

Dynamic mechanical studies of nitrocellulose/nitroglycerine mixtures

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Dynamic mechanical measurements were made over a frequency range from 0.03 Hz to 30 Hz and over a temperature range from 173 to 373 K for nitrocellulose (NC) (12.2% nitrated) with varying levels of nitroglycerine (NG), up to 60 wt% NG. Two principal relaxation processes were observed, their variation with NG concentration is reported. It was necessary to anneal samples for 60 min at 353 K to obtain reproducible results. The high temperature process, which does not appear to be a true glass-to-rubber transition, is complex and related to sample stress history. The low temperature transition is dependent solely upon the NG concentration. Both processes are thermally activated. The activation energies as a function of NG concentration are reported. A model relating the behaviour of the low temperature process to NG content is proposed.

(Keywords: nitrocellulose; nitroglycerine; dynamic mechanical relaxations; activation energies; microstructure; adsorption)

INTRODUCTION

The basic ingredients in many propellants are nitrocellulose (NC), nitroglycerine (NG) and energetic crystalline fillers such as picrite (nitroguanidine). Little is known concerning the manner in which a plasticizer, such as NG, or fillers affect the dynamic mechanical properties of the final propellant. Varying the NG content has been shown to have a pronounced effect upon the dielectric properties of the NC matrix¹ as does the water content of the NC². Physical properties such as brittleness, ultimate tensile strength and total strain capability are strongly influenced by the filler and plasticizers used in the formulation. A study of the dynamic mechanical properties is therefore of considerable technological interest.

Recently the existence of two major relaxation processes, one alpha, occurring at high temperatures (+40°C) and the other, beta, at lower temperatures (-35°C), has been discovered. Work by Townend and Warren³ has suggested the presence of a third small peak at around -80°C. Its origin is in some doubt and may be due to residual solvent in the system. Their work was carried out on a Du Pont resonance machine and therefore it was not possible to obtain activation energies or directly compare peak positions.

This paper will report the influence of NG upon the dynamic mechanical and thermal mechanical properties of the NC matrix and discuss its significance in relation to complementary studies involving dielectric relaxation spectroscopy. Experimental difficulties and adopted solutions also will be described.

EXPERIMENTAL

Materials

The type of NC used throughout this paper was a commercial sample used in rolled solventless propellant. It was manufactured by immersion of purified wood pulp

in mixed nitric-sulphuric acids and stabilized by the normal procedure of extended boiling in aqueous media⁴. Its nitrogen content as measured by a Lunge nitrometer was 12.2%, and its molecular weight, measured viscometrically, was approximately 250 000, with a polydispersity in the range 5-6.

Sample preparation

Nitrocellulose, a fibrous material, is made into a slurry with water and to this is added the nitroglycerine. The water is filtered off and the resultant wet 'paste' is subsequently dried.

Samples of pure NC/NG containing in excess of 30% NG were made by cutting samples (22 × 2.5 × 5 mm) from sheets formed by passing the dried paste through a hot rolling mill. The rolling schedule was 30 passes through a nip of 1 mm, five more at a nip of 0.5 mm, and, finally, four passes at a nip of 2.5 mm.

Samples containing less than 30% NG were made by incorporating dried paste with a suitable solvent system, such as acetone/alcohol. After the material gelatinized, the dough was extruded into cords of 2 mm diameter using a laboratory-scale capillary extrusion rheometer^{5,6}.

The resulting samples were dried in an oven for 21 days at 45°C.

Thermal mechanical measurement

The thermal mechanical measurements were made using a Perkin-Elmer TMS-2 Precision Thermal Mechanical Analysis unit. The analyser is capable of measuring thermal expansion coefficients over a temperature range of -180° to +325°C.

The apparatus was monitored by a microcomputer which stored and displayed experimental data. Analysis routines were employed to find the temperatures at which transitions occurred, and to calculate expansion coefficients for a given temperature range.

The temperature scanning rate used for the samples was 3°C min⁻¹.

Dynamic mechanical measurements

The dynamic Young's modulus E' and loss modulus E'' were measured using a Polymer Laboratories Dynamic Mechanical Thermal Analyser (DMTA). The DMTA is a fixed-frequency device that can operate over a frequency range of 0.03 to 90 Hz and a temperature range of -150 to $+350^\circ\text{C}$. The DMTA operates by applying a sinusoidal force to the midpoint of a sample, securely mounted as a dual cantilever. A constant strain rate is maintained as the temperature changes. Values of E' and $\tan \delta$ are generated as both analogue and digital signals and passed via BNC or IEEE-488 connectors to a microcomputer. The microcomputer controls the DMTA, logs the results and stores the data on disc. This allows the data to be graphically displayed and analysed as and when required.

The temperature scanning rate used for the samples was $0.4^\circ\text{C min}^{-1}$.

It was observed whilst calibrating the DMTA that there was a slight zeroing error at frequencies above 3 Hz. These errors are corrected within our software but would have proved awkward had the data been recorded on a chart recorder. The software supplied by the manufacturer also corrects for these errors.

Difficulties

It was found that the results generated by the DMTA were subject to sudden changes in $\tan \delta$. These changes took the form of a sudden sharp rise followed by a slow decay. This gave the loss modulus *versus* temperature plot a generally sawtooth appearance, and rendered accurate analysis impossible. It was realized that the DMTA keeps the strain rate within a small 'window' of acceptable values. For materials with large variations in the magnitude of E' , the machine must control the strain rate very tightly ($\pm 3\%$) to obtain acceptable results. The manufacturers now supply additional EPROMs making such tight control possible.

Occasionally it was observed that there were still sudden changes in the recorded $\tan \delta$ values. In general these occurred during temperature scans covering more than 100°C . The changes were attributed to differential expansion between the sample and the clamps, leading to the sample 'slipping'. The problem was alleviated by reducing the temperature range for any individual experiment to less than 100°C and roughening the clamp surface slightly to ensure better sample/clamp contact.

Reproducibility

During preliminary experimentation, a range of sample types were examined. The results showed that, in general, the temperature at which the alpha and beta peaks occurred varied by $\pm 6^\circ\text{C}$ and $\pm 1^\circ\text{C}$ respectively for a given sample. Indeed two samples from a strand of extrudate could have greatly differing alpha peak positions despite apparently identical compositions and history⁷. Lengthy investigations showed that more reproducible results were produced if the samples were heated to 80°C for around one hour. The heating of the sample brought about irreversible changes in the position, breadth and height of the alpha peak (Figure 1). In one case, a rocket motor composition, the alpha process was seen to decrease in temperature by 18°C , and increase in breadth and diminish in intensity. The rate at which this change occurred was dependent on the

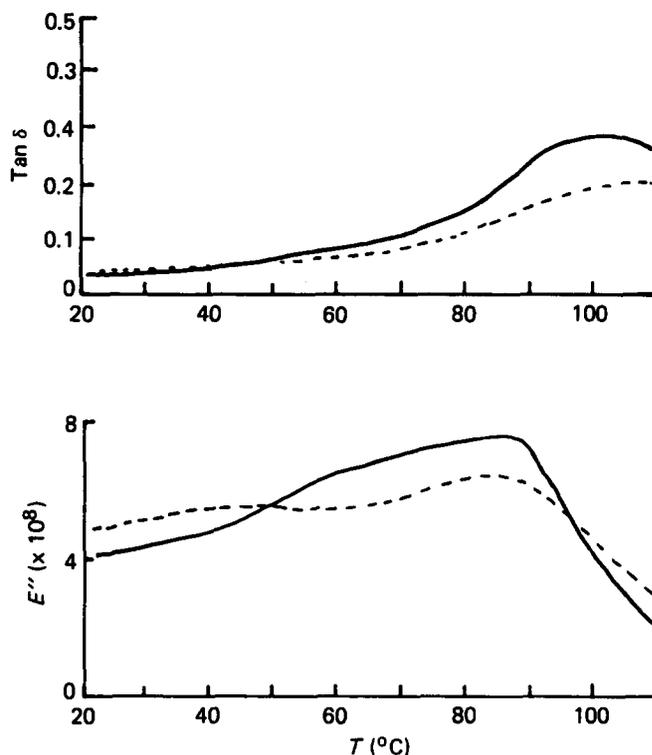


Figure 1 $\tan \delta$ and E'' versus temperature for annealed (----) and unannealed (—) 10% NG samples

sample's composition. Samples containing high levels of NG 'annealed' more quickly.

Townend and Warren³ noted the need for samples to be annealed prior to applying t.m.a. techniques, but make no reference to such a requirement for dynamic measurements. Samples of the batches discussed by Townend and Warren were still available from Mr R. E. Carter at RO (WA), who together with Warren was responsible for their manufacture. These samples showed changes upon annealing, thus suggesting that the results reported by Townend and Warren should be treated with caution.

RESULTS

Dynamic properties

Two major relaxations were observed in all samples examined, corresponding to the alpha and beta peaks described earlier. Evidence was found for the presence of a lower-temperature, -80°C , peak, but the amplitude was small, $\tan \delta$ being less than 0.01. It has not been observed in any sample other than a 10% NG sample, and may be due to residual solvent.

Examination of the alpha process, both annealed and unannealed, over a range of frequencies showed that the peak consisted of at least two components. The components seemed to obey different temperature laws separating or merging as the frequency was increased. It has been found also that the alpha peak position and shape were strongly influenced by material processing, whilst the beta peak was essentially unchanged by the manner of sample preparation.

After annealing the samples it was found that both the alpha and beta peaks appear to obey an Arrhenius law (Figure 2), the pre-exponential factor of which is determined by the NG content of the sample. The alpha

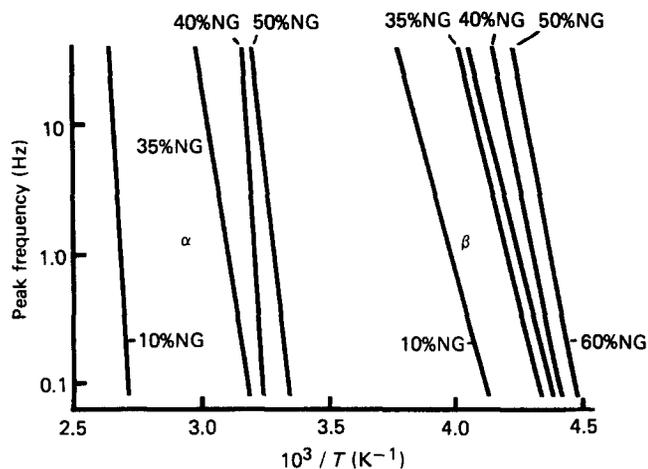


Figure 2 Arrhenius plots for both the alpha and beta processes

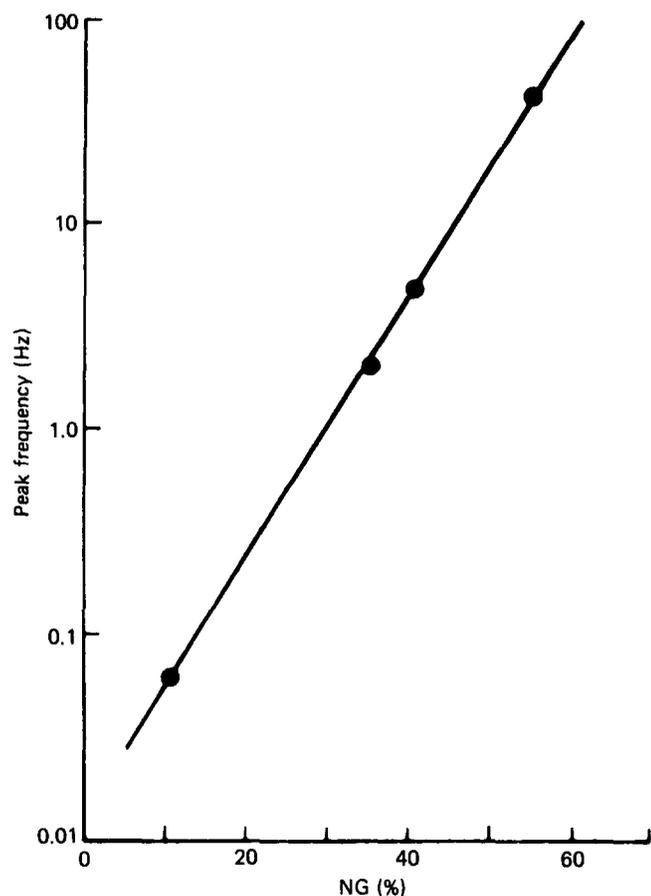


Figure 3 $\log F_0$ versus NG concentration at 238 K

process gave activation energies from 50 to 150 kcal mol⁻¹ and the beta process from 33 to 52 kcal mol⁻¹. In the case of the beta process the activation energies were higher than those observed for the transition occurring in the dielectric relaxation process and did not show any sign of antiplasticization at low NG levels (Figure 3).

It was noted that the drop in modulus at the alpha peak was much greater than that for the beta peak (Figure 4). It was further found that the amplitudes of the $\tan \delta$ peaks were closely related to the NG content (Figure 5). The loss curves showed however that even at 10% NG the loss due to the beta peak was equal to that of the alpha peak, and at higher NG levels the beta peak was as much as three times the size of the alpha peak.

Thermal mechanical properties

Initial results suggested that two transitions were present within the temperature range -100 to $+100^\circ\text{C}$, one at around -40°C and the other at $+80^\circ\text{C}$. The latter, however, underwent an irreversible change and vanished when the sample was heated to around 80°C for an hour (Figure 6). It was found that such high-temperature transitions could be induced by the very act of cutting samples for the TMA at room temperature. To avoid creating such stress artifacts, samples were cut at low temperatures, approximately -150°C .

No such artifacts were found to occur for samples prepared for the DMTA machine and hence it was not necessary to cut samples at these low temperatures.

The results showed that propellant formulations were

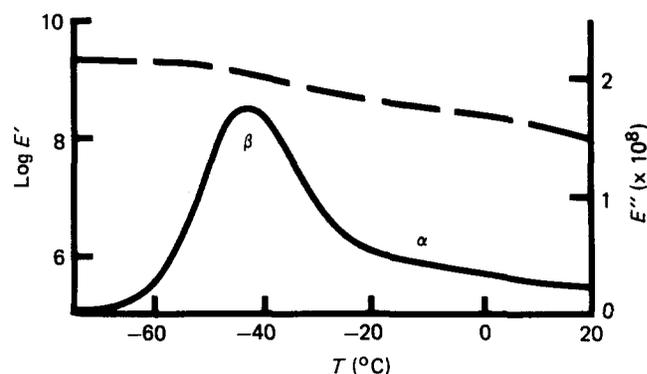


Figure 4 E' (-----) and E'' (—) versus temperature for an annealed 60% NG sample

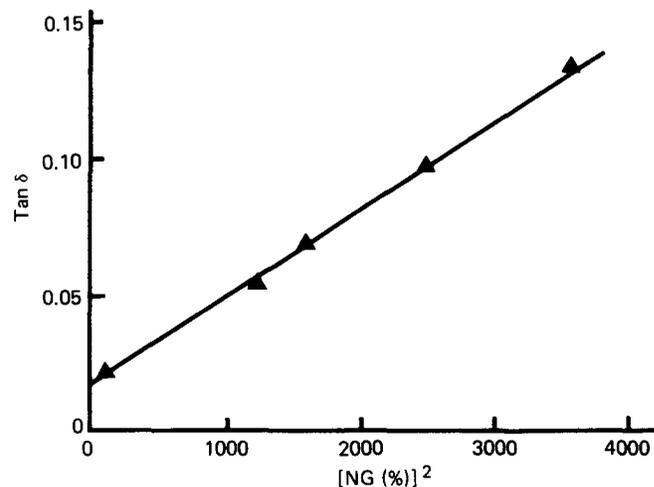


Figure 5 $\tan \delta$ versus the square of the NG concentration for the beta process

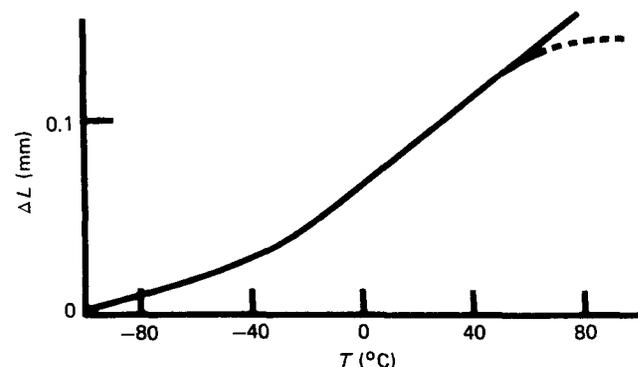


Figure 6 Sample length versus temperature for annealed (—) and unannealed (-----) 35% NG samples

capable of retaining a memory of their stress history if stressed at ambient temperature. Examination of some very old samples suggested that the memory be considered long-term, taking many years to decay at room temperature.

The low-temperature TMA transition was found to be totally reversible and may be considered to represent a free-volume change unrelated to the sample stress history. The transition temperature was a function of the NG content and thus can be related to both the beta process measured on the DMTA and to the dielectric relaxation.

DISCUSSION

The dynamic mechanical results show that the largest change in modulus occurs at the alpha transition, and that the change in modulus for the beta process is quite small. The assumption would be made that the glass to rubber transition (T_g) is represented by the alpha relaxation. If this were true then a large change in the coefficient of expansion would be expected to occur at high temperatures, above 60°C for these samples, as a result of the large change in free volume. From the TMA it is clear that there is no sudden change in the coefficient of expansion due to free-volume changes at these high temperatures. The nitrocellulose may behave as an extended chain molecule, or as a system of extended chains in microcrystalline form, and the transition is due to the movement of these systems through NG, which acts as a lubricant.

There is sufficient evidence from the hydroxypropyl-cellulose work and the findings from the dielectric relaxation spectra of NC/NG matrix to indicate that there exists in the matrix a considerable amount of structure of a fibrillar and crystalline nature.

In the case of an electric stress field it was found that the dipolar relaxation of the nitrocellulose was modified as nitroglycerine was added to it. Indeed the relaxation process at first slowed down, reaching a minimum at 27% loading. Above this value the frequency rapidly increased. From a consideration of the dielectric properties, it was proposed that the plasticizer at first filled sites existing in the nitrocellulose; when these are full the NG forms successive layers upon itself, just as in multilayer adsorption. Corroborative evidence for this is to be found in the work of Lotmentsev *et al.*⁸

The fact that the beta loss mechanism, like the dielectric relaxation, was insensitive to processing conditions would suggest a link between them. Equations exist^{9,10} for converting the response derived from an electric field to one for a mechanical stress field. Neither the alpha nor beta processes allow such a conversion. Neither process obeys the same temperature laws. The beta process is related only to the NG concentration, just as observed for the dielectric response.

Examination of the frequency response of the beta peak as a function of the plasticizer content showed that, unlike the dielectric process, the mechanical loss did not go through a minimum in frequency. The frequency decreased steadily with decreasing NG concentration (Figure 3).

The question must be addressed as to how the mechanical stress field is coupled through the sample. To this end, a model has been devised for the beta relaxation process.

The assumption is made that the relaxation time is a function of the 'microviscosity' of the system, and will therefore be a function of the shear stress and shear rate imposed on the sample.

Thus the viscosity is given by:

$$\eta = \sigma/\dot{\gamma} \quad (1)$$

where η is the viscosity, σ the shear stress applied and $\dot{\gamma}$ the shear rate.

The assumption is now made that the viscosity is an exponential function of the concentration of the plasticizer. Thus:

$$\eta = Ae^{-Bc} \quad (2)$$

where c is the concentration of the plasticizer, A is a constant and B is a constant and is a function of temperature.

Now:

$$\dot{\gamma} = \sigma/\eta = \sigma Ae^{Bc} \quad (3)$$

But $\dot{\gamma}$ is a measure of frequency, so that at the relaxation peak:

$$\dot{\gamma} = F_0 \quad (4)$$

Thus the frequency (F_0) at which the maximum relaxation occurs is given by:

$$F_0 = \sigma_0 Ae^{Bc} \quad (5)$$

But the shear stress σ_0 is a function of both the strain imposed on the sample and its modulus at F_0 . Therefore:

$$\sigma_0 = G\varepsilon_0 \quad (6)$$

where G is the rigidity modulus, which of course is related to Young's modulus E , and ε_0 is the imposed strain. Hence:

$$F_0 = G\varepsilon_0 Ae^{Bc} \quad (7)$$

Therefore:

$$\ln F_0 = \ln(G\varepsilon_0 A) + Bc \quad (8)$$

Now the beta peak behaves according to the Arrhenius law. Thus:

$$\ln F_0 = K - (E^*/RT) \quad (9)$$

where K is the pre-exponential term containing entropic data, E^* is the activation energy of the process, R is the universal gas constant and T is temperature.

Combining (8) and (9), the activation energy can be expressed as a function of the shear modulus (hence Young's modulus), the strain imposed and the concentration of plasticizer:

$$-E^* = RT \ln(G\varepsilon_0 A) + RT(Bc - K) \quad (10)$$

From Figure 7:

$$K = K'c + D \quad (11)$$

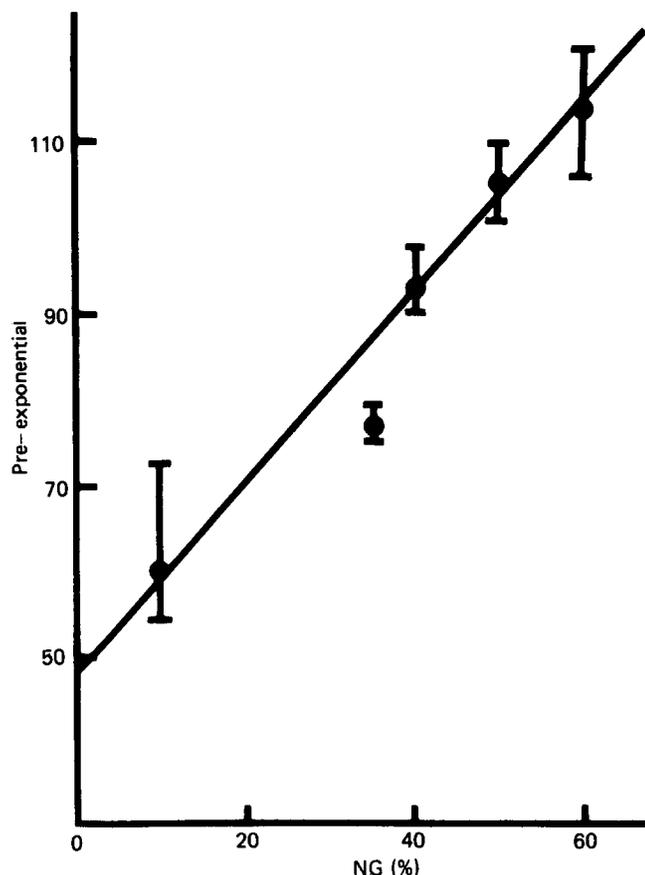


Figure 7 Pre-exponential factor as a function of NG concentration

where K' and D are constants. Then:

$$-E^* = RT[\ln(G\epsilon_0 A) - D] + RT(B - K')c \quad (12)$$

Now if $B = K'$ then $-E^*$ will not be a function of concentration
 if $B > K'$ then $-E^*$ will be a positive function of concentration
 if $B < K'$ then $-E^*$ will be a negative function of concentration

From this equation two predictions can be made, namely that the activation energy of the process may be a linear function of the plasticizer concentration, and that it should be a function of the product of strain and modulus. From Figure 8 it appears that activation energy approximates to a linear function of NG concentration as predicted, and that the viscosity constant B is greater than the constant K' . It is evident from the equation that changing the strain by a factor of 16 will not alter the value of the logarithm in the equation. It is not surprising, therefore, that the expected change in activation energy with strain cannot be observed and is lost in the scatter of the results.

From Table 1 it can be seen that the modulus remains constant over a 16-fold increase in strain. This indicates that the sample is within its linear elastic region.

According to equation (8), the logarithm of the frequency at which the maximum occurs for the relaxation process should be a linear function of the NG concentration, and as can be seen from Figure 3 this is true. The equation also predicts that the frequency should be a function of the product of modulus and strain, but

since the modulus remains constant over the strains measured, it should be a function of the strain for a given concentration of NG. Once again, however, there was too much scatter in the results either to verify or contradict this prediction. Table 2 lists the activation energies and pre-exponential factors for different NG concentrations and imposed strains.

It would seem that, although not absolutely proven, the model based on microviscosity, wherein the NG acts

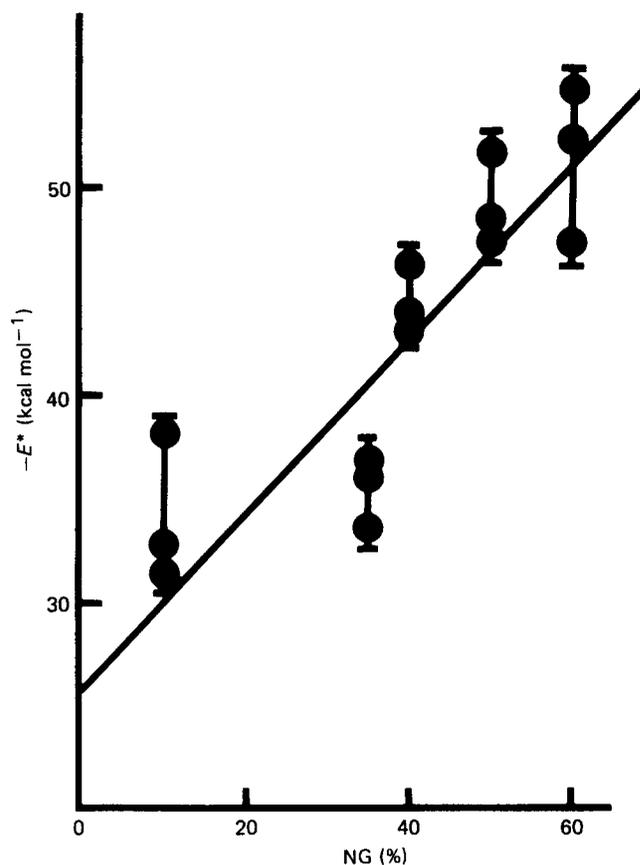


Figure 8 Activation energy as a function of NG concentration

Table 1 Values of Young's modulus

At 0.33 Hz

NG (%)	Strain	Log E'
10	$\times 1$	9.044
10	$\times 4$	9.049
10	$\times 16$	9.049
40	$\times 1$	8.984
40	$\times 4$	8.984
40	$\times 16$	8.984
60	$\times 1$	8.970
60	$\times 4$	8.970
60	$\times 16$	8.970

At 30 Hz

NG (%)	Strain	Log E'
10	$\times 1$	9.046
10	$\times 4$	9.049
10	$\times 16$	9.046
40	$\times 1$	9.015
40	$\times 4$	9.015
40	$\times 16$	9.010
60	$\times 1$	9.076
60	$\times 4$	9.076
60	$\times 16$	9.057

Table 2 Activation energies and pre-exponential factors

NG (%)	Strain	Act. energy (cal mol ⁻¹)	Pre-exponential factor
10	×1	-32 300	66.0
10	×4	-38 100	77.7
10	×16	-31 300	64.4
35	×1	-36 700	77.4
35	×4	-36 800	77.7
35	×16	-33 500	70.3
40	×1	-43 600	91.3
40	×4	-43 900	92.0
40	×16	-46 100	96.4
50	×1	-51 500	110.2
50	×4	-48 700	104.3
50	×16	-47 000	100.7
60	×1	-54 800	121.2
60	×4	-52 400	116.0
60	×16	-47 400	104.8
Mean values			
10	-	-33 900	69.3
35	-	-35 700	75.1
40	-	-44 500	93.2
50	-	-49 000	105.1
60	-	-51 600	114.0

as the medium through which the stress field is transported through the system, is tenable.

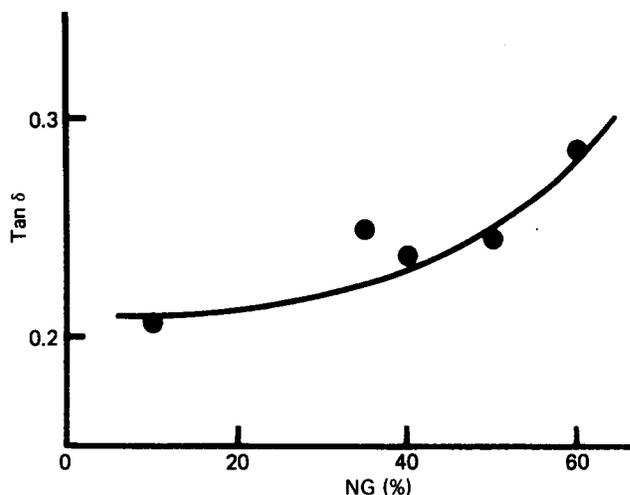
The $\tan \delta$ peak height of the beta process appears to be linearly related to the square of the NG concentration (Figure 5). This would suggest that the loss mechanism is related to the collision of 'particles' and is not therefore at variance with the 'microviscosity' hypothesis.

It is difficult to arrive at a model which would explain the origin of the alpha peak. There is no doubt that the annealing effect must be associated with reorientation of entities within the system. The activation energies do not follow a simple relationship with plasticizer concentration, yet the position of the alpha peak is governed by the amount of NG present (Figure 2). There is evidence that more than one process is occurring, and this may explain the large variation in activation energy with NG content. It does seem also that the peak height of $\tan \delta$ follows a similar law to that found for the beta process (Figure 9) though the data are rather scattered.

Finally it should be noted that the modulus changes by approximately a factor of 50 at the alpha process but much less at the beta relaxation. If the beta relaxation is due mainly to the freeing of the NG molecules then possibly a large change in modulus would not be expected, whereas if large systems of fibrils or microcrystals move, then although this may not be accompanied by a sudden change in expansion coefficient—the free volume being created by the NG—large changes in modulus would be expected.

CONCLUSIONS

At least two major relaxation phenomena have been found for the NC/NG system. There is a low-temperature

**Figure 9** $\tan \delta$ versus NG concentration for the alpha process at 0.3 Hz

beta process, the position of which is independent on how the material was processed, and dependent only on the NG concentration. A model based on microviscosity predicting some of the experimental observations for this relaxation has been put forward.

The higher-temperature alpha process is complex. Its position is dependent not only on the NG content but also on processing. This would support the hypothesis that this process is associated with the movement of large ordered structures, which may or may not be crystalline in nature. Indeed during the process it is perfectly possible that structures of different sizes are moving and or forming or re-forming.

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