in d.s.c. traces and was attributed to an increase in flexibility of the NC molecule.

(Keywords: nitrocellulose; nitroglycerine; glass transition; dynamic mechanical analysis; d.s.c.; cooperative motion)

INTRODUCTION

The first practical nitrocellulose (NC) propellant was developed in 1884, and double base propellants consisting of NC and nitroglycerine (NG) were developed soon after. In the intervening 100 years there have been few published studies on the physical properties of these propellants. Recently a number of significant studies were reported to the Conference on Nitrocellulose Characterisation at Waltham Abbey, UK, in 1980. Dynamic mechanical[1], thermomechanical[2] and dielectric spectroscopy[3] studies on double base propellants with a range of compositions were reported, and molecular mechanisms were proposed[4]. As conference proceedings were not published, some of this work, plus additional data, was recently published in this Journal[5].

The dynamic mechanical work demonstrated that double base propellants generally have two loss processes, one at about -30°C designated β, and another above 30°C designated α. A third loss process, designated γ, was found in pure NC and in low NG content propellants at about -90°C. These results were recently confirmed by Baker and Privett[6], who reported that the α transition was affected by annealing the propellant at 80°C for 1 h. They also attributed the γ transition to retained solvent. However, because the magnitude of the γ transition was found to increase as the solvent was removed[5], it is difficult to see how this attribution could be correct. Further work is in hand to try to settle this matter.

Similar behaviour has been reported for plasticised and unplasticised cellulose acetate butyrate (CAB)[7], and cellulose acetate (CA)[8,9].

The most significant result from these studies was that a single glass transition did not appear to exist for double base propellants. Many polymeric systems have multiple transitions or loss processes, but most have one transition that can be clearly identified as a glass transition[10]. Instead the α and β processes in double base propellants each had some of the characteristics of a glass transition. A large change in modulus accompanied the α process, but there was no sharp change in expansion coefficient nor any evidence for the process in d.s.c. traces. In contrast, with the β transition there was a large change in expansion coefficient and a step in the d.s.c. trace, which normally indicates a glass transition, but only a small change in modulus.

Dielectric studies of the NC/NG system have also been reported[3,11] in which the dependence on temperature and frequency of the dielectric loss associated with the β process was investigated. A study of the temperature dependence of birefringence of these materials has also been made[12]. None of these studies has provided an explanation for the apparent absence of a single glass transition in double base propellants.

It is possible that the mechanism of the interaction between NC and NG could be elucidated by studying high NG content materials, but this was rejected for safety reasons. This restriction does not apply to inert plasticisers, so it was decided to study the dynamic mechanical properties and d.s.c. response of mixtures of NC with several inert plasticisers, as well as energetic plasticisers, in an attempt to explain the transition behaviour of double base propellants.

EXPERIMENTAL

Materials

The nitrocellulose (NC) was a commercial propellant grade made from wood cellulose nitrated to a nitrogen level of 12.6%, which corresponds to a degree of substitution of 2.44. The NG, triacetin (TA) and diethylene glycol dinitrate (DEGDN) were commercial

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propellant grades, while the dimethylacetamide (DMAc) was laboratory grade.

The materials studied consisted of mixtures of NC and the following plasticisers. Concentrations of plasticisers are in percentage by weight.

NG	0, 10, 20, 35, 45%
TA	20, 35, 50, 55, 70, 80, 90, 100%
DEGDN	35%
DMAc	35, 40, 45%

One per cent stabiliser was added in most cases, and previous experience indicated that the stabiliser would not significantly affect transition behaviour.

Specimen preparation

The NC–NG, NC–20% TA, NC–35% TA, and NC–35% DEGDN mixtures were prepared by mixing the NC, plasticiser and processing solvents in a 1.5 kg Winkworth Incorporator for 4 h at 50°C. The processing solvents were acetone–ethanol mixtures chosen to give a readily processable dough. After mixing, the dough was extruded through a die of cross-section 3 × 35 mm. The slabs were stoved for 3 weeks at 50°C to remove the solvents. Previous experience with propellants had indicated that this procedure caused negligible plasticiser loss in the bulk of the material. Specimens for dynamic mechanical analysis (d.m.a.) in the single cantilever mode were machined from the extruded slabs of material to dimensions of 2 × 6 × 30 mm. The dimensions of the NC–0% NG and NC–10% NG specimens were 1.5 × 6 × 30 mm.

The NC–DMAc, NC–50% TA and NC–55% TA mixtures were of sufficiently low viscosity for them to be mixed in the Winkworth Incorporator without solvents, and they were not extruded. D.m.a. specimens were made by pressing 2 mm thick slabs of material which were sealed between plates and annealed at 55–60°C for 30 min. Specimens were cut 10 mm wide and 30 mm long, wrapped in two layers of thin polyethylene film to prevent evaporation of the DMAc or TA, and tested immediately.

NC–TA specimens containing 70, 80 and 90% TA for low temperature d.s.c. measurements were made by placing the NC and TA in tubes mounted vertically. Mixing was achieved by inverting the tubes at regular intervals until the mixture was homogeneous.

Experimental techniques

Measurements of Young's modulus and tan δ were made with a Polymer Laboratories dynamic mechanical thermal analyser. The specimens were tested in the single cantilever mode over a span of 8 or 13 mm. The test frequencies were 0.33, 3, and 30 Hz, and the temperature was scanned at a rate of 5°C min^{-1}.

D.s.c. measurements were made with a Perkin-Elmer DSC-2 instrument controlled by a Model 3600 data station. Specimens of 20 mg were sealed in vapour-tight pans. The temperature scan rate was 20°C min^{-1}.

RESULTS AND DISCUSSION

The α and β processes and the glass transition

The effect of NG concentration on the dynamic mechanical loss of NC was the same as observed previously[5]. There were two loss peaks below ambient temperature, one at −80 to −90°C, which has previously been designated γ, and another at 0 to −40°C which has been designated β.

The γ peak only occurred for NG contents of 0 and 10%. The β peak appeared in all the materials, and the magnitude increased with increasing NG content. The β peak has been previously attributed to the motion of NG molecules associated with NC sidegroups[4,5,11].

At temperatures above 0°C there was a large peak which has previously been designated α (ref. 5). The temperature of the α peak, T_α, varied from above 133°C for pure NC down to 56°C for 45% NG. A small peak due to a first-order transition was observed at 50–60°C for pure NC and low NG/NC mixtures. A similar peak has been reported in CA[8,9], which will be discussed later.

Tan δ for NC–20% TA is illustrated in *Figure 1*, together with tan δ for NC plasticised with 35% DEGDN. In each case there were α and β peaks. The NC–35% DEGDN behaved in a very similar manner to NC–35% NG.

The effect of higher concentrations of TA is shown in *Figure 2*. NC–35% TA had α and β peaks, but there was considerable overlap. There was a single peak for NC–50% TA and NC–55% TA. Greater amounts of TA gave materials which were too soft for d.m.a. measurements.

The peaks in tan δ of NC plasticised with DMAc are shown in *Figure 3*. For DMAc concentrations of 35 and 40% there were α and β peaks but they were not well resolved. NC–45% DMAc had only a single loss peak.

The frequency of 0.33 Hz was chosen to illustrate the loss behaviour because the loss peaks were most clearly separated at this frequency. Similar loss curves were obtained at frequencies of 3 and 30 Hz, with the temperatures of all peaks, except for the first-order transition peak, increasing by 10–20°C for an increase in frequency of a factor of 91.

A plot of temperature of peak tan δ *versus* plasticiser concentration for various mixtures of NC and NG is given in *Figure 4*, along with the one result obtained for NC and DEGDN. Both T_α and T_β, for NG concentrations above 20%, decreased with increasing plasticiser concentration. The form of the curves above 45% NG was not determined because of safety considerations. However, the glass transition

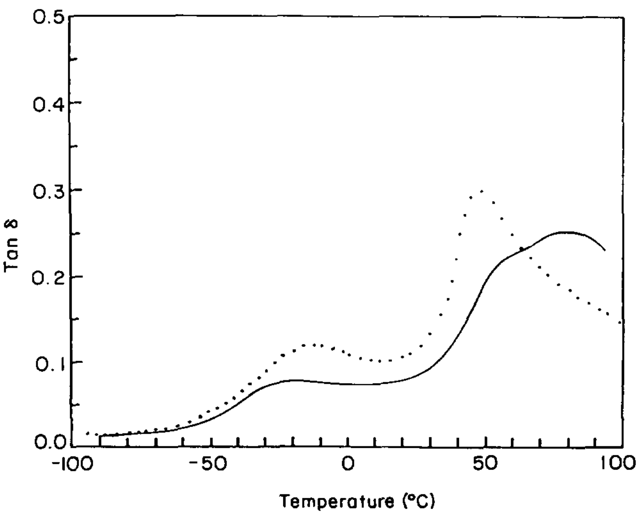

Figure 1 The mechanical loss of NC–20% TA (···) and NC–35% DEGDN (——) at 0.33 Hz

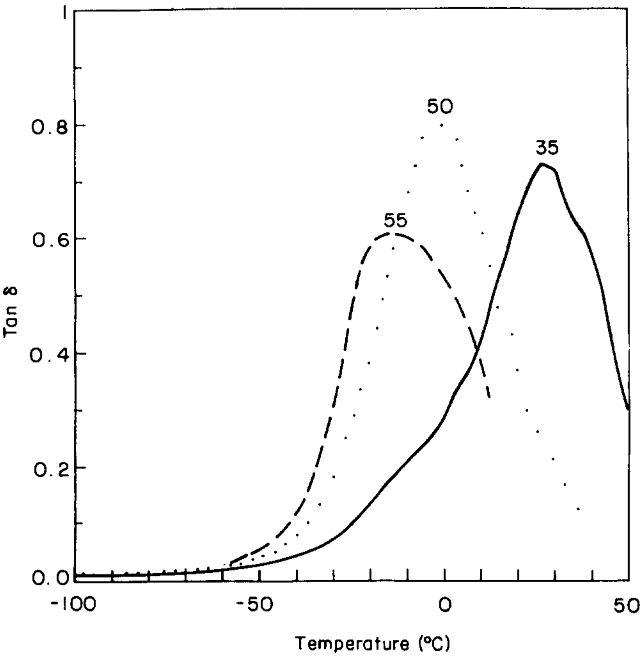

Figure 2 The effect of TA on the mechanical loss of NC–TA (0.33 Hz). Numerals indicate TA content (%)

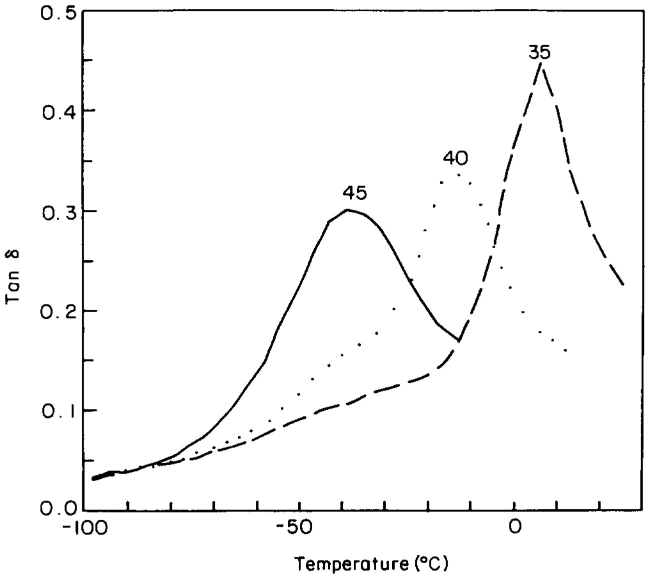

Figure 3 The effect of DMAc on the mechanical loss of NC–DMAc (0.33 Hz). Numerals indicate DMAc content (%)

temperature of NG is known to be about −70°C, so it might be expected that the curves should approach this temperature at high NG concentrations. This is confirmed by a reported study on volume dilatometry of NC–NG[13]. The data have been replotted in *Figure 4* for comparison, where it can be seen that the transitions merge into a single transition at about −75°C for NG contents above 80%.

A plot of the temperature of peak tan δ *versus* concentration for NC–TA is given in *Figure 5*. The α and β peaks are evident at low plasticiser concentrations. Also plotted are the transition temperatures measured by d.s.c. The d.s.c. values are about 40°C below T_β from d.m.a., but show the same downward trend with increasing plasticiser content. The lower temperatures for d.s.c. are probably due to the lower effective measuring frequency of the d.s.c. process. The materials containing 50–60% TA were inadvertently made without stabiliser, and had to be disposed of before the d.s.c. measurements could be made.

A plot of the temperature of peak tan δ *versus* concentration for NC–DMAc is also given in *Figure 5*. Again, the α and β peaks merge into a single peak at high plasticiser concentration. The T_g of DMAc was too low, about −110°C, for accurate d.s.c. data to be obtained for NC–DMAc mixtures.

An important observation was that there was no indication of the α transition in any of the d.s.c. traces, which confirms the previous observations on double base propellants[5].

These observations indicate that for plasticised NC materials at high plasticiser concentrations there is only a single glass transition, and that as the plasticiser concentration drops, the glass transition splits into two processes. This suggests that below a certain plasticiser concentration, which is different for each plasticiser, a single glass transition does not exist. The reason for this can be derived from a consideration of the mechanism of the glass transition.

The classical explanation of the glass transition is based on the behaviour of flexible, amorphous polymer

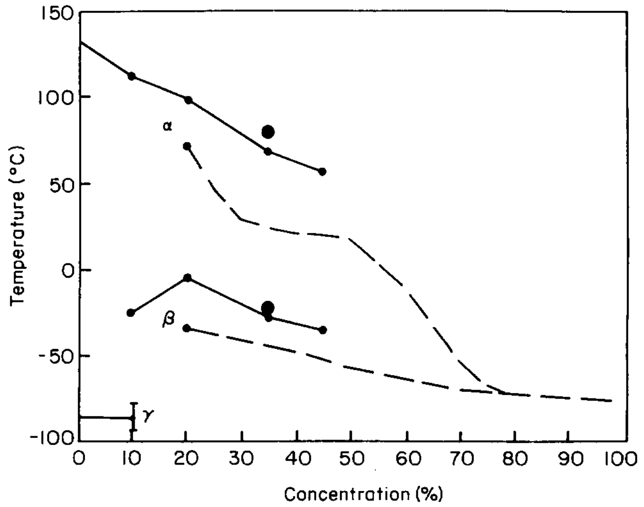

Figure 4 Temperature of peak mechanical loss *versus* temperature for NC plasticised with: NG (——), DEGDN (●) and dilatometry data replotted from ref. 14 (– – –)

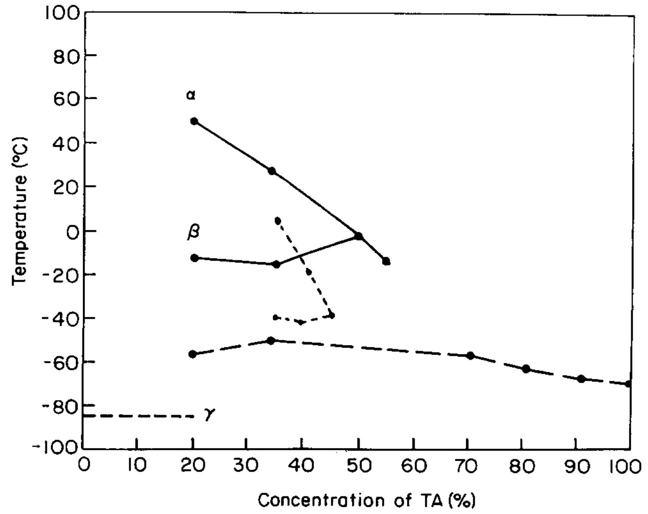

Figure 5 Temperature of peak mechanical loss and d.s.c. transition temperature for NC plasticised with TA and DMAc: NC–TA mechanical (——), NC–DMAc mechanical (– – –) and NC–TA d.s.c. transition temperature (— — —)

chains[10]. Short segments of the chains move as a result of thermal energy, and above the glass transition there is sufficient free volume for cooperative motion of a number of segments to occur. This cooperative motion allows large scale deformations of the material, and also reduces the modulus. Addition of a plasticiser reduces the interaction between the polymer molecules, and the resulting cooperative motion of the plasticiser and polymer molecules increases the amount of free volume, and hence lowers T_g.

The application of the classical picture to NC is not necessarily justified. Rather than being a flexible polymer, various techniques have shown NC to be a stiff molecule. It has a persistence length in dilute solutions in the range 110–165 nm[14,15]. Hence a major requirement for the existence of a single glass transition may not occur in plasticised NC.

A plausible explanation for the glass transition behaviour of plasticised NC is given by the following discussion. At high plasticiser concentrations the overall molecular motion is controlled by the plasticiser molecules, and there is sufficient free volume at high temperatures for the NC and plasticiser molecules to move cooperatively. As the temperature is lowered, the system undergoes a normal glass transition. However, for lower plasticiser contents, the ability of the plasticiser molecules to maintain cooperativity of motion along the length of the stiff NC chains would be reduced, and the cooperative motion of the NC molecules and plasticiser molecules would break down. The system would then consist of regions of plasticiser molecules effectively isolated along the NC chain, but moving cooperatively with each other and the NC nitrate sidechains, as previously described[5,11]. The plasticiser molecules would hence have their own glass transition, the β transition. The plasticiser molecules would have a viscosity controlled by free volume, as described by the theory of Doolittle[16]. This viscosity would undergo a sudden change at T_g because of the change of free volume as measured by t.m.a. Baker and Privett derived alternative expressions for the temperature and frequency dependence of viscosity.[6]

An explanation for the α process is less definite. It appears that the effect of the stiff NC molecules is similar to the effect of other high aspect ratio fillers in a polymeric binder. At sufficiently high temperatures the reinforcement becomes less effective, and the modulus decreases. Hence the α process may be better described as a relaxation, rather than a transition.

The first-order loss process

A different type of process from those considered above occurred at about 50°C. The process is frequency insensitive and has an enthalpy of melting, so it will be termed a first-order transition to differentiate it from the other transitions, which are sometimes referred to as second-order transitions.

The effect of the first-order transition on mechanical loss is shown in *Figure 1*, where tan δ for NC containing 35% DEGDN shows a shoulder on the α peak at about 50°C. A similar shoulder was seen on curves for NG contents of 0–20% in the temperature range 50–60°C, and for 35% NG there was a slight shoulder on the α peak at the same temperature, but at higher plasticiser contents the α peak overlapped the shoulder. Baker and Privett reported that the α transition may consist of two processes, but they gave no details[6].

The transition temperature did not depend on measuring frequency over the range 0.33–30 Hz. The fact that the transition occurs in the same temperature range for all frequencies, and for different plasticiser types and concentrations, indicates that the mechanism of first-order transition relates to the NC molecule alone, and not to NC–plasticiser interactions.

An endothermic peak occurred at a similar temperature in d.s.c. traces of NC–DMAc mixtures containing between 42.5% and 60% NC, and the height of the peak depended on the NC content[17]. The peak was absent if the sample was rerun immediately, but reappeared on annealing at room temperature for several hours. It was previously attributed to a liquid crystal transition, but it is now believed this may not be correct.

The transition has the characteristics of a form of melting, and to test this possibility d.s.c. measurements were made on double base propellants. D.s.c. scans of samples of NC plasticised with NG at levels of 20, 35, and 45% showed endothermic peak at a temperature of about 45–55°C. The enthalpy change varied with thermal history of the sample, but was about 0.5–0.9 J g^{-1}.

To determine the rate of reformation of the structure which underwent the melting, d.s.c. runs were made in the following manner on 45% NG samples. After a normal heating run to above the transition temperature, the specimen was cooled at maximum rate to 20°C. The specimen was allowed to equilibrate for the nominated time and then a further run made. The peak temperature of the virgin material varied for different samples, possibly reflecting different thermal histories. Typical traces are given in *Figure 6*. It can be seen that as the annealing time increased the peak height increased, and the peak moved to higher temperatures. Note that there was no evidence of a step in the trace associated with the α transition.

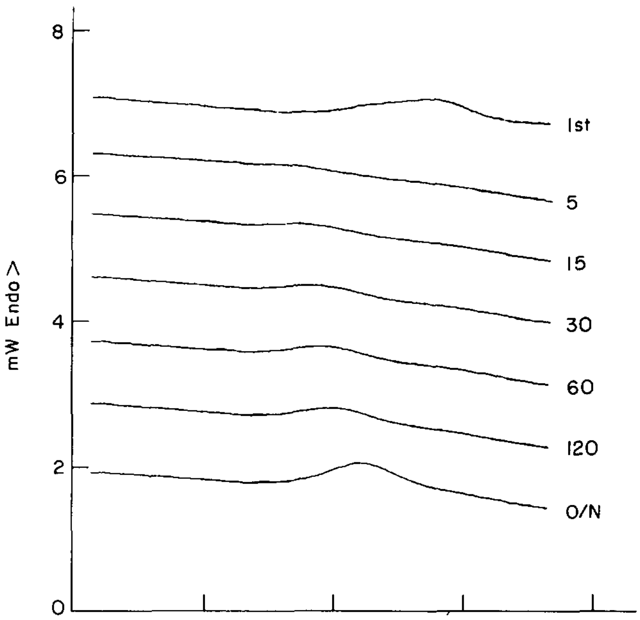

Figure 6 Effect of annealing time on the recovery of the first-order peak in d.s.c. traces. From top to bottom: virgin sample, then delay times of 5, 15, 30, 60, 120 min and overnight (O/N, 16 h)

Table 1 Increase in ΔH of the first-order transition of NC plasticised with 45% NG as function of annealing time

Time (min)	ΔH ($J g^{-1}$)
5	0.25
15	0.36
30	0.45
60	0.55
120	0.59
1000	0.90

The increase in enthalpy change, and hence order or structure, with time at 20°C is given in *Table 1*.

The form of the relation between time and enthalpy change could not be fitted with a simple rate constant. There was a large increase in structure or order in the first 30 min, to about half the total which was developed with the longer time limit. It would be expected that the finite cooling rate would allow some annealing to occur during cooling, and so the short time values may be overestimated.

A similar transition has recently been reported in CA[8,9], and it was attributed to the loss of water from the sample. To test this possibility, an unplasticised NC was heated to 80°C for 15 min and then a d.m.a. run made immediately. The first order peak disappeared, but the α peak was unaffected. If water had been lost from the sample, it would be expected that the α peak would have moved to a higher temperature because the overall plasticiser content would have been lower. As a further test for water loss, t.g.a. runs were made on unplasticised NC from 20 to 100°C, and there was no evidence of weight loss which could be associated with the first-order transition.

The bulk of the evidence suggests that the first-order transition is associated with the NC, and that it involves large scale movement of the NC molecule, since a finite time is required for the order to reform after cooling. However, it would be expected that the plasticiser concentration would affect the recovery rate by altering the rate at which the NC molecules can move. The recovery time of poorly plasticised materials may be very long, and annealing may appear to be irreversible. However, over the long times that a propellant may be in service, up to 30 years, significant changes in properties may occur. This effect requires further study.

The first-order transition is undoubtedly responsible for the abrupt changes in thermal expansion coefficient above 50°C observed during t.m.a. runs, and which necessitated annealing of the samples[3,5]. Baker and Privett noticed similar behaviour[6]. It is also likely that the change in the NC molecule caused by the first-order transition could account for part of the effect of annealing, which was reported by Baker and Privett[6].

CONCLUSIONS

An explanation for the apparent anomaly in the glass transition behaviour reported for NC plasticised with NG has been developed. At high plasticiser concentrations the materials have a single glass transition in common with other plasticised polymeric systems. However, at low plasticiser concentrations the stiffness of the NC molecule causes a breakdown of the cooperative motion of the NC and plasticiser molecules, and two loss processes occur. The low temperature process is related to the glass transition of the plasticiser, and the high temperature process relates to the motion of the NC component.

A second type of loss process has been identified at a temperature of about 50°C. The process appeared to be independent of measuring frequency and plasticiser type or concentration, and it produced an endothermic peak on d.s.c. traces. It is suggested that the process is some form of first-order process, and is possibly caused by an increase in NC molecule flexibility.

REFERENCES

1 Townend, D. J. 'The Dynamic Mechanical Analysis of Nitrocellulose and Cast Double Base Propellant', Conference on Nitrocellulose Characterisation and Double Base Propellant Structure, Propellants, Explosives and Rocket Motor Establishment, Waltham Abbey, UK, 1980
2 Warren, R. C. 'TMA Studies of the NC/NG System', *ibid.*
3 Baker, F. S. 'Dielectric Relaxation Spectroscopy of Nitrocellulose/Nitroglycerine Pastes', *ibid.*
4 Warren, R. C. 'The Interaction of Nitroglycerine with Nitrocellulose', *ibid.*
5 Townend, D. J. and Warren, R. C. *Polymer* 1985, **26**, 79
6 Baker, F. S. and Privett, G. J. *Polymer* 1987, **28**, 1121
7 Seymour, R. W. and Minter, J. R. *Polym. Eng. Sci.* 1980, **20**, 1188
8 Scandola, M. and Ceccorulli, G. *Polymer* 1985, **26**, 1953
9 Scandola, M. and Ceccorulli, G. *Polymer* 1985, **26**, 1958
10 Bueche, F. 'Physical Properties of Polymers', Interscience Publishers, New York, 1962, p. 85, 116
11 Baker, F. S., Jones, M., Lewis, T. J., Privett, G., Crofton, D. J. and Pethrick, R. A. *Polymer* 1984, **25**, 815
12 Ash, C. and Lewis, T. J. *Polymer* 1985, **26**, 643
13 Lotmentsev, Yu. M. and Shneerson, R. N. *Tr. Khim. Khimich. Teknol.* 1974, **1**, 126
14 Isles, M. and Jennings, B. R. *Br. Polym. J.* 1976, March, 43
15 Gupta, A. K., Marchal, E. and Burchard, W. *Macromolecules* 1975, **8**, 843
16 Bueche, F. 'Physical Properties of Polymers', Interscience Publishers, New York, 1962, p. 104
17 Warren, R. C. *Rheol. Acta* 1984, **23**, 544