SYNTHESIS, FIRE RETARDANCY AND DIELECTRIC PROPERTIES OF CYCLOTRIPHOSPHAZENE DERIVATIVES BLENDED WITH EPOXY RESIN

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FACULTY OF SCIENCE AND NATURAL RESOURCES
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ABSTRACT

Cyclotriphosphazene is a ring compound consisting of alternating phosphorus and nitrogen atoms. Since cyclotriphosphazene compound was claimed to have excellent fire-retardant properties, this compound was used to overcome the problem of epoxy resin, which was reported to have poor fire ability. Epoxy resin was used widely in many industrial areas but restrained its further application in areas with high-fire resistance requirements. The research project concludes with four key objectives achieved, each contributing to the advancement and characterization of novel hexasubstituted cyclotriphosphazene compounds with promising applications across various domains. Firstly, a successful synthesis was achieved for hexasubstituted cyclotriphosphazene compounds featuring Schiff base and ester linking units, accomplished through multiple chemical pathways. Notably, the alkylation reaction of 4-hydroxybenzaldehyde with pentyl and tetradecylbromide produced intermediates **1a-b**, while condensation of p-substituted benzaldehyde with 4-aminophenol led to intermediates **2a-b**. Intermediate **3** emerged from a substitution reaction of methyl-4-hydroxybenzoate with hexachlorocyclotriphosphazene (HCCP), subsequently yielding intermediate **4**. Esterification of **2a-e** and **4** resulted in compounds **5a-e**, distinguished by Schiff base and ester linking units with varying terminal chain lengths. These synthesized compounds hold substantial potential as versatile constituents for further investigations and practical applications. Secondly, thorough characterization of both intermediates and final compounds was carried out employing diverse spectroscopic techniques, encompassing Fourier transform infra-red spectroscopy (FT-IR), nuclear magnetic resonance spectroscopy (NMR), and CHN elemental analysis. The FT-IR spectra of compounds **5a-e** revealed significant absorption bands at 1617 cm^{-1} (C=N stretching), 1535 cm^{-1} (C=C stretching), and 1238 cm^{-1} (C-O stretching). P=N stretching appeared at 1182 cm^{-1}, while P-O-C bending occurred at 1011 cm^{-1}. Notably, compound-specific characteristics such as C-H sp^3 stretching (2924-2850 cm^{-1}) for **5a** and **5b**, and C-Cl bending (842 cm^{-1}) for **5c**, were observed. The ^{1}H NMR analysis exposed a distinctive proton peak of Schiff base proton at ~ δ 8.50 ppm and various aromatic protons, which resonated in the region of δ 6.50-8.50 ppm. Similarly, ^{13}C and ^{31}P NMR spectra provided insights into carbon and phosphorus environments, demonstrating consistent trends in chemical shifts. Thirdly, the fire retardant properties of these hexasubstituted cyclotriphosphazene compounds, when incorporated into epoxy resin, were investigated. Both thermogravimetric analysis (TGA) and limiting oxygen index (LOI) measurements exhibited improved fire resistance. Compound **5d**, featuring a nitro terminal group, displayed the highest char residue with 34.2% at 700 °C. Notably, LOI testing revealed that compound **5d** had the highest LOI value of 26.71%, indicating enhanced fire retardancy. The dielectric strength of these compounds was also evaluated using AC breakdown voltage, with **5d** exhibiting the highest value of 24.31 kV/mm, suggesting its potential for electrical insulation applications. Lastly, the determination of dielectric strength through AC breakdown voltage measurements provided valuable data on the compounds' electrical properties. Breakdown voltages for different compounds were measured, with alkyl chain-containing compounds exhibiting lower values (21.13-23.51 kV/mm) compared to those with electron-withdrawing groups (-Cl, $-NO_2$, -OH) (23.51-

24.31 kV/mm). The synthesized compounds' diverse performances in terms of breakdown voltage could lead to applications in electrical insulation or capacitor materials, depending on specific requirements. In summary, this research project successfully achieved its objectives of synthesizing, characterizing, and exploring the potential applications of hexasubstituted cyclotriphosphazene compounds. The findings suggest these compounds hold promise in diverse fields ranging from material science to fire safety application and electrical insulation.

ABSTRAK

SINTESIS, KETAHANAN API DAN SIFAT DIELEKTRIK TERBITAN SIKLOTRIFOSFAZENA DICAMPUR DENGAN RESIN EPOKSI

*Siklotrifisfazena adalah sebatian cincin yang terdiri daripada atom fosforus dan nitrogen yang bergantian. Oleh kerana sebatian siklotrifisfazena mempunyai sifat ketahanan api yang sangat baik, sebatian ini digunakan untuk mengatasi masalah resin epoksi, yang dilaporkan mempunyai keupayaan api yang lemah. Resin epoksi digunakan secara meluas dalam pelbagai bidang industri tetapi terhad penggunaannya dalam bidang yang memerlukan ketahanan api yang tinggi. Projek penyelidikan ini disimpulkan dengan empat objektif utama yang dicapai, setiap satu menyumbang kepada pembangunan dan pencirian sebatian siklotrifosfazena tertukarganti heksa yang baru dengan aplikasi yang meyakinkan di pelbagai bidang. Pertama, sintesis berjaya dicapai untuk sebatian siklotrifosfazena tertukarganti heksa yang menampilkan unit penyambung bes Schiff dan ester, dilakukan melalui pelbagai laluan kimia. Tindak balas alkilasi 4-hidroksibenzenaldehid dengan pentil dan tetradesilbromida menghasilkan perantaraan **1a-b**, manakala kondensasi benzaldehid tertukarganti-p dengan 4-aminofenol menghasilkan perantaraan **2a-b**. Perantaraan **3** muncul daripada tindak balas penggantian metil-4-hidroksibenzoat dengan heksaklorosiklotrifosfazena (HCCP), kemudiannya menghasilkan perantaraan **4**. Esterifikasi **2a-e** dan **4** menghasilkan sebatian **5a-e**, mempunyai unit penyambung bes Schiff dan ester dengan panjang rantaian terminal yang berbeza. Sebatian-sabatian yang disintesis ini mempunyai potensi yang besar sebagai bahan-bahan pelbagai untuk penyelidikan lanjutan dan aplikasi praktikal. Kedua, pencirian menyeluruh terhadap perantaraan dan sebatian akhir dilakukan dengan menggunakan pelbagai teknik spektroskopi, termasuk spektroskopi inframerah transformasi Fourier (FT-IR), spektroskopi nuklear resonan magnetik (NMR), dan analisis elemen CHN. Spektra FT-IR sebatian **5a-e** menunjukkan jalur serapan yang signifikan pada 1617 cm^{-1} (peregangan C=N), 1535 cm^{-1} (peregangan C=C), dan 1238 cm^{-1} (peregangan C-O). Peregangan P=N muncul pada 1182 cm^{-1}, manakala lenturan P-O-C berlaku pada 1011 cm^{-1}. Amat penting, ciri-ciri tertentu sebatian seperti peregangan C-H sp^3 (2924-2850 cm^{-1}) untuk **5a** dan **5b**, dan lenturan C-Cl (842 cm^{-1}) untuk **5c**, diperhatikan. Analisis ^1H NMR mendedahkan puncak proton khas iaitu proton bes Schiff pada ~ δ 8.50 ppm dan pelbagai proton aromatik, yang bergema di kawasan δ 6.50-8.50 ppm. Demikian juga, spektra ^{13}C dan ^{31}P NMR memberikan pendedahan ke dalam persekitaran karbon dan fosforus, menunjukkan corak ketetapan kimia yang konsisten. Ketiga, ciri kalis api sebatian siklotrifosfazena tertukarganti heksa ini apabila dicampurkan ke dalam resin epoksi, telah disiasat. Seterusnya, analisis termogravimetri (TGA) dan pengukuran indeks oksigen (LOI) menunjukkan peningkatan ketahanan api.*

*Sebatian **5d**, yang mempunyai kumpulan terminal nitro, menunjukkan jumlah sisa karbon tertinggi dengan 34.2% pada 700°C. Secara signifikan, ujian LOI menunjukkan bahawa sebatian **5d** mempunyai nilai LOI tertinggi iaitu 26.71%, menunjukkan sifat ketahanan api yang lebih baik. Kekuatan dielektrik sebatian-sebatian ini juga dinilai menggunakan voltan pecah AC, dengan **5d** menunjukkan nilai tertinggi iaitu 24.31 kV/mm, mencadangkan potensinya untuk aplikasi penebat elektrik. Akhirnya, penentuan kekuatan dielektrik melalui pengukuran voltan pecah AC memberikan data berharga mengenai sifat elektrik sebatian-sebatian ini. Voltan pecah untuk sebatian-sebatian yang berbeza diukur, dengan sebatian yang mengandungi rantaian alkil menunjukkan nilai yang lebih rendah (21.13-23.51 kV/mm) berbanding dengan yang mempunyai kumpulan penarik elektron (-Cl, -NO_2, -OH) (23.51-24.31 kV/mm). Prestasi yang pelbagai dalam hal voltan pecah bagi sebatian-sebatian yang disintesis ini boleh membawa kepada aplikasi dalam bahan penebat elektrik atau kapasitor, bergantung kepada keperluan yang spesifik. Ringkasnya, projek penyelidikan ini berjaya mencapai objektifnya untuk mensintesis, mencirikan, dan meneroka aplikasi berpotensi sebatian siklotrifosfazena tertukarganti heksa. Penemuan ini mencadangkan bahawa sebatian-sebatian ini mempunyai potensi dalam pelbagai bidang dari sains bahan sehingga aplikasi keselamatan kebakaran dan penebat elektrik.*

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^{1}H-NMR	-	Proton nuclear magnetic resonance
^{13}C-NMR	-	Carbon nuclear magnetic resonance
^{31}P-NMR	-	Phosphorus nuclear magnetic resonance
$CDCl_3$	-	Deuterated chloroform
CHN	-	Carbon Hydrogen Nitrogen
COSY	-	Correlation Spectroscopy
DCC	-	N,N-dicyclohexylcarbodimide
DCM	-	Dichloromethane
DEPT	-	Distortionless enchancement by polarization transfer
DMAP	-	4-dimethylaminopyridine
DMF	-	Dimethylformamide
DMSO-d_6	-	Deuterated dimethyl sulfoxide
FT-IR	-	Fourier Transform Infrared
HCCP	-	Hexachlorocyclotriphosphazene
HSQC	-	Heteronuclear Single Quantum Correlation
LOI	-	Limiting oxygen index
NMR	-	Nuclear Magnetic Resonance
TLC	-	Thin Layer Chromatography
%	-	percentage
δ	-	chemical shift
^{o}C	-	degree Celcius
C_F	-	Oxygen concentration of final test
cm^{-1}	-	Per centimetre
d	-	Oxygen concentration increment
d	-	Doublet
g	-	Gram
h	-	Hour
J	-	Coupling constant
k	-	Factor obtained from the manual book Fire Testing Technology
m	-	Multiplet

MHz	-	Megahertz
mL	-	Millilitre
ppm	-	Part per million
rt	-	Room terperature
s	-	Singlet
t	-	Triplet

CHAPTER 1

INTRODUCTION

1.1 Cyclotriphosphazene

The discovery of organic chemistry led to the new material sciences area. In the early years, the cyclotriphosphazane compound was extensively explored and greatly impacted innovation in the chemistry field. Cyclotriphosphazane compound was first investigated in the mid-1950 by Allcock and his co-workers. Hexachlorocylotriphosphazene, HCCP ($N_3P_3Cl_6$) (Figure 1.1a) is a versatile starting compound for synthesizing phosphazene-based polymers. This compound contains a planar non-delocalized cyclic ring with an alternating of two atoms, which is phosphorus and nitrogen (Devaraju *et al.,* 2018), whereby the chlorine atoms that attached to the phosphorus atom can be replaced with any nucleophile by the substitution reaction (Moriya *et al.,* 1995) (Figure 1.1b). The nucleophilic substitution reaction of cyclotriphosphazene typically involves the replacement of P-Cl bonds by various nucleophiles such as phenols (Lyon *et al.,* 2003), amine (Allcock *et al.,* 1966) and aromatic azo (Bartlett *et al.,* 2006). Previous research has been done by changing the side group of phosphazene such as $-NH_2$, $-OR$, $-OC_6H_5$, or fluorinated derivatives can improve oxidative and thermal stabilities (Allcock, 2012).

(a) (b)

Figure 1.1: Chemical structure of cyclotriphosphazene derivatives; (a) HCCP and (b) hexasubstituted cyclotriphosphazene

It was also reported that the compound containing phosphazene compound core system attached to different substrates exhibited different chemical and physical properties (Allcock, 2004). Due to this reason, the cyclotriphosphazene derivatives compound are widely used in many application such as liquid crystal (Jamain *et al.,* 2021), flame retardant (Allen, 1993), dielectric devices and application (Koran *et al.,* 2014), electrode membrane (Gu *et al.,* 2011) and biomaterials (Sudhakar & Sellinger, 2006). Due to these excellent properties, this compound is still being explored to make it more useful in modern technology and used in the enhancement of the properties of several polymers.

1.2 Fire Retardancy of Cyclotriphosphazene

Fire retardant materials play an important role in preventing property from being damaged. Flame retardancy can be defined as a process to inhibit or stop the combustion process. Fire retardation occurs due to the removal of heat from the materials that can burn and char formation during the fire, interrupting the contact from combustion (Shin *et al.,* 2010). Before this, halogen substances were used as effective fire retardants' substances, but later the halogen halides were deemed too toxic and unstable as a fire retardant (Jiang *et al.,* 2019). It will negatively impact the environment due to its toxicity properties. In light of this, phosphorus and nitrogen are two active components found in current flame retardants. The combination of these two elements in the same compound leads to a synergistic effect wherein the combined effect of two components is greater than a simple additive combination of their individual fire-retardant effects (Liu *et al.,* 2020). Consequently, this puts cyclotriphosphazene compound in the limelight as a high-potential fire retardant that is environmentally friendly since it has low smoke emission, non-toxic, and excellent fire retardancy properties (Wu *et al.,* 2003).

In recent years, phosphazene-based materials have gained a lot of attention because they not only have a wide variety of thermal and chemical stabilities, but they can also boost the thermal and fire-retardant properties of polymers and composites (Kumar *et al.,* 1983). Many researchers have recently discovered that the phosphazene-based family of materials has a wide variety of thermal and chemical stabilities and improved thermal and fire retardant properties to polymers and their composites. Phosphazene compound cores incorporated into the network of thermoset polymers exhibits unusual properties such as flame retardancy and self-extinguishability due to the synergistic effect of two containing atom which is phosphorus and nitrogen (Xu *et al.,* 2016).

1.3 Dielectric Property of Cyclotriphosphazene

Dielectric materials can be referred to as non-metallic substances with a high specific resistance, a negative temperature coefficient of resistance, and a substantial insulating resistance. The dielectric material can also be defined as a non-conducting material that stores electrical charges. When a dielectric is placed in an electric field, the electric charges do not flow through the materials. Electric charges slightly shift from their average equilibrium positions, causing dielectric polarization (Thakur & Kessler, 2014). Positive charges flow in the direction of the field, while negative charges shift in the opposite direction of the field due to dielectric polarization. This phenomenon yields an internal electric field, which in turn reduces the overall electric field within the dielectric materials. Dielectric properties such as dielectric loss, dielectric constant, and breakdown voltage are the most common properties that are extensively studied in order to evaluate solid materials. Dielectrics are of vital importance for the performance of capacitors, sensors, field effect transistors, and touch screen panels, which are widely used in many fields, including microelectronics, electrical equipment, portable or mobile devices, and hybrid vehicles (Tao *et al.,* 2021).

The significance of phosphazene compounds in the dielectric field has increased due to their remarkable dielectric properties. A study reported that the phosphazene compound contains good dielectric properties, and this compound is promising candidate material in multifunctional and optoelectronic devices (Koran *et al.,* 2014). Even though the research related to cyclotriphopshazene in the dielectric is still limited, this compound possesses remarkable attributes, making it a prime candidate for serving as a basic insulating material in cutting-edge electric and electrical equipment. Its stability is particularly valuable in meeting the stringent operational requirements of these fields. Therefore, further enhancing this compound's dielectric properties, especially in epoxy polymer, is crucial for enhancing the performance and reliability of advanced polymers.

1.4 Epoxy Resin

Epoxy resin is a versatile and widely used thermosetting polymer that exhibits excellent adhesion, chemical resistance, and mechanical properties. It is composed of two main components: epoxy resin and a hardener. When these components are mixed, a chemical reaction occurs, leading to cross-linking and the formation of a rigid and durable material.

Epoxy resins find applications in various industries, such as construction, aerospace, automotive, electronics, and marine, due to their outstanding properties (Cheng *et al.,* 2020). They are commonly used as adhesives, coatings, and composites, providing strong bonding capabilities, and protecting surfaces from environmental factors. However, epoxy resins have limitations when it comes to high-fire requirement application (Liu *et al.,* 2010). The main drawbacks are low resistance to high temperatures. Epoxy resins tend to degrade at elevated temperatures, and when exposed to intense heat, they can lose their structural integrity. This makes them unsuitable for applications where fire resistance is critical, such as in fire-rated constructions or fire protection systems. In addition, epoxy resins are flammable, which means they can ignite and support combustion under certain conditions. In high-fire requirement environments, materials need to have low flammability to prevent the rapid spread of flames. Other than that, the combustion of epoxy resins releases toxic gases, such as carbon monoxide and various volatile organic compounds. These emissions pose serious health hazards to occupants and responders during a fire event.

Due to these limitations, epoxy resins are not recommended for applications where high fire resistance and low smoke and toxic gas emissions are essential. In such cases, other fire-resistant materials like intumescent coatings, fire-retardant polymers, or ceramic composites may be preferred to meet the stringent fire safety requirements.

1.5 Problem Statement

Hexasubstituted cyclotriphosphazene compounds have been widely synthesized and studied to evaluate their fire-retardant properties. Various linking units have been explored to gain a better understanding of how the compound's structure influences its enhanced properties. In recent years, studies have been done to enhance the properties of polymer polyester resin incorporated with hexasubsituted cyclotriphosphazene containing Schiff base and ester linking units. Since epoxy resin has been widely used as advanced composites matrices in various areas due to its outstanding properties, this research aims to enhance the properties of epoxy resin, especially in fire retardant and dielectric properties, as it is reported to have poor fire performance and limitation in electrical application materials. Overall, enhancing the fire retardant and dielectric properties of epoxy resins can lead to safer, more reliable, and efficient products and structures, benefiting various industries such as electronics, aerospace, construction, transportation, and more. It enables the use of epoxy resins in applications where fire safety and electrical insulation are critical considerations. The most desirable solution to this problem is to develop a new compound that can enhance epoxy resin properties