

Mechanochemical effects in degradation of nitrocellulose and nitrocellulose–diphenylamine mixture

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Abstract

Dynamic mechanical analysis is combined with mass spectrometry to study nitrocellulose and nitrocellulose–diphenylamine films 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 a 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. Addition of 2 mass% of diphenylamine markedly enhances the resistance of nitrocellulose to mechanochemical degradation. At 160 °C, the process has been initiated only after significant exposure times to high frequencies: 67 min at 200 Hz, 36 min at 300 Hz and 29 min at 400 Hz.

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1. Introduction

Mechanical stimulation is capable of initiating various solid-state processes such as phase transitions [1–3], solid–solid reactions [4–8], decompositions [9,10] as well as degradation [11–13] and amorphization [14] of polymers. Mechanically activated processes are most commonly studied by using ball mills. By producing high strain fields, the mills allow for initiating the aforementioned processes without heating [15–18]. While easy to operate, the ball mills do not provide any simple ways of in situ monitoring the processes as well as measuring the values of strain and stress in the transforming materials. These problems can be resolved by using the method 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 while exposing them to a range of dynamic parameters that include frequency, strain and temperature [19]. DMA is extensively used in studies of the

relaxation behavior of polymers. It generates moderate strain fields that may be insufficient to cause fracture of glassy or crystalline polymers. Still, fracture can occur as a result of decreasing modulus with increasing temperature. There are two major mechanisms by which fracture of polymers may take place. These are chain slippage and bond breaking [20]. The long-range molecular motion of polymer chains is suppressed below the glass transition temperature, thus making chain slippage practically impossible. For this reason, bond breaking is the most likely mechanism of fracture in glassy polymers. Loading polystyrene [21] and polycarbonate [22] in tension to fracture has been demonstrated to yield gaseous products consistent with bond scission. Similar phenomena have been observed while microtoming polyethylene [23] and drilling poly(methyl methacrylate) [24]. The emission of ions, electrons or neutral species associated with the deformation and fracture of polymers is also known as the phenomenon of fractoemission [25]. Although the role of chain slippage increases in the rubbery and molten state, shearing of polymers above the glass transition temperature may still cause mechanochemical degradation [26]. The process has even been reported for solutions of polymers [27,28].

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By combining DMA with mass spectrometry (MS) in our laboratories, we have pioneered [29] a new method of detecting mechanochemical degradation. The present paper provides a detailed account of the method and focuses on the mechanochemical effects in degradation of nitrocellulose (NC) and its mixture with diphenylamine (DPA). DPA is a common stabilizer that is widely used in NC propellants [30]. The aminogroup of DPA is capable of binding the nitro-degradation products (e.g., NO_2 , HNO_3 , etc.) by forming nitrosoamines whose rearrangement and oxidation results in the formation nitro-DPA [31]. Because NC is an important energetic material, its thermal degradation has been extensively studied [30,32,33]. Although there is a strong practical interest in the behavior of energetic materials in high stress fields [34,35] characteristic of shock waves, the effect of moderate stresses is largely unexplored. It has been, however, reported [36] that extruding NC based propellants results in scission NC chains as detected by measuring the molecular weight of NC by gel permeation chromatography. In this paper, we use our novel DMA–MS method to explore the effect of moderate stress on degradation of NC materials.

2. Experimental

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). A mixture of NC with DPA (Fisher Sci.) was prepared by adding 2 mass% of DPA to the aforementioned NC solution. The resulting mixtures were stirred with a magnetic stir bar in a closed flask for 1 h to accomplish a homogeneous solution. The solution was cast in a Petri dish and carefully evaporated under the hood at ambient temperature for 24 h. This procedure allowed us to obtain tough, clear and uniform films of ~ 0.3 mm thick. NC films were colorless, whereas NC–DPA films were light green. DMA samples were prepared by cutting the film into ~ 11 mm by 9 mm pieces that were clamped into the DMA frame (Fig. 1, bottom). A Tritec 2000 (Triton Technology Ltd.) DMA apparatus was used to study the NC films in a tensile mode in a wide range of frequencies varying from a fraction to several hundred Hertz. 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 non-isothermal linear (2°C min^{-1}) heating. Blank DMA runs were carried out without applying the tensile deformation, 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 films.

A ThermoStar (Pfeiffer Vacuum) time-of-flight mass spectrometer was used for monitoring the degradation prod-

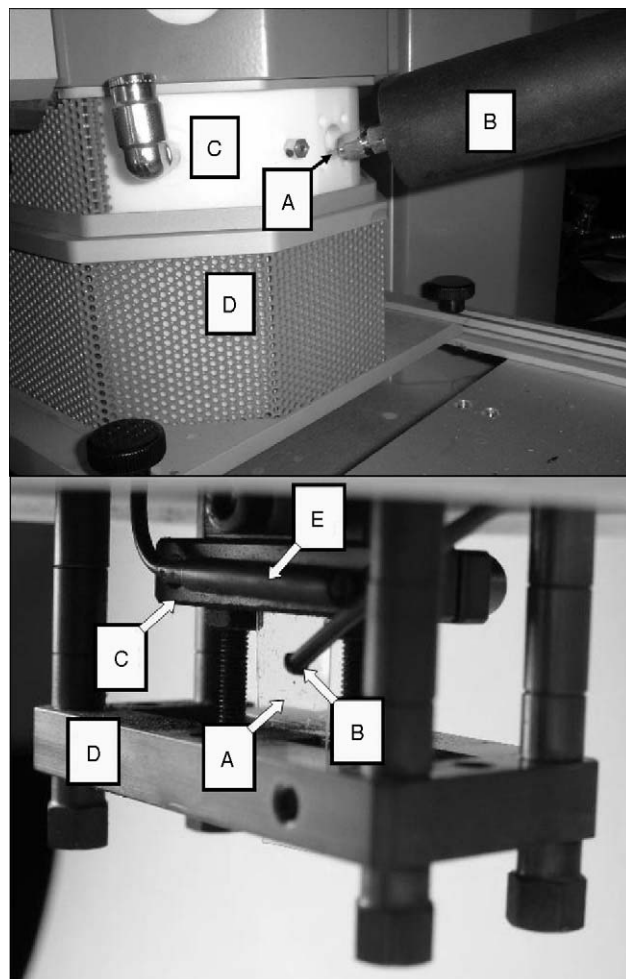


Fig. 1. DMA–MS setup. Top: (A) port; (B) heated line; (C) Teflon wall; (D) furnace. Bottom: (A) NC film; (B) MS “sniffer” (quartz capillary wrapped in PEEK sleeve); (C) moving clamp; (D) steady clamp; (E) thermal sensor.

ucts. The instrument was connected (Fig. 1, top) to the DMA apparatus via a heated (190°C) transfer line. The latter 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 (Fig. 1, bottom). The products of the thermal degradation of NC are known to include NO_2 , CH_2O , $\text{C}_2\text{H}_4\text{O}$ [32,30]. The most intense MS peaks were observed at $m/z = 44$ ($\text{C}_2\text{H}_4\text{O}^+$, CO_2^+ , N_2O^+) and 30 (NO^+ , CH_2O^+). The ion signal at 46 amu (NO_2^+) was markedly weaker. It is known [37] that NO_2 is detected in the mass spectrometer predominantly as NO^+ because of fragmentation of NO_2^+ in the ion source. Establishing the unique identities of the species associated with the peaks at $m/z = 44$ and 30 was not intended in the present work as the simple detection of these peaks provided sufficient evidence of NC degradation. It should be noted that the signals at $m/z = 44$ and 30 showed identical behavior in all our experiments. The most intense peaks for the thermal degradation of neat DPA occur at $m/z = 169$, 77 and 51 [38]. Although we observed these signals in our test run on pure DPA, they

were not detected during mechanochemical degradation of NC–DPA films.

A Mettler-Toledo 851^e thermogravimetric analyzer (TGA) was used to measure mass loss of NC during its thermal decomposition in ambient atmosphere. For this purpose, ~6 mg samples were placed in 40 μ L Al pans and heated under either isothermal (150 and 160 $^{\circ}$ C) or linear heating (2° C min^{-1}) conditions.

3. Results and discussion

3.1. Neat NC film

Our initial runs were conducted at ambient temperature and did not result in detecting any degradation products in spite of our attempts to increase the strain and frequency to the maximum values allowed by the DMA instrument. Obviously, the accomplished strain fields were insufficient to initiate any significant changes such as crazing or fracturing.

The kinetic theory of fracture [39] suggests that the life time, τ , of a solid under tensile stress, σ , and temperature, T , can be described by the following equation:

$$\tau = \tau_0 \exp \left[\frac{U_0 - \gamma\sigma}{RT} \right] \quad (1)$$

where U_0 is the activation energy for scission of an interatomic bond, τ_0 the period of the thermal oscillations of the bonded atoms and γ is the structural coefficient which represents the actual loads in the stressed body. According to this theory, fracture involves three steps: (1) deformation of interatomic bonds that causes the energy for bond scissions to decrease to $U = U_0 - \gamma\sigma$; (2) scission of the strained bonds by thermal fluctuations; (3) nucleation of microcracks as a result of the scission of macromolecules [39]. Eq. (1) does not directly include the frequency. However, the stress in a material under forced vibrations depends [20] on the strain as well as on the strain rate, which is proportional to the frequency. Another important feature of Eq. (1) is that the contributions of the thermal and mechanical energy are coupled. That is, if the delivered amounts of mechanical energy are insufficient to initiate degradation at a room temperature, they may become sufficient at higher temperatures. In other words, the frequency and temperature are two major parameters of mechanochemical degradation.

The temperature interval for further runs was chosen based on thermal degradation data obtained by using TGA. It is seen (Fig. 2) that appreciable degradation (>1 mass% loss) starts above 170 $^{\circ}$ C. Therefore, we chose to explore the temperature region from 160 $^{\circ}$ C down to lower temperatures in 10 $^{\circ}$ C decrements. The results of an experiment at 160 $^{\circ}$ C are shown in Fig. 3. In the DMA instrument, the preset isothermal temperature has been reached for approximately 12 min. After this warm-up period, we started to strain our sample at various frequencies. The frequencies were increased manually. A short wait period was allowed at each frequency in

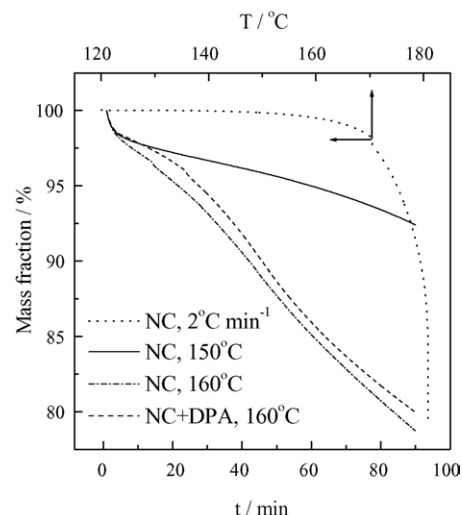


Fig. 2. Isothermal and linear heating TGA experiments in ambient atmosphere. Dotted line: linear heating of NC at 2° C min^{-1} ; solid line: isothermal heating of NC at 150 $^{\circ}$ C; dash-dot line: isothermal heating of NC at 160 $^{\circ}$ C; dashed line isothermal heating of NC mixture with 2% of DPA at 160 $^{\circ}$ C.

order to observe possible degradation products. The modulus showed a regular increase with increasing the frequency, but remained practically constant (10^8 – 10^9 Pa) within each of the constant frequency periods. The first degradation products were detected when the frequency was raised from 100 to 200 Hz at the 18th minute. A more intense release of the degradation products occurred when switching from 300 to 400 Hz at the 22nd minute. At that moment the modulus started to decrease and dropped sharply 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. Fig. 3 also displays a blank run for heating a NC sample without straining. The blank run yielded no degradation products that suggests that the observed degradation was initiated by mechanical activation. Note that the small first peak was not reproduced in repetitive experiments.

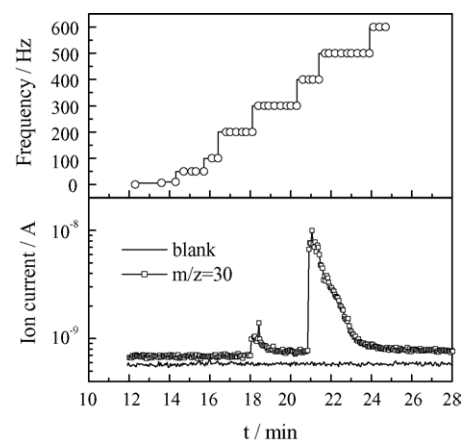


Fig. 3. Isothermal DMA–MS run of NC at 160 $^{\circ}$ C.

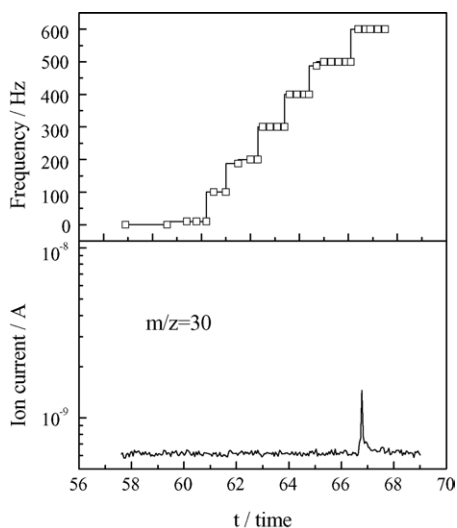


Fig. 4. Isothermal DMA–MS run of NC at 150 °C.

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 (Fig. 3), the sample may have thermally degraded to some extent. Obviously, at 150 °C the thermal degradation would occur to a lesser extent for the same period of time. In order to evaluate the effect of the thermal degradation, we used TGA data for isothermal runs at 150 and 160 °C. The results of these experiments are shown in Fig. 2. It can be seen that by the time a sample reaches 21–22 min at 160 °C it loses almost 5% of its mass. Note that about 2% of this mass loss occurs during the first 4 min while a sample reaches the preset temperature and is most likely associated with out-gassing residual moisture and solvents. At 150 °C a similar extent of the mass loss would be reached for ~60 min of the run (Fig. 2). Based on these data we performed two runs at 150 °C when the oscillating strain was turned on at ~60 min. In both cases, we detected degradation products when the frequency reached 500–600 Hz (Fig. 4). At that moment, the modulus dropped dramatically signaling fracture of the film. The thermal sensor did not detect any temperature increase associated with this process. The fractured film was examined under the 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 (Fig. 5).

In addition to the isothermal runs, we have conducted several linear heating runs at various frequencies. A typical run is shown in Fig. 6. 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 suggest-

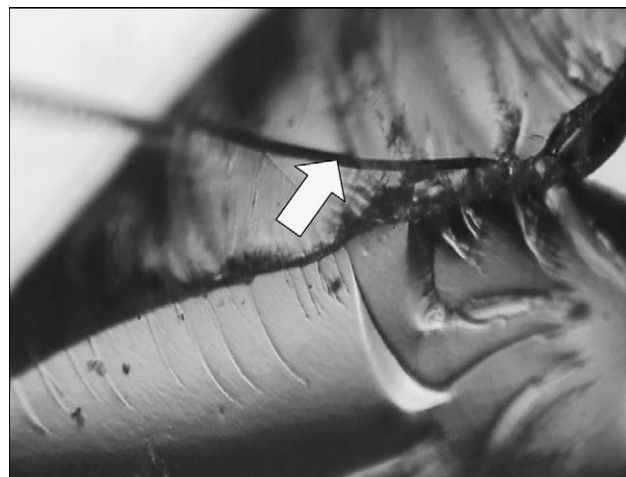


Fig. 5. Reflected light micrograph of the fracture front in NC film. Arrow shows the crack that runs through the front and the film bulk (left). The actual image size is 1.0 mm × 0.7 mm.

ing 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 observed a significant increase in temperature and obtained 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 that the higher

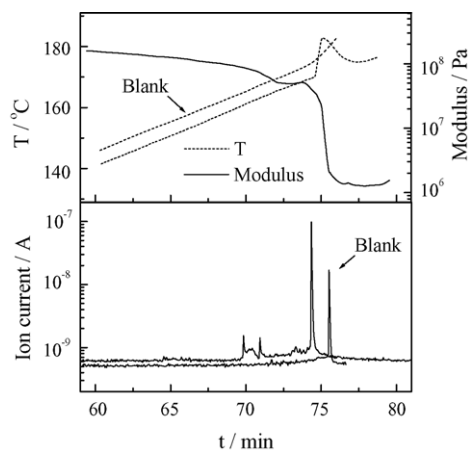


Fig. 6. Linear heating DMA–MS run ($m/z=30$) of NC at 2 °C min⁻¹. DMA run is performed at frequency 10 Hz.

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 [40].

3.2. NC–DPA film

Our first experiments were focused on detecting degradation products under conditions similar to those used for neat NC, i.e., by raising the frequency in steps up to 600 Hz at 160 °C. In spite of using various types of up-jumps and delay times, no degradation products were detected. Non-isothermal runs performed at different frequencies also did not show any clear-cut effect of frequency. The material simply demonstrated ignition above 180 °C that was accompanied by an abrupt fall in the modulus and a sharp increase in the temperature.

After more than two dozens of unsuccessful isothermal and non-isothermal runs we became almost convinced that degradation of the NC–DPA could not be accomplished by mechanical activation. The breakthrough came in one of the isothermal experiments performed at 160 °C and 600 Hz. About 30 min in the run the frequency was switched from 600 to 60 Hz that was followed by the appearance of a MS peak at $m/z=30$ and 44. The effect was reproducible and was also observed on the down-jumps from 500 to 50 Hz and from 400 to 40 Hz. Note that the effect was not unique to the NC–DPA film and was also produced on the neat NC film. The discovery of this effect prompted us to explore its dependence on the base frequency and the frequency exposure time before a down-jump. In order to accomplish this, we performed a series of isothermal runs at 160 °C at the base frequencies 400, 300, 200 and 100 Hz. In all of these runs the frequency was turned on after the temperature stabilized at 160 ± 1 °C. This generally occurred at ~ 16 min after heating was started. The samples were exposed to the base frequencies for approximately 20, 30, 40, 60 and 70 min, after which a 10-fold down-jump in frequency was initiated. Main results of these experiments are presented in Figs. 7–10.

Fig. 7 presents DMA–MS data for the 400–40 Hz down-jump runs at different exposure times that were roughly 20, 29, 40 and 67 min. At the exposure time 20 min (Fig. 7A), MS seems to detect a very small peak just above 36 min, i.e., about ~ 30 s after the frequency jump at 35.7 min that suggest that the effect may be caused by the jump. On the other hand, the peak intensity is only about two times larger than the noise amplitude so that no reliable conclusion can be drawn. A much stronger peak was detected at the exposure time 29 min, i.e., after the frequency switch at 44.8 min (Fig. 7B). The effect was accompanied by breaking the film that was detected as an instantaneous drop in the modulus value. Immediately after that the run was terminated. The broken film was removed and examined under the microscope. The observed fracture front (Fig. 8) looked similar to that observed for neat NC including a crack running through

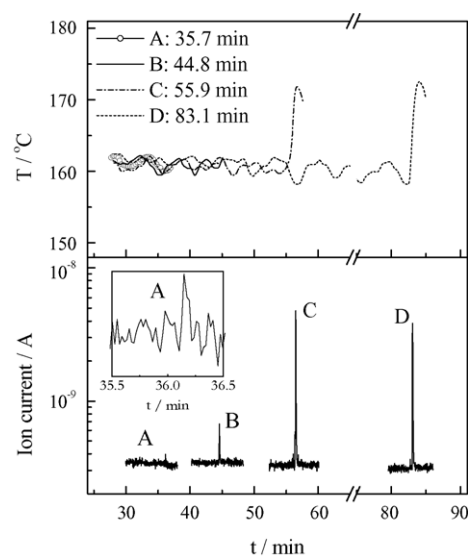


Fig. 7. (A–D) DMA–MS runs ($m/z=30$) performed on NC–DPA films at 160 °C and at 400 Hz. Numbers by the letters represent the total times when the frequency jump was carried out. The actual frequency exposure time is 16 min less. Inset shows a blow-up for run A.

the film bulk. No increase in temperature was detected by the thermal sensor of DMA. More profound MS peaks were observed at the exposure times 40 and 67 min. As seen from Fig. 7C and D, the peak intensity is about an order of magnitude larger than that detected for the peak B at the exposure time 29 min. The significant increase in intensity was associated with ignition of the film and was detected by the thermal sensor of DMA as ~ 10 °C jump in temperature. Upon terminating the runs, we opened DMA and found a charred residue in the DMA clamps.

The next series of runs was performed at the base frequency of 300 Hz (Fig. 9). The runs demonstrated that it is markedly more difficult to initiate degradation at this frequency than at 400 Hz. No $m/z=30$ and 44 peaks were

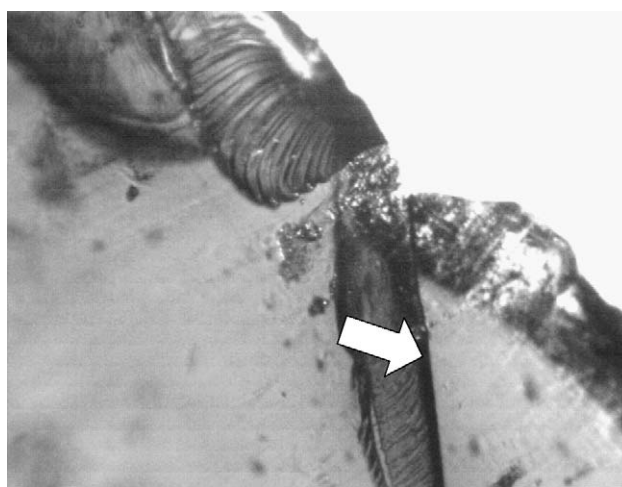


Fig. 8. Reflected light micrograph of the fracture front in NC–DPA film. Arrow shows a crack in the film bulk (left). The actual image size is 1.0 mm \times 0.7 mm.

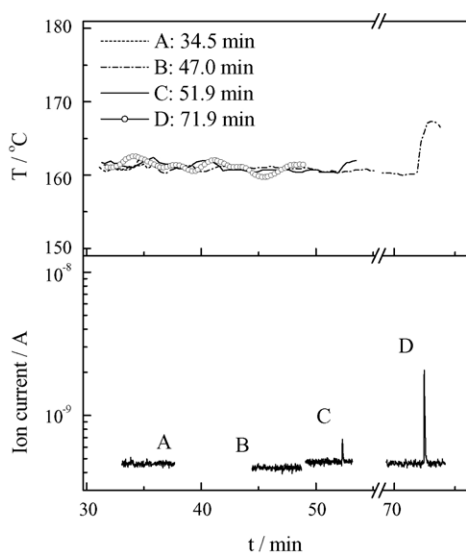


Fig. 9. (A–D) DMA–MS runs ($m/z=30$) performed on NC–DPA films at 160 °C and at 300 Hz. Numbers by the letters represent the total times when the frequency jump was carried out. The actual frequency exposure time is 16 min less.

detected by MS at the exposure times 19 and 31 min (Fig. 9A and B) in several repetitive runs. However, degradation was initiated at the 300–30 Hz frequency down-jump performed at 51.9 min (exposure time 36 min). The effect was detected as a MS peak (Fig. 9C) and was accompanied by a sharp drop in modulus measured by DMA. No sharp increase in temperature was observed. Upon opening the DMA apparatus we found a broken film in the clamps. A sharp increase in temperature was observed in the next run when switching the frequency at the exposure time 56 min (Fig. 9D). The film ignited and left a charred residue in the clamps. The respec-

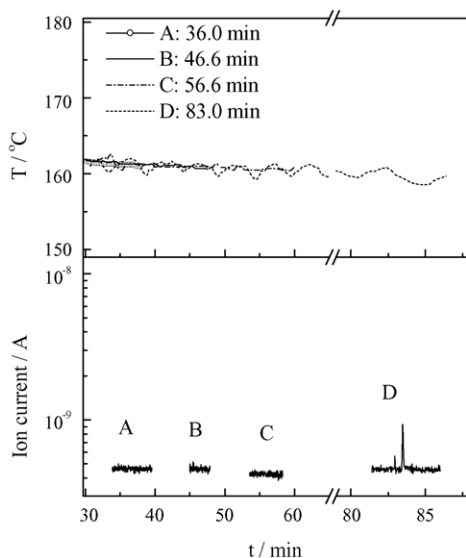


Fig. 10. (A–D) DMA–MS runs ($m/z=30$) performed on NC–DPA films at 160 °C and at 200 Hz. Numbers by the letters represent the total times when the frequency jump was carried out. The actual frequency exposure time is 16 min less.

tive degradation process gave rise to a MS peak that is about an order of magnitude larger than the peak detected at the exposure time 36 min.

The results of a series of experiments performed at the base frequency 200 Hz are shown in Fig. 10. Initiation of degradation at this frequency was even more difficult than at 300 Hz. No degradation was detected at the 200–20 Hz down-jumps performed at exposure times 20 min (Fig. 10A), 31 min (Fig. 10B) and 41 min (Fig. 10C), although we carried out several repetitive runs at the longer exposure time. Nevertheless, degradation was initiated at the exposure time 67 min as witnessed by a MS peak (Fig. 10D). DMA did not detect any significant increase in temperature, but a sharp drop in modulus, signaling that the film broke. The broken film was found in the DMA clamps upon opening the apparatus.

We also conducted a few runs at the base frequency 100 Hz and exposure times 60–80 min. In neither of these runs, 100–10 Hz down-jumps were we able to initiate degradation.

Our experiments with the NC–DPA films demonstrate that it is significantly more difficult to initiate mechanochemical degradation in this system than in the neat NC films. Apparently, DPA prevents quite effectively degradation of NC. Another important observation is that initiation of mechanochemical degradation in the NC–DPA films depends strongly on the base frequency. For instance, at the exposure time around 40 min, we cannot initiate degradation at 200 Hz, however we initiate film breakage and degradation at 300 Hz and film ignition at 400 Hz.

The strong dependence on the base frequency at similar exposure times suggests that we deal with the cumulative effect of cyclic deformation also known as fatigue [41]. The time to fatigue failure depends not only on the stress but also on the number of cycles, which is the product of the frequency and the exposure time. This phenomenon explains why we were not able to initiate mechanochemical degradation in our initial experiments when using frequency up-jumps. These experiments were performed at lower frequencies and apparently never reached the exposure time needed for developing any significant fatigue that might result in initiation of degradation. In the higher frequency down-jump runs, fatigue develops much faster so that the jump in force associated with the frequency switch is sufficient to initiate instant failure that results in degradation or ignition of the NC–DPA films.

4. Conclusions

A combination of DMA with MS provides a new approach to detecting mechanochemical degradation under moderate strain fields. The mechanochemical degradation has been initiated in NC at temperatures as low as 150 °C. 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. It is significantly more difficult to initiate mechanochemical degradation in the NC–DPA samples. The process shows a strong dependence on the frequency and could only be initiated after significant exposure times at the frequencies 200 Hz and above. The combined DMA–MS technique may provide a valuable tool for evaluating mechanochemical stability in energetics and other solid materials.

Acknowledgements

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