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Binder/HMX interaction in PBX9501 at Elevated Temperatures

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Plastic bonded explosives (PBX) generally consist of 85 - 95 % by weight energetic material, such as HMX, and 5 - 15 % polymeric binder. Understanding of the structure and morphology at elevated temperatures and pressures is important for predicting of PBX behavior in accident scenarios. The crystallographic behavior of pure HMX has been measured as functions of temperature and grain size. The investigation is extended to the high temperature behavior of PBX 9501 (95% HMX, 2.5 % Estane, 2.5 % BDNPA/F). The results show that the HMX β-phase to δ-phase transition in PBX 9501 is similar to that in neat HMX. However, in the presence of the PBX 9501 binder, δ-phase HMX readily converts back to β-phase during cooling. Using the same temperature profile, the conversion rate decreases for each subsequent heating and cooling cycle. As observed in earlier experiments, no reverse conversion is observed without the polymer binder. It is proposed that the reversion of δ-phase to β-phase is due to changes in the surface molecular potential caused by the influence of the polymer binder on the surface molecules of the δ-phase. Upon thermal cycling, the polymer binder segregates from the HMX particles and thus reduces the influence of the binder on the surface molecules. This segregation increases the resistance for the δ-phase to β-phase transition, as demonstrated in an aged PBX 9501 material for which the reversion is not observed.

INTRODUCTION

Previous investigations[1,2] of the kinetic behavior of neat HMX (octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine) indicated that the freshly prepared sample has a monoclinic structure, which is the β-phase, and when heated to 160-170° C, it converts to a hexagonal structure, which is the δ-phase. At elevated temperatures, the coefficient of thermal expansion of neat HMX crystals is independent of particle size and the number of temperature cycles, even though the conversion temperature is observed to be higher for small particle size HMX than for large particle size HMX[1]. Upon cooling, the δ-phase does not convert back to the original β-phase. The circumstances governing this phase conversion are critical to the understanding of the thermal ignition, impact sensitivity, and the violence of thermal explosion processes. These properties also have a direct correlation with the microstructure, e.g. voids, domain clustering and crystal arrangements. The changes of the microstructure with time, temperature and pressure are dictated by the phase behavior.

It has been reported[3] that the density of neat HMX reduces by 5% (from 1.901 to 1.801 gm/cc[3]) over a period of just 7 days at 160 °C in the β-phase. With no phase change, this behavior is attributed to the presence of defects and voids. Mang et. al.[4] also reported that the voids present in pressed PBX 9501 display a tri-modal distribution. This change in microstructure and hence the degree of sensitivity of PBX 9501 can be correlated to the change in crystal structure of HMX over time and temperature. The conversion behavior of β- and δ- phases of HMX certainly influences the stability and the safety of the high explosive materials.

Several studies[1,2,5] have clearly identified the conversion from monoclinic β-phase to hexagonal δ-phase as the temperature is increased from room temperature to 160-170°C[1,2]. There were no observations of δ- back to β-phase conversion. However, there are two related papers[6,7] in which the authors reported the phase conversion of HMX from β- to δ- and then back to β-phase using the Second Harmonic Generation (SHG) technique. A theoretical model was also provided describing this behavior. The experimental data in support of the reversion is actually obtained from HMX in PBX 9501. No reversion has thus far been observed in neat HMX.

The present work focuses on the phase reversion behavior of HMX in PBX 9501 and compares the results with that of neat HMX reported earlier[2]. This result will provide information on the effect of polymer binder and plasticizer on the phase behavior of HMX. This investigation also monitors the phase changes during several temperature cycles, providing information on the effect of aging on PBX 9501.

SAMPLES

In this report, two PBX 9501 samples are studied. PBX 9501 is a composite of 95 % HMX and 5 % polymeric binder by weight with a little processing aid (Irganox 1010). The binder is made up of 2.5 % Estane and 2.5 % nitroplasticizer (BDNPA/F). Sample (A) from LLNL labeled as C-214 was purchased from Pantex in 1986 (Lot #730-010, class 2), and sample (B) is a more recent sample from LANL labeled as "reverted" (Lot#90-B731002). This sample was treated with a temperature of 170 °C, thus converting to δ-phase and slowly cooled to room temperature to the β-phase. The LLNL sample is labeled as 'old' and the LANL sample is labeled as 'new'. The major component in PBX 9501 is obviously HMX, so the scattering signal is essentially from the HMX crystals. HMX's β-phase is monoclinic with a=6.54 Å, *b*=11.05 Å and *c*=8.702 Å, and β=124.443, and its δ-phase is hexagonal with *a*=7.71 Å, *c*=32.55 Å[8].

EXPERIMENTAL PROCEDURE

The experimental setup uses an INEL curved position sensitive detector system mounted on an in-house sealed tube x-ray generator. The generator is set at 40 KeV and 30 MA. An incident Ge monochromator is used to select only the $\mathrm{CuK}_{\alpha 1}$ radiation. This unit enables the acquisition of the full 120 °(2θ) angular range simultaneously. For heating, an INEL capillary furnace is used. The samples are loaded into capillary tubes 0.7 - 1.0 mm diameter and 2 mm long. Approximately 1.4 mg of explosive material is used. To avoid a preferred orientation, the capillary tube is kept spinning at all times.

The temperature controller and the data acquisition are computer controlled. The temperature profile used is as follows: the sample is first heated to 170 °C for 20 minutes; then it is cooled to and maintained at 130 °C for at least 2 hours; and finally it is cooled to room temperature. Data acquisition time per scan is selected to be 10 minutes with a temperature step of 10°C.

RESULTS AND DISCUSSION

Figure 1 shows the diffraction patterns of PBX 9501 as a function of temperature along with the ICDD listing for β- and δ-phases. Clearly, all the lines can be accounted for by either the β- or δ-phases. The changes of the lattice parameters and the coefficients of thermal expansion have been discussed previously[2]. The scattering signal from the binder is relatively weak and therefore is not observed in the spectra. The phase conversion from β- to δ- can be observed at 170 °C, which is a slightly higher temperature than that was reported for neat HMX. On continued heating and then cooling to 130 °C, δ-phase remained. There was no reversion of δ-phase back to β-phase during cooling. In fact, this behavior is similar to that observed earlier[2] for the neat HMX. It can then be concluded that the HMX in the 'old' PBX9501 sample behaves like neat HMX. Thus the binder in this material seems to have no significant influence on conversion from β- to δ- phase.

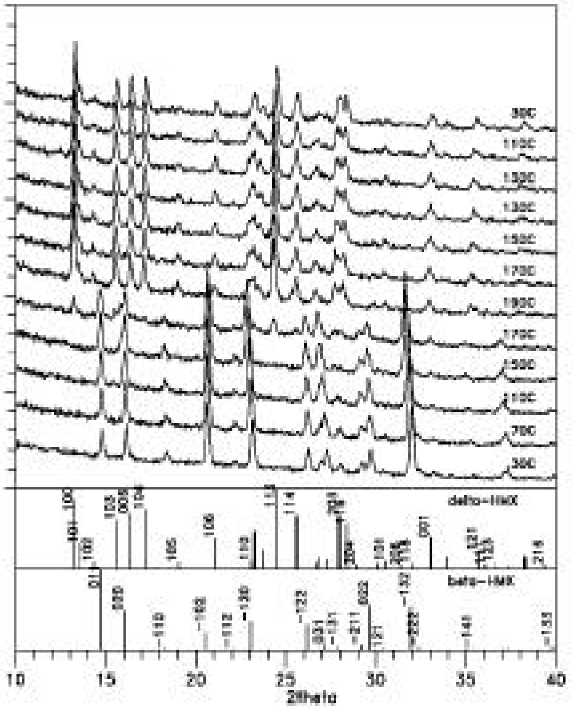

Figure 1. XRD patterns of the old sample as a function of temperature as indicated by the arrow. Some scans are omitted for the purpose of clarity.

It should be noted that, at the transformation temperature, the diffraction peaks of the β-phase diminish in intensity, while the peaks belonging to the δ-phase increase in intensity. The two phases can co-exist since the development of δ-phase does not require the complete destruction of β-phase. There are no major changes in peak widths for either the β- or δ-phase during the conversion, indicating that the average crystallite size does not change during the conversion. This result suggests that the conversion from β- to δ-phase occurs one crystallite at a time, which may explain an observation of fine structures in the DSC curves[9]. Weese et al.[9] attribute this to uneven contact of the powder with the sample pan.

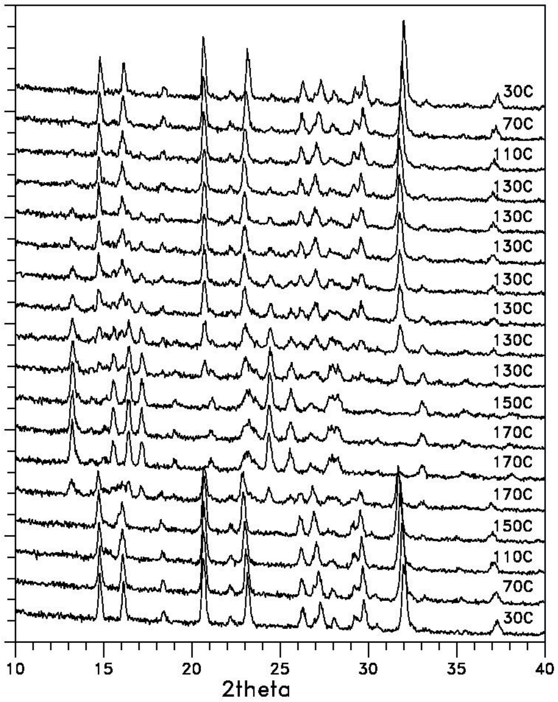

Figure 2. XRD spectra of new reverted PBX9501 sample indicating the reversion of the δ- to β-phase. Some spectra are omitted for clarity.

Figure 2 shows the diffraction patterns of the 'new' PBX 9501 sample, indicating a transformation of the β-phase to δ-phase at about 170 °C and then the reversion of the δ-phase back to the original β-phase starting at about 130 °C during cooling. The reversion process during cooling is similar to the conversion process during heating. That is, at 130 °C, both phases co-exist. There is no shift in the peak positions apart from thermal expansion effects. The peak intensities of the δ-phase increase while those of β-phase decrease. The reversion to the β-phase requires at least 2 hours, while the conversion to δ-phase occurs in the first 10 minutes at 170 °C.

At room temperature, there is no evidence of δ-phase as indicated by the absence of the (100) peak and at 170 °C, the β- phase in fully converted to δ-phase as indicated by the absence of the (-102) peak. By taking the peak intensities of these peaks, the concentration ratio over time and temperature can be extracted. Figure 3 shows the conversion rate of the β- to δ-phase and back to β- phase.

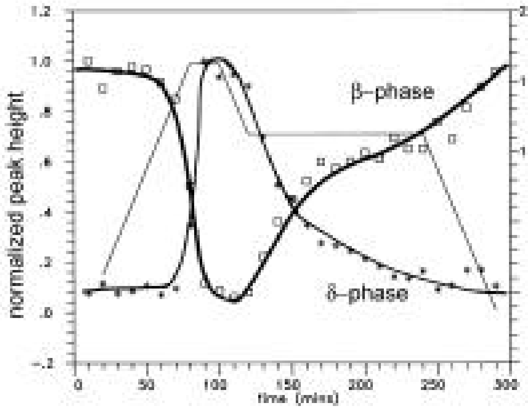

Figure 3. Conversion rate of β- (open square) and δ-phase (*) (dark lines are visual aids) and the light line shows the temperature profile used.

Even though cooling at 130 °C for 2 hours does not appear to completely revert the δ-phase back to the β-phase, the reversion process is definitely underway. This observed reversion process is in agreement with earlier reports[5-7] using the SHG technique.

The aging experiment is performed by cycling the temperature using the same profile several times. As for the 'new' sample, the β-phase is observed to convert to δ-phase and δ-phase reverts back to β-phase upon cooling. With each subsequent cycle, the reversion back to β-phase requires a longer time than the one before. A typical plot shows the changes in the (-102) peak intensity in Figure 4 for the 2nd, 3rd, 4th and 5th cycles. The intensity of the β-phase decreases after each subsequent cycle, indicating that not all the β-phase is reverted during the previous cycle. The conversion from β- to δ- phase is complete at about 100 minutes or 10 minutes after reaching 170 °C. Upon cooling to room temperature, at a total time of 290 minutes, not all the β-phase is recovered, even though all the β-phase is converted to δ-phase at the 110 minute mark. Therefore the degree of β-phase reversion decreases with each cycle.

CONCLUSIONS

X-ray diffraction technique is used to monitor the phase transformation of β- to δ- and back to the β-phase of HMX in PBX9501. The fact that HMX does not revert back to β-phase during cooling leads to the conclusion the phase reversion of HMX in PBX 9501 is influenced by the polymer binder.

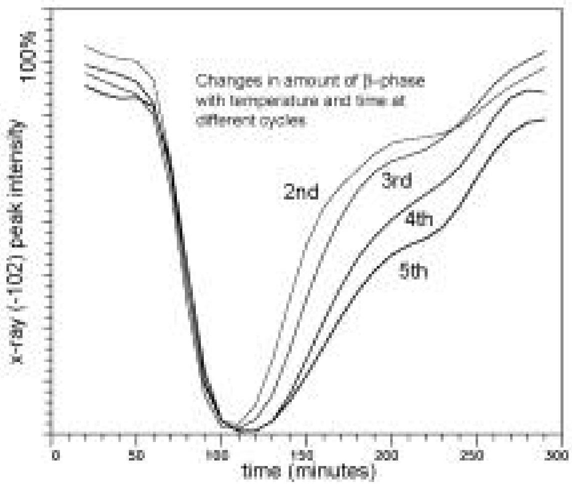

Figure 4. Conversion and reversion of β-phase during and cooling. The same temperature profile as indicated in Figure 3 is used.

When heated to 170 °C, the β-phase fully converts to the δ-phase within the first ten minutes. However, reversion back to β-phase requires at least 2 hours at 130 °C. This reversion time is shown to take longer with each subsequent heating and cooling cycle. This indicates that thermal aging of HMX has a direct correlation with reversion time.

As was described earlier[2], the phase conversion of HMX highly depends on the grain size and therefore on the amount of surface area. This suggests that changes in the surface molecular potentials trigger the phase conversion. Similarly, the current results imply that the surface molecular potentials are influenced by the polymer binder. On each subsequent heating and cooling cycle, this influence is reduced due to the segregation of the binder. Over a long period of time as the polymer binder continues to segregate, this influence may become non-existent. This is demonstrated by the 'old' PBX 9501 sample, for which the phase conversion is observed to be similar to that of neat HMX.

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