Dielectric studies of nitrocellulose/nitroglycerine interaction

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Dielectric relaxation studies have been made of nitrocellulose/nitroglycerine mixtures over a wide range of frequencies (100 mHz to 40 kHz) and temperatures (-70 to $+20°C$). The results obtained for 13.4%N nitrocellulose DOS 2.74 and the 12.2%N nitrocellulose DOS 2.32, suggest that the nitroglycerine is adsorbed onto the pyranose rings present on the surface of the ultimate (elementary) fibrils present in the nitrocellulose. This contradicts the popular hypothesis that the prime sites for nitroglycerine adsorption are the residual hydroxyl groups present in the nitrocellulose.

(Keywords: nitrocellulose; nitroglycerine; dielectric relaxation studies; pyranose rings)

INTRODUCTION

Nitrocellulose (NC) may be considered to be a partially ordered semicrystalline polymer. The order present may exist over a range of scales. It may extend over a few Angstroms, being associated with the ultimate crystalline microfibril of the cellulose precursor, or it may be associated with the incompletely disintegrated fibres ($\approx 1 \mu m$) as frequently observed in thin sections of propellant in the polarizing microscope[1].

Until recently, little was known concerning the manner in which a plasticizer, such as nitroglycerine (NG), is dispersed in the NC matrix. A number of techniques have been employed to investigate this subject including thermal mechanical analysis (t.m.a.), dynamic mechanical analysis (d.m.a.), dielectric relaxation spectroscopy and n.m.r. Detailed discussions concerning the findings from these studies have been reported elsewhere[2-6].

Studies on the dielectric response of 12.2%N NC/NG mixtures have shown that a high frequency relaxation process exists. The magnitude and frequency of this process is a strong function of the NG concentration. Analysis of the results suggested that the plasticizer was adsorbed onto sites extant on the NC. The process very much resembled multilayer adsorption[4], the first monolayer being completed at a concentration of 27% of NG.

These observations carried out at a 12.2% nitration level, were consistent with n.m.r. and vapour phase adsorption studies. The specific sites probably exist at the surface of the microfibrils or in areas of disorder in the microfibrillar structure of the NC.

The present study has been undertaken in an attempt to elucidate more exactly the nature of these sites. At a nitration level of 13.4% there are fewer hydroxyl groups remaining and it would be expected that if the NG is associated with these groups the number of available sites should decrease and be measurable.

EXPERIMENTAL

Materials

The NC used in this study was a commercial sample of the type used in propellant manufacture. It was prepared by immersion of purified cotton linters in mixed nitric–sulphuric acid and stabilized by the normal procedure of extended boiling in a succession of aqueous media. The nitrogen content as measured by a Lunge nitrometer was 13.4%.

Sample preparation

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

The percentage of nitrogen in the NC is usually quoted; however, 12.2%N NC is equivalent to a cellulose structure in which 2.32 of the hydroxyl groups have been substituted, similarly the degree of substitution for 13.4% N NC is 2.74.

The samples were prepared by loading the wet paste into a small press, and subjecting it to a pressure of 85 MPa for at least 15 min. During this time the excess water was expressed from the sample and removed. The biscuit so formed was extracted from the press and subsequently dried for 2 weeks in an oven maintained at 45°C. It was found that the mass of the disc reached a constant value within this period. The dried biscuits were stored in a desiccator. For safety reasons, all the samples contained 1% of a stabilizer 1,3-diphenyl-1,3-diethyl urea, added after the addition of NG.

The sample consisting of 13.4% N NC and 50% NG w/w was made by the hot rolling of a paste containing a small percentage of solvent. The solvent was subsequently removed by drying the sample as above.

The NC used in these studies had a $\bar{M}_w \approx 220\,000$ with a polydispersity of approximately 3.
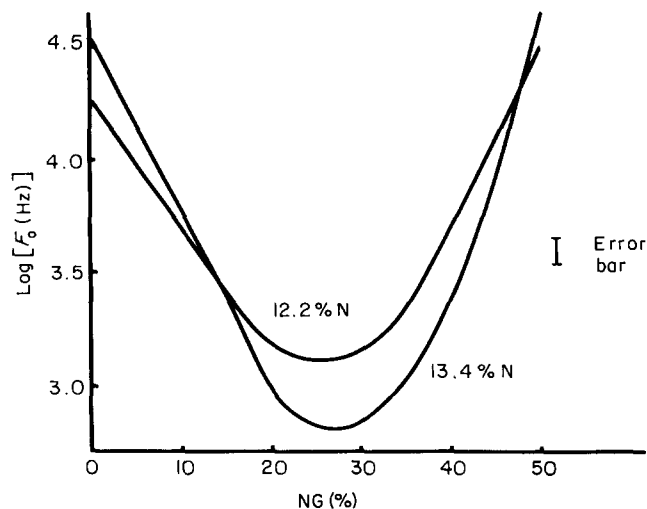
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Figure 1 Log fundamental frequency (F_0) (Hz) *versus* NG concentration (w/w) at 253 K
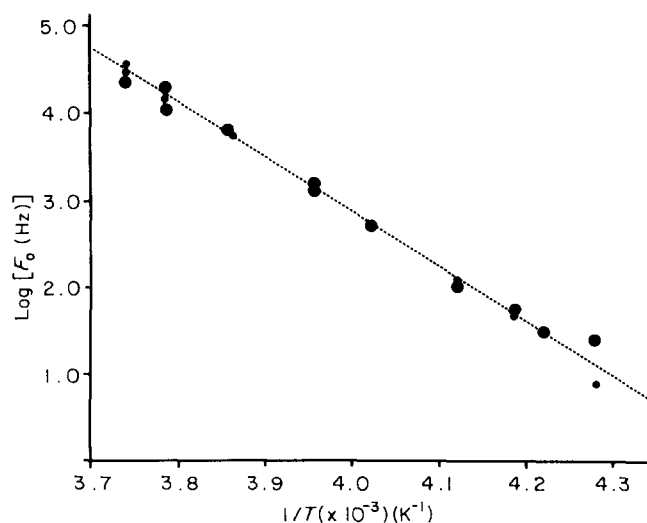

Figure 2 Arrhenius plot (log F_0 *versus* $1/T$) for sample 21520 (30% NG). ●, observed; ●, calculated

Dielectric measurements

The dielectric constant and the dielectric loss were measured using a three terminal cell, which could function over the temperature range −70 to +60°C[7].

The measurements were made using a General Radio AC Bridge 1616 driven by a Rohde and Schwartz RC Generator Type BN 40581. This combination gave an effective frequency range of 10 Hz–60 kHz. Lower frequency measurements were obtained using a Solarton Frequency Response Analyser in the manner described by Hayward *et al.*[8]

The data were analysed in terms of a Havriliak–Negami five-parameter fit described by Baker *et al.*[7]

RESULTS

A relaxation process was observed similar to that found during the 12.2% N study. The magnitude and the frequency of the loss process was a strong function of the NG content, and was unaffected by the method of processing.

The variation of the frequency of the dielectric loss peak as a function of NG concentration is shown in *Figure 1*.

The minimum at approximately 27% indicates that the dipoles experience their greatest hindrance to motion at this concentration. The decrease in frequency as the NG content increased can be explained by a concentration-dependent Kirkwood 'g' factor[9].

Varying the temperature of the observations gave a linear plot of log(F) against $1/T$, a typical example is shown in *Figure 2*. The relaxation corresponds, therefore, to a simple thermally activated process as described by Arrhenius. The change in the activation energy as a function of NG content is shown in *Figure 3*, the value rises sharply initially but less slowly above 40% NG.

The dielectric loss peaks were analysed using the Havriliak–Negami formulism[10]

$$\varepsilon^*(\omega) = \varepsilon_i + (\varepsilon_0 - \varepsilon_i) \times \frac{1}{(1 + (i\omega\tau_0)^{1-\alpha})^\beta}$$

where ε_0 is the static dielectric constant and ε_i is its limiting value at high frequency. The variables α and β are a measure of the broadness and skewness of the loss peak. In all cases, the data could be fitted using only the parameter α. Furthermore, the breadth of the peak as measured by α depended on the NG content. The value decreased as the NG concentration increased. The value of α also increased with decreasing temperature, indicating that the distribution of relaxation times broadened as the temperature was lowered (*Figure 4*).

The Havriliak–Negami analysis gave also an estimate of the constants ε_0 and ε_i. The difference between these two components, defined as the dielectric increment, is proportional to the number of dipoles taking part in the relaxation process and also their effective activity. In a condensed phase, the increment is a function of the extent of the interaction with the neighbouring dipoles, and this is indicated by the value of the Kirkwood 'g' factor, which can vary with concentration. To correct for the variation in bulk density from sample to sample, the experimentally
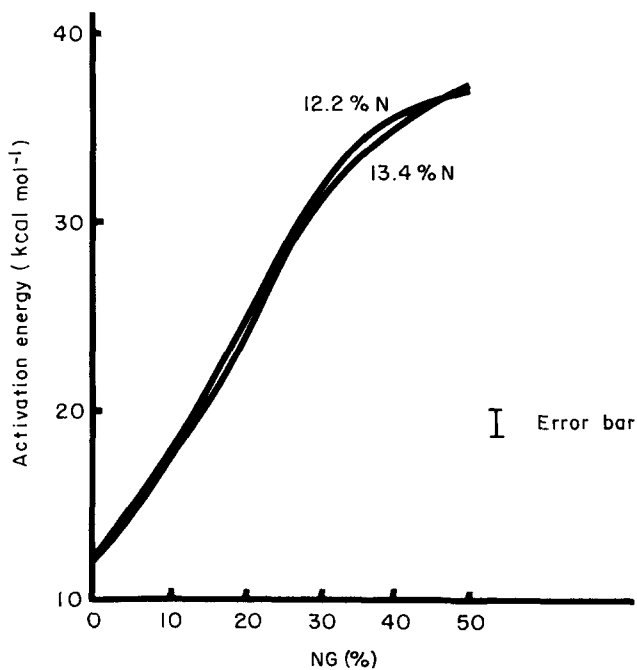

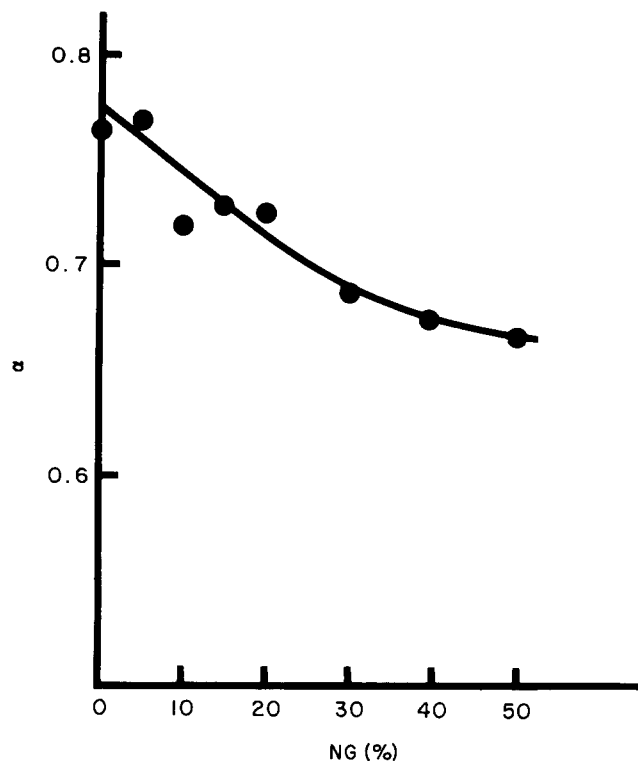**Figure 3** Activation energy *versus* NG concentration

Figure 4 Havriliak–Negami parameter, α versus NG concentration at 253 K

determined increments were normalized to the theoretical density expected for each sample. A plot of the normalized increment against NG concentration is shown in *Figure 5*. The curve shows that the number of dipoles responding to the electric field increased markedly after the addition of approximately 30% of plasticizer. This is in accord with n.m.r. studies[6] in which it was shown that the contribution to the relaxation was due to the NG only.

The response of the 13.4% N NC to an electrical stress field was very similar to that observed for the 12.2% N NC. There are however a number of significant differences.

It was previously believed that the sites occupied by the NG molecules were probably associated with the hydroxyl groups and that once these were filled, multilayer adsorption began with a resultant increase of mobility in the relaxing species. If this were true, then with increasing nitration the minimum in the log frequency vs. NG concentration plot should occur at a lower concentration. Also, the start of the plateau in the activation energy as a function of NG content should occur at a lower concentration. Neither phenomenon was observed.

It is known that NG does not penetrate the crystal lattice[11]. The adsorption of the NG must, therefore, take place on the surfaces of the microcrystals. Calculations[5] on the number of available sites further support this hypothesis by suggesting that monolayer coverage will be reached at 37% NG concentration. A model can now be proposed for explaining the observed phenomena for 12.2 and 13.4% NC.

It is assumed that after the solvent has been driven off from the propellant, the microcrystalline nature of the NC has been preserved. This hypothesis is strongly supported by the work of Trommel[11] where the d lattice

spacing has been unaltered by precipitation from a solution in acetone.

Since it is highly unlikely that the microcrystals have been destroyed by the mixing or rolling processes used in the manufacture of propellants, then the adsorption sites remain practically unaffected either by the solvent or solventless techniques used in producing propellants. This explains why the dielectric loss and the loss modulus of the high frequency/low temperature transitions are not influenced by the processing conditions.

Further support for the model comes from the observation that the broadness of the loss mechanism, as measured by the Havriliak–Negami constant, α, increased as the NG content decreases for the 13.4% NC; but rises to a maximum for the 12.2% NC. The fact that the distribution of relaxation times for the 13.4% NC are greater than the 12.2% NC would indicate that there are more degrees of freedom for the movement of the dipoles extant in the system. This would be expected for a more open structure, which of course the 13.4% NC has, as measured by X-ray diffraction work[11].

The addition of NG to the system may have two opposing effects dependent upon the extent to which coupling exists between NG groups. If coupling is extensive it may be anticipated that the degrees of freedom will be reduced as each molecule is influenced by those nearby. On the other hand if coupling/steric hindrance is not significant for all sites, the addition of NG might lead to a wider range of possible movements for the NG molecule and hence an increase in the degrees of freedom. Trommel's work[11] shows that the d spacing in the NC crystal increases with nitrogen level, hence it is not unreasonable to expect that the degree of coupling between sites will vary as a function of substitution. The observed difference in broadness of the relaxation processes with plasticizer concentration as a function of nitration level can be explained by the following argument.
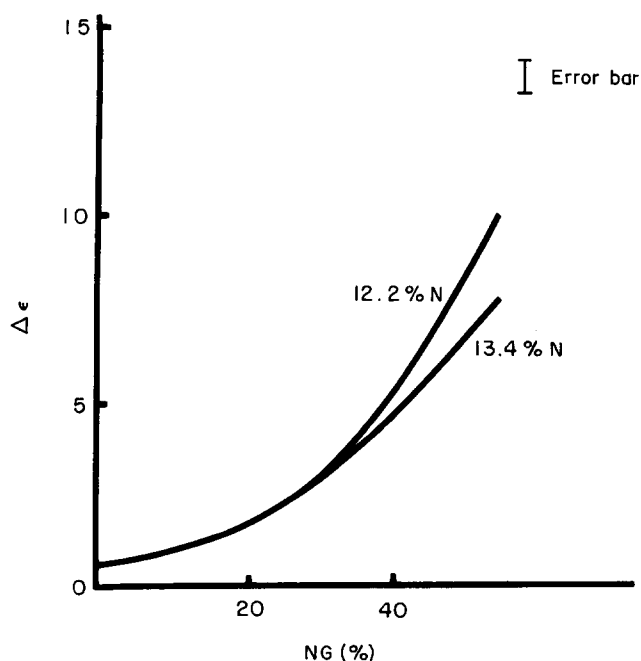

Figure 5 Dielectric increment ($\Delta\varepsilon = \varepsilon_0 - \varepsilon_i$) versus NG concentration (corrected for density)

In the case of the 12.2% N NC, as the NG is added, so will it find sites on the crystallites. Initially these will adopt positions as far apart as possible to reduce the energy of the system. Since they are independent of each other, they are likely to move with the imposed electric field in a similar manner and have similar relaxation times. As the sites become increasingly filled, clusters of the molecules begin to interact. The result will be to increase the distribution of relaxation times, hence α will progressively increase in magnitude. Once half the available sites have been occupied, the NG molecules will become more tightly packed resulting in an increasing cooperative interaction between clusters. The relaxation time distribution will steadily decrease and approach the value for the liquid state. Thus, α will steadily decrease and approach a steady value once the first layer of molecules has covered all the available surface sites.

Since it is thought that monolayer coverage is complete at a weight concentration of NG of 27%, the above hypothesis is supported by the observation that α reaches a maximum at approximately 15%.

In the case of the 13.4% N, the distribution gradually narrows with concentration of NG, although there may be a slight inflection at 15% NG content. It is possible that in this case the lattice distance is large enough to allow the pyranose rings to move more independently of each other than in 12.2% N NC. At low concentrations of plasticizers, therefore, the distribution of relaxation times will be large. As the NG is added the interaction between other sites will increase as described, and the distribution of relaxation times will narrow as observed.

Some consideration should be given to the nature of the adsorption site. From the data, it would appear that the sites are resident on the surface of the microcrystals present in the NC.

Although NC has groups with very strong dipole moments (2.95 Debye) they will not all be active. If the assumption is made that the pyranose ring does not move, then only the primary ester group will undergo a change in dipole moment with the imposed electric field, the secondary ester groups will not undergo a net change in dipole moment since they can only spin about their own axis. The primary groups will experience different environments depending on whether they are on the central chain in the microcrystal or on the surface. In this case, coupling between the motion of the internal primary groups with those on the surface would be weak. Two relaxation phenomena or at least a skew distribution should be observed. In particular, the difference between the two motions should become more evident as the NG couples with these surface groups. The fact that this is not observed indicates that the loss process is not solely due to the relaxation of the primary group, and that the NG does not interact exclusively with the surface primary groups.

If the pyranose ring is allowed to oscillate about the ether linkage then there will be a change in dipole moment, since the resultant dipole vector points 70° away from the c axis of the chain[5]. The rate of relaxation of the inner chain may be different from the surface chains in the lattice[1]. It is likely, however, that the relaxation times

would not be too different, since some coupling would be expected as a result of steric effects. A single broad non-skew distribution would be expected if this model is correct, and the loss would not split into two processes nor become increasingly skew as NG is added.

Finally, another source of dipole moment change to be considered is oscillations of the pyranose ring between chair and boat form[12]. Such oscillations are probably sterically forbidden.

From the above analysis, it is evident that the data fit best the hypothesis that the NG is adsorbed onto the pyranose rings existing on the surfaces of the ultimate fibrils present in the NC.

CONCLUSION

Examination of the interaction of NG with NC has shown that the hypothesis that the plasticizer interacts directly via hydrogen bonding to the primary group in NC is incorrect. The data presented support the hypothesis that the NG is adsorbed onto the pyranose rings existing on the surfaces of the ultimate fibril present in NC. The nature of the adsorption would seem to be physical, Van der Waal's forces, or weak chemisorption, since NG is known to migrate out of NC by heating at low temperatures, i.e. 363 K.

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