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Stability - Summary of KF and TGA Results

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A Progress Report for a 44-month Aging Study on Nitroplasticizer (NP) Stability – Summary of KF and TGA Results

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Abstract: In the past few years, a 44-month long aging experiment was conducted under various aging conditions. The properties of aged nitroplasticizer (NP) samples were analyzed using Fourier transform infrared spectroscopy, Karl Fischer (KF) titration, thermogravimetric analysis (TGA), liquid chromatography tandem quadrupole time of flight mass spectrometry, and ion chromatography. In this progress report, complete KF and TGA results are reported and discussed.

1. Introduction

In polymer bonded explosive (PBX) 9501 formulation, a binder that consists of 5% nitroplasticizer (NP) and polymer, is commonly used to bind energetic crystals together for propellant and explosive fabrications. The purpose of using binder is to lower the shock sensitivity and to improve the manufacturability of the PBX 9501 materials. NP studied here is a eutectic mixture of bis-2,2-dinitropropyl acetal (BDNPA) and bis-2,2-dinitropropyl formal (BDNPF), with a weight ratio of approximately 1:1 [1, 2]. NP also contains a trace amount of N-phenyl-2-naphthylamine (PBNA) (~0.1 wt%) for the purpose of long-term storage, which was added after NP production for scavenging NO_x radicals generated from NP degradation [3]. Like many plasticizers with a low molecular weight, at moderate temperatures after prolonged aging, NP tends to diffuse out of the PBX matrix and decompose into reactive by-products, such as NO, NO₂, H₂O, HONO, HNO₃, N₂O, and other NP residuals. Through oxidation and hydrolysis, the reactive molecules can further degrade NP, NP residues, and nearby polymeric materials, which cause undesired impacts. To better understand and mimic the aging conditions similar to real world applications, we conducted the present four-year aging experiment with improved experimental design. Although the environments and temperatures were identical to those used previously [4, 5], the headspace volume of the aging sample containers was greatly reduced (headspace volume/NP volume reduced from >30 to <0.2) and the headspace composition was not allowed to freely exchange with the surrounding atmosphere both during the aging and sample removal processes. Because water plays a key role in both HONO elimination and NP hydrolysis, monitoring its changes in the aged NP samples was an important improvement in the current study. To precisely monitor the changes in water content in the aged sample, coulometric Karl Fisher (KF) titration and Near Infrared (NIR) measurements at an accuracy in 10th ppm level were applied. Thermogravimetric analysis (TGA) was applied to the aged samples. In this progress report, complete KF and TGA data are documented and discussed.

2. Experimental

Baseline NP was obtained from a newly opened drum (lot number OCP-A/F-XB 8/8), which was made around 1965 and stored at LANL. This lot passed qualification tests except for the depletion of PBNA (as low as ~ 760 mM) and increased water concentration (as high as ~ 800 ppm (wt/wt)), compared to the pristine NP that contains 0.1 wt% PBNA ($= 6.33$ mM) and < 600 ppm water [6]. Baseline NP was used to prepare aged samples, which had been aged in air and nitrogen (N_2) conditions (called dry samples), and in direct contact with deionized (DI) water (called wet samples). Each set of samples was loaded into two different types of containers: one type - IR cells (32 SIR1, Firefly Sci.com) for NIR measurements in a pseudo-in-situ mode; and second type - glass vials (12x32 clean vials with screw caps, Fisher) for TGA, KF, and other measurements. The samples aged inside the cells were capped with a Teflon stopper secured with two layers of Teflon tape. Evidentially, this seal was imperfect so that some volatiles were able to leak out of the cells, hence they are also referred to as leaked samples. For the vial samples, Teflon tape was added between the thread and the cap to ensure the tightness of the seal, hence they were referred to as sealed samples. All cell and vial samples were kept inside Teflon containers. Four sets of samples were respectively heated at 38, 45, 55, and 64°C in ovens up to 44 months. The photos of these samples and sample containers are illustrated in Figure 1.

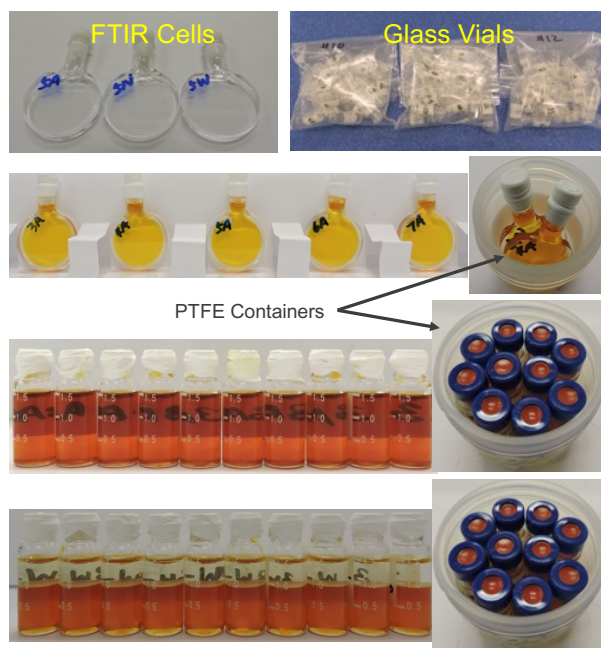


Figure 1. NP samples were prepared in 240 glass vials and 16 NIR quartz cells. Three headspace environments were used: Air, N_2 , and water.

KF titration was used to determine the water concentrations in the aged samples using a Mettler Toledo compact coulometric titrator (model C30S). TGA was conducted using a TA Instruments Q500 TGA. Samples (25–30 mg) were heated in standard aluminum pans from RT to 300°C , at $5^\circ\text{C}/\text{min}$ and under nitrogen purge (60 mL/min).

3. Results and Discussion

3.1. KF Results - Water concentration in aged NP samples

3.1.1. Aged under Dry Conditions

Figure 2 shows the water concentration profiles of two sets of samples aged under dry environments and at various temperatures for the entire experiment - 44 months. Inset photos show the appearance of the aged NP samples for 33 months at various temperatures. Figure 2 (left) shows the change in water concentrations of the cell samples, determined by the NIR measurement over the aging process [7]. The concentration profile exhibits three periods: 1) monotonic decrease; 2) slight fluctuation around a “mean” value, indicated by a horizontal line; and 3) large fluctuation. The duration of each stage is shortened as the temperature increases. Upon heating, in the first stage, NP loses its free water mainly through diffusion which regulates the duration of the first stage for the temperatures at 55°C and below [7]. The slower decreasing rate of the 64°C samples indicates that some water was generated to compensate the water loss through water diffusion. It is suspected that HONO elimination/decomposition already occurred in this early stage when NP is heated at 64°C [7, 8]. After losing this trace amount of free water, the water concentration reaches the minimal concentration in the aged samples, which is referred to as bonded water and can't be removed without degrading NP. The amount of this bonded water in NP decreases as the temperature decreases [7]. NP degradation starts in the second and eventually progresses into the third stage. Overall degradation in the second stage is insignificant so that the structural change in NP is not detectable in their MIR spectra [4], but is detectable in the LC/QTOF/MS and IC results because of their high sensitivity [9].

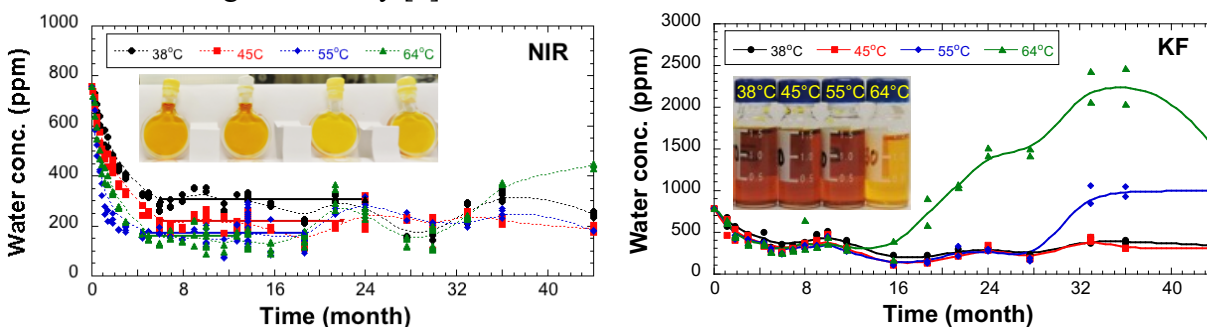


Figure 2. Water concentration in the NP samples aged at various conditions as a function of time - (left) for the cell samples. Flat lines indicate approximated mean values of the water concentrations in the samples in the second stage at various temperatures; and (right) for the vial samples. Both insets are the photos of the 33-month aged samples at different temperatures.

Figure 2 (right) shows the change in water concentration of the vial samples over the aging process, determined by KF titration. Similar to the cell samples, their water concentrations also exhibit three stages with respect to time. The behaviors of two sets of samples are identical in the first stage, dominated by the water diffusing out of the condensed phase into the headspace in these vial samples. We have hypothesized that the water loss triggers more HONO elimination and then decomposition through $\text{HONO} \rightarrow \text{NO} + \text{NO}_2 + \text{H}_2\text{O}$ [10], which in turn generates more water, and causes the water concentration fluctuation [7, 8]. Eventually an equilibrium is reached between the

condensed phase and the headspace (i.e., after 33 months) for the samples aged at 38°C and 45°C. Owing to the protection of PBNA, which scavenges the generated NO₂ [11]. Overall, the degradation at 38 and 45°C samples are minimal (not detectable in the MIR spectra). On the contrary, at 55 and 64°C, the more NO₂ generated from HONO decomposition aggressively depletes the antioxidant efficiency of PBNA and its nitrated derivatives over the aging process [11]. HNO₃ starts to form together with water formation, which results in NP hydrolysis [12]. For example, at 55°C, the water concentration increases rapidly at 28 months, and then remains relatively constant (~1000 ppm) for the rest of aging process. Again, water concentration would be balanced through water generation via HONO decomposition and bonded water dissociation, and consumption via NP hydrolysis [7]. At 64°C, the water concentration increases rapidly after 15 months and reaches 2500 ppm, and then starts to decrease after 33 months, indicating great NP hydrolysis. Also, water loss after 36 months due to the damaged cap in the vial sample might contribute to the decreased water concentration after the prolonged aging at 55 and 64°C.

Different water concentrations between the cell and vial samples can be attributed to the different headspace compositions. For the cell samples, the imperfect seal results in severe losses of volatiles (such as NO_x and water) at elevated temperatures. The depletion of these volatiles introduces two contradicting effects: 1) moves the HONO elimination and decomposition forward through chemical equilibrium, and 2) reduces the concentration of water and oxidants inside the cells, which reduces their catalytic effects on NP degradation. Similarly, for the vial samples, the accumulation of reactive products also brings two contradicting effects: 1) slows down HONO elimination and decomposition through chemical equilibrium, and 2) increases the catalytic effect of water and oxidants on NP degradation. These contradicting effects result in the non-monotonic profiles of water concentration over the aging process and alter the cascaded reaction pathways in these two settings.

3.1.2. Aged in Direct Contact with Water

Figure 3 shows the water concentration of the wet samples when aged inside the vials. The inset photo shows the appearance of these NP samples aged for 36 months at various temperatures. Due to the high density of NP (1.39 g/cm³) and immiscibility with water, the NP phase stays at the bottom of the vial. Despite the hydrophobic characteristic of NP, water solubility in NP increases from 2500 ppm to 5500 ppm as the temperature increases from room temperature to 70°C, which agrees with the earlier findings [13, 14]. During a period of 44 months, once water reaches its saturation in the NP phase, its concentration almost remains a constant at 38°C and 45°C. The color and volume of both NP and aqueous phases do not change, suggesting that the interactions between water and NP mainly remain as the physical interactions at these low temperatures.

At 55°C, the water concentration increases slightly after 36 months. At 64°C, the water concentration increases slightly after 12 months, then increases quickly between 12 and 33 months, followed by a rapid decrease at 44 months. Accordingly, the color of NP phase lightens and the volume of NP phase decreases as the volume of the aqueous increases, as indicated by the yellow arrows in the photo in Figure 3. These observations suggest that, after extended aging at 55°C and above, the interactions between water and NP change from physical to chemical. The water

concentration increases after 6 months at 64°C is an indication of complex reactions. The previous study suggests that when PBNA and its nitrated derivatives deplete, HNO_3 forms and dissociates into ionic forms, which triggers the acid-catalyzed hydrolysis [5, 11]. As proposed in Figure 4, depending on the degree of the hydrolysis, various alcohols, aldehydes, and organic acids can form [8, 9]. Since the alcohols and organic acids have different solubility in NP and aqueous phase, their distribute between these two phases changes accordingly. As the concentrations of the degraded products increases in both phases, their solubilities in both phases are changed, which explains the high concentration of water in the NP phase (as high as 2.8 wt%) though the strong acidity might affect the accuracy of the KF measurement. Simultaneously, as more organic acidic molecules are formed and extracted into the aqueous phase, the color of the aqueous phase changes from originally clear to yellowish. The large decreased water concentration after 36 months suggests the large degree of NP hydrolysis and possible loss to evaporation due to the damaged cap of the vial after a long-term aging at 64°C, which is similar to what was observed in the dry condition, as discussed in Section 3.1.1.

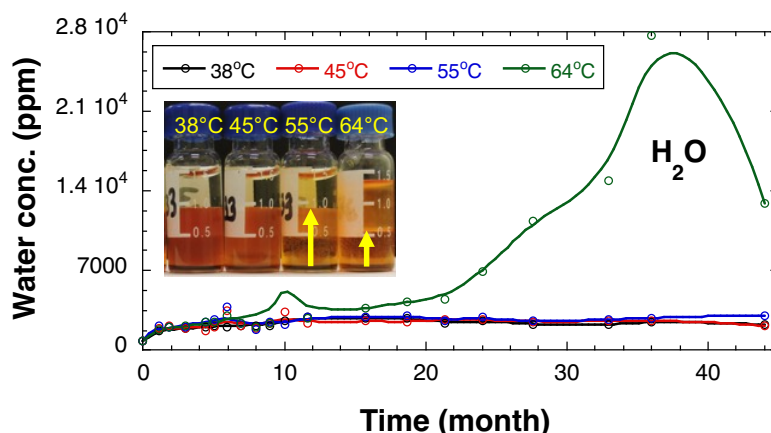


Figure 3. Water concentration in the NP samples aged in direct contact with water at various temperatures. The inset is the photo of the wet samples aged at various temperatures for 36 months. The yellow arrows indicate the interface between aqueous and NP phases.

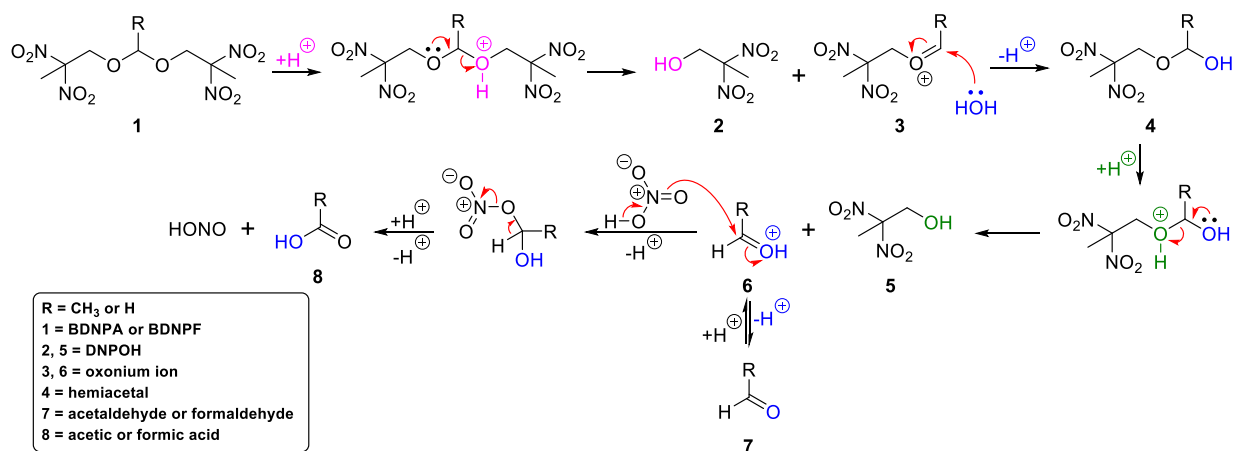


Figure 4. Acid-catalyzed acetal/formal hydrolysis of NP into DNPOH, acetic/formic acids, and other products in the later stage of NP aging [9, 15-18].

3.2. TGA Results of Aged Samples

3.2.1. Aged under Dry Conditions

Figure 5 shows the TGA results of the air samples after aging for 28, 36, and 44 months at various temperatures. The decomposition (and evaporation) temperature (DT) of the sample aged at 38°C for 44 months is ~2°C higher than that of baseline NP (234°C). This is likely due to the loss of a trace amount of water through diffusion and/or other volatiles from these earlier aged sample. For the sample aged at 45°C for 44 months, the DT (233°C) becomes lower than that of baseline NP (234°C) with a different (bimodal) shape on the DTG curve, signaling different thermal behaviors, which might be associated with the formation of NP isomers, such as nitroso alcohol with -OH and -NO groups through HONO addition due to a cage effect when the sample was sealed in a confined container [4, 10]. Since those isomers are the intermediate products, their existence has a higher possibility at low temperatures than at high temperatures, and can change the thermal stability of aged NP. Nevertheless, aging at 38°C and 45°C for 44 months does not significantly change the TGA results below 200°C, compared to that of the baseline NP.

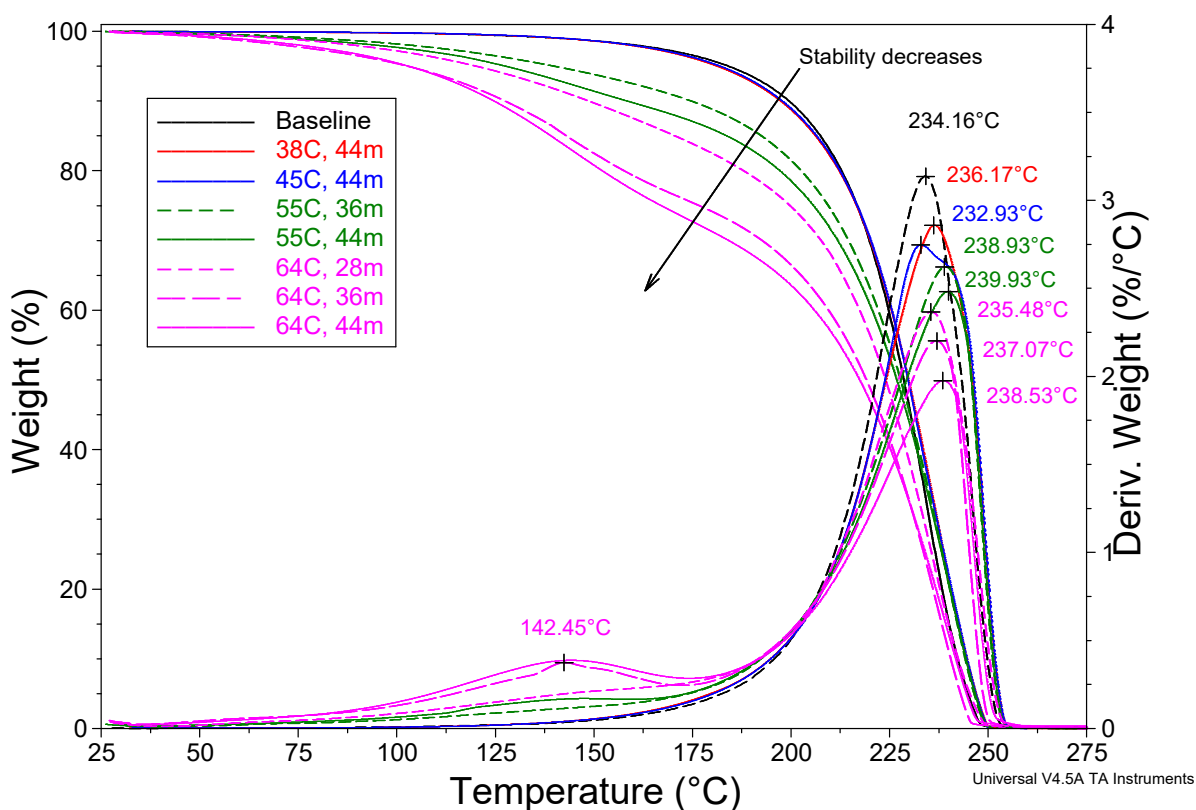


Figure 5. TGA results of baseline NP and air samples aged for 28, 36, and 44 months at various temperatures. The left Y-axis is the weight percentage of the sample, and the right Y-axis is the first derivative of the weight over temperature (the DTG curve).

Aging at 55 and 64°C for more than 28 months, their TGA traces clearly deviate from that of the baseline NP, and deviate more as aging proceeds. It is especially true for the weight loss below 175°C because a new peak with a long tail at low temperature zone is detected, suggesting that

compounds with a lower DT at 143°C are formed in the aged samples. As the time increases from 28 to 44 months, the intensity of this broad peak increases. The weight loss of the aged samples at 175°C increases from ~5 to >35 wt%. On the other hand, the DT of the original peak increases from 234 to 239°C at 36 months, and 240°C at 44 months when the samples were aged at 55°C. In the previous study [6], we found that the DT of BDNPF (237°C) differs by ~5°C from BDNPA (232°C). We also concluded that more degradation of BDNPA over BDNPF, which might result in the dominant thermal characteristic of BDNPF in the aged samples [4, 5]. However, the unchanged BDNPA/BDNPF ratio was found in the samples aged at 55°C for up to 44 months [9]. Therefore, the increased DT in the aged samples might be due to reasons other than more BDNPA degradation, namely the formation of molecules with a higher molecular weight than NP through possible dimerization between degraded NP, or even dinitro-/trinitro-PBNA formation. As the temperature increases to 64°C, while the DT of the aged samples decreases, the BDNPA/BDNPF ratio largely decreases over time, suggesting that BDNPA degrades more than BDNPF, which is mainly due to the NP hydrolysis at the elevated temperatures.

3.2.2. Aged in Direct Contact with Water

Since NP is aged in direct contact with liquid water, poor miscibility between water and NP results in two separated phases: NP and aqueous phases, which are analyzed separately.

3.2.2.1. TGA of the NP phase

Compared to baseline NP, samples aged at 38 and 55°C do not yield much different results, suggesting that their thermal stability does not alter much during the aging process. As expected, elevated temperature does increase water solubility, as shown in Figure 3. At 64°C, the increased water solubility is mostly responsible for the increased weight loss below 100°C within the first 12 months [8]. As the aging time increases from 12 months to 44 months, the following changes are found in the TGA traces presented in Figure 6: 1) DT varies between 233°C and 239°C. This is likely due to isomer formation/degradation; 2) a shoulder grows in the DTG trace at temperatures below 175°C, ultimately forming the broad peak at 142°C after 24 months, suggesting the formation of hydrolyzed products, such as 2,2-dinitropropan-1-ol (DNPOH) [12]; 3) a peak emerges at 55°C after 28 months. Such a low temperature ought to be associated with volatiles, such as HONO, HNO₃, and organic acids [9]. This is a rather unique peak for the wet samples because the volatiles are preserved well by the aqueous layer. On the contrary, in the dry samples, those volatiles were able to escape into the vapor phase, explaining its absence in Figure 5. Based on the weight loss at 87°C, the estimated volatile content 6.5 wt% in the wet sample and only less than 3.0 wt% in the dry sample after 44 months of aging at 64°C; and 4) the intensity of the peak at 142°C and the shoulder at 55°C decrease from 36 to 44 months, suggesting a decreased amount of the volatiles and degraded products. Reasons for their depletion could be a) hydrolyzed products (at ~142°C) are extracted from the NP phase into the aqueous phase, b) degraded products continually react with water to form alcohols from acetaldehyde/formaldehyde with decreased volatility, and c) some volatiles (below 87°C) escape through the damaged vial cap after a long-term aging at 64°C.

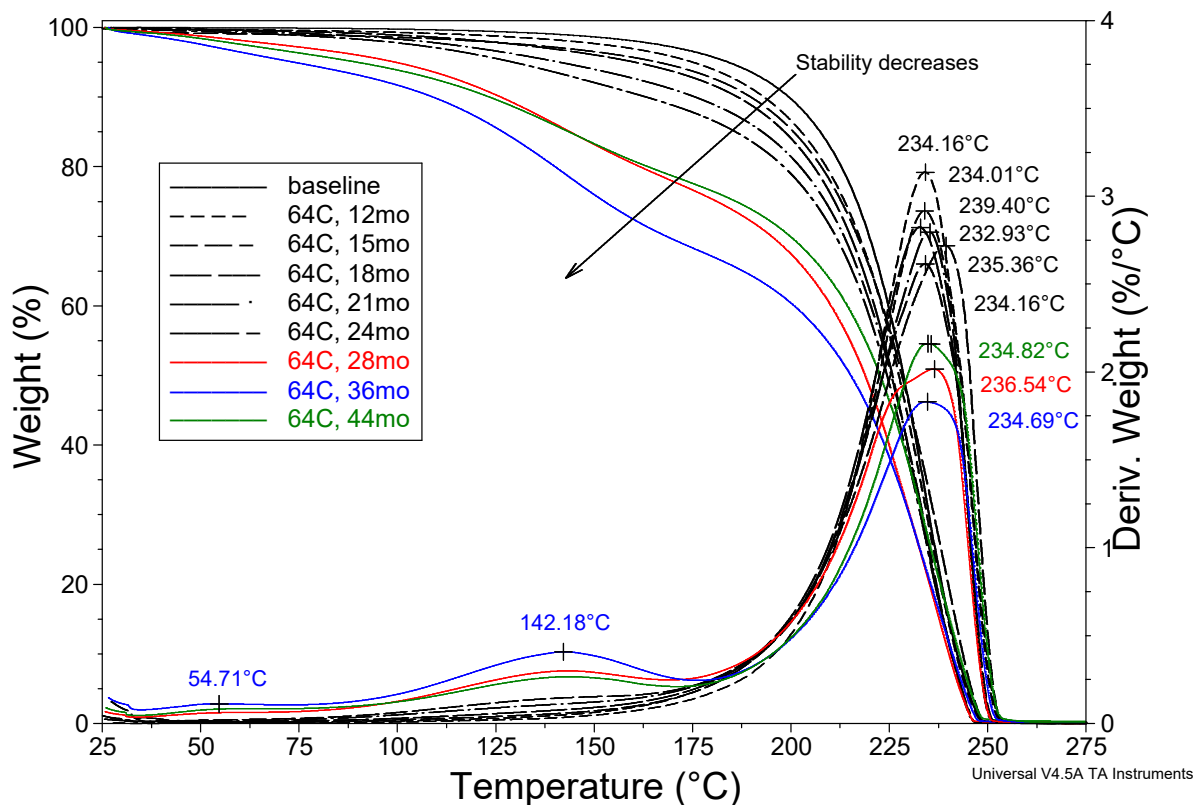


Figure 6. TGA results of the baseline and wet samples aged at 64°C for different ages.

3.2.2.2. TGA of the aqueous phase

Figure 7 (left) shows a set of photos which illustrate the color change in the aqueous phases collected from the samples aged at various conditions. At time zero, 0.5 mL of DI water was added into each vial; this volume remains approximately constant when the samples were aged at 38, 45 and 55°C. Small deviations from 0.5 mL is predominantly due to variation in the procedure applied to separate the aqueous phase from the NP phase. Conversely, at 64°C, the volume of the aqueous samples noticeably increases after 28 months. As aging proceeds and temperature increases, the color of the aqueous phase changes from colorless to light yellow, yellow, brown, and to dark brown, suggesting that more degraded fragments were extracted into the aqueous phase. Of course, the damaged cap allowed some volatiles to escape from the vial, which is primarily responsible for the decreased volume of the aqueous samples aged at 55 and 64°C for 36 months and after.

Figure 7 (right) shows the TGA results of the aqueous samples aged at 64°C for 0 to 44 months. The boiling (or evaporation) point of the aqueous sample decreases from 89°C to 70°C after 44 months. Accordingly, the weight loss at 175°C increases from 0 to ~7 wt%, confirming the increased amount of chemicals extracted from the NP phase. Depending on the degree of NP degradation, newly produced chemicals give rise to one, two, or even three new peaks in the DTG curves, suggesting that these chemicals exhibit different volatilities and thermal stabilities. While the concentration of HNO₃ determines the peak position below 89°C, fragments degraded from NP are responsible for the peaks at 107, 125, and 147°C. The 147°C peak is of particular interest

because it is likely related to one of hydrolytic products, DNPOH. The DT of DNPOH was measured at 148°C. The 142°C peak detected in the corresponding NP phase might be also associated with the product from NP hydrolysis, i.e.: hemiacetal (with DT of ~142°C). To confirm their chemical structures, the LC/QTOF/MS and IC analyses were conducted and reported in Ref. [9].

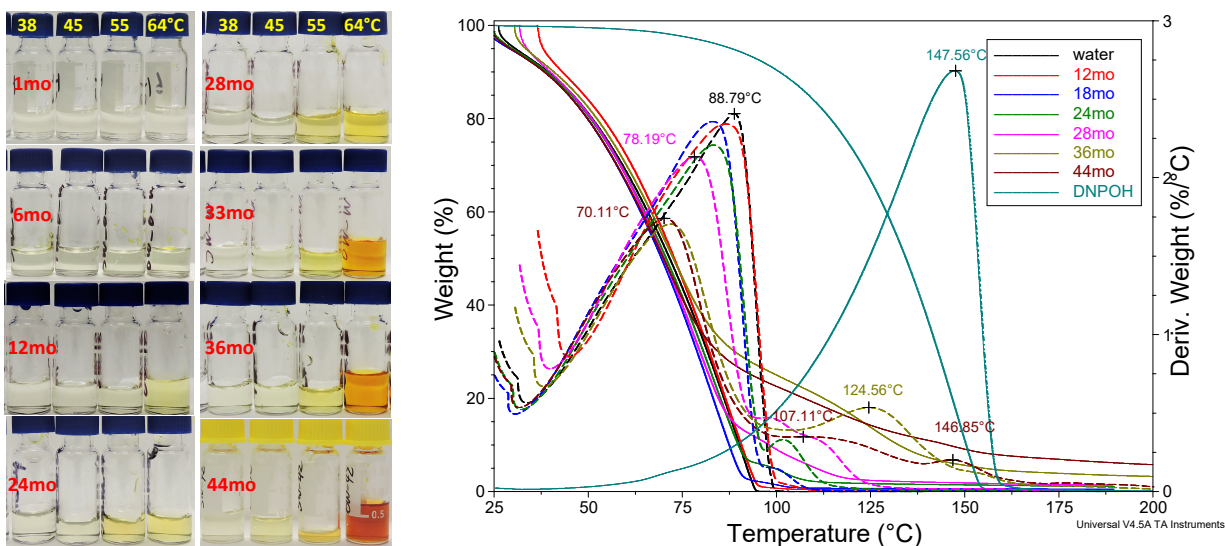


Figure 7. The color changes in the aqueous phase after being aged for different conditions (left) and TGA results of the aqueous samples aged at 64°C for different times (right).

3.2.3. Environment Effect on Thermal Stability of Aged Samples

Again, at 45°C and below, the environment has minimal effect on the thermal stability of NP. Figure 8 shows the TGA results of the samples aged in air, N₂, and water at 55 and 64°C for 44 months. At 55°C, the weight loss at 175°C is 27.3, 24.5, or 22.3 wt% from the air, N₂, or wet samples, respectively. The results suggest that NP degradation is more important in the dry samples than in the wet sample. On the other hand, compared to the dry samples, the wet sample contains more volatiles with the boiling point less than 87°C. This behavior supports the argument that water captures NO_x by converting it to HNO_x, which reduces the severity of NO_x radicals toward NP and its residuals in the wet sample as the radicals were extracted into the aqueous phase when they were aged at 55°C and below. At 64°C, NP greatly degrades regardless of aging conditions. For the wet sample, the more weight loss at the temperature below 87°C is due to the trapped volatiles whereas the less weight loss between 87°C and 175°C is due to the extraction of DNPOH into the aqueous phase.

Clearly, NP aging in contact with water introduces complications in NP degradation. While some harmful species removed by water can reduce the acidity in NP phase, preventing NP from hydrolysis at low temperatures, water in NP at elevated temperatures definitely accelerates NP hydrolysis. Therefore, one must be mindful about the impact of water addition on the aging behavior of NP.

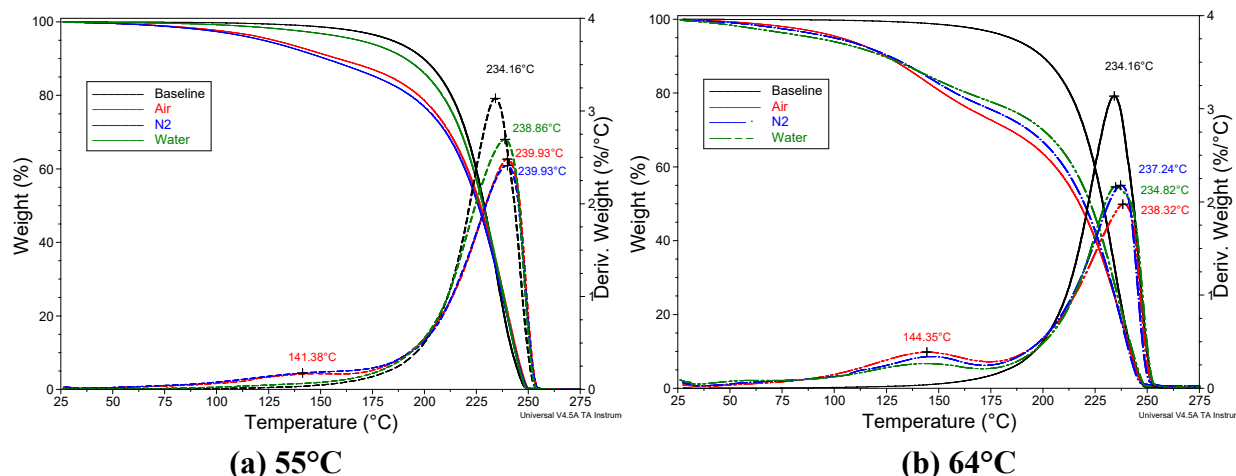


Figure 8. TGA results of baseline NP and samples aged in air, N₂, and water at (a) 55°C, and (b) 64°C for 44 months.

4. Summary

The KF results reveal that the trends of water concentrations in the aged NP samples exhibit three stages, which are governed by water diffusion, HONO elimination/decomposition, bonded water dissociation, and NP hydrolysis. The temperature and headspace environment regulate the duration of each stage. While HONO elimination dominates NP degradation in the early stage of aging, NP hydrolysis dominates NP degradation in the later stage of aging.

The TGA results reveal that the thermal stability of NP aged under the dry condition is lower than that under the wet condition when the samples were aged at 55°C and below within 44 months of aging. As the temperature reaches 55°C and above, the new peaks and noticeable weight loss are observed below 175°C in the TGA results. While the acid species are responsible for the weight loss below 87°C, DNPOH and other NP hydrolyzed molecules are responsible for the weight loss between 140 and 150°C. Overall, water plays an important role in altering the behavior of NP aging at different temperatures and different headspace conditions.

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