PYRO NITROCELLULOSE: MOLECULAR WEIGHT DISTRIBUTION AND PROCESSABILITY

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ABSTRACT

    Problems in processing 12.6% N Pyro nitrocellulose into certain types of
casting powder have been identified as due to unusual molecular weight distri-
butions. Critical in the formation of a good propellant dough is the presence
of a low molecular weight fraction which is solvent soluble and acts as an
adhesive between fibres. Because of this, processability is a function more
of number average than of weight average, and a simple viscometric test which
measures both these values is described.

INTRODUCTION

    About five years ago considerable difficulty was experienced in processing
many batches of 12.6% N Pyro nitrocellulose into certain casting powders. The
phenomenon was one of poor "dough-up". Using the traditional ethanol—acetone
solvent system the mixtures remained somewhat friable in the incorporators,
and this resulted in the extruded propellants having poor densities and
ballistics. These difficulties coincided with an enforced change in the
suppliers of the cotton linters — from Lansil to Holden Vale. Both the linters
from the new suppliers and the nitrocellulose produced therefrom were within
specification. However, it was not a clear—cut situation. Not all batches of
nitrocellulose produced from the linters from the new suppliers was unprocessable,
and we were never sure that the cause of the trouble was not inadvertent changes
on the plant during nitration and stabilisation.
    NEC Ltd had developed an empirical test, called the lead β resorcylate
(or LBR) test, which, from long experience over many production batches, gave
a good indication as to whether a particular nitrocellulose would process well

in the critical ballistic modifier/solvent system. In this test (and in the slightly different PERME modification) the increase in the viscosity of a solution of nitrocellulose in ethanol/acetone (3 g NC dissolved in 70 ml absolute ethanol and 50 ml acetone) by the addition of lead β resorcylate (0.2 g) is measured. Viscosities are determined by the time of fall of a steel ball. Standard mixing conditions must be maintained, and measurements are usually taken 2 hours after the introduction of LBR. The temperature of the solutions is kept at all times at $20^{\circ}C$. Viscosity increase is expressed as a percentage, and this is called the "LBR value". Those nitrocellulose batches having an LBR value below about 200 always processed well. Those batches with an LBR value above about 300 were found to be unprocessable, and would be used in other modifier/solvent systems.

Because of its empirical nature the LBR test could tell us nothing of why certain batches of nitrocellulose would not process. But we felt that if we could relate LBR values to some more fundamental property we would be able to define more precisely the desirable characteristics of a propellant grade NC, and to advise the manufacturers of both the linters and the nitrocellulose of the plant conditions likely to give acceptable material.

The viscosity increase is obviously due to cross-linking in solution. The effect is well-known, and occurs with a number of lead and, to a lesser extent, calcium salts. There appeared to be two main possibilities – (1) that cross-linking was due to interaction with specific impurity groups and that the concentration of these groups determined the LBR value, and (2) it was entirely a molecular weight effect, but one which was not paralleled exactly by the molecular weight function measured by the 3% viscosity blanks. Much time was spent attempting to relate LBR values with impurity levels, entirely without success. On the other hand a rough correlation, though very rough, was found between LBR value and both weight and number average molecular weight as measured by GPC and with the molecular weight function as measured by the 3% viscosity blanks. Because of this molecular weight dependence the belief grew up that what was causing processing problems in the NC was the high molecular weight component of the distribution. The purpose of the present paper is to show how a careful comparison of LBR value with number average (measured by osmometry) and weight average (measured by intrinsic viscosity, calibrated against light scattering) has caused us to abandon this hypothesis and to replace it with another. We now believe that it is the low molecular weight part of the distribution which is the most important. The critical requirement is an adequate amount of low molecular weight material which is solvent-soluble and acts as an adhesive between fibres, allows work to be done on the system, and is responsible for the matrix essential in the formation of a good dough.

EXPERIMENTAL

A number of samples of nitrocellulose with a large range of polydispersity were prepared. This was achieved both by nitrating linters of different fluidities and mixing the resulting nitrocelluloses, or mixing the linters themselves before nitration. This enabled us to make a clear distinction between number and weight average molecular weight when comparisons were made with the LBR values. All nitrations were made in nitric/sulphuric acid mixtures. Nitrogen content ranged from 12.3 to 12.7%, and account of this was taken in the interpretation of the viscometric data.

Intrinsic viscosity, osmotic measurements, and LBR tests were carried out on all samples and correlation sought. The LBR test is described in the previous section. Viscosity measurements were made in n-butyl acetate solution. The intrinsic viscosities so obtained were first converted to equivalent values in acetone by the method of Doyle,[1] and to the equivalent value of a 14.1% N sample by the method of Lindsley and Frank.[2] Although there have been a number of papers relating equivalent viscosity in acetone to light scattering molecular weight,[3,4] the majority deal with samples of much higher molecular weight than those normally used in the propellant range. The five samples of lowest molecular weight described by Holtzer et al were finally selected, and the equation used was

$$\left[\eta\right]_{T,Ac} = 1.78 \times 10^{-5} \; \bar{M}_w$$

The values of $\bar{M}_w$ so obtained were reconverted back to the corresponding molecular weight at the particular nitrogen concentration of the sample.

Osmotic measurements were made on a Hewlett-Packard 502 membrane osmometer. Schleicher and Schull regenerated cellulose membranes were used.

Further details of all methods are being published elsewhere.[5]

RESULTS AND DISCUSSION

Fig 1 shows the relationship between the logarithm of the LBR value (log LBR) and $\bar{M}_w$, as obtained from intrinsic viscosity. Fig 2 shows log LBR against $\bar{M}_n$ obtained from osmometry. It can be seen that the correlation with $\bar{M}_n$ is by far the better (correlation coefficient of 0.950 against 0.809). The LBR value is reflecting the number average of the pyro nitrocellulose sample. Since number average is controlled largely by the low molecular weight fraction of the distribution curve, this completely altered our ideas of the type of distribution required to give a processable sample. The trouble was being caused, not by the presence of high molecular weight material, but by the absence of a low molecular weight fraction. A wide
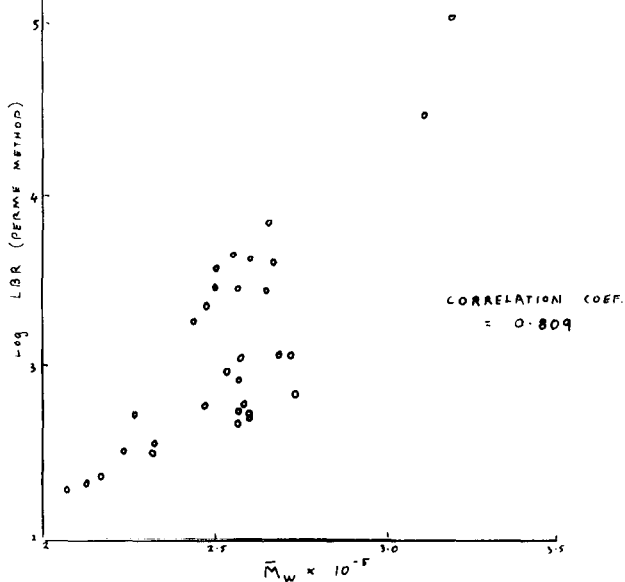
Fig 1. Log (LBR value) v weight average molecular weight.
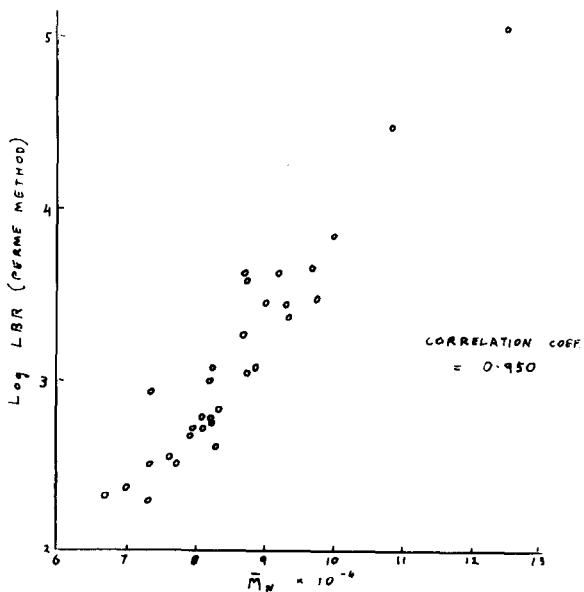

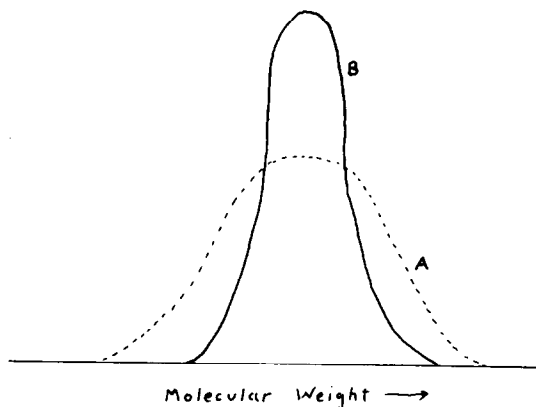Fig 2. Log (LBR value) v number average molecular weight.

Fig 3. Types of molecular weight distribution.

distribution (high polydispersity) is now favoured. In Fig 3, previously we
would have said that sample A was poor because with its wide distribution it
contained more high molecular weight material. We would now say such a
sample is good because it also has a large low molecular weight fraction.
It is now believed that this low molecular weight fraction is necessary
since it is this fraction which, on the addition of solvent, dissolves
up forming an adhesive which binds the fibrous material together to form a
coherent dough.

The results presented so far summarise our case that it is the low
molecular weight fraction which is critical and that number average is more
significant than weight average. However, in studying the LBR test we also
questioned what the 3% blanks were measuring. Miles[6] gives the equation

$$P = A \log \eta + B$$

where P is the degree of polymerisation, η the viscosity of a concentrated
solution, and A and B are constants. However, he admitted that he did not
know whether P represented a weight or number average. A number of other
equations have appeared in the literature for polymers in general, one of
the best-known being the Lyons-Tobolsky[7] equation:-

$$\ln \frac{\eta_{sp}}{[\eta] c} = \frac{k [\eta] c}{1 - bc}$$

where c is the concentration and k and b are constants. However, the main

interest of most workers has been the variation in η_{sp}, the specific
viscosity, with c. It is doubtful whether a series of samples with a
sufficient range of polydispersity has ever been studied to say whether
which is a function of viscosity average molecular weight (or in the case
of nitrocellulose, weight average), could with advantage be replaced by some
other molecular weight function. With this in mind we plotted the 3% viscosi-
ties against weight average and number average, as shown in Figs 4 and 5.
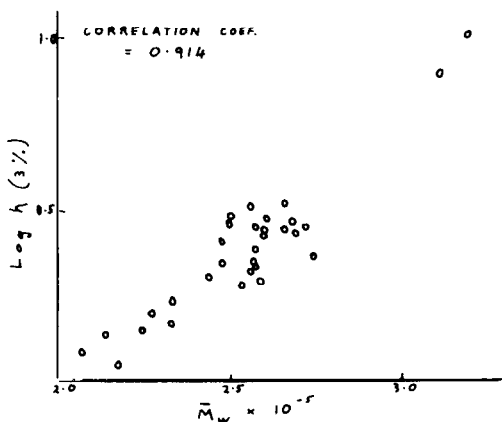Each gave a correlation

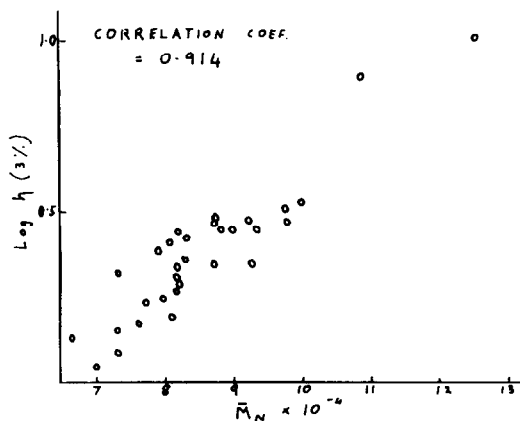Fig 4. Log (3% viscosity) v weight average molecular weight.

Fig 5. Log (3% viscosity) v number average molecular weight.

coefficient of 0.914. However, when the 3% viscosities were plotted against the geometric mean of number and weight average $(\bar{M}_n \cdot \bar{M}_w)^{\frac{1}{2}}$, the correlation coefficient improved to 0.963 (Fig 6). We would not, of course, claim that this relationship is precise; some other function intermediate between weight and number average would probably fit equally well. However, using the relationship shown in Fig 6, we
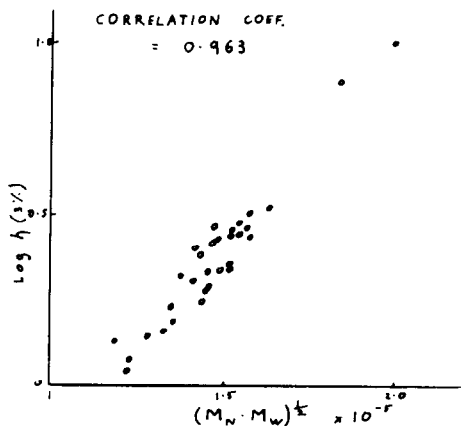

Fig 6. Log (3% viscosity) v $(\bar{M}_n \bar{M}_w)^{\frac{1}{2}}$.

are now in a position to obtain from the LBR test $(\bar{M}_n \bar{M}_w)^{\frac{1}{2}}$ from the blank, and $\bar{M}_n$ from the LBR value itself. $\bar{M}_w$ and α, the polydispersity can obviously be calculated. This operation has been carried out on a number of fractionated samples, and polydispersities in the range 1.1 – 1.4 have been obtained. These are of the same order as have been obtained by the separate measurement of $\bar{M}_n$ and $\bar{M}_w$ by osmometry and light scattering. GPC persists in showing poly-dispersities of 2 and above for these same samples.

Returning to the original problem of unprocessable nitrocellulose, the question still remains unanswered as to whether the unusual molecular weight distributions which we have shown to be present in poorly processable material originate from the linters themselves or from some inadvertent change in the nitration and stabilisation conditions. It is known that molecular weight degradation occurs during these processes, but it is also known that the fluidity of the linters influences the molecular weight of the derived nitrocellulose. Lansil linters have a lower molecular weight than either Holden Vale or Temmings 4419/20 material. This is observed by both the fluidity measurements and by GPC in cardoxen solution[8]. Holden Vale and Temmings 4419/20 have similar fluidities but the Temmings material has a much narrower molecular weight distribution. It has always been our

experience that Temmings 4419/20 linters do not produce nitrocellulose which processes under our incorporation conditions, whereas Holden Vale material is marginal, sometimes processing and sometimes not. (This is no reflection on the quality of Temmings linters. Other grades would process and 4419/20 would process in other solvent systems.) But this is some slight evidence that distributions are not masked by the molecular weight changes occurring during nitration and stabilisation, and that a narrow distribution in the linters results in a narrow distribution in the nitrocellulose. Osmotic measurements have not been carried out on Temming 4419/20 nitrocellulose, but using the LBR test measurement of $\bar{M}_n$ and $\bar{M}_w$ described in this paper, Temmings 4419/20 nitrocellulose does indeed have a high $\bar{M}_n$ but a normal $\bar{M}_w$.

CONCLUSIONS

1   The LBR test is a sensitive, if empirical, method of measuring both the $\bar{M}_n$ and $\bar{M}_w$ of 12.6% N Pyro nitrocellulose. The LBR value itself reflects number average, $\bar{M}_n$, and the 3% viscosity blanks reflect the geometric mean of number and weight average, $(\bar{M}_n \bar{M}_w)^{\frac{1}{2}}$.

2   The fact that processability is a function of LBR value (and hence $\bar{M}_n$) indicates that it is the low molecular weight fraction which is critical in the production of propellant doughs. It is suggested that an appreciable proportion of low molecular weight material must be present, since this is solvent soluble and acts as an adhesive between fibres during incorporation.

3   It follows from conclusion 2 that for a given weight average a high poly-dispersity is favoured. If, for any reason, polydispersity is low, a low molecular weight fraction could still be obtained if the whole distribution curve could be shifted towards lower molecular weights. This can be done by extended boiling.

4   There is some evidence that the polydispersity of the nitrocellulose is a direct reflection of the polydispersity of the linters.

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