Relaxation spectra and x-ray diffraction of plasticized nitrocellulose

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Introduction

The degree of plasticization of nitrocellulose has an effect on its mechanical properties and its combustion properties [1]. However, measuring the degree of plasticization of nitrocellulose based propellants poses a real challenge.

Nitrocellulose possesses a micro fibrillar structure that results from that of the cellulose source used to make it [2]. The destruction of those fibrils during mixing both due to the action of the solvent as well as the action of the shear produced by the mixer and the action of plasticizers is what is referred to as the plasticization of the nitrocellulose.

X-ray diffraction (XRD) has been used to characterize the crystalline and amorphous parts of nitrocellulose [3]. This could be used to track morphological changes.

Torque is difficult to use as a quality check for propellants given the nature of the mixing operation. The work unit can however be useful as a measure of the mechanical energy imparted to the propellant [4].

It is expected that XRD and the relaxation spectra which depends on the microstructural features of a material [5] would yield important information on the degree of plasticization of nitrocellulose.

Figure 1. Nitrocellulose, 13.25% nitrogen content in a sigma type mixer prior to addition of solvents and plasticizers.

Materials and methods

- X-ray diffraction: commercial (12% N) nitrocellulose and Camphor 90/10 (m/m). Internal mixer (Brabender, 30 cm^3).
- Dynamic mechanical analysis & relaxation spectra: grade B (13.25% N) nitrocellulose and acetyl triethyl citrate ATEC 89/10 (m/m). 1% ethyl centralite used as stabilizer. Sigma blade mixer, 2.65 L.
- Solvent incorporation method used for all mixes. Subsequent ram extrusion of the 13.25% nitrocellulose mixes. Pressed samples used for the nitrocellulose/camphor mixes.

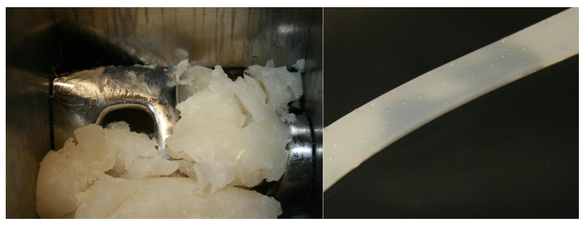

Figure 2. Mixing of and extruded nitrocellulose based propellant

- Energy added to the propellant calculated through work units (Wu).

$$Wu = \frac{2\pi N}{m}\int_{t_1}^{t_2} T(t)dt$$

- Relaxation spectra calculated with the NLREG software from dynamic mechanical analysis (DMA) modulus using frequency sweeps and time-temperature superposition (TTS) to obtain at least 6 decades of frequency.

Results

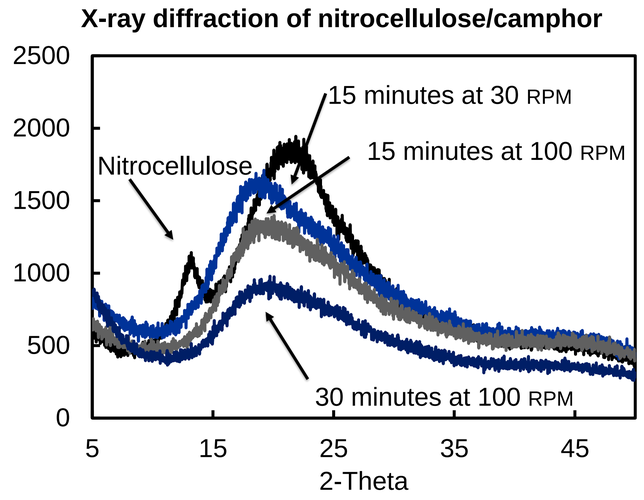

Figure 3. XRD on plasticized nitrocellulose, the crystalline content of pure nitrocellulose can be seen at 13 2-theta. The broad peak represents the amorphous content.

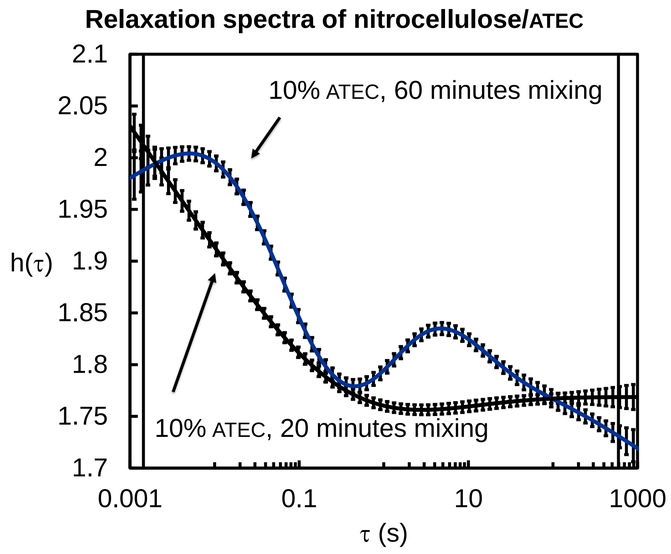

Figure 5. Relaxation spectra of plasticized nitrocellulose, the two vertical black bars indicate the interval for which the relaxation spectra was calculated.

The initial crystalline content of the nitrocellulose is easily distinguished on Figure 3. The expected loss of crystallinity due to the destruction of the fibrils is also easily observed. However, the expected slow decrease in crystallinity with increased mixing wasn't present.

The torque data, Figure 4, can be used to provide a measure of the amount of mechanical energy imparted to a propellant during the mixing stage.

$Wu_{20\ minutes} = 363\ J/g$ $\qquad$ $Wu_{60\ minutes} = 775\ J/g$

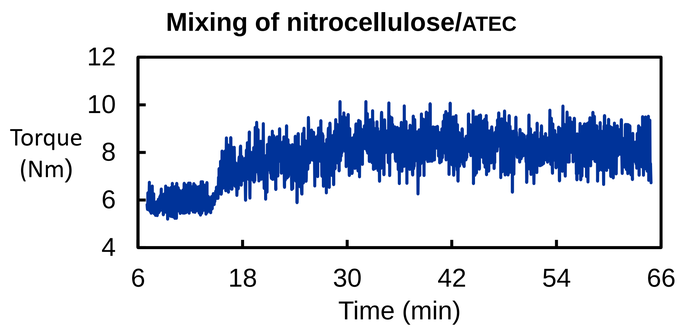

Figure 4. Torque during the mixing stage, notice how "noisy" the data is.

The relaxation spectra, Figure 5, shows that a change in the microstructure of the propellant occurred upon further mixing. The extra mechanical energy imparted to the propellant and the action of the solvents during the mixing stage clearly caused changes.

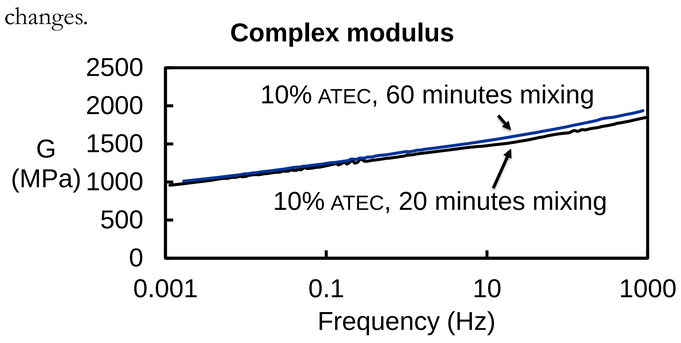

Figure 6. Complex modulus from DMA experiments, the complex modulus is shown as it represents both the storage and loss moduli and for readability. The use of TTS generated a little bit of noise in the curves, this could be improved with more precise testing apparatus.

Conclusions

- X-ray diffraction can be used to characterize the changes in nitrocellulose during the initial mixing stages.
- X-ray diffraction will highlight any residual crystallinity if present.
- Military grade NC has lower crystallinity than commercial NC and XRD characterization will likely prove more difficult as a result.
- Peak deconvolution on the XRD data may provide more insight into the morphology of the propellant. It was the case for pure nitrocellulose [3].
- The relaxation spectra provides insight as to the changes in the microstructure of nitrocellulose. This technique warrants further investigations!
- Stiff fibrils are expected to have short relaxation times while long chains resulting from the breakdown of the fibrils would show longer relaxation times. This is seen in Figure 5.
- A decrease in the longest relaxation times would indicate destruction of some of the longest nitrocellulose polymer chains during the mixing.
- Time-temperature superposition may not hold for all NC based propellants, this needs to be verified prior to performing the relaxation spectra calculations.
- The micro fibrillar structure of NC is dependent on the source (wood essence, cotton, etc.). Differences are expected between sources of the NC even after mixing. This needs to be verified!
- Time-relaxation experiments could be used as alternative measurement technique to measure the relaxation spectra through the relaxation modulus G(t) or to validate the calculated relaxation spectra.
- The experiments to calculate the relaxation spectra are lengthy, but the resulting changes could be linked to the number work units imparted. This would be highly dependent on the mixing conditions of the nitrocellulose however.

Literature cited

[1] Carter, R.E. and Warren, R.C., Extrusion stresses, die swell and viscous heating effects in double-base propellants, *Journal of Rheology, 31, 151-173, 1987.*

[2] Baker, F.S. *et al.*, The interaction of dibutyl phthalate with 12.6% nitrocellulose, *Polymer International*, 54, 54-57, 2005.

[3] Herrmann, M. *et al.*, Microstructure of nitrocellulose investigated by x-ray diffraction, *42nd International annual conference of ICT*, 53.1-53.7, 2011.

[4] Baker, F.S., Carter, R.E., Processing characteristics of gun propellants, *Propellants, Explosives, Pyrotechnics*, 7, 139-147, 1982

[5] Honerkamp, J., Weese, J., A nonlinear regularization method for the calculation of relaxation spectra, *Rheologica Acta*, 32, 65-73, 1993

Acknowledgments

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