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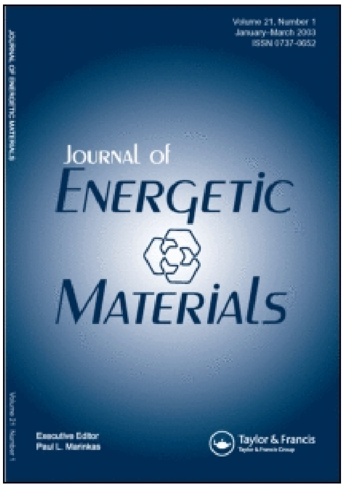

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Various nitrocellulose, NC, based propellant formulations need to be processed using new and more environmentally friendly solvent combinations on the one hand and using continuous processing methodologies on the other hand. A detailed understanding of the significant changes that take place in the structure and hence the rheological behavior of NC based formulations during manufacture is required to minimize the use of organic solvents and to revert to safer and green solvents. Towards achieving these objectives, experimental methodologies were developed for the first time to enable the accurate characterization and thus fingerprinting of the rheological behavior of NC gels. In these methodologies linear viscoelastic measurements are employed. The concentration of the solvents existing in the gel sample during rheological

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characterization is concomitantly monitored to allow the documentation of the major source of error associated with the rapid loss of the typical solvents, which generally exhibit relatively high vapor pressures. These measurements have indicated that the source of the NC fibers and the treatment method alter the rheological behavior and can be tracked. The rheological properties of the NC gels can be linked to their manufacturability and such data can be used to pinpoint optimum geometries and processing conditions. The processability of the NC based formulations can also be tailored on the basis of rheological characterization, allowing the manufacturers greater latitude for reducing costs and environmental footprint during manufacture, as well as improving the quality of their NC based energetic formulations.

Keywords: energetic, nitrocellulose, rhelogy, viscoelasticity

Background

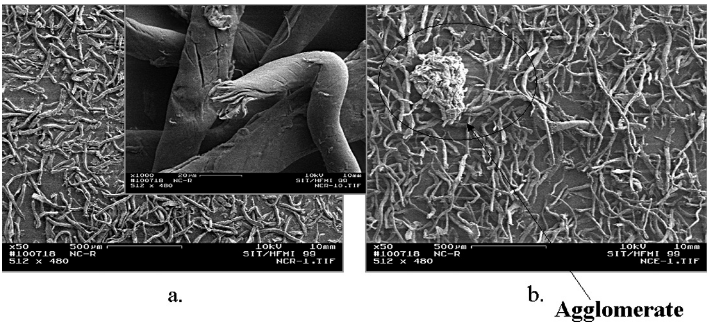
Nitrocellulose (NC) is manufactured upon controlled nitration of cellulose [1–3]. Most of the microstructural characteristics of NC are inherited from the base cellulose used; however, the structure of the NC is also affected by the conditions used during manufacture including the nitration, stabilization, pulping, and poaching stages [1]. The structural characteristics include the backbone of the molecular configuration and molecular weight distribution; molecular conformation and packing in the crystallographic unit cell; degree of crystallinity and its distribution in the cellulosic fibrils; and the binding arrangement of the fibrils in the cellulosic fibers [1–3].

The structure of cellulose fibers and the effects of various processing steps on cellulose structure have been reviewed by Stockmann [3]. Native cellulose fibers occur in the form of elementary fibrils with typical thicknesses 40 Å [3]. In the absence of encrustants cementing fibrils together the fibrils possess a certain degree of freedom to undertake position changes independently. The pulping process alters the spatial distributions of cellulose molecules within the fibrils and the fibril within the fibers [3].

During processing the original native structure is transformed into a two-phase organization [3]. In a disordered region, the end-to-end distances of the segments are shorter than the contour lengths of the segments. Because a transforming fibril develops disordered regions, a transformation is associated with a longitudinal contraction of the fibril [3]. If the tendency to contract longitudinally is opposed by an external restraint, the fibril retains its thermodynamically unfavorable structure despite sufficient molecular mobility. A fibril in this condition is then in a state of longitudinal tension. For example, the encrustation of a cellulose fibril by lignin and hemicellulose is believed to be a restraining medium. Because lignin and hemicellulose are removed during pulping, a pre-existing longitudinal tension will produce a longitudinal contraction of the fibril. The longitudinal contraction materializes whenever the intermolecular cohesion within a fibril has been weakened and the contraction is not opposed by any outside restraint. This mechanism can account for the molecular rearrangements within a fibril. The mechanism triggers fibrillar rearrangements as well because of the helical orientation of fibrils. Fibrils leave their native positions to release the longitudinal tension that develops within a fibril [3].

These arguments [1–3] suggest that depending first on the source of the cellulose used in the manufacture of the NC and second on the processing and treatment conditions, that are applied to different NC fibers, changes in the structure NC will be generated. For example, various typical photomicrographs of two sets of monolayer samples of NC are shown in Fig. 1. In the first case the fiber diameter varies from 15 μm to 45 μm, with an average of 20 μm. In the second case the fiber diameter varies from 15 μm to 30 μm with an average of 20 μm. The range of the fiber lengths is from 200 μm to 800 μm, with bimodal characteristics, with an average fiber length of around 500 μm for the first case. On the other hand, the fiber-length distribution in the second sample is more uniform and varies from 200 μm to 500 μm, with an average of around 400 μm.

Agglomeration is also an important factor. As shown in Fig. 1b one of the NC samples investigated here contains a



a. b.

Figure 1. Scanning electron micrographs of nitrocellulose fibers.

significant number of agglomerated fiber ‘‘grains’’ (encircled in the figure to distinguish) that typically range from 200 µm to 400 µm in size. At high magnifications these agglomerated grains exhibit traces of a binder material. These grains are most likely the leftover agglomerates that form during pagination. The volume content of these ‘‘grains’’ in this sample is estimated to be 10% to 20%. These ‘‘grains’’ would survive subsequent processing and cause non-uniformities in the ultimate properties of the energetic product. The differences in the statistics of the fiber aspect ratio, the deformation behavior of the fibers as associated with the orientation of the fibers around the fiber axis and the frequency and the nature of the agglomerated fibers will also affect the solvation kinetics upon being incorporated with solvents and the other ingredients of NC based propellant formulations as well as the rheology, i.e., the flow and deformation behavior during the processing stage. The conditions used during the manufacturing of the nitrocellulose, including for example, the nitration conditions which are utilized to allow the acid system to diffuse into the fibers, especially the nitration temperature, also affect the ultimate rheological behavior of the nitrocellulose [1].

Solvation and Rheological Behavior

The solvation of the NC with the solvents and other ingredients of the typical NC based formulations constitute again important manufacturing stages. During the solvation step the feeding order, the aging profile, the geometry, and the set of operating parameters used, including the degree of fill of the mixer and the rotational speed of the blades, and the specific energy imparted as a function of mixing time, are all important in controlling the structure. Clearly a given degree of gelation and degree of mixedness would occur at a critical specific energy input. Some of the NC is solvated to form the binder and the rest of NC remains as fibers to act as the rigid filler of the formulation. In the solvation process the temperature is generally not considered an important factor due to the large quantities of the solvent present. Generally blending of the different NC grades is used as the method to generate a desired final degree of nitration. Since the solubility of the NC is dependent on its nitrogen content it is natural that there will be a distribution of the solubility in the fibers leading to composite characteristics with the undissolved NC fibers acting as reinforcements and the dissolved NC acting as the binder [1].

Upon mixing of the NC with the solvents, including diethyl ether, acetone, or alcohols, a gel starts to develop. In the inset of Fig. 2 a sample of NC/solvent gel is shown, confined in between two parallel disks, one of which is rotating and the second is stationary at a strain amplitude >100%. The formation of the gel is indicated here by the presence of a wall slip in a steady torsional flow. In Fig. 2 the wall slip is indicated by the discontinuity in the straight line marker line used to mark the free surface of the gel and the edges of the discs used to deform the NC/solvent system in simple shear flow [4–6].

The small-amplitude oscillatory shear data can be collected on NC samples to characterize the elasticity and the viscous behavior of such gels. In our experiments the linear viscoelastic material functions were characterized using 8 mm parallel plates under small-amplitude oscillatory shear in conjunction with an AR 2000 ARES rheometer from TA Instruments.

The relationship between the shear stress, $\tau_{yx}(t)$, and the strain, γ_{yx}, imposed on the material during small-amplitude oscillatory shearing is given by the following [7]:

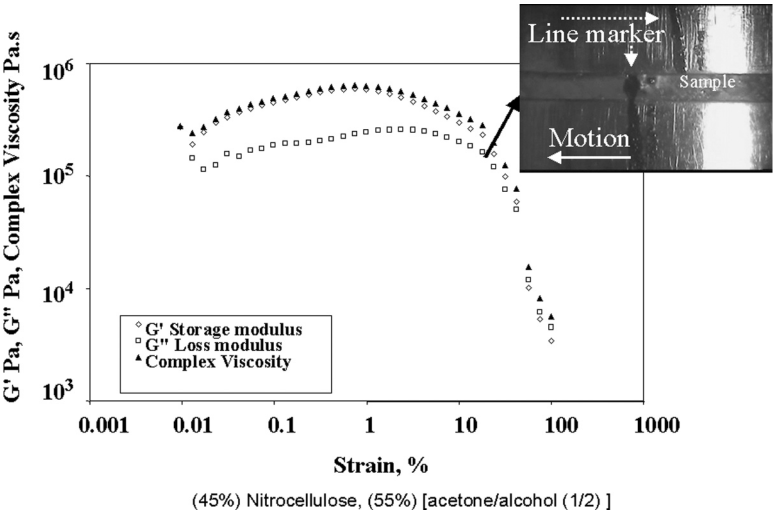


Figure 2. Dynamic properties as a function of strain amplitude for solvated nitrocellulose.

$$\tau_{\mathrm{yx}}(\mathrm{t}) = -\left[\int_0^{\infty} \mathrm{G(s)} \cos \omega \mathrm{s}\, \mathrm{ds}\right] \dot{\gamma}_{\mathrm{yx}}^{0} \cos \omega \mathrm{t} - \left[\int_0^{\infty} \mathrm{G(s)} \sin \omega \mathrm{s}\, \mathrm{ds}\right] \dot{\gamma}_{\mathrm{yx}}^{0} \sin \omega \mathrm{t} \qquad (1)$$

where $\dot{\gamma}_{\mathrm{yx}}^{0}$ is the shear rate amplitude, ω is the frequency, t is time, G is the relaxation modulus, and s is the elapsed time. The first term in the brackets on the right hand side represents the loss modulus, G″, and the second term in the brackets represents the storage modulus, G′, i.e.,

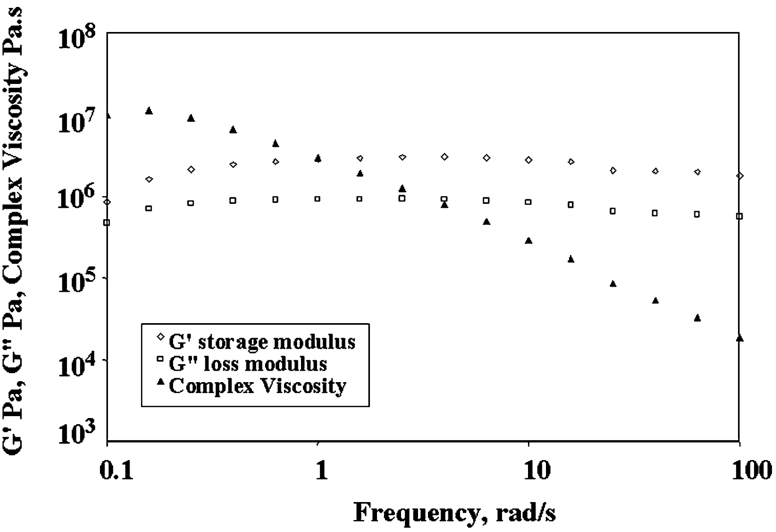
$$\tau_{\mathrm{yx}}(\mathrm{t}) = -\mathrm{G}''\gamma^{0} \cos \omega \mathrm{t} - \mathrm{G}'\gamma^{0} \sin \omega \mathrm{t} \qquad (2)$$

The shear strain changes with time according to $\gamma_{\mathrm{yx}} = \gamma_{\mathrm{yx}}^{0} \sin \omega \mathrm{t}$, where γ^{0} is the strain amplitude. Thus, the oscillatory shear at different frequency values, ω, provides both the storage, G′, and the loss modulus, G″, values. The magnitude of complex viscosity, $|\eta^{*}|$, is defined as $((\boldsymbol{G}'/\omega)^{2} + (\boldsymbol{G}''/\omega)^{2})^{0.5}$.

The storage modulus, G′, is indicative of the energy conserved through elasticity during a cycle of deformation. The loss modulus, G″, is indicative of the energy dissipated as heat during a cycle of deformation. The magnitude of complex viscosity approaches the steady shear viscosity of the material as the frequency and the shear rate both diminish to zero. As noted earlier, the on-set of the decrease of the linear viscoelastic properties at a critical shear strain, can be associated with the onset of a strong slip at the wall of the rheometer. Generally, one expects the linear viscoelastic properties to be independent of the imposed strain amplitude up to this critical shear strain value, defining the linear viscoelastic region. However, as shown in Fig. 2, the small-amplitude oscillatory shear data of the NC gels do not follow the conventional behavior of linear systems, i.e., the dynamic properties are not independent of strain amplitude.

With the solvated NC samples the dynamic properties first increase with the increasing strain, which normally one would not have observed with stable samples (Fig. 2). This increase is caused by the decrease in the solvent concentration of the NC as a function of time as the experiment progresses. The decreases of the dynamic properties upon further increases in strain amplitude, i.e., at and above a strain amplitude of about 1%, are associated with wall slip and with non-linearity effects. Thus, the solvent concentration changes during the course of the experiment and needs to be kept track of at all times. From Fig. 2 one can again see that it is not unreasonable to take a strain which is less than 1%, as the strain at which the NC solutions behave as linear viscoelastic material, provided that the solvent loss can be monitored and accounted for appropriately. In our subsequent experiments we used the strain amplitude of 0.2%.

The typical frequency scan is shown in Fig. 3, and represents the conventional experiment which is generally carried out to probe the viscoelasticity of a sample as a function of a series of characteristic times for deformation (reciprocal frequency) and hence a series of Deborah numbers. As noted earlier, the G′ and G″ remain more or less parallel to each other



(45%) Nitrocellulose, (55%) [acetone/alcohol (1/2)]

Figure 3. Dynamic properties as a function of frequency for solvated nitrocellulose.

during the experiment reflecting the gel-like characteristic of the solution. For the entire frequency range, the G′ values remain greater than G″ indicating that the bulk of the energy associated with the deformation is stored as elastic energy and not dissipated as heat (as noted earlier, the storage modulus, G′, is proportional to the energy stored and the loss modulus, G″, is proportional to the energy dissipated as heat during one cycle of deformation in the small amplitude oscillatory shear). It should again be noted that in the frequency scan test, there is also continuous loss of the solvent during the experiment (Fig. 3). Thus, it is necessary to device a method for the determination of the solvent concentration as a function of time during the rheological characterization so that the changes in the dynamic properties associated with the solvent loss can be quantified. The decrease of the magnitude of the complex viscosity (which approaches the shear viscosity of the solution as the frequency and the shear rate both approach zero) is also shown in Fig. 3 and reveals the pseudoplastic nature (decreasing viscosity with increasing shear rate).

The typical frequency-dependent behavior of the NC based systems (NC incorporated with acetone/ethyl alcohol with the solvents at a ratio of 2:1) (Fig. 3) and formulations that are based on NC, for example the single base formulation (Fig. 4) are indicative of the gel type behavior of NC and solvent systems. As shown in Figs. 3 and 4 the storage modulus, G′, values are significantly greater than the loss modulus, G″, values. The greater values of G′ and the parallel nature of the G′ and G″ data are precursors to the formation of gels [8]. The abundant frequency dependent data provide accurate fingerprints of the solvent concentration as well as the structure of the solvated NC gels, as affected by various properties of the NC fibers employed. The characterization of such dynamic properties can be used as the means to characterize and fingerprint the rheological behavior of NC based gels. The fingerprinting of the NC gels on the basis of their small-amplitude oscillatory

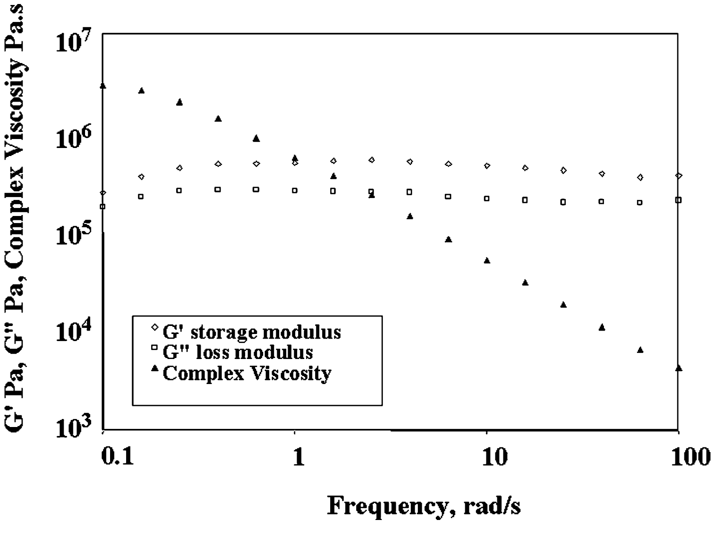


Figure 4. Dynamic properties as a function of frequency for single base propellant.

shear behavior can thus provide the requisite conditions for the solvation to be successfully and reproducibly completed as well as providing information on the effects of the conditioning, blending, and processing methods and the source of the cellulose employed.

Thus, overall the characterization of the small-amplitude oscillatory shear behavior can generate a set of experiments which can provide the basic guidance and the scientific wherewithal necessary to determine the optimum mixing procedures including the order of the addition of the ingredients, the aging and the stability of the NC, the mixing conditions etc. These conditions can then be used to determine the mixing conditions in the process necessary to generate the requisite specific energy input, to furnish the production rates and the associated economics of the processing operation in conjunction with the new environmentally benign solvents.

However, as noted there is a significant problem, which arises during such rheological characterization. The solvent concentration in the specimen continuously changes upon the diffusion and the evaporation of the solvents as the rheological characterization progresses. This renders the conventional method of the collection of data, using continuous sweeps of strain and frequency as shown in Figs. 2–4 unreliable and unacceptable. What can be done to alleviate this problem and provide reliable and reproducible data that the manufacturers can employ? This is addressed next.

Methodologies Developed for Rheological Characterization which Accommodate the Loss of Solvent during the Measurements

Procedure for Handling

It was noted from previous studies that the amount of water in the NC specimens would have a direct effect on the rheological behavior of the solution. Therefore, the NC samples were all first dried in a vacuum oven at 100°C. The dried samples were then incorporated with acetone and ethyl alcohol at a solvent ratio of (acetone/ethyl alcohol) 2:1. Upon incorporation with the solvent the white color of the NC disappears and the solution attains the transparency associated with typical gels. Upon mixing the NC samples with the solvents, none of the NC gels generated became completely transparent, suggesting that some of the NC in all cases remained insoluble in the solvents. This was true even for NC samples that were designated to be 99% dissolvable. For some NC samples the NC fibers were still visible upon the completion of the mixing process.

The mixing of the ingredients of the formulation is a lengthy process (the typical mixing could take three hours in the batch mixer) and during the course of this mixing some of the solvent will be evaporated. In our experiments the initial solvent concentration upon mixing was kept arbitrarily at 65% of the total mass. Thus, the typical solution contained 35% by weight of NC and 65% by weight of solvents. However, the concentration of the solvent changed during the course of the handling of the material prior to and during the rheological characterization. Thus, the concentration of the solvent was continuously monitored on a routine basis using gravimetric analysis during the course of the sample preparation, loading into the rheometer, and during rheological characterization experiments.

The procedure followed in the rheological characterization experiments involved the following steps:

1. The NC specimens were mixed with the solvents at relatively high solvent concentrations (around 65% solvents at a solvent ratio of acetone/ethyl alcohol of 2:1). The solvent was allowed to evaporate to the desired solvent concentration as determined thermo-gravimetrically and then the sample was mixed quickly a second time to assure the uniformity of the distribution of the solvent upon evaporation.
2. The solvated NC sample was loaded to the rheometer upon sample preparation (mixing/solvation) and its solvent concentration values at the beginning and at the end of the experiment were determined. This was done thermo-gravimetrically by weighing immediately

the captured samples and then drying them off completely to enable the determination of the concentration of the solvent in the specimen at the point the sample was collected.

3. The loading of the sample into the rheometer was always carried out using the same procedures and always within the same time frame.
4. For all of the samples 8 mm parallel plate fixtures and an ARES rotational rheometer were used. This is the smallest fixture that was available and allowed the use of the smallest amount of NC in any given run, which was an important safety aspect.
5. As part of the experiment, conductive gloves, conductive lab coat, and goggles were used. The rheometer was grounded. Typically the sample was divided into two; the first one was used for the solvent concentration analysis and the second one was used for the rheological analysis. The specimen was always prepared fresh for each of the experiments and thus was not allowed to age.
6. A cotton screen with a polymer backing was used to surround the specimen during the experiment without altering the torque and the normal force readings. This loose screen was soaked in the solvents used in the formulation to decrease the driving force (concentration difference) between the sample and its immediate surroundings to minimize the diffusion of the solvent out of the specimen. However, although this procedure slowed the rate of the solvent loss, it did not eliminate it.
7. Upon the completion of the experiment the sample was recovered and immediately weighed. Its solvent content was completely evaporated in the vacuum oven to enable the solvent concentration at the end of the experiment to be determined.
8. The time-dependent collection of the linear viscoelastic properties of the NC gels was not carried-out for relatively long durations of time but only over relatively short time intervals. This allowed us to go directly to solvent concentrations of interest without having to

generate solvent concentration distributions within the specimen, which would have been problematic.

The typical time scan of the NC solution is shown in Fig. 5. These experiments are carried out at a frequency of 1 rps and a strain amplitude of 0.2%. With increasing time, as the solvent evaporates all the dynamic properties increase. Within 1000 seconds upon the initiation of this run, all of the dynamic properties of the material increased approximately by an order of magnitude as the solvent concentration decreased from 54% at the beginning of the experiment to 39% at the end, as indicated in Fig. 5. For the entire time range G′ ≫ G″ and the difference between the two increase with increasing time, thus with decreasing solvent concentration. The magnitude of complex viscosity values also increase parallel to G′ as expected on the basis of G′ ≫ G″.

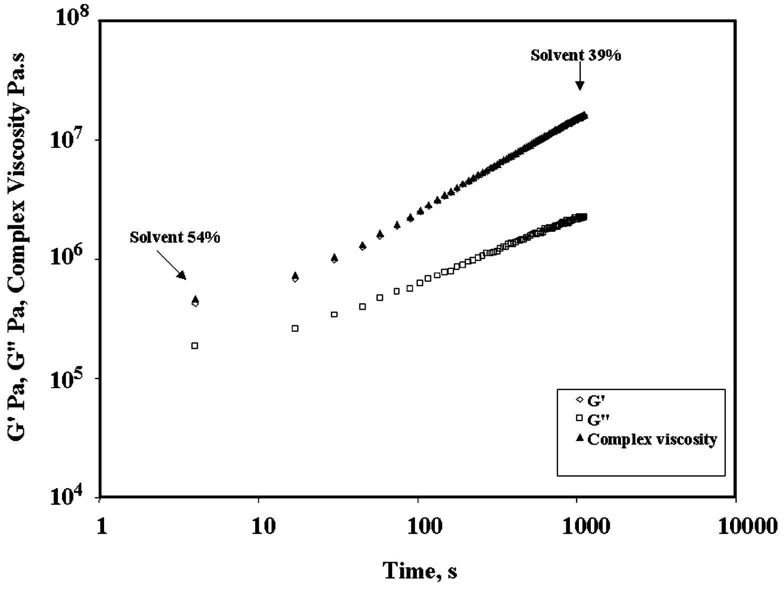


Figure 5. Dynamic properties as a function of time at 1 rps for solvated NC (solvent concentrations at the beginning and at the end of the experiment are indicated).

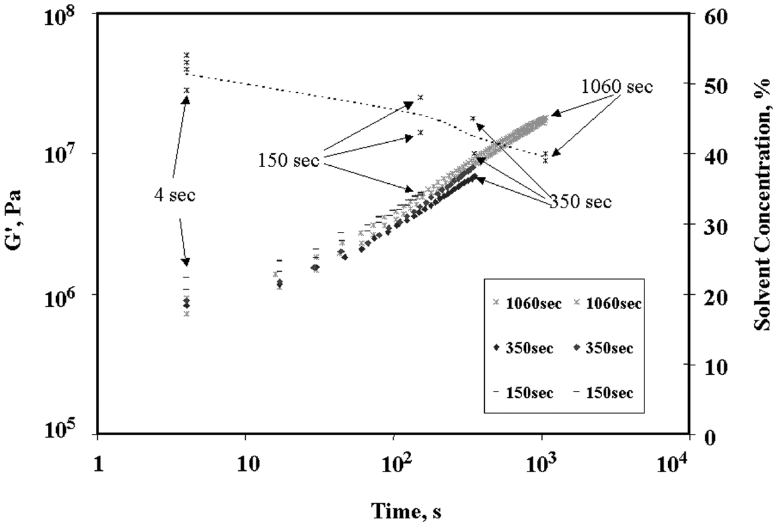


Figure 6. Storage modulus, G′, versus time and corresponding solvent concentration for solvated NC.

The dynamic properties over a wide range of solvent concentrations were determined for all of the NC samples at a frequency of 1 rps. Typical data are shown in Figs. 6 and 7. The time dependence of the solvent loss and the change in the storage modulus were fitted with polynomial expressions (Fig. 7). It appears that the rate of the solvent loss and the associated rate of change of the storage modulus (which is indicative of the elasticity of the solution so that higher storage modulus values indicate greater elasticity) decrease with increasing time. This suggests that the resistance to diffusion and the loss of solvent increases as the amount of the solvent in the specimen is depleted. It is expected that during the mixing process the loss of the solvent will also alter the rheological behavior and hence the processability of the solvated NC. The rheological behavior and the processability will change in a nonlinear fashion as the solvent is being depleted in the mixture, akin to what is observed in Figs. 6 and 7. In Fig. 7 the results from two separate runs carried out under similar conditions were included and suggest that the time dependent behavior is indeed reproducible.

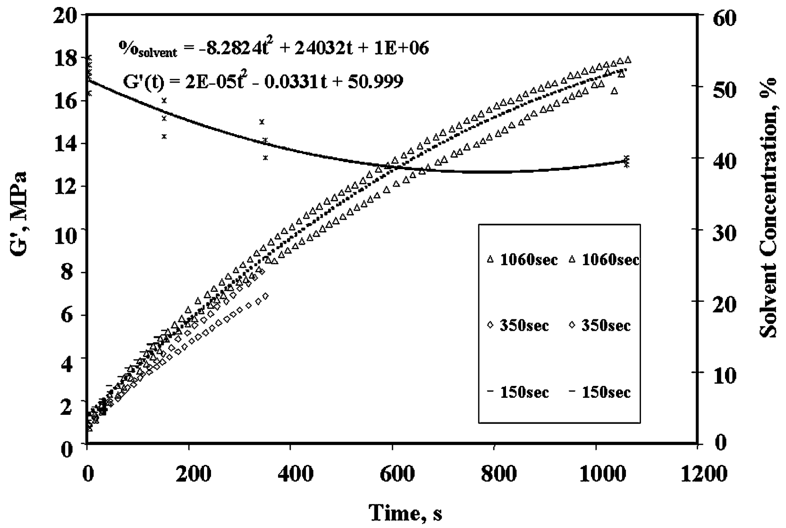


Figure 7. Time dependent fit of storage modulus, G′, versus time and corresponding solvent concentration for solvated NC. Two parallel runs were carried out to check reproducibility.

The control of the solvent levels during the mixing process and proper adjustments on the basis of the characteristics of the NC may allow the operator of the manufacturing plant to achieve the same end result in terms of rheological behavior and the processability of the binder (NC solution). This is suggested from the observation that the rheological behavior is very sensitive to the concentration of the solvent. Thus, the ability to determine the solvent concentration at the point the rheological characterization is carried out is a key. Is it possible to compare the rheological behavior of the NC solutions fairly to determine if there is any dependency on the starting material characteristics of the NC?

Comparisons of the Viscoelastic Properties of 17 NC Specimens

Table 1 shows the properties and the sources of the NC samples received from Canadian and US manufacturers of NC. There

Table 1
Properties and origins of the NC samples characterized

Sample designation	Country of origin	Grade	Fiber origin	Stability KI (min)	Stability MVP (min)	Fineness (ml)	N2 content (% P/P)	Solubility Ether/ Alcool (% P/P)	Acetone insolubles (% P/P)	Ash (% P/P)	Viscosity (sec)	Moisture content (% P/P)
A-1	USA	A	Wood	35	30	93	12.64	99+	0.00	0.04	14	30.4
C-1	USA	C	Wood	45+	30	90	13.14	42	0.00	0.03	13	29.8
A-2	USA	A	Wood	35	30	85	12.66	99	0.00	0.05	11	31.3
C-2	USA	C	Wood	35	30	88	13.16	38	0.00	0.06	12	28.5
A-3	USA	A	Cotton	35	30	89	12.69	99	0.00	0.04	22	26.0
C-3	France	C	Cotton	60+	30+	100	13.15	37	0.00	0.04	9	31.4
A-4	France	A	Cotton	60+	30+	98	12.60	99+	0.00	—	17	30.0
C-4	Tchek Republic	C	Cotton	40	—	96	13.12	35.6	0.12	0.07	12	29.8
C-5	China	C	Cotton	35	31	94	13.11	37.8	0.06	0.16	10	30.2
A-5	South Africa	A	Cotton	40	40	94	12.59	99.1	0.20	0.20	6	31.5
C-6	Yugoslavia	C	Unknown	35	30	86	13.14	41	0.20	0.10	12	30.0
C-7	Australia	C	Wood	—	30	105	13.13	38.5	0.10	—	12	—
A-6	Australia	A	Wood	50+	30	105	12.59	99+	0.10	0.02	11	—
C-8		C	Pulp				13.23	29.47				
C-9		C	Pulp				13.11	40.75				
D-1		D	Lint				12.12	99+				
A-7		A	Pulp				12.62	99+				

are seventeen NC samples, seven of which pertain to Grade A, nine are Grade C, and one is designated to be Grade D. The origins of the cellulose fibers, i.e., from wood, lint, cotton, and the values of the stability and the N content tests are also provided. The side-by-side comparisons of the dynamic properties of various NC solutions were carried out on the basis of the characterization of the dynamic properties as a function of the solvent concentration.

In Figs. 8–10 the solvent concentration-dependent values of the storage modulus G′, loss modulus, G″, and the magnitude of the complex viscosity of the 17 specimens obtained from different sources are shown. It is very interesting to note that some of the NC samples exhibit significantly lower elasticity (lower values of the storage modulus G′), and lower values of shear viscosity (lower values of loss modulus, G″, and magnitude of the complex viscosity) at similar solvent concentrations in comparison to other NC samples from other sources. The $\tan\delta = G''/G'$ values also exhibit similar significant differences.

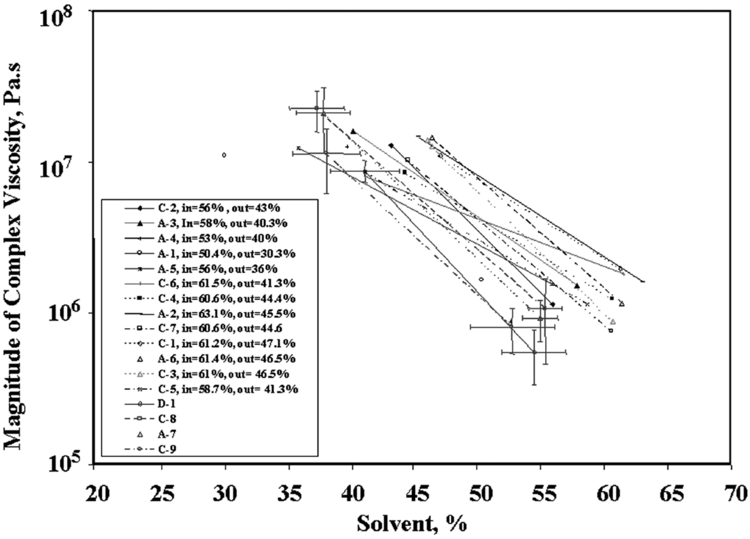


Figure 8. Magnitude of complex viscosity versus solvent concentration behavior of various NC samples at 1 rps and 20°C.

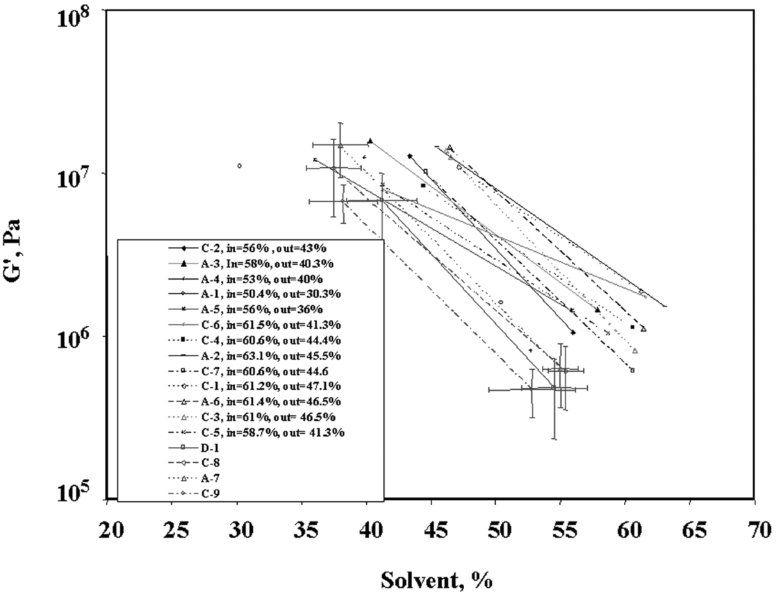


Figure 9. Storage modulus, G′, versus solvent concentration behavior of various NC samples at 1 rps and 20°C.

Overall, these results suggest that the differences in the way NC is produced, including, for example, the nitration, stabilization, pulping, and poaching conditions are reflected in their rheological behavior, since the dynamic properties are very accurate fingerprints of the structure of the NC gels.

The differences between the Class A and Class C samples are also clearly observed. The comparisons are shown in Figs. 11–13. The vertical and horizontal ranges are included to indicate the differences in behavior associated with the samples of each class. At the same solvent concentration the Class C NC samples exhibit greater elasticity (higher values of storage modulus G′) than Class A samples, as affected by differences in nitration levels and the resulting solubility differences. The two grades appear to be losing solvents at different rates also. Especially at the low solvent concentrations the loss modulus and values of the Class A samples are also greater than Class C

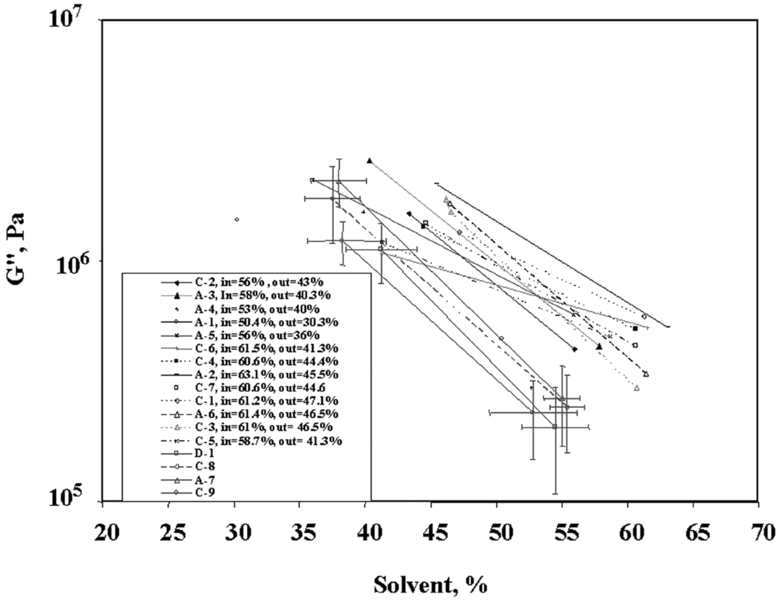


Figure 10. Loss modulus, G″, versus solvent concentration behavior of various NC samples at 1 rps and 20°C.

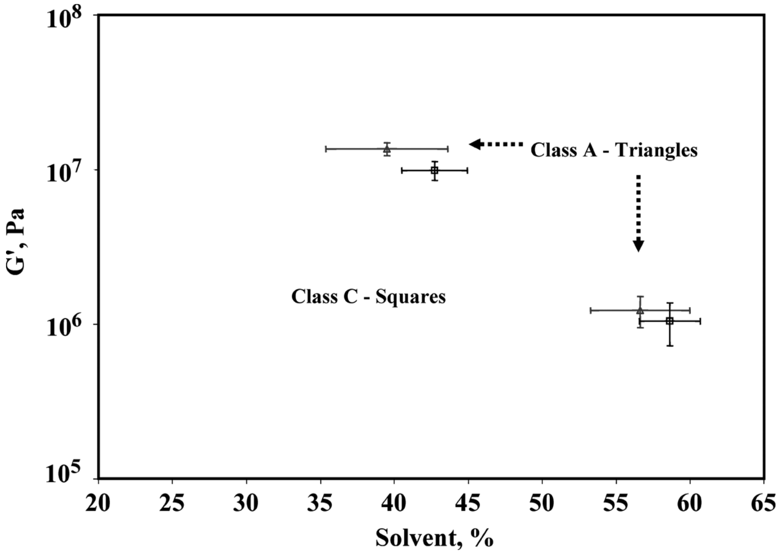


Figure 11. Storage modulus, G′, versus solvent concentration behavior of various NC grades at 1 rps and 20°C.

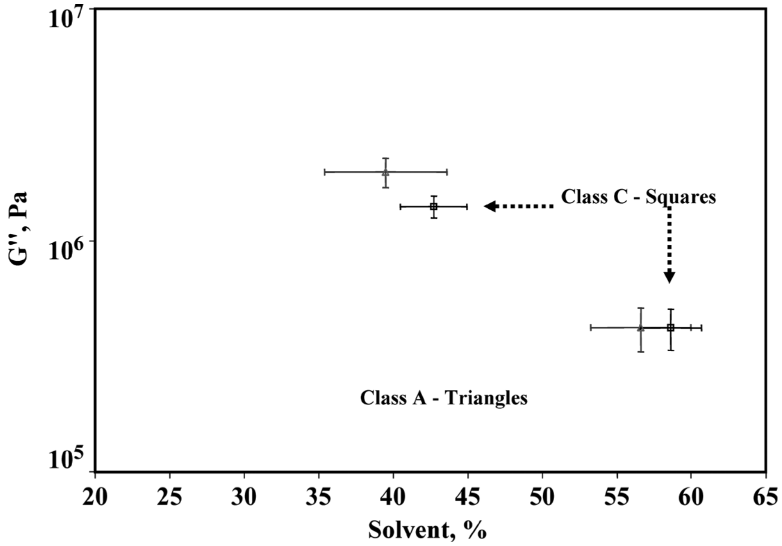


Figure 12. Loss modulus, G″, versus solvent concentration behavior of various NC grades at 1 rps and 20°C.

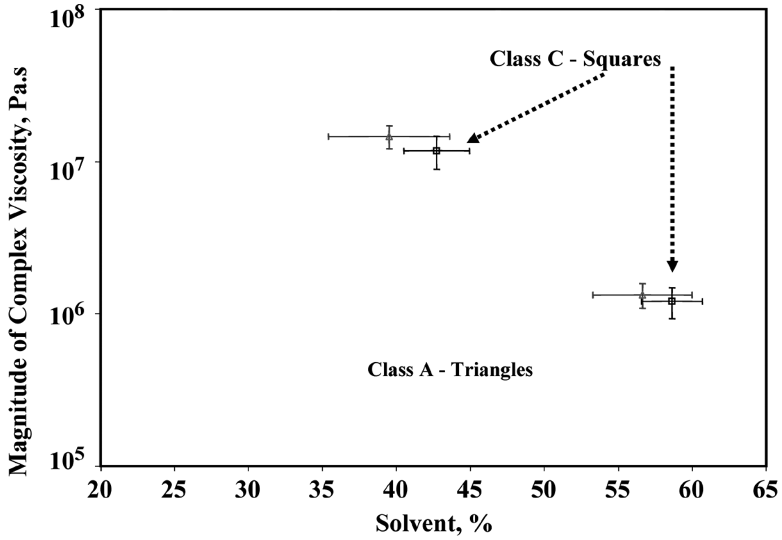


Figure 13. Magnitude of complex viscosity versus solvent concentration behavior of various NC grades at 1 rps and 20°C.

samples. These differences are understandable on the basis of the different nitration levels and different degrees of solubility of the two classes and indicate that the differences in the rheological behavior of the two grades may necessitate changes in the processing conditions of the two grades of NC. The ability to fingerprint the elasticity and the viscosity of the NC gels should facilitate the optimization of the processing conditions for the gels of Class A and C NC fibers.

Conclusions

1. A new method, which has the capability to define and discriminate the linear viscoelastic material functions of NC gels, is developed. This method accommodates the rapid loss of solvent during rheological characterization.
2. Samples of NC were procured from various sources. The total number of the samples received and characterized was 17. The new methods were demonstrated on all 17 NC samples. The data on its own are significant and allows for the first time a side-by-side comparison of the processability and rheological material functions of NC products manufactured with differing methods and with different primary characteristics including the source of the cellulosic raw materials.
3. All of the findings were reported on the basis of a side-by-side comparison of the rheological behavior of the NC samples employing the solvent concentration dependent values of the storage modulus G$'$, loss modulus, G$''$, and the magnitude of the complex viscosity, $|\eta^*|$. The storage modulus is indicative of the energy stored as elastic energy during one cycle of deformation, the loss modulus is indicative of the energy dissipated as heat during deformation, the magnitude of complex viscosity approaches the shear viscosity of the gel as the frequency and the shear rate approach zero in small-amplitude oscillatory shear and steady torsional experiments, respectively.

4. It is very interesting to note that the NC samples from various sources generate a broad distribution of behavior at different solvent levels. The maximum values of the dynamic properties for the NC samples were as high as 10 times the minimum values at similar concentration values. The significant differences indicate that there are appreciable effects of grade and source of NC and the manufacturing methods/procedures used on the rheological behavior of the NC gels. Consequently, the processability of the NC gel is expected to change with the grade, the source of the NC, and the manufacturing method, thus necessitating changes in the processing conditions and the geometries as the NC source and manufacturing methods are modified.
5. Overall, there are differences in the viscoelasticity of Class A and Class C samples. At the same solvent concentration the Class C NC samples exhibit greater elasticity (higher values of storage modulus G') than Class A samples. The two grades appear to be losing solvents at different rates also. Especially at the low solvent concentrations the loss modulus values of the Class A samples are also greater than Class C samples. These differences are understandable on the basis of the different nitration levels and hence the solubility behavior of the two classes and indicate that the differences in the rheological behavior of the two grades may necessitate changes in the processing conditions of the two grades of NC. The ability to fingerprint the elasticity and the viscosity of the NC gels should facilitate a better selection of the processing conditions for the gels of Class A and C NC fibers.

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References

[1] Urbanski, T. 1967. *Chemistry and Technology of Explosives*. Vol. 3. New York: Pergamon Press.

[2] Bice, H. C. and C. R. Thombs. June 1, 1956. Nitrocellulose, Indiana Arsenal Report PE-1.

[3] Stockmann, V. E. 1971. Effect of packing on cellulose structure. *J. Tappi*, 54: 2033–2037.

[4] Kalyon, D. M., P. Yaras, B. Aral, and U. Yilmazer. 1993. Rheological behavior of concentrated suspensions: A solid rocket fuel simulant. *J. Rheology*, 37: 35–53.

[5] Aral, B. and D. M. Kalyon. 1994. Effects of temperature and surface roughness on time-dependent development of wall slip in torsional flow of concentrated suspensions. *J. Rheol.*, 38(4): 957–972.

[6] Kalyon, D. 2005. Apparent slip and viscoplasticity of concentrated suspensions. *J. Rheology*, 49(3): 621–640.

[7] Bird, B., R. Armstrong, and O. Hassager. 1987. *Dynamics of Polymeric Liquids*. Vol. 1, 2nd ed. New York: Wiley.

[8] Winter, H. and F. Chambon. 1986. Analysis of the linear viscoelasticity of a crosslinking polymer at the gel point. *J. Rheology*, 30: 367–382.