Dielectric studies of the effect of water on the relaxation properties of nitroglycerine–nitrocellulose mixtures

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Dielectric relaxation and water adsorption data are reported on mixtures of nitrocellulose and nitroglycerine which have been exposed to moisture to varying degrees. It was observed that the characteristics of these systems depend on the level of nitrogen in the base polymer. At 10.9% hydroxyl sites still exist which can effectively interact with the moisture, whereas at 12.9% the free hydroxyls appear to be incorporated into the ordered semi-crystalline regions of the polymer. The addition of water to nitroglycerine–nitrocellulose mixtures has little effect on the dominant beta relaxation other than to narrow the distribution of relaxations. The relaxation process is, in this case, associated with a cooperative relaxation of nitroglycerine moieties. Water has the effect of decreasing the cooperativity of the beta relaxation process.

(Keywords: dielectric relaxation; nitrocellulose; nitroglycerine; water adsorption; effect of water)

INTRODUCTION

The dielectric relaxation of nitrocellulose (NC) plasticized with nitroglycerine (NG) has been described recently[1]. The general conclusion was that the main contribution to the relaxation process observed in the 10 to 5 MHz range was attributed to the nitroglycerine. Comparison of the expected dielectric relaxation strength associated with the nitrate group in NC with that predicted theoretically indicated that either the polymer is very stiff and/or that cancelling of dipolar contributions occurs due to two possible conformers leading to a small net contribution. The concentration dependence of the NG relaxation was consistent with a model in which at low concentrations the NG is adsorbed onto sites extant in the NC forming a monolayer. Further addition produces a multilayer which gradually assumes the characteristics of liquid NG.

The behaviour described is similar to that observed for the dielectric relaxation of cellulose acetate plasticized with glycerol[2] and water[3]. In the case of cellulose acetate, it has been possible to define the extent to which a crystalline structure exists in the material and observations from the dielectric relaxation are consistent with the existence of ordered regions.

Formulations of NG/NC are prepared from aqueous slurries hence it is important to ascertain the effect that water has on the properties of this particular relaxation process. Additionally, two sets of samples containing different degrees of nitrogen were examined to ascertain the effect of residual hydroxyl groups attached to the NC on the relaxation behaviour.

EXPERIMENTAL

Materials

Two samples of NC were used in this study; one having a nitrogen level of 10.9% and obtained from British Drug Houses Ltd. This grade of material is commonly used in the manufacture of celluloid film. The other sample had a nitrogen content of 12.2% and is used in military applications. The nitrogen content of the samples was measured using a Lange nitrometer and the molecular weight of the polymer was determined viscometrically to be 2.5×10^5 with a dispersivity of between 4 to 5.

Sample preparation

The military grade nitrocellulose (12.2%) was made into a slurry with water to which was added the desired quantity of NG. The mixture was then agitated and the resultant paste filtered and dried. The dried material was then passed through heated rollers where it was formed into sheets ~3 mm thick. Discs some 75 mm in diameter were cut from the sheet and used for the dielectric measurements. Samples containing 35, 40, 50 and 60% of NG were prepared in this manner.

Dielectric measurements on the 10.9% nitrogen containing sample were obtained on solvent cast films. The original sample was provided as a dispersion in solvent (isopropyl alcohol). Films ~2 mm thick were obtained by casting in square moulds. The films so obtained were dried for 24 h in a vacuum oven to remove residual solvent.

Addition of water to samples

The discs of rolled NC/NG were stored at ambient temperature and 100% humidity for a period of at least one month before measurements were performed. Any

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surface condensate on the discs was removed with absorbent tissue prior to measurements being performed. The sample was then weighed, placed in the dielectric cell[4] and quickly cooled to below 273 K. The dielectric properties were then determined as has been described previously[1,4]. The rate of water loss from these samples when exposed to ambient RH was determined by monitoring the weight loss as a function of time, until an equilibrium value was attained.

In addition to the above measurements, discs of both the high and low nitrogen content NC were 'dried' for a week in a specially designed oven (Laboratory Thermal Equipment-type F) equipped with a pressure release and a thermal safety cut out control. These previously dried samples were stored at constant relative humidity of 53% for various lengths of time. The amount of water absorbed was varied by altering the time of exposure. The degree of water uptake was estimated by weighing the disc before and after the hydration procedure. A maximum water uptake of 4% could be achieved in this manner. Higher water contents (4–10%) were obtained by placing the discs in a dessicator containing distilled water (100% humidity). In order to achieve the highest levels of water uptake, it was necessary to agitate the system with a magnetic stirrer.

Dielectric measurements

As indicated above, the measurements were performed on discs of the material. Variable temperature-fixed frequency observations were made using a Teradyne C357 bridge operating at a frequency of ~1 kHz. Variable frequency (10 Hz–100 kHz) measurements were made using a Rohde and Schwartz RC generator type BN 40851 driving a General Radio AC bridge type 1616. Higher frequencies (100 kHz–5 MHz) were measured using a Wayne Kerr A.C. Bridge B602, driven by a Wayne Kerr Source and Detector S2268. The samples studied were placed in sealed cells, one of which contained drying agent in order to avoid problems associated with condensation of moisture on electrodes, the other being filled with dry nitrogen gas. The weight of the sample before and after the experiments was monitored in order that the exact level of hydration of the samples was known.

RESULTS AND DISCUSSION

Adsorption and desorption of water from the NC/NG mixtures

The water desorption from four samples of differing NG content was also recorded, *Figure 1(a)*. The desorption experiments from 100% humidity indicate that the higher the NG content the larger was the amount of water which had been absorbed. Analysis of the absorption data indicated that it was initially Fickian[5] and yields values of the diffusion coefficient of 1.017×10^{-4} and $0.711 \times 10^{-4}\ m^2\ s^{-1}$ respectively for the 2 and 15% NG samples, *Figure 1(b)*. The values of the diffusion coefficients are much higher than those observed for water absorption in other cellulose materials[3] and reflects both the hygroscopic and plasticized nature of this material. From the water desorption experiments carried out on the samples containing NG levels ranging from 35% to 60%, it can be seen that the level of water in the samples during the measurements of the dielectric properties is as shown in *Table 1*.

Effect of the addition of water to NC films on the dielectric loss

The temperature dependence of the dielectric loss (ε'') was measured at 1 kHz as a function of water content and is shown in *Figures 2* and *3*. In the case of the 12.6% N sample, the beta relaxation position is essentially unaffected by the addition of water. In previous studies of NC/NG mixtures, the data were interpreted in terms of an adsorption model in which molecules of NG in the first monolayer strongly interact with the NC and an upward shift in temperature was observed in the beta process at low concentrations. In the present situation, addition of water has little effect other than to increase the amplitude of the beta process and at high concentrations to produce a large loss contribution associated with ionic conduction. This behaviour is similar to that observed previously in our studies of water adsorption on to cellulose acetate[2,3].

In contrast, the 10.9% NC does exhibit a downward shift in the position of the beta peak in addition to the expected increase in the higher temperature loss associated with conduction. A downward shift in the beta peak is indicative of more facile motion being generated as a consequence of a component of the relaxation process possessing a lower activation energy. The relaxation in water doped cellulose derivatives occurs at a lower temperature than that for water in NC and hence a downward shift is consistent with the occurrence of water interactions directly with residual hydroxyl groups. In the case of the 12.6% NC, residual hydroxyl groups may be assumed to be structure generators and hence are not accessible to the water, hence the difference in the behaviour presented in *Figures 2* and *3*.

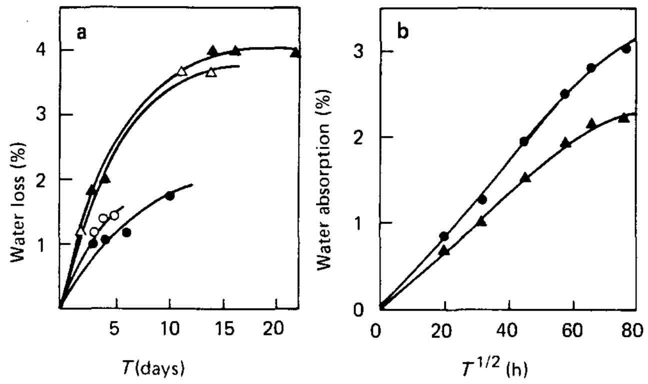

Figure 1 Water adsorption and desorption as a function of time for various NC/NG mixtures. The NC contains 12.2% nitrogen. (▲) 2% NG/NC; (●) 15% NG/NC; (●) 40/60 NG/NC; (○) 50/50 NG/NC; (△) 60/40 NG/NC; (▲) 65/35 NG/NC

Table 1 Activation energies for wet and dry NG/NC mixtures

	Activation energy		Water composition of wet samples	
Sample %NG	Dry kJ mol^{-1}	Wet (H_2O) kJ mol^{-1}	%NG	%H_2O
35	144	139	35	1.5
40	140	144	40	2.0
50	154	162	50	3.5
60	145	135	60	4.0

Estimated error ±8 kJ mol^{-1}

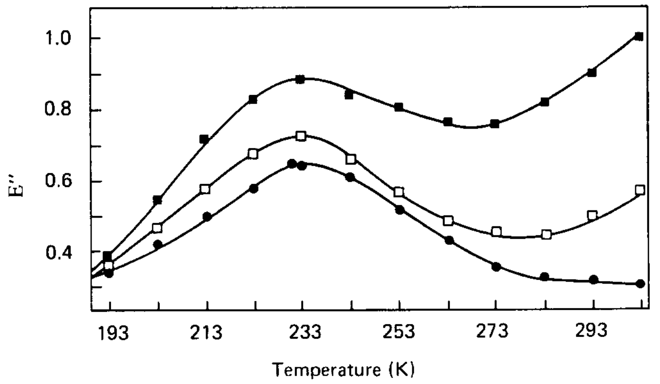

Figure 2 Temperature dependence of the dielectric loss in NC (12.6% N) as a function of water content. (●) 0% H_2O, (□) 1.2% H_2O and (■) 2.8% H_2O

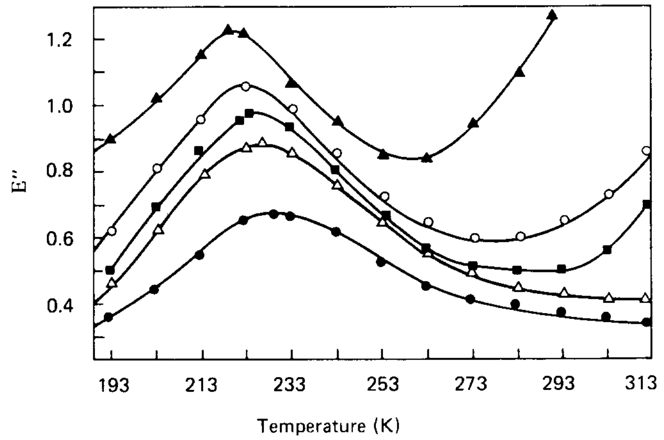

Figure 3 Temperature dependence of the dielectric loss (ε'') for NC (10.9% N) as a function of water content. (●) 0% H_2O; (△) 0.8% H_2O; (■) 1.3% H_2O; (○) 2.5% H_2O and (▲) 3.7% H_2O

Temperature dependent dielectric measurements in NC/NG mixtures

In order to rapidly assess the effects of water on the relaxation of NC (12.6% N)/NG mixtures, the temperature scans of the dielectric loss (ε'') were obtained at 1 kHz, *Figures 4* and *5*. It is apparent that the addition of low levels of water leads to an increase in the amplitude of the beta relaxation peak and also a rapid increase in the conductivity at high temperature. In the interpretation of the NC/NG mixture carried out previously[1] it was inferred that NG is adsorbed onto ordered regions of NC. The data presented here indicates that the water appears to be either combined with the NG relaxation or its effect on the local field experienced by the NG is to alter the effective Kirkwood '*g*' factor[6,7]. Local field effects are usually accompanied by a shift of the relaxation on the temperature frequency plane which is contrary to the evidence presented and hence an interpretation based on a cooperative relaxation of NG and water is preferred. No evidence was found for the existence of a specific H_2O/NC relaxation process. The only effect of the addition of water on the relaxation was to narrow the distribution of relaxation times for the system and to increase the dielectric increment, see *Table 2*.

Frequency dependent dielectric studies on NC/NG pastes

A typical set of data for an NC/NG (50/50) paste

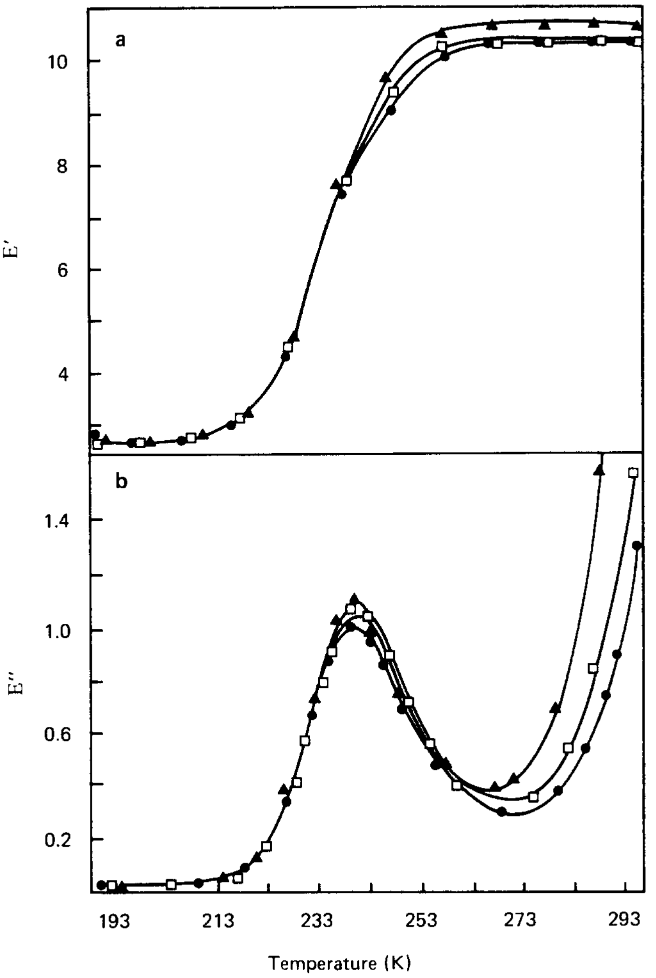

Figure 4 Variation of (a) permittivity (ε') and (b) dielectric loss (ε'') as a function of temperature for a 60% NG/NC (12.2% N) paste containing (●) 0% H_2O, (□) 0.3% H_2O and (▲) 0.5% H_2O

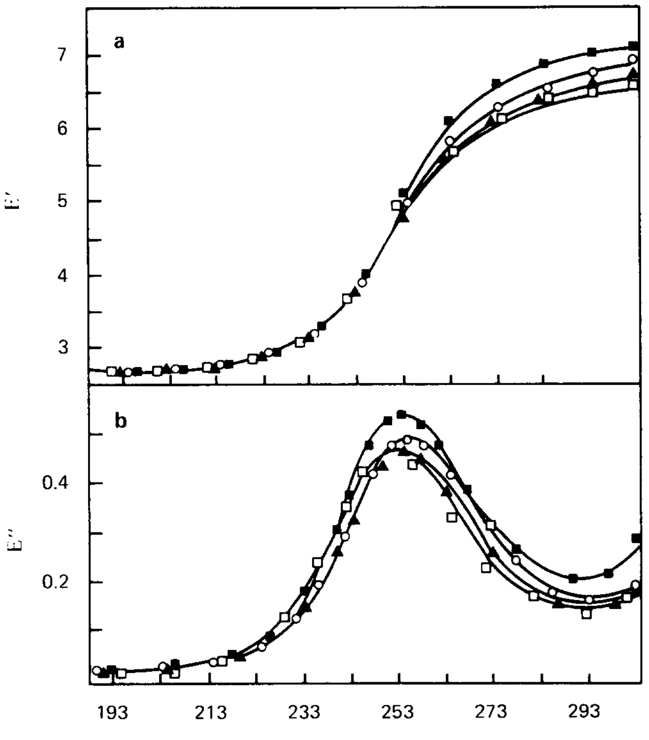

Figure 5 Variation of the (a) permettivity (ε') and (b) dielectric loss (ε'') as a function of temperarture for a 40% NG/NC (12.2% N) paste containing (□) 0% H_2O, (▲) 0.08% H_2O, (○) 0.27% H_2O and (■) 0.55% H_2O

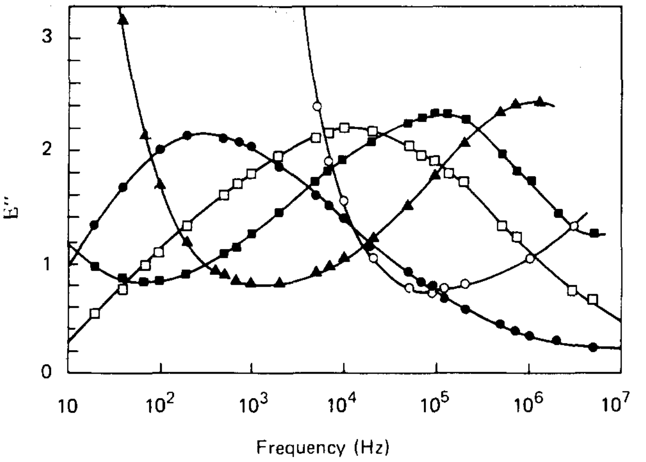

Figure 6 Plot of dielectric loss ε'' as a function of frequency and temperature for a (12.2% N) paste 35% NG. (▲○) 263 K; (○△) 253 K; (■) 243 K; (○) 233 K

containing approximately 3.5% water is shown in *Figure 6*. The large low frequency loss at high temperature is consistent with the occurrence of proton conduction within the sample. The presence of this conduction loss limits the temperature–frequency range available for study and hence increases the uncertainty in the activation parameters obtained. A more detailed examination of samples containing 40% and 60% NG (*Figures 4* and *5*) in the temperature plane indicates a slight upwards movement in the relaxation peak consistent with the idea that water plasticizes the system. The dielectric data were analysed using an iterative fitting[4] of the Havriliak–Negami (HN) equation 8,1. The frequencies obtained from the analysis confirmed that the process followed Arrhenius Rate Law. The activation energies for the various samples studied are listed in *Table 1*. The differences observed are within experimental error.

The results of the HN analysis are summarized in *Table 2*. It is apparent that the relaxation distribution is narrower in the wet sample compared with the corresponding dry. Increase in the temperature causes the distribution to be narrowed in both cases. A value of the distribution parameter in the range 0.6–0.75 is indicative of the occurrence of a highly cooperative motion of the NG dipole. The observed change in the distribution parameter implies that the extent of the cooperation of the relaxation is reduced by the addition of water or by an increase in the temperature. These observations are consistent with the idea that the water is dispersed in the NG phase and has in the highest nitrogen containing NC little or no interaction with the cellulose.

Table 2 Results of Havriliak–Negami analysis of wet and dry NG/NC samples

NG composition (%)	Temperature	α parameter		$(\varepsilon_0-\varepsilon_\infty)$	
		Dry	Wet	Dry	Wet
35	263	0.73	0.66	4.4	6.5
	253	0.72	0.68	4.3	5.9
	243	0.73	0.70	4.1	4.9
40	263	0.69	0.65	5.7	10.8
	253	0.71	0.67	5.5	9.3
	243	0.72	0.69	5.5	8.4
	233	0.73	0.70	4.7	7.6
50	253	0.65	0.63	9.7	14.9
	243	0.66	0.65	9.9	12.6
	233	0.68	0.65	9.2	12.2
60	243	0.63	0.63	12.3	20.5
	233	0.63	0.63	12.1	18.4

CONCLUSION

The addition of water to NC/NG mixtures leads to a slight narrowing of the distribution of relaxations without significantly modifying either the frequency or activation energy associated with the relaxation process. Comparison of the data obtained as a function of the degree of nitration indicates that in the case of 12.6% NC, addition of water has little effect apart from an increase in the dielectric loss due to ionic conduction at high temperatures. In contrast, the 10.9% NC contains sufficient accessible hydroxyl groups for the addition of water to influence the distribution of relaxation processes. This latter observation is consistent with similar observations on the addition of water to cellulose derivatives.

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