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Abstract

Pentaerythritol tetranitrate (PETN) is a secondary explosive used extensively in military and commercial applications. Coarsening of PETN during long-term storage changes the physical properties such as surface area and particle morphology which are important factors in initiation and performance. Doping of impurities has been proposed to slow the coarsening process since impurities have been shown to modify both the kinetic and thermodynamic properties. In this paper, we discuss how doping of PETN with its homologs of dipentaerythritol hexanitrate (diPEHN) and tripentaerytritol octanitrate (triPEON) affect kinetic and thermodynamic parameters. Pure and homolog doped PETN single crystals were prepared by solvent evaporation in acetone at room temperature. Doping concentrations for this study were 1000 ppm, 5000 ppm and 10000 ppm. Activation energy and vapor pressure of pure, and doped PETN, single crystals were obtained from thermogravimetric analysis data.

Key Words: Single crystal, PETN, DiPEHN, TriPEON, Kinetic and Thermodynamic property, vapor pressure.

1. Introduction

Pentaerythritol tetranitrate (PETN) is one of the most powerful explosives used in military applications and mining. PETN is normally used as a powder with a very high surface area and has a high heat of detonation of 1.5kcal/gm compared to other common explosives [1]. Detonation of PETN depends on the particle size distribution of the PETN powder, porosity, particle morphology, surface area, etc. Changes in the morphology, surface area and particle size distribution is proposed to take place by coarsening mechanisms such as sublimation and recrystallization during long term storage [2-8]. Thus, the aging process of PETN is controlled by coarsening which eventually increases the particle size. Performance of PETN is negatively affected with the deterioration of surface area. The initial morphology is dependent on crystal growth kinetics, dislocation and defects in the crystal, temperature and presence of foreign particles. The stability is dependent on how well these parameters are controlled during the growth process of the crystal [9]. By exploiting these properties it should be feasible to make PETN more stable during long term storage with the addition of impurities.

Doping with impurities is widely used to modify the properties of crystalline products [9-13]. These reports summarize that the effect of impurities depend on the chemical nature of both impurity and the crystal face. Sangwal surveyed the adsorption and effect of the impurities on the growth process of bulk crystals extensively [14-16]. Mathematical models associated with the effect of impurities were also reported in those surveys. At lower concentration, impurities modify growth structures such as spirals and hillocks by adsorbing at the kink site, or step edge, and at higher concentration, impurities are randomly distributed on the surface and can be the growth center for initiating new layers. Pitchimani *et al.* investigated morphology changes of PETN crystals doped with cations of zinc, calcium, and sodium [9]. They also qualitatively showed that doping PETN with Zinc ions can increase the thermal stability at both the macro and nano scale. Mridha *et al.* conducted a more detailed study on thermal stability of PETN doped with Zinc ions [17]. They reported that presence of Zinc ions changed the thermodynamic and kinetic properties in PETN showing improved stability. While metal ions have been shown to potentially decrease coarsening in PETN, under long term storage, there may be incompatabilities with the metals, limiting their use. The homologs of PETN are better candidates for stabilization. Both the dimer, dipentaerythritol hexanitrate (diPEHN), and the trimer, tripentaerytritol octanitrate (triPEON), are produced during synthesis of PETN [18] and are more thermally stable compared to PETN [19]. Therefore, doping PETN single crystals with diPEHN and triPEON should be more suitable candidates for stabilizing PETN.

In this paper, kinetic and thermodynamic properties of PETN single crystals doped with diPEHN and triPEON are reported. Single crystals of PETN, and doped crystals, are grown from acetone solution. Thermogravimetry is used to evaluate thermodynamic and kinetic parameters. The vapor pressure data of the pure and PETN homolog doped PETN single crystals is also reported.

1.1 Theory

Thermogravimetric Analysis (TGA) is one of the simplest ways to study the sublimation of a compound. Kinetics of the sublimation process during the isothermal heating in TGA was analyzed by the Arrhenius equation

$$K = K_o e^{\frac{-E_a}{RT}} \tag{1}$$

where E_a is the Activation Energy and K_o is the Arrhenius parameter known as the pre exponential factor, T is the absolute temperature and R is the gas constant. For a zero order process, the Arrhenius equation can be rearranged as

$$ln\frac{dm}{dt} = lnK_o - \frac{-E_a}{RT} \tag{2}$$

where $\frac{dm}{dt}$ is the of mass loss per unit surface area in mg.sec^{-1}.mm^{-2}. The activation energy for sublimation can be determined by the slope of the plot of $ln\frac{dm}{dt}$ vs $1/T$.

TGA can also be used to measure the vapor pressure of various compounds [20-25]. Data from the TGA is incorporated with the Langmuir equation [26] to calculate the vapor pressure given by

$$\frac{dm}{dt} = p\alpha\sqrt{\frac{M}{2\pi RT}} \tag{3}$$

where $\frac{dm}{dt}$ in kg.sec^{-1}.m^{-2}, p is the vapor pressure in Pa, α is the vaporization coefficient which is assume to be 1 in vacuum, M is the molecular weight of the vapor in kg mol^{-1}. In the presence of a foreign gas, the vaporization constant, α, cannot be assumed to be 1. To obtain an accurate vaporization constant, a standard material with known vapor pressure is used. Benzoic acid and

Naphthalene are used as the standard material for this study. Since α cannot be determined a priori, a modified form of the Langmuir equation is used

$$p = V\phi \tag{4}$$

where $V = \frac{\sqrt{2\pi R}}{\alpha}$ and $\phi = \frac{dm}{dt}\sqrt{\frac{T}{M}}$. The vaporization constant is calculated in the form of '*V*'. The value of *V* does not depend on the material or rate of mass loss, it only depends on the coefficient of the vaporization constant which is dependent on the experimental set up. Therefore, the value of *V* obtained from the standard materials should be the same in each experimental setup. The vapor molecular weight, *M*, was the molecular weight of the PETN since the vapor phase is assumed to contain very little amount of doping compound.

Another way to relate vapor pressure and temperature is by the Antoine equation which is written as

$$\log P = A - \frac{B}{T+C} \tag{6}$$

where *A*, *B* and *C* are constants, *T* is the absolute temperature and *P* is the vapor pressure [27]. However, for low vapor pressure compounds like PETN, a modified form of Antoine equation [28] can be used

$$\log P = A - \frac{B}{T} \tag{7}$$

Coefficients of *A* and *B* were calculated using equation (7) for pure and doped PETN single crystals for the temperature range of this study.

2. Experimental

Single crystals of PETN, and doped analogs, were grown in acetone by solvent evaporation. PETN, diPEHN and triPEON were provided from Lawrence Livermore National Laboratory. The solution of PETN was allowed to evaporate slowly to make a supersaturated solution from which the single crystals were grown. Doping concentrations of diPEHN and triPEON were 1000 ppm, 5000 ppm and 10000 ppm with respect to the weight of PETN. The surface area of each crystal was measured for calculating sublimation rate per unit surface area using optical images which were collected with an Olympus SZH stereomicroscope and Image J software [29]. The rate of sublimation of the single crystal was collected using an Instrument Specialist Incorporated (WI, USA) TGA. Data from the TGA was normalized by the surface area of each crystal to obtain sublimation rate per unit area. Single crystals were heated from 100℃, to 135℃, in steps of 5℃, isothermally, from 60 minutes to 260 minutes. Nitrogen gas was used as the purge gas in the TGA and the flow rate was 15 cc/min. Benzoic acid and Naphthalene were used as standard materials for calculating coefficient of vaporization and were obtained from Scholar Chemistry.

3. Result and Discussion

3.1 Kinetic Analysis

The kinetic mechanism of the mass loss, of pure and doped PETN, with isothermal annealing was studied using the Arrhenius equation. The Arrhenius plot for diPEHN and triPEON doped PETN crystals are presented in Figure 1. The evaporation rate for pure and doped PETN crystals increased consistently with temperature. Linearity of the curves shows the rate of mass loss is a zero order process for all samples. Zero order kinetics suggests that the only process taking place during the mass loss is sublimation. The high flow of nitrogen in the TGA, and the zero order kinetics observed, also assured that recrystallization did not take place during the sublimation process. Figure 1 also shows that rate of mass loss per unit surface area for diPEHN and triPEON doped PETN were reduced compared to pure PETN crystal. Pitchimani *et al.* showed that doping with inorganic salt changed the evaporation rate as well as Arrhenius parameters [30]. Rogers *et al.* studied triPEON doped PETN crystals using differential scanning calorimeter (DSC) and Differential Thermal Analysis (DTA) [31]. They reported that the presence of triPEON in PETN can decrease the evaporation rate at lower temperature (<120 ^{o}C). They also showed that increasing the triPEON concentration (>mole fraction 0.02) reduced the heat of fusion significantly. The activation energy of pure, diPEHN doped and triPEON doped single PETN crystals are shown in table 1. A pair wise T-test was conducted between each group that showed there is no significant change at the 95% confidence level. However, there is a general decreasing trend in the activation energy as the doping concentration increases, which is consistent with the result reported by Rogers and Dinegar [31].

3.2.1 Calculation of the Vaporization Coefficient

The vaporization coefficient in the form of '*V*' was calculated using equation (4). The vapor pressure (*P*) and ϕ $(\phi = \frac{dm}{dt}\sqrt{\frac{T}{M}})$ for the standard materials (benzoic acid and naphthalene) were fitted in equation (4) (figure 2) and '*V*' is obtained by the slope of the plot. The vapor pressure of benzoic acid was calculated using the Antoine equation. The coefficient of the Antoine equation for benzoic acid and vapor pressure data of naphthalene were obtained from literature [32, 33]. These standard materials were used since the vapor pressure was in the sublimation range of PETN. The '*V*' value from benzoic acid is was used to calculate the vapor pressure of the material of interest in this study and average '*V*' value was 175641 Pa $kg^{0.5}$ $mol^{0.5}$ sec^{-1} m^{-2}. Naphthalene was used to check the consistency of the '*V*' values. The results showed that '*V*' was similar for both materials.

3.2.2 Vapor pressure of pure and doped PETN single crystals

Figure 3 shows a comparison of the vapor pressure between pure PETN crystal obtained from this study and that of a powder sample by extrapolated by Burnham *et al.* [34] to the same temperature range of this study. Coefficients for the extrapolation were obtained in the temperature range of 30°C to 90°C [34]. The results showed that vapor pressure data obtained from PETN single crystals is lower than that observed on a powder sample. This is not surprising since it is expected that the powders have higher surface area per unit mass compared to a single crystal. In addition, the surface area of the single crystal was only measured at initiation of the experiment and is expected to reduce over time leading to a source of error.

As explained in the experimental section, the doping level was controlled in solution where PETN crystals were grown. It is not claimed that the concentration of doping compound incorporated with the PETN crystal is the same as in the solution. It is not in the scope of this particular study if the doping compound is incorporated into the PETN crystal and the mechanisms may be different for the diPHEN and triPEON doped crystals [5-6]. Vapor pressure data of pure, diPEHN doped and triPEON doped PETN is presented in table 2. The vapor pressure of 1000 ppm diPEHN doped PETN crystals are similar to that of pure PETN crystals at temperatures <130°C. With an increase in DiPEHN concentration to 10000 ppm, vapor pressure of the diPEHN doped PETN crystals decreases. For triPEON doped PETN, the vapor pressure of

PETN crystals grown in 1000 ppm triPEON solution was reduced compared to the pure PETN. With the increase of triPEON doping, the vapor pressure of triPEON doped PETN crystals did not statistically change compared to the 1000 ppm triPEON doping.

Statistical analysis was also performed on the data in table 2 through a pair wise T-test. At the 95% confidence level, all samples, apart from the 1000 ppm diPHEN doped were statistically different than the pure PETN. In addition, all diPHEN doped samples were observed to be statistically different from each other. However, all triPEON doped samples were not statistically different from each other.

Vapor pressure data obtained from this experiment was fitted with the modified Antoine equation as written in equation (7). Parameters (*A* and B) calculated using equation 7 are presented in table 3. These parameters are obtained only in the temperature range of 100^{o}C to 135^{o}C. As PETN has a very low vapor pressure, these parameters should reasonably predict the correct value below 100^{o}C to room temperature. Using the calculated coefficient from the experimental data, vapor pressure of pure PETN at room temperature (25^{o}C) is predicted to be 2.26X10^{-6} Pa which is similar to the literature value (1.82 X10^{-6} Pa) [35].

4. Conclusion

Sublimation properties of pure PETN single crystals and PETN crystals grown in the presence of homologs were investigated using TGA. The results show that the sublimation rate was decreased due to doping with these impurities. Vapor pressure data were obtained for pure and doped PETN crystals at temperatures from 100^{o}C to 135 ^{o}C in steps of 5 ^{o}C. Vapor pressure of doped PETN single crystals was found to be reduced in general with the addition of the impurities. Activation energy of the pure and doped PETN single crystals were also presented in this report where a slight decrease in the activation energy was observed but was not found to be statistically significant. Although the actual concentration of doping compound into the crystal was not measured, changes in the vapor pressure, and rate of sublimation, indicate the presence of doping compound alters the physical properties of PETN. Further analyses are required to quantify how much doping compound is incorporated in the crystal structure and the location of doping compound within the crystal. However this investigation revealed that controlled doping with impurities such as diPEHN and triPEON, which have a similar chemical structure with PETN, can reduce the sublimation rate, thereby slowing the coarsening of PETN.

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Figure 1 Arrhenius plot of diPEHN and triPEON doped PETN crystals. 1(A): Arrhenius plot of pure and diPEHN doped PETN. Figure 1(B): Arrhenius plot of pure and triPEON doped PETN.

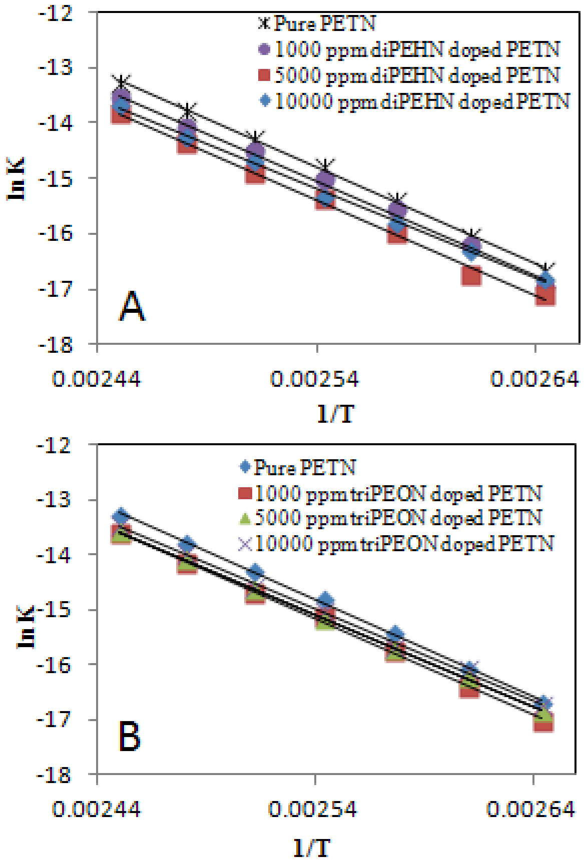

Table 1: Activation Energy of the pure and doped PETN single crystals

Sample	Activation Energy E (kJoule.mole^{-1})
Pure PETN crystal	143.6
1000ppm diPEHN doped PETN	142.7
5000ppm diPEHN doped PETN	140.9
10000ppm diPEHN doped PETN	140.0
1000ppm triPEON doped PETN	144.6
5000ppm triPEON doped PETN	138.7
10000ppm triPEON doped PETN	140.4

Figure 2: Determination of the coefficient of evaporation using the standard materials

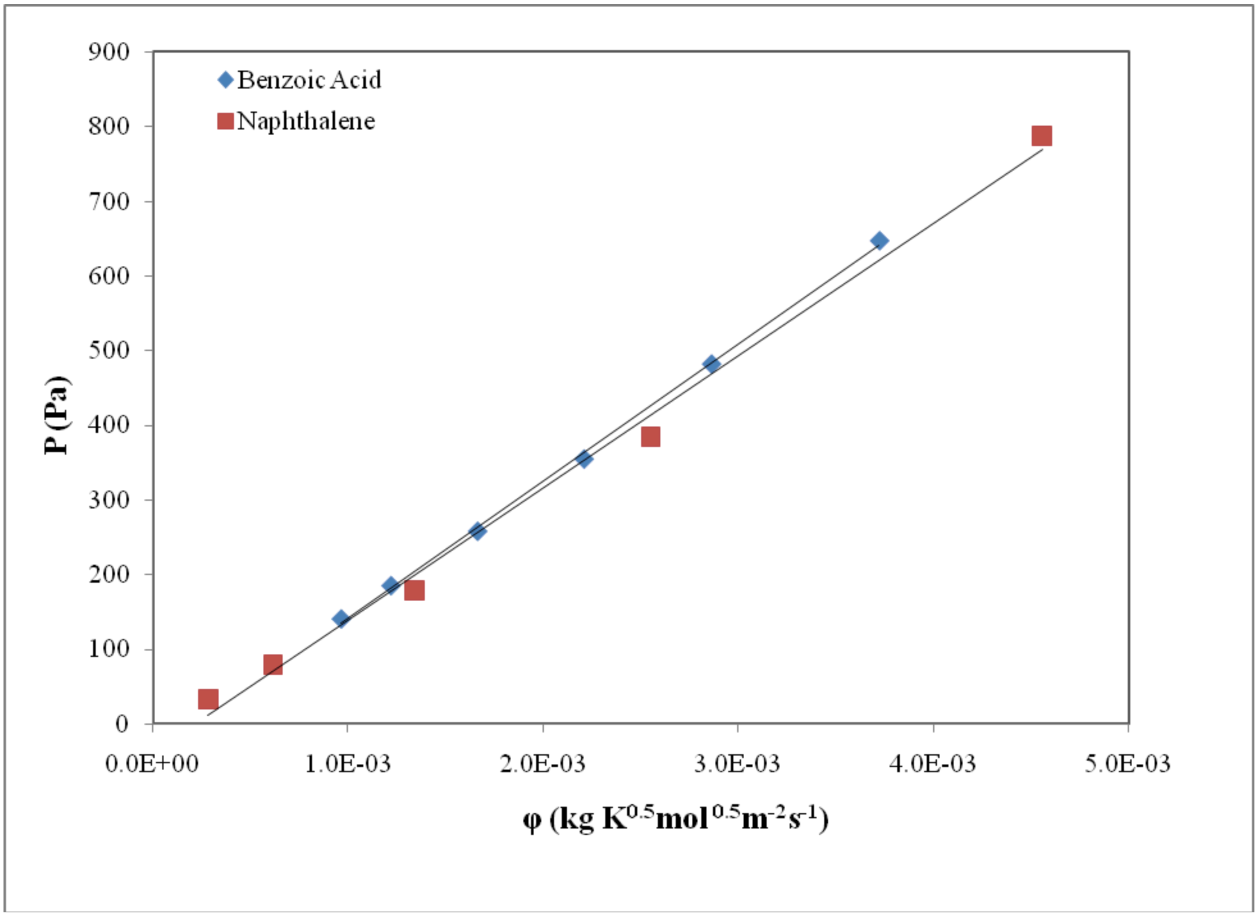

Figure 3: Comparison vapor pressure from the experiment and the literature [33]

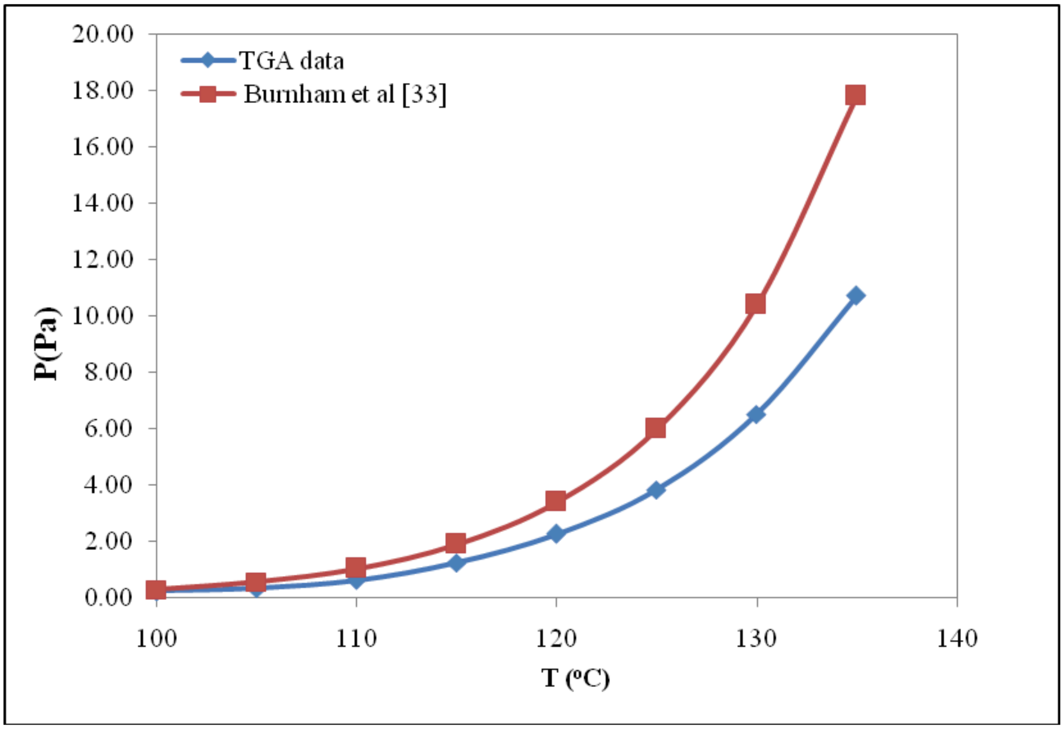

Table 2: Vapor pressure of Pure, diPEHN doped and triPEON doped PETN single crystals.

Temperature (^{o}C)	Vapor Pressure						
	Pure PETN (Pa)	1000 ppm diPEHN doped PETN (Pa)	5000 ppm diPEHN doped PETN (Pa)	10000 ppm diPEHN doped PETN (Pa)	1000 ppm triPEON doped PETN (Pa)	5000 ppm triPEON doped PETN (Pa)	10000 ppm triPEON doped PETN (Pa)
100	0.25	0.20	0.15	0.18	0.19	0.18	0.20
105	0.35	0.31	0.31	0.27	0.29	0.31	0.37
110	0.65	0.59	0.62	0.50	0.51	0.53	0.61
115	1.27	1.19	1.05	1.04	0.94	0.94	1.02
120	2.29	2.26	1.75	1.50	1.69	1.66	1.96
125	3.86	3.74	3.17	2.60	2.91	2.79	2.94
130	6.53	6.51	5.42	4.42	4.89	4.64	5.37
135	10.74	9.68	8.83	7.64	8.37	8.75	9.04

Table 3: Parameters of the Equation $\log p(Pa) = A - \frac{B}{T(K)}$ for pure and doped PETN crystals obtained in the temperature of 100^{o}C --135^{o}C

Parameters	Pure PETN	1000 ppm diPEHN doped PETN	5000 ppm diPEHN doped PETN	10000 ppm diPEHN doped PETN	1000 ppm triPEON doped PETN	5000 ppm triPEON doped PETN	10000 ppm triPEON doped PETN
A	19.12	19.82	19.60	18.45	18.82	18.99	18.40
B	7384	7670	7606	7171	7310.4	7376.5	7128