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13. ABSTRACT (Maximum 200 words)

Dynamic mechanical analysis is combined with mass spectrometry to study nitrocellulose under oscillating strain. At a constant temperature (150 – 160°C) and frequency 400 – 600 Hz nitrocellulose fractures demonstrating a modulus drop and release of products with m/z=30 and 44. At linear heating (2°C min-1) and frequency 10 – 50 Hz similar products are released in two steps, the second of which demonstrates a modulus drop and a temperature increase indicating ignition.

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FINAL REPORT

Title “A method of monitoring explosive under cyclic mechanical stress”

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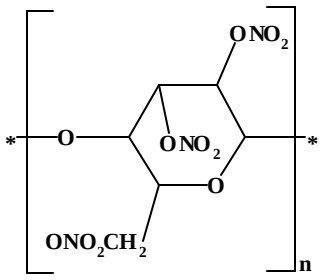
Statement of the problem studied

Mechanically activated processes are studied by the rapidly developing field of mechanochemistry.[1,2,3,4] Ball mills provide one of the most common tools for mechanical stimulation of solid state processes such as phase transitions,[5,6,7] solid-solid reactions[8,9,10,11,12] decompositions,[13,14] as well as degradation[15,16,17] and amorphization[18] of polymers. Ball mills are capable of producing high strain fields that allow for initiating the aforementioned processes without heating. The disadvantages of using the ball mills include the difficulty of monitoring the processes *in situ* as well as the practical impossibility of measuring the values of strain and stress in the transforming materials. These disadvantages can be overcome when using the techniques of dynamic mechanical analysis (DMA). The DMA instruments are designed to measure the mechanical modulus (i.e., the stress to strain ratio) of solid materials under various dynamic conditions that include a range of frequencies, strains, and temperatures.[19] DMA is widely used to study the relaxation behavior of polymers in moderate strain fields that may be insufficient to cause fracture of solid (i.e., glassy or crystalline) polymers. Nevertheless fracture may take place in moderate strain fields as a result of decreasing modulus with increasing temperature. Fracture of polymers occurs via two major mechanisms that include chain slippage and bond breaking.[20] The later mechanism dominates below the glass transition temperature where chain slippage may not occur because of the suppressed long range molecular motion. It has been demonstrated that loading polystyrene[21] and polycarbonate[22] in tension to fracture results in releasing gaseous products consistent with bond scissions. Similar phenomena have been reported for microtoming of polyethylene[23] and drilling of poly(methyl metacrylate).[24] The deformation and failure of polymers or other solids may result in the emission of ions, electrons as well as neutral species that is known as the phenomenon of fractoemission.[25] Although above the glass transition temperature the role of chain slippage increases, shearing of polymers may still result in mechanochemical degradation.[26] Mechanochemical degradation has even been reported to occur in solutions of polymers.[27,28]

In the present study, we combine DMA with mass-spectrometry (MS) to detect mechanochemical degradation of an important polymeric material, nitrocellulose (NC). NC is produced by nitration of cellulose and has the following repeat unit



To our knowledge, DMA has not yet been applied to studying mechanochemical degradation. MS has been used to detect mechanochemical degradation of polymeric[21,22] and other materials.[29,30] However, we are not aware of any previous reports of combining DMA with MS. Because of its importance as an energetic material, the thermal degradation of NC has been extensively studied.[31,32,33] Surprisingly, there seem to have been no studies on the mechanochemical degradation of NC or on the effect of the mechanical stress on the thermal degradation of this material.

Summary of the most important results

A NC fiber sample (12.4% N) was purchased from Firefox Enterprises, Inc. About 4 g of NC was dissolved in 250 ml of a mixture of diethyl ether and ethanol (1:1). The mixture was stirred until a homogeneous solution was obtained. The solution was cast in a Petrie dish and carefully evaporated under the hood at 80°C for 24 hrs. This procedure allowed us to obtain tough, clear and uniform films of ~0.3 mm thick. DMA samples were prepared by cutting the film into ~ 11 by 9 mm pieces that were clamped into the DMA frame.

A Tritec 2000 (Triton Technology Ltd.) DMA apparatus was used to study the NC films in a tensile mode in wide range of frequencies varying from fraction to several hundred Hz. The use of higher frequencies (up to 600 Hz) has allowed us to accomplish relatively high strain rates (i.e., several mm s^{-1}) under rather moderate strain amplitude of 0.05 mm. DMA runs were performed under isothermal and nonisothermal linear (2°C min^{-1}) heating. Blank DMA runs were carried out without applying the tensile deformation that was accomplished by not clamping one of the sample ends. The sample temperature was controlled by the thermal sensor of the DMA instrument positioned in a close proximity of the sample. All the runs were conducted under ambient atmosphere and pressure. An Olympus BX51 polarized light microscope was used to take pictures of the fractured NC films.

A ThermoStar (Pfeiffer Vacuum) time-of-flight mass-spectrometer was used for monitoring the degradation products. The instrument was connected to the DMA apparatus via a heated (190°C) transfer line (quartz capillary). The later was introduced inside the DMA apparatus through a small port in the wall of the DMA instrument. The opening of the capillary was placed within ~1 mm from the film sample. The products of the thermal degradation of NC are known to include NO_2, CH_2O, C_2H_4O.[31,33] In agreement with this, we observed most intense peaks at m/z=44 ($C_2H_4O^+$) and 30 (NO^+, CH_2O^+). The ion signal at 46 amu (NO_2^+) was markedly weaker. It is known[34] that NO_2 is detected in the mass spectrometer predominantly as NO^+ because of fragmentation of NO_2^+ in the ion source. Therefore, the signals at m/z=44 and 30 were used for monitoring of degradation and showed practically identical behavior in all our experiments.

A Mettler-Toledo 851^e thermogravimetric analyzer (TGA) was used to measure mass loss of NC during its thermal decomposition in air flow (80 ml min^{-1}). For this purpose, ~2 mg samples were placed in 40 µl Al pans and heated under either isothermal or linear heating (2°C min^{-1}) conditions.

Our initial runs were performed at a room temperature. These runs did not show any degradation products in spite of our attempts to increase the strain and frequency to the maximum values allowed by the instrument. Obviously the strain fields were insufficient to initiate any significant mechanical changes such as crazing or fracturing.

According to the kinetic theory of fracture[35] the life time t of a solid under tensile stress s and temperature T is given by the following equation

$$t = t_0 \exp\left[\frac{U - g s}{RT}\right] \qquad (1)$$

where U is the activation energy for scission of an interatomic bond, t_0 is the period of the thermal oscillations of the bonded atoms, and g is a structural coefficient which represents the actual loads in the stressed body. Equation 1 suggests that the contributions of the thermal and

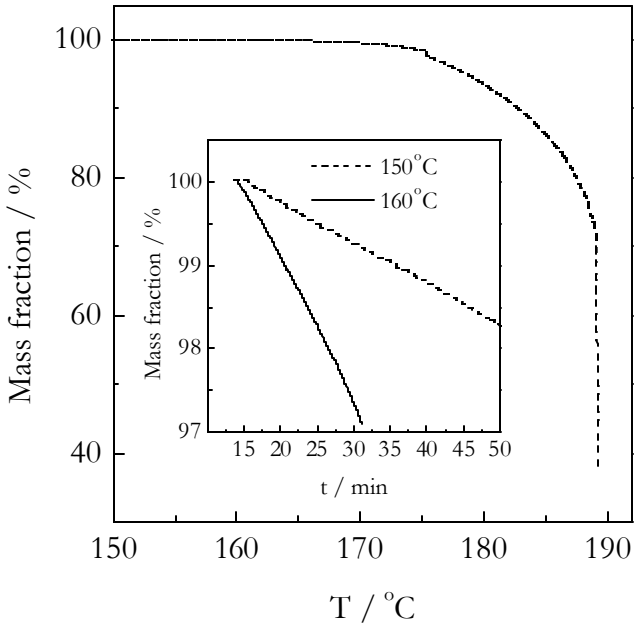


Figure 1.

Linear heating TGA run at 2°C min^{-1}. Inset shows TGA simulation of the heating programs realized in the DMA runs at 150 and 160°C

mechanical energy complement each other. That is if the delivered levels of mechanical energy are insufficient to initiate degradation at a room temperature, they may become sufficient at higher temperatures.

The temperature interval for further runs was chosen based on thermal degradation data obtained by using TGA. It is seen (Figure 1) that appreciable degradation (> 1% mass loss) starts above 170°C. Therefore, we chose to explore the temperature region from 160°C down to lower temperatures in 10°C decrements. The results of an experiment at 160°C are shown in Figure 2. In the DMA instrument the preset isothermal temperature has been reached for approximately 12 min. After this warm-up period, we have started to strain sample at various frequencies. The frequencies were increased manually. A short wait period was allowed at each frequency in order to observe possible degradation products. The first degradation products were detected when the frequency was raised from 100 to 200 Hz at the 18^{th} minute. The next more intense release of the degradation products occurred when switching from 300 to 400 Hz at the 22^{nd} minute. At that moment the modulus started to decrease and dropped instantaneously at the 24^{th} minute when the sample fractured in the middle in the direction perpendicular to the strain. No temperature increase was detected by the temperature sensor during any of these processes. Figure 2 also displays a blank run for heating a NC sample without straining. The blank run yielded no degradation product that suggests that the observed degradation was initiated by mechanical activation. Note that the small first peak was not reproduced in repetitive experiments.

When performing similar experiments below 150°C, no degradation products were detected. It should be noted that the sample was strained immediately after reaching 150°C, i.e., at roughly the same time as in the run at 160°C. However, it is likely that by the time we observed the effect at 21-22 min (Figure 2), the sample may have thermally degraded to some extent. Obviously, at 150°C the thermal degradation would occur to lesser extent for the same period of time. In order to evaluate the effect of the thermal degradation, we simulated in TGA a heating program similar to that observed in DMA for isothermal runs at 150 and 160°C. This

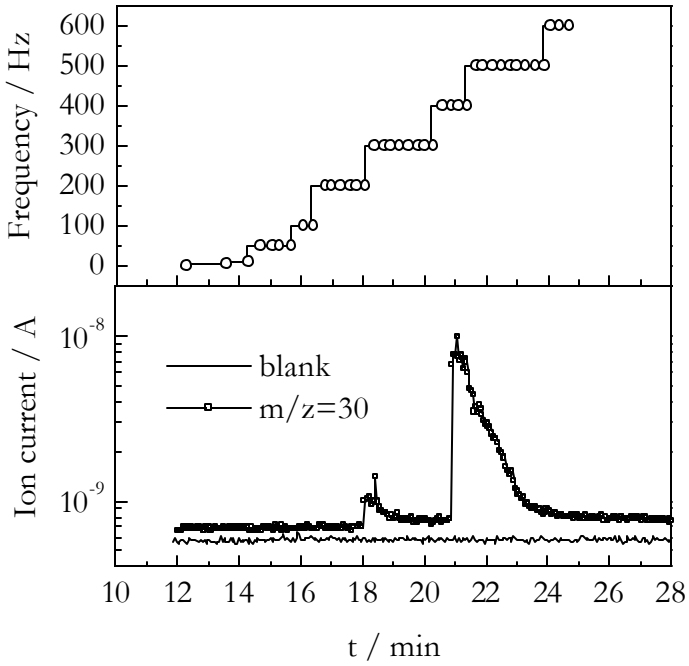


Figure 2.

Isothermal DMA-MS run at 160°C.

program was approximated by heating at 10°C min^{-1} to the isothermal temperature and holding at it for about one hour. The results of these experiments are shown in Figure 1. It is seen that by the time a sample reaches 21-22 min at 160°C it loses slightly more than 1% of its mass. At 150°C a similar extent of thermal degradation would be reached after 40 min of the run. Based on this data we performed two runs at 150°C when the oscillating strain was turned on after 45 min. In both cases we detected degradation product when the frequency reached 500 – 600Hz. At that moment the modulus dropped dramatically signaling fracture of the film. The thermal sensor

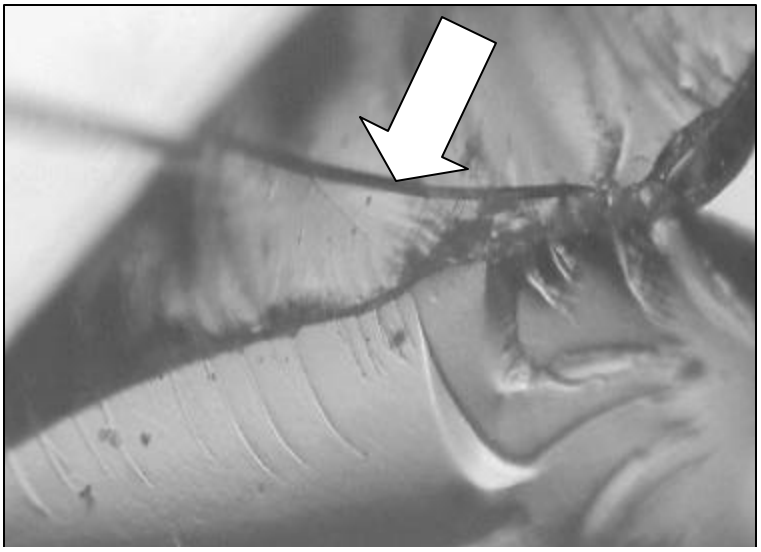


Figure 3.

Optical micrograph of the fracture front in reflected light. Arrow shows the crack that runs through the front and the film bulk (left). The actual image size is 1.0 x 0.7 mm.

did not detect any temperature increase associated with this process. The fractured film was examined under a microscope. Examination showed that the fracture front looked similar to that of a broken window glass with a few cracks running under an angle to the front (Figure 3).

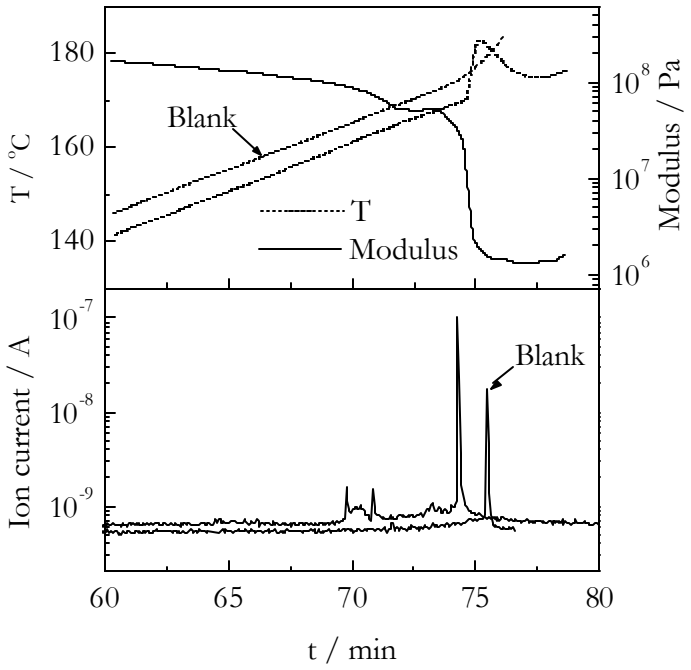


Figure 4.

Linear heating DMA-MS run at 2°C min^{-1}. DMA run is performed at frequency 10 Hz.

In addition to the isothermal runs, we have conducted several linear heating runs at various frequencies. A typical run is shown in Figure 4. In this figure we can see that the degradation products become detectable by MS at the 70th minute of the experiment that corresponds approximately to 160°C. It should be noted that this first degradation peak is associated with a change in the mechanical modulus as measured by DMA. However, the thermal sensor of DMA does not detect any changes in the sample temperature suggesting that the degradation products are most likely associated with mechanical action. The first peak is followed by another large peak that appears at the 74th minute of the experiment that corresponds to the temperature ~169°C. The respective degradation occurs very quickly and is accompanied by a dramatic decrease in the modulus and by a large (~13°C) increase in the temperature. After opening the DMA apparatus, we found that the NC film was gone and only some charred residue was left inside the clamps. This indicates that the fast degradation resulted in ignition. A blank run performed on an unclamped sample showed a single intense MS peak at the 75th minute that corresponds to ~175°C. As in the case of the second degradation peak for the clamped sample, we also observe a significant increase in temperature and obtain a charred residue that points at the similarity of the respective degradation processes. Since the lower temperature peak is found only in the strained sample we can conclude that the respective degradation process was initiated by mechanical activation. It is also noteworthy the higher temperature peak in the strained sample occurs at a lower temperature than in the blank. This appears to indicate that the tensile stress may accelerate the process of thermal degradation. A similar effect has been reported for photodegradation of polymers.[36]

Conclusions

A combination of DMA with MS provides a new approach to detecting mechanochemical degradation under moderate strain fields. The mechanochemical degradation has been detected for NC at temperatures that are noticeably lower than the temperatures of regular thermal degradation. The effect is accompanied by releasing degradation products detectable by MS and by decreasing modulus detectable by DMA. No significant change in temperature has been detected for this process, which is, however, associated with cracking and fracturing of the NC sample. The proposed approach may prove valuable in detecting mechanochemical degradations in other polymeric materials. Further efforts will be focused on examining the mechanochemical degradation of NC with stabilizers and on quantitatively describing the process.

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