The effect of ageing and annealing on the physical properties of nitrocellulose plasticized with nitroglycerine

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Dynamic mechanical measurements and thermal expansion measurements were made on samples of nitrocellulose plasticized with nitroglycerine. Samples were prepared either by roll milling into sheets or by extruding into strips. The rolled materials that had been aged for 20 weeks at room temperature showed a strong first-order type of transition. Extruded materials also showed some evidence of the first-order transition as well as the commonly observed α-relaxation. The state of the aged rolled material was changed by annealing in such a way that the first-order transition disappeared and was replaced by the frequency-dependent α-transition. However, the first-order transition slowly reappeared on ageing at room temperature. It appears that the α-relaxation reported previously does not occur in the equilibrium state of this type of material.

(Keywords: nitrocellulose; nitroglycerine; dynamic mechanical analysis; transitions; annealing; ageing)

INTRODUCTION

Recent studies of the dynamic mechanical behaviour of plasticized nitrocellulose (NC), and in particular of double-base propellants consisting of NC plasticized with nitroglycerine (NG), have demonstrated that there are at least two mechanical loss processes in this type of material; a low-temperature process designated β, which is essentially the glass transition of the plasticizer, and a second process, designated α, which is associated with the motion of the NC molecules and occurs above ambient temperature[1–3]. While no evidence of any effect of thermal annealing on the β-transition has been found, some evidence for an irreversible change in the α-relaxation has been reported[3].

Recently a transition at a temperature of about 50°C was reported in double-base propellants[1]. This transition produced an endothermic peak in differential scanning calorimetry (d.s.c.) traces, and a shoulder on the α-peak on curves of mechanical loss. The temperature of the process responsible for the shoulder appeared to be independent of frequency, and this fact, together with the presence of the peak in d.s.c. traces, indicated that the 50°C transition was some form of thermodynamic first-order melting-type process.

The magnitude of the first-order process was relatively small in the materials studied previously. However, it was subsequently found that double-base materials containing 45% NG and aged under ambient conditions for several months showed a large first-order transition, which occurred in place of the α-relaxation. Annealing at 80°C caused the first-order process to disappear and be replaced by the α-relaxation. The results of an investigation of this phenomenon are presented in this paper.

A second variable studied in this work was the degree of gelatinization, which was found to have a significant influence on properties. The term 'gelatinization' is used in the propellant industry to denote the process of breaking down the fibrous structure of NC and converting it to a consolidated, 'plastic', solid. The degree to which the conversion has occurred is the degree of gelatinization, but at present there is no quantitative measure of it, so subjective assessments have to be made based on various criteria that indicate the degree of structural breakdown. It would be expected that degree of gelatinization would have a significant effect on dynamic mechanical properties, but little quantitative information is available. However, a study has been reported of the effect of gelatinization on the extrusion behaviour of double-base propellants that contained processing solvents[4]. Significant differences in viscosity and elasticity were found in materials with different degrees of gelatinization.

This paper gives results of a study of the effect of annealing, ageing and degree of gelatinization on the dynamic mechanical and thermal expansion behaviour of one type of double-base propellant.

EXPERIMENTAL

Materials

The composition by weight of the double-base propellant material was:

Nitrocellulose	44%
Nitroglycerine	54%
Ethyl centralite	2%

One kilogram lots were mixed with a processing liquid for 30 min at 25–30°C in a propellant incorporator, and then dried on trays in an oven at 50°C for 24 h. The processing liquid type, percentage weight on NC, and

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Table 1 Concentration of processing liquids before and after mixing and drying

Liquid	Wt% on NC in mix	Wt% residual volatiles
Water	30	0.30
Ethanol	30	0.20
Heptane	30	0.25
Ether/ethanol (68/32)	80	0.20
Acetone/ethanol (44/56)	40	0.86
Ether	30	0.50
Ethyl acetate	45	0.57

residual total volatile matter after drying are given in *Table 1*.

The physical form of the resulting material was affected by the type of liquid used. The material processed with acetone/ethanol was in the form of lumps about 20 mm in diameter, and that processed with ethyl acetate was in lumps about 5 mm in diameter. With all of the other processing liquids the fibrous texture of the NC was retained. The longer diffusion path for the liquids to diffuse out of the lumpy materials may explain their higher amount of residual volatile matter as shown in *Table 1*.

One lot of material processed using each liquid was consolidated into a sheet by roll milling in an even-speed roll mill at a temperature of 50°C. The material was repeatedly passed through a 1.52 mm nip until it married up into a consolidated sheet. Sheets with an approximate thickness of 2 mm were produced, and aged under ambient conditions for at least 20 weeks before testing.

A second lot of each material was produced by extruding through a slit die $2 \times 20\,\mathrm{mm}^2$ in section and 18 mm long. The die was attached to an extrusion rheometer with a barrel diameter of 32 mm. The load on the rheometer ram was monitored as the extrusion rate was varied over apparent shear rates from 4 to 400 s^{-1}.

Testing

Dynamic Young's modulus and tan δ were measured using a Polymer Laboratories Dynamic Mechanical Thermal Analyser. Frequencies of 0.33, 3 and 30 Hz were used, and the temperature was scanned at a rate of 2°C min^{-1}. The samples were bars with a cross-section of approximately $2 \times 10\,\mathrm{mm}^2$, and they were tested using a span of 14 mm. The strain amplitude was approximately 0.1%.

Thermal expansion was measured with a Perkin–Elmer TMS-2 Thermomechanical Analyser. The samples were cubes with a side of approximately 2 mm, and the temperature was scanned at a rate of 5°C min^{-1}.

Weight loss over the temperature range 20–100°C was measured with a Perkin–Elmer TGS-2 Thermogravimetric Analyser. The temperature was scanned at a rate of 5°C min^{-1}.

RESULTS

General

The materials processed with water, heptane, ether and ethanol were all fibrous. When they were rolled or extruded they all behaved in a similar manner, and they gave similar results in the tests described here. These materials were obviously poorly gelatinized in the sense described in the 'Introduction'. To facilitate the following discussion, these materials will be grouped together and designated PG, for 'poorly gelatinized'. On the other hand, the acetone/ethanol material was in the form of consolidated lumps, and it subsequently behaved like a well gelatinized material, so it will be designated WG. The ethyl acetate material had intermediate properties, and it will be designated moderately gelatinized, or MG. The ether/ethanol material appeared to be only slightly more gelatinized than the PG material.

Dynamic mechanical properties

Rolled materials. The rolled materials were not tested immediately after they were made, but after they had aged under ambient conditions for at least 20 weeks. They all showed a β-transition similar to that reported previously for other double-base propellants. Since no differences were seen in the β-transition between each of the materials investigated, this transition will not be considered further here.

A most striking difference from previous studies was the presence of a strong loss process at about 55°C. This process was quite different from the α-transition because the temperature of peak tan δ was independent of frequency over the frequency range 0.33–30 Hz, whereas the temperature of the α-transition was frequency-dependent[1]. The new loss process appeared to be associated with the so-called first-order process.

The well gelatinized material, WG, most clearly showed the effect of the first-order process, and the dynamic mechanical behaviour is illustrated in *Figures 1a* and *2a*. The peak in tan δ was relatively sharp, and the shift in peak temperature between different frequencies was insignificant, being of the order of several degrees. Concurrently, the modulus showed a sharp step of an order of magnitude in the temperature range from 30 to 60°C, and the temperature of the step was essentially independent of frequency. However, the magnitude of the step increased with decreasing frequency.

The effect of annealing the WG material at 80°C for 1 h is shown in *Figures 1b* and *2b*. The loss process above ambient temperature became frequency-dependent, with the transition temperature increasing by about 15°C for an increase in frequency from 0.33 to 30 Hz. The drop in modulus was also much broader. The loss process now appeared to be the α-transition seen previously. After ageing the annealed material at ambient temperature for 19 days, the tan δ and modulus curves became more like the unannealed curves and the tan δ peaks for the different frequencies moved closer together. The drop in modulus also became sharper (see *Figure 2c*).

The degree of gelatinization of the material also affected the transition behaviour. Curves of tan δ and modulus of WG, MG and PG materials measured at a frequency of 0.33 Hz are given in *Figures 3* and *4*. Similar curves were obtained at other frequencies, but the differences between the materials were most apparent at 0.33 Hz. Curves for ether/ethanol materials were close to PG curves, and were not included for the sake of clarity. The unannealed materials all had a peak tan δ at about 55°C, with the PG material having the lowest peak loss. All materials showed a sharp drop in modulus at high temperatures, and the magnitude of the drop increased with increasing gelatinization. The higher modulus of the poorly gelatinized materials indicated

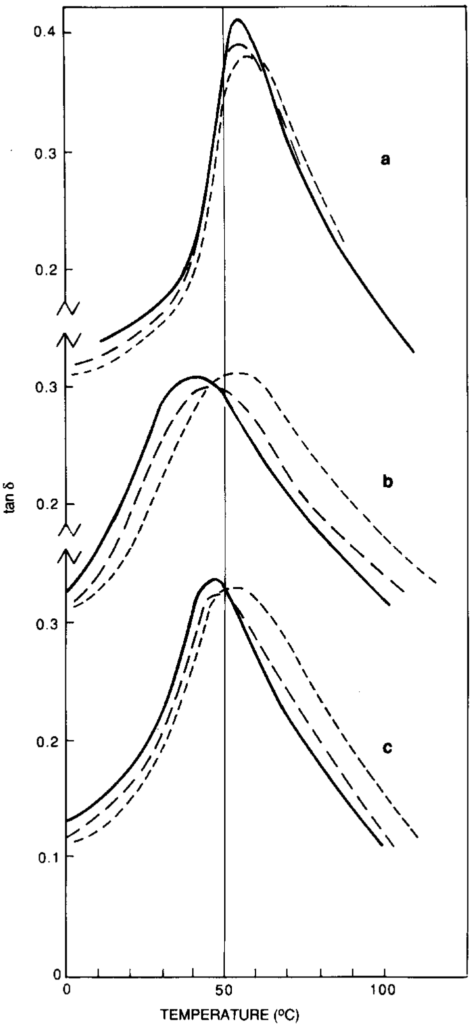

Figure 1 Tan δ vs. temperature for well gelatinized rolled materials: a, aged approximately 20 weeks; b, annealed at 80°C for 1 h; c, aged 19 days after annealing. ———, 0.33 Hz; – – – –, 3.0 Hz; -------, 30 Hz

that they had a more rigid structure than the well gelatinized materials.

The effect of annealing at 80°C, and then ageing, was similar for all degrees of gelatinization: the peak in tan δ was shifted to a lower temperature, the drop in modulus was smeared out over a wider temperature range (see *Figures 3a* and *4b*) and the effects were partially reversed after 19 days (see *Figures 3c* and *4c*).

The degree of gelatinization had a significant effect at higher temperatures. The PG material had a pronounced shoulder on the tan δ curve at about 90°C, but the shoulder was weaker on the MG material and did not appear on the WG material. When the PG material was annealed at 70°C there was a shoulder on the tan δ curve at about 80°C. Hence, it appears that the poorly gelatinized materials can exist in several states at elevated temperatures, and these can be frozen-in after moderately fast cooling. These states did not correspond to the equilibrium state at lower temperatures, as is evidenced by the decrease in magnitude of the shoulders on the tan δ curves over the period of 19 days.

Annealing at 50°C had a much smaller effect on the first-order peak. *Figure 5* shows curves of tan δ of WG and PG materials annealed at 50°C for 1 h. The first-order peak of the WG material was not significantly affected, but the magnitude of the peak of the PG material was reduced slightly. The main effect of annealing was the appearance of a shoulder on the curves at about 30°C, which was more pronounced at lower frequencies, especially in the PG material.

Extruded materials. Well and poorly gelatinized materials were extruded both at low shear rates ($\sim 10\ s^{-1}$) and at moderate shear rates ($\sim 100\ s^{-1}$), at temperatures of 50 and 70°C. The curves of tan δ at different frequencies for the materials extruded slowly are given in *Figures 6* and 7. The WG material showed the greatest influence of frequency on the position of peak tan δ, which increased by about 15°C when the frequency increased from 0.33 to 30 Hz. The PG material had a shoulder on the tan δ curve at about 40°C, which was more pronounced at the higher extrusion temperature. The 70°C curves also showed a peak at about 75°C, which was very pronounced in the PG material. Hence it appears that the state of the materials that were extruded at high temperature was similar to the state of the rolled materials after high-temperature annealing.

The degree of dependence of peak temperature on frequency of the materials extruded at 50°C was minimal (see *Figures 6* and 7). This result is in agreement with the observation that annealing the rolled materials at 50°C had little effect on dynamic mechanical behaviour (see *Figure 5*).

The effect of extrusion conditions on tan δ at 0.33 Hz, for WG and PG materials, is given in *Figure 8*. The tan δ

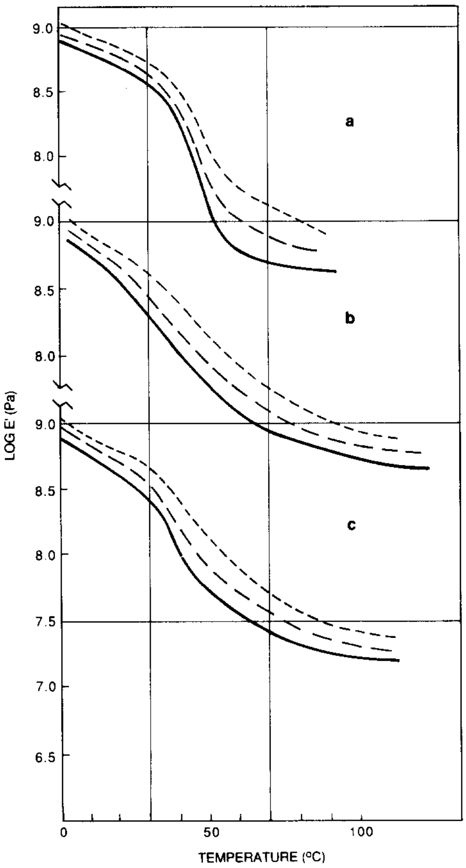

Figure 2 Log Young's modulus vs. temperature for well gelatinized rolled materials: a, aged approximately 20 weeks; b, annealed at 80°C for 1 h; c, aged 19 days after annealing. ———, 0.33 Hz; – – – –, 3 Hz; -------, 30 Hz

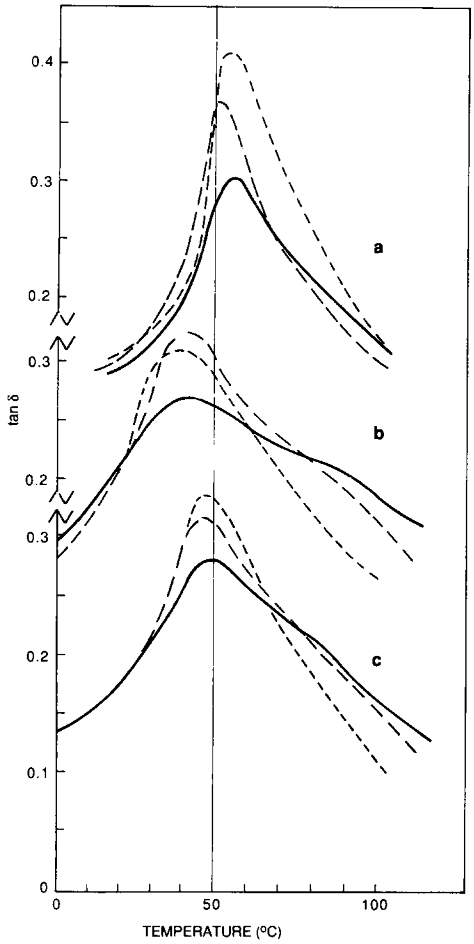

Figure 3 Effect of degree of gelatinization on tan δ of rolled materials: a, aged approximately 20 weeks; b, annealed at 80°C for 1 h; c, aged 19 days after annealing. -------, Well gelatinized; ———, moderately gelatinized; ———, poorly gelatinized

curves for the slow extrusion confirm the observations made from *Figure 6*. However, for the fast extrusion the magnitude of tan δ near 70°C was much lower than for the slow extrusion.

Thermal expansion

There was considerable variation in thermal expansion behaviour in different samples of the same material, and similar variation has been seen previously[2]. This variation may have been due to slight compositional or orientational inhomogeneities, or perhaps to frozen-in stresses in the samples. However, all samples showed the same qualitative behaviour, and a typical example is given in *Figure 9*, which shows the thermal expansion of extruded WG material tested in the direction perpendicular to extrusion. As the temperature was increased from 0 to ~25°C the expansion curve was linear. Above 25°C the curve showed a trough, with a minimum at ~50°C. Above 50°C the curve showed a marked increase in rate of expansion, with an expansion coefficient approximately twice that below 25°C. On cooling from 100 to 0°C the curve was almost linear with a slope similar to the slope of the initial curve below 25°C, and the reheating curve was almost identical to the cooling curve. The higher expansion rate seen on the initial heating run indicates that the state of the material was changing continuously as the temperature increased. The same behaviour was seen in samples cut in three orthogonal directions, so the measured decrease in linear dimensions corresponded to a decrease in volume.

In a separate experiment a study was made of the effect of heating to an intermediate temperature, cooling and then reheating to a higher temperature. A similar sample-to-sample variability to that seen in the simple expansion measurements was also found. A typical example of heating a WG rolled sample to two intermediate temperatures is illustrated in *Figure 10*. It can be seen that if the intermediate cooling and heating sections are ignored, the curve has a similar shape to the first heating curve in *Figure 9*. This observation suggests that the state of the material changes continuously with increasing temperature, and that for short times cooling and reheating does not affect the state of the material. However, heating above the highest previously attained temperature continues the process of changing the state of the material.

Extrusion behaviour

The load on the ram of the extrusion rheometer, measured during the extrusion of each material through the slit die at 70°C, is plotted as a function of shear rate in *Figure 11*. The curves are all roughly parallel, and they move to increasing loads with increasing degree of gelatinization. The curves for water, heptane and ether, which have no gelatinizing action, superimpose closely. Ethanol is a very poor solvent for NC, and the ethanol

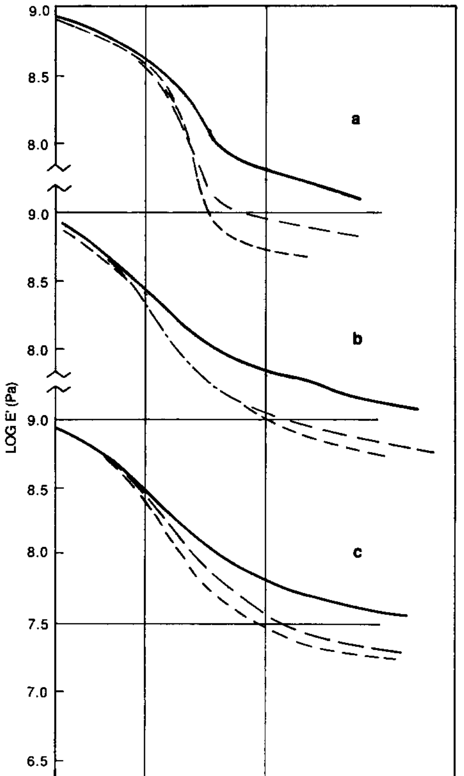

Figure 4 Effect of degree of gelatinization on log Young's modulus of rolled materials: a, aged approximately 20 weeks; b, annealed at 80°C for 1 h; c, aged 19 days after annealing; frequency 0.33 Hz. -------, Well gelatinized; ———, moderately gelatinized; ———, poorly gelatinized

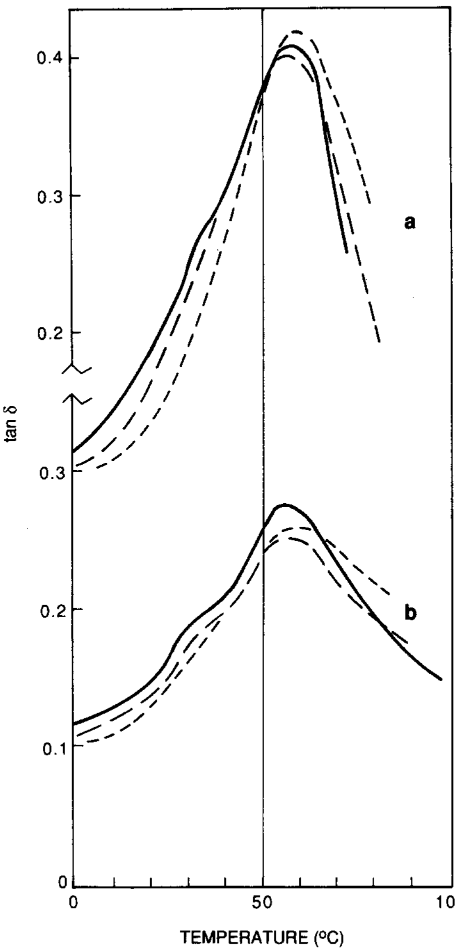

Figure 5 Tan δ vs. temperature for rolled materials annealed at 50°C for 1 h; a, well gelatinized materials; b, poorly gelatinized materials. ———, 0.33 Hz; – – – –, 3.0 Hz; -------, 30 Hz

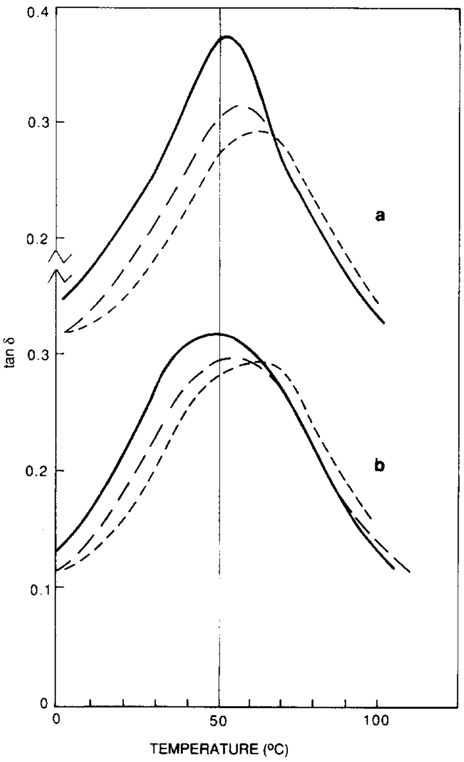

Figure 6 Tan δ vs. temperature for extruded well gelatinized materials: a, extrusion temperature 50°C; b, extrusion temperature 70°C. ———, 0.33 Hz; – – – –, 3.0 Hz; -------, 30 Hz

curve is slightly above the curves for the PG materials. The curve for the ether/ethanol material is intermediate between the WG and PG curves. The loads for the WG material are twice the corresponding loads for the PG materials.

Attempts were made to measure the die swell of WG and PG materials as a function of extrusion rate. Die swell is the degree to which an extrudate swells on issuing from a die, and is strongly related to the elasticity of the material. However, the very high viscosity of the materials made the measurements difficult with the available equipment because the pressures required for extrusion were too high. Moderately good-quality cords were obtained from the WG material when it was extruded through a die approximately 1 mm diameter and 2 mm long, at a temperature of 83°C. The cord diameter at a shear rate of 1000 s^{-1} was 12% greater than at the lowest rates. Under the same conditions the PG material did not consolidate into smooth cords, but formed very stringy distorted cords, which continually broke into short lengths. The extrusion pressures were about one-third of the pressures for the WG materials, in line with the pressures in the slit die used to prepare samples for dynamic mechanical analysis.

Weight loss

Thermogravimetric (t.g.a.) measurements were made on 10 mg samples of all the rolled materials over the temperature range 20–100°C at a scan rate of 5°C min^{-1}. The weight vs. temperature curves were linear over the whole range, and the maximum weight loss was 1%. There was no evidence of any weight loss that could be associated with the first-order transition.

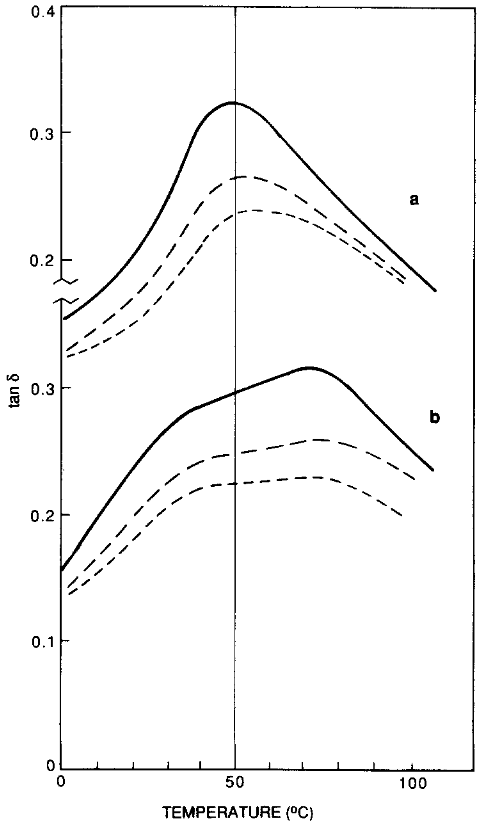

Figure 7 Tan δ vs. temperature for extruded poorly gelatinized materials: a, extrusion temperature 50°C; b, extrusion temperature 70°C. ———, 0.33 Hz; – – – –, 3.0 Hz; -------, 30 Hz

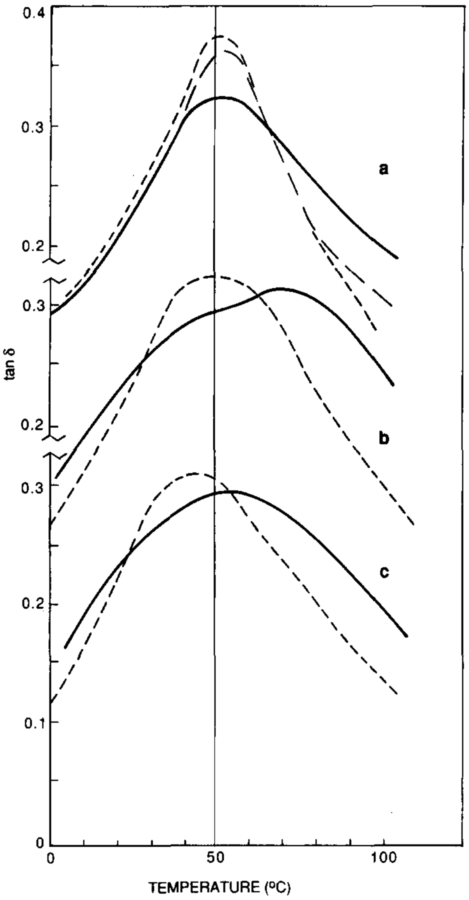

Figure 8 Effect of extrusion conditions on tan δ of extruded materials; a, 50°C, low extrusion rate; b, 70°C, low extrusion rate; c, 70°C, moderate extrusion rate; frequency 0.33 Hz. ———, Well gelatinized; – – – –, moderately gelatinized; - - - - - - -, poorly gelatinized

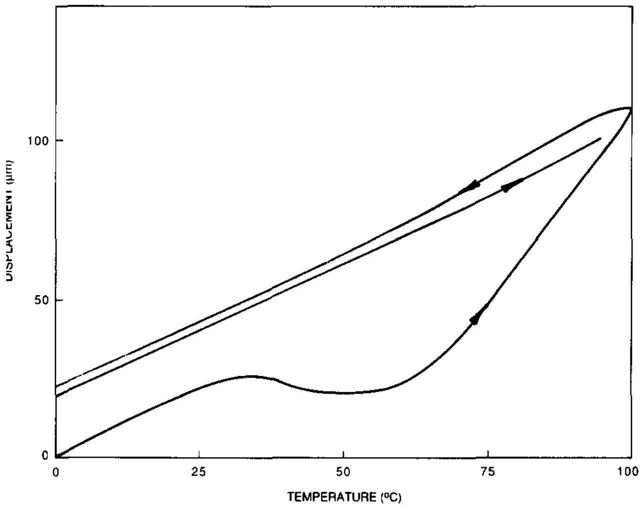

Figure 9 Thermal expansion of extruded well gelatinized material perpendicular to extrusion direction. Arrows indicate direction of temperature change

DISCUSSION

It has been shown that the thermal history of double-base propellants has a significant effect both on thermophysical properties and on small-strain dynamic mechanical properties. A suggestion in the literature[3] that these materials should be annealed before testing appears to be misguided, as the behaviour induced by annealing is reversible, indicating that the annealed state is not the equilibrium state. Hence it would appear to be preferable to age the materials under standard conditions in order to allow an equilibrium state to form before testing. In most cases reported previously the first-order transition was either not present, or was very small in magnitude, possibly because the materials were tested too soon after manufacture and before the equilibrium state was reached. Also, many materials were processed with solvents, and non-equilibrium structures may have been locked in as the solvents were removed.

It is desirable when testing materials that the effects of variations in thermal history be minimized without having to wait long periods for an equilibrium state to be reached. It was hoped that the approach to the equilibrium state could be speeded up by annealing the materials at a relatively low temperature. An annealing temperature of 50°C was chosen because it should give the maximum molecular mobility while still remaining below the first-order transition temperature. Samples were annealed at 80°C for 1 h and then 24 h at 50°C. Unfortunately it was found that the extra 50°C annealing had no significant additional effect on the dynamic mechanical behaviour.

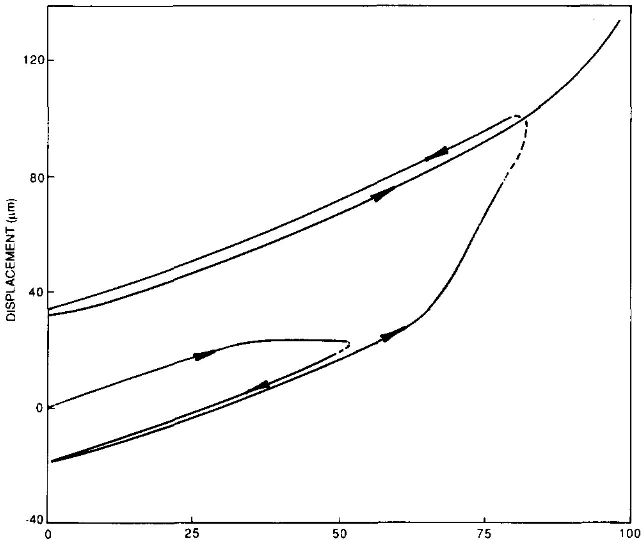

Figure 10 Thermal expansion of rolled well gelatinized material during thermal cycling to increasing temperatures. Arrows indicate direction of temperature change

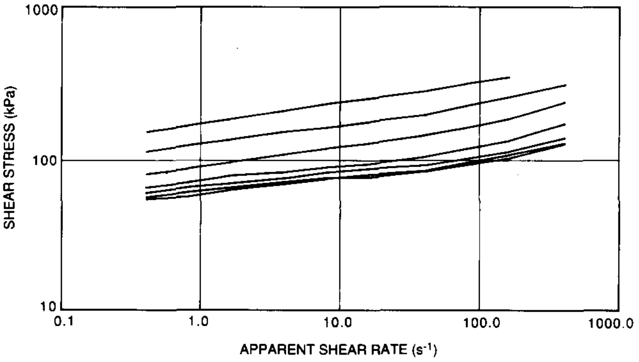

Figure 11 Effect of degree of gelatinization on extrusion pressure, with following liquids (from top to bottom): acetone/ethanol, ethyl acetate, ether/ethanol, ethanol, ether, water and heptane

There were large differences in dynamic mechanical behaviour between materials which were pretreated with water only and those which were pretreated with the strong solvents ethyl acetate and acetone. These results show that it is necessary to differentiate between materials made by roll milling water-wet ingredients and materials made by a solvent process. This difference was not appreciated by Baker and Privett in their study[3], where they determined the effect of varying the NG concentration on mechanical properties by using samples prepared by roll milling at high NG concentrations, and samples prepared by solvent incorporation at low NG concentrations.

The fact that the grossly non-linear thermal expansion occurred only with unannealed samples, and also that the maximum in the non-linear effect occurred at the temperature of the first-order transition, indicated that the first-order transition caused the non-linear behaviour. Hence it is apparent that one major effect of the first-order transition is to decrease the volume of the material. The lack of reproducibility of the thermal expansion results impedes their interpretation. One possibility for improvement may be to use volume dilatometry, rather than linear dilatometry, so that orientation effects would be averaged out.

The results of the interrupted thermal expansion measurements suggest a mechanism for the shoulders on the tan δ curves at 80 and 90°C, which occurred when the materials were annealed at 70 and 80°C. It was seen that when a sample had been heated to a particular temperature and cooled, the state of the material at that temperature was frozen in. Reheating did not appear to change the state of the material until the previous maximum temperature was exceeded. It appears that annealing the dynamic mechanical samples and then cooling them would have frozen in the state at the annealing temperature. The sample would stay in the annealed state during a measurement run until the test temperature exceeded the annealing temperature. At higher temperatures the state of the sample would continue to change, which would affect the dynamic mechanical response and cause the shoulders on the tan δ curves. Hence the shoulders do not indicate the presence of any fundamental transitions, but are only an artifact related to thermal history.

The degree of gelatinization had opposite effects at low and high strains. At the low strains ($\sim$0.1%) involved in d.m.t.a. measurements, the WG material had lower modulus and loss than the PG material, indicating that the WG was less elastic and less viscous. However, at the high strains encountered in extrusion, the WG material showed higher extrusion stresses, indicating that it had a more entangled structure and was more viscous. A previous study of double-base materials containing solvents showed that the die swell, and hence elasticity, of WG materials was much greater than the die swell of PG materials[4]. Hence it is apparent that dynamic mechanical behaviour may not be used to predict extrusion behaviour. However, low-temperature brittle fracture occurs at low strains, usually much less than 5%, and so d.m.t.a. data may be useful in detecting different structures and monitoring thermal history effects that are relevant to fracture.

The differences in mechanical response at high and low strains obviously reflect different structures and molecular motions in the materials. In well gelatinized materials the fibre structure of the original NC fibres has been broken down, allowing the NC molecules to form an amorphous, entangled structure. This structure would have high viscosity and elasticity. In poorly gelatinized materials on the other hand, many NC molecules are locked into the fibrils remaining from the original cellulose structure, and hence these molecules are not available to form an entangled elastic network. It is not clear what the nature of the deformation mechanism is in PG materials at low strains, but it may be that the fibrils act as reinforcing fillers, and stiffen the structure. Large-strain deformations, e.g. extrusion, would occur by fibrils sliding past each other, and this would give rise to viscous, but not necessarily elastic, effects. The α-relaxation is clearly not a crystal melting transition, so it must be associated with the amorphous phase, and it may well be related to some form of entanglement slippage.

The dynamic mechanical and thermal expansion behaviour reported here, and the d.s.c. and dynamic mechanical data reported previously[1], taken together show that the first-order transition occurs at a temperature that is not significantly affected by plasticizer type or concentration. Hence it appears that the transition temperature is determined largely by the NC component alone. Intermolecular factors are not important, since plasticizers change the intermolecular environment. One possible molecular mechanism that would give behaviour consistent with the observed results would be the formation of a hydrogen bond from an unnitrated hydroxyl across the β-linkage between adjacent pyranose rings. The 12.6% nitrogen NC used here has a degree of substitution of 2.45, and hence would have a considerable fraction of unnitrated hydroxyls. Molecular conformation studies of NC by Winkler[5] have indicated that the lowest-energy conformation of the inter-ring bridge would allow the formation of a hydrogen bond between the oxygen attached to the C3 atom and the O5 in the adjacent ring. This mechanism could also explain a similar transition reported at the same temperature in cellulose acetate with a degree of esterification of 2.44[6].

Large-scale molecular mobility is required for the formation of the structure that gives rise to the first-order transition, as is evidenced by the long time (several weeks) required for the structure to form. The structure could form in the following way. At temperatures below 50°C the segments of the molecules would undergo random thermal motions until adjacent segments moved into position to form a rigid intersegment link. The process would continue until the molecules were packed in local domains of ordered molecules. This packing may give a more rigid structure, which would have a higher modulus than an amorphous structure at temperatures below the transition temperature, as illustrated in *Figure 4*. It would also be expected that the packing of rigid molecules would require a greater volume than packing flexible molecules, and hence the volume of the material would decrease when it went through the first-order transition.

CONCLUSIONS

A double-base propellant consisting of nitrocellulose plasticized with nitroglycerine in the ratio 55:45 has been found to exist in at least two states, and these states give rise to different transitions in the dynamic mechanical response. The state that was formed on long-term ageing gave a first-order transition at about 55°C. Annealing the aged material at 80°C for 1 h caused the first-order transition to disappear and be replaced by another type of transition, the temperature of which was dependent on measuring frequency. This transition was previously designated the α-relaxation. Ageing the annealed material for 19 days under ambient conditions partially reversed the effect of annealing. The long-term aged material also showed a drop in thermal expansion coefficient associated with the first-order transition, but no corresponding drop was present in the annealed material. The main implication of these findings is that the thermal history has an important effect on the dynamic mechanical behaviour, and it must be controlled if reproducible results are to be obtained.

The degree to which the fibrous structure of the nitrocellulose was broken down, known as the degree of gelatinization, affected both the dynamic mechanical behaviour and the pressure required to extrude the material. The dynamic modulus at high temperature decreased with increasing degree of gelatinization, but the extrusion pressure increased. This behaviour indicates that different mechanisms are responsible for small-strain deformations and large-scale deformations.

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