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Thermal hazard analyses of organic peroxides and inorganic peroxides by calorimetric approaches

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Abstract Organic peroxides (OPs) and inorganic peroxides (IPs) are usually employed as an initiator for polymerization, a source of free radicals, a hardener, and a linking agent in low density polyethylene (LDPE), polyvinyl chloride (PVC), controlled-rheology polypropylene (CR-PP), and styrene industries. Worldwide, due to their unstably reactive natures, OPs and IPs have caused many serious thermal explosions and runaway reaction incidents. This study was conducted to elucidate its essentially hazardous characteristics. To analyze the runaway behavior of OPs and IPs in the traditional process, thermokinetic parameters including heat of decomposition (ΔH_d), exothermic onset temperature (T_0), self-accelerating decomposition temperature (SADT), time to maximum rate (TMR), critical temperature (T_c), etc., were measured by calorimetric approaches involving differential scanning calorimetry (DSC), vent sizing package 2 (VSP2), and calculation method. Safety and health handling information of hazardous materials and toxic substances is noted in material safety data sheets (MSDS) and was applied to analyze in process safety management (PSM) in the chemical industries, but MSDS are not providing important handling indicators concerning the SADT, TMR, T_c, etc. In view of loss prevention, more useful indicators must be provided in the sheets or guide book.

Keywords Differential scanning calorimetry · Inorganic peroxides · Material safety data sheets · Organic peroxides · Runaway reaction

List of symbols

A	Frequency factor, sec^{-1} M^{1-n}
C_p	Liquid specific heat at constant pressure, kJ kg^{-1} °C^{-1}
C_0	Initial concentration, mol L^{-1}
E_a	Activation energy, kJ mol^{-1}
K	Pre-exponential factor, s^{-1}
M	Mass of reactant, g
$P_{\max}$	Maximum pressure during overall reaction, psig
Q	Calorific capacity, J g^{-1}.
$\dot{Q}$	heat flow, W g^{-1}
R	Gas constant, 8.314 J mol^{-1} K^{-1}
S	Wetted surface area, m^2
SADT	Self-accelerating decomposition temperature, °C
T	Temperature, °C
T_{A}	Final adjusted temperature, K
T_{A0}	Initial adjusted temperature, K
T_f	Final temperature, °C
T_{M}	Final measured temperature, K
$T_{\max}$	Maximum temperature during overall reaction, °C
T_{M0}	Initial measured temperature, K
T_{NR}	Temperature of no return, °C
T_{wall}	Temperature on the wall, °C

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$\mathrm{TMR}_{\mathrm{ad}}$	Time to maximum rate under adiabatic system, min, h
U	Heat transfer coefficient, kJ min^{-1} m^{-2} K^{-1}
a	Vessel wetted surface area, m^2
k_i	Rate at stage i, s^{-1}
m	Mass of reactor, kg
n	Order of reaction, dimensionless
α	Degree of conversion, dimensionless
β	Heating rate, °C min^{-1}
λ	Heat conductivity, J ms K^{-1}
φ	Thermal inertia, dimensionless
ΔH_d	Heat of decomposition, J g^{-1}
$(\mathrm{d}T\ \mathrm{d}t^{-1})$	Self-heating rate, °C min^{-1}
$(\mathrm{d}T\ \mathrm{d}t^{-1})_{\mathrm{A}}$	Actual self-heating rate, °C min^{-1}

Introduction

Organic peroxides (OPs) and inorganic peroxides (IPs) have the common characteristic of the peroxy bond (–O–O–). The hazardous characteristics of the –O–O– bond show that it is a thermally unstable structure including (a) being very sensitive to thermal sources, (b) yielding a large amount of heat during decomposition reaction, (c) generating a large amount of gases and mists during decomposition reaction, (d) being very susceptible to contaminants, such as inorganic acids (H_2SO_4, H_3PO_4, HCl, or HNO_3), alkali, Fe_2O_3, and so on, (e) inducing radicals under decomposition reaction, and (f) possessing oxidizing ability [1, 2]. The members of DIERS (Design Institute for Emergency Relief Systems) under AIChE have emphasized researches on the characteristics of pressure relief for OPs. The exothermic threshold temperature of many OPs is usually around 50–120 °C. Calorimetric and related methodologies for forestalling thermal hazards of OPs have been proposed.

Numerous studies of induced thermal hazards by OPs have been performed worldwide [3–5]. The United Nations (UN) has suggested that an OPs supplier must make a precise test of self-accelerating decomposition temperature (SADT) in any specific commercial package. According to Recommendations on the Transport of Dangerous Goods (TDG), Manual of Tests and Criteria of the UN, SADT is defined as the lowest ambient temperature at which self-accelerating decomposition may take place in the packaging for transportation purposes. TDG of the UN provides four methods to determine SADT value: the United States SADT test (US SADT test), adiabatic storage test (AST), isothermal storage test (IST), and heat accelerating storage test (Dewar test) [6, 7]. Lin et al. [7] provide an SADT calculation method dependent on the Semenov explosion model. Therefore, Lin et al. use vent sizing package 2 (VSP2) (AST method by TDG of UN) to determine the thermokinetics and to calculate SADT. Li and Koseki [6] suggest that thermal activity monitor (TAM) (IST method by TDG of UN) be applied to calculate SADT value. Eq. 1 shows the SADT calculation model in previous articles.

$$\mathrm{SADT} = T_{\mathrm{NR}} - \frac{R(T_{\mathrm{NR}} + 273.15)^2}{E_a} \tag{1}$$

Activation energy (E_a), frequency factor (A), temperature of no return (T_{NR}) Eq. 2, heat transfer coefficient (U), vessel-wetted surface area (a), etc., are employed to calculate SADT. Therefore, T_{NR} can be calculated via the relationship between the heat generation rate and heat removal rate. When the maximum self-heating rate compared with the time constant is the same in the system, then the temperature will rise to T_{NR} [8]. The E_a and A is developed from Arrhenius equation that is displayed in Eq. 3. The E_a calculation value should be compared with differential calorimeter.

$$(T_{\mathrm{NR}} + 273.15)^2 = \frac{mE_a \Delta H A e^{-E_a/R(T_{\mathrm{NR}}+273.15)}}{RU(1.8)a} \tag{2}$$

$$k = A\exp\left(\frac{-E_a}{RT}\right). \tag{3}$$

This study was employed to explain the E_a calculation method by non-isothermal, isothermal, and adiabatic calorimeter. Lin et al. [7] provide an E_a calculation method using an adiabatic calorimeter depending on self-heating rate that is shown in Eq. 4. Equation 3 was applied to develop and to calculate the reaction rate (k), E_a,, and A that were described in Eq. 4.

$$\ln k = \ln A - E_a/RT = \ln\left(\frac{\mathrm{d}T/\mathrm{d}t}{T_f - T}\right) \tag{4}$$

Li and Koseki [6] describe the E_a calculation method employing an isothermal calorimeter depending on various isothermal temperatures that is noted in Eq. 5.

$$\frac{qm}{D_0} = -\Delta H \beta k \alpha_m^{1-x}(1-\alpha_m)^{1-y} = A\exp(-E_a/RT) \tag{5}$$

You et al. [9] suggest an E_a calculation method by the Kissinger method and Ozawa method, employing a non-isothermal calorimeter (such as differential scanning calorimeter, DSC) depending on various heating rates that is noted in Eqs. 6 and 7

$$\frac{2.303\mathrm{d}\left[\log\left(\beta/T_{\max}^2\right)\right]}{\mathrm{d}(1/T_{\max})} = -E_a/R \tag{6}$$

where $T_{\max}$ is the temperature corresponding to the maximum in the DSC exothermic at a specific heating rate (β). From the slope of the linear curve of log ($\beta\ T_{\max}^{-2}$) again $T_{\max}^{-1}$, E_a can be calculated.

$$\frac{2.15\mathrm{d}[\log(\beta)]}{\mathrm{d}(1/T_{\max})} = -E_a/R \tag{7}$$

where E_a is obtained from the slope of the drawing of log β against $T_{\max}^{-1}$.

The OPs have caused a number of serious thermal explosions in Taiwan. Thermal explosion model was developed four decades ago in Taiwan. Thermal explosion development model was concerned by the Semenov and Frank–Kamenetskii method. The behavior of thermal explosions or runaway reactions has been broadly studied for years. In a reactor with an exothermic reaction, it is very easy to accumulate energy and temperature when the heat generation rate (Q_g) exceeds the heat removal rate (Q_r) by Semenov theory. Eqs. 8–13 are used to assess the critical situation in the Semenov model [10–15].

$$Q_g = qVr_b \tag{8}$$

where Q_g is the heat generation rate used to depict thermal development in a reactor.

$$Q_r = hS(T - T_a) \tag{9}$$

where Q_r is the heat removal rate that is called the Newton cooling law.

$$r_b = kC_0^n \tag{10}$$

where r_b is reaction rate.

$$r_b = kC_0^n = A\mathrm{e}^{-E_a/RT}C_0^n \tag{11}$$

$$Q_g = qVA\mathrm{e}^{-E_a/RT}C_0^n \tag{12}$$

$$Q_{\mathrm{acc}} = Q_g - Q_r = qVA\mathrm{e}^{-E_a/RT}C_0^n - hS(T - T_a) \tag{13}$$

where Q_{acc} is heat of accumulation that was used to investigate the critical development in three cooling system circumstances.

Typically, time to maximum rate (TMR) is adopted to analyze the degree of safety, perniciousness, etc. TMR provides an indication of how imminent the reaction is, or a specific time for a reaction to occur approaches. The TMR determination for a runaway reaction can provide firefighters information about the emergency response time. Equations 14 and 15 are used to compute the TMR [8]:

$$\mathrm{TMR} = \frac{RT^2}{AE_a\Delta T_{\mathrm{ad}}}\mathrm{e}^{\frac{-Ea}{RT}} \tag{14}$$

$$\Delta T_{\mathrm{ad}} = \frac{Q}{C_p} \tag{15}$$

SADT, T_c, T_{NR}, TMR, and other thermokinetics are applied to control and to handle chemical reaction in the process or industries.

Experimental method

Samples

The TBPO, BPO, TBPBZ, CaO_2, MgO_2, and Na_2O_2 were directly purchased from the Fluka Co., and both density and concentration were measured. Then, those OPs were stored in a refrigerator at 4 °C. Acetone (99.5 mass%), H_2O_2 (65 mass%), and 18 M H_2SO_4 were applied to manufacture TATP under 0 °C ambient temperature. The TATP must be stored in 4 °C environment temperature and must be kept from fire and thermal sources.

Differential scanning calorimetry (DSC)

Temperature-programmed screening experiments were performed on a Mettler TA8000 system DSC821. Heating rate chosen for the temperature-programmed ramp was 4 °C min^{-1}, to maintain better thermal equilibrium. The tests were conducted between 30–300 °C with TBPO, TBPBZ, BPO, TATP, CaO_2, MgO_2, and Na_2O_2. The test used a pipet to inject at about 3–7 mg of seven of the OPs. The DSC is regarded as a useful tool for evaluating thermal hazards and investigating decomposition mechanisms of reactive chemicals if the experiments are carried out carefully. The experimental conditions were as follows:

(a) Heating rates: 1–10 °C min^{-1}.
(b) Materials mass: 3–7 mg.
(c) Temperature range: 30–300 °C.
(d) Test cell: These gold-plated high-pressure crucibles, which can be pressed together, have proven to be very useful for safety investigation, but they can only be used for one measurement with a maximum pressure of 15 MPa. The lid is pressed into the crucible with a pressure of about a ton so that the seal tightens the crucible. A toggle press is employed to close the crucible.

Vent sizing package 2 (VSP2)

VSP2, a PC-controlled adiabatic calorimeter manufactured by Fauske & Associates, Inc., was employed to obtain thermokinetic and thermal hazard data, such as temperature and pressure traces versus time. The heat-wait-search (H-W-S) mode for detecting the self-heating rate was adopted for VSP2. If the self-heating rate is larger than 0.1 °C min^{-1}, the H-W-S and main heater will be immediately terminated for measuring the original phenomenon of self-exothermic behavior. The low heat capacity of the cell ensured that all the reaction heat released remained within the tested sample. Thermokinetic and pressure behavior in the same test cell (112 mL) usually could be tested, without any difficult extrapolation to the process scale due to the low thermal inertia factor (Φ) of about 1.05 to 1.32. The low Φ allows for bench scale simulation of the worst credible case, such as incorrect dosing, cooling failure, or external fire conditions.

Results and discussion

Methyl ethyl ketone peroxide (MEKPO)

MEKPO is a typical OPs produced by methyl ethyl ketone (MEK) with hydrogen peroxide (H_2O_2) used as a radical source for initiation and cross-linking agent during polymerization. MEKPO has caused many serious accidents in Taiwan, Japan, China, Korea, etc. [16]. Thirty mass% of MEKPO decomposes at 30–40 °C (first peak) and has three peaks of decomposition by DSC using 3–7 mg of MEKPO. Main decomposition temperature was analyzed to be 100 °C (second peak). E_a of MEKPO was determined to be 110–116 kJ mol^{-1} [7]. The SADT of MEKPO in 55 gallon drum was calculated to be 80 °C [7]. Lin et al. suggest that 40 mass% MEKPO should be used in storage or transportation in Taiwan [7]. According to incompatible reaction of MEKPO, Chang et al. used MEKPO mixed with NaOH and H_2SO_4 and analyzed the exothermic onset temperature (T_0) as about 70 °C of 31 mass% MEKPO mixed with acid and base. Results indicated that mixing MEKPO with base and acid was prohibited [16]. Chang et al. describe the degree of hazard as follows:

$$\mathrm{MEKPO} + \mathrm{Fe}^{2+}\ \mathrm{or}\ \mathrm{Fe}^{3+} > \mathrm{MEKPO} + \mathrm{OH}^- > \mathrm{MEKPO} + \mathrm{H}^+ > \mathrm{MEKPO}$$

T_0 of MEKPO mixed with $FeSO_4$ or $FeCl_3$ was calculated to be 30 °C [17]. T_0 of MEKPO with HCl and NaCl was determined to be 68 and 77 °C, respectively [18]. Acetone was utilized to mix with MEKPO by Lin et al. Therefore, acetone was analyzed as a diluent in MEKPO solution [19]. Safety parameters of OPs are shown in Table 1.

Di-tert-butyl peroxide (DTBP)

DTBP is a crucial industrial chemical that acts as an initiator for radical polymerization, initiators, hardeners, and linking agents. It is a clear and colorless to yellow liquid material. When used to link with other OPs, it is a powerful oxidizer that reacts with reducing agents and is subject to decomposition when exposed to thermal sources. Ninety eight mass% DTBP decomposes at 120 °C. When DTBP is mixed with HCl or H_2SO_4, its T_0 is reduced about 100 °C. ΔH_d of DTBP was determined to be 1,200 J g^{-1} [20]. Li and Koseki indicate that the reaction order of DTBP was analyzed to be first order. SADT of DTBP is determined about 80 °C [6].

Cumene hydroperoxide (CHP)

Cumene hydroperoxide (CHP) has been broadly employed in the chemical industry and is easily recognized as a typical thermally unstable and hazardous substance. Numbers of thermal explosions have been induced by CHP on oxidation reactors or storage tanks in Taiwan. Exothermic runaway reactions may occur when impurities or alien materials are present in the reactors, storage tanks, or pipelines. During any stage, thermal energy could accumulate via self-acceleration decomposition, or thermal polymerization, and is subject to various upsets or abnormal conditions, such as cooling failure, mischarging, overdosing, or external fire exposure [21, 22].

SADT of CHP was noted at 80 °C [23]. Reaction order of CHP was calculated to be 0.5. Chen et al. use a liquid thermal explosion (LTE) simulation model to simulate a storage tank ($H = 1.2$ m and $r = 0.4$ m) and 50 gallon

Table 1 Safety parameter collection for ten OPs

Chemical	T_0/°C	ΔH_d/J g^{-1}	SADT/°C	E_a/kJ mol^{-1}	n
TATP	50	2,500	*	*	1
Di-tert-butyl peroxide (DTBP)	115	1,200	80	80	1
Cumene hydroperoxide (CHP)	110	1,500	80	*	0.5
Dicumyl peroxide (DCPO)	110	700	80	*	1
Methyl ethyl ketone peroxide (MEKPO)	100	1,200	80	110	1
Tert-butyl hydroperoxide (TBHP)	65	1,600	*	*	1
Lauroyl peroxide (LPO)	70	576	*	*	1
Benzoyl peroxide (BPO)	105	1,000	70	188	0.9
Tert-butyl peroxybenzoate (TBPBZ)	100	1,100	65	*	1
Tert-butyl peroxide (TBPO)	110	1,105	*	136	1

* Not applicable (NA)

drum of 88 mass% CHP. Emergency response time for a storage tank ($H = 1.2$ m and $r = 0.4$ m) and 50 gallon drum of 88 mass% CHP was determined to be 80 and 100 min, respectively [1]. T_0 of 80 mass% CHP was determined to be 110 °C [21]. Over 90% of CHP produced in the world is applied in the production of phenol and acetone. T_0 of CHP mixed with phenol in batch reactor was determined to be 98 °C [22]. When CHP mixed with NaOH, T_0 was determined to significantly reduce at 40 °C [24]. Moreover, T_0 of CHP compared with NaOH, H_2SO_4, and Na_2SO_3 was analyzed to be 40, 53, and 137 °C, respectively. ΔH_d of CHP mixed with NaOH, H_2SO_4, and Na_2SO_3 was investigated to be 800, 1,300, and 1,100 J g^{-1}, respectively [25].

T_0 of CHP compared with t-BuONa, KOH, LiOH, and NH_3 was analyzed to be 46, 55, 55, and 54 °C, respectively. CHP mixed with aqueous hydroxides generated unstable intermedia that could lead to a lower SADT, which then is susceptible to triggering a thermal runaway hazard [26].

Dicumyl peroxide (DCPO)

Dicumyl peroxide (DCPO) is a white crystalline solid substance. When used to link with other chemicals, such as polyethylene (PE), ethylene vinyl acetate (EVA) copolymer, and ethylene propylene terpolymer (EPT), it is a potent initiator which can readily be an oxidizer and react with reducing agents. If the DCPO product, a white crystalline solid, is properly maintained at low temperature during transportation and storage, it will not initiate any prominent runaway reaction, unless it goes through the melting stage under higher temperature. However, it is likely to result in accidents in a chemical process under higher temperature, incompatible substances, improper temperature control, human error, and so forth. The CHP and DCPO are important reactive reactants in the DCPO manufacturing process. The DCPO manufacturing process uses low concentration or a small amount of CHP compared with CA and acids in a batch reactor. The DCPO process should indicate a temperature under T_0 of CHP. In practice, these data are necessary for safe application, storage, and transportation of a chemical product. Ninety-nine mass% DCPO is decomposed at 110 °C in a runaway reaction [2].

Tert-butyl hydroperoxide (TBHP)

Tert-butyl hydroperoxide (TBHP) is a typical alkyl hydroperoxide for commercial and industrial applications. It is extremely sensitive and incompatible to acids, bases, metal ions, and other impurities. It is one of the initiators for emulsion and suspension polymerization of ethylene, vinyl acetate, acrylates, polyvinyl chloride (PVC), or curing agent for unsaturated polyesters in the petrochemical industry. The TBHP decomposes at 75 °C. T_0 of TBHP mixed with NaOH, KOH, LiOH, and NaCl were calculated to 40 °C. T_0 of TBHP compared with NH_4OH was analyzed to be 60 °C [27]. T_0 of TBHP in water, nonane, and tert-butanol was determined to be 75, 75, and 100 °C, respectively. ΔH_d of TBHP was determined to be 1,600 J g^{-1} [28].

Lauroyl peroxide (LPO)

Lauroyl peroxide (LPO) is applied as bleaching agent, drying agent for fats, oils, and waxes, as a catalyst and vulcanizing agent. Thus, small amounts of LPO are employed in food packaging. It is an oxidizing agent, and it can ignite organic materials; hence, it has dangerous fire and explosion risk. Strongly reduced materials, such as sulfides, nitrides, and hydrides may react explosively. It decomposes rapidly, causing fire and explosion hazard, upon heating and under influence of light [9]. According to You et al., E_a of 95 mass% LPO was determined to be 100 kJ mol^{-1}. The Reaction order (n) of LPO was analyzed to be first order. Therefore, T_0 of 95 mass% LPO was determined to be 70 °C.

Hydrogen peroxide (H_2O_2)

Hydrogen peroxide (H_2O_2) has been used to bleach textiles, article products, manufactured or processed foods, minerals, petrochemicals, and consumer products (detergents). It was used for pollution control on municipal wastewater applications in the 1970's, industrial waste/wastewater applications in the 1980's, and more recently, air applications since the 1990's. The H_2O_2 is readily available throughout the world, in drums, wet tasks totes, mini-bulk, and bulk quantities in concentrations of 35 or 50 mass%.

The physical and chemical properties of H_2O_2 have the hazardous structure of H–O–O–H, and can be dissolved in water and alcohol, but not in petroleum ether. Generally speaking, H_2O_2 can be solidly crystallized under low temperature (−261 to 0 °C) [29]. T_0 of 31 mass% H_2O_2 is determined to be 80 °C. When H_2O_2 was mixed with H_2SO_4, T_0 reduced to room temperature and released a number of heats in solution [30].

Tert-butyl peroxide (TBPO)

Tert-butyl peroxide (TBPO) is a typical OPs that is employed as an initiator in the chemical industry. Ninety-eight mass% TBPO was employed to analyze its thermal

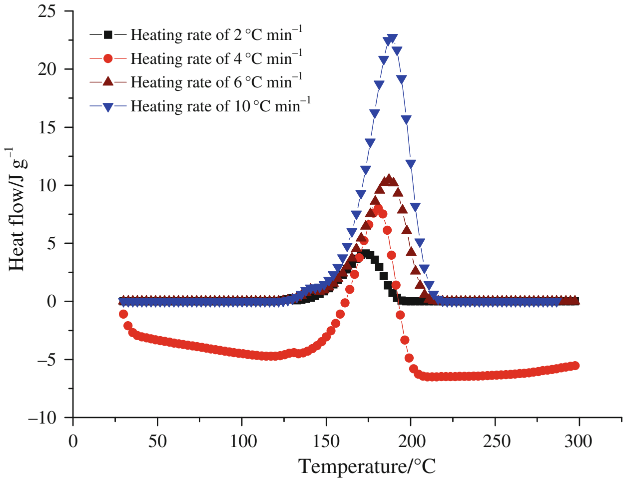

Fig. 1 Thermal decomposition evaluation of TBPO under various heating rates by DSC

hazard by DSC under various heating rates. According to the thermal curve (Fig. 1; Table 2), 98 mass% TBPO decomposed the ΔH_d about 1,105 J g^{-1}. The T_0 of 98 mass% TBPO was calculated at 110 °C. The DSC was utilized to determine reactor index for operator use in the manufacturing process. The use of various heating rates by DSC handling made it easy to calculate the E_a. According to all the thermal curves by DSC tests, the T_0 was about 110–130 °C. Process engineers and operators must control the temperature of a reactor under less than T_0 (110 °C). To prevent thermal accumulation, the temperature of the cooling system must be kept low in a reactor. To avoid incompatible behavior, 98 mass% TBPO mixing with acid or base is prohibited. Ninety-eight mass% TBPO released a ΔH_d about 1,105 J g^{-1}, and the reaction order was noted as about 1 (Table 1).

This study was used to evaluate safety parameters of TBPO compared with various containments by DSC. When TBPO was mixed with HNO_3 and HCl in DSC tests, the T_0 was detected to be 84 and 87 °C, respectively. According to thermal curves, T_{max} of all of tests was 183 °C (Fig. 2; Table 3). The *n* value of TBPO was calculated to be 1 by DSC model. The degree hazard of TBPO mixed with containments was as follows:

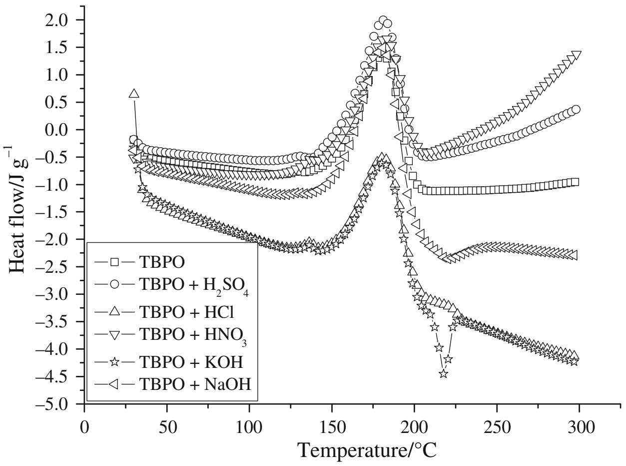

Fig. 2 Thermal decomposition analysis of TBPO mixed with various containments by DSC

$$\mathrm{TBPO + NaOH > TBPO + HCl > TBPO + KOH > TBPO > TBPO + H_2SO_4}$$

Benzoyl peroxide (BPO)

Benzoyl peroxide (BPO), broadly used in organic chemistry, is generally considered to be a relatively inert compound and few precautions are ordinarily taken while handling it. In Taiwan and Japan, however, several severe fire and explosion incidents have occurred due to its thermal reactivity and explosive properties. For example, a serious accident occurred at Fu-Kao Chemical Plant on May 18, 2001 in Taiwan. The immediate cause turned out to be a vapor cloud explosion, and the blast mass was estimated to be equivalent to 1,000 kg of TNT. Polymerization initiators utilize OPs, such as BPO, that can thermally decompose to form primary free radicals [31]. The reaction order of BPO was determined to be 0.9, and that by the Arrhenius equation was measured to be $E_a = 188$ kJ mol^{-1}. The T_{NR} values of BPO were determined to be 63.9 °C. The SADT of BPO was determined to be 70 °C [6]. The abovementioned values are relatively close to the literature values. In summary, practical suggestions can be provided to prevent accidents, especially at low temperature conditions during storage and transportation.

Table 2 Safety parameters of TBPO under various heating rates by DSC tests

β/°C min^{-1}	Mass/mg	T_0/°C	ΔH_d/J g^{-1}	T_{max}/°C	*n*	E_a of Kissinger/kJ mol^{-1}	E_a of Ozawa/kJ mol^{-1}
2	3.3	118	1190	173	1	138.6	136.5
4	4.2	120	1153	180	1	138.6	136.5
6	3.6	125	942	187	1	138.6	136.5
10	5.2	130	848	191	1	138.6	136.5

Table 3 Safety parameters of TBPO mixed with containments by DSC tests under 4 °C min^{-1} of β

	Mass/ mg	T_0/ °C	ΔH_d/ J g^{-1}	T_{max}/ °C	n
TBPO	5.8	118	1,100	182	1
TBPO + H_2SO_4 (6 N)	6.8	106	1,100	183	1
TBPO + HCl (6 N)	3.3	87	1,233	183	1
TBPO + HNO_3 (6 N)	3.8	84	967	183	1
TBPO + KOH (6 N)	3.3	114	1,165	183	1
TBPO + NaOH (6 N)	6.3	100	1,705	181	1

This study was used to determine safety parameters of BPO mixed with three chemicals that are displayed in Table 4 and Fig. 3. T_0 of BPO was determined to be 103 °C in this study. When HCl was added to BPO solution, ΔH_d of BPO/HCl was determined to be 2,390 J g^{-1}. The HCl is prohibited from being mixed with BPO. The n value was calculated to be 0.9 by DSC model.

Tert-butyl peroxybenzoate (TBPBZ)

Tert-butyl peroxybenzoate (TBPBZ) is used as the cross-linker for combining with calcium, unsaturated pitch (UP), and other materials. The SADT of TBPBZ was determined to be 65.8 °C. ΔH_d and T_0 of 98 mass% TBPBZ were calculated to be 1100–1300 J g^{-1} and 86–100 °C, respectively [32].

Thermal tests using various heating rates (1, 2, 4, and 10 °C min^{-1}) by DSC were applied to assess the thermokinetics of TBPBZ that are shown in Table 5 and Fig. 4. T_0 of 98 mass% TBPBZ is determined about 70–90 °C. The n value of TBPBZ is the first order reaction.

Triacetone triperoxide (TATP)

Thirty-one mass% H_2O_2, 99 mass% propanone (so-called acetone), and 6 NH_2SO_4 are employed to generate diacetone diperoxide (DADP) or triacetone triperoxide (TATP) [33]. Owing to high energy reason and the ease of making, DADP or TATP is used as an initiator for explosive materials for terrorist attacks worldwide [34].

Table 4 Safety parameters of BPO mixed with containments by DSC tests under 4 °C min^{-1} of β

	Mass/mg	T_0/°C	ΔH_d/J g^{-1}	T_{max}/°C	n
BPO	1.2	103	1,332	111	0.9
BPO + H_2SO_4	6.3	103	239	110	0.9
BPO + HCl	1.1	118	2,390	118	0.9
BPO + NaOH	6.8	105	140	108	0.9

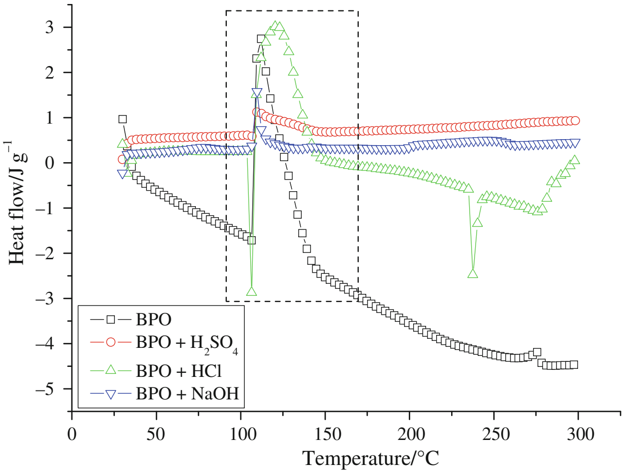

Fig. 3 Thermal decomposition evaluation of BPO mixed with three containments by DSC

Table 5 Safety parameters of TBPBZ under various heating rates by DSC tests

β/°C min^{-1}	Mass/ mg	T_0/ °C	ΔH_d/ J g^{-1}	T_{max}/ °C	n	E_a/ kJ mol^{-1}
1	2.8	70	1,130	145	1	65
2	3.2	75	1,134	146	1	70
4	2.2	80	1,167	151	1	77
10	2.5	90	1,177	164	1	80

The DSC was employed to analyze the thermal behavior of TATP and various heating rates were applied including 1, 2, 4, 10 °C min^{-1} to simulate an external fire situation. The TATP is a white solid that decomposes at 50–60 °C with differential scanning rate. According to thermal curves, TATP decomposed rapidly and the completion of decomposition was calculated before 200 °C. The ΔH_d of TATP

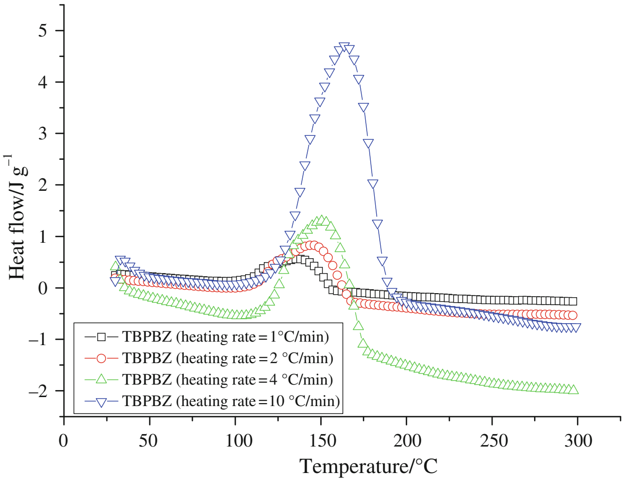

Fig. 4 Thermal decomposition evaluation of TBPBZ under various heating rates by DSC

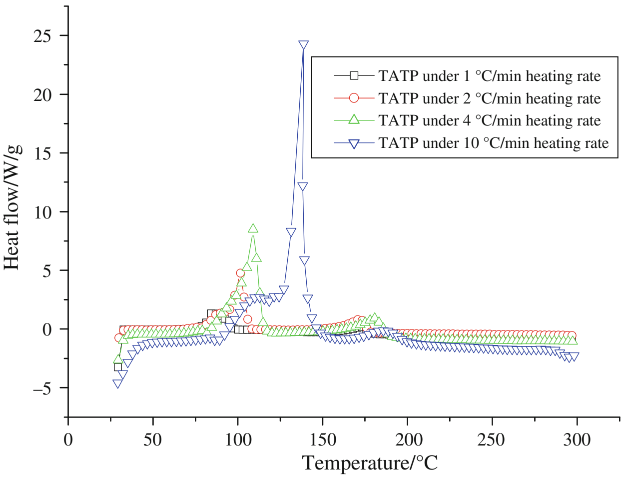

Fig. 5 Thermal decomposition evaluation of TATP under various heating rates by DSC

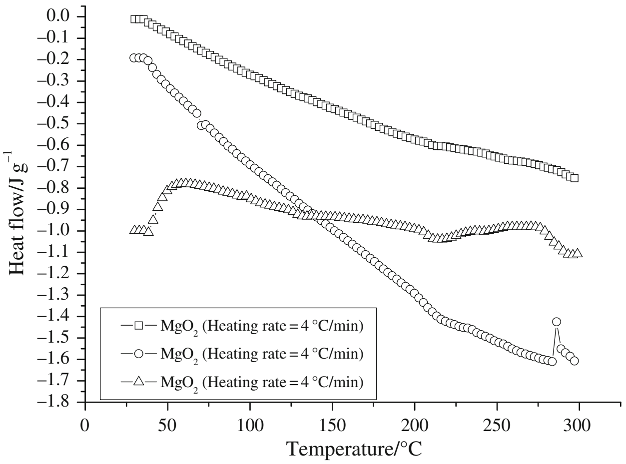

Fig. 7 Thermal decomposition evaluation of MgO_2 under three heating rates by DSC

was investigated to be 2,500 J g^{-1} (Fig. 5) that was analyzed as 4th degree of exothermic score by Kao et al. [35].

Calcium peroxide (CaO_2)

Calcium peroxide (CaO_2) is a solid of peroxide with a white or yellowish color. For all practical purposes, calcium peroxide is insoluble in water but will dissolve in acid to form hydrogen peroxide. When in contact with water it will immediately start to decompose, releasing oxygen. CaO_2 is manufactured to varying specifications and purity and can be used in different areas of industry and agriculture. In agriculture, it is used as an oxygen fertilizer, and is also used in the presowing treatments of rice seed. Furthermore, calcium peroxide has found use in the aquaculture industry, as it is used to oxygenate and disinfect water, and in the ecological restoration industry, as it is used in the treatment of soils. CaO_2 is used in a similar manner to magnesium peroxide for environmental restoration programs. It is used to restore soil and groundwater contaminated with petroleum hydrocarbons by stimulating aerobic microbial degradation of the contaminants in a process known as Enhanced In Situ Bioremediation [36]. According to thermal curves, CaO_2 was evaluated by using 1, 2, and 4 °C min^{-1} by DSC. CaO_2 was determined without decomposition behavior by DSC curve (Fig. 6).

Magnesium peroxide (MgO_2)

Magnesium peroxide (MgO_2) is a fine powder of peroxide with a white to white-off color. It is similar to calcium peroxide because magnesium peroxide also releases oxygen by breaking down at a controlled rate with a hydrous fluid. It can also be used in bleaching, disinfecting, and deodorizing. MgO_2 is environmentally benign and its

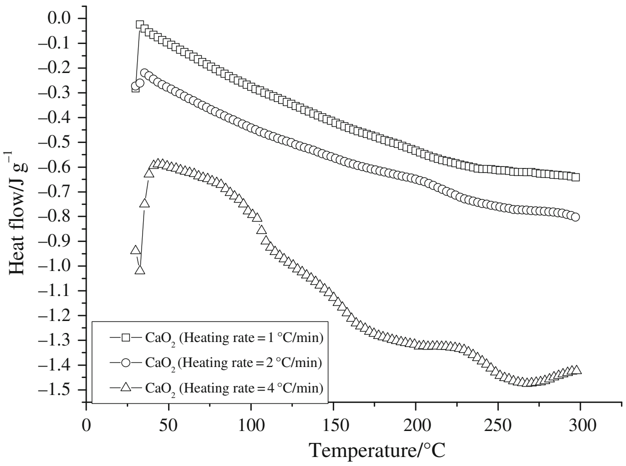

Fig. 6 Thermal decomposition evaluation of CaO_2 under three heating rates by DSC

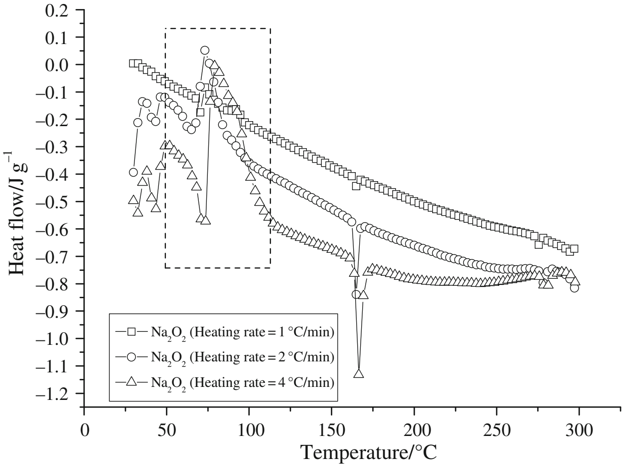

Fig. 8 Thermal decomposition evaluation of NaO_2 under three heating rates by DSC

Table 6 Safety parameters of peroxides by VSP2 tests

	T_0/°C	T_{max}/°C	P_{max}/bar	$(dT\ dt^{-1})_{max}$/°C	$(dP\ dt^{-1})_{max}$/bar	TMR/min	Ref.
CHP (20 mass%)	141	200	13	3	0.5	80	[38]
MEKPO (20 mass%)	90	263	34	83	134	90	[7]
DCPO (25 mass%)	110	175	21	2	0.6	110	[2]
TBPO (20 mass%)	140	211	20	35	8	20	[39]
H_2O_2 (20 mass%)	80	158	60	8	7	70	[40]

stable oxygen release is used widely in the cosmetic, agricultural, pharmaceutical, and environmental industries. It is used to reduce contaminant levels in groundwater. MgO_2 is used in the bioremediation of contaminated soil and can improve the soil quality for plant growth and metabolism. It is also used in the aquaculture industry for bioremediation. Commercially, magnesium peroxide exists as a form of compound of MgO_2 and magnesium hydroxide [36]. MgO_2 was evaluated without decomposition behavior by DSC curve as shown in Fig. 7.

Sodium peroxide (Na_2O_2)

Sodium peroxide (Na_2O_2) is hydrolyzed by water to form sodium hydroxide plus hydrogen peroxide. Na_2O_2 thus formed decomposes rapidly in the ensuing basic solution, producing water and oxygen. The reaction is substantially exothermic and can set fire to combustible materials. Na_2O_2 will also set fire to many organic liquids on contact (particularly alcohols and glycols), and reacts violently with powdered metals and numerous other compounds after minimal initiation. Given its strong oxidation characteristics, Na_2O_2 is used to bleach wood pulp for the production of article. It has also been used for the extraction of minerals from various ores. In chemistry preparations, Na_2O_2 is used as an oxidizing agent. It is also used as an oxygen source by reacting it with carbon dioxide to produce oxygen and sodium carbonate; it is thus particularly useful in scuba gear, submarines, etc. [37].

Na_2O_2 was investigated under three of β by DSC (Fig. 8). Na_2O_2 may have a serious exothermic reaction below 50 °C. There are three exothermic reactions in Na_2O_2 decomposition behavior. It is more dangerous than MgO_2 and CaO_2. The boiling point (decomposition temperature) was evaluated to be 350 °C [36]. The characteristic of MgO_2 and CaO_2 are the same and are stable under 300 °C without mixing water. The decomposition reaction mechanism of Na_2O_2 was illustrated in Eq. 16. Na_2O_2 decomposed to release oxygen (O_2) and sodium oxide (Na_2O) [37]. Na_2O_2 and Na_2O were identified as unstable materials that were easy to react with heat.

$$2Na_2O_2 \rightarrow 2Na_2O + O_2 \tag{16}$$

Conclusions

Material safety data sheets (MSDS) were widely utilized to protect and prevent thermal hazard and reactive hazard of chemicals in industries that was planed as sixteen sheets. This study suggested that thermal hazard and reactive information including the SADT, TMR, T_0, etc., of peroxides should be evaluated in MSDS. Tables 1 and 6 were applied to display the MSDS data that can be employed for supplier, operator, and engineers.

This study was used to analyze thermal hazard that was shown as follows:

a. When 98 mass% TBPO was mixed with 6 N HNO_3 and 6 N HCl in DSC tests, the T_0 was detected to be 84 and 87 °C, respectively. According to thermal curves, T_{max} of all of tests was 183 °C. The n value of TBPO was calculated to be 1 by DSC model. The degree hazard of TBPO mixed with containments was as follows: TBPO + NaOH > TBPO + HCl > TBPO + KOH > TBPO > TBPO + H_2SO_4.
b. T_0 of BPO was determined to be 103 °C in this study. When HCl was added to BPO solution, ΔH_d of BPO/HCl was found to be 2,390 J g^{-1}. The HCl is prohibited from being mixed with BPO. The n value of BPO was calculated to be 0.9 by DSC model.
c. T_0 of TBPBZ was determined to be about 70–90 °C. The n value of TBPBZ is the first order reaction.
d. The TATP is a white solid and decomposes at 50–60 °C with differential scanning rate. According to thermal curves, TATP decomposed rapidly and final decomposition was calculated below 200 °C. Heat of decomposition (ΔH_d) of TATP was investigated as about 2,500 J/g.
e. MgO_2 and CaO_2 were evaluated without decomposition behavior by DSC curve. Na_2O_2 may have a serious exothermic reaction below 50 °C. There are three exothermic reactions in Na_2O_2 decomposition behavior. It is more dangerous than MgO_2 and CaO_2.

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