

Exothermic behaviors in decomposition of three solid organic peroxides by DSC and VSP2

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Abstract The decomposition of organic peroxides by their relatively weak oxygen linkage and hydroperoxide radical in the presence of reaction solution is one of the thermal hazards for triggering a runaway reaction. Runaway incidents may occur in oxidation reactors, vacuum condensation reactors, tank lorries, or storage tanks. In NFPA 432 organic peroxides in NFPA 432 are classified as flammable. The exothermic behaviors of solid organic peroxides, dicumene peroxide, benzoyl peroxide, and lauroyl peroxide, were determined by differential scanning calorimetry (DSC), and vent sizing package 2 (VSP2). Relevant data detected by DSC provided thermal stability information, such as exothermic onset temperature (T_0), maximum heat-releasing peak (T_{\max}), and heat of decomposition (ΔH_d). VSP2 was used to perform the bench scale situation for pushing the expected or unexpected reaction to undergo runaway reaction. Onset temperature, maximum pressure, self-heating rate ($(dT dt^{-1})_{\max}$), and pressure-release rate ($(dP dt^{-1})_{\max}$) were therefore obtained and explained. These results are essentially crucial in process design for an inherently safer approach.

Keywords Differential scanning calorimetry (DSC) · Exothermic behaviors · Runaway incidents · Solid organic peroxide · Vent sizing package 2 (VSP2)

Introduction

Organic peroxides (OPs), including solid organic peroxides (SOPs), and liquid organic peroxides (LOPs), are widely used in industrial processes for the initiation of polymerization and as curing or cross-linking agents [1, 2]. However, a critical factor for OPs, which have relatively weak oxygen linkage and hydroperoxide radical in the presence of reaction solution, is one of thermal hazards in triggering a runaway incident [3–5].

Lauroyl peroxide (LPO), benzoyl peroxide (BPO), and dicumyl peroxide (DCPO) are SOPs usually applied in many chemical reactions. These SOPs can be used for copolymerization and polymerization so that the reaction temperature is usually around 100–140 °C [1]. The threshold temperatures of many exothermic SOPs are below 120 °C and sometimes even as low as ambient temperature [6]. For this reason, many runaway accidents may occur on oxidation reactors or storage tanks.

LPO is a white solid with a soapy fragrance. It has a powerful free radical source containing more than 4.0 mass% of active oxygen and is applied as a polymerization initiator or polymerization catalyst [7]. It has been used in bleaching agents, waxes, and catalysts. It decomposes rapidly and causes fire and explosion hazard, upon heating and under influence of light or mixing with incompatible chemicals [8].

BPO, which is widely applied in the chemical industry, is a non-toxic, colorless, and tasteless solid that generally contains less than 5 mass% or 15–50 mass% water in commercial products [9]. BPO is essentially thermally

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unstable and susceptible degrades to form organic acid such as benzoic acid [10].

DCPO is one of the most applied peroxides in polymers [11]. It is broadly employed in cross-linking agent for ethylene vinyl acetate (EVA) copolymers, ethylene propylene terpolymer (EPT), and curing agent for unsaturated polystyrene (PS) [12, 13]. DCPO is also applied to enhance physical properties in architectural materials, electronics, and electric insulators [12].

Our aim was to apply differential scanning calorimetry (DSC) and VSP2 to confirm the thermokinetic parameters, such as maximum temperature (T_{\max}), onset temperature (T_0), temperature of no return (T_{NR}), maximum pressure (P_{\max}), maximum temperature rise ($(dT dt^{-1})_{\max}$), and maximum pressure rise ($(dP dt^{-1})_{\max}$). The results could provide thermal hazard information about LPO, BPO, and DCPO in the process industries to establish a proactive emergency program.

Experimental and method

Samples

As listed in Table 1, three SOPs, LPO, BPO, and DCPO, were selected for this study. The experimental samples were LPO of 95 mass%, BPO of 75 mass%, and DCPO of 98 mass%, which appeared as white crystalline solid and were stored in a refrigerator at 4 °C. The experimental method, such as preparatory estimate, DSC, and VSP2, was proposed earlier [10–13].

Differential scanning calorimetry (DSC) tests

Dynamic scanning experiments were performed on a Mettler TA8000 system coupled with a DSC 821° measuring test crucible (Mettler ME-26732) that could withstand relatively high pressure ca. 100 bar. For the sake of acceptable thermal equilibrium, a heating rate (β) was chosen by 4 °C min⁻¹ and the test cell was fastened by a special kit and then dynamic scanning was performed by initiating the programmed setting.

DSC is a very popular tool for evaluating thermal hazards and investigation mechanisms of reactive chemicals [14–16]. The experimental conditions were as follows:

- (1) Heating rate: 4 °C min⁻¹.
- (2) Materials mass: ca. 5 mg.
- (3) Temperature range: 30–300 °C.
- (4) Test cell: These gold-plated high-pressure crucibles, which can be pressed together, have been confirmed to be very potent for thermal safety investigation. However, they can only be used for one measurement with a maximum pressure of 15 MPa. The lid is pressed onto the crucible with a pressure of about a ton; therefore the seal tightens the crucible. A toggle press is used to close the crucible.

VSP2 tests

VSP2, which is a PC-governed adiabatic calorimeter system manufactured by Fauske and Associates, LLC (FAI) [17], was used to acquire thermokinetic and thermal hazard data, such as self-heating rate ($(dT dt^{-1})_{\max}$), and pressure-release rate ($(dP dt^{-1})_{\max}$) [18]. The low heat capacity of the cell warranted that all the reaction heat released remained within the tested sample [19, 20]. Thermokinetic and pressure phenomena in the same test cell (112 mL) usually could be tested without any difficult extrapolation to the process scale because of the low thermal inertia factor (Φ) of ca. 1.05–1.32 [21, 22].

In this study, we manufactured a new type of test cell for solid samples such as LPO, BPO, and DCPO and to avoid bursting the VSP2. For the exothermic data, the VSP2 tests were run with ca. 5 g SOPs. Here, all the results showed that the three crystalline SOPs were first melted, followed by runaway excursion as temperature and pressure increased with time.

Results and discussion

Thermal analysis by DSC tests

The initially exothermal T_0 , T_{\max} , ΔH_d of LPO, BPO, and DCPO with H₂SO₄ or NaOH were obtained by DSC. The scanned results are in Figs. 1, 2, 3 and Tables 1, 2, 3. The heat release rate versus temperature for the thermal decomposition of 98 mass% LPO mixed with H₂SO₄ or

Table 1 Thermokinetic parameters of 98 mass% LPO by DSC at heating rate of 4 °C min⁻¹

SOPs		Incompatibility		$T_0/^\circ\text{C}$	$T_{\max}/^\circ\text{C}$	$\Delta H_d/\text{J g}^{-1}$
Material	Mass/mg	Material	Mass/mg			
LPO 98 mass%	4.7	–	–	88	109	581
	5.0	6 N H ₂ SO ₄	1.41	62	109	559
	4.97	6 N NaOH	1.46	90	112	527

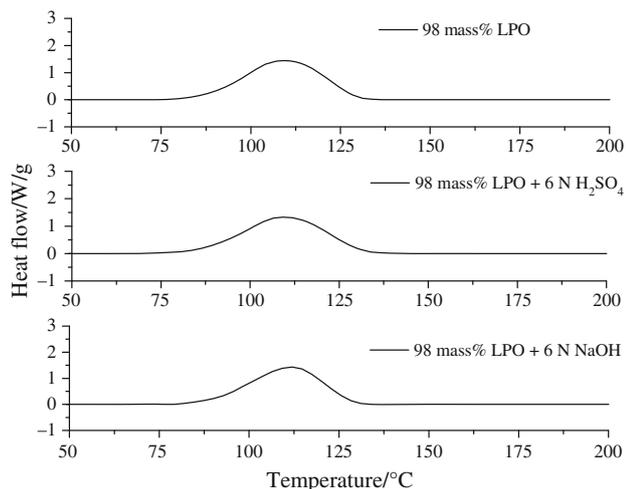


Fig. 1 Thermal curves of various incompatible solutions mixed with LPO by DSC at 4 °C min⁻¹

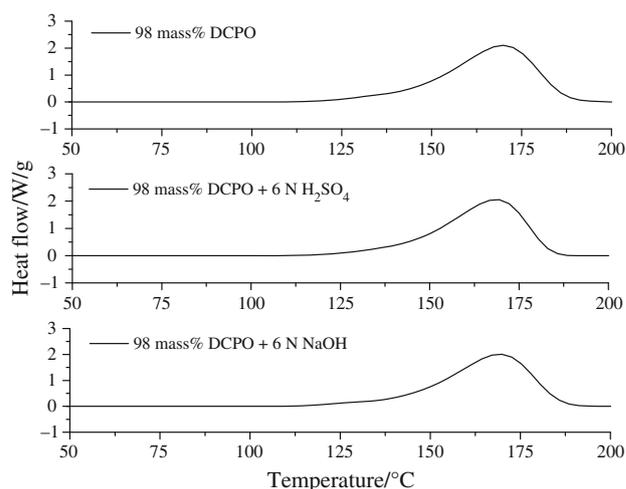


Fig. 3 Thermal curve of various incompatible solutions mixed with DCPO by DSC at 4 °C min⁻¹

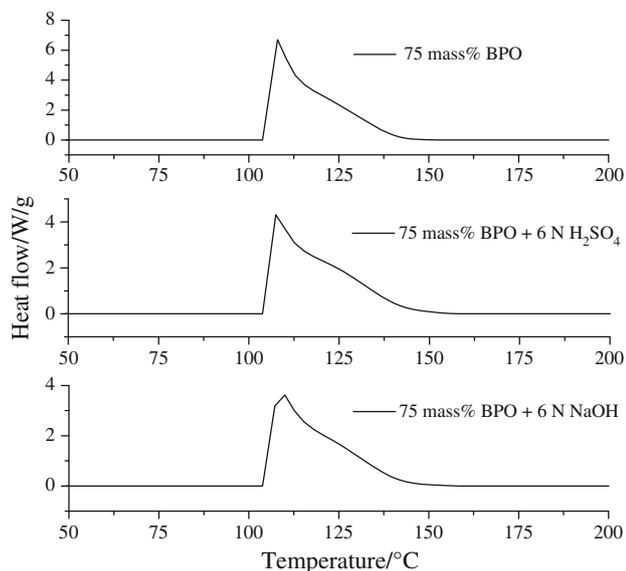


Fig. 2 Thermal curves of various incompatible solutions mixed with BPO by DSC at 4 °C min⁻¹

NaOH is summarized in Fig. 1. The T_0 and ΔH_d are reported in Table 1.

Figure 1 shows the typical heat flow curves versus temperature for the thermal decomposition of 98 mass% LPO in H_2SO_4 or NaOH. Instead of severe exothermic reaction, when LPO was mixed with H_2SO_4 or NaOH, the results indicated that all exothermic peaks were mild. However, as likely the LPO mixed with acid for which T_0 occurred earlier than NaOH, as given in Table 1. According to the results of DSC tests, the T_0 noticeably reduced and pushed the reaction process to be unstable. LPO mixed with H_2SO_4 will be more dangerous because of lower T_0 that will exacerbate the thermal hazard or increase the hazard risk of handling LPO.

To investigate the thermal decomposition hazard of 75 mass% BPO, DSC at 4 °C min⁻¹ heating rate was applied to determine the hazard information, as shown in Table 2 and Fig. 2. The BPO exothermic results are given in Table 2. Lu et al. [9] also measured the BPO decomposition reaction of 50, 75, and 98 mass% BPO by DSC. They described the ΔH_d changed with different concentration as 771.1–1047.8 J g⁻¹. According to our experimental results, which show the ΔH_d of BPO, BPO mixed with H_2SO_4 , and BPO mixed with NaOH are equal to 1,045, 1,229, and 975 J g⁻¹, respectively. The results reveal that when BPO was mixed with H_2SO_4 , the ΔH_d was increased from 1,045 to 1,229 J g⁻¹. Zaman et al. [10] described the BPO with weak oxygen bond, which when broken leads to a tendency toward more stable substance.

Wu et al. [23] measured the heat of decomposition reaction of 99.3 mass% DCPO using DSC. The results of ΔH_d and T_0 were 741 J g⁻¹ and 112 °C. According to our experiments evaluating the thermal hazard of 98 mass% DCPO, DSC at 4 °C min⁻¹ of heating rate was applied to acquire thermal hazard information, as displayed in Table 3 and Fig. 3. Figure 3 shows that DCPO decomposed reaction was at ca. 112 °C. The thermokinetic parameters of 98 mass% DCPO are given in Table 3. T_0 of DCPO mixed with incompatible solutions showed that the exothermic reaction was determined to be about 911, 850, and 863 J g⁻¹, respectively, for DCPO, DCPO mixed with H_2SO_4 , and DCPO mixed with NaOH.

Thermal analysis by VSP2 tests

We attempted to partially validate the similarity of DSC results by VSP2. Furthermore, we could understand the

Table 2 Thermokinetic parameters of 75 mass% BPO by DSC at 4 °C min⁻¹ of heating rate

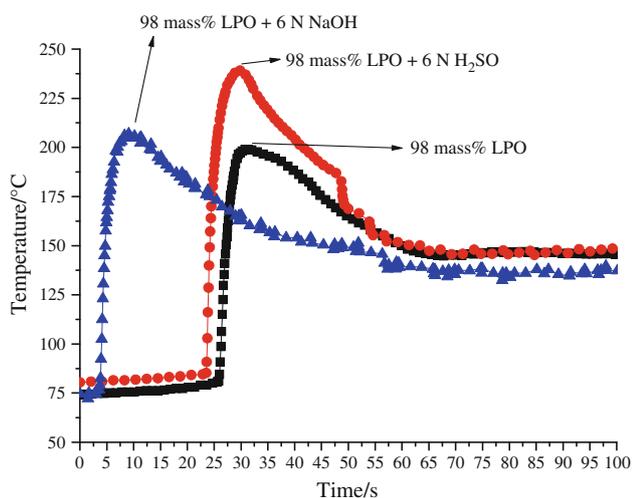
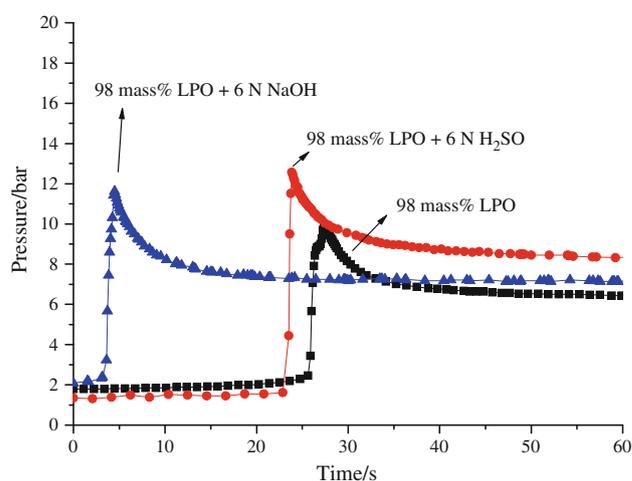
SOPs		Incompatibility		$T_0/^\circ\text{C}$	$T_{\text{max}}/^\circ\text{C}$	$\Delta H_d/\text{J g}^{-1}$
Material	Mass/mg	Material	Mass/mg			
BPO 75 mass%	5.12	–	–	102	107	1,045
	4.94	6 N H ₂ SO ₄	1.44	104	107	1,229
	5.43	6 N NaOH	2.07	105	108	975

Table 3 Thermokinetic parameters of 98 mass% DCPO by DSC at heating rate of 4 °C min⁻¹

SOPs		Incompatibility		$T_0/^\circ\text{C}$	$T_{\text{max}}/^\circ\text{C}$	$\Delta H_d/\text{J g}^{-1}$
Material	Mass/mg	Material	Mass/mg			
DCPO 98 mass%	5.13	–	–	113	169	911
	5.03	6 N H ₂ SO ₄	1.5	112	169	850
	5.04	6 N NaOH	1.74	112	169	863

Table 4 VSP2 test results for 98 mass% LPO mixed with various incompatibilities

SOPs		Incompatibility		$T_0/^\circ\text{C}$	$T_{\text{max}}/^\circ\text{C}$	$P_{\text{max}}/\text{bar}$	$(dT/dt)_{\text{max}}/^\circ\text{C min}^{-1}$	$(dP/dt)_{\text{max}}/\text{bar min}^{-1}$
Material	Mass/mg	Material	Mass/mg					
LPO 98 mass%	5	–	–	66	199	10	5,366	579
		6 N H ₂ SO ₄	2.5	65	239	13	6,784	1,035
		6 N NaOH	2.5	72	205	12	5,539	812

**Fig. 4** Temperature versus time for thermal decomposition of 98 mass% LPO and LPO mixed with 6 N H₂SO₄ or 6 N NaOH by VSP2**Fig. 5** Pressure versus time for thermal decomposition of 98 mass% LPO and LPO mixed with 6 N H₂SO₄ or 6 N NaOH by VSP2

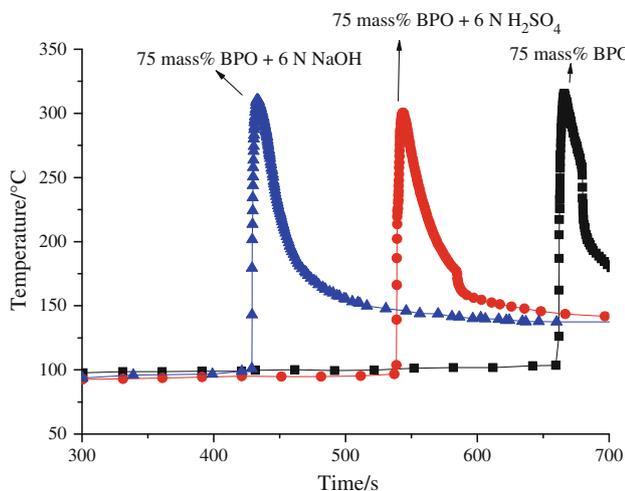
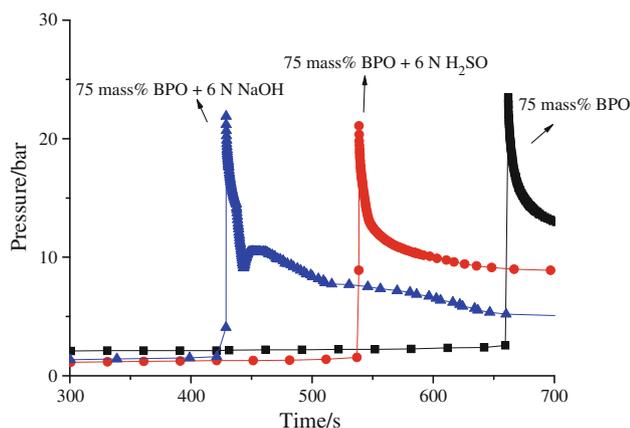
thermal hazard phenomena, when the runaway reaction increased or reduced the disasters potential.

Table 4 lists the thermal safety parameters T_0 , T_{max} , maximum pressure (P_{max}), $((dT/dt)_{\text{max}})$, and $((dP/dt)_{\text{max}})$ of 98 mass % LPO by VSP2. Figures 4 and

5 show the thermal decomposition of 98 mass% LPO mixed with H₂SO₄ or NaOH by VSP2. When LPO was mixed with incompatible solutions, it resulted in rapid increases in pressure and temperature. LPO demonstrated greater degree of thermal hazard and instability, and the

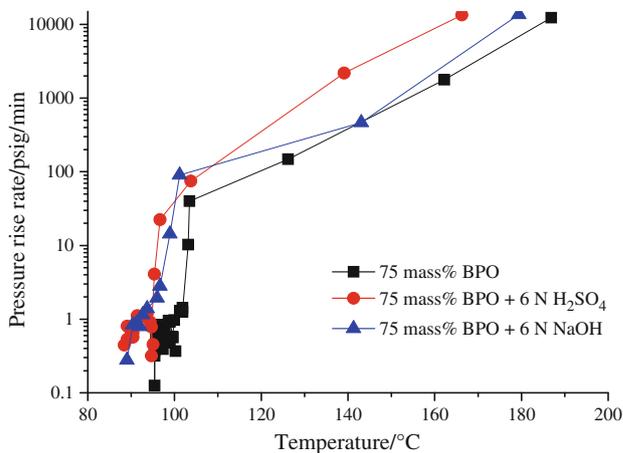
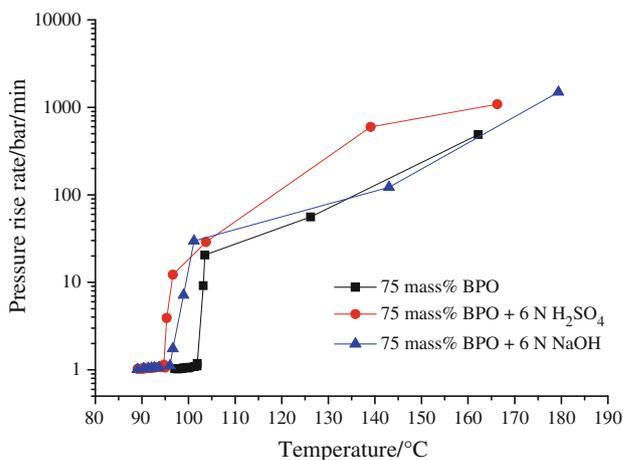
Table 5 VSP2 test results for 75 mass% BPO mixed with various incompatibilities

SOPs		Incompatibility		$T_0/^\circ\text{C}$	$T_{\max}/^\circ\text{C}$	P_{\max}/bar	$(dT/dt)_{\max}/^\circ\text{C min}^{-1}$	$(dP/dt)_{\max}/\text{bar min}^{-1}$
Material	Mass/mg	Material	Mass/mg					
BPO 75 mass%	5	–	–	94	316	23	12,354	490
		6 N H ₂ SO ₄	2.5	88	300	21	16,451	1,089
		6 N NaOH	2.5	89	310	22	13,612	1,495

**Fig. 6** Temperature versus time for thermal decomposition of 75 mass% BPO and BPO mixed with 6 N H₂SO₄ or 6 N NaOH by VSP2**Fig. 7** Pressure versus time for thermal decomposition of 75 mass% BPO and BPO mixed with 6 N H₂SO₄ or 6 N NaOH by VSP2

rate of temperature increase in temperature and pressure happened earlier than LPO alone. In the adiabatic environment, the results of LPO mixed with H₂SO₄ could cause thermal decomposition and release a large amount of gas.

Table 5 lists the thermal safety parameters of 98 mass% BPO and BPO mixed with 6 N H₂SO₄ or 6 N NaOH by VSP2. Figure 8 shows the temperature versus time for thermal decomposition of 75 mass% BPO mixed with H₂SO₄ or NaOH by VSP2. According to time versus

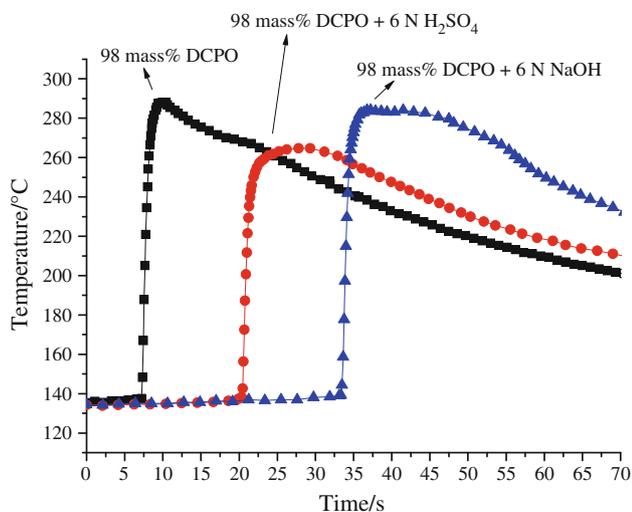
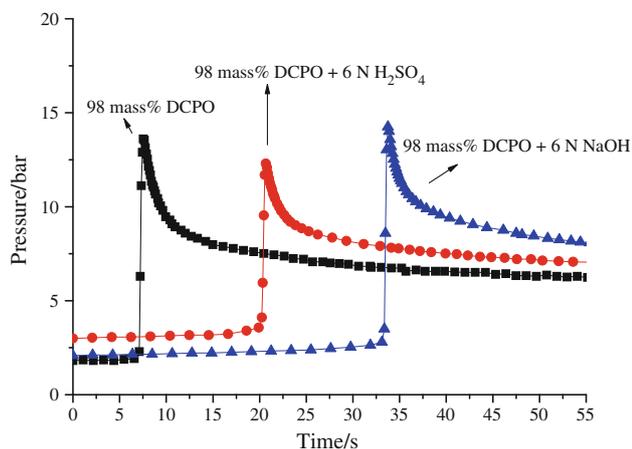
**Fig. 8** $(dT/dt)_{\max}$ versus temperature of BPO by VSP2**Fig. 9** $(dP/dt)_{\max}$ versus temperature of BPO by VSP2

temperature and pressure from Figs. 6 and 7, 8, and 9 show that the $((dT/dt)_{\max})$, and $((dP/dt)_{\max})$, BPO mixed with incompatibilities solutions is more dangerous than BPO. It is confirmed that the decomposition occurred by breaking the weak oxygen linkage bonds by protons [10]. Therefore, no matter how much of the BPO mixed acid or alkali, the adiabatic results could cause terrible thermal decomposition and release a huge amount of gas in a few seconds.

Table 6 lists the T_0 , T_{\max} , P_{\max} , $((dT/dt)_{\max})$, and $((dP/dt)_{\max})$ of 98 mass% DCPO conducted by VSP2.

Table 6 VSP2 test results for 98 mass% DCPO mixed with various incompatibilities

SOPs		Incompatibility		$T_0/^\circ\text{C}$	$T_{\text{max}}/^\circ\text{C}$	$P_{\text{max}}/\text{bar}$	$(dT/dt)_{\text{max}}/^\circ\text{C min}^{-1}$	$(dP/dt)_{\text{max}}/\text{bar min}^{-1}$
Material	Mass/mg	Material	Mass/mg					
DCPO 98 mass%	5	–	–	130	291	14	10,249	1,604
		6 N H ₂ SO ₄	2.5	125	265	12	8,068	2,004
		6 N NaOH	2.5	125	284	14	8,629	1,281

**Fig. 10** Temperature versus time for thermal decomposition of 98 mass% DCPO and DCPO mixed with 6 N H₂SO₄ or 6 N NaOH by VSP2**Fig. 11** Pressure versus time for thermal decomposition of 98 mass% DCPO and DCPO mixed with 6 N H₂SO₄ or 6 N NaOH by VSP2

Figures 10 and 11 show the thermal decomposition curves of 98 mass% DCPO mixed with H₂SO₄ or NaOH by VSP2. When DCPO was mixed with incompatible solutions, T_0 and T_{max} occurred earlier than DCPO alone, but the rate of temperature increase in temperature and pressure was lower than the DCPO alone.

Conclusions

From the tests, the runaway reaction of LPO, BPO, and DCPO mixed with incompatible solutions, the thermal hazard information was confirmed by DSC and VSP2. According to DSC experimental results of 6 N H₂SO₄ as a typical acid, LPO decompositions took place at 88 °C; when LPO was mixed with H₂SO₄ the T_0 was advanced at 66 °C. As BPO was mixed with H₂SO₄ the ΔH_d was ca. 1,229 J g⁻¹, which was higher than BPO. On the other hand, for VSP2 tests SOPs mixed with incompatible solutions, the results were also more dangerous and unstable than SOPs alone. Therefore, our results from thermal curves and experimental data provided evidence to show that the degree of hazard increased when the LPO, BPO, and DCPO were mixed with incompatible solutions, such as 6 N H₂SO₄, as an example of acids and 6 N NaOH, as an example of alkaline.

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