การพัฒนาพอลิคาร์บอเนตที่มีความหน่วงไฟ 5วีบี

นายอาทิตย์ เพิ่มเติมสิน

วิทยานิพนธ์นี้เป็นส่วนหนึ่งของการศึกษาตามหลักสูตรปริญญาวิทยาศาสตรมหาบัณฑิต
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DEVELOPMENT OF POLYCARBONATE WITH 5VB FLAME RETARDANCY

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A Thesis Submitted in Partial Fulfillment of the Requirements

for the Degree of Master of Science Program in Petrochemistry and Polymer Science

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Thesis Title   DEVELOPMENT OF POLYCARBONATE WITH 5VB
                    FLAME RETARDANCY
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อาทิตย์ เพิ่มเติมสิน : การพัฒนาพอลิคาร์บอเนตที่มีความหน่วงไฟ 5วีบี. (DEVELOP-MENT OF POLYCARBONATE WITH 5VB FLAME RETARDANCY)   อ.ที่ปรึกษาวิทยานิพนธ์หลัก : รศ.ดร.ศุภวรรณ ตันตยานนท์, อ.ที่ปรึกษาวิทยานิพนธ์ร่วม : ผศ.ดร.พูนทรัพย์ ตรีภพนาถกูล, 71 หน้า.

งานวิจัยนี้ศึกษาสมบัติการหน่วงไฟของบิสฟีนอลเอพอลิคาร์บอเนต (PC) โดยมีการเติมสารปรุงแต่ง (additives) ที่มีสมบัติหน่วงไฟ ตั้งแต่หนึ่งถึงสี่ชนิดเข้าไป แล้วนำไปทดสอบหาค่า limiting oxygen index (LOI) และวิธี UL94 ที่ระดับการทนไฟ 5VB จากการทดลอง ได้สารผสมสองสูตร ที่มีสมบัติผ่านเกณฑ์ UL94 ที่ระดับการทนไฟ 5VB ที่ความหนาของตัวอย่าง 2.0 มิลลิเมตร และมีค่า LOI ที่สูงกว่า PC ประมาณ 20% สูตรแรกมีเตตระโบรโมบิสฟีนอล-เอ (TBBA) ปริมาณ 15% โดยน้ำหนัก และสามารถปรับลดปริมาณลงให้เหลือ 10% ผนวกกับการเติม 5% บิสฟีนอล-เอ บิส(ไดฟีนิลฟอสเฟต) (BDP) เข้าไปในส่วนผสมสูตรที่สอง สมบัติการหน่วงไฟของ PC ที่เพิ่มขึ้นนี้ แสดงให้เห็นว่าส่วนประกอบของสารหน่วงไฟที่เติมเข้าไปเกิดปฏิกิริยาเสริมกัน และเพิ่มการหน่วงไฟ ของ PC ให้ดียิ่งขึ้น นอกจากนี้ได้นำสองสูตรที่ผ่านเกณฑ์นี้ไปศึกษาลักษณะเฉพาะของสารผสมโดย เทคนิค TGA, FTIR, Raman spectroscopy และ SEM จากการทดสอบสมบัติทางกายภาพ พบว่า การเติมสารหน่วงไฟในปริมาณสูง จะทำให้สมบัติทางกายภาพ เช่น ความแข็งแรงด้านการทนแรง กระแทกลดลงอย่างมีนัยสำคัญ อย่างไรก็ตามในงานวิจัยนี้สามารถแก้ไขได้โดยการเติมสารปรุงแต่ง ที่เพิ่มสมบัติการทนแรงกระแทกเข้าไปในส่วนผสมโดยยังคงความหน่วงไฟในระดับ 5VB

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KEYWORDS : POLYCARBONATE / FLAME RETARDANCY / 5VB RATING / TETRABROMO BISPHENOL-A / BISPHENOL-A-BIS(DIPHENYLPHOSPHATE)

ARTHIT PHERMTERMSIN : DEVELOPMENT OF POLYCARBONATE WITH 5VB FLAME RETARDANCY. ADVISOR : ASSOC. PROF. SUPAWAN TANTAYANON, Ph.D., CO-ADVISOR : ASST. PROF. POONSUB THREEPOPNATKUL, D.Eng., 71 pp.

The flame retardancy of bisphenol A polycarbonates (PC) containing one to four flame retardants (FRs) was determined by limiting oxygen index (LOI) measurement and UL 94 5VB rating test. Two of the formulations were complied with UL94 5VB rating at 2.0 mm thick with 20% higher LOI value than the neat PC. Interestingly, the first formulation containing 15% by weight of tetrabromo bisphenol-A (TBBA) can be reduced to 10% by adding 5% of bisphenol-A bis(diphenyl phosphate) (BDP) to form the second formulation. The improvement in flame retardancy of PC compositions arose from synergistic interaction of these additives. These two formulations were characterized by TGA, FTIR, Raman spectroscopy, SEM and mechanical properties. The high content of FRs of the selected samples reduced the mechanical property especially the impact strength significantly. Surprisingly, this can be improved by adding of the impact modifier while maintaining the flame retardancy of PC.

Field of Study : Petrochemistry and   Student's Signature ....
                 Polymer Science   Advisor's Signature ....
Academic Year :   2011   Co-advisor's Signature ....

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CONTENTS

LIST OF TABLES

LIST OF FIGURES

FIGURE   **PAGE**

LIST OF ABBREVIATIONS

ABS	:	Acrylonitril butadiene styrene polymer
ATR	:	Attenuated total reflectance mode
BDP	:	Bisphenol-A bis(diphenylphosphate)
EB	:	Elongation at break
FM	:	Flexural modulus
FR	:	Flame retardant
FT-IR	:	Fourier-transform infrared spectrometer
ISO	:	International standardization and organization
KBPFS	:	Potassium butyl perfluorosulfonate
LOI	:	Limiting oxygen Index
PC	:	Bis-phenol A polycarbonate or Polycarbonate
PET	:	Polyethylene terephthalate
PTFE	:	Polytetrafluoroethylene
SAN	:	Styrene acrylonitrile polymer
SEM	:	Scanning electron microscope
TBBA	:	Tetrabromo bisphenol-A
TGA	:	Thermogravimetric analysis
TS	:	Tensile strength at break
UL	:	Underwriters Laboratories Inc.
VB	:	Vertical burning
°C	:	Degree celsius
hr	:	Hour
J/m^2	:	Joules/square meter
min	:	Minute
mL	:	Milliliter
MPa	:	Mega pascal
T_{max}	:	The temperature of the maximum rate of degradation
T_{onset}	:	The onset degradation temperature
μL	:	Microliter

wt   :   Weight

wt%   :   % by weight

CHAPTER I

INTRODUCTION

1.1 Purpose of investigation

Nowadays, synthetic polymers are widely used and very important for daily life. The synthetic polymers are widely used to replace the traditional materials such as ceramics, metals, wood, cotton, rubber and etc. Furthermore, synthetic polymers are developing continually to improve their properties to be better or same as traditional materials. Almost synthetic polymers are combustible. Thus, the polymer-containing end products, for example, compressor parts, electric plugs, motor pumps, and etc. must have a high degree of flammability resistance to fire and also maintain the public safety.

Bisphenol-A polycarbonate or Polycarbonate (PC) is one of the most important commercial aromatic polycarbonates [1,2], widely used as an engineering thermoplastic. It is an amorphous polymer with outstanding thermal and mechanical properties; including good transparency, high mechanical strength, good dimensional stability, high gloss, high heat distortion temperature, flame retardancy, high glass and high degree of thermal stability. The unique properties of PC make it the polymer choice in a wide variety of applications such as electronic and electrical devices, construction, automobiles, aircraft, medical and packaging parts [1-6]. Even PC exhibits a limiting oxygen index of approximately 24 - 27% and V-2 rating of 3.2 mm thick in UL94 vertical burning test [4-9], a higher rating of flame retardancy is required in many applications of PC.

Four flame retardants (FRs) such as tetrabromo bisphenol-A (TBBA), bisphenol-A bis(diphenylphosphate) (BDP), potassium butyl perfluorosulfonate (KBPFS), and polytetrafluoroethylene (PTFE) are selected to improve the flame

retardancy of PC. Their functions are different in mechanisms which are chosen to study the synergistic interaction with neat PC.

1.2 Objective of research

To improve the flame retardancy of PC complying with UL94 5VB rating of 2 mm thick by optimizing flame retardants content in PC.

CHAPTER II

THEORY AND LITERATURE REVIEWS

Polycarbonate (PC) is produced from the polymer condensation reaction. The chemical structure of PC consists of benzene rings and quaternary carbon atoms in the molecules, which promote the high heat deflection temperature, rigidity, strength and creep resistance. The bulky chains of the polymer are normally amorphous and transparency, also high ductility and impact resistance due to the free volume. These characteristics lead to the good properties of PC such as high percent elongation, heat deflection temperature, heat resistance, impact strength, optical clarity and toughness. Therefore, PC applications are widely used in many areas. They are manufactured, for example, as consumer articles, household, laser-optical data-storage systems, photograph, optical equipment and sporting goods [4,7,8].

PC resin has usually been imparted with flame retardancy by being incorporated with flame retardants and flame retardant aid. There are many types of flame retardants can be used with PC which will be reviewed in this chapter.

2.1 Inherent flammability of polymer groups summary [10]

2.1.1 Inherently flame retardant polymers

Main structures of these inherently flame retardant polymers contain either aromatic groups or halogen which have good thermal stability and the ability to form char during combustion. The examples of polymers family in this group are polytetrafluoroethylene (PTFE), aromatic polyimide, aromatic polyamide, aromatic polyester, aromatic polyether and aromatic polyethersulfone.

2.1.2 Less flame retardant polymers

The polymers family of this group is relatively less flame retardant such as silicone, polysulfone, and liquid crystal polymers. Therefore, appropriate flame retardants such as minerals and other flame retardant additives are used to improve their flame retardancy.

2.1.3 Flammable polymers

The low thermal stability and forming large quantities of fuel with fast decomposition are subjected to classify this polymers family as flammable polymers. Polystyrene (PS), polyacetal (POM), polyamide (PA), polycarbonate (PC), polyethylene (PE), polypropylene (PP), polyurethane (PU), polyvinyl chloride (PVC), acrylic, cellulose, ionomer, Acrylonitrile-butadiene-styrene (ABS) and Styrene-acrylonitrile (SAN) are flammable polymers.

2.2 Introduction of polycarbonate

In 1953, Dr. H. Schnell at Bayer AG (Germany) discovered the PC by the synthesis reaction between bisphenol-A (BPA) and diphenyl carbonate or carbonyl chloride (as named is phosgene gas). It is almost the same period as discovered by Dr. Dan Fox of General Electric. In the late 1950s, the first commercial production of PC was available in the market [11]. At the present, PC was produced from many companies such as Bayer (Makrolon®), Chi Mei (Wonderlite®), Dow(Calibre®), DSM (Xantar®), Formosa (PC®), GE (Lexan®), LG (Lupoy®), Mitsubishi (Iupilon®) , Samsung (Staren®), Sam Yang Kasei (Trirex®), and Teijin (Panlite®) [12].

Polymerization processes of PC are well commercially produced by the reactions of interfacial process (Figure 2.1) and the melt process (Figure 2.2). Both reactions are shown below.
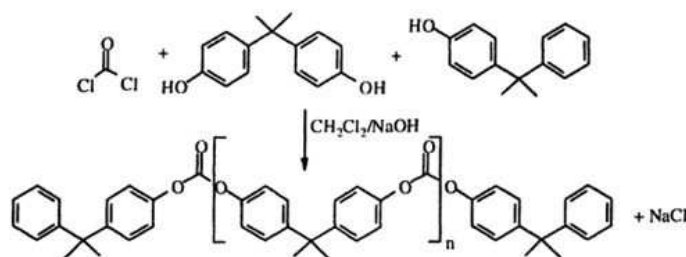
Figure 2.1 General synthesis of BPA-PC by the interfacial process [13].
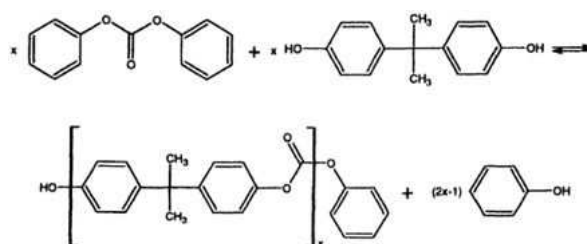
Figure 2.2 General synthesis of BPA-PC by the melt process [13].

PC has many desirable properties such as good thermal stability, transparency, high glass transition temperatures (T_g =140-150°C), high mechanical strength, colorability, electrical insulation, weathering resistance and high charring polymer showing a V-2 rating in the UL94 test. It can be widely used such as drinking bottle, optical disc, switching box, control parts (push buttons, dials), extruded parts, automobiles, electrical and electric devices, haemodialysis filter membrane, surgical instrument handles, needle-free injection, and etc. PC is also advanced material that comply with biocompatibility testing of ISO 10993-1 and USP Class VI [11-12]. However, high efficiency on flame retardancy while maintaining PC properties is required in industrials, therefore many research groups intent to study of flame retardancy for PC and its blend [3].

2.3 Polymer combustion and flame retardancy

2.3.1 Polymer combustion

Combustion or thermal oxidative degradation of polymers occurs in a gas phase involving a fuel and oxygen as shown in Figure 2.3 [14]. This process is difficult to control. Therefore, the preventing during early combustion stage or stop rapidly if the combustion has been occurred, is the important of flame retardant strategy [15].
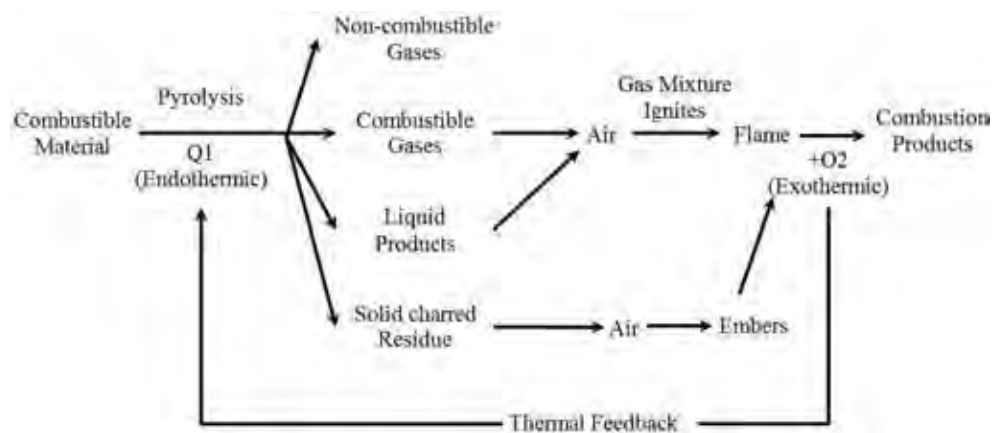
Figure 2.3 The steps of the combustion process [14].

Polymers which made up from carbon and hydrogen are highly combustible. The combustion reaction mainly consists of combustibles (reducing agents) and a combustive (oxidizing agent). The processes start with increasing a temperature and then induce polymer bond scissions to produce a combustible gaseous mixture of the polymer fragments. The gaseous mixture ignites when reach the auto-ignition temperature and then generating heat. Alternatively, the fuel can also ignite at a lower temperature upon reaction with an external source of intense energy [15]. Thus, the combustion cycle is maintained, and called a fire triangle as shown in Figure 2.4.
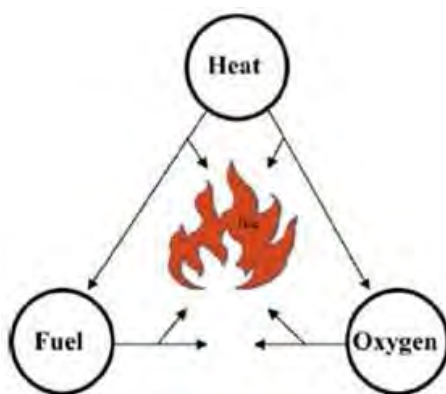
Figure 2.4 The classical fire triangle [16].

2.3.2 Flame retardancy [17]

Flame retardants can be classified in two categories:

1. Additive flame retardants

This category is generally incorporated during the transformation process. These additives do not react with the polymer until the temperature reaches the ignition temperature. Examples of these additives are organic compounds and mineral fillers.

2. Reactive flame retardants

This category is usually incorporated at the beginning of the polymer synthesis (as monomers or precursor polymers) or in a post-reaction process (e.g. via chemical grafting). Such flame retardants are integrated in the polymer chains.

Flame retardant systems (FRS) are intended to stop or to inhibit the combustion process. The function of FRS can either act physically (by fuel dilution, cooling, or formation of a protective layer) or chemically (reaction in the condensed or gas phase). They can interfere with many processes during combustion process (heating, ignition, pyrolysis, and propagation of thermal degradation). The mechanism of actions of FRS are reported and discussed below.

2.3.2.1 Physical action

Physical characteristics and chemical composition of materials have the influence on combustion behavior. Surface area, heat transfer of the flame, oxygen and materials can influence the rate and extent of combustion [15]. Some flame retardant additives exhibit the endothermic decomposition which decrease a temperature by heat consumption which endothermic decomposition of some flame retardant additives decreases a temperature by heat consumption. This involves some cooling of the reaction medium to below the polymer combustion temperature. The formation of gases (H_2O, CO_2, NH_3, etc.) which has occurred during the flame retardants decomposition can dilute the combustible gas mixture resulting to reduce the concentration of the gas mixture and the possibility of ignition. Moreover, some flame retardant additives can be able to form a protective solid or gaseous layer between the gas phase where combustion takes place and the solid phase where thermal degradation occurs. The protective layer inhibits the transfer of combustible volatile gases and oxygen resulting in reduction of decomposition gases produced, significantly. In addition, the fuel gases can be physically separated from the oxygen, which prevents the combustion process being sustained [17].

2.3.2.2 Chemical action [17]

Mechanism of chemical action of flame retardancy can occur in both the gas phase and the condensed phase. The mechanism of the combustion process can be stopped by the incorporation of flame retardant additives that mainly release specific free radicals such as chloride free radical ($Cl^{\bullet}$) and bromide free radical ($Br^{\bullet}$) in the gas phase. These radicals can react with highly reactive free radical species, such as hydrogen free radical ($H^{\bullet}$) and hydroxyl free radical ($OH^{\bullet}$) to form inert or less reactive molecules. This combustion pathway leads to decrease in the exothermic reaction, temperature and the fuel production. In the condensed phase, the flame retardants can accelerate the scission of the polymer chains. In this case, the polymer drips and thus moves away from the flame action zone. Alternatively, the flame retardant can induce the formation of a carbonized or vitreous layer at the polymer's

surface by chemical transformation of the degrading polymer chains. This vitrified layer or char acts as a physical insulating layer between the gas phase and the condensed phase.

2.4 Mechanisms of flame retardant action [15]

2.4.1 Condensed phase

In the condensed phase, three types of processes can take place:

1) Polymer breakdown, which can be accelerated by flame retardants, leads to its pronounced flow which decreases the impact of the flame.

2) Flame retardants can form a carbon layer (charring) on the surface of polymer. This phenomenon occurs by the dehydration of the flame retardant resulting in double bonds occurs in the polymer. These processes form through cyclization and cross linking as shown in Figure 2.5.

3) Heat absorption. Some materials such as alumina trihydrate (ATH) have a very high heat capacity to absorb heat and then reduce the combustion process to be continued.
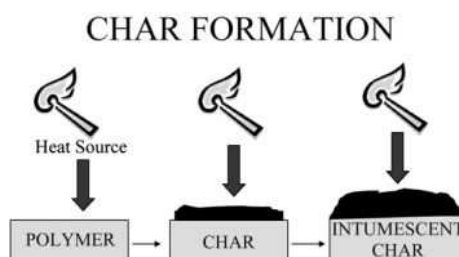
Figure 2.5 Char and intumescence formation.

During intumescence formation, the amount of fuel produced is greatly decreased and carbon char is formed. The char constitutes a two-way barrier, both for hindering the passage of combustible gases and molten polymer to the flame as well as for shielding the polymer from the heat of the flame. These can be generally formulated to consist of three basic ingredients:

1. A promoting charring (catalyst).
2. A charring agent,
3. A blowing agent (spumific compound).

Once ignition occurs, the rate of burning will depend on two factors:

1. The rate of flame spread over the surface. Flame spread can be seen as a repeated series of ignitions, and thus the parameters governing ignitability also control flame spread.

2. The rate of penetration of the flame front into the bulk of the fuel. The heat flux from the flame will drive the production of volatiles. If the flame is above the material, radiant heat transfer will predominate. If gas phase inhibition occurs, this will result in more soot and hence more radiation and greater heat transfer to the fuel. As the rate of fuel pyrolysis increases, so the heat flux from the flame will increase, leading to a greater peak in the heat release as a function of time.

2.4.2 Gas phase

The combustion process in the gas phase is slowed by reactive free radical species that interact chemically with the propagation process of the fire. The flame retardants themselves (or species derived from them) interfere with the free radical mechanism of the combustion process. This slows or stops the exothermic processes that occur in the gas phase and results in a cooling of the system and a reduction in the supply of flammable gases. Hydrogen halides, HX (X = Br or Cl), produced by the reaction of halogenated organic compounds (R–X). With a polymer, P–H, can react with the excited state $HO^{\bullet}$ and $H^{\bullet}$ free radicals to produce the less reactive halogen free radicals ($X^{\bullet}$) leading to an overall decrease in the kinetics of the combustion. See the reaction scheme outlined below:

$$R\text{-}X + P\text{-}H \rightarrow HX + RP$$
$$HX + H^{\bullet} \rightarrow H_2 + X^{\bullet}$$
$$HX + OH^{\bullet} \rightarrow H_2O + X^{\bullet}$$
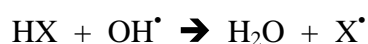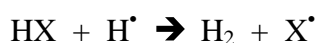
In the presence of halogenated flame retardants, the active free radical species such as OH$^{\bullet}$, O$^{\bullet}$, and H$^{\bullet}$ can be quenched in the gas phase to form less reactive species such as H_2O, H_2, and HX, in the combustion cycle. Mechanisms of action of flame retardants are shown in Figure 2.6.
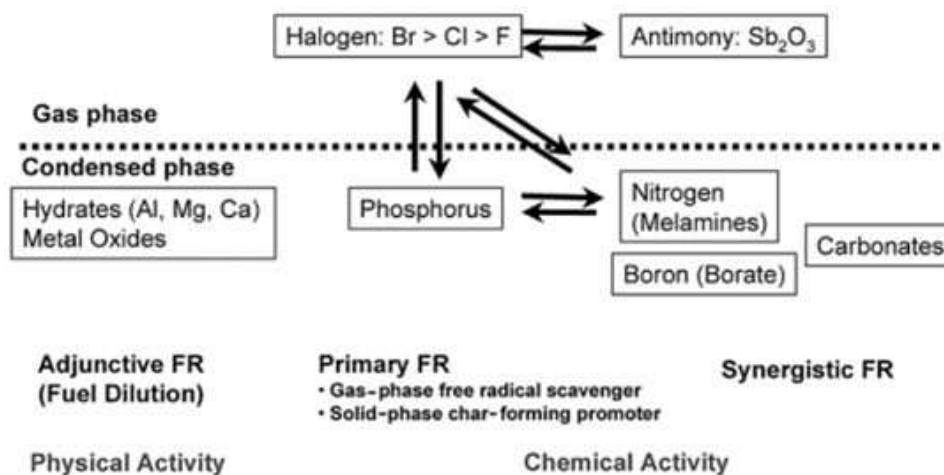
Figure 2.6 The chemical mechanism of flame retardance [10].

2.5 Degradation paths of PC [18]

The polymer degradation behavior is closely related to its flame retardancy. In order to accomplish effective flame retardancy, the degradation pathway of the polymer must be prerequisite understood. The thermal degradation pathways of PC occur by several complicated reactions [19-20]. The chemical structure of PC is polyester unique form of multi-carbon ester linkages which is same as polybutylene terephthalate (PBT) and polyethylene terephthalate (PET). The ester linkage in PC is shown in Figure 2.7. This unique characteristic gives PC decomposed in many routes. The end chain scission, de-carbonation, dehydrogenation, and Fries rearrangement are typical reactions in the initial stage. Successively, cross linking, cyclization and many other side reactions occur. Examples of chemical reactions are described in Figure 2.8 - 2.10. [11,18].

Although there are many routes and the reactions are very complicated, the final products are limited. Some major products are bisphenol-A, alkyl phenols, and a

cyclic compound. Thus, only the main routes were selected among these known mechanisms as shown in Figure 2.11.

PBT ester linkage   **PET ester linkage**   **PC ester linkages**

$$\underset{\displaystyle C}{\overset{\displaystyle O}{\parallel}}-O-CH_2CH_2CH_2CH_2-O- \qquad \underset{\displaystyle C}{\overset{\displaystyle O}{\parallel}}-O-CH_2CH_2-O- \qquad -O-\underset{\displaystyle C}{\overset{\displaystyle O}{\parallel}}-O-$$
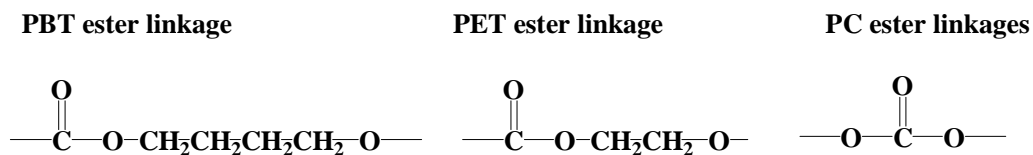
Figure 2.7 Esters linkages [11]
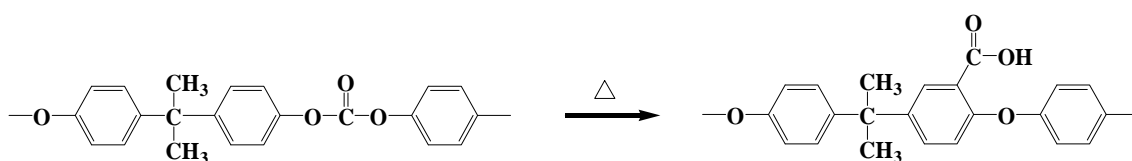
Figure 2.8 Initial Fries rearrangement of the para-carbonyl to the ortho position, ready for cross linking. [11].

$$R_1–CH_2–CH_2–R_2 \;\Rightarrow\; R_1–CH_2^{\bullet} + {}^{\bullet}CH_2–R_2$$

$$R_1–CH_2–CH_2–CH_2–R_2 \;\Rightarrow\; R_1–CH = CH_2 + CH_3–R_2$$
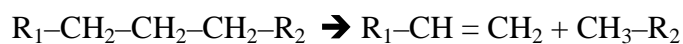
Figure 2.9 Chain scission of 2 reactions forming free radicals and two stable molecules [17].
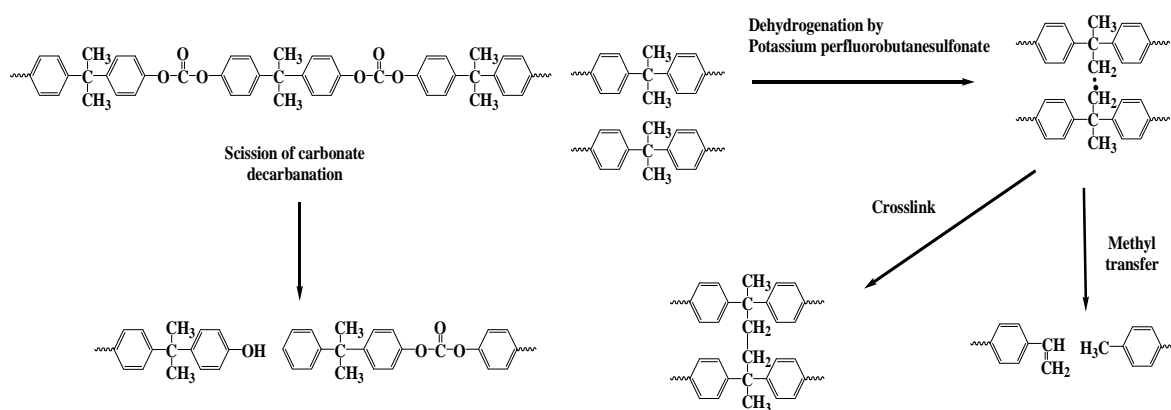
Figure 2.10 Simple de-carbonation (left) and

cross linking reaction (right) of PC main chain [18].
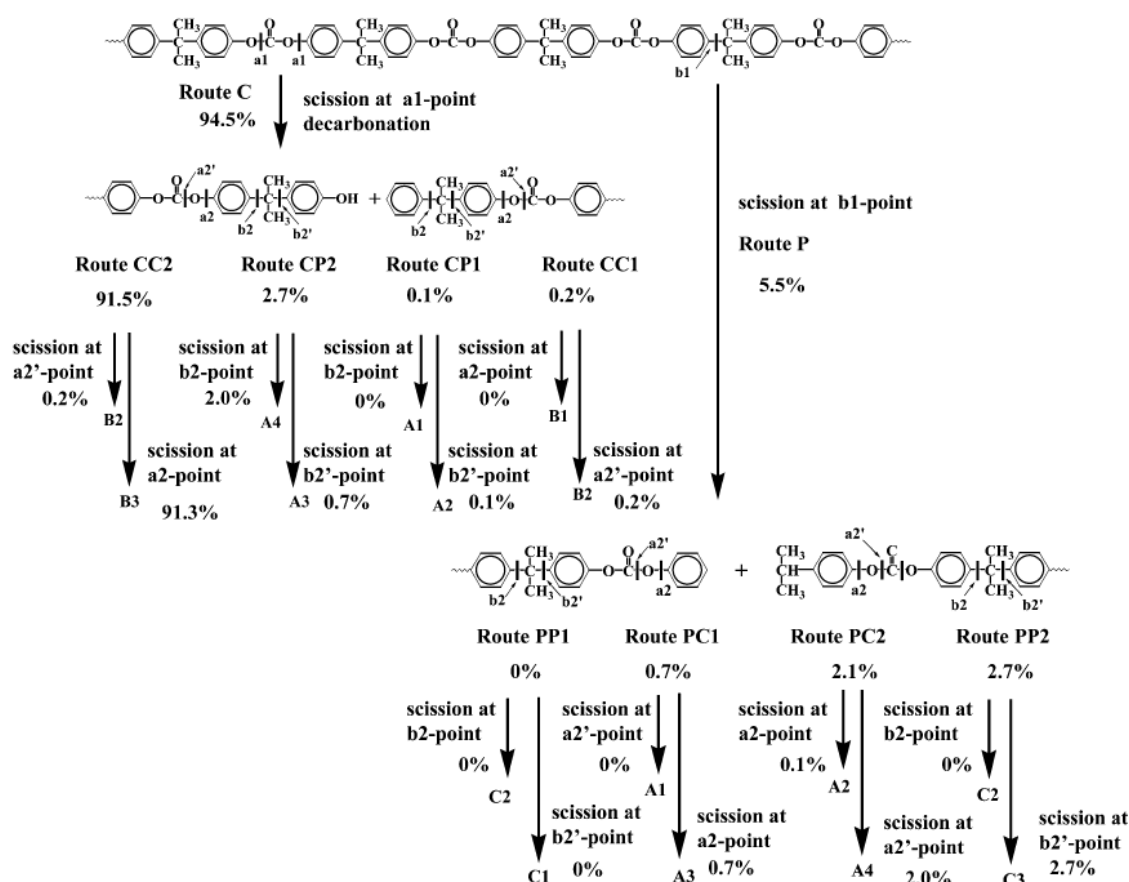
Figure 2.11 Simplified degradation paths of PC and the
degradation ration of each path of neat PC at 495 ^{0}C [18]

2.6 Estimated char structures of PC

C/H ratio, before and after combustion, is observed after burn of burnt charring polymer. The data from previous paragraph exhibited that reaction_was occurred at the initial combustion stage and followed by dehydration or dehyroxy-reaction. Figure 2.12 shows the C/H ratio of neat PC is 1.17 and those of the two intermediates are 1.17 and 1.33, respectively. The final structure is presumed to be the char structure of neat PC after degradation with the C/H ratio of 5.64 which is nearly the same as the experiment data at 800°C (C/H ratio is 5.51). KBPFS is one of flame retardants that increase the char structure as shown in the experiment data at 800°C (C/H ratio is 5.99), thus it will be concluded that the KBPFS is flame retardant that act in the condense phase. [10,18]
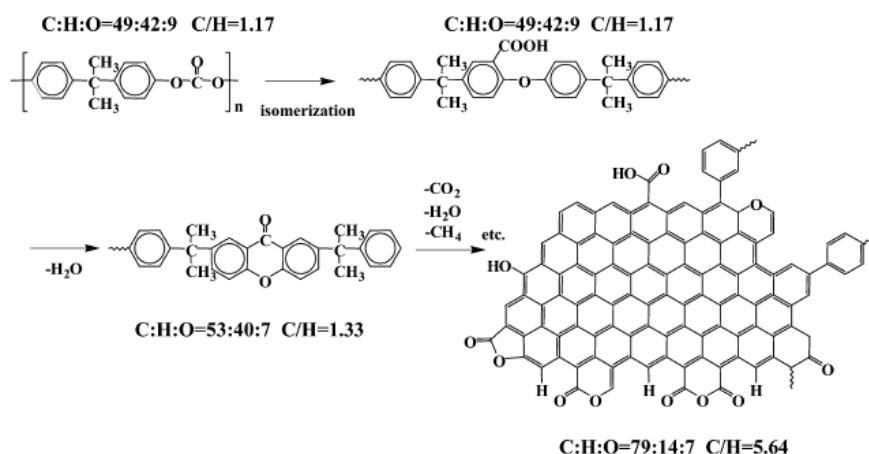
Figure 2.12 Estimated char formation process at the initial stage of degradation [18]

2.7   Classification of flame retardants

FRs have many classifications, some FRs will be discussed below.

2.7.1   Halogenated flame retardant

The mechanism of halogen flame retardant is quite complicated. A radical trap mechanism occurs in the gas phase, which interferes in the burning process, resulting in decrease systematic temperature and reduced reaction rate for the fire-sustaining chemical process retardance. Therefore halogen flame retardant is introduced to use as an advantage function in gas phase. Brominated and chlorinated organic compounds are widely used as flame retardants. Iodine-containing materials are avoided due to less stable than others. In the flame of temperature range, the polymer as a fuel degrades into volatile combustible products would react with halogen flame retardant as an inhibitor in the gas phase consistent with the "right place at the right time" principle [15].

Brominated flame retardants (BFRs) are organohalogens with more than 75 types because of their low cost and high performance [21]. Several classes BFRs, namely bis(2,4,6-tribromophenoxy)ethane (BTBPE), hexabromocyclododecane (HBCCD), polybrominated biphenyls (PBBs), polybrominated diphenylethers

(PBDEs), tetrabromo bisphenol-A (TBBA), and tris(2,3-dibromopropyl)phosphate (Tris) [22].

TBBA, containing approximately 58% bromine, is a phenolic, weakly acidic and hydrophobic compound (pH dependent). It's produced via bromination of bisphenol A in an organic solvent as shown in Figure 2.13 [14]. TBBA ranging from 3-5%, will be reacted with PC by a covalent bond to produce TBBA-PC which is widely used as a reactive flame retardant in electrical & electronic equipment such as cell phones, computers, fax machines, printing of circuit boards, TVs, printers, videos, washing machines and etc. [14].
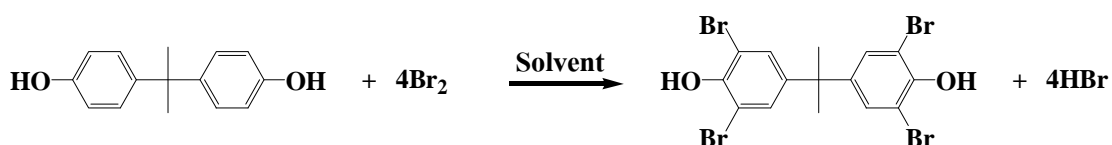
Figure 2.13 TBBA synthesis [14].

2.7.2 Phosphorus-containing flame retardant [15]

The mechanisms of action of phosphorus depend to a large extent on its chemical environment. Under conditions when no hetero elements are present other than oxygen, phosphoric or phosphonic acids are formed. These accelerate the loss of volatile groups from the burning polymer chain and provide a less combustible vapor barrier. The formation of reactive phosphorus based species (such as $PO^{\bullet}$, $P^{\bullet}$, and HPO) in the gas phase are capable to remove the free radicals that can drive combustion. The reaction scheme outlined for a triaryl phosphate as shown below:

$$R_3P{=}O \quad\quad \rightarrow \quad\quad PO^{\bullet}, P^{\bullet}$$
$$H^{\bullet} + PO^{\bullet} + M \quad \rightarrow \quad HPO + M$$
$$HO^{\bullet} + PO^{\bullet} \quad\quad \rightarrow \quad\quad HPO + 1/2\ O_2$$
$$HPO + H^{\bullet} \quad\quad \rightarrow \quad\quad H_2 + PO^{\bullet}$$
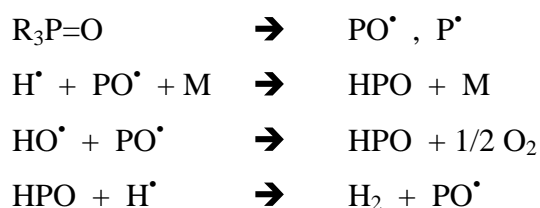
Bisphenol-A bis(diphenyl phosphate) or BDP is a phosphorus-containing flame retardant. It's colorless liquid or clear powder form. BDP is excellent compatibility with the PC, high thermal and hydrolytic stability. The mechanism of BDP on FR is mainly occurring in both condensed phase and gas phase action. BDP chemical structure is shown in Figure 2.14 [7].

Feng et al. have reported that BDP acts as a catalyst during decomposition in the earlier stage, phosphoric acid is formed and catalyze the PC to dehydrate and esterify to form char. Also aryl phosphate group in BDP will further react with PC become a part of char due to the cross-linking reaction, the reaction is shown in Figure 2.15 [7].
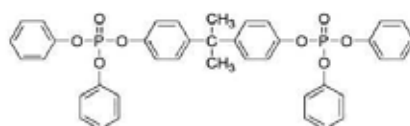
Figure 2.14 Chemical structure of BDP [7].
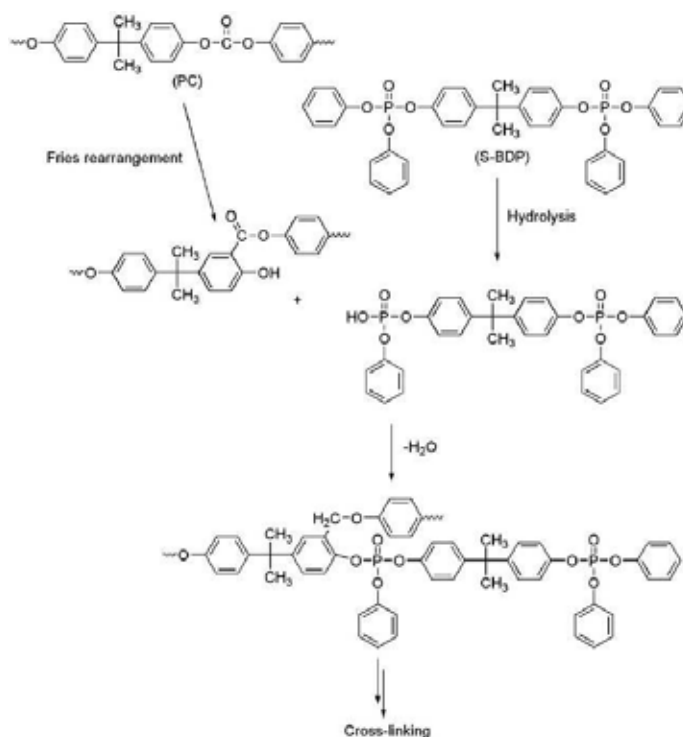
Figure 2.15 Reaction between PC and BDP during thermal decomposition [7]

2.7.3 Poly-tetrafluoroethylene [23]

PTFE was discovered by Roy Plunkett of Dupont in 1938. The physical and chemical properties of this polymer are thermal stability, low coefficients of friction, chemical inertness, and high toughness [24]. PTFE has several forms; high molecular weight (MW) PTFE and low MW PTFE, both of them exhibits with different functions. The mechanism of high PTFE in polymers is to suppress the dripping during combustion, which reduces the spreading of flame and function as an additive to increase melt tension and viscosity of some thermoplastics. The low MW PTFE is for other as improvement functions of wear and friction in plastic that is not presented in this work. The recommended particle size of PTFE is typically 10-20 µm which is easily to "picked" out of the plastic surface during rubbing. Thus the PTFE particle size should be small enough so it is not visible but large enough that it remains embedded in the plastic during rubbing. In general commercial process of irradiation of PTFE in air leads to the formation of carboxylic acid and acid fluoride end group. The presence of these polar groups increases the PTFE surface energy enough to improve the compatibility with other thermoplastics. PTFE chemical structure is shown in Figure 2.16.
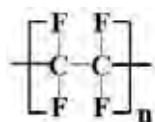
Figure 2.16 Chemical structure of PTFE.

2.7.4 Sulfonated flame retardants [11]

The sulfonate FR mechanism is described as cross linking which different from the three classical mechanisms of FR technology (radical-trapping, intumescence and endothermic). Specialized sulfone-sulfonate flame retardants technology is typically added less than 1% loading. This preserves the polycarbonate properties while allowing the production of compound meeting UL94 V-0 rating

flame retardancy requirements. In contrast, the flame retardant mechanism of the sulfone-sulfonate PC flame retardant is not well understood.

Potassium butylperfluorosulfonate (KBPFS), a sulfonated flame retardant, is a type of cross linking sulfonate flame retardant compound used in PC formulations, supplied by 3M, Bayer and Miteni of Italy, for examples. KBPFS is an effective FR for PC. The use level is usually quite low (0.06-0.1wt.%) to obtain a UL94 V-0 rating of 3.2 mm thick. A chemical structure of KBPFS is shown in Figure 2.17. The mechanism of KBPFS occurs by sulfonates promote cross linking of the PC substrate during thermal degradation. Unfortunately, the high cost of KBPFS limits its use. To solve this economic problem, many compounders have combined to use of 0.02% KBPFS and 0.3% potassium diphenylsulfone sulfonate (KSS) to achieve a good UL94 V-0 rating while improving the transparency and color of a PC. Although there is not yet proven conclusively, fluorine ions may act in the vapor phase as radical traps quenching of the flame.

$$K^{+} \; {}^{-}O-\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle O}{\|}}{S}}-\overset{\overset{\displaystyle F}{|}}{\underset{\underset{\displaystyle F}{|}}{C}}-\overset{\overset{\displaystyle F}{|}}{\underset{\underset{\displaystyle F}{|}}{C}}-\overset{\overset{\displaystyle F}{|}}{\underset{\underset{\displaystyle F}{|}}{C}}-\overset{\overset{\displaystyle F}{|}}{\underset{\underset{\displaystyle F}{|}}{C}}-F$$
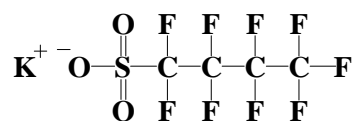
Figure 2.17 Potassium butylperfluorosulfonate.

2.8 Synergistic interaction of flame retardants

It is well known that, there is no ideal FR. Then, more than one FR are incorporated into the polymer matrix during blend. The application of reactive flame retardants involves either the design of new, intrinsically flame retarding polymers or modification of existing polymers through co-polymerization with a flame retarding unit either in the chain or as a pendent group. To synergistic improvement of PC properties with others flames retardancy, various frame retardants were incorporated into PC polymer by physical blend with different ratio and then to investigate PC properties, flame retardancy and thermal stability that will be further discussed in this paper

TBBA is cost efficient and melt blendable in PC. TBBA is not just an additive FR but is also a "reactive" FR. This means that the FR is actually chemically reacted into the polymer matrix such as unsaturated polyester and epoxy resins [16]. TBBA reacts with high reactive free radical of $HO^{\bullet}$ and $H^{\bullet}$ which prevented the thermal decomposition of polymer during combustion. However, thermal stability of polymer was decreased [25]. Although, the halogenated FR has been known to be hazardous to human health and the environment after decomposition [26] but it still be used in various industrial applications. Further study to reduce or replace halogenated FR with environmentally friendly FR is still in research.

Pawlowski and Schartel [27] studied the thermal decomposition and the pyrolysis behavior of aryl phosphates (TPP, RDP, and BDP) in PC/ABS. The result showed that the combination of gas and condensed phase action of BDP results in a slightly superior performance in terms of fire load and decreasing the flame spread than others. They also reported that PTFE is a good additive that synergistic with BDP in terms of flame spread and fire load that made its blend complied with UL94 V-0 rating. He et al. [3] investigated synergistic effects of polyhedral oligomeric silsesquioxane (POSS) and BDP on thermal and flame retardant properties of PC. The addition of TPOSS and BDP significantly affect the thermal degradation and combustion behaviors. The results indicated that combination of TPOSS with BDP in the optimal ratio can enhance the thermal stability of the PC matrix under inert and air atmosphere. Further, addition of both TPOSS and BDP copolymers significantly improves the flame retardant properties of the matrixes, more than the addition of BDP alone. The synergistic effect of BDP and TPOSS significantly decreased the value of peak heat release rate (PHRR) of the hybrids; but the introduction of TPOSS induces the ignition of the hybrids. And the addition of 2 wt% TPOSS and 3 wt% BDP leads to the maximum decrease of the PHRR.

The effect of phosphorus based FR on flame retardancy in PC have been previously reported as good thermal stability and effectively increasing the char residue after thermal decomposition [28]. Moreover J. Green [9] observed the synergistic effect on flame retardancy of a brominated phosphate FR in PC. It's further enhanced comparing with individual phosphorus or bromine compound of HIP, ABS, PET fiber, PC, PC/ABS and PC/PET blend.

Huang et al. [6] reported that the interaction of KBPFS in PC showed the ability to prevent the dripping of melt polymers, generated carbon dioxide to form an intumescent flame retardant effect and help accelerated the char forming. The addition of KBPFS 0.1 wt%. in PC, increased the LOI value to 10 units and then accomplished to the level of the V-0 rating. However, a high amount of KBPFS affected to impact strength of PC [29].

PTFE is one of FR as a function of anti-dripping agent that exists in the PC/FRs blends. Siripurapu et al. [29] used PTFE at 0.4% by weight in the PC/ABS blends with resorcinol bis(diphenyl phosphate) (RDP) and KBPFS. Its combination can be complied with UL94 5VB rating of 3.0 mm thick. In addition PTFE was fixed at 0.4% to prevent the dripping that present in Feng et al. work [7]. They studied thermal stability and flame retardancy of BDP, organo-montmonrillonite (OMMT) and PTFE in PC matrix. BDP with the existing of OMMT and PTFE exhibit a synergistic effect in the UL94 and enhance the thermal stability of the PC. The best two formulations in this study are PC/8%BDP/0.4%PTFE and PC/6%BDP/2%OMMT/0.4%PTFE. These can be complied with the UL94 V-0 rating of 3.0 mm thick with % LOI value of 29.4 and 27.6, respectively.

2.9 Analysis techniques for PC/FRs blends

2.9.1 Raman spectroscopy

In 1928, Chandrashekhara Venkata Raman discovered the phenomenon of inelastic scattering of light as known of the Raman effect. This effect is shift in wavelength of a small fraction of radiation scattered by molecules, having different frequency from that of the incident beam. This shift in wavelength depends upon the chemical structure of the molecules responsible for scattering [30].

Raman spectroscopy has been used in a great number of studies to analyze the vibrational properties and characteristics of numerous materials. Vibrational spectroscopy has proven itself to be a valuable contributor in the study of various fields of science, primarily due to the extraordinary versatility of sampling methods. In particular, it appears to be fast, nondestructive, and very useful method to

characterize the structure of polymers. Raman measurement gives the vibrational spectrum of the analyte, which can be treated as its "fingerprint," allows easy interpretation and identification [30].

Raman band shifts, the energy difference between the incident and scattered photons, are typically described in wavenumber. The unit of wavenumber is cm^{-1}, and it is equivalent to joule by a conversion factor (hc), where h is the Planck constant and c is the speed of light. A typical laboratory Raman spectroscopy system is shown in Figure 2.18 [31]. Raman spectrum and Raman frequency of PC are shown in Figure 2.19 and Table 2.1, respectively [32].
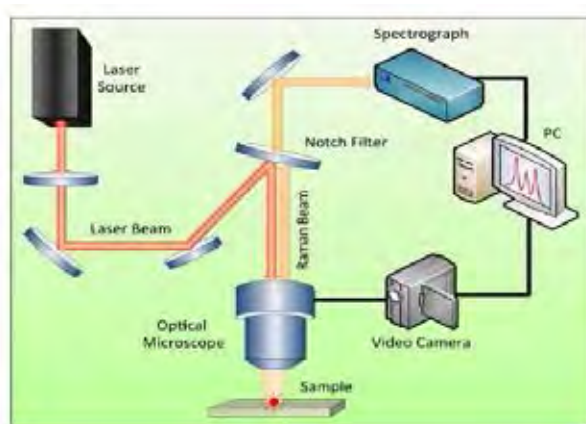
Figure 2.18 A typical laboratory Raman spectroscopy system [31].
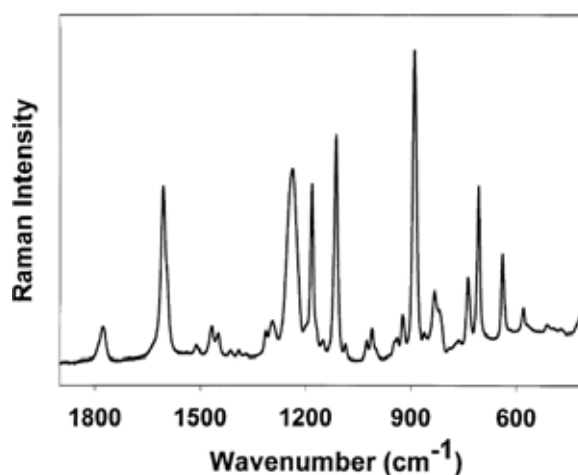
Figure 2.19 Raman spectrum of PC [32].

Table 2.1 Raman frequencies of PC (i.p., in-plane; o.p., out of plane) [32]

Vibration	Raman (polymer)	Intensity [a]
C=O stretch	1777	w
Ring stretch	1606	s
Ring stretch	1592	sh
CH def*	1468	vw
C-O stretch	1235 (broad)	s
CH wag (i.p.)	1180	s
CH wag (i.p.)	1111	s
C-O stretch	1025	vw
Ring stretch	1012	w
CH wag (o.p.)	936	vw
C-CH$_3$ stretch	923	w
C-CH$_3$ stretch	889	s
CH wag (o.p.)	885	sh
CH wag (o.p.)	821	w
Ring def (o.p.)	710	m
Ring def (i.p.)	643	m

[a] w, weak; m, medium; s, strong; v, very; and sh, should.
* deformation band.

The advantages of Raman scattering technique is that it has remarkable resolution and ease of implementation for samples in different physical states (solutions, suspensions, gels, precipitates, fibers, single crystals, amorphous solids, etc.), applicability to large supramolecular assemblies, a spectroscopic time scale (~10^{-14} s) that is fast in comparison to both biomolecular structure transformations and protium/deuterium (H/D) exchanges, non-destructiveness of data collection protocols, relatively low mass (<1 mg) and volume (~1 µL) requirements for most sampling protocols, and freedom from the need for chemical labels or probes. Moreover, the confocality can lead to a three-dimensional analysis of various materials [33-35].

Raman mapping technique is applied to characterize the dispersion of different chemicals that mix together in one material. It is software development of Raman manufacturer for the special technique and easy for user operation. The different spectra of each chemical will be compared. The dominant peak of each spectrum is selected for Raman scanning in the specified area. The sample is placed under the microscope. A 780 nm laser is used to image scanning with a cross section of specified area to allow Raman images to be generated which reveal the location of the different polymer species and also their domain size. The Raman images were generated based on chemical and reference spectra such as PTFE (red) and PC (green)

are shown in Figure 2.20. The Raman images can be combined to show the relative species location. The remaining dark regions represent surface contaminants which produce fluorescence [36].
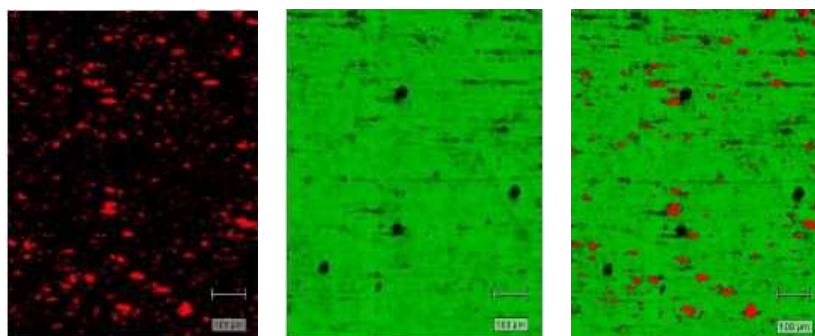
Figure 2.20 Raman images of PTFE (red), PC (green)
and combined PTFE and PC.

2.9.2 Fourier transform infrared spectroscopy

Infrared (IR) spectrum is formed as a consequence of the absorption of electromagnetic radiation at frequencies that correlate to the vibration of specific sets of chemical bonds within a molecule. It is important to reflect on the distribution of energy possessed by a molecule at any given moment, defined as the sum of the contributing energy terms:

$$E_{total} = E_{electronic} + E_{vibrational} + E_{rotational} + E_{translational}$$

The translational energy relates to the displacement of molecules in space as a function of the normal thermal motions of matter. Rotational energy, which gives rise to its own form of spectroscopy, is observed as the tumbling motion of a molecule, which is the result of the absorption of energy within the microwave region. The vibrational energy component is a higher energy term and corresponds to the absorption of energy by a molecule as the component atoms vibrate about the mean center of their chemical bonds. The electronic component is linked to the energy transitions of electrons as they are distributed throughout the molecule, either localized within specific bonds, or delocalized over structures, such as an aromatic

ring. In order to observe such electronic transitions, it is necessary to apply energy in the form of visible and ultraviolet radiation:

$$E = h\nu = \frac{hc}{\lambda}$$

where: h = Planck's constant (6.6256×10^{-34} Js)

The fundamental requirement for infrared activity, leading to absorption of infrared radiation, is that there must be a net change in dipole moment during the vibration for the molecule or the functional group under study [37].

Fourier transform infrared attenuated total reflection (FTIR-ATR) has been extensively used to investigate adsorption and reactions on surfaces and at interfaces. Unlike other techniques, such as fluorescence, radio-labeling, and electrochemical detection, FTIR-ATR needs no extra labels and can provide a wealth of information on system. Main characteristic group absorptions of PC are shown in Table 2.2.

Table 2.2 Main characteristic group absorptions present in FTIR spectra of Poly(bisphenol A carbonate) Durolon samples [38].

Frequency (cm^{-1})	Bonds	Vibrational mode
3529	OH (phenolic hydroxyl)	Stretching
3039	C—H (aromatic ring)	Stretching
2969	C—H (methyl groups)	Symmetrical stretching
2500–1800	Aromatic ring	Combination bands
1773	O—(C—O)—O (carbonyl)	Stretching
1602 and 1465	C—C (aromatic ring)	Stretching
1506	C—H (aromatic ring)	In-plane bending
1387	C—H (methyl groups)	Symmetrical bending
1232	C—O—(C—O)—O—C	Asymmetrical stretching
757	C—H (aromatic ring)	Out-of-plane bending
667	C—C (aromatic ring)	Out-of-plane bending

2.9.3 Thermogravimetric analysis

Thermogravimetric analysis (TGA) is an analytical technique that measures the weight of a small sample (typically 10 mg or less) as a function of time or temperature and hence gives a quantitative description of the thermal stability of the material and the amount of the corresponding residue. The technique can characterize materials that exhibit weight loss or gain due to decomposition, oxidation, or dehydration. TGA can used to study the composition of multicomponent systems such as thermal stability of materials, oxidative stability of materials, estimated lifetime of a product, decomposition kinetics of materials, the effect of reactive or corrosive atmospheres on materials, moisture and volatiles content of materials [39].

The measurement is normally carried out in an atmosphere such as N_2/helium/argon or in air, O_2, to understand the thermal stability of the materials in an inert atmosphere or to study their thermo-oxidative stability, respectively. TGA experiments can be carried out as either isothermal or non-isothermal (i.e., dynamic) weight-loss measurements. The isothermal method requires almost instantaneous heating of the polymer sample to the desired temperature, followed by maintaining that temperature for a specified time. On the other hand, non-isothermal method requires a program with a linear increase in sample temperature with respect to time. [40].

2.9.4 Laboratory flame testing

The flammability resistance of polymers can be characterized such as by their ignition ability, radiant heat transfer test, vertical burning rate, flame-spread rate and heat release rate. These depend on the targeted application of the polymeric material. At least one of the flammability criteria needs to be measured by appropriate flammability tests. Those may find it surprising to learn that there are so many FR products virtually all around them. UL standards test methods and Limiting oxygen index (LOI) will be briefly reviewed in this paper.

2.9.4.1 Limiting oxygen index

LOI test is used to indicate the relative flammability of materials that was first proposed in 1966 by Fenimore and Martin. LOI had been standardized by France (NF T 51-071) and United States (ASTM D 2863) which are now subjected to an international standard (ISO 4589) [17]. The limiting oxygen index (LOI) or oxygen index (OI) is a method for evaluation of the flammability of materials. LOI is defined as the minimum concentration of oxygen in oxygen–nitrogen mixtures, required to sustain burning of a vertically mounted specimen. Thus, the more oxygen required (higher LOI), the stronger the flame retardancy effect. The oxygen index of the air is 21, it means that the material with an LOI value below 21 it's very fast combustion, on the other hand the material with an LOI value above 21 it's self-extinguishing. Thus, the higher of the LOI value, the better in FR property [39]. LOI apparatus is shown in Figure 2.21. The LOI values for some selected polymers are shown in Table 2.3.

The LOI is expressed as:

$$LOI = 100 \times [O_2] / [O_2] + [N_2]$$

Where; O_2 = volumetric flow of oxygen at concentration determined

N_2 = volumetric flow of nitrogen
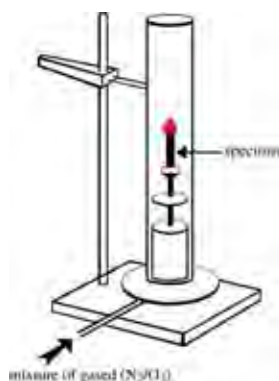
Figure 2.21 Experimental set-up for LOI measurement [17]**.**

Table 2.3 Limiting oxygen index values for selected polymers [15]

Material	LOI	Material	LOI
Polyoxymethylene	15.7	Neoprene	26.3–40
Polyurethane foam (flexible)	16.5	Nomex	26.7–28.5
Natural rubber foam	17.2	Modacrylic fibers	26.8
Polymethylmethacrylate	17.3	Leather	34.8
Polyethylene	17.4	Phenol–formaldehyde resin	35
Polypropylene	17.4	PVC	37–42
Polyacrylonitrile	18	Polyvinylidene chloride	60
ABS	18.3–18.8	Polytetrafluoroethylene	95
Cellulose	19	Polystyrene	18–19
Nylon	20.1–26	Styrene–acrylonitrile	19
Wood (birch)	20.5	Polyethylene terephthalate	20–23
Polycarbonate	22.5–28	Epoxy	21–25
Wood (red oak)	23	Polyvinylidene fluoride	44
Wool	23.8	Fluorinated ethylene propylene copolymer	>95

2.9.4.2 Underwriters Laboratories

Underwriters Laboratories (UL) is an independent organization that provides product safety testing and certification. Their UL94 testing procedures and rating system for thermoplastics flammability are the generally accepted standard throughout most of the world. Different UL94 ratings are given based on variations of the test method and results.

The set of UL94 tests has been approved by the ''Underwriters' Laboratories'' as tests of the flammability of plastic materials for parts in devices and appliances. It includes a range of flammability tests (small and large flame vertical tests, horizontal tests for bulk and foamed materials, radiant panel flame-spread test). In terms of practice and usage, the most commonly used test is UL94 V for measuring the ignitability and flame-spread of vertical bulk materials exposed to a small or large flame. It is a vertical combustion that classifies materials as V-0, V-1, V-2, HB, 5V, 5VA and 5VB as shown in Table 2.4.

Table 2.4 UL94 Flammability classifications summary [10]

UL 94 Rating Flame		Spread Flame	Extinguishing	Limits Flame Drips
HB	Slow burning on a horizontal specimen: burning rate less than 3.0 in./min for wall thickness less than 0.12 in.			
		1.5 in./min	0.12 in. < thickness > 0.50 in.	OK
		3.0 in./min	< 3.0 in. spread > 0.12 in. thick	
V0	Burning stops within 10 seconds on a vertical specimen; no drips allowed			
		Flame or glow cannot reach clamp	< 10 s for any flame application	No drops
			< 50 s for ten flame applications glow out < 30 s	
V1	Burning stops within 30 seconds on a vertical specimen; no drips allowed			
		Flame or glow cannot reach clamp	< 30 s for any flame application	No drops
			< 250 s for ten flame applications glow out < 60 s	
V2	Burning stops within 30 seconds on a vertical specimen; drips of flaming particles are allowed			
		Flame or glow cannot reach clamp	< 30 s for any flame application	OK
			< 250 s for ten flame applications glow out < 60 s	
5V	Burning stops within 60 seconds after fire applications of a flame larger than used in "V" testing each of 5seconds, to a test bar			
		Flame or glow cannot reach clamp	< 60 s for five flame applications glow out	No drops
5VB	Plaque specimens may have a burn-through (have a hole)			
		Flame or glow cannot reach clamp	< 60 s for five flame applications glow out	No drops
5VA	Plaque specimens may not have a burn-through (no hole); highest UL rating			
		Flame or glow cannot reach clamp	< 60 s for five flame applications glow out	No drops

Several ratings can be applied based on the rate of burning, time to extinguish, ability to resist dripping, and whether or not drips are burning. Each polymer compounded material tested may receive several rating based on color and/or wall thickness. When specifying a material for an application, the UL rating should be applicable for the thickness used in the wall section in the plastic molded product. The UL94 flammability rating tests are dependent on the wall thickness of the specimen. For example, one specific material could have several UL94 flammability ratings, 5V for 0.125 in thick, V-0 for 0.062 in thick and V-2 for 0.03 in thick. The UL rating should always be reported including the wall thickness; just reporting the UL rating without mentioning wall thickness is insufficient.

The corresponding experimental device of UL94 5V rating is shown in Figure 2.22. The test specimens can take two forms, 0.50 x 5.0 in. bars or 6.0 x 6.0 in plaques. The burner is controlled to produce a flame height with a 5 in. The blue core flame with 1.5 in. is applied to the lower corners of the specimen. The flame is applied for 5 second and removed for 5 second. This process is repeated five times application. Duration of flaming time plus glowing time, the distance of the burned specimen and dripping of the specimen are observed and recorded.
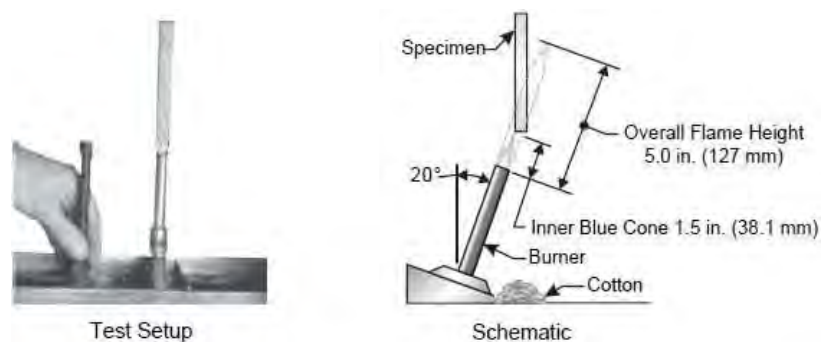
Figure 2.22 Vertical burning test setup and schematic, UL94 5V rating [10].

2.9.5 Scanning electron microscope

Scanning electron microscope (SEM) is utilized in various industrial fields as medical science, biology, materials development, metallic materials, ceramics, and semiconductors [41]. The SEM permits the observation of materials in macro and submicron ranges. The instrument is capable of generating three-dimensional images for analysis of topographic features. An SEM generates high energy electrons and focuses them on a specimen. The electron beam is scanned over the surface of the specimen in a motion similar to a television camera to produce a rasterized digital image. Electrons are speeded up in a vacuum until their wavelength is extremely short, only one hundred-thousandth that of white light. Beams of these fast-moving electrons are focused on a sample and are absorbed or scattered by the specimen and electronically processed into an image. Most electron microscopes used to study materials can image down to about 10 angstroms (0.001 microns) [42].

2.9.6 Mechanical properties testing

Plastics are different from metals because of mechanical characteristics come from the inherent nature of the plastic themselves. Therefore, mechanical properties such as impact strength, tensile and flexural properties are introduced to measure the PC/FRs blend in this paper.

2.9.6.1 Impact strength

ISO 179 is a method for determining the Charpy impact strength of plastics under defined conditions [43-44]. This method is used to investigate the behavior of specified types of specimen under the impact conditions defined and for estimating the brittleness or toughness of specimens within the limitations inherent in the test conditions. This method is more suitable for the testing of materials showing inter laminar shear fracture or of materials exhibiting surface effects due to environmental factors. The method is suitable for use with many types of materials, such as; [43]

1) Rigid thermoplastic molding and extrusion materials, including filled and reinforced compounds in addition to unfilled types; rigid thermoplastics sheets.

2) Rigid thermosetting molding materials, including filled and reinforced compounds; rigid thermosetting sheets including laminates.

3) Fiber-reinforced thermosetting and thermoplastic composites incorporating unidirectional or non-unidirectional reinforcements such as mat, woven fabrics, woven rovings, chopped strands, combination and hybrid reinforcements, rovings and milled fibers, sheet made from pre-impregnated materials (prepregs), including filled and reinforced compounds.

4) Thermotropic liquid-crystal polymers.

2.9.6.2 Tensile properties

ISO 527 is the test for determining the tensile properties of molding and extrusion plastics. These properties include ultimate strength, strain at failure, and modulus. The mechanical properties of plastics can change dramatically when certain additives are incorporated into the formulation. Some of these properties include strength, ductility, and toughness. For the measurement of modulus of elasticity, the speed of testing should be taken from the standard. The following groups of materials are suitable for use with this method.

1) Rigid and semi-rigid thermoplastics molding, extrusion and cast materials in their unfilled form. This includes reinforced materials with short fibers, small rods, plates, or granules, but excludes textile fibers.

2) Rigid and semi-rigid thermosetting molding and cast materials which include reinforced with filler and reinforced compounds, but excludes textile fibers.

3) Thermoplastic liquid crystal polymers. [45]

2.9.6.3 Flexural properties

ISO 178 determines flexural properties of reinforced and unreinforced plastics including high modulus composites and insulating materials for electronics using a three point loading system. The specimen tested are thin rectangular bars either from sheets, plates or molded shapes and the test data results in flexural properties

including max fiber stress, flexural yield, flexural strength, max strain, modulus of elasticity and stress as a function of strain which are important for qualitative characterization, research and development, quality control and other plastics engineering design purposes. ISO 178, Procedure A uses a strain rate of 1%/min and is for specimen that fails under relatively small deflections. ISO 178, Procedure B uses two different strain rates, 5%/min or 50%/min depending on the material's ductility [46]. The ISO 178 test method is suitable for use with the following range of materials.

1) Thermoplastic molding and extrusion materials, including filled and reinforced compounds in addition to unfilled types.

2) Rigid thermoplastic sheets.

3) Thermosetting molding materials, including filled and reinforced compounds.

4) Thermosetting sheets [47].

CHAPTER III

EXPERIMENTAL

3.1 Chemicals

The chemicals composition of the polycarbonate, flame retardant materials studied in this work are following.

3.1.1 Bisphenol-A polycarbonate (PC), powder form, from Thai Polycarbonate Co., Ltd. The number and weight average molecular weight of PC are 10,500 and 27,000 Daltons, respectively, relative to polystyrene standard.

3.1.2 Tetrabromo bisphenol-A (TBBA), powder form, from Mitsubishi Engineering Plastics Corporation.

3.1.3 Bisphenol-A bis(diphenyl-phosphate) (BDP), liquid form, from Adeka Corporation.

3.1.4 Potassium butyl perfluorosulfonate (KBPFS), powder form, from Lanxess Deutschland and GmbH.

3.1.5 Polytetrafluoroethylene (PTFE), powder form, from Daikin Fluorochemicals Co., Ltd.

3.16 Impact modifier as block terpolymers of siloxane-alkylacrylate-SAN, powder form, from Mitsubishi Rayon Co., Ltd.

3.2 Experiment apparatus / Analytical equipment / Machines

3.2.1 Twin screw extruder; Toshiba machine TEM37BS, Japan.

3.2.2 Tumbler mixer; capacity 30 liter.

3.2.3 Injection molding machine; Nissei 80 Ton.

3.2.4   Limiting Oxygen Index apparatus (LOI) which was equipped according to the standard test method of Oxygen index, ASTM D2863-06.

3.2.5   Flammability tester; ATLAS HVUL, USA, which was equipped according to UL94 5V standard test method.

3.2.6   Thermogravimetric analyzer (TGA); Mettler SDTA851, Switzerland.

3.2.7   Fourier transform infrared spectrophotometer (FTIR); Perkin Elmer Spectrum 2000 Explorer, USA, using with Attenuated total reflectance mode (ATR).

3.2.8   Raman spectrophotometer; Renishaw inVia Raman Microscope, UK, using with Raman mapping mode.

3.2.9   Scanning electron microscope (SEM); Phillips XK20, UK, using Energy dispersive X-ray detector.

3.2.10 Digital impact tester, Toyoseiki DG-CB, Japan.

3.2.11 Universal testing machine, Autograph AG-50kNG, Japan.

3.3   Experimental procedure

3.3.1 Preparation of PC/FRs blends

PC and 4 types of flame retardants (TBBA, BDP, KBPFS, PTFE) after weighing were mechanical mixed for 20 min in a tumbler mixer. The mixtures of PC/FRs blends are in powder form.

3.3.2 Preparation of samples (test specimens)

PC and one or more of flame retardants were melt blended at $250^{o}C$ in twin screw extruder (Toshiba TEM-58BS, Japan) to form pellet. The pellets after dried in oven at $80^{o}C$ for 4 hrs, were molded in injection molding machine (Nissei NEX-110W, Japan) at 50 - $260^{o}C$ into rectangular sheets; 6.5 x 3 x 70 mm and 13 x 2 x 125 mm for LOI and UL94 5VB measurement respectively. The amount of each FRs was varied as shown in Table 3.1. The test condition of twin screw extruder and injection molding machine are shown in Table 3.2 and 3.3, respectively.

Table 3.1 Recipes of PC/FR blends

Blend No.	PC (%)	Additive content (% by wt.)				
		TBBA	BDP	KBPFS	PTFE	Impact modifier
PC	100.00	0.00	0.00	0.00	0.00	0.00
PC1	84.55	15.00	0.00	0.05	0.40	0.00
PC2	84.55	10.00	5.00	0.05	0.40	0.00
PC3	84.55	7.50	7.50	0.05	0.40	0.00
PC4	84.55	5.00	10.00	0.05	0.40	0.00
PC5	84.55	0.00	15.00	0.05	0.40	0.00
PC6	85.00	15.00	0.00	0.00	0.00	0.00
PC7	85.00	0.00	15.00	0.00	0.00	0.00
PC8	99.95	0.00	0.00	0.05	0.00	0.00
PC9	99.60	0.00	0.00	0.00	0.40	0.00
PC10	82.05	15.00	0.00	0.05	0.40	2.50
PC11	81.55	10.00	5.00	0.05	0.40	3.00

Table 3.2 The test condition of twin screw extruder (TEM37BS)

Parameter	Setting value	Unit
C1	250	°C
C2	250	°C
C3	250	°C
C4	250	°C
C5	250	°C
Die	250	°C
Pressure at Vent port	-0.7	bar
Resin Temperature	315-320	°C
Screw speed	250	rpm
Through put	40-50	kg/hr

Table 3.3 The test condition of injection molding machine (Nissei NEX80)

Parameter	Setting value	Unit
Cylinder temp	260-260-250-240-240-50	°C
Mold Temp	80	°C
Injection speed	10	%
V/P Change position	10	mm
Pressure injection time	0	sec
Cooling time	10	sec
Suck back	2	mm
Holding pressure	31	%
Pressure speed	36	%
Measure distance	45	mm
Measure time	10	sec
Back Pressure	2	Mpa
Screw speed back	17	%
Cushion	6-7	mm
Cycle time	40	sec

3.4 Characterization

3.4.1 Raman analysis

The dispersion of FRs in each PC/FRs blend sample was characterized by Raman spectrophotometer (Renishaw inVia Raman Microscope, UK) with Raman mapping mode; Laser beam at wave length 785 nm. and surface scan area of 100 x 120 micron.

3.4.2 FTIR-ATR analysis

External solid combustion residues according to UL94 5VB test were characterized by fourier transform infrared spectrophotometer (FTIR) (Perkin Elmer Spectrum 2000 Explorer, USA) using attenuated total reflectance mode (ATR).

3.4.3 Thermogravimetric analysis

The thermal decomposition of PC/FRs blend samples were carried out with thermogravimetry analyzer from Mettler (SDTA851, Switzerland). Each 10 mg of samples was placed into the crucible and was heated from ambient temperature to 800 ^{0}C with the heating rate of 20^{0}C/min under nitrogen atmosphere at flow rate of 100 ml/min. T_{onset}, T_{max} and residues were obtained from the TGA curve.

3.4.4 Limiting oxygen index measurement

The LOI values were measured by LOI apparatus which was equipped according to the standard test method of Oxygen index, ASTM D2863-91. The value of oxygen in balance nitrogen will be recorded in percent unit (%) after burning of test specimen reaches of 3 min.

3.4.5 UL94 5VB rating measurement

The measurement of each blend, 5 rectangular sheets were performed by Flammability tester (ATLAS HVUL, USA) with 125 mm of flame length according to UL94 standard test method. Criteria for judgment of 5VB rating; after flame time applied, cotton ignited by flaming particles drop should not allow and flame shall

extinguished within 60 second. Vertical burning of flame application of UL94 5VB is opposite site from LOI test.

3.4.6 Scanning electron microscope analysis

Morphology of external solid residues according to the UL94 5VB were characterized by scanning electron microscopy; SEM-EDX (Phillips XL20, UK) at 30 kV. The residues were mounted on a SEM stub using a double-side tape then sputtered with a thin gold layer before measurement.

3.5 Mechanical properties test

3.5.1 Charpy impact strength

Load direction of test specimen with notched for impact strength testing according to ISO 179 is shown in Figure 3.1. The results were obtained from the excess energy remaining in the pendulum 4 J. after samples were broken that was measured by digital impact tester (Toyoseiki DG-CB, Japan). Specimen size is 80 x 10 x 3 mm.
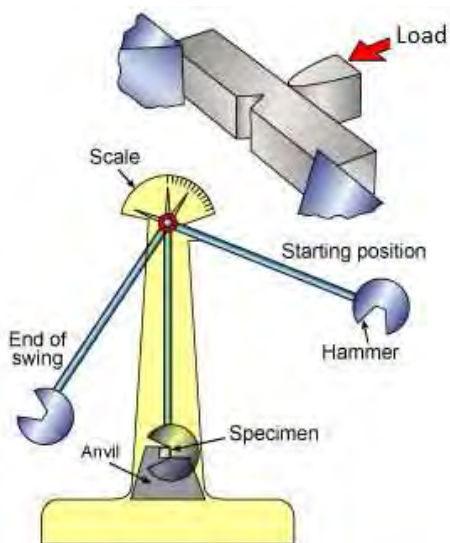
Figure 3.1 Charpy testing machine [48].

3.5.2 Tensile properties

Dimension of test specimen for tensile strength testing according to ISO 527 is shown in Figure 3.2. The results were obtained from universal testing machine (Autograph AG-50kNG, Japan) with a cross head speed 50 mm/min and load capacity 50 kN.
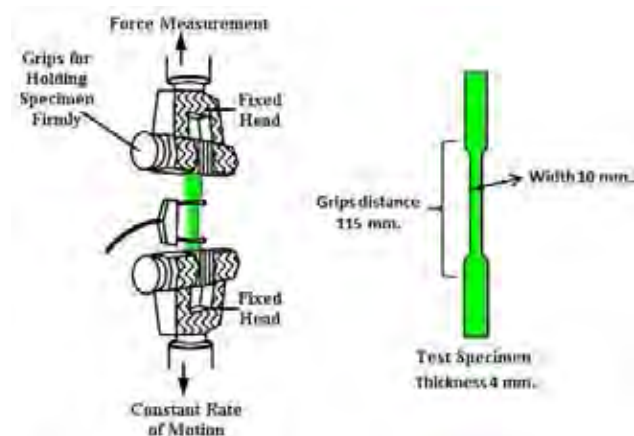
Figure 3.2 Tensile testing direction [49].

3.5.3 Flexural properties

Load direction of test specimen for flexural properties testing according to ISO 178 is shown in Figure 3.3. The results were measured using 3-points blending in a Universal testing machine (Autograph AG-50kNG, Japan) at a cross head speed 2 mm/min. Stress was applied until 64 mm (span length) or fracture by a centrally 1 kN load cell. Specimen size is 80 x 10 x 4 mm.
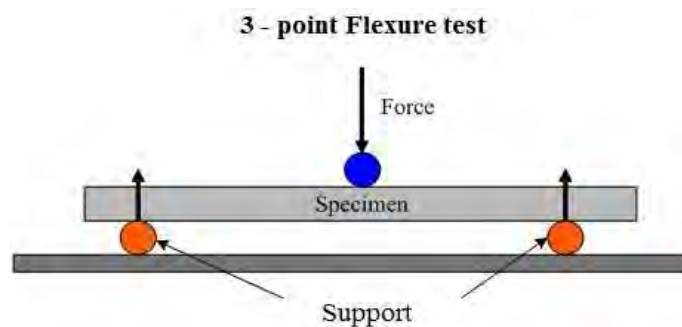
Figure 3.3 Flexural testing direction [50].

CHAPTER IV

RESULTS AND DISCUSSION

4.1 Raman spectroscopy

Raman imaging technique is well known and employ to characterize the compositions and morphologies of polymer blends [34,51,52]. This technique is used to observe the dispersion of the additives mixed with PC matrix at the surface of samples. The blend of PC/10%TBBA/10%BDP (PC10) was used as representative of all blend samples which was useful to confirm the homogeneity of additives in PC matrix. Therefore, TBBA, BDP and neat PC were analyzed by Raman technique comparing with the blend sample of PC10.

The Raman spectra of TBBA, BDP and PC10 comparing to neat PC are shown in Figure 4.1. The strong characteristic Raman absorption bands of neat PC, TBBA and BDP were observed and selected for further investigation. Aromatic C-H bending of sp^2 of neat PC at region 694 – 717 cm^{-1} [32] and P-O stretching of BDP at region 996 – 1019 cm^{-1} [28,37,53] were used to identify their presence in the blend. For TBBA, aryl bromo peak was observed at region 1025-1075 cm^{-1} [53]. Unfortunately this region is nearly the same as P-O peak of BDP but weaker. Therefore, the un-identified region 229 – 259 cm^{-1} of TBBA was used instead to identify the presence of TBBA in the blend.
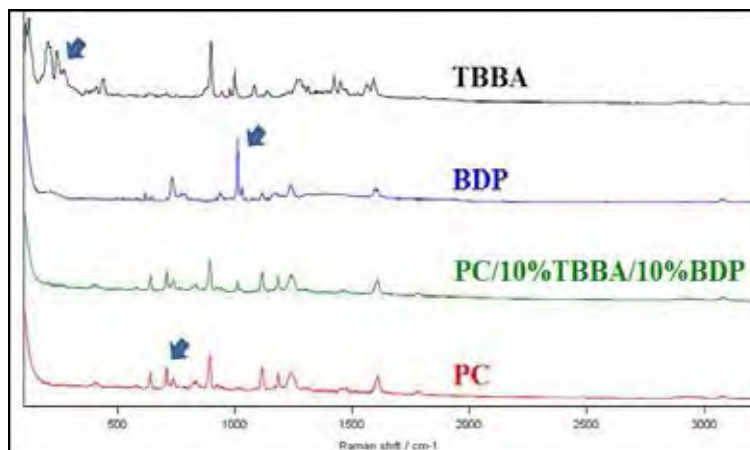
Figure 4.1 Raman spectra of TBBA, BDP, PC/10%TBBA/10%BDP blend and neat PC.

The Raman imaging of PC10 is shown in Figure 4.2. It was obviously observed that TBBA and BDP dispersed well in the PC matrix which represented in three colors; blue, red and green for TBBA, BDP and neat PC, respectively.
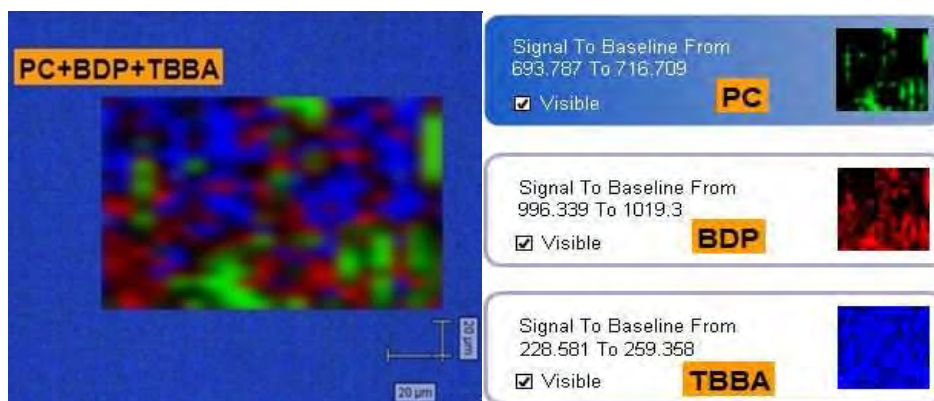
Figure 4.2 Raman image of PC/10%TBBA/10%BDP blend.

4.2 Limiting Oxygen Index

Flame retardancy of neat PC and PC/FRs blend was determined by the limited oxygen index (LOI) method, which detected the minimum oxygen concentration needed to support combustion after ignition. The LOI values of PC, and PC1 – PC9 were measured according to the standard test method of oxygen index, ASTM D2863-06. The LOI values and compositions of these samples are shown in Table 4.1.

Table 4.1 LOI values and UL94 5VB tested results of neat PC and PC1 – PC9.

Blend No.	PC (%)	Additive content (% by wt.)				LOI (%)	5VB at 2 mm
		TBBA	BDP	KBPFS	PTFE		
Neat PC	100.00	0.00	0.00	0.00	0.00	24.3	Not pass
PC1	**84.55**	**15.00**	**0.00**	**0.05**	**0.40**	**44.2**	**Pass**
PC2	**84.55**	**10.00**	**5.00**	**0.05**	**0.40**	**45.8**	**Pass**
PC3	84.55	7.50	7.50	0.05	0.40	45.2	Not pass
PC4	84.55	5.00	10.00	0.05	0.40	44.0	Not pass
PC5	84.55	0.00	15.00	0.05	0.40	38.5	Not pass
PC6	85.00	15.00	0.00	0.00	0.00	43.0	Not pass
PC7	85.00	0.00	15.00	0.00	0.00	38.2	Not pass
PC8	99.95	0.00	0.00	0.05	0.00	26.8	n/a*
PC9	99.60	0.00	0.00	0.00	0.40	27.8	n/a*

*n/a : not analysis
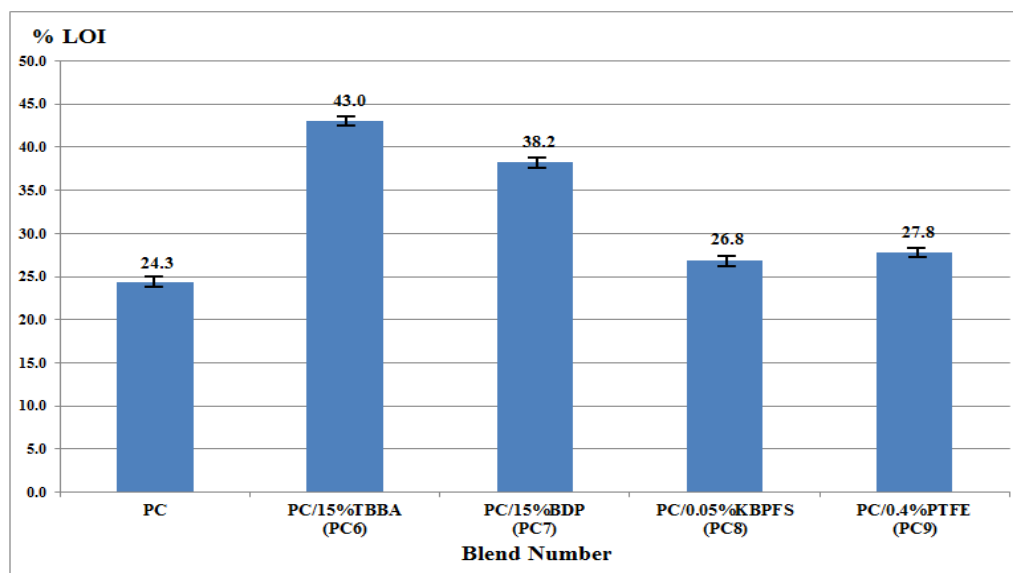
Figure 4.3 The effect of different flame retardants on LOI values of neat PC and PC6 – PC9.

The effect of different flame retardants on LOI values of neat PC and PC6 – PC9 is shown in Figure 4.3. The LOI value of PC6 – PC9 were higher than the neat PC which PC6 showed the highest LOI value of 43.0%, following by PC7, PC9, PC8 and neat PC with the LOI values of 38.2%, 27.8%, 26.8% and 24.3%, respectively. These results correspond with many reports that halogenated FRs have extremely high flame retardancy [4,6,8]. Also J. Green [9] reported that the LOI values increased with high loading of both TBBA and aryl phosphorus FRs into PC/ABS and PC/PET blends.
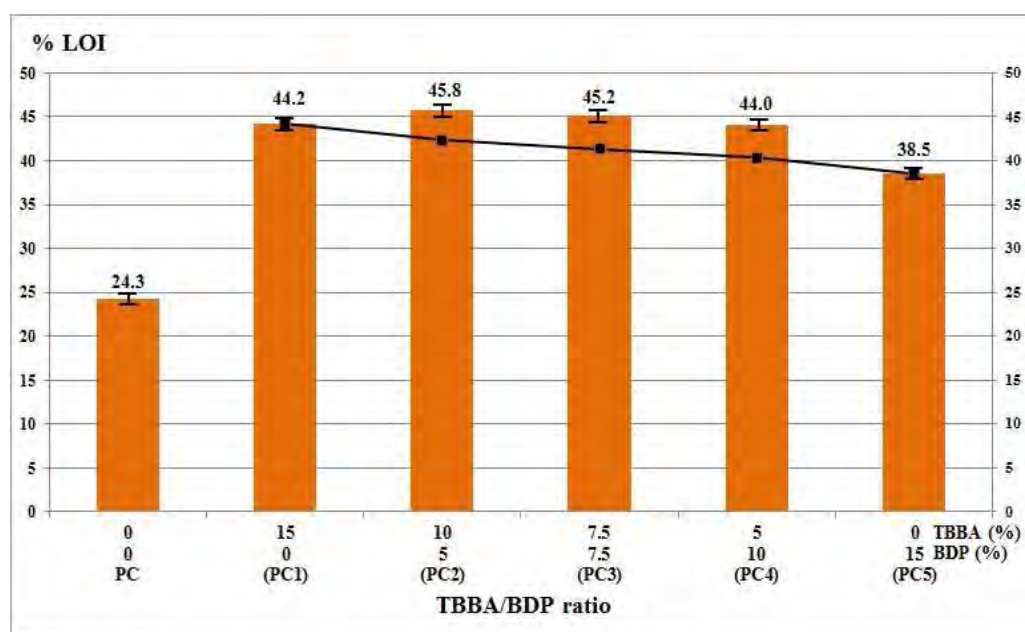
Figure 4.4 Effect of TBBA and BDP content on LOI values of
PC/0.05%KBPFS/0.4%PTEF.

Sample PC1 – PC5 containing various ratios of TBBA, BDP and fixed ratios of KBPFS and PTFE with total amount of 15.45% by weight were further investigated (see Table 4.1 and Figure 4.4). Comparing the efficiency on flame retardancy between PC/15%TBBA/0.05%KBPFS/0.4%PTFE (PC1) and PC/15%BDP/0.05%KBPFS/0.4%PTFE (PC5), the LOI values of PC1 was higher than PC5 by 5.7%, which was significant and similar to the results reported by Green [9]. Based on the environmental concern [21,26], reducing halogenated FR (TBBA)

and replacing with phosphorus-containing flame retardant (BDP) into the formulations was studied. In preparation processes, BDP was added to replace TBBA at amount of 5%, 7.5% and 10% by weight to formulate PC2, PC3 and PC4, respectively. The results showed that PC2 and PC3 had a higher LOI values than PC1 by 1.6% and 1.0% respectively, while PC4 is nearly the same as PC1. The linear curve that shown in Figure 4.4 is a representative of the calculation data of rule of mixture which represent the theoretical LOI for these blends of the two flame retardants. The theoretical LOI for each sample was calculated by below equation.

$$LOI_{sample} = x_1 LOI_1 + x_2 LOI_2 \ldots\ldots\ldots\ldots\ldots(1)$$

where LOI_{sample} is the limiting oxygen index of PC1 – PC5, x_1 is the weight fraction of TBBA, LOI_1 is the limiting oxygen index of PC1, x_2 is the weight fraction of BDP, LOI_2 is the limiting oxygen index of PC5. It was found that the experiment LOI values are higher than theoretical LOI values, demonstrating that TBBA and BDP are synergistic interaction. The BDP can be used to reduce the amount of TBBA to support the environmental issue while maintaining good LOI values.

4.3 UL94 5VB rating measurement

In this study, UL94 5VB vertical burning test was used to carry out with a flammability tester (ATLAS HVUL, USA) with 125 mm of flame length according to the UL94 5VB standard test method.

The results of UL94 5VB rating were summarized in Table 4.1. PC/15%TBBA (PC6) and PC/15%BDP (PC7) did not pass the UL94 5VB rating. However, when KBPFS and PTFE were added into the blend to formulate PC/15%TBBA/0.04%KBPFS/0.4%PTFE (PC1) improved the flame retardancy of neat PC and pass the UL94 5VB rating of 2 mm thick, while PC/15%BDP/0.04%KBPFS/0.4%PTFE (PC5) did not pass. These results indicated the suitable incorporation of TBBA, KBPFS and PTFE with neat PC could increase a better flame retardancy and passed the 5VB criteria. TBBA and KBPFS showed good mechanisms on flame retardancy in gas phase action [6,15] which prevent the cotton to ignite. While PTFE increased the dripping time that make the TBBA and KBPFS

extinguish the flame and not ignite once the flame particle reaches the cotton. Good examples of PTFE function well with other flame retardants were showed in Figure 4.5 according to the UL94 5VB test. In case of PC5, the result revealed the inappropriate formulation of the blend that made it did not pass the UL94 5VB rating.

Remarkably, incorporation of the 15%TBBA by weight in a PC1 can be reduced to 10% by adding 5%BDP as shown in PC2. It can be concluded that PC1 and PC2 have the most efficient flame retardancy in the present work. This observation indicates that the optimum addition of FRs into PC blend to formulate PC1 and PC2 can enhance the flame retardancy by synergistic interaction The good results of PC1 and PC2 are from the incorporation action of FRs in both gas phase and condensed phase during ignition and combustion which correspond with previous reports [7,15,27].
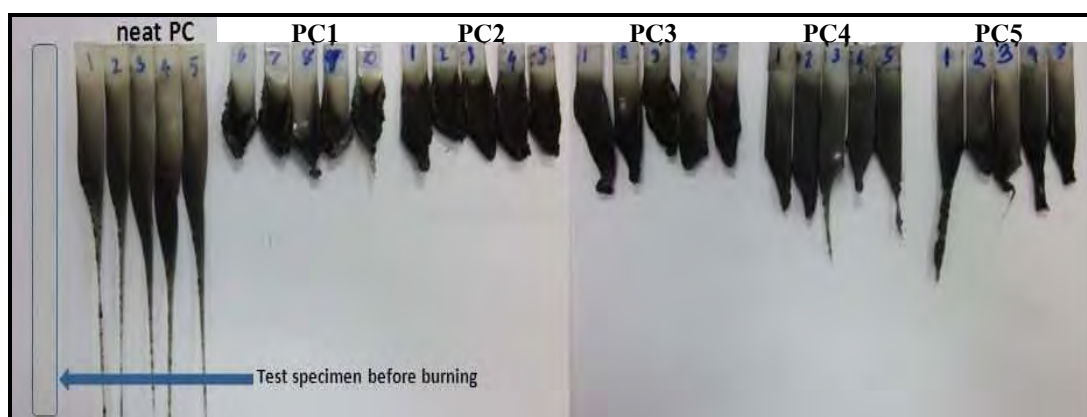
Figure 4.5 Photos of 5 pieces of selected samples after burning, according to UL94 5VB test; neat PC and PC1 - PC5.

The burning characteristic of tested sample sheets of PC1 – PC5 and neat PC according to the UL94 5VB test are shown in Figure 4.5. Neat PC shows the longest spread of tested sample sheets, dripping with cotton ignite during test. Therefore, it did not pass the UL94 5VB rating. For PC1 – PC5, all of them were dripping and shrinkage. It will be explained that the active function of additives in PC/FRs blends work well. Comparing among of PC1 to PC5, it is noticed that the burning sheets of PC1 and PC2 are shorter than those of PC3, PC4 and PC5. These might facilitate to extinguish the flame before cotton ignition which could pass the UL94 5VB criteria.

4.4 FTIR-ATR spectroscopy

FTIR-ATR spectra of external solid combustion residues of PC1 – PC5 according to the UL94 5VB test were recorded and compared with the FTIR-ATR spectrum of neat PC before burning as shown in Figure 4.6. The spectra of PC1 – PC5 exhibit the absorption patterns similar to the neat PC before burning, but the intensity of the absorption bands was relatively decreased from PC1 – PC5.

The IR peaks of PC1 and PC2 were clearly observed, C-H stretching of sp^2 and sp^3 at region 2850-3050 cm^{-1} , C=O stretching of carbonate group at 1769 cm^{-1}, C=C stretching of aromatic at 1503 cm^{-1} and C-O stretching of carbonate group in region 1013-1218 cm^{-1} which were stronger than those found in PC3 - PC5. These results indicated that the amount of PC matrix remained on the surface of PC1 and PC2 more than neat PC and PC3 - PC5 which supported the results of the UL94 5VB rating.

P-O stretching peak is found on PC2 – PC5 at 957 cm^{-1} [28,37]. The P-O stretching peak is also found by Raman technique as shown in Figure 4.1 which proved the remaining of BDP after burning. In conclusion, the flame retardant system in PC1 and PC2 are more effective on flame retardancy than other formulations.
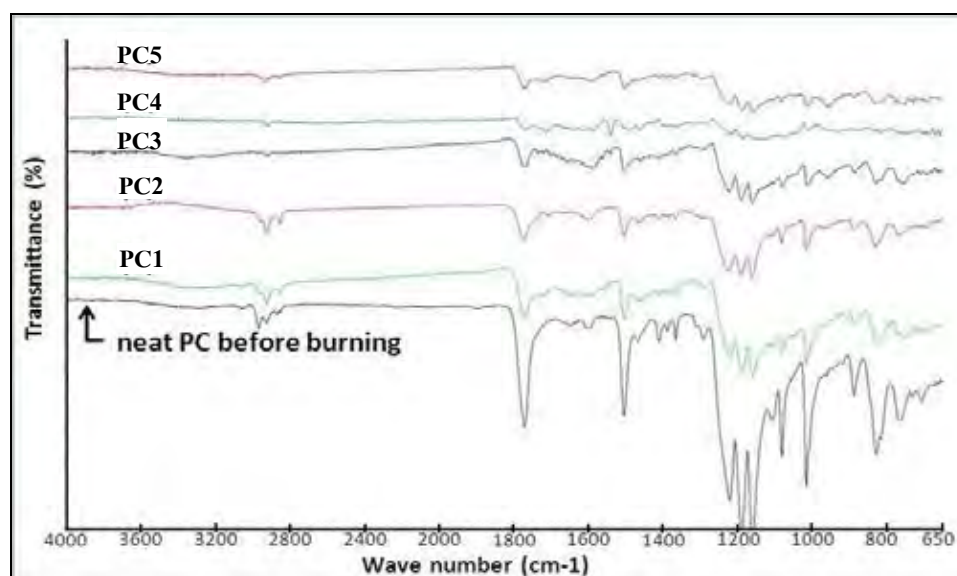
Figure 4.6 FTIR-ATR spectra of solid combustion residues of PC1 - PC5 after UL94 5VB test comparing with neat PC before burning.

4.5 Thermogravimetric analysis

Thermal stability of neat PC and PC/FRs selected blends were characterized by thermogravimetric analysis (TGA) method, analyzing the thermal decomposition temperature of the blends. The thermogravimetric curves of the neat PC, PC1 and PC2 were observed in nitrogen flow at the heating rate from ambient temperature to 800 ^{o}C are given in Figure 4.7. The results showed that all of them are decomposed in one step around 450 – 600 ^{o}C. The onset degradation temperature (T_{onset}) and the temperature of the maximum rate of degradation (T_{max}) of the 3 samples including the solid combustion residue at 800 ^{o}C were obtained from the TGA curve as shown in Figure 4.8. T_{onset} and T_{max} of neat PC are 506.3 ^{o}C and 531.3 ^{o}C, respectively. During the thermal decomposition of PC, it has many complicate chemical reactions occur, including the chain scission of isopropylidene linkages, hydrolysis and alcoholysis of carbonate linkages, rearrangement of carbonate linkages to form ether linkages and cross-linking reaction to form char [7]. Although there is no noticeable weight loss below 450 ^{o}C, a small amount of evolved gases may be detected by FTIR, but no mass loss can be detected by TGA. When compare the PC1 and PC2 with neat PC. TGA curves of both samples are a bit lower than neat PC which T_{onset} reduces by 14.1 and 17.0 ^{o}C and T_{max} reduces by 8.3 and 6.0 ^{o}C, respectively, while T_{onset} and T_{max} of PC1 and PC2 are not significant difference. It can be assumed that the presence of TBBA and BDP reduce the decomposition temperature of neat PC in the earlier stage of these FRs during thermal decomposition. Similar observations were reported by the other research groups [7,28,54].

The main mass loss regions of PC1 and PC2 end at about 550 ^{o}C, which were the same as neat PC. Considering the remain mass percentage of the solid residues after combustion at 800 ^{o}C, the neat PC, PC1 and PC2 as shown in Figure 4.8 are 18.0%, 20.2% and 22.0%, respectively. It can be explained that the higher percentage of solid residue in case of PC1 and PC2 were from the additional additives, especially for the PC2, the residues increase because BDP functions as a char forming agent [7,28]. The generation of char residues further prevents PC/FRs blend burning.
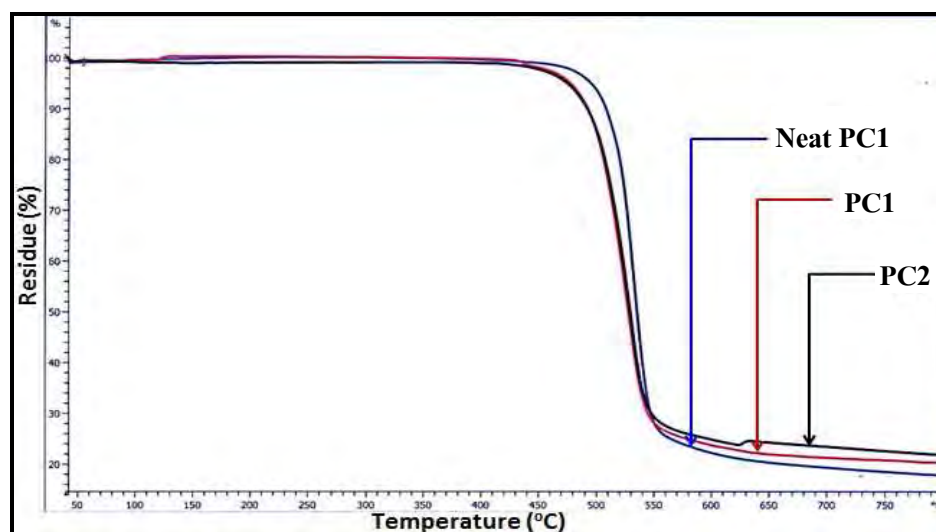
Figure 4.7 TGA curves of PC/FRs blends of neat PC, PC1 and PC2.
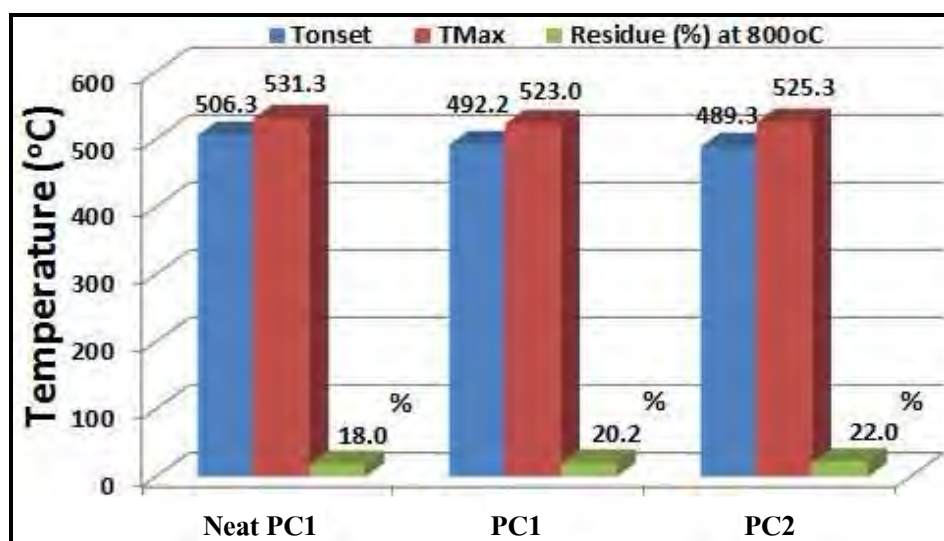
Figure 4.8 Decomposition temperature of PC/FRs blends of neat PC, PC1 and PC2 which including T_{onset}, T_{max} and residues(%) at 800°C.

4.6 Morphology of solid combustion residues of PC/FRs blend

SEM images of external solid combustion residues according to the UL94 5VB test are shown in Figure 4.9.
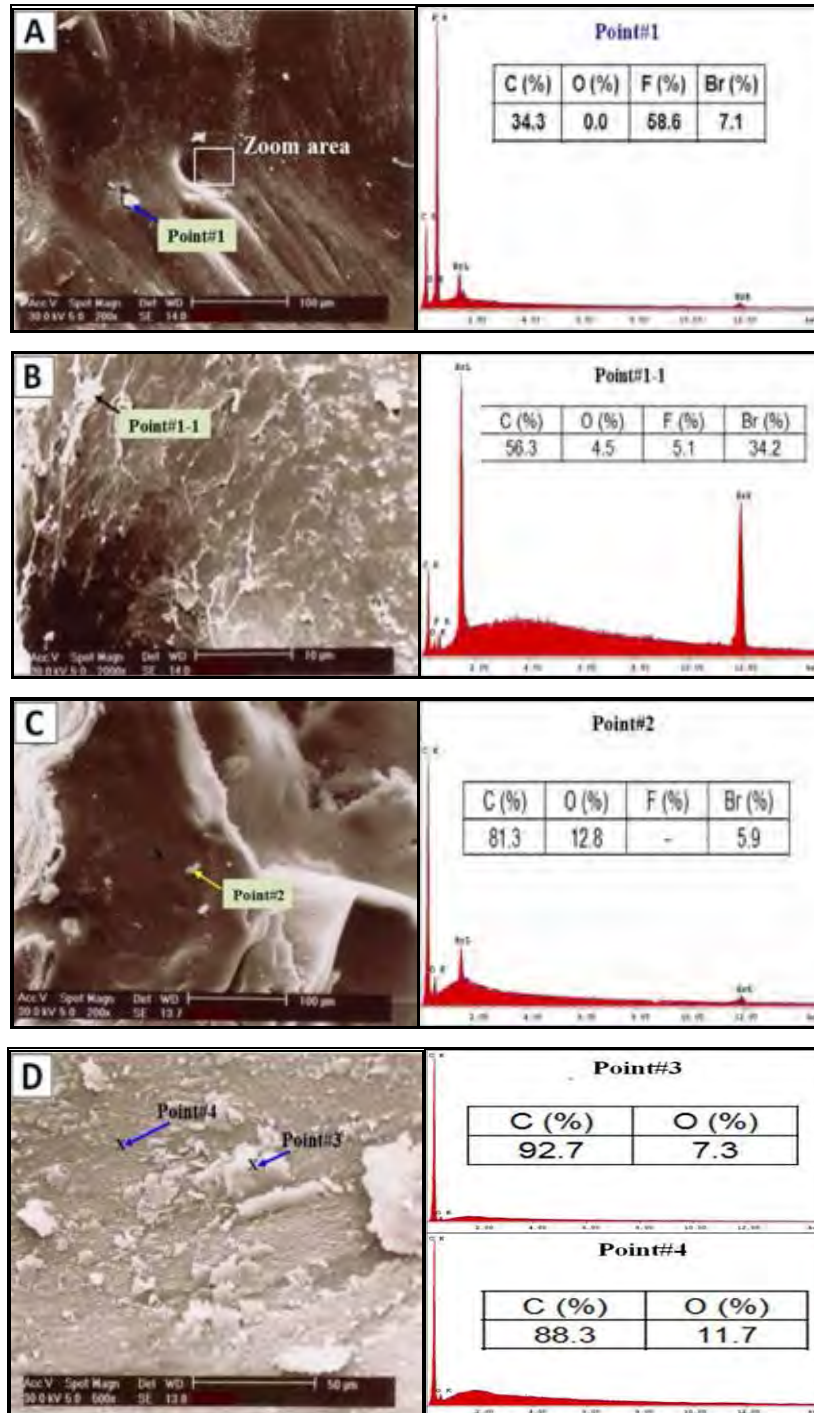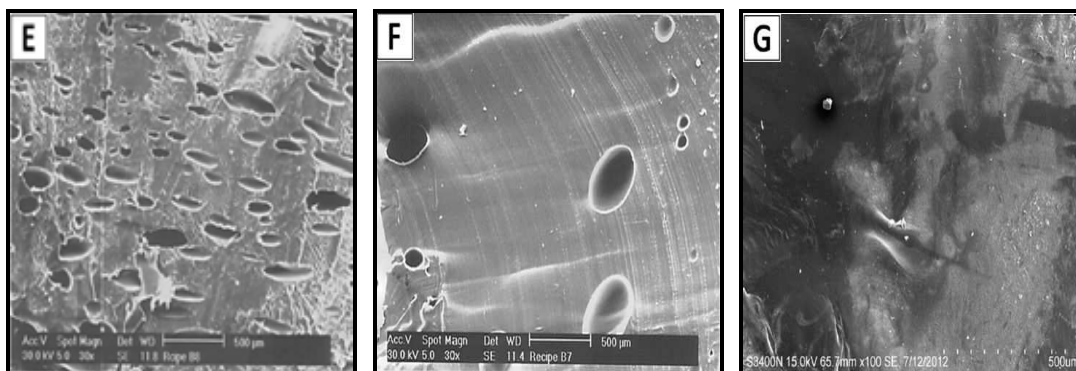
Figure 4.9 SEM images and spectra of solid combustion residues according to the UL94 5VB test. A) PC1, B) PC1 at the zoom area with 2000 magnification, C) PC2, D) neat PC, E) cross section of PC1 and F) cross section of PC5.

With SEM-EDX thermogram of Figure 4.9A, bromine and fluorine at point #1 were detected in % by area normalization technique, indicating the presence of TBBA and PTFE of PC1. While Figure 4.9C at point #2 indicates the presence of TBBA of PC2 only. It is assumed that the PTFE in PC2 was decomposed after combustion. In Figure 4.9B, fibrillation of PTFE, formed after combustion, can be seen clearly. These can be confirmed the effectiveness of their functions as flame retardant and anti-dripping agent as well.

The surface of neat PC, PC1 and PC2 after burning are observed under SEM as seen in Figure 4.9. It's revealed that the surface of neat PC shows rough skin surface and has many small pieces of fractures on the surface whereas the surface of PC1 and PC2 are smoother than the neat PC. PC2 also shows the surface fracture from burning. This phenomenon may be come from different compositions in the blends which can be evident to the existent of their flame retardants as well.

Figure 4.9E, 4.9F and 4.9G show the cross section of PC1, PC5 and neat PC after burning, respectively. The specimens were cut at 2 mm from the tip of the residue. Micro-sized pores can be observed in both samples that which should come from mass and heat transfer [7] of flame retardants after combustion. PC1 shows a lot of pores with size smaller than those of PC5 while pores cannot be found from neat PC. This result confirms that the main action of TBBA occurs in gas phase [15,54], by generating HBr gas which reacts with high reactive radicals to form H_2 and H_2O as shown in equation (2) and (3), respectively. While BDP, mainly occurs in condensed

phase by char forming and partly occurs in gas phase, $PO^{\bullet}$, $P^{\bullet}$ and HPO were generated and reacted with high reactive free radicals [7,9,15]. Different pore sizes might also confirm the different gas types that come from different molecular weight and vapor pressure during combustion.

With the above results of Raman, LOI, UL94 5VB rating, FTIR and SEM in this study, it could be observed the collaborated interaction of each additives as a function of flame retardant and anti-dripping agent.

TBBA as a function of radical quenching mainly reacts in gas phase through free radical process which hydrogen bromide (HBr) was emitted from TBBA after decomposition. It reacted with, $H^{\bullet}$ and $OH^{\bullet}$ from decomposed PC, high reactive free radicals become H_2 and H_2O, respectively, as shown the reactions of hydrogen halide during thermal decomposition in polymer below. The bromide free radical ($Br^{\bullet}$) was produced which is lower reactive free radicals then can prevent the propagation of PC decomposition reaction. This reduces the rate of heat transfer back to the polymer matrix, which decreases the burning rate and leads to extinction of the flame

$$H^{\bullet} + HBr \rightarrow H_2 + Br^{\bullet} \quad ....(2)$$

$$OH^{\bullet} + HBr \rightarrow H_2O + Br^{\bullet} \quad ....(3)$$
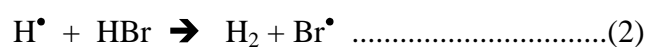
KBPFS [6] and BDP [7,9] mainly show condensed phase action as well as gas phase action. The mechanism of KBPFS is to accelerate the evolution of CO_2 after decomposed which retards the flame by its dilution into the gas phase and induces the intumescent char forming in condensed phase. While BDP itself after thermal decomposition, the char is formed by cross-linking reactions then generated phosphoric that catalyzed the carbon char formation of the neat PC during thermal decomposition. The chars act as a barrier for the unburned polymer matrix against heat and oxygen as well as hindering the diffusion of pyrolysis gases. This is rather favorable to enhance the flame retardancy of PC. The char of sample PC1 is mainly from neat PC while the char of sample PC2 is increased from neat PC and BDP. This confirms the formation of char could shield the underlying matrix from heat and oxygen. And also slowing down the thermal-oxidative decomposition of polymer matrix.

PTFE mainly reacted in the condensed phase. The fibril structure of PTFE is generated during shear under heat condition as combustion [24]. It's a key to improve the anti-drip property [6-7]. The fibril structure is believed that is a network to support the formation of a char upon burning. The char inhibits the dripping of burning polymer which can be observed in this paper.

4.7 Mechanical properties of PC/FRs blends

The PC1 and PC2 sheets which passed the UL94 5VB test were selected for further mechanical tests by charpy impact strength, tensile and flexural properties. The formulations and results were summarized in Table 4.2 and Table 4.3, respectively. Charpy impact strength, tensile strength and elongation at break of the PC1 and PC2 are lower than neat PC especially for charpy impact strength can be seen obviously. The charpy impact strength may come from the miscible blend of additives; TBBA and BDP, with high content in PC. However, flexural strength and flexural modulus of PC1 and PC2 are higher than the neat PC. The higher value may come from the good compatibility of miscible blend sample. The additives are mixed well with neat PC and improve the toughness of the PC blend samples which correspond with the Raman image of Figure 4.2. Interestingly, the lower charpy impact strength of PC1 and PC2 is improved by adding impact modifier. Block terpolymers of siloxane-alkylacrylate-SAN is selected with the amount of 2.5% and 3.0 % by weight adding in PC10 and PC11, respectively. The charpy impact strength of both PC1 and PC2 is increased significantly to 51.6 and 55.6 kJ/m^2, respectively. Furthermore, the amounts of impact modifier, which added into the blends, still maintain the good results of UL94 5VB rating. The data is shown in Table 4.3. The pictures of UL94 5VB test of PC10 and PC11 samples are shown in Figure 4.10 and Figure 4.11, respectively.

Table 4.2 Formulation of PC/FRs blends

Blend	PC	Additives content (% by wt.)				
No.	(%)	TBBA	BDP	KBPFS	PTFE	Impact modifier
Neat PC	100.00	0.00	0.00	0.00	0.00	0.00
PC1	84.55	15.00	0.00	0.05	0.40	0.00
PC2	84.55	10.00	5.00	0.05	0.40	0.00
PC10	82.05	15.00	0.00	0.05	0.40	2.50
PC11	81.55	10.00	5.00	0.05	0.40	3.00

Table 4.3 Test results of mechanical properties of PC/FRs blends.

Samples	5VB at 2mm	Charpy Impact (KJ/m^2)	Tensile strength (MPa)	Elongation at break (%)	Flexural Strength (MPa)	Flexural Modulus (MPa)
Neat PC	Not pass	67.0	71.9	125.2	96.9	2,314
PC1	Pass	3.4	66.7	101.7	106.0	2,402
PC2	Pass	6.7	60.6	87.7	113.0	2,564
PC10	Pass	51.6	68.4	112.5	101.3	2,257
PC11	Pass	55.6	67.9	106.9	106.1	2,419

Figure 4.10 Sample specimens of PC10 according to UL94 5VB test.

Figure 4.11 Sample specimens of PC11 according to UL94 5VB test.

CHAPTER V

CONCLUSIONS AND SUGGESTION

5.1 Conclusion

Flame retardancy of PC was improved by addition with conventional halogen and/or halogen-free flame retardants. In this study, the two blend formulations which showed the highest flame retardancy property were formulated. There were PC/15%TBBA/0.05%KBPFS/0.4%PTFE (PC1) and PC/10%TBBA/5%BDP/ 0.05%KBPFS/0.4%PTFE (PC2). These two blend formulations can be complied with UL94 5VB rating of 2.0 mm thick with the LOI greater than 44%.

TBBA, an example of halogenated flame retardant, is the main composition in the blends in this work which showed effectiveness on UL94 5VB rating when the BDP, KBPFS and PTFE were incorporated into the formulations. In addition, the amount of TBBA which was incorporated into the blend can be reduced by adding BDP to create a more environmental friendly plastic. Furthermore, TGA, SEM and FTIR-ATR results also confirmed the flame retardancy enhancement in PC of both PC1 and PC2.

Moreover, balancing of flame retardancy and mechanical property need to be concerned for various applications in industrial fields. High content of flame retardants in PC1 and PC2 decreased the charpy impact strength significantly. Therefore, an impact modifier, block terpolymers of siloxane-alkylacrylate-SAN was added into the PC1 and PC2 at 2.5 and 3.0 % by weight, respectively.

5.2 Suggestion for the future works

Even though the blend samples in this work can pass the criteria as the 5VB level, however, they contain the halogenated flame retardant which is hazardous chemical to human and environment [24]. Regarding to the good combination of phosphorus and bromine on flame retardancy and the ability for enhancement of the PC properties according to this work, then the various types of phosphorus-bromine compound incorporated into PC will be further investigated.

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APPENDICES

Appendix A

Raman spectrum of additives and PC/FRs blends

Figure A-1 Raman spectrum of TBBA
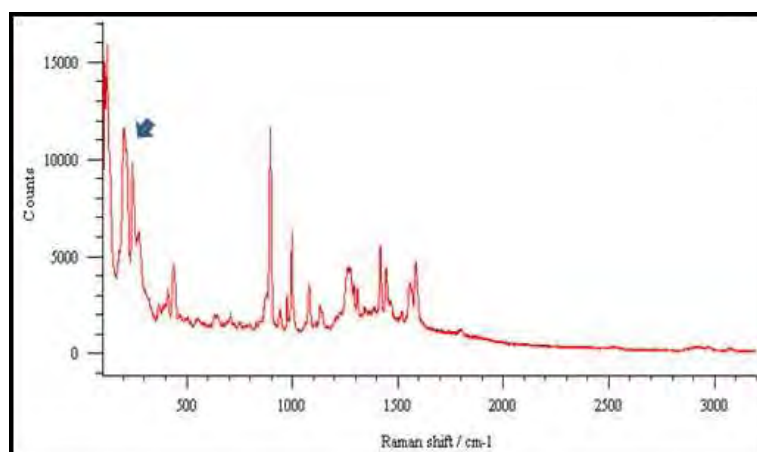
Figure A-2 Raman spectrum of BDP
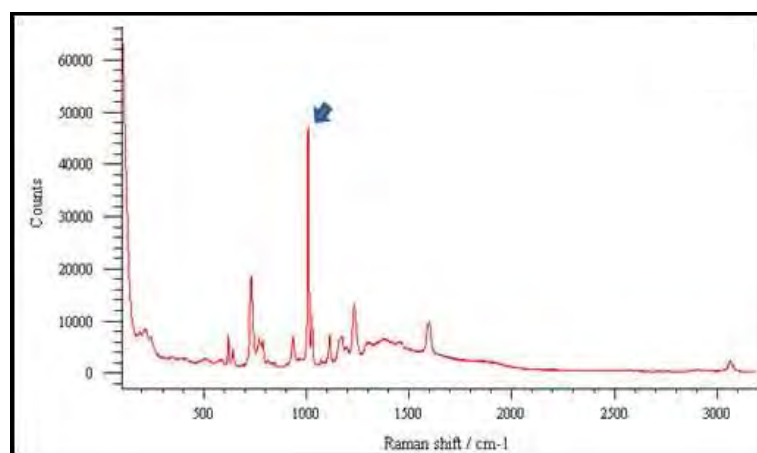
Figure A-3 Raman spectra of neat PC and PC/FRs blend at various ratio of TBBA
as 10% and 20%
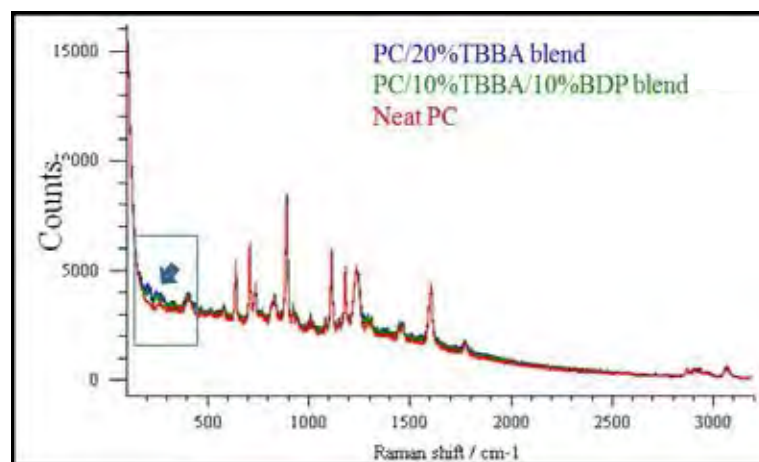
The intensity of Raman spectrum at region 229 – 259 cm^{-1} of TBBA were
relatively increased when TBBA content in the blends increase.

Appendix B

Data of LOI of PC/FRs blends

Table B-1 Data of limiting oxygen index (LOI) of PC/FRs blends

Specimen No.	Limiting oxygen index (%)									
	Neat PC	PC1	PC2	PC3	PC4	PC5	PC6	PC7	PC8	PC9
1	24.0	44.0	45.5	45.0	44.0	38.0	42.5	38.0	26.5	27.5
2	25.0	44.5	46.0	45.0	44.0	38.5	43.5	38.0	27.0	28.0
3	24.0	44.0	46.0	45.5	44.0	39.0	43.0	38.5	27.0	28.0
Min	24.0	44.0	45.5	45.0	44.0	38.0	42.5	38.0	26.5	27.5
Max	25.0	44.5	46.0	45.5	44.0	39.0	43.5	38.5	27.0	28.0
Mean	24.3	44.2	45.8	45.2	44.0	38.5	43.0	38.2	26.8	27.8
SD	1.4	0.7	0.7	0.7	0.00	1.2	1.2	0.7	0.7	0.7
%RSD	5.81	1.60	1.54	1.57	0.00	3.18	2.85	1.85	2.64	2.54

Appendix C

Data of UL94 5VB of PC/FRs blends

Table C-1 Data of UL94 5VB of PC/FRs blends

Blend no.	After flame time (5 applications)	Dripping (pcs/5)	Cotton ignite (pcs/5)	Judgment
PC	0 / 0	5 / 5	5 / 5	Not pass
PC1	1 / 1	5 / 5	0 / 0	Pass
PC2	1 / 1	5 / 5	0 / 0	Pass
PC3	1 / 1	5 / 5	3 / 2	Not pass
PC4	3 / 2	5 / 5	1 / 2	Not pass
PC5	2 / 3	5 / 5	4 / 3	Not pass
PC6	0 / 0	5 / 5	5 / 5	Not pass
PC7	0 / 0	5 / 5	5 / 5	Not pass
PC10	1 / 1	0 / 1	0 / 0	Pass
PC11	1 / 1	1 / 1	0 / 0	Pass

* 1st test / 2nd test

Appendix D

Data of Mechanical Properties of PC/FRs blends

Table D-1 Data of charpy impact strength of PC/FRs blends

Specimen	Charpy impact strength (KJ / m^2)				
No.	Neat PC	PC1	PC2	PC10	PC11
1	66.3	3.4	6.7	51.5	55.5
2	67.4	3.3	6.6	51.5	54.6
3	68.4	3.4	6.6	50.6	56.0
4	66.9	3.3	6.6	52.7	55.6
5	66.9	3.4	6.8	51.4	56.8
6	66.0	3.3	6.8	50.5	56.4
7	67.4	3.6	7.0	52.3	54.9
8	66.5	3.3	6.8	52.1	55.9
9	66.8	3.3	6.8	53.0	55.2
10	67.4	3.4	6.7	50.6	54.9
Min	**66.0**	**3.3**	**6.6**	**50.5**	**54.6**
Max	**68.4**	**3.6**	**7.0**	**53.0**	**56.8**
Mean	**67.0**	**3.4**	**6.7**	**51.6**	**55.6**
SD	**2.0**	**0.2**	**0.3**	**2.5**	**2.0**
% RSD	**2.93**	**6.94**	**4.98**	**4.84**	**3.67**

Table D-2 Data of tensile strength at break of PC/FRs blends

Specimen	Tensile strength (MPa)				
No.	Neat PC	PC1	PC2	PC10	PC11
1	71.2	69.0	62.0	67.4	68.8
2	71.9	66.2	63.5	69.7	69.2
3	71.3	66.8	58.7	69.4	67.4
4	73.3	64.8	60.3	67.5	69.6
5	71.8	66.7	58.6	67.9	64.4
Min	**71.2**	**64.8**	**58.6**	**67.4**	**64.4**
Max	**73.3**	**69.0**	**63.5**	**69.7**	**69.6**
Mean	**71.9**	**66.7**	**60.6**	**68.4**	**67.9**
SD	**0.7**	**1.4**	**1.9**	**1.0**	**1.9**
% RSD	**1.02**	**2.04**	**3.13**	**1.43**	**2.76**

Table D-3 Data of elongation at break of PC/FRs blends

Specimen	Elongation at break (%)				
No.	Neat PC	PC1	PC2	PC10	PC11
1	124.9	111.4	85.9	109.1	110.9
2	125.0	98.1	93.0	118.2	109.6
3	122.9	100.9	85.4	116.0	105.4
4	129.0	97.2	87.0	110.3	109.7
5	124.0	100.9	87.5	109.0	99.1
Min	**122.9**	**97.2**	**85.4**	**109.0**	**99.1**
Max	**129.0**	**111.4**	**93.0**	**118.2**	**110.9**
Mean	**125.2**	**101.7**	**87.7**	**112.5**	**106.9**
SD	**2.0**	**5.0**	**2.7**	**3.8**	**4.4**
% RSD	**1.63**	**4.97**	**3.10**	**3.42**	**4.07**

Table D-4 Data of flexural strength of PC/FRs blends

Specimen	Flexural strength (Mpa)				
No.	Neat PC	PC1	PC2	PC10	PC11
1	96.8	106.2	113.7	101.3	104.7
2	97.2	106.1	113.5	101.9	105.3
3	96.3	106.0	112.9	101.3	107.3
4	96.7	105.9	112.4	101.1	105.2
5	97.3	105.7	112.7	101.2	107.9
Min	**96.3**	**105.7**	**112.4**	**101.1**	**104.7**
Max	**97.3**	**106.2**	**113.7**	**101.9**	**107.9**
Mean	**96.9**	**106.0**	**113.0**	**101.3**	**106.1**
SD	**0.4**	**0.2**	**0.5**	**0.3**	**1.3**
% RSD	**0.40**	**0.17**	**0.42**	**0.26**	**1.19**

Table D-5 Data of flexural modulus of PC/FRs blends

Specimen	Flexural modulus (MPa)				
No.	Neat PC	PC1	PC2	PC10	PC11
1	2366	2365	2520	2256	2462
2	2315	2412	2524	2303	2341
3	2282	2395	2571	2280	2389
4	2306	2387	2590	2219	2444
5	2302	2450	2621	2227	2461
Min	**2282**	**2365**	**2520**	**2219**	**2341**
Max	**2366**	**2450**	**2621**	**2303**	**2462**
Mean	**2314**	**2402**	**2565**	**2257**	**2419**
SD	**28**	**29**	**38**	**32**	**47**
% RSD	**1.21**	**1.19**	**1.50**	**1.40**	**1.96**

BIOGRAPHY

Mr. Arthit Phermtermsin was born on December 10th, 1972 in Khonkaen, Thailand. He was graduated with a Bachelor's Degree of Science in Chemistry from Department of Chemistry, Faculty of Science, Kasetsart University since 1994. He works at Thai Polycarbonate Co., Ltd. He has studied for Master Degree in the Program of Petrochemistry and Polymer Science, Faculty of Science, Chulalongkorn University since 2010. His manuscript was published in proceedings of the 6th Pure and Applied Chemistry International Conference (PACCON 2012) that was held at the Empress convention center, Chiang Mai, Thailand on January 11th - 13th, 2012 and finished his study in 2012.