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COMPATIBILITY STUDY OF 1,3,3-TRINITROAZETIDINE WITH SOME ENERGETIC COMPONENTS AND INERT MATERIALS

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The compatibility of 1,3,3-trinitroazetidine (TNAZ) with some energetic components and inert materials of solid propellants was studied by using the pressure DSC method. Where, cyclotetramethylenetetranitroamine (HMX), cyclotrimethylenetrinitramine (RDX), nitrocellulose (NC), nitroglycerine (NG), 1.25/1-NC/NG mixture, lead 3-nitro-1,2,4-triazol-5-onate (NTO-Pb), aluminum powder (Al powder) and N-nitrodihydroxyethylaminedinitrate (DINA) were used as energetic components and hydroxyl terminated polybutadiene (HTPB), carboxyl terminated polybutadiene (CTPB), polyethylene glycol (PEG), polyoxytetramethylene-co-oxyethylene (PET), addition product of hexamethylene diisocyanate and water (N-100), 2-nitrodianiline (2-NDPA), 1,3-dimethyl-1,3-diphenyl urea (C_2), carbon black (C.B.), aluminum oxide (Al_2O_3), cupric 2,4-dihydroxybenzoate (β-Cu), cupric adipate (AD-Cu) and lead phthalate (φ-Pb) were used as inert materials. The results showed that the binary systems of TNAZ with HMX, NC, NG, NC+NG and DINA are compatible, with RDX and Al powder are slightly sensitive, with NTO-Pb, β-Cu, AD-Cu, C.B. and Al_2O_3 are sensitive, and with HTPB, CTPB, PEG, PET, N-100, 2-NDPA, C_2 and φ-Pb are incompatible.

Keywords: *compatibility, DSC, energetic components, inert materials, 1,3,3-trinitroazetidine (TNAZ)*

Introduction

1,3,3-Trinitroazetidine (TNAZ) is an energetic compound containing one nitroamine and one geminal-dinitroalkyl group, which can be used as a main ingredient of cast explosives and propellants [1]. The reactivity or compatibility of TNAZ with some energetic components and inert materials is one of the most aspects of TNAZ in practical application. There are a few reports on the thermal behavior of TNAZ and its compatibility with some materials [2–9], seldom, however, has the compatibility of TNAZ with some energetic components and inert materials used in propellants been reported. In this work, their compatibilities under non-isothermal condition investigated by means of pressure DSC [10–15] are reported.

Experimental

Materials

1,3,3-Trinitroazetidine (TNAZ) was prepared by Xi'an Modern Chemistry Research Institute. Its purity was more than 99.4%. Cyclotetramethylenetetranitroamine (HMX), cyclotrimethylenetrinitramine (RDX), nitrocellulose (NC, 12.3%N), nitroglycerine (NG), 1.25/1–NC/NG mixture, lead 3-nitro-1,2,4-triazol-5-onate (NTO-Pb), aluminum powder (Al powder, 13.8 μm) and N-nitrodihydroxyethylaminedinitrate (DINA) used as energetic components, and hydroxyl terminated polybutadiene (HTPB, M=3000), carboxyl terminated polybutadiene (CTPB, M=4500), polyethylene glycol (PEG, M=6000), polyoxytetramethylene-co-oxyethylene (PET, M=4000), addition product of hexamethylene diisocyanate and water (N-100), 2-nitrodianiline (2-NDPA), 1,3-dimethyl-1,3-diphenyl urea (C_2), carbon black (C.B.), aluminum oxide (Al_2O_3), cupric 2,4-dihydroxybenzoate (β-Cu), cupric adipate (AD-Cu) and lead phthalate (φ-Pb) used as inert materials were industrially procured. Mixtures of TNAZ and energetic component or inert material were prepared with 50% TNAZ.

Experimental equipment and conditions

All measurements were made with a model DSC 910S differential scanning calorimeter made in American TA Company.

The conditions of DSC were as follows: sample mass, about 2.00 mg; heating rate, 10°C min^{-1}; atmosphere, static nitrogen, 1 MPa; reference sample, α-Al_2O_3. The TNAZ, energetic component or inert material of 2.00 mg or mixture of 50/50-TNAZ/energetic component or 50/50-TNAZ/inert material of 1.00 mg/1.00 mg was sealed in a sealed aluminum cell.

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Table 1 Data of the energetic component and 50/50-TNAZ/energetic component binary system obtained by pressure DSC*

System		Rating		
mixture system	single system	T_{p2}/°C	T_{p1}/°C	ΔT_p/°C
50/50-TNAZ/HMX	TNAZ	285.33	264.68	–20.65
50/50-TNAZ/RDX	RDX	235.40	238.89	3.49
50/50-TNAZ/NC	NC	207.70	209.46	1.76
50/50-TNAZ/NG	NG	207.55	203.76	–3.79
50/50-TNAZ/(NC+NG)	NC+NG	207.62	204.20	–3.42
50/50-TNAZ/Al	TNAZ	260.75	264.68	3.93
50/50-TNAZ/NTO-Pb	NTO-Pb	238.33	248.70	10.37
50/50-TNAZ/DINA	DINA	211.97	210.38	–1.59

*Mixture system, 50/50-TNAZ/energetic component binary system; single system, system of the neat energetic component, which exothermic peak temperature is smaller of the two neat components; T_{p1}, the maximum exothermic peak temperature of single system; T_{p2}, the maximum exothermic peak temperature of mixture system; $\Delta T_p = T_{p1} - T_{p2}$

Results and discussion

Compatibility of TNAZ with some energetic components

Typical DSC curves of systems 1–17 are shown in Fig. 1. Their maximum exothermic peak temperatures are shown in Table 1, and the evaluated standards of compatibility for explosive and contacted materials [10] are listed in Table 2.

From Fig. 1 and Table 1, the following observations can be made.

- The DSC curve of the TNAZ-DINA mixture shows one endothermic peak and three exothermic peaks. The endothermic peak of 44.82°C without change in composition is the eutectic point for the system TNAZ/DINA at 1 MPa. When TNAZ and DINA were mixed, the binary eutectic solid system came into being, which melting point is much lower than that of neat TNAZ (99.78°C) and of neat DINA (50.87°C).
- DSC curve of HMX consists of two endothermic peaks and one exothermic peak. The first peak at 194.76°C is due to the crystal transformation from α to δ. The second endothermic peak at 280.02°C is the phase change from solid to liquid. The exothermic peak at 286.05°C is caused by the rapid decomposition reaction.
- The endothermic peaks of TNAZ, RDX and DINA are caused by the phase change from solid to liquid. The endothermic peaks of binary systems **1–17** are due to the melting process of TNAZ.
- The exothermic peak temperature of the TNAZ-HMX mixture is higher 20.65°C than that of neat TNAZ and 0.72°C than that of neat HMX, which suggests that the presence of HMX stabilized TNAZ and TNAZ has little influence on HMX.
- The maximum exothermic peak temperature different between TNAZ and TNAZ- HMX mixture (ΔT_p) is –20.65°C. The values of ΔT_p are 1.76°C between NC and TNAZ-NC binary system, –3.79°C between NG and TNAZ-NG binary system, –3.42°C between NC-NG mixture and TNAZ-NC-NG mixture and –1.59°C between DINA and TNAZ-DINA binary system. According to the standards of compatibility evaluated in Table 2, we think that the binary systems TNAZ-HMX, TNAZ-NG, TNAZ-DINA and TNAZ-(NC+NG) have good compatibility because ΔT_p is less than 2°C.
- The values ΔT_p of between RDX and TNAZ-RDX mixture, and Al powder and TNAZ-Al mixture are 3.49 and 3.93°C, respectively. This phenomenon indicates that the decomposition reaction of the mixture is ready to take place and the mixture has fair compatibility.
- The value of ΔT_p between NTO-Pb and TNAZ-(NTO-Pb) mixture is 10.37°C which is consistent with the destabilization of NTO-Pb by the presence of TNAZ . This means an increase in reactive ability and a decrease in the thermal stability of the mixture. The compatibility of NTO-Pb with TNAZ is poor over 230°C.

Table 2 Evaluated standards of compatibility for explosive and contacted materials

Criteria	Rating*	
ΔT_p/°C		
less than or equal to 2	A	compatible or good compatibility
3–5	B	slightly sensitized or fair compatibility
6–15	C	sensitized or poor compatibility
15–above	D	hazardous or bad compatibility

*A – safe for use in any explosive design; B – safe for use in testing, when the device will be used in a very short period of time, not to be used as a binder material, or when long-term storage is desired; C – not recommended for use with explosive items; D – hazardous, do not use under any conditions

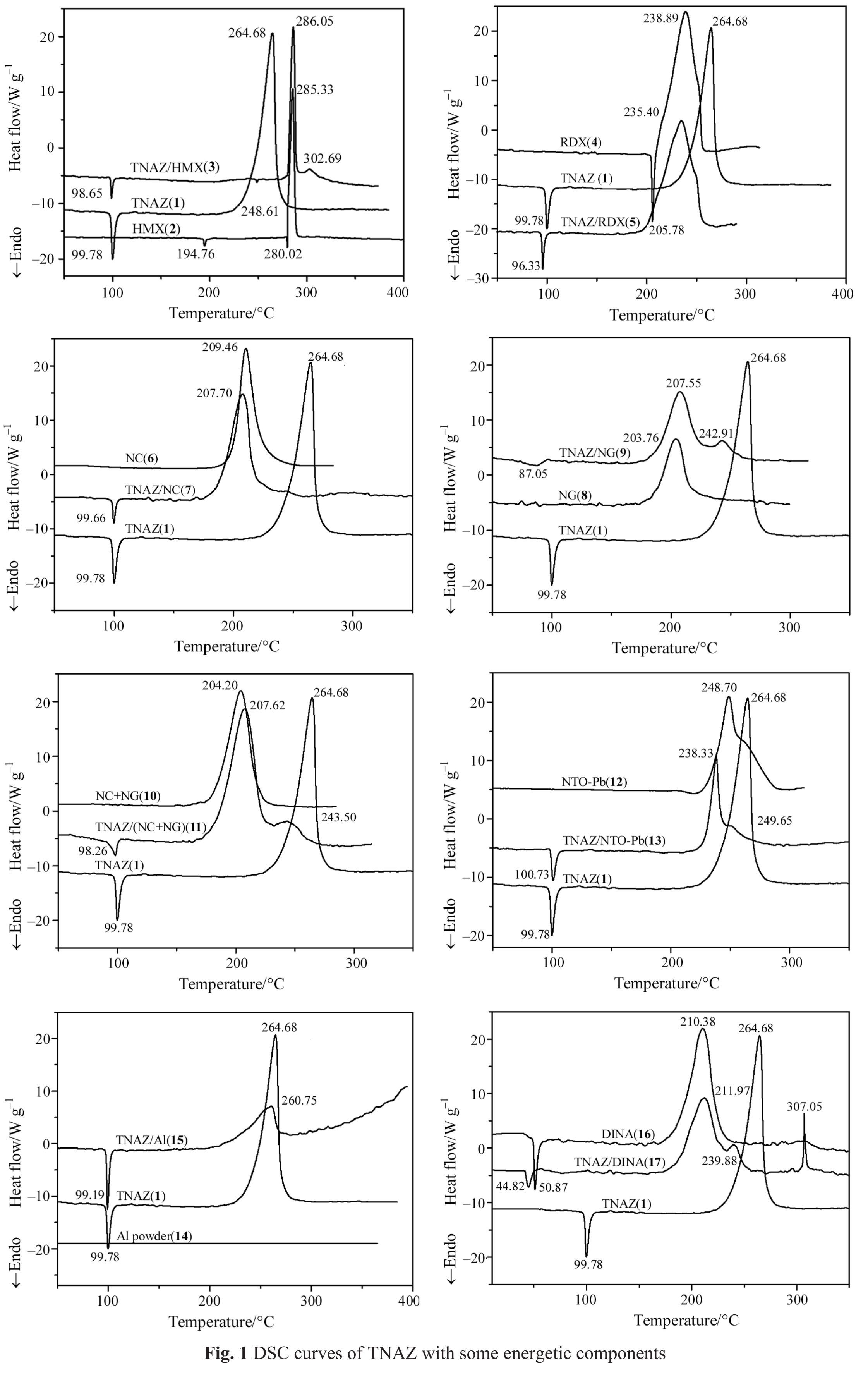

Fig. 1 DSC curves of TNAZ with some energetic components

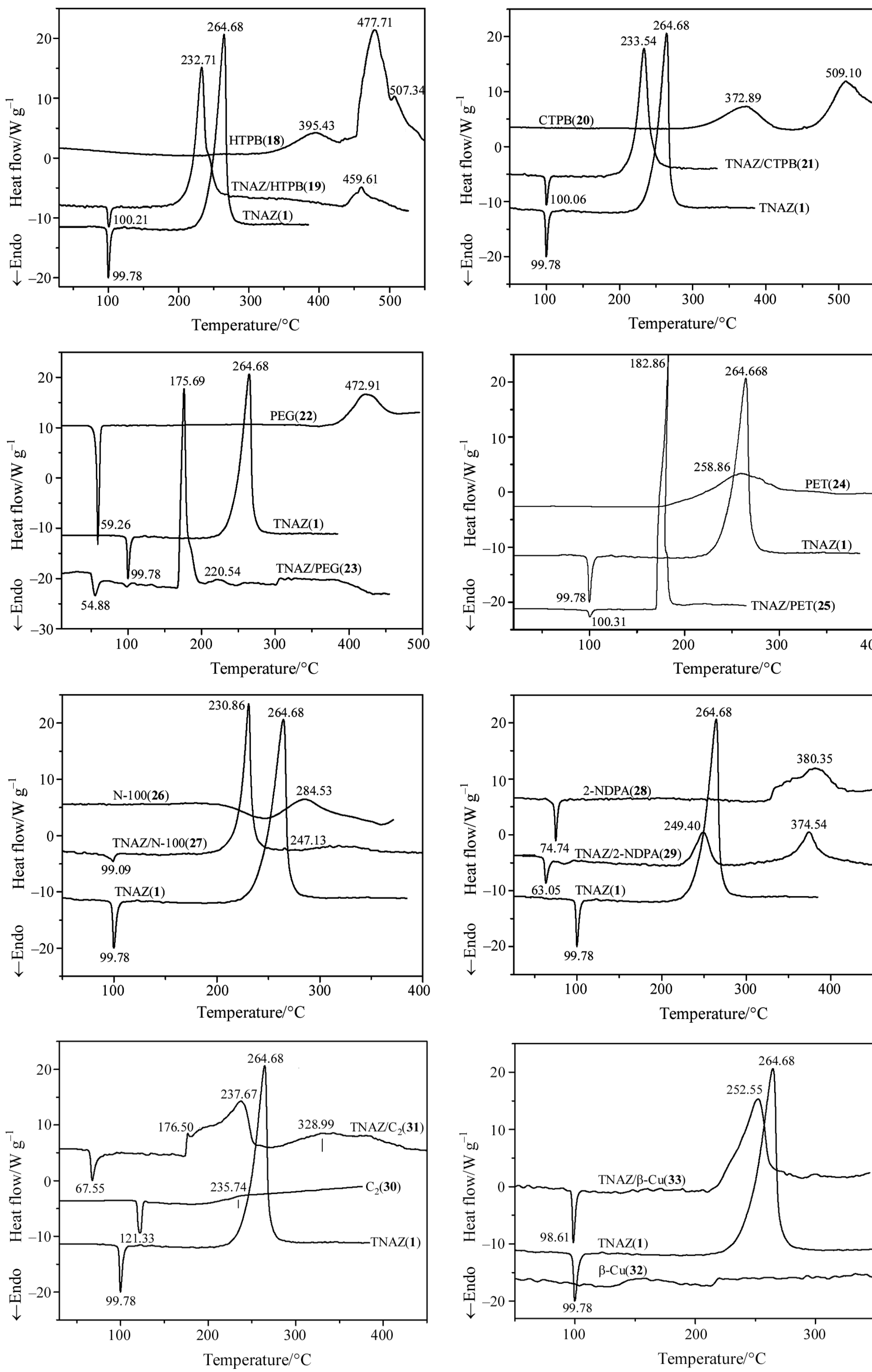

Fig. 2a DSC curves of TNAZ with some inert materials

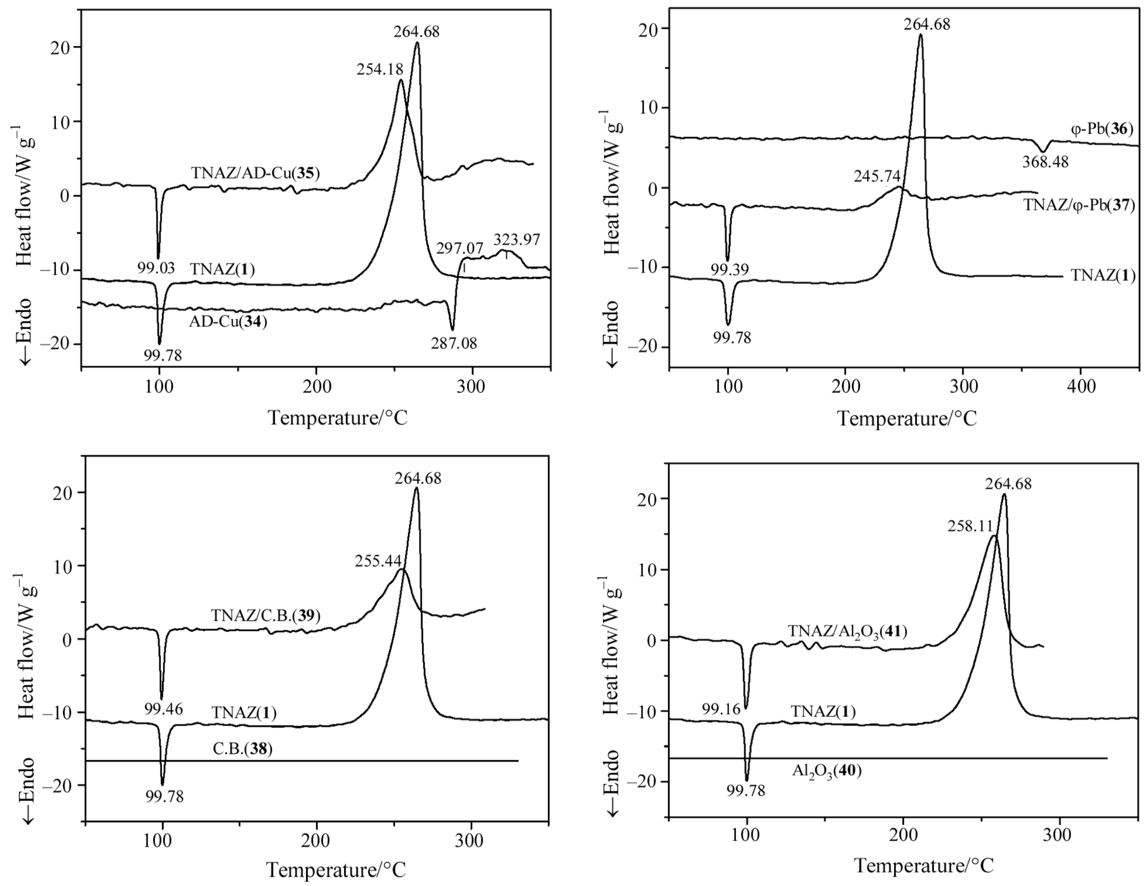

Fig. 2b DSC curves of TNAZ with some inert materials

Table 3 Data of the inert material and 50/50-TNAZ/inert material binary system obtained by pressure DSC*

System		Rating		
mixture system	single system	T_{p2}/°C	T_{p1}/°C	ΔT_p/°C
50/50-TNAZ/HTPB	TNAZ	232.71	264.68	31.97
50/50-TNAZ/CTPB	TNAZ	233.54	264.68	31.14
50/50-TNAZ/PEG	TNAZ	175.69	264.68	88.99
50/50-TNAZ/PET	PET	182.86	258.86	76.00
50/50-TNAZ/N-100	TNAZ	230.86	264.68	33.82
50/50-TNAZ/2-NDPA	TNAZ	249.40	264.68	15.28
50/50-TNAZ/C_2	C_2	176.50	235.74	77.24
50/50-TNAZ/β-Cu	TNAZ	252.55	264.68	12.13
50/50-TNAZ/AD-Cu	TNAZ	254.18	264.68	10.50
50/50-TNAZ/φ-Pb	TNAZ	245.74	264.68	18.94
50/50-TNAZ/C.B.	TNAZ	255.44	264.68	9.24
50/50-TNAZ/Al_2O_3	TNAZ	258.11	264.68	6.57

*the meanings of marks in Table 3 are same as in Table 1

- The compatibility of binary systems TNAZ/energetic component decrease in the order **3**>**9**>**11**>**17**>**7**>**5**>**15**>**13**.
- The relative thermal stability of binary systems TNAZ/energetic component decreases in the order **3**>**15**>**13**>**5**>**17**>**7**≈**11**≈**9**.

The compatibility of TNAZ with some inert materials

Typical DSC curves of systems 18–41 are shown in Fig. 2. Their maximum exothermic peak temperatures are shown in Table 3.

From Fig. 2 and Table 3, the following observations can be made.

- The DSC curves of TNAZ-PEG, TNAZ-(2-NDPA), TNAZ-C_2 mixtures show one endothermic peak each. The endothermic peaks temperatures 54.88, 63.05 and 67.55°C are the eutectic points for the systems TNAZ/PEG, TNAZ/2-NDPA and TNAZ/C_2, respectively.
- The values of ΔT_p between TNAZ with TNAZ-(β-Cu), TNAZ-(AD-Cu), TNAZ-C.B. and TNAZ-Al_2O_3 are 12.13, 10.50, 9.24 and 6.57°C, respectively, showing that the increase of the rate of the decomposition reaction or reactivity and the poor compatibility of the mixture.
- The values of ΔT_p between TNAZ or C_2 and TNAZ-HTPB, TNAZ-CTPB, TNAZ-PEG, TNAZ-PET, TNAZ-(N-100), TNAZ-(2-NDPA), TNAZ-C_2 and TNAZ-(φ-Pb) mixtures are greater than 15°C, indicating that these binary systems are extremely incompatible.
- All the inert materials examined promoted the decomposition of TNAZ in a certain extent.
- The compatibility of binary systems TNAZ/inert material decrease in the order **41**>**39**>**35**>**33**>**29**>**37**>**21**>**19**>**27**>**25**>**31**>**23**.

Conclusions

The reactivity or compatibility of the TNAZ-energetic component mixture and TNAZ-inert material mixture under the liner temperature increase condition at a heating rate of 10°C min^{-1} at 1 MPa had been investigated by means of pressure differential scanning calorimetry. According to the evaluated standard of compatibility, we considered that the TNAZ-HMX, TNAZ-NC, TNAZ-NG, TNAZ-(NC+NG) and TNAZ-DINA binary mixtures have good compatibility, and the TNAZ-RDX and TNAZ-Al binary mixtures have fair compatibility, but the compatibilities of the TNAZ-(NTO-Pb), TNAZ-(β-Cu), TNAZ-(AD-Cu), TNAZ-C.B. and TNAZ-Al_2O_3 binary mixtures are poor. The compatibilities of the TNAZ-HTPB, TNAZ-CTPB, TNAZ-PEG, TNAZ-PET, TNAZ-(N-100), TNAZ-(2-NDPA), TNAZ-C_2 and TNAZ-(φ-Pb) mixtures are bad.

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