

Relaxations in double base propellants

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Double base propellants are composed of nitrocellulose (NC) plasticized with various amounts of nitroglycerine (NG). A series of propellants was made with NG contents of 10%, 35% and 60% by incorporating with solvents, extruding into cords and then drying. A study of relaxation behaviour of these propellants was made using dynamic mechanical analysis, thermomechanical analysis and differential scanning calorimetry (d.s.c.). Three relaxations were observed, one at about -80°C designated γ , one in the temperature range -10° to -60°C designated β , and one above 35°C designated α . The γ relaxation is attributed to motion of the pendant nitrate side groups of NC. The β relaxation is attributed to motion of NC molecule side groups and associated NG molecules. It causes a peak in mechanical loss, and changes in modulus, thermal expansion and heat capacity. The β relaxation has previously been reported as the glass transition, but there is some doubt and this may be incorrect. The α relaxation occurs in the same temperature range as the glass transition reported in other plasticized cellulosic polymers, but it is unusual in that it involves a large change in modulus and mechanical loss, but no change in thermal expansion or heat capacity.

(Keywords: relaxations; double base propellants; nitrocellulose; nitroglycerine)

INTRODUCTION

Double base propellants are composed of nitrocellulose (NC) plasticized with various amounts of nitroglycerine (NG), and they have been in service for many years in both gun and rocket applications. Recently, concern has been expressed about the low temperature fracture properties of gun propellants, because the high ignition pulses in modern guns can cause propellant grain fracture in low temperature firings. An understanding of the factors influencing low temperature fracture properties is required, but only a few studies have been made of the molecular mechanisms governing propellant physical behaviour. Pulsed proton n.m.r.^{1,2}, dielectric spectroscopy³, and thermal expansion⁴ have indicated the presence of a molecular relaxation in the temperature range -60° to -20°C . The relaxation was reported as the glass transition⁴. However, the glass transition is a second order thermodynamic transition, and its relation to molecular relaxation processes can be complex.

It would be expected that double base propellants would show relaxation behaviour similar to other plasticized cellulosic systems. Studies have been made of cellulose⁵, cellulose acetate (CA)⁶, cellulose acetate-propionate (CAP) and acetate-butyrates (CAB)⁷, and CAB⁸. In all cases, a glass transition was found in dynamic mechanical response or thermal expansion at temperatures above 80°C , while secondary relaxations were found at lower temperatures. The high temperature of T_g for other cellulosic materials conflicts with the lower value reported for double base propellants.

Double base propellants have an added complication over most other polymeric systems in that much of the biological structure of the original cellulose is retained

during the manufacture of NC, and also of propellants. NC fibres are made up of layered structures of fibrils, which in turn are made up of ordered layers of molecules. The progressive breakdown of this structure during propellant processing is known in the industry as gellatinization, and the degree to which it has occurred in a particular propellant is the degree of gelatinization. The use of the term gelatinization can be misleading, as it does not imply the existence of a network structure in the propellant.

It would be expected that the physical properties of propellants would depend on the degree of gelatinization and NG content, as well as molecular relaxations in the NC, so propellants with a range of NG contents and degrees of gelatinizations were studied.

EXPERIMENTAL

Two types of NC were used in this study, one derived from wood cellulose nitrated by the displacement process to a nitrogen level of 12.2%, designated 12.2%N-NC, and one derived from cotton cellulose nitrated by the mechanical process to a nitrogen level of 12.6%, designated 12.6%N-NC. A nitrogen level of 12.2% corresponds to a degree of substitution of 2.32, and 12.6% to 2.45.

Propellants containing 10, 35 and 60% NG by weight were made by incorporating a premixed NC-NG paste with acetone/ethanol as a processing solvent. The resulting dough was extruded as cords 4 mm in diameter, which were stored at 45°C for at least 21 days to remove solvent. The degree of gelatinization was controlled by varying the acetone/ethanol ratio with high acetone contents giving greater gelatinization. For each NG level, propellants

Table 1 Solvent compositions in propellant manufacture

Nitrocellulose Source	Nitrogen (%)*	Nitroglycerine (%)	Stabilizer (%)	Acetone in solvent (%)
Wood	12.2	10	1	95, 35, 20
		35	1	90, 45, 14
		60	1	80, 20, 10
Cotton	12.6	10	1	90, 50, 35
		95	1	90, 65, 40
		60	1	80, 30, 10

*All concentrations are w/w

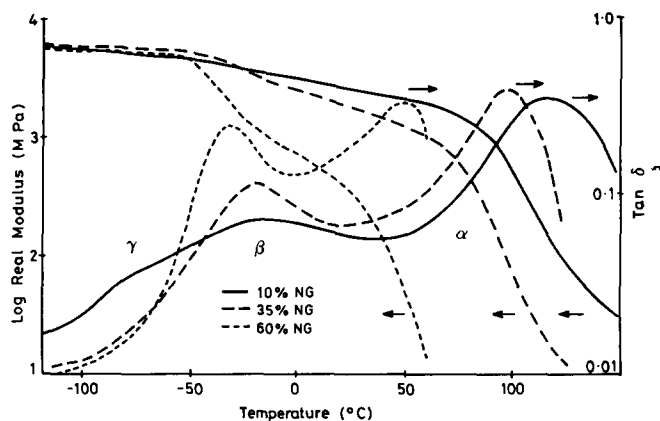


Figure 1 Effect of NG content on real modulus and $\tan(\delta)$ of solvent processed moderately gelatinized propellant made from 12.2%N-NC

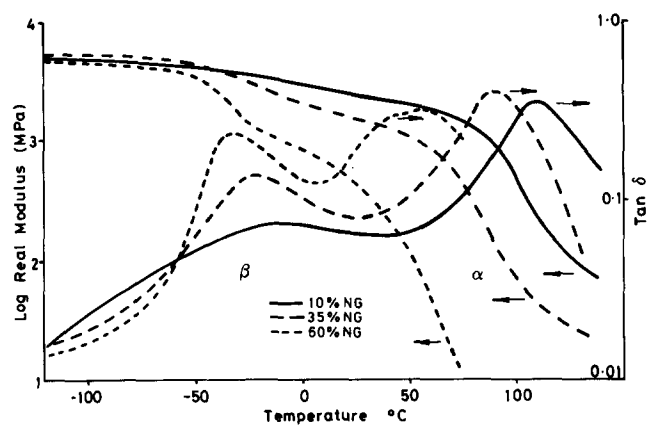


Figure 2 Effect of NG content on real modulus and $\tan(\delta)$ of solvent processed moderately gelatinized propellant made from 12.6%N-NC

were made which were poorly, moderately and well gelatinized. Details of solvents used are given in Table 1.

Films of pure NC were made by casting from acetone solution. They were dried by water steeping at 60°C for 3 days followed by vacuum drying at 60°C for 20 days.

Dynamic mechanical properties were measured on a Dupont 980 Dynamic Mechanical Analyser (DMA) over the temperature range -180°C to at least 100°C. The temperature scan rate was 5°C min⁻¹. This instrument operates in a resonance mode with a variable frequency ranging from 60 to 3Hz. To minimize the effect of frequency variation, testing was carried out on similar sized rectangular samples (1.6 × 3 × 17 mm) machined from sections of the extruded cord. Data from the 12.6% N-NC propellants was obtained manually, while the 12.2%N-NC propellant data was obtained from a micro-processor controlled system.

Thermal expansions were determined on a Perkin-Elmer TMS-2 Thermomechanical Analyser over the temperature range -180°C to 100°C, at a temperature scan rate of 5°C min⁻¹. It was necessary to anneal the samples, 3 mm lengths of cord, at 90°C for 1 min in order to obtain reproducible results.

Differential scanning calorimetry (d.s.c.) was carried out with a Perkin-Elmer DSC 1b instrument over the temperature range -120°C to 120°C at a scan rate of 32°C min⁻¹. The samples were pieces of cord weighing approximately 30 mg.

RESULTS

Dynamic mechanical analysis

Three relaxations were observed in the 10%NG, 12.2% N-NC propellants, and two relaxations in all other

propellants. Relaxations occurring above 30°C will be designated α , between 0°C and -50°C β , and those about -80°C will be designated γ , following the usual convention.

The variation of real modulus and $\tan(\delta)$ with temperature is illustrated for moderately gelatinized propellants in Figures 1 and 2. The curves for the other propellants are similar. The relaxation temperatures for all propellants are similar. The relaxation temperatures for all propellants summarized in Table 2.

As a check that the propellants were not degrading at the higher measurement temperatures, repeat runs were made on several samples. The results were found to be unchanged on the second run.

The temperature of the α relaxation, $T\alpha$, was strongly dependent on NG contents, see Table 2. $T\alpha$ varies by about 60°C for a change in NG contents of 50%. However, the magnitude of $\tan(\delta)$ at $T\alpha$ was unaffected by NG contents, see Figures 1 and 2.

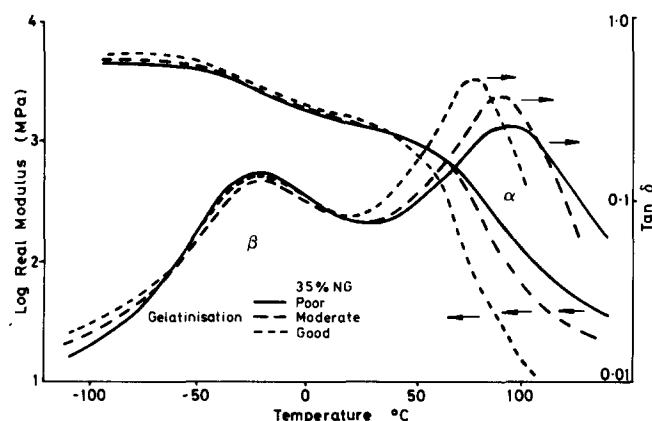
The value of $T\beta$ was also dependent on NG contents, but to a lesser degree than $T\alpha$. $T\beta$ varied by about 20°C for a change in NG content of 50%. Unlike the α relaxation, the magnitude of the β relaxation was dependent on NG content. $\tan \delta$ at $T\beta$ determined from Figure 2 was 0.087 for 10% NG, 0.13 for 35% NG and 0.23 for 60% NG. These values were typical of all propellants studied, and show that peak $\tan \delta$ for 35% NG propellants was about 50% greater than 10% NG propellants, for 60% NG propellants it was 250% greater. The greater increase in magnitude of peak $\tan \delta$ with higher NG contents was associated with larger increments in real modulus. The width of the relaxations decreased with increasing NG content.

Table 2 (a) D.m.a. relaxation temperatures of 12.2%N-NC propellants

NG content (%)	Degree of gelatinization	Relaxation temperature (°C)		
		α	β	γ
10	High	110	-12	-80
	Moderate	117	-14	-80
	Low	120	-11	-80
35	High	91	-22	-
	Moderate	93	-20	-
	Low	93	-24	-
60	High	37	-33	-
	Moderate	49	-32	-
	Low	51	-32	-

(b) D.m.a. relaxation temperatures of 12.6%N-NC propellants

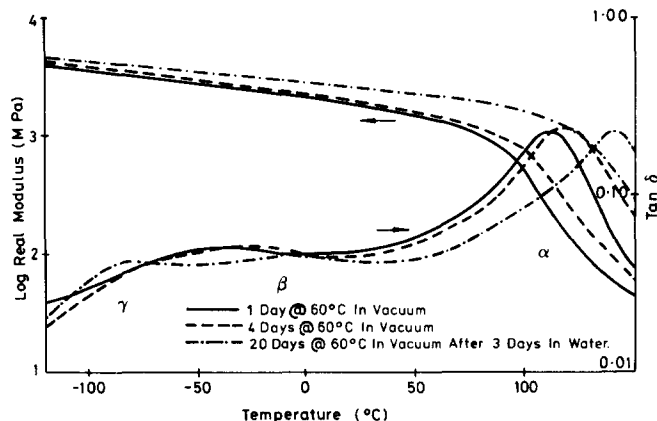
NG content (%)	Degree of gelatinization	Relaxation temperature		
		α	β	γ
0	-	140	0	-80
10	High	98	-12	-
	Moderate	110	-15	-
	Low	114	-14.5	-
35	High	77	-25	-
	Moderate	90	-23	-
	Low	94	-24	-
60	High	38	-36	-
	Moderate	55	-33	-
	Low	-	-	-


Figure 3 Effect of gelatinization on real modulus and $\tan(\delta)$ of solvent processed propellant made from 12.6%N-NC

The γ relaxation was small, and was seen only in the 10% NG, 12.2%N-NC propellants, although $\tan \delta$ at about -180°C in 12.6%N-NC propellants was greater than for higher NG content propellants. The reason for the apparent absence of a sharp γ relaxation in 12.6%N-NC propellants may be due to the data being obtained manually at 5°C intervals, whereas the 12.2%N-NC data was obtained with a microprocessor controlled digital system at 1°C intervals.

The effect of different degrees of gelatinization on real modulus and $\tan(\delta)$ of 12.6%N-NC propellants containing 35% NG is illustrated in *Figure 3*. The effect of gelatinization on the relaxation temperatures of all propellants can be determined from *Table 2*.

T_β was unaffected by gelatinization within experimental scatter. However, T_α changed by nearly 20°C from the best to the poorest gelatinized propellant. Some variation


Figure 4 Real modulus and $\tan(\delta)$ of films of 12.6%N-NC

in the magnitude of the α relaxation occurred, but it did not depend upon the degree of gelatinization in any consistent manner.

The temperatures listed for each relaxation in *Table 2* do not show any significant differences that could be attributed to types of NC used.

Plots of real modulus and $\tan \delta$ for a film of 12.6%N-NC at various stages of acetone removal are given in *Figure 4*. It can be seen that pure dry NC has a γ and an α relaxation. The temperature of the α relaxation increased as the acetone was removed. There is also a small peak at about 0°C , which may be due to a relaxation in NC. However, the peak may also be due to the presence of a small amount of residual acetone, since it is virtually impossible to remove all acetone from NC films. It is much easier to remove solvents from propellants, and the effect of any residual solvent would be much less in propellants.

Table 3 Relaxation temperatures of double base 12.2%N-NC propellants measured by thermal expansion and d.s.c.

Nitroglycerine (%)	Transition temperature (°C)	
	Thermal expansion	d.s.c.
10	-120	-
35	-40	-35
60	-60	-50

Thermal expansion and d.s.c.

Thermal expansion and d.s.c. relaxation temperatures of 12.2%N-NC propellants are summarized in Table 3, while thermal expansion data for the 12.6%N-NC propellants are illustrated in Figure 5. There were no differences in thermal expansion between propellants made from 12.2%N-NC and 12.6%N-NC. Thermal expansion and d.s.c. both showed the presence of the β relaxation in propellants containing 35% or more NG. The relaxation temperatures are lower than those observed by d.m.a. as the effective measuring frequencies are lower. The γ relaxation was manifested in lower NG content propellants as a deviation from linearity at about -100°C . However, there was no indication of the α relaxation in any of the propellants, which is surprising in view of the large magnitude of the α relaxation in mechanical loss.

DISCUSSION

The frequency variation during the measurement of mechanical properties by d.m.a. caused by the changing modulus introduces some uncertainty in the relaxation temperatures. However, the results are sufficiently accurate to show the presence of the relaxations, and to show differences between similar samples.

The relaxation designated here as β has been previously reported as the glass transition of double base propellants on the basis of thermal expansion measurements⁴. It is also well known in the propellant industry that double base propellants have a brittle to ductile transition in the temperature range -50°C to 0°C , and this transition has been attributed to the glass transition⁹. However, this work has shown that the major relaxation in the mechanical properties of double base propellants occurs above 35°C , in the same temperature range as the T_g of other cellulosic systems. Hence the assignment of the β relaxation as the glass transition would appear to be erroneous.

The occurrence of the brittle to ductile transition near $T\beta$ of double base propellants is similar to the behaviour of plasticized CAB, where the fracture properties at 23°C were related to $T\beta$, rather than $T\alpha$ ⁸. This suggests that the low temperature mechanical properties of double base propellants may be influenced by the β relaxation, and an investigation of the influence of $T\beta$ on the fracture properties of double base propellants is being undertaken.

The γ relaxation has been reported previously in several cellulosic polymers. A small relaxation was seen in dielectric loss of 12.6%N-NC at 1000 Hz at -45°C ¹⁰. Bradley and Carr observed a relaxation at -90°C in regenerated cellulose which they attributed to motion of methylol groups⁵. Russel and van Kerpel observed a relaxation in cellulose triacetate at -45°C which they attributed to motion of the acetate groups⁶. However,

Seymour *et al.* observed a γ relaxation at -40°C in CAB, which they attributed to ring motion⁷. If the relaxation was due to ring motion, it would be expected that some mobility would be detected in the pulse proton n.m.r. response from pure NC. Such mobility has not been detected¹, so it is suggested that the γ relaxation in NC is due to nitrate side group motion. N.m.r. studies using C^{13} and N^{15} may be able to confirm this assignment.

A relaxation has been observed in pulsed proton n.m.r. at an effective measuring frequency of 10 kHz^{1,2}. The temperature of onset of mobility decreased from -10°C for 20% NG content to -35°C for 60% NG content. Peak dielectric loss at 10 kHz varied from -15°C for 35% NG content to -30°C for 60% NG content³. Allowing for the difference in measuring frequencies, these relaxations are the same as the β relaxations seen with d.m.a.

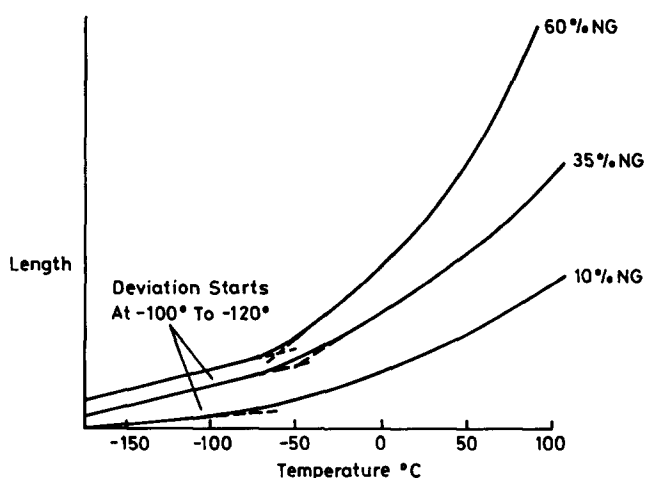
The β relaxation progressively replaced the γ relaxation as the NG content was raised. Similar behaviour has been reported by Bradley and Carr for regenerated cellulose plasticized with water⁵, by Janacek and Kolarik for poly(methacrylic acid) esters plasticized with low molecular weight compounds^{11,12}, and by Seymour *et al.* for CAB plasticized with various compounds⁷. In the first two cases the β relaxation was attributed to motion of side groups to which plasticizer molecules had become associated. Seymour *et al.* attributed the β relaxation to interaction between the plasticizer and the polymer ring.

If the γ relaxation in NC and double base propellants is due to side group motion, it is likely that the β relaxation is due to motion of NC side groups with associated NG molecules.

The fact that the α relaxation is not observed in thermal expansion, d.s.c. or in proton n.m.r. is puzzling. It is observed in dilatometry of CA^{6,7}, CAP and CAB⁷, and also in d.s.c. of plasticized CAB⁸. The α relaxation, unlike the β and γ relaxations, is strongly affected by degree of gelatinization, which reflects the number of fibrils in the propellant. Poorly gelatinized propellants have a large number of fibrils and higher $T\alpha$ s, and so the α relaxation may involve fibrils acting as reinforcing fillers. However, further work is required to elucidate the mechanism of the α relaxation.

CONCLUSIONS

Three relaxations have been observed in double base propellants. The γ relaxation occurred at about -80°C ,

**Figure 5** Thermal expansion of double base propellants

causing a small change in real modulus and $\tan(\delta)$, and an increase in thermal expansion. It was seen only in NC and low NG content propellants, and may be due to motion of pendant nitrate groups of NC.

The β relaxation occurred in the temperature range -10°C to -60°C , and is the relaxation previously reported as the glass transition. It is associated with a moderate change in real modulus and a moderate peak in $\tan(\delta)$, and with changes in dielectric loss and proton n.m.r. relaxation times. In propellants containing 35% or more NG, the β relaxation was associated with changes in thermal expansion coefficient and heat capacity. The magnitude and temperature of the relaxation are dependent on NG content, but are unaffected by gelatinization. The relaxation is attributed to motion of NC side groups to which NG molecules have become associated, and is therefore not the glass transition.

The α relaxation occurred above 35°C , and had the largest effect on real modulus and $\tan(\delta)$. However, it caused no changes in heat capacity, thermal expansion or proton n.m.r. relaxation times. $T\alpha$ was strongly dependent on NG content. The process responsible for the α relaxation could not be determined.

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