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THERMAL HAZARD STUDIES FOR DICUMYL PEROXIDE BY DSC AND TAM

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A differential scanning calorimetry (DSC) and thermal activity monitor (TAM) were used to study the thermo–kinetic parameters for dicumyl peroxide (DCPO) at various concentrations. The potential thermal hazards of intermediates and end products whose concentrations were at approximately 50, 70, 94 and 99.3 mass%, respectively, in the process of operating DCPO were investigated. Thermoanalytical curves indicate that the average heat of decomposition of various DCPO samples in a manufacturing process was 762 to 1200 J g^{-1} which made it an inherently hazardous material. In the incompatibilities study, significant thermal hazards appeared in the presence of H_2SO_4. From the TAM experiments, the synthetic process of DCPO could result in an unexpected reaction in the condition of batch addition with reactants and H_2SO_4.

Keywords: *dicumyl peroxide, thermal hazards, unexpected reaction*

Introduction

Thermal runaway reactions can occur when the total rate of heat generated exceeds the rate of heat removed in a reactive system [1]. Under such a circumstance, a thermal runaway reaction may be caused by a violent exothermic decomposition or polymerization. It will cause a thermal explosion when pressure rises or external fire exposure is encountered under an uncontrollable situation. Historically, many thermal runaway incidents have been caused by organic peroxides owing to the peroxy functional group (–O–O–) which is sensitive to heat and incompatible with many materials, such as acids, bases, metals, irons, etc. [2].

In principle, dicumyl peroxide (DCPO) belongs to dialkyl peroxides that are among the more stable types of all the commercially available organic peroxides. In industry, it can be used as a curing agent or initiator for unsaturated polyester and polystyrene (PS). In addition, DCPO is used in various resins for improving physical properties in many commodity or specialty chemicals.

In petrochemistry, after the production procedure of cumene, three major steps are used to produce DCPO, as the following equations show. Cumene is used to generate cumene hydroperoxide (CHP) by oxidization process, and then, after concentration procedure, the concentrated CHP is achieved at approximately 80–83 mass%. Second, a mixture of sodium sulfite (Na_2SO_3) and CHP is reacted to produce cumyl alcohol (CA) and sodium sulfate (Na_2SO_4) by the redox reaction. Finally, CHP is added to CA by a dehydration reaction to form crude DCPO with sulfuric acid (H_2SO_4, 5M) as catalyst.

Oxidization reaction:

$$C_5H_5CH(CH_3)_2 + O_2 \xrightarrow{heat} C_6H_5C(CH_3)_2OOH \quad (1)$$

Redox reaction:

$$C_6H_5C(CH_3)_2OOH + Na_2SO_3 \rightarrow C_6H_5C(CH_3)_2OH + Na_2SO_4 \qquad (2)$$

Dehydration reaction:

$$C_6H_5C(CH_3)_2OOH + C_6H_5C(CH_3)_2OH \rightarrow C_6H_5C(CH_3)_2OOC(CH_3)_2C_6H_5 + H_2O \qquad (3)$$

Through a dehydration reaction, the concentration of DCPO was increased to approximately 50 mass%. During alkalization, crystallization, and purification, the concentrations of DCPO sequentially were enhanced to approximately 70, 94 and 99.3 mass%, respectively. In this study, differential scanning calorimetry (DSC) was used to investigate the sensitivity of related hazardous properties of DCPO during the manufacturing process, even under upset conditions. On the other hand, by TAM with titration ampoule, the possibilities of thermal

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hazard phenomena in the DCPO synthetic process incurred by incompatibilities were simulated, analyzed, and evaluated to a deeper degree.

Experimental materials and apparatus

Samples

The DCPO was obtained directly from the production site, which includes few intermediates and side products; the various concentrations of DCPO are approximately 50, 70, 94 and 99.3 mass%. The incompatibilities, sulfuric acid (H_2SO_4, 96 mass%), sodium hydroxide (NaOH, 1 N), and rust (Fe_2O_3) had been acquired from the producer company of Baker and Riede-de Haën, and chosen as might appear during the manufacturing process. In addition, the melting point of highly pure indium (In) was used to calibrate the sensitivity of the apparatus [3], DSC and then 98 mass% di-tert-butyl peroxide (DTBP) was used, which was purchased from Aldrich to identify the accuracy of temperature and heat flow of the test method. DTBP in a toluene mixture is also recommended as a standard sample for estimating the performance of several calorimeters. Because of its range of application, the thermal decomposition and its kinetics under both isothermal and adiabatic conditions have been intensively researched in the past [4].

Differential scanning calorimetry (DSC)

The dynamic screening experiments, which were performed on a Mettler TA8000 system coupled with a DSC821^e measuring cell, can withstand relatively high pressure (100 bar). Disposable high pressure gold-plated steel crucibles (ME-26732) were used for acquiring thermal curves and isothermal traces. STAR^e software was adopted for acquiring the DSC curves and analyzing kinetics. For better thermal equilibrium, the scanning rates chosen for the temperature range from 25–400°C were 4 K min^{-1} – strictly for purposes of accuracy.

Thermal activity monitor (TAM) and titration ampoule

The LKB thermal activity monitor is a micro-calorimetric system designed to monitor a wide range of chemical and biological reactions. Reactions can be detected within 12–90°C, the working temperature range of this thermostat. The thermal stability is maintained at a fixed temperature, constant to within $\pm 2\cdot 10^{-4}$°C, which allows fractions of a microwatt to be measured effectively [5]. Before testing, both static calibration and dynamic calibration were performed to ensure the data represented the true response of the sample.

The reactants (CA+CHP) were injected into the stainless containers, capped, and then placed in the measuring chambers. In addition, the reference chambers placed an empty one. The catalyst (96 mass% sulfuric acid) was dispensed into the titration ampoule. Measurement was conducted at 54°C, which simulated the real DCPO process conditions.

Results and discussion

Results of thermal scanning tests

To calibrate the DSC prior to the scanning tests, we first validated the accuracy of this study with standard decomposition reactions of DTBP, and then applied it to the studies on the intermediates and end products of DCPO [2, 6]. In summary, the decomposition of DTBP was determined as first order [7]; the kinetic parameters are delineated in Table 1.

The thermal decomposition hazards of different DCPO concentrations were characterized by using the non-isothermal method. The onset temperature and heat of decomposition of various DCPO concentrations can be acquired easily by using DSC programmed scanning [8]. Physical data on thermal analyses are listed in Table 2. In practice, the average onset temperature DCPO decomposition is 125°C, which was tested and validated by this study. In addition, the heat of decomposition was between 762 to 1200 J g^{-1} which is judged as an inherently hazardous material when the heat of reaction exceeds 250 J g^{-1} [9]. The heat of decomposition (ΔH) of 50 mass% DCPO is largest,

Table 1 Kinetic parameters for the decomposition of DTBP by DSC 821^e

Material	Instrument	Conditions	β/K min^{-1}	E_a/kJ mol^{-1}	lnk_0/s^{-1}	n
DTBP	DSC	pure (98 mass%, 3.9 mg)	10	142.5	32.2	1
DTBP	DSC	20 mass% in toluene (4.0 mg)	10	152.3	34.7	1
DTBP	DSC	20 mass% in toluene (8.8 mg)	10	158.2	36.2	1
DTBP	DSC	20 mass% in toluene (7.4 mg)	4	156.3	36.1	1
DTBP	DSC	20 mass% in toluene (3.5 mg)	4	150.8	34.6	1

due to its including more CHP solvent, the heat of decomposition of 1500 J g^{-1} (80 mass% CHP) determined by DSC [2].

Incompatibilities of DCPO intermediates

The other purpose of the experiments was to identify and assess the incompatibility hazards of inadvertent mixing with incompatible chemicals during the DCPO manufacturing process. As planned, the incompatibilities or additives were strong acid (H_2SO_4), strong base (NaOH) or iron rust (Fe_2O_3), which may be the kinds of impurities encountered in a process. Table 3 displays all the heats of decompositions and initial exothermic temperatures of DCPO mixed with various incompatible substances. By an incompatibility test, both Fe_2O_3 and NaOH did not increase thermal hazards, but the H_2SO_4 conspicuously decreased the onset temperature. For example, the onset temperature of 50 mass% DCPO was 123°C; when with the additive H_2SO_4, it decreased to 96°C. Figures 1 and 2 represent the DSC curves when DCPO was mixed with various incompatibilities. Other incompatibilities and significant thermal hazards will appear in the presence of inorganic acids that not only decrease the onset temperature but also trigger unexpected exothermic reactions at higher temperature. Both figures show the same phenomena; for DCPO with incompatible H_2SO_4, the onset temperature decreased and unexpected reaction occurred.

Thermal hazard phenomena in DCPO synthetic process

In the DCPO synthetic process, we used the CHP and CA as reactants, for which the concentrations were approximately 80 mass%, with strong organic acid as

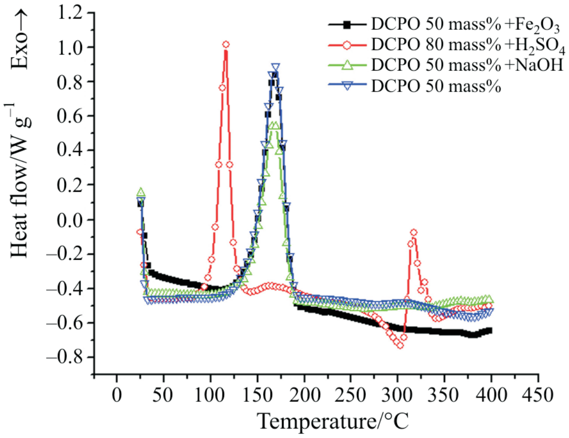

Fig. 1 Thermal decomposition of DCPO intermediate (50 mass%) with various incompatibilities by DSC

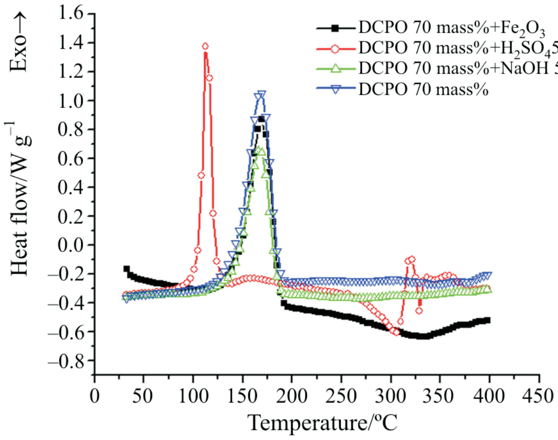

Fig. 2 Thermal decomposition of DCPO intermediate (70 mass%) with various incompatibilities by DSC

Table 2 Scanning test of various DCPO concentrations by DSC 821^e

Concentrations/mass%	β/K min^{-1}	Dosage/mg	T_0/°C	T_{max}/°C	Δ*H*/J g^{-1}
50	4	3.6	127	170	1200
70	4	6.6	130	169	862
94	4	3.2	125	170	756
99.3	4	7.2	119	169	762

Table 3 Experimental data of DCPO intermediates mixed with various incompatibilities[a]; β=4 K min^{-1}

Sample		Incompatibilities		Curve data (for one peak)		
Mass%	Dosage/mg	Substance	Dosage/mg	T_0/°C	T_{max}/°C	Δ*H*/J g^{-1}
50	8.3	–	–	123	169	1149
	8.9	Fe_2O_3	0.5	122	169	1117
	7.1	H_2SO_4	5.5	96	116	851
	10.1	NaOH	1.1	107	168	883
70	7.3	–	–	125	168	814
	5.0	Fe_2O_3	2.4	121	169	772
	4.4	H_2SO_4	7.3	105	115	692
	9.8	NaOH	1.1	109	168	625

[a] Mettler DSC 821^e STAR^e

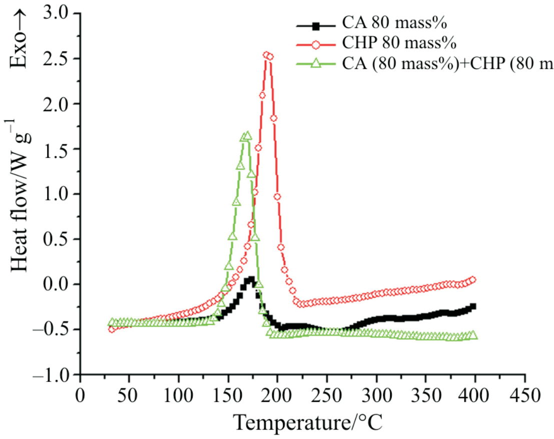

Fig. 3 Comparison of DSC scanning tests on CA, CHP and its mixture

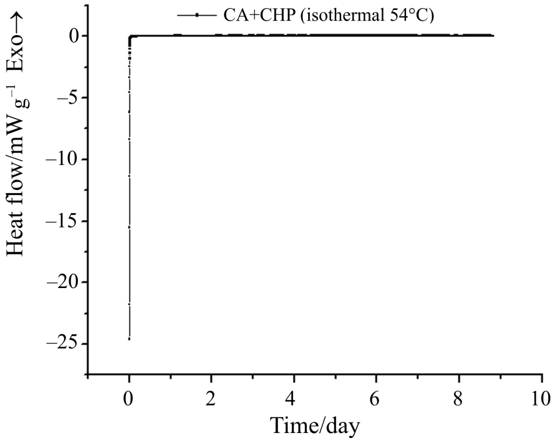

Fig. 4 The thermal curve of mixture sample under isothermal condition at 54°C – a blank test by TAM

catalyst during 50–56°C isothermal conditions. From the DSC test, the result shows the product, DCPO, had potential hazards when mixed with H_2SO_4, which was the necessary catalyst in the DCPO synthesizing process; two peaks of decomposition reaction showed a complicated reaction mechanism and thermal hazard; and the exothermic onset temperature was conspicuously reduced. In addition, to realize the potential hazards of CHP and CA, dynamic screening experiments were performed on DSC tests. Thermoanalytical curves conducted in Fig. 3 show the exothermic characteristics of the mixed sample between the CA and CHP that provide the compatible phenomena, which had no unexpected reaction appearing, and the heat of decomposition of mixture came mainly from CHP.

Furthermore, we tried to narrow the production conditions of the factory to investigate the incompatible tests between reactants (CA+CHP and CA) and catalyst (H_2SO_4) by the same proportion; the tests were performed in a beaker to investigate the preliminary hazards. According to the US Coast Guard CHRIS Systems [10], if the difference between onset temperature and maximum temperature is more than 25°C while reactants are mixed with each other, the reaction could be defined as an incompatibly reaction. By measuring the change of temperature and time elapsed to identify the incompatible hazards, our experimental data demonstrate that incompatibilities may result in a violent runaway reaction, during which the reactive temperature rose fast after an initial exothermic peak [11]. All the experimental data and the calculated parameters are summarized in Table 4.

To closely observe the thermal hazard phenomena in the DCPO synthetic process, we used an isothermal micro-calorimeter, TAM, combined with titration equipment to simulate the reaction system. Isothermal temperature was chosen as 54°C, the typical operating temperature in a plant. Then through a blank test, the mixture sample (CA+CHP) was observed as to whether it would result in any unexpected thermal runaway hazard at such a condition. Through time elapsed, no unexpected phenomena occurred, as indicated in Fig. 4. It demonstrates that the mixture without adding catalyst was compatible. According to the results from the blank test as the baseline, we could observe the potential thermal runaway hazard when any mistake occurred in dosing the catalyst or incompatible chemical receipt by using a titration ampoule. When the catalyst was entering the reactive system, the exothermic reaction was quite violent in a very short period. Furthermore, the exothermic peak exceeded the limit of the isothermal mi-

Table 4 Experimental results of incompatibility tests with H_2SO_4

Reactant	Dosage/mL	H_2SO_4/M, mL	Δ*T*/°C	β/K min^{-1}	Observed phenomena
CA+CHP	25	(10, 0.56)	41.4	16.6	1. charging rate for catalyst: fast speed 2. unexpected reaction being occurred
CA+CHP	25	(10, 0.56)	29.9	12.0	1. charging rate for catalyst: middle speed 2. no unexpected reaction being occurred
CA+CHP	25	(10, 0.56)	15.7	31.4	1. charging rate for catalyst: very fast speed 2. no unexpected reaction being occurred
CA	25	(10, 0.56)	8.9	8.9	1. charging rate for catalyst: fast speed 2. no unexpected reaction being occurred
CA+CHP	25	(5, 0.56)	1.4	0.1	1. charging rate for catalyst: fast speed 2. no unexpected reaction being occurred

cro-calorimeter, TAM, which could detect a maximum power of 3000 [4]. On the other hand, when the reactions proceeded for approximately 21.6 h, it detected an unexpected exothermic phenomenon, as demonstrated in Fig. 5. Figures 6 and 7 are the magnifying-scale for the titration experiment.

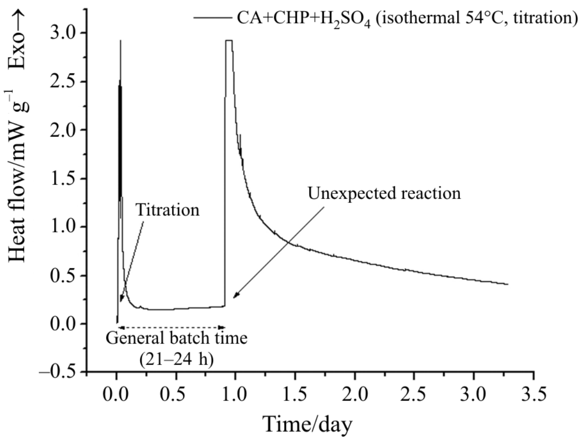

Fig. 5 The synthetic process conducted by TAM under isothermal conditions with titration at 54°C

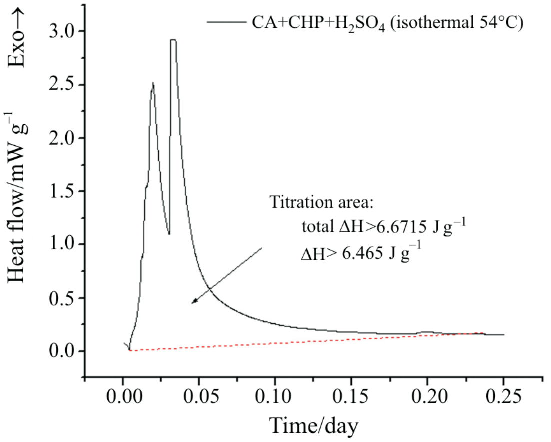

Fig. 6 A magnifying-scale of titration reaction

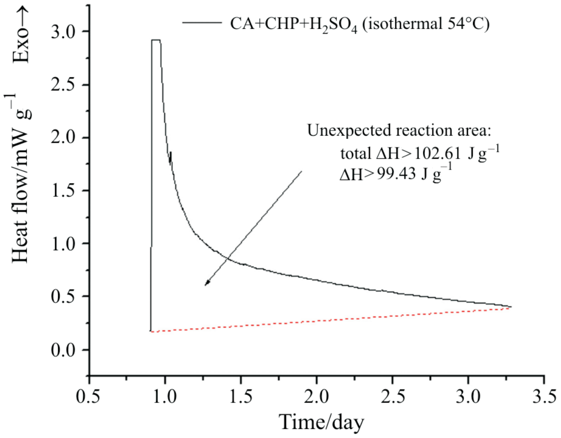

Fig. 7 A magnifying-scale of unexpected reaction

Conclusions

Compared to other organic peroxides, such as CHP or methyl ethyl ketone peroxide (MEKPO), DCPO is safer, but it may become hazardous in manufacturing procedures under various upset scenarios, such as mixing with incompatible chemicals. By means of DSC curves, the average heat of decomposition of various DCPO samples in the manufacturing process is 762 to 1200 J g^{-1}, which makes it a dangerous material. In the incompatibilities study, by using the DCPO mixtures to simulate the real thermal hazard when contaminated with Fe_2O_3, NaOH and H_2SO_4, the labile or unstable sequences are:

DCPO<DCPO+Fe_2O_3<DCPO+NaOH<DCPO+H_2SO_4

From the TAM experiments, the synthetic process of DCPO may result in an unexpected reaction, although the real reason behind it is not clearly known yet.

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