Journal of Thermal Analysis, Vol. 36 (1990) 1155-1160

THERMAL BEHAVIOUR ON 2,2,2-TRINITROETHYL-4,4,4-TRINITROBUTYRATE

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(Received October 30, 1989)

The enthalpies of the crystal transformation from I to II and from II to III and the melting enthalpy of 2,2,2-trinitroethyl-4,4,4-trinitrobutyrate (TNETB) are determined by means of Calvet microcalorimeter. On cooling, the supercooing from liquid to solid does not appear, and form II will transform to form I when 71.8°C is reached. The phase diagrams of TNETB-2,4,6-trinitrotoluene (TNT) and TNETB-polyester systems have been constructed by differential scanning calorimetry (DSC). The eutectic temperatures are 56°C and 34°C respectively. The compositions corresponding to the eutectic points are 52 and 46 weight percent TNETB respectively.

2,2,2-trinitroethyl-4,4,4-trinitrobutyrate (TNETB) is a main ingredient of cast explosives. Three polymorphic crystalline forms of TNETB have been observed by Rosen [1]. The aim of this paper is to study the crystal transformation of TNETB and its phase change from solid to liquid and to characterize its thermal behaviour below 100°. In this work, the phase diagrams of TNETB-2,4,6-trinitrotoluene (TNT) and TNETB-polyester systems have also been drawn by differential scanning calorimetry (DSC). From the point of view of casting process of explosive, these phase diagrams are of great importance, especially with respect to liquidus and solidus curves, the eutectic points and other melting temperatures.

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Experimental

TNETB was prepared by our Institute and purified by recrystallization in acetone before use. Its purity was more than 99.5%. Polyester (M = 2500) and TNT were industrially procured. TNT was also purified by recrystallization in acetone before use.

The enthalpies of the crystal transformation of TNETB and the melting enthalpies of TNETB and TNT were measured using a Tian-Calvet type microcalorimeter from Setaram, France, which has a sensitivity of 66.5 μv/mw and equipped with two 15 ml - vessels. The precision of enthalpy measurement is 2%. Sample size used was about 100 mg.

The measurement of the phase diagram for the binary systems TNETB-TNT and TNETB-polyester was carried out on a Shanghai Balance Manufactures' CDR-1 differential scanning calorimeter, using a Ni/Cr-Ni/Si thermoelement and working under static ambient conditions. The heating rate is 2 deg/min. The error in reading of temperature is less than 0.25°.

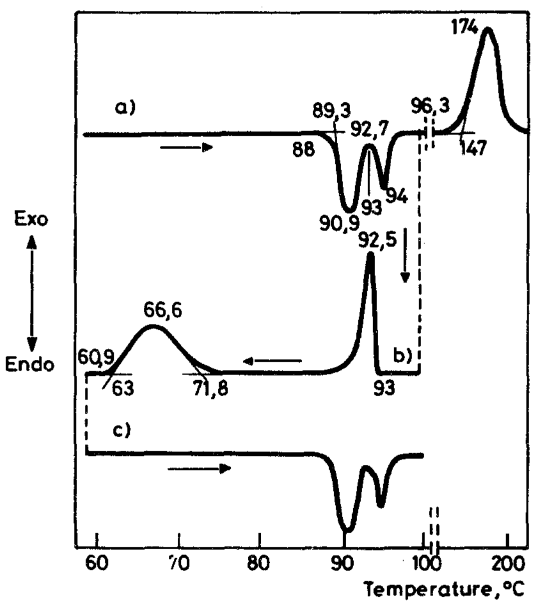

Fig. 1 DSC curves of TNETB. (a) upon heating (4.7 deg/h); (b) upon cooling (3.4 deg/h); (c) upon heating once more (4.7 deg/h)

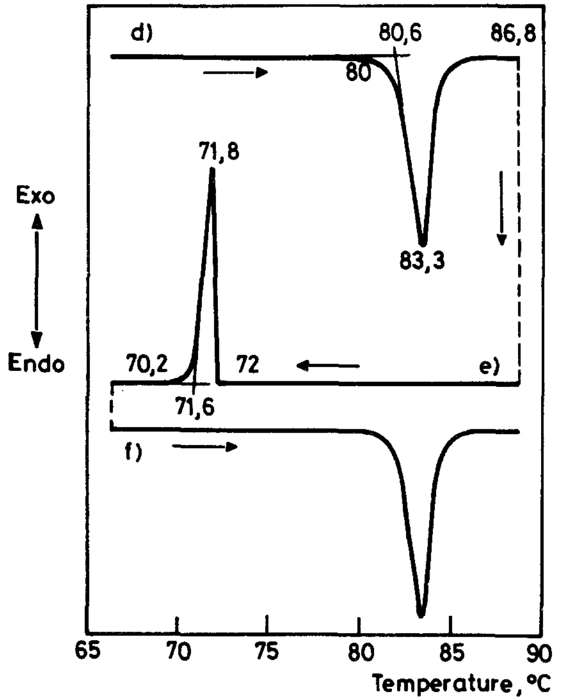

Fig. 2 DSC curves of TNT. (d) upon heating (7.8 deg/h); (e) upon cooling (15.5 deg/h); (f) upon heating once more (7.8 deg/h)

Aluminum oxide is used as reference material. Mixed samples were prepared by mixing varying amounts of TNETB and TNT (or polyester).

Results and discussion

Thermal behaviour of TNETB

Figure 1 shows the DSC curves of TNETB. The curve (a) consists of three endothermic peaks and one exothermic peak. The first endothermic peak begins at 89.3° with summit peak at 90.9°.It is due to the crystal transformation from I to II. The second endothermic peak at 93° is the crystal transformation from II to III. From Fig. 1 it can be seen that form III appears to be stable over a very narrow temperature range on the order of 0.2 to 0.3° deg near 93°. The third endothermic peak at 94° is the phase change from solid to liquid. The exothermic peak at 174° is caused by the rapid decomposition reaction.

Table 1 The melting points for TNETB-TNT and TNETB-polyester systems

TNETB-TNT		TNETB-polyester	
TNETB, wt %	Melting point, °C	TNETB, wt %	Melting point, °C
0.00	80.6	0.00	51.0
3.50	80.0	3.00	50.2
7.50	79.2	6.85	48.5
11.5	77.5	10.7	47.0
15.0	76.8	14.1	46.0
18.3	75.5	17.1	45.1
21.8	74.1	21.3	44.5
25.4	72.5	25.0	43.7
29.5	70.7	28.8	42.5
33.8	68.5	32.9	40.9
37.9	66.3	36.5	39.0
41.9	63.9	39.8	37.4
45.5	61.6	42.8	35.8
48.1	59.1	46.0	34.0
52.5	56.0	47.1	43.4
55.6	59.0	49.3	60.8
58.1	61.7	51.5	73.7
62.1	65.0	56.2	79.5
65.9	68.3	60.5	80.7
69.8	71.5	65.0	81.4
73.5	74.2	68.5	81.8
77.8	77.1	73.2	82.5
81.6	79.5	77.9	83.5
85.3	81.7	82.6	84.5
89.5	84.1	86.8	85.7
93.2	86.4	90.1	86.6
95.7	87.8	93.1	87.8
97.3	89.0	95.5	88.8
98.8	90.7	98.0	90.4
100	94.0	100	94.0

The enthalpies of the crystal transformation from I to II and from II to III for TNETB are 29.00 ± 0.32 and 0.90 ± 0.01 kJ/mol respectively. The melting enthalpy and the decomposition heat of TNETB are 5.02 ± 0.06 and 572 kJ/mol respectively.

On cooling, the supercooling from liquid to solid does not appear, and form II will transform to form I when 71.8° is reached. The curve (c) obtained upon second heating is the same as curve (a).

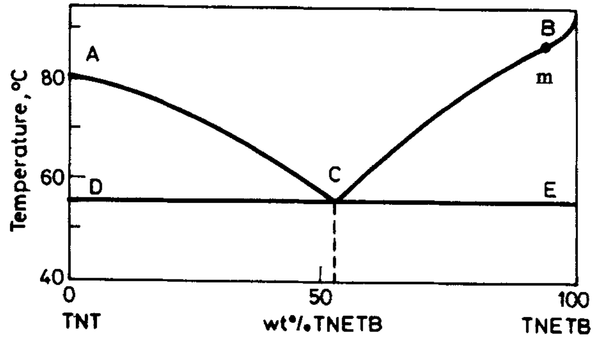

Fig. 3 Phase diagram for binary system TNETB-TNT

The DSC curves of TNT are shown in Fig.2. An endothermic peak begins at its melting point (80.6°) with summit peak at 83.3° and an exothermic peak at 72° with summit peak at 71.8°.

The solidifying point of TNT is 80.6° (= 72° observed plus 8.6° for supercooling). The melting enthalpy and the solidification heat for TNT are 22.41 and 22.40 kJ/mol respectively.

The phase diagrams of binary systems TNETB-TNT and TNETB - polyester

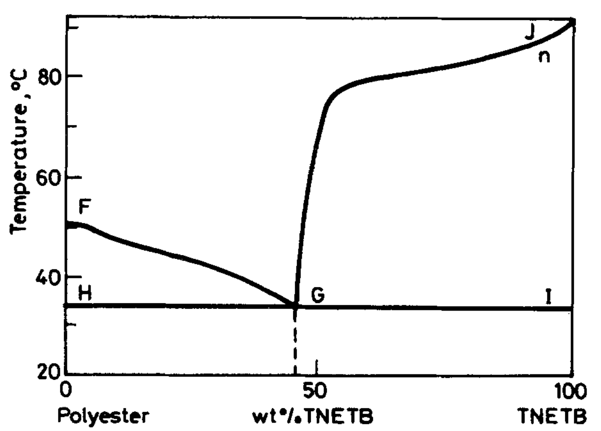

Fig. 4 Phase diagram for binary system TNETB-polyester

Table 1 lists the melting points for two pairs of organic compounds, TNETB-TNT and TNETB-polyester. The phase diagrams obtained by data in Table 1 show in Figs 3 and 4.

The curve AC in Fig. 3 gives the melting points of TNT when in contact with TNETB. The curve CB gives the melting points of TNETB when in contact with TNT. The curves AD, DE and EB are solidus curves for the system TNETB-TNT. The point C of 56^{o} without change in composition is the eutectic point for the system TNETB-TNT at atmospheric pressure. The composition corresponding to the point C is 52 ±0.5 weight percent TNETB.

In Fig. 4 are given the liquidus and solidus curves for TNETB-polyester system. The points F and J are the melting point of polyester and TNETB respectively. The point G of 34^{o} is the eutectic point for the system TNETB-polyester. It corresponds to 46 weight percent TNETB.

The transition points m and n in curves CB and GJ are attributed to the crystalline transition of TNETB.

Reference

1 AD 764-340 (1971) p 376.

Zusammenfassung — Mittels eines Calvet-Mikrokalorimeters wurden die Enthalpien für die Kristallumwandlungen I/II bzw. II/III sowie die Schmelzenthalpie von 2,2,2-Trinitroethyl-4,4,4-trinitrobutyrat (TNETB) bestimmt. Beim Abkühlen tritt keine Unterkühlung der flüssigen Phase auf und bei Erreichen von 71.8°C wandelt sich Form II in Form I um. Mittels DSC wurden die Phasendiagramme von TNETB - 2,4,6-Trinitrotoluol sowie einiger TNETB-Polyester-Systeme ermittelt. Eutektika treten bei 56°C bzw. 34°C auf. Die Zusammensetzung im Eutektikum beträgt 52 bzw. 46 Massenprozente TNETB.