Thermochimica Acta 620 (2015) 36–39

Contents lists available at ScienceDirect

Thermochimica Acta

journal homepage: www.elsevier.com/locate/tca

Short Communication

The glass transition of trinitrotoluene (TNT) by flash DSC

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ARTICLE INFO

Article history:
Received 25 August 2015
Received in revised form 4 October 2015
Accepted 5 October 2015
Available online 22 October 2015

Keywords:
TNT
Glass transition
Chip calorimetry
Flash DSC
Cold crystallization

ABSTRACT

Flash differential scanning calorimetry has been used to determine the glass transition response of the rapidly crystallizing energetic material, TNT. After heating at 600 K/s, it was found that for cooling rates from 1000 K/s to 10 K/s the glass transition changes from 247.5 K to 239.3 K. The dynamic fragility index was determined to be $m = 62 \pm 6$ and the activation energy determined from the range of cooling rates in which vitrification occurred was found to be 290 ± 16 kJ/mol. Crystallization was found to occur during cooling at rates below 0.3 K/s, whereas cold crystallization was found on subsequent heating after cooling between 10 K/s and 30 K/s. At cooling rates of 100 K/s and above, and for the same heating rate of 600 K/s investigated, the glass transition event was observed, but cold crystallization during heating did not occur. Hence, the crystallization behavior of the fully amorphous TNT upon heating depends on the cooling rate and vitrification path.

1. Introduction

There is significant interest in creating novel materials through physical, rather than chemical, methods. In this respect, taking a rapidly crystallizing material that is generally used in the crystalline state, one may find advantages if the material can be made vitreous by avoiding crystallization. To this end, we have begun a series of works to attempt to make energetic materials that are vitreous in nature with the intent that the defect nature of the glassy material may provide improved properties, such as improved handling and stability or enhanced combustion properties.

In the present work, we use a baseline energetic material, trinitrotoluene (TNT) to demonstrate that such a material can be made vitreous, i.e., can be made into a glass. The method chosen for the demonstration is to use flash differential scanning calorimetry (DSC) to provide a means of cooling the material at a sufficiently high rate that vitrification will occur rather than crystallization. As shown subsequently, the rate at which TNT can be cooled to form a glass is outside the range of cooling rates achievable by normal DSC, but not so high that the flash-type of chip calorimeter is pushed to its limits, i.e., the required cooling rate is nearer to 10 K/s rather than 10^4 K/s that can be achieved with such a calorimeter. In addition to the first direct observation and reporting of the glass transition temperature behavior of TNT, we also find that the crystallization behavior of the TNT from the glassy state is different depending on the cooling rate used to make the glass. While this is a finding that has been seen in, e.g., metallic glass-formers, its observation in the mono-component TNT suggests that fully understanding such phenomena will provide a potential path to control material behavior by varying the route to vitrification.

2. Experimental methods

2.1. Materials

The TNT used in this project was provided by Austin Explosives Company and was used in the present experiment after purification by crystallization from acetone. Silver paste from Ted Pella, Inc. (PELCO High Performance Silver Paste, Product number 16047) was used to create a “reservoir” for the TNT on the chip calorimeter to hold the TNT in place when it was in the liquid state.

2.2. Calorimetry

The calorimetric measurements were made using a Mettler Toledo Flash DSC 1 with Freon intercooler and nitrogen purge. Both heating and cooling scans were made over a temperature range from 178.2 K to 372.2 K (−95 °C to 99 °C). The cooling rates varied from 0.1 K/s to 1000 K/s while the heating rate was kept constant at 600 K/s. (For comparison, conventional DSC is commonly used at ranges of heating or cooling rates from 0.01 to 30 K/min, i.e., 1.7×10^{-4} to 0.5 K/s. [1]). Calibration of the instrument was performed following the manufacturer procedures and using indium as described by Gao et al. [2].

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http://dx.doi.org/10.1016/j.tca.2015.10.003
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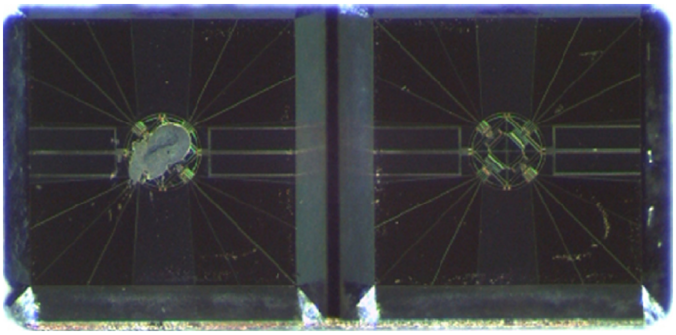

Fig. 1. Image of calorimetery chip sensor showing the silver paste with TNT sample in middle (left side image) along with the reference sensor (right side image).

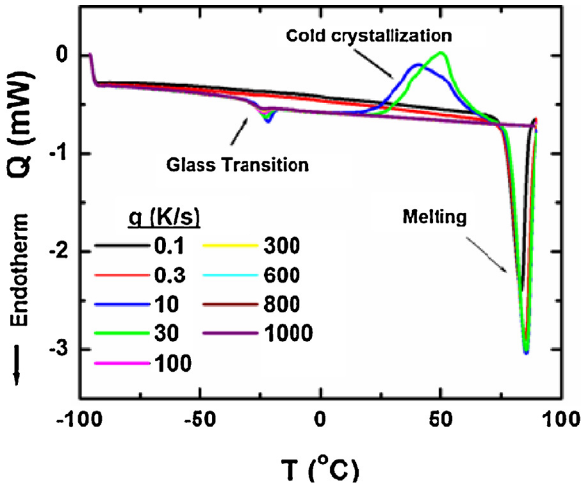

Fig. 2. Heat flow curves for TNT as a function of cooling rate q, as indicated. Heating rate is 600 K/s. Note three regimes: $q > 100$ K/s only glass transition is observed. 10 K/s $< q < 100$ K/s, glass transition, cold crystallization and melting are observed. 0.1 K/s $< q < 10$ K/s, only melting is observed, no glass transition or cold crystallization are observed.

The silver paste was applied in a thin layer to the chip within the borders of the inner "diamond" of approximately 0.5 mm × 0.5 mm area. This paste was applied using an animal hair provided with the instrument. Because the paste dries rapidly, the small crystal (approximately 0.3 mm × 0.3 mm) of TNT was placed onto the paste with the animal hair in a way that a slight indent was created such that the liquid TNT when melted would not flow off of the sensor area. Fig. 1 shows an image of the DSC chip with the silver paste and TNT sample along with the reference side of the chip showing no sample on the sensor portion.

2.3. Analysis

The glass transition temperatures were determined from the fictive temperatures T_f obtained on heating as a function of the cooling rate where the glass was formed, i.e., we use $T_f = T_g$ [1]. At the high cooling rates used in the flash DSC, the overshoots in enthalpy can be large, which can lead to large errors in the values of T_f unless care is taken in the analysis to match the liquid lines and the glass lines when comparing the responses at different cooling rates. In our methodology, we superpose all of the liquid and glass lines for all of the runs of a given sample for the different cooling rates. This technique also provides good liquid lines for samples cooled at low rates. The fictive temperatures are then determined using the same liquid and glass lines for all of the runs.

The values of T_f were obtained using the Moynihan area matching method, which, through integration of Eq. (1), determines T_f as the point of intersection of the glassy enthalpy with the extrapolated equilibrium enthalpy line [1,3]:

$$\int_{T_f}^{T \gg T_g} (C_{p,l} - C_{p,g})dT = \int_{T \ll T_g}^{T \gg T_g} (C_p - C_{p,g})dT \tag{1}$$

where $C_{p,l}$ is the liquid state heat capacity, $C_{p,g}$ is the glass state heat capacity, C_p is the apparent heat capacity as a function of temperature, T is temperature, T_f is fictive temperature and T_g is the glass transition temperature.

The glass temperature is a function of cooling rate and can be analyzed in the context of the Vogel [4], Fulcher [5], Tammann [6] (VFT) equation as:

$$q(T_g) = q_0 \exp\left[\frac{-B}{T_g - T_0}\right] \tag{2}$$

where $q(T_g)$ is the cooling rate associated with a given glass transition temperature T_g (or fictive temperature T_f), q_0, B, and T_0 are fitting parameters, with the latter two having some physical significance and the other being thought of as a prefactor. In particular, for the VFT temperature dependence of the behavior, the B parameter has a role similar to an activation energy/R (the universal gas constant), and the parameter T_0 is the VFT temperature where the relaxation time or viscosity would diverge to infinity, perhaps at an 'ideal' glass transition. Furthermore, from the VFT parameters, one can determine the activation energy at the glass temperature E_g and the dynamic fragility m of the material through the equations [7–10]:

$$E_g = \frac{RB}{\left[1 - T_0/T_g\right]^2} \tag{3}$$

$$m = \frac{B/T_g}{\ln(10)\left[1 - T_0/T_g\right]^2} \tag{4}$$

When the range of glass transition temperatures to be investigated is small enough (curvature on the plot of $\ln q$ vs. $1/T_f$ is low), as the case here, the VFT equation can be replaced with an Arrhenius equation, in which case the data can be analyzed using the following equations [11,12]:

$$q(T_g) = q_0 \exp\left(\frac{-E}{RT_g}\right) \tag{5}$$

$$m = \frac{E_g}{\ln 10\, RT_g} \tag{6}$$

3. Results

3.1. Glass transition temperature of TNT

Fig. 2 shows the heat flow curves that result upon heating the TNT material after cooling at rates from 0.1 K/s to 1000 K/s. The first thing we remark upon is that for cooling rates of 100 K/s or above, we did not get crystallization of the TNT upon reheating at 600 K/s. Only the glass transition is seen upon reheating of the TNT at 600 K/s. At lower cooling rates two types of behavior are seen. First, at 10 K/s and 30 K/s we see that there is a glass transition event and, at somewhat higher temperatures, one sees a cold crystallization exotherm followed by a melting endotherm. At even lower cooling rates ($q = 0.1$ and 0.3 K/s) one does not see the glass transition event and only melting is seen upon reheating, indicating that full crystallization of the TNT occurred during cooling before the heating scan.

The cooling rate dependence of the fictive temperature for rates at and above 10 K/s where a glass transition event was observed is shown in Fig. 3. Using the fact that $T_g = T_f$ we find that the