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Phase diagram and compatibility of the binary systems TNT–polyester and TNT–picric acid ☆

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Abstract

The phase diagrams of 2,4,6-trinitroluene (TNT)–polyester and TNT–picric acid (PA) are constructed by differential scanning calorimetry (DSC). Their eutectic temperatures are 49.5 and 61.5°C, respectively. The compositions corresponding to the eutectic points are 44.4 and 68.4 wt.% of TNT respectively. The compatibility of TNT–polyester and TNT–PA systems has also been investigated. The experimental data indicate that the TNT–polyester system has poor compatibility above 240°C, but the TNT–PA system has good compatibility both at ambient temperature and higher temperatures.

Keywords: Binary system; Compatibility; Phase diagram; Picric acid; Polyester; TNT

1. Introduction

2,4,6-Trinitrotoluene (TNT), polyester and picric acid (PA) are widely used as composite explosives. However, the thermodynamic characteristics and compatibilities of TNT–polyester and TNT–PA systems at higher temperatures have not yet been reported. In this work, the binary phase diagrams of TNT–polyester and TNT–PA systems are constructed and the compatibilities of the systems have been estimated by means of DSC. These phase diagrams and compatibilities are very useful for casting and storage of explosives.

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2. Experimental

TNT, polyester ($M = 2500$) and PA were commercially procured. Mixed samples were prepared by mixing various percentages of TNT and polyester or PA.

The measurements were carried out in a CDR-1 differential scanning calorimeter (Shanghai Balance Instrument Factory, China) using a Ni/Cr–Ni/Si thermoelement. The instrument reads temperature to within 0.25°C. When the measurements for the phase diagram were made, the experimental conditions were as follows: DSC sensitivity ± 20.92 mJ s^{-1}; sample mass, 10 mg; heating rate, 2°C min^{-1}; paper speed, 20 mm min^{-1}; atmosphere, static air; reference material, α-Al_2O_3; crucibles of aluminium (diameter 5 mm × 3 mm) were used. When the compatibility experiments of TNT–polyester and TNT–PA systems were conducted, 1.0 mg of TNT, 1.0 mg/1.0 mg of TNT–polyester or TNT–PA mixture were sealed in a stainless steel crucible. The heating rate was calculated according to the actual rate at which the temperature rose from 50°C to the end of the reaction. Other experimental conditions were the same as mentioned above. The apparent activation energy was calculated according to the Kissinger equation using the linear least squares method [1].

3. Results and discussion

3.1. Construction of phase diagram for TNT–polyester and TNT–PA systems

The results in Table 1 show the eutectic compositions and temperatures of TNT–polyester and TNT–PA binary systems. The phase diagrams obtained using the data in Table 1 are shown in Figs. 1 and 2.

The points A and B in Fig. 1 are the melting points of polyester and TNT respectively. The curve AC in Fig. 1 shows the melting points of polyester in contact with TNT. The curve CB gives the melting points of TNT in contact with polyester. The curves AD, DE and EB are solidus lines for the TNT–polyester system. The point C of 49.5°C with constant composition is the eutectic point for the TNT–polyester system under atmospheric pressure. The composition corresponding to point C is 44.4 wt.% of TNT.

In Fig. 2, the liquidus and solidus lines for the TNT–PA system are given. The points A′ and B′ are the melting point of PA and TNT respectively. The point C′ of 61.5°C is the eutectic point for the system TNT–PA. It corresponds to 68.4 wt.% of TNT.

3.2. The compatibility of TNT–polyester and TNT–PA systems

Typical DSC curves of pure polyester, PA, TNT and 50/50 TNT–polyester or 50/50 TNT–PA mixtures are shown in Fig. 3. The DSC curve of TNT (curve III) contains one endothermic peak and one exothermic peak. The endothermic peak at 79.00°C is caused by the phase change of TNT from solid to liquid. The decompo-

Table 1
Melting points for TNT–polyester and TNT–PA systems

TNT–polyester		TNT–PA	
TNT/wt.%	Melting point/°C	TNT/wt.%	Melting point/°C
0.0	52.8	0.0	122.0
6.4	52.9	5.0	118.0
11.7	51.8	11.0	114.0
15.0	51.5	17.5	110.0
19.8	51.3	24.0	106.0
26.7	51.0	29.0	102.0
34.9	50.5	34.0	98.0
40.9	50.3	44.2	89.3
44.4	49.5	55.0	79.5
51.8	75.0	59.5	73.8
59.5	75.5	66.0	63.5
65.0	75.8	68.4	61.5
69.8	76.5	72.0	65.0
74.8	76.8	74.0	66.3
84.9	77.0	80.0	70.5
89.7	78.5	84.6	74.0
94.9	79.5	96.0	78.0
100	80.5	100	80.5

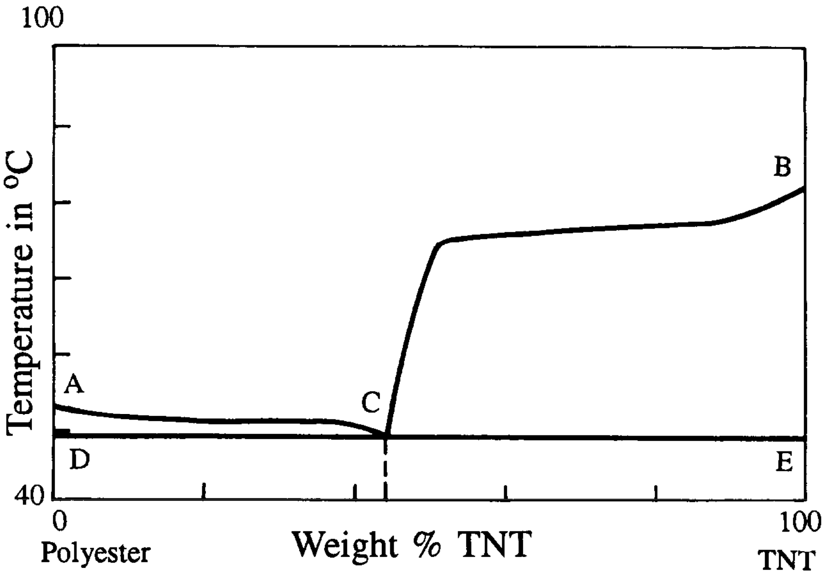

Fig. 1. Phase diagram for the TNT–polyester binary system.

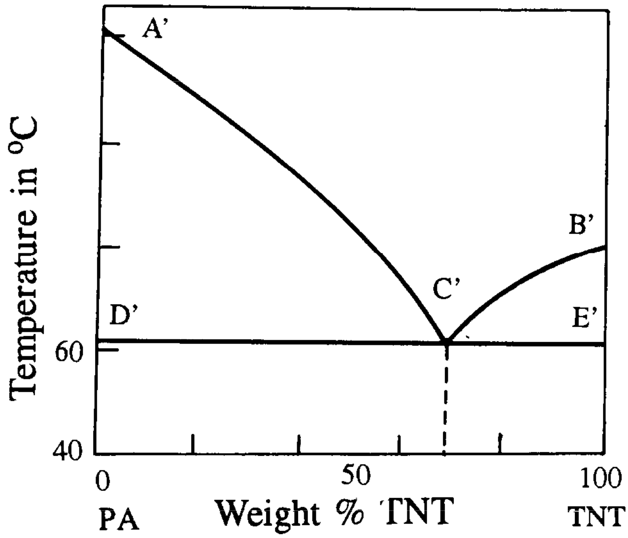

Fig. 2. Phase diagram for the TNT–PA binary system.

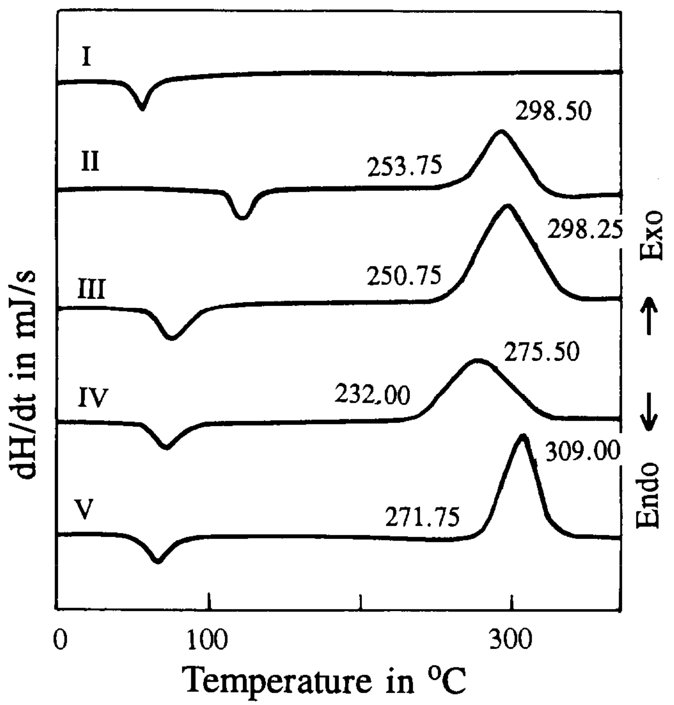

Fig. 3. Typical DSC curves of pure polyester (I), PA (II), TNT (III), TNT–polyester (IV) and TNT–PA (V) (heating rate 5°C min^{-1}).

Table 2
Evaluated standards of compatibility for explosive and contacted material [2]

Criteria		
ΔT_m/°C	$\frac{\Delta E}{E}$/%	Rating
Less than or equal to 2	Less than 20	Good compatibility
Less than or equal to 2	Greater than 20	Fair compatibility
Greater than 2	Less than 20	Poor compatibility
Greater than 2	Greater than 20	Bad compatibility

sition of TNT begins at 250.75°C with a summit peak at 298.50°C. For TNT–polyester mixture (curve IV), the decomposition begins at 232.00°C with summit peak at 275.50°C. The maximum exothermic peak temperature difference between TNT and TNT–polyester mixture (ΔT_m) is −23.0°C.

The apparent activation energies obtained by Kissinger's equation for pure TNT and TNT–polyester mixture are 99.21 and 96.34 kJ mol^{-1} respectively. The percentage change of the apparent activation energy $\Delta E/E$ between pure TNT and TNT–polyester mixture is 2.89%.

From curve V, it can been seen that decomposition reaction of the TNT–PA mixture begins at 271.75°C with the summit exothermic peak at 309.00°C. The maximum exothermic peak temperature difference between pure TNT and TNT–PA mixture is +10.5°C.

The apparent activation energy obtained by Kissinger's equation for TNT–PA mixture is 114.76 kJ mol^{-1}. The percentage change of the apparent activation energy between pure TNT and TNT–PA mixture ($\Delta E/E$) is 15.68%. The value of ΔT_m for the TNT–polyester mixture is greater than 2°C and $\Delta E/E$ is less than 20%. According to the standards of compatibility evaluated in Table 2, we think that the compatibility of TNT with polyester is poor over 240°C. The experimental data obtained by the weight loss method show that the compatibility of TNT–polyester mixture at 100°C is good. The TNT–PA mixture must have good compatibility because ΔT_m is less than 2°C and the value of $\Delta E/E$ is less than 20%.

4. Conclusions

(1) The phase diagrams of systems TNT–polyester and TNT–PA are constructed by differential scanning calorimetry (DSC). Their eutectic points are 49.5 and 61.5°C respectively. The compositions corresponding to the eutectic points are 44.4 and 68.4 wt.% of TNT.

(2) According to the evaluated standard of compatibility, we think that the TNT–polyester mixture has a poor compatibility over 240°C, but the compatibility of the TNT–PA mixture is good.

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