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FLAMMABILITY PROPERTIES OF METHYLPHENYLCARBONATE IN DIPHENYLCARBONATE PRODUCTION PROCESS

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ABSTRACT

This article is aimed for investigating the flammability properties of methylphenylcarbonate (MPC) such as explosion limits (LEL, lower explosion limit and UEL, upper explosion limit) and maximum explosion pressure (P_{max}), according to its practical operating condition (1 atm, 250ºC) by 20-L apparatus. MPC acts as a critical intermediate with potential flammability hazard during the manufacturing process of diphenylcarbonate (DPC), which has been regarded as a potential substitute material for highly toxic phosgene to produce polycarbonate (PC).

It was concluded that important flammability characteristics like explosion limits and P_{max}, the explosion hazard degree of MPC were first proposed by our flammability test. This original and primary research could help to understand and provide MPC's safety-related parameters specifically; so as to avoid accidents resulting from fires and explosions for safe storage, transportation and operation in such relevant processes.

Key words: Methylphenylcarbonate (MPC), Diphenylcarbonate (DPC), Flammability characteristics, Fires, Explosions

INTRODUCTION

In recent years, the most critical objective for industrial fires and explosions prevention is to create effective procedures for flammability hazard protection and control. First, to be familiar with the flammability properties of materials is exactly the primary

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step to alleviate fire and explosion accidents[1]. Especially, investigating and recognizing the explosion limits (lower explosion limit, LEL; upper explosion limit, UEL) and explosion pressure hazard degree (maximum explosion pressure, P_{max}) for a specified chemical material preferably under its surrounding process scenarios would be a prior obligation to prevent accidents resulting from fires and explosions for safe storage, transportation, and operation[1].

Polycarbonate (PC) is one kind of widely and quite substantially used chemical material in the petrochemical industrial process nowadays[2, 3]. Generally speaking, it can be generated directly by the reaction of phosgene and bisphenol A (BPA)[4]. whereas, this highly toxic phosgene-needed process might result in severe health issue[5]. For environment, safety and health concern, another more benign and environmentally route was proposed. Diphenylcarbonate (DPC) has been viewed as an appropriate substitute material for replacing toxic phosgene, reacting with bisphenol A (BPA) in a phosgene-free process to produce PC since the 1970s[5–8].

However, each approach has its own advantages and disadvantages, i.e., for synthesizing DPC by this route, methylphenylcarbonate (MPC, or also called PMC, phenylmethylcarbonate industrially) is an intermediate with potential flammability hazard. In fact, MPC is considered as the combustible liquid according to NFPA 30[9] with probable fire and explosion danger. Once it sparks or burns, it might cause serious fire and explosion accidents, that would be an urgent and earnest emergency at a plant. Nevertheless, even up to date, the rudimentary flammability characteristics, such as explosion limits (LEL and UEL) and P_{max} based on MPC's practical operating conditions, still lack awareness and recognition in the open literature[3-7, 10].

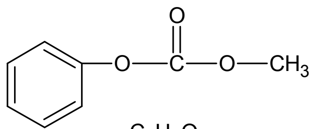
Ensuring the fire and explosion safety of combustible or flammable substances used in processes is unlikely without a detailed understanding for their flammability characteristics and relevant hazards[11,12]. Since those safety knowledge for MPC has generally been insufficient and has not been proposed[10] at present, we attempted to foremost investigating the basic but crucial safety-related parameters of MPC, including explosion limits (LEL/UEL), explosion range and P_{max}. Fire tests were carried out according to its practical operating conditions (1 atm, 250°C) by means of a 20 liter vessel (20 L apparatus) for measuring desired flammability characteristics.

Finally, our concerted efforts on surveying flammability properties of MPC in this work do help. We first inaugurated and proposed MPC's explosion limits and explosion pressure specifically. It is anticipated that this study could recommend, and even forestall any unexpected fires and explosions from such pertinent processes.

EXPERIMENTAL

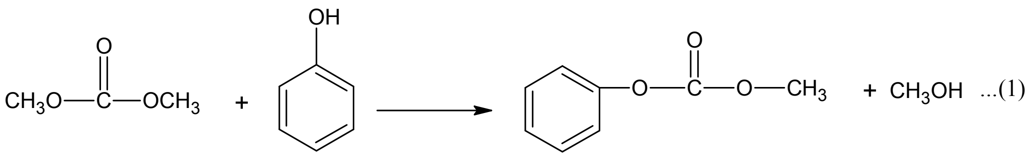
Reagent (MPC)

MPC, which looks in liquid state with colorless appearance at room temperature, has the chemical formula of $C_8H_8O_3$. Fig. 1[10] presents its chemical structure. In this study, 100 Vol.% MPC sample was provided by Chimei-Asahi Co., Ltd. in Taiwan.



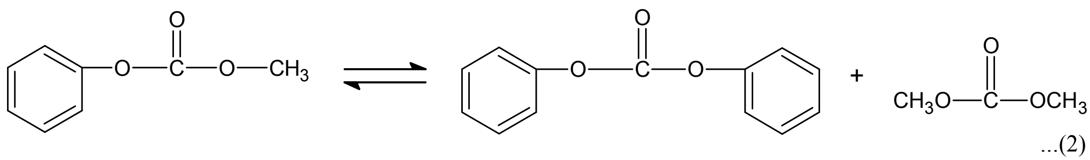
$C_8H_8O_3$

Methylphenylcarbonate (MPC)



$C_3H_6O_3$ (DMC) + C_6H_5OH (Phenol) → $C_8H_8O_3$ (MPC) + CH_4O (Methanol) ...(1)

1 atm, 100-250ºC and normal 21 O_2 vol. % condition DMC, dimethylcarbonate; MPC, methylphenylcarbonate; DPC, diphenylcarbonate



$C_8H_8O_3$ (MPC) ⇌ $C_{13}H_{10}O_3$ (DPC) + $C_3H_6O_3$ (DMC) ...(2)

Industrially, MPC is an intermediate generated from transesterification of DMC and phenol for synthesizing DPC. In general, its continuous reaction routes are given in Equations (1) and (2)[7]. The process conditions are the following: high reaction temperature (100–250°C); low or normal pressure (1 atm)[7]. Hence, based on real industrial operating conditions, we deliberately set the initial pressure and temperature at 1 atm and 250°C, which refers to the highest operating temperatures between 100–250°C, and normal process pressure at 1 atm.

20 Liter spherical explosion vessel (20 L apparatus)

The experiments were carried out in a closed spherical system with a 20 liter vessel, as normally recognized and known as the so-called 20 liter spherical explosion vessel (20-L-Apparatus). It was purchased from Adolf Kühner AG and available for this study as illustrated in Fig. 2[13, 14]. A sight glass was bracketed in the middle of the device for observing the blinker light of combustion.

Fig. 2: 20-L-Apparatus for determining flammability characteristics of MPC[13, 14]

The test chamber is a stainless steel hollow sphere with a general acceptance of the personal computer interface connected with the 20-L-Apparatus. The mixtures are ignited by a pyrotechnic igniter, which has a total of 10 J electric current employed as ignition source for the gas/vapor system, and placed at the center of this vessel[15–17]. The top of the spherical explosion vessel cover contains holes for the lead wires to the ignition system. The opening provides for ignition by a condenser discharging with an auxiliary spark gap, which is controlled by the KSEP 320 unit of the 20-L-Apparatus[11,18]. The KSEP 332 unit uses two "Kistler" piezoelectric pressure sensors on the flange to measure the pressure as function of time[17, 19]. A comprehensive software package KSEP 6.0 was available, which allowed safe operation of the test equipment and an optimum evaluation of the explosion test results[11, 20].

The 20-L-Apparatus has the highest reliability because of its standard spherical shape[21,22] compared with another measurement apparatus for fire and explosion characteristics that have been brought out[17]. The test system enables to determine a material's inherent safety properties in accordance with internationally recognized test procedures, e.g., ASTM 1226 (American Society for Testing and Materials, USA) and VDI 2263 (Verein Deutscher Ingenieure, Germany)[11], as displayed in Table 1[11,16,17]. Essentially, it is suitable for measuring explosion behaviors of combustible materials, such as solvent vapors, flammable gases, or combustible dusts and deriving the flammability properties of LEL, UEL, P_{max}, maximum rate of explosion pressure rise ($(dp\ dt^{-1})_{max}$), gas or vapor explosion constant (K_g), and minimum oxygen concentration (MOC) in the series of test procedures[17].

Table 1. The criteria for the observed reaction behavior in the 20-L-Apparatus[11, 16, 17].

IE = 10 J	P_{ex} (bar)	P_m (bar)	Decision
UEL and LEL testing	< 0.1	< 0.1	No ignition
	≧0.1	≧0.1	Ignition

E: Ignition energy; P_{ex}: Explosion overpressure; P_m: Corrected explosion overpressure

LEL, UEL and P_{max} detection for gas and solvent vapors

Explosion limits consists of the LEL and UEL. The explosion range is from LEL to UEL of a specific substance. Vapor-air mixtures will ignite and burn only over a well-specified range of compositions[1]. The LEL/UEL of gas or vapor is the lowest/highest concentration at which gas or vapor explosion is not detected in three successive tests[17]. Generally, for a material, the lower LEL or broader explosion range; the greater its flammability hazard degree would be[23].

As for the explosion indices, P_{max}, defined as the mean values of the maximum values of all three series[17].

RESULTS AND DISCUSSION

Through our investigations on flammability characteristics for MPC in a normal air condition of O_2 21 Vol.%, 1 atm, and 250°C, these experimentally derived data had been proposed and also given in Table 2, indicating its properties in such required scenarios: each explosion limit was 1.33 (LEL) and 8.02 Vol.% (UEL), so that the explosion range was 6.69 Vol.%. Correspondingly, MPC had a P_{max} for 4.8 bar.

Furthermore, Fig. 3 shows the relationship between MPC and its fitted P_{max}, all at 21 O_2 Vol.%, 250°C, and 1 atm scenarios, which clearly indicated that the LEL was even less than 2 Vol.%. As we know, the lesser the LEL or broader the explosion range, the greater the flammability hazard degree for a flammable material[23]. Besides, the most crucial merit or benefit of this study is that we initially discovered MPC's critical fire and explosion characteristics, such as the explosion limits and pressure. In other words, we inaugurated the discovery for the potential flammability hazard of MPC concretely.

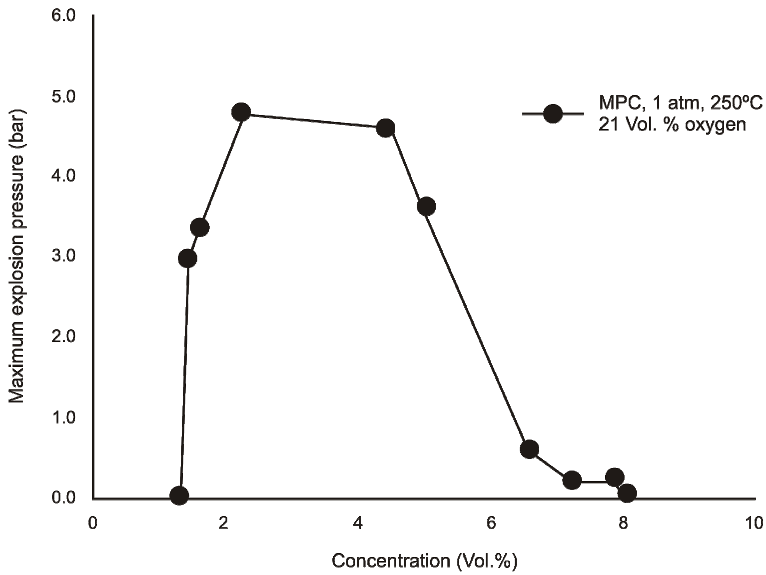


Fig. 3: P_{max} *vs.* 100 Vol.% MPC at 21 O_2 Vol.%, 250℃ and 1 atm

CONCLUSIONS

According to the experimental initial conditions of 1 atm, 250℃ and regular oxygen concentration 21 Vol.%, we found that pure MPC's explosion limits, explosion range and P_{max} were 1.33 (LEL), 8.02 (UEL), 6.69 Vol.% (explosion range) and 4.8 bar (P_{max}), respectively.

Through these experimental flammability investigations, essential and significant flammability characteristics of MPC were first detected. We initially elucidated that

MPC's flammability properties and first proposed its potential flammability hazard practically. Furthermore, this study could recommend, and even present any unexpected fires and explosions from such relevant processes.

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