SYNTHESIS AND CHARACTERIZATION OF NEW HYBRID HEXASUBSTITUTED CYCLOTRIPHOSPHAZENE-SCHIFF BASES AND ITS EFFECT ON THE FIRE RETARDANCY OF EPOXY RESIN COMPOSITE

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NUR ATIKA BINTI WALDIN

THESIS SUBMITTED IN FULFILMENT OF THE REQUIREMENTS FOR THE DEGREE MASTER OF SCIENCE

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DECLARATION

I declare that this thesis was composed solely by myself except where stated otherwise by references and acknowledgement.

24 July 2023

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CERTIFICATION

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ABSTRACT

Broad research in hexasubstituted cyclotriphosphazene derivatives has become a great investment especially in science and technology. Cyclotriphoshazene poses high thermal properties and self-extinguish ability, making it a valuable additive as fire-retardant. A series of new fire-retardant compounds based hexasubstituted cyclotriphosphazene with Schiff bases linkage was successfully synthesized. These compounds, labelled **4a-e**, having different alkyl length terminal end (pentyl, nonyl, decyl, dodecyl and tetradecyl) through nucleophilic substitution. All synthesized compounds were obtained in high percentage yield within the range of 81.45% - 95.68%. The structures of these compounds were characterized using Fourier transform infrared (FTIR) spectroscopy, nuclear magnetic resonance (NMR) spectroscopy and CHN elemental analysis revealed a well fitted data compared to each compound structure and showed high purity. To have better insight on their fire-retardant and mechanical behaviour, epoxy resin (EP) was used as polymer matrix. The thermal stability of the compounds was evaluated using thermogravimetric analysis (TGA). The char yield percentage at 600°C was increased gradually as the alkyl chain length at the end terminal of the compound increased. The incorporation of fire-retardant additives, **2a-e**, **3**, and **4a-e** significantly increased the limiting oxygen index (LOI) compared to pure EP, which exhibited a LOI value of 22.75%. Compound **4e** attached to tetradecyl terminal alkyl group gave the highest LOI value of 26.71%. The surface morphology of char residues from the LOI test was analyzed using field emission scanning electron microscopy (FESEM) showed a good improvement on a compact char residue formed as physical barrier to the matrix which decelerate the heat transfer. Moreover, the mechanical property of synthesized compounds was also investigated. The effect of fire-retardant compounds of hexasubstituted cyclotriphosphazene, **4a-e** to epoxy resin proved an increased mechanical property compared to pure EP with tensile strength of 8.06 MPa. The incorporation of compound **4a** to EP showed the highest tensile strength with 24.61 MPa followed by **4e** with 21.48 MPa. This study concluded that it is essential to maintain both the mechanical properties and fire retardancy of polymers in order to achieve satisfactory safety and high functionality.

Keyword: Cyclotriphosphazene; Schiff-base; fire retardant; mechanical property.

ABSTRAK

SINTESIS DAN CIRI-CIRI HIBRID BAHARU SIKLOTRIFOSFAZENA TERTUKARGANTI HEKSA-BES SCHIFF DAN KESANNYA TERHADAP RENTANG KEBAKARAN KOMPOSIT RESIN EPOKSI

*Penyelidikan yang meluas dalam terbitan siklotrifosfazena tertukarganti heksa kini menjadi pulangan yang bermanfaat terutama dalam bidang sains dan teknologi. Siklotrifosfazena mempunyai sifat kestabilan haba yang tinggi dan keupayaan pemadaman sendiri, menjadikannya bahan tambahan yang penting sebagai kalis api. Satu siri bahan cegah kebakaran yang baharu berasaskan sebatian siklotrifosfazena tertukarganti heksa dihubungkan dengan jaringan bes Schiff telah berjaya disintesis. Sebatian ini, berlabel **4a-e** mempunyai hujung terminal panjang alkil berbeza (pentil, nonil, desil, dodesil dan tetradodesil) melalui tindakbalas penggantian nukleofilik. Semua sebatian yang disintesis memperoleh peratusan hasil yang tinggi dalam julat 81.45% - 95.68%. Struktur sebatian ini telah dicirikan menggunakan spektroskopi inframerah transformasi Fourier (FTIR), spektroskopi nuklear resonan magnetik (NMR) dan analisis unsur CHN membuktikan data yang tepat dibandingkan dengan setiap struktur sebatian dan menunjukkan ketulenan yang tinggi. Untuk mendapatkan gambaran jelas tentang ciri cegah kebakaran dan sifat mekanikal, resin epoksi (EP) digunakan sebagai matriks polimer. Kestabilan haba sebatian telah dinilai menggunakan kaedah analisis termogravimetri (TGA). Peratusan hasil arang pada suhu 600°C meningkat secara beransur apabila panjang rantai alkil pada terminal akhir sebatian meningkat. Penggabungan bahan tambah cegah kebakaran, **2a-e**, **3** dan **4a-e** menunjukkan peningkatan ketara dalam pengukuran indeks oksigen (LOI) dibandingkan dengan resin epoksi tanpa bahan tambah dengan nilai LOI sebanyak 22.75%. Sebatian **4e** dengan terminal kumpulan alkil tetradodekil menunjukkan nilai LOI tertinggi iaitu 26.71%. Morfologi permukaan sisa arang daripada ujian LOI dianalisis menggunakan pancaran medan mikroskopi electron pengimbasan (FESEM) menunjukkan peningkatan pembentukan sisa arang yang padat sebagai penghalang fizikal kepada matriks sekaligus memperlahankan tindakbalas haba. Selain itu, sifat mekanikal sebatian juga dikaji. Kesan siklotrifosfazena tertukarganti heksa kepada EP telah meningkatkan sifat mekanikal bahan. Penggabungan sebatian **4a** menunjukkan kekuatan tegangan tertinggi dengan 24.61 MPa diikuti dengan sebatian **4e** dengan 21.48 MPa. Kajian ini merumuskan bahawa adalah penting untuk mengekalkan kedua-dua sifat mekanikal dan tahan api polimer untuk memenuhi ciri keselamatan dan kebolehfungsian yang lebih baik.*

Kata kunci: *Siklotrifosfazena; bes Schiff; bahan cegah kebakaran; sifat mekanikal*

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LIST OF SYMBOLS

ε	-	Tensile Strain
σ	-	Tensile Strength
E	-	Modulus of Elasticity/Young's Modulus
%	-	Percentage
°C	-	Degree Celsius

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LIST OF ABBREVIATION

HCCP	-	Hexachlorocyclotriphosphazene
P-Cl	-	Phosphorus-Chlorine
EP	-	Epoxy Resin
ABS	-	Acrylonitrile Butadiene Styrene
PA6	-	Polyamide 6
$Al(OH)_3$	-	Aluminium Hydroxide
$Mg(OH)_2$	-	Magnesium Hydroxide
Br_2	-	Bromine
Cl_2	-	Chlorine
FT-IR	-	Fourier Transform-Infra Red
NMR	-	Nuclear Magnetic Resonance
CHN	-	Carbon, Hydrogen, Nitrogen
TGA	-	Thermogravimetric Analysis
LOI	-	Limiting Oxygen Index
FESEM	-	Field Emission Scanning Electron Microscopy
o-	-	Ortho
m-	-	Meta
p-	-	Para
DGEBA	-	Bisphenol A Diglycidyl Ether
ROAC	-	Ring-Opening Alternating Copolymerization
PA	-	Phthalic Anhydride
PET	-	Poly(Ethylene Terepthalene)
HSPCTP	-	Silicon-Containing Cyclotriphosphazene
BODIPY	-	Bearing Mono- And Distyryl(Pyrene) Borondipyrromethene
BPS-BPP	-	Bisphenol-S Bridged Penta(Anilino)Cyclotriphosphazene
PCBs	-	Printed Circuit Boards
LCD	-	Liquid Crystal Display
LED	-	Light Emitting Diode

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XPS/EPS	-	Expended/Extruded Polystyrene
FR	-	Fire-Retardants
TBBPA	-	Tetrabromobisphenol A
HBCD	-	Hexabromocyclododecane
Deca-BDE	-	Decabromodiphenyl Ether
ISO	-	International Organization For Standardization
PLA	-	Poly(Lactic Acid)
HAP-DOPS	-	Hexa(4-9,10-Dihydro-9-Oxa-10-Phosphaphenanthrene-10-Sulfide)-Hydroxymethylphenoxy)Cyclotriphosphazene
HCCP-EP	-	Hexa(Ethylene Oxide) Cyclotriphosphazene
ABCP	-	Aminobenzothiazole-Substituted Cyclotriphosphazene
LDPE	-	Low-Density Polyethylene
EVA	-	Poly(Ethylene-Co-Vinyl Acetate)
HSPCTP	-	Silicon-Containing Cyclotriphosphazene
PC	-	Polycarbonate
APP	-	Ammonium Polyphosphate
HNTP	-	Hexakis(4-Nitrophenoxy) Cyclotriphosphazene
POM	-	Polyformaldehyde
HIPS	-	High Impact Polystyrene
ASTM	-	American Society for Testing And Materials
BICP	-	Benzimidazolyl Substituted Cyclotriphophazene
CTP-EP	-	Hexa[4-(Glycidyloxycarbonyl)Phenoxy] Cyclotriphosphazene
DMF	-	N,N-Dimethylformamide
DCM	-	Dichloromethane
K_2CO_3	-	Potassium Carbonate
KI	-	Potassium Iodide
TLC	-	Thin Layer Chromatography

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RF	-	Retention Factor
IR	-	Infra-Red
$CDCl_3$	-	Deuterated Chloroform
DMSO-d_6	-	Deuterated Dimethyl Sulfoxide
TGA/DSC	-	Thermogravimetric Analysis/Differential Scanning Calorimetry
UTM	-	Universal Tensile Machine
ppm	-	Parts Per Million
s	-	Singlet
d	-	Doublet
t	-	Triplet
q	-	Quadruplet/Quartet
m	-	Multiplet
Hz	-	Hertz
MHz	-	Megahertz
Et_3N	-	Triethylamine
EtOH	-	Ethanol
MeOH	-	Methanol
rt	-	Room Temperature
wt.%	-	Weight Percent

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CHAPTER 1

INTRODUCTION

1.1 Research Background

The development of synthetic chemistry contributes a huge role in modern industry. Synthesis involves sequences of reactions derived from available starting materials to form complex molecules with desirable multifunction applications. Thus, synthetic chemistry gives high impact in most industries include plastic and polymers, cosmetics, electric and electronics as well as other high-tech industry (Nicolaou, 2016). Some synthetic chemistry used in improvising and enhancing the properties of a composite regarding to their safety, resiliency, flexibility, toughness and more.

The synthesis of phosphazene derivatives have drawn much attention and have been reviewed over the years since 19th century (Zibarov *et al.*, 2021). The uniqueness of these compounds which are readily attach to a variety substituent bonded to the phosphorus atoms exhibit highly customizable biological, physical and chemical characteristics. Interestingly, a broad research based on this compound designed desired applications in different fields such as fire-retardant (Mohd Taip *et al.*, 2022), anti-cancer (Pharma *et al.*, 2011), liquid crystal (Jamain *et al.*, 2020a), fluorescent dye (Liu *et al.*, 2021) and dielectric (Selvi *et al.*, 2019).

Phosphazene exist in either cyclic or linear chain inorganic compounds containing of alternate phosphorus (P) and nitrogen (N) atoms, $(\text{-P=N-})_n$ as shown in Figure 1.1.

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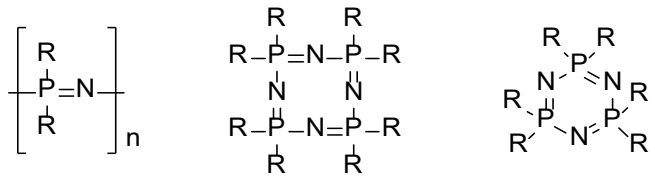
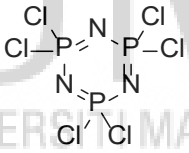


(a) (b) (c)

R = any nucleophiles/alkyl group

Figure 1.1: Phosphazene structures

Phosphonitrilic chloride trimer, also known as hexachlorocyclotriphosphazene, HCCP, $N_3P_3Cl_6$ (Figure 1.2) is one of the most popular starting materials used to form cyclotriphosphazene derivatives. It is noticeable that cyclotriphospazene can behave as excellent fire-retardant with high thermal stability due to the presence of P and N atoms. The content of P acting as radical scavengers and nitrogen which responsible as charring agent by releasing inert gaseous by-product during combustion can greatly enhanced the fire resistance of a material (Fontenot *et al.*, 2015; Jamain *et al.*, 2019).



HCCP

Figure 1.2: Structure of hexachlorocyclotriphosphazene (HCCP)

The high reactivity between P-Cl bond makes it eligible to substitute any side arm by undergo nucleophilic substitution reaction between nucleophiles and the chlorine atom attached to the phosphorus. It is important role in obtaining different desirable properties or to improve their properties depending on the characteristic of the substituted groups (İbişoğlu *et al.*, 2019; Shin *et al.*, 2010). Wide range applications can be explored by incorporating different side-group containing organic, inorganic, or organometallic to form a cyclotriphosphazene derivates.

On the other hand, Schiff base known as azomethine (-C=N-) was formed by the reaction of amine with carbonyl either aldehyde or ketone. Nonetheless, the synthesis of the reaction is more easily initiated from aldehyde due to their reactivity

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primarily due to the less steric hindrance. As for ketone, the presence of two alkyl groups attached to the carbonyl carbon can reduce its electrophilicity thus reducing the rate of reaction (Senthil Kumar Raju *et al.*, 2022; Tuna Subasi, 2023). Schiff base create an efficient cross-linking route to form a highly stable compound to be used as fire-retardant additive (Jamain *et al.*, 2020b). Plus, the special structure of C=N group can self-crosslink to form a relatively stable cross-linked network at relatively low temperature makes them ideal for use as charring agents' promoter (Fan *et al.*, 2020).

In polymer industries, the outstanding properties of cyclotriphosphazene derivatives were used to enhance the thermal and fire-retardant properties and improve the performance of polymer such as epoxy resin (EP) (Chen *et al.*, 2022), acrylonitrile butadiene styrene (ABS) (Shin *et al.*, 2018) and polyamide 6 (PA6) (Malkappa *et al.*, 2020). In the past decades, an approach to improve polymer's fire-retardant properties by incorporating traditional HCCP either by reactive or additive. Although it was proven to improve their flammability shortage, it is however exhibit massive environmental issue.

Phosphorus-based materials are thermally stable and versatile exhibit effective fire-retardant activity by introducing hexachlorocyclotriphosphazene (HCCP, $N_3P_3Cl_6$) into the compound. However, the use of existing HCCP as fire-retardant have a massive environmental issue during combustion as it released toxic chlorine gas (Meng *et al.*, 2021). Therefore, an approach to overcome these issues is by using alternative halogen-free hexasubstituted cyclotriphosphazene derived from the traditional HCCP.

1.2 Problem Statement

The interest in hexasubstituted cyclotriphosphazene had become a great investment in science and technology field. The unusual thermal properties such as fire-retardant and self-extinguish of cyclotriphosphazene has several advantages used as an additive or reactive to increase the resistance of a material towards ignition and reduce fire spread. The statistic of fire breakout is increasing years by years

demanding the urge in research and development (R&D) on flame-retardant compound mainly associated to fire safety (El Gouri *et al.*, 2009).

Polymeric materials are essential components of a wide range of products in our modern world. These covers from manufacturing in automotive, electric and electronics, construction, textile as well as in medical industry. However, most polymeric materials are based on organic compounds which are thermodynamically unstable in an oxidative environment, which poses instability toward fire. The flammability of polymeric materials poses a threat to both product integrity and human health. This is why there is a need for fire-retardants and inherently inflammable polymers.

Halogen-containing cyclotriphosphazene is the most popular fire-retardant. However, it is banned due to their toxicity which released toxic gas such as bromine, chlorine and dibenzofuran when burned (Meng *et al.*, 2021; Zhou *et al.*, 2020). Other conventional halogen free fire-retardant such as aluminium hydroxide, $Al(OH)_3$ and magnesium hydroxide, $Mg(OH)_2$ eventually resulting in a deterioration of mechanical properties to some polymers (Yang *et al.*, 2020; Yang *et al.*, 2017). Therefore, a modification of HCCP with halogen-free compound is necessary to overcome this issue as well to improve their properties.

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1.3 Objectives of Study

The following objectives are part of this study:

1. To synthesize a series of new hybrid hexasubstituted cyclotriphosphazene bearing of two Schiff-bases having different alkyl chain terminal end via nucleophilic substitution.
2. To characterize the intermediates and targeted compounds using Fourier transform infrared spectroscopy (FT-IR), nuclear magnetic resonance spectroscopy (NMR) and CHN elemental analysis.
3. To investigate the fire-retardant properties of targeted compounds by thermogravimetric analysis (TGA) and limiting oxygen index (LOI) test as well as char residue analysis using field emission scanning electron microscopy (FESEM).
4. To determine the mechanical properties of all targeted compounds, includes tensile strength, elongation at break and Young's modulus.