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GRADUATE SCHOOL OF SCIENCE AND ENGINEERING

SYNTHESIS OF FUNCTIONAL POLYAMINOBORANES AND THEIR APPLICATIONS

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MASTER OF SCIENCE THESIS

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Dedicated to my family

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LIST OF SYMBOLS

°C	Celsius degree
cm	Centimeter
eV	Electronvolt
g	Gram
g/mol	Gram per mol
kJ	Kilojoules
kW	Kilowatt
L	Liter
µ	Micrometers or microns
ml	Milliliter
mmol	Millimole
min	Minutes
M	Molar
MW	Molecular Weight
nm	Nanometer
N	Newton
ppm	Parts per million
%	Percent
PDI	Polydispersity Index

LIST OF ABBREVIATIONS

APMES	3-aminopropyl trimethoxysilane
BH_3:THF	Borane–Tetrahydrofuran Complex
BN	Boron Nitride
DCM	Dichloromethane
DIAB	Diisopropylaminoborane
DLS	Dynamic Light Scattering
DMF	Dimethylformamide
EDA	Ethylene diamine
EDX	Energy Dispersive X-Ray Analysis
EEC	European Council Regulation
GPC	Gel permeation chromatography
LOI	Limiting Oxygen Index
$MgSO_4$	Magnesium Sulfate
MMAB	Mono Methyl Amino Borane
NaOH	Sodium hydroxide
NMR	Nuclear magnetic resonance spectroscopy
PAB	Polyaminoborane
PDMS	Polydimethylsiloxane
SEM	Scanning Electron Microscope
TEA	Triethylamine
TGA	Thermogravimetric Analysis
THF	Tetrahydrofuran
WHO	World Health Organization
XPS	X-ray photoelectron spectroscopy
XRD	X-Ray diffraction analysis

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ABSTRACT

Synthesis of Functional Polyaminoboranes and Their Applications

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Chemistry Program (English)

Master of Science Thesis

Supervisor: Prof. Dr. Tarık EREN

Polyaminoboranes have various applications, such as serving as initiators in ceramics, being used in boron nitride (BN) production, hydrogen storage, and energetic materials. They exhibit a synergistic effect and are non-combustible due to the presence of boron and nitrogen. These polymers can also be utilized to synthesize organic-inorganic hybrid boron nitride ceramics, similar to the inorganic analog of polyolefins. Boron nitride is a highly stable layered material that is ideal for coatings with excellent thermal conductivity. Within the thesis, the synthesis of BN was conducted using polyaminoboranes as precursors. BN is a non-oxide ceramic with unique properties determined by its crystal structure. Cubic BN is the second hardest material known after diamond, demonstrating exceptional chemical resistance and thermal stability. Hexagonal BN (h-BN) resembles graphite but distinguishes itself with high thermal conductivity, low thermal expansion, thermal shock resistance, high electrical resistance, non-toxicity, workability, lubricity, and chemical stability. These properties make boron nitride suitable for various industries, including aerospace, automotive, electronics, semiconductors, metalworking, and cosmetics. The thesis involved the synthesis of three different polyaminoborane homopolymers: (i) methyl-functional aminoborane, (ii)

phosphorus-functional aminoborane, and (iii) silane-functional aminoborane. The polymers were characterized using techniques such as ^{1}H NMR, ^{13}C NMR, ^{11}B NMR, FTIR, TGA, and GPC. Subsequently, the functional polyaminoborane polymers were pyrolyzed to obtain ceramic structures based on B-N, P-B-N, and Si-B-N. The resulting structures were characterized through SEM and XPS analysis. In terms of surface coating, carbon fiber was coated using the dip coating method, and surface characterization was performed using SEM-EDX and XPS methods. The flame resistance of the polymer structures was investigated in wood surface applications. It is anticipated that the obtained polymer structures will exhibit multifunctional surface coating properties, such as flame retardancy, chemical and oxidative stability.

Keywords: Polyaminoborane synthesis, flame retardants, boron, boron nitride, coatings

ÖZET

Fonksiyonel Poliaminoboranların Sentezi ve Uygulamaları

Mert Burak ŞEN

Kimya Anabilim Dalı

Yüksek Lisans Tezi

Danışman: Prof. Dr. Tarık EREN

Poliaminoboranlar, seramik yapımında başlatıcı olarak veya bir seramik hazırlanmasında, bor nitrür (BN) üretiminde, dihidrojen depolanmasında ve/veya hidrojen pilleri veya enerjetik malzemeler olarak kullanılabilmektedir. Bunun yanında B ve N sinerjistik etkisi ile kendiliğinden yanmaz özellikte olan polimerler içinde bir örnek teşkil edebilmektedir. Ayrıca, poliolefinlerin inorganik analoğu olan poliaminoboranlar, organik-inorganik hibrit bor nitrür seramiklerin sentezlenmesinde kullanılabilir. Bor nitrür, olağanüstü termal iletkenliğe sahip kaplamalar için ideal olan, yüksek termal ve kimyasal stabiliteye sahip katmanlı bir malzemedir. poliaminoboranlar BN-esaslı malzemelere öncü bileşikler olduklarından tez kapsamında BN sentezi gerçekleştirilmiştir. BN, kristal yapısına bağlı olarak benzersiz özellikler gösteren oksit olmayan bir seramiktir. Kübik formunda, kimyasallara karşı olağanüstü bir dirence ve termal stabilite özelliklerine sahip olması ile elmastan sonra bilinen en sert ikinci malzemedir. Altıgen BN (h-BN) grafite benzer ve yüksek ısı iletkenliği, düşük termal genleşme, termal şok direnci, yüksek elektrik direnci, toksik olmayan, kolayca işlenebilirlik, kayganlık, kimyasal kararlılık göstererek diğer metal ve metal tuzlarından önemli bir ayırt edici özelliği bulunmaktadır. Bu, bor nitrürü havacılık, otomotiv, elektronik, yarı iletkenler, metal işleme ve hatta kozmetik dahil olmak üzere çeşitli endüstri dallarında farklı özellikler sergileyen üretilebilir bir malzeme haline getirmektedir. Tez kapsamında 3 farklı poliaminoboran homopolimeri

sentezlenmiştir. Bunlar (i) metil fonksiyonel aminoborane, (ii) fosfor fonksiyonel aminoborane, (iii) silane fonksiyonel aminoborane monomer ve polimerlerin karakterizasyona ^{1}H NMR, ^{13}C NMR, ^{11}B NMR, FTIR, TGA, GPC teknikleri ile yapılmıştır. Fonksiyonel poliaminoboran polimerleri daha sonra piroliz fırınında piroliz edilerek B-N, P-B-N, Si-B-N esaslı seramik yapılar elde edilmiştir. SEM ve XPS analizleri ile yapılar karakterize edilmiştir. Yüzey kaplama kapsamında karbon fiber daldırma method ile kaplanmış ve yüzey karakterizasyonu SEM-EDX ve XPS metodları ile karakterizasyonu incelenmiştir. Ahşap yüzey uygulamasında aleve karşı direnç inccelenmiştir. Ortaya çıkan polimer yapılarının, çok işlevli yüzey kaplama özelliklerinin, aleve dayanım, kimyasal ve oksidatif stabilite gibi, elde edilmesine kullanılabilir.

Anahtar Kelimeler: Poliaminoboran sentezi, alev geciktiriciler, bor, bor nitrür, kaplamalar

1
INTRODUCTION

1.1 Literature Survey

With an annual growth rate of 5-6%, polyolefins, [RCH-CH_2]n, are currently one of the most significant synthetic polymer markets [1]. Polyaminoboranes are polymers that are inorganic analogues of polyolefins. The history of chemistry has been greatly influenced by the isoelectronic interaction between B-N and C-C bonds [2]. Polyaminoboranes have a variety of applications, including boron nitride (BN) synthesis, dihydrogen storage, hydrogen cells, and energetic materials. In addition, polyaminoboranes, thanks to synergistic effect of B and N, can be an example among polymers that have flame retardant properties.

However, despite efforts made in the 1950s and 1960s, it was not possible to synthesize a soluble polyaminoborane [RNH-BH_2]n (BN analog of polyolefins) with high molecular weight and suitable characterization [3]. BN linkages in the structure also contribute to the formation of transition metal coordination polymers. The catalytic dehydrogenation of primary amine-boranes and ammonia-boranes has offered a potential pathway for the production of analog of polyaminoboranes. Using [Rh(μ-Cl)(1,5-cod)]$_2$ as a catalyst, a catalytic dehydrocoupling/dehydrogenation reaction was carried out with 1 equivalent of the complex as shown in Figure 1.1, and the aim was to obtain high molecular weight polyphosphinoboranes [4].

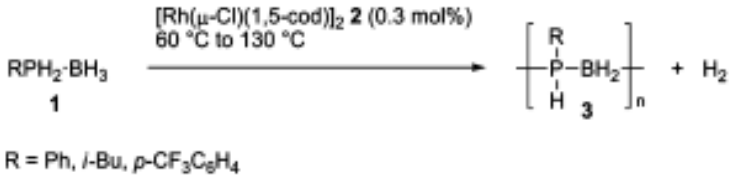


Figure 1.1 Synthesis of polyphosphinoboranes [4]

However, in this reaction with hydrogen, the desired result could not be achieved. Instead, the presence of the BN structure in this study led to the formation of weakly insoluble and branched oligomeric materials [5].

$NH_3 \cdot BH_3$, a cyclic pentamer followed by $[NH_2BH_2]_5$, was synthesized using Brookhart's IrH_2POCOP catalyst as shown in Figure 1.2. This development has facilitated similar

studies in the preparation of soluble polyaminoboranes with primary amine borane additives [6].

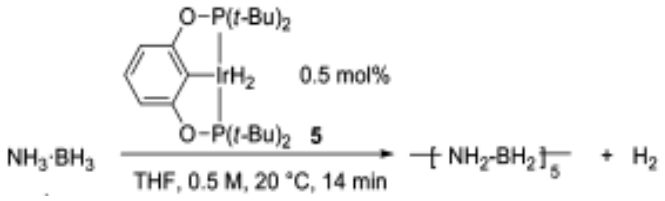


Figure 1.2 Synthesis of polyaminoboranes with Brookhart's IRH_2POCOP catalyst [6]

Several ferrocenylphosphine-borane adducts, in which amines readily react with BH_3, were prepared. The needed phosphine-borane was made using the appropriate ammonium salt, and the associated ferrocenyl-substituted P-B-based polymers have been produced using RhI-catalyzed dehydroconjugation [7]. Similar to the previously described catalytic dehydroconjugation/dehydrogenation of primary phosphine borane adducts, the catalytic dehydrogenation of primary amine-boranes and ammonia-boranes offers a possible pathway to polyaminoboranes.

An analogous method to the previously described catalytic dehydroconjugation/dehydrogenation of primary phosphine borane adducts is used for the catalytic dehydrogenation of primary amine-boranes and ammonia-boranes to polyaminoboranes. This offers a potential route for synthesis. Manners and colleagues demonstrated the success of polyaminoborane synthesis by conducting Rh-catalyzed dehydroconjugation of primary phosphine-borane adducts. They achieved this synthesis by utilizing an amine-borane adduct such as CH_3NH_2:BH_3 at ambient temperature in the presence of a catalyst. This approach led to the identification of well-characterized, high molecular weight, soluble polyaminoboranes, and it was achieved through the room temperature reaction of $MeNH_2 \cdot BH_3$, one of the readily available amine-borane additive precursors [2-8] as shown in Figure 1.3.

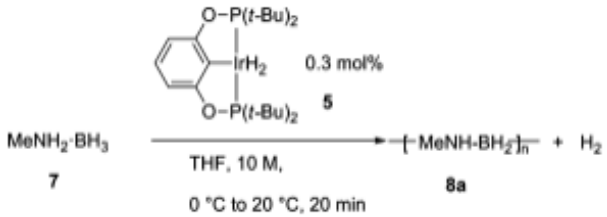


Figure 1.3 Synthesis of first well-characterized and soluble polyaminoboranes [2-8]

The dehydropolymerization of N-methylaminoborane using Brookhart's Ir-catalyst in Figure 1.3 results in high molecular weight and the formation of soluble poly(N-methylaminoborane). This approach was confirmed through characterization techniques such as GPC, DLS, and NMR. Although the catalyst's efficiency is 60%, its development remains crucial for this polymer synthesis. As a result, studies are being conducted on Ru, Rh, and Pd catalysis in various manners to explore alternative options.

The mechanism-led design of novel systems for the dehydropolymerization of amine-boranes is difficult despite the wide range of available catalyst alternatives. It is challenging because every catalyst system has a dual duty [9], holistically managing two fundamental steps of this cascade-like polymerization [10]: First dehydrogenation of an amine-borane to make a transitory and extremely reactive aminoborane, and the subsequent dehydrogenation of an aminoborane to produce a polymer. The mechanism-led design of novel systems for the dehydropolymerization of amine-boranes is difficult despite the wide range of available catalyst alternatives. It is challenging because any catalyst system mediates two fundamental steps of this cascade-like polymerization, including the initial dehydrogenation of an amine-borane to create a fleeting and extremely reactive aminoborane. It has been demonstrated that $MLn(iPr_2PCH_2CH_2)_2NH$)-type systems, which function via ligand cooperative amine-borane dehydrogenation pathways, may be used to expand chain-length control to potentially more robust systems [11]. Controlling the degree of polymerization and subsequently exploring the physical characteristics of polymers is possible by using the boron salt $[H_2B(NMe_2H)_2]Cl$ as an easy chain control agent. Although this work offers promising chain propagation in shown Figure 1.4 for synthesis of polyaminoboranes, there is still need for more new methods and new catalyst.

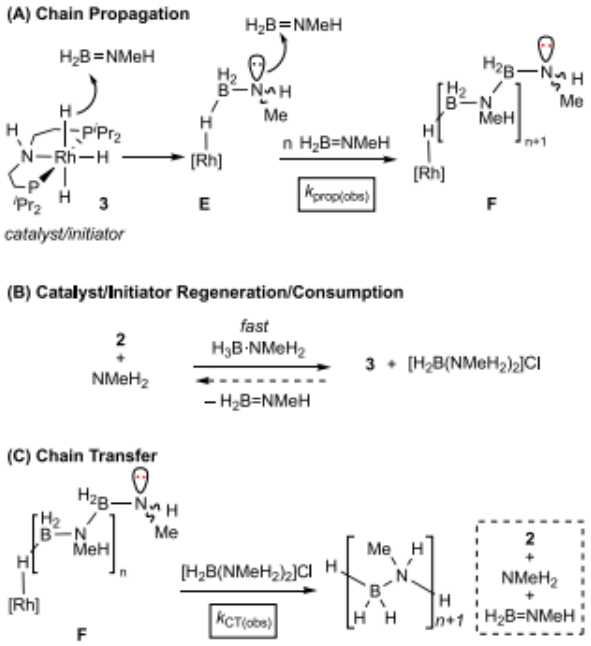


Figure 1.4 Proposed chain propagation [12]

1.1.1 Noncatalyst Route for the Synthesis of Polyaminoboranes

Additionally, Alcaraz et al. have successfully synthesized the polymer without the use of any catalyst, providing an alternative approach [13]. Diisopropylaminoborane (iPr_2NBH_2; DIAB) served as the monomer precursor in the procedure outlined (Figure 1.5). DIAB and a primary amine were combined in a process that took place at -40 °C. It is assumed that the secondary amine unit, iPr_2N, and the primary amine engage in an exchange process, potentially creating adduct 6 in Figure 1.5. The in situ produced monomer 7 shown in Figure 1.5, in contrast to the sterically hindered iPr_2NBH_2, is thermally unstable and polymerizes right away. DIAB can be used as a precursor for species of highly reactive aminoborane. This method of synthetic synthesis produces polymers with extremely high molecular weights without the use of solvents or metal catalysts.

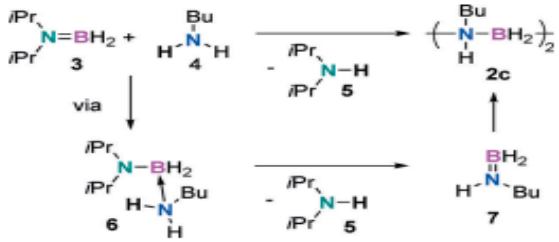


Figure 1.5 Solvent-free polymerization to obtain polyaminoboranes [13]

Perhaps the variation in the oxidation state of the pre-monomer is what distinguishes the catalytic dehydrocoupling polymerization process from the new, uncatalyzed polymerization induced by amine-aminoborane exchange: In the first method, hydrogen is removed, but in the second method, neither the oxidation state of nitrogen nor that of boron is altered. The functional group tolerance of both reactions is impacted by this difference. While such side reactions are obviously not a problem for the polymerization induced by amine-aminoborane exchange, the freed dihydrogen in a catalytic dehydrocoupling process may react once again with double bonds and other easily reducible functional groups [14].

1.2 Purpose of Thesis

Polyaminoboranes are inherently flame-retardant polymers that possess unique properties. Due to the B-N bond, they have partial ionic character and have a clear distinction between the valence and conductivity bands. Due to their superior combustion retardation characteristics, they are strong prospects for next semiconductor systems. Furthermore, the presence of boron in the polymer matrix gives it the capacity to absorb neutrons, creating a substance that is both neutron-capturing and inflammable. This characteristic helps to create materials that are versatile and have a variety of useful features.

Over 1.5 million tons of flame retardants are consumed annually on the world market, at an estimated cost of about 2.4 billion dollars. The market for flame retardants is expanding at a consistent 5% yearly rate. The rising use of plastic in numerous sectors is the main cause of this rise [15]. Due to its harmful effects, PCB (polychlorinated biphenyls), one of the first flame retardants, was outlawed in 1977. Bromine-based flame retardants are currently utilized frequently, although their use is restricted due to the negative effects they are connected with. Beginning in 2008, the bulk of PDBEs (polybrominated diphenyl ethers) were outlawed by the European Union. Flame retardants present a number of problems on a global scale, including their effects on the environment, the buildup of inorganic materials in organisms, the possibility of long-term environmental and human harm, and the emission of unwelcome gases during combustion. Since 2000, there have been sporadic limits or outright bans on the use of goods containing flame retardants made of chlorine and bromine due to the risk that these compounds bring to the environment and human health when they burn. Due to this, new

generation flame retardant compounds are being investigated by the chemical industry. These materials are well-dispersed in polymers and have a low likelihood of igniting and emitting harmful waste. As a result, there has been a considerable emphasis on creating flame retardant materials with better qualities.

In addition to polyaminoboranes, the thesis aims to synthesize phosphorus-boron and silane-boron-containing polymers with self-inflammability properties. These polymers can serve as additives or commercial product as flame retardant polymers. The application of these synthesized polymers in the polymer matrix enhances surface dispersion and prevents surface emissions. Additionally, these polymers represent a new generation of flame retardants.

Polyaminoboranes are precursor for boron nitride. Here, we also conducted to synthesize P-BN and Si-BN as functional boron nitride that can be phosphorous (P-BN) and silane (Si-BN) coated onto carbon fiber surface. Furthermore, they can also be utilized as raw materials for the production of polyaminoborane boron nitride. In this context, the development and production of new ceramic materials based on functional boron nitride is achieved. Our expectation is that these products will find significant applications, particularly in the defense industry, where they can serve as raw materials for high-value-added products.

In conclusion, our process intends to create ceramers—organic-inorganic hybrid ceramics made to withstand harsh conditions. The initial area of focus for our research is synthesis of functional polyaminoboranes possesing silane, phosphorus and methyl functionality at the backbone. We employed homopolymers of polyaminoboranes, which have already been exploited as boron nitride precursors, to create organic-inorganic ceramics. Carbon fiber, wood, and glass surfaces are coated for this study's use to increase the surface's toughness. With this application procedure, the polymer structure won't be broken down and will instead be heated to high temperatures and transformed into a ceramic structure. The characterization of the monomers and polymers at each stage led to the discovery that the intended structures were produced. Characterization proved that we used the dipping approach on our materials to produce a high degree of boron nitride coating.

1.3 Hypothesis

The utilization of polymeric compounds containing boron and nitrogen in the synthesis of functional BN-based materials has gained considerable interest in recent times. Ceramic polymers offer a significant advantage in terms of their high processability potential, allowing for the production of complex-shaped components or structures. They also enable various fabrication processes such as sol-gel coating. The field of BN ceramic polymers primarily involves polymers derived from borazine. However, this method requires an inert atmosphere and necessitates the use of super dry solvents, which poses challenges due to the sensitivity of borazine initiators to moisture and their high reactivity. Polyaminoboranes have emerged as a promising alternative in the realm of BN ceramic polymers.

One of the significant advantages of polyaminoboranes is their inherent flame-retardant property due to their polymer structure. Currently, inorganic-based additives are commonly used in polymers to impart flame retardant characteristics. For instance, zinc borate is utilized as an additive in polymers and paints. However, inorganic additives have certain drawbacks, such as the tendency to form aggregates within the polymer matrix, poor distribution resulting in phase separation, and abrasion in extruder machines. Additionally, the release of inorganic additives from the surface over time can impact the long-term flame retardancy of the material and pose environmental concerns.

Similar environmental concerns apply to low molecular weight organic-based additives as well. Moreover, the effects of halogen-based additives on the environment and human health have prompted the need for new flame-retardant materials. The development of new standards addressing flammability, considering environmental conditions and human health, as well as the implementation of new regulations in this regard, have further emphasized the importance of flame-retardant studies.

Currently, there is a growing focus on exploring the flame resistance of polymers without the use of flame-retardant additives. In the scope of this research, functionalized polyaminoborane, silane functional, phosphorous functional polymers with flame retardant properties is synthesized and P-BN, Si-BN, boron nitride type ceramic is obtained thanks to these polymers. Alkoxysilane groups are preferred for polymers containing end groups that can be hydrolyzed by synthesizing Si-based poly(siliconaminoboranes), which is thought to be able to provide silicon and boron

synergy, due to their wide spectrum of use in the field of polysiloxanes or silicones. Hybrid polyaminoborane/polysiloxane polymers that are likely to contain additives of interest and are likely to interact with various surfaces, particles or devices for coating or layering, to be obtained in finely shaped ceramics by appropriate heat treatment have been developed. The synthesis of new P-based poly(phosphoamidatamineborane)s is proposed, which are expected to exhibit a synergistic effect between phosphorus and nitrogen (PN). The use of halogenated flame-retardant compounds, such as those containing bromine and chlorine, has been increasingly restricted or even banned since the 2000s due to their harmful and toxic waste emissions into the environment. This has prompted the exploration of environmentally friendly alternatives that do not produce toxic by-products, can be uniformly dispersed in polymers, and expand the potential applications of these compounds. The primary objective of our research is to synthesize these new functional polymers, that demonstrate multifunctional properties, the phenomenon of luminescence (both for fluorescent or phosphorescent) with phosphor, self-lubricant properties and anti-corrosion with silane, improved physical properties with boron and flame-retardant properties, without the need for additional additives.

2
FLAME RETARDANTS

Anywhere in the world, a fire might break out, resulting in human casualties, material losses, and the destruction of priceless works of art and history. Experts claim that the usage of flame retardants significantly reduces the risk of fire spreading. The National Fire Protection Association reported that there were 1,348,500 fires in the United States in 2009, resulting in 3,010 fatalities, 17,050 injuries, and $12.5 million in property damage [16].

Our nation's fast industrialization, uncontrolled urbanization, and population expansion all contribute to an increase in fires and the consequent damage each year. Every 30 seconds, a fire doubles in size, and in the first 4 minutes, it can spread by about 1100%. 80% of all fires are house fires. Fire danger persists at all times as long as combustible materials are present in our workplaces, industries, and structures. Based on the construction of the building and the quantity of combustible materials available, the likelihood that a fire may occur there (fire risk) rises. Aside from industrial facilities, such as factories, hotels, business centers, and shopping centers, the growth and modernization of our buildings, the use of sophisticated electromechanical systems, and the increased density of energy and control cables have all increased the fire load and risk. If a fire is not put out in the beginning, it spreads quickly by taking advantage of cracks, crevices, shafts, and openings inside the structure. To determine the minimal amount of fire protection that is appropriate, several nations have set rules. In particular, having flame retardant qualities that support safety precautions in the case of a fire is one of the core specifications for construction materials. The emphasis that the European Union placed on this subject has led to the creation of several rules, including the Building Materials Regulation 89/106/EEC.

2.1 Current Research on Flame Retardants

Flame retardants are essential for halting the spread of fire or preventing its initiation in a variety of materials. They are combined with substances like synthetic and natural polymers, which have excellent thermal, mechanical, structural, optical, and electrical qualities and are employed extensively in the twenty-first century. These polymers are

widely used in construction, home decor, furniture, electronics, autos, the railway and aviation sectors, coatings, and other products. Unfortunately, polymers are prone to fire risks, which can result in casualties and damage to property. New substances called as flame retardants have been created to solve this problem. They are made to increase escape time, decrease flame propagation, and improve ignition resistance. Halogenated and non-halogenated flame retardants are the two primary categories that they fall under. The categorization also covers exfoliated or intercalated nanocomposites, such as polymer clay composites, that are phosphorus-based, mineral-filled, nitrogen-based, silicone-based or boron-based and come under the category of inorganic flame retardants and condensed ash systems. The research in this field is continuously growing, particularly without the use of any additives. There is a noticeable increase in studies focused on polymers with flame retardant properties. Fire-related deaths have been an undeniable and significant problem throughout human history.

Thermo-oxidative stability, decreased flammability, enhanced strength at high temperatures, greater resistance to corrosion and fatigue, and lower expenses for tooling and simplicity of manufacturing are all significant aspects in material selection [17]. Small amounts of inorganic flame retardants, such as silicon dioxides, are frequently employed, although they can be costly and need the mixing of additional elements. Due to the addition of nanoscale spheres, rods, or plates into the polymer matrix, nanocomposite flame retardants, notably polymer-clay composites, provide promising features. However, because to their intrinsic nanoscale structure, nanocomposites may perform poorly over time and might be difficult to achieve homogeneity in. Furthermore, nanocomposites might have complicated rheological and surface area assessments [18].

Flame retardant chemicals are frequently used in carried out commercial polymer-based products and are required. For flame retardancy, the industry formerly mainly used halogenated substances. As flame retardants, halogen-based organic molecules like brominated or chlorinated compounds performed particularly well. However, their continuous usage in the industry has been constrained due to the environmental and health risks connected with these substances. Additionally, restrictions and risk evaluations for several components, such as the prohibition of specific halogenated flame retardants, have been published by the World Health Organization (WHO) [19].

Boron-containing flame retardants can effectively prevent fire by working in the dense phase and forming a boron silicate layer. Boron-based molecules, like zinc borate and boric acid, are benefited as fireproofing agents. The synthesis of various boron derivatives and polymers is conducted to explore their high strength and flame-retardant properties. This shielding layer successfully absorbs fumes, acts as an anti-alloying agent, and captures oxygen. Boron-based polymers exhibit high strength and stability at high temperatures, and their matrix displays various properties, including neutron absorption. Silicone-based flame retardants, such as polysiloxanes and related polymers, are bonded by strong silicon-oxygen bonds with a dissociation energy of 513 kJ/mol, surpassing the dissociation energy of the carbon-oxygen bond at 348 kJ/mol. This bond energy in polysiloxanes contributes to heat transfer, resulting in high performance, flexibility, and permeability [19]. Specifically, compounds containing phosphorus and silicon, along with other nitrogen-containing functional groups, exhibit enhanced flame retardancy in both the gas phase and dense phase, demonstrating significant effects [17]. Dialkyl H-phosphonate and dimethyldichlorosilane, two monomers with two functional groups, can be used to create silicon-containing poly (alkylene H-phosphonate), another silicone-based polymer [20]. Ash-containing condensed phase mechanisms or gas phase flame suppression mechanisms are how phosphorus-based flame retardants work [21].

Epoxy-based bis-biphenoxy phenyl phosphine oxide has an ash content of 26.1% and a limiting oxygen index (LOI) of 30.5% [22]. The LOI value for polyols and polyurethanes with phosphorus in the P-N ring is 31.4% [23]. According to the results of the thermogravimetric analysis (TGA), pure polymethylmethacrylate (PMMA) does not create ash. However, the ash content can rise to 36% when an acrylate-containing phosphonate is applied in the right quantities [24]. Organoboron compounds function in the condensed phase, where carbon production rather than CO or CO_2 is the result of breakdown. A barrier that stops oxygen from entering and carbon from oxidizing is created by the creation of protective ash. Carboranes are good flame retardants due to their high boron concentration and thermal stability. A high ash yield of 91.5% at 1000°C in air is produced by the thermal copolymerization of carborane-containing acetylenic monomers and acetylene-terminated imide monomers. Adding carboranes to the siloxane backbone greatly improves thermal stability overall with an unusually high ash yield [25]. As candidates for flame retardants, carboranes are favored. However, their chemical pathways could require difficult synthesis processes and limited solubility. Some

oligomer combinations can become porous and brittle when they are carborane-cured [26]. Carboranes are example of organic-inorganic type of structure. (Figure 2.1)

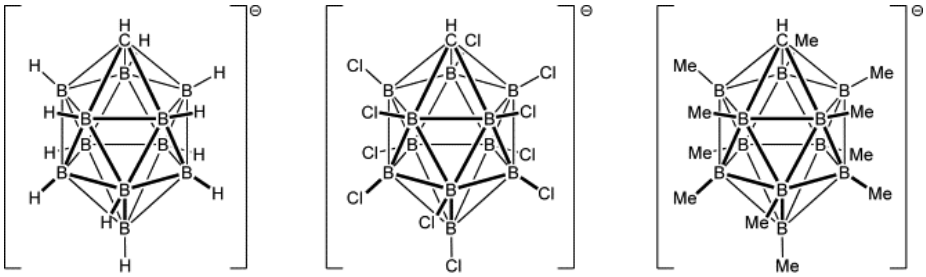


Figure 2.1 Carborane structures

Most polymers are flammable, and non-reactive organic additives tend to migrate or release into the polymer during use, resulting in changes in flame retardancy. To achieve both stable transparency and flame retardancy, it is necessary to chemically bond organic additives to the polymer [27]. The use of new flame-retardant compounds is imperative for health and environmental reasons. Therefore, there is an urgent need for polymers with inherent flame resistance that do not contain halogens in their matrix. The generation of highly toxic gases during thermal decomposition has led to the development of non-halogen flame retardants. Additionally, there is growing interest in flame testing and flame-retardant studies for new polymers without the use of additives. This research holds promise and importance in the field. Two main aspects related to polymeric flame retardancy can be emphasized. First, whether the synthesized material possesses inherent flame retardancy, and second, whether the addition of synthesized flame retardants contributes to the thermal stability and flame retardancy properties of other polymers.

The manufacturers' claim is correct that one of the common approaches to make a polymer flame resistant is by incorporating flame retardant chemicals. Flame retardants can be categorized into reactive and additive types. Reactive flame retardants contain heteroatoms, such as phosphorus or nitrogen, which chemically interact with the polymer molecules. These flame retardants undergo chemical reactions during the combustion process, producing by-products that act as flame suppressants. By incorporating reactive flame retardants, the polymer's chemical structure is modified to enhance its fire resistance. On the other hand, additive flame retardants are physically mixed with the polymer without undergoing chemical reactions. These flame retardants work by releasing gases or forming a protective barrier on the polymer surface during a fire, thus

reducing the flammability and slowing down the combustion process. Commonly used flame-retardant elements include boron, aluminum, phosphorus, antimony, chloride, and bromide. These elements or their compounds can provide different mechanisms of flame retardancy, such as forming char, releasing flame-inhibiting gases, or interrupting the combustion reaction. Both reactive and additive flame retardants have their advantages and limitations, and the selection of the appropriate flame retardant depends on the specific requirements and properties desired for the polymer and its intended applications.

The world market of flame retardants incorporated into commercial polymers is shown in Table 2.1. 1.8 million tons of flame retardants, with a market worth of around 4.2 billion dollars, were used in 2007, according to statistics. Due to the consequences on both human and environmental health, it appears that the use of flame retardants that include bromine will be prohibited in the upcoming years. There is a need to look for other flame retardants since inorganic additives often produce a heterogeneous matrix in the polymer matrix and are not properly shared there.

Table 2.1 Consumption percentages of flame-retardant materials in USA and Western Europe [28]

Types of Flame Retardants	USA	Western-Europe
Aluminum Hydroxide	**39**	**47**
Bromine	**27**	**13**
Phosphorus	**12**	**23**
Chlorine	**11**	**3**
Antimony Oxide	**8**	**7**
Magnesium Hydroxide	**1**	**2**
Zinc Borate	**2**	**5**

Figure 2.2 indicates that the use of flame retardants is experiencing an annual increase of approximately 5%. This trend can be attributed to several factors, including the growing demand for fire safety measures in various industries, the development of stricter regulations regarding flame retardancy, and the increasing awareness of the importance of human health and environmental considerations.

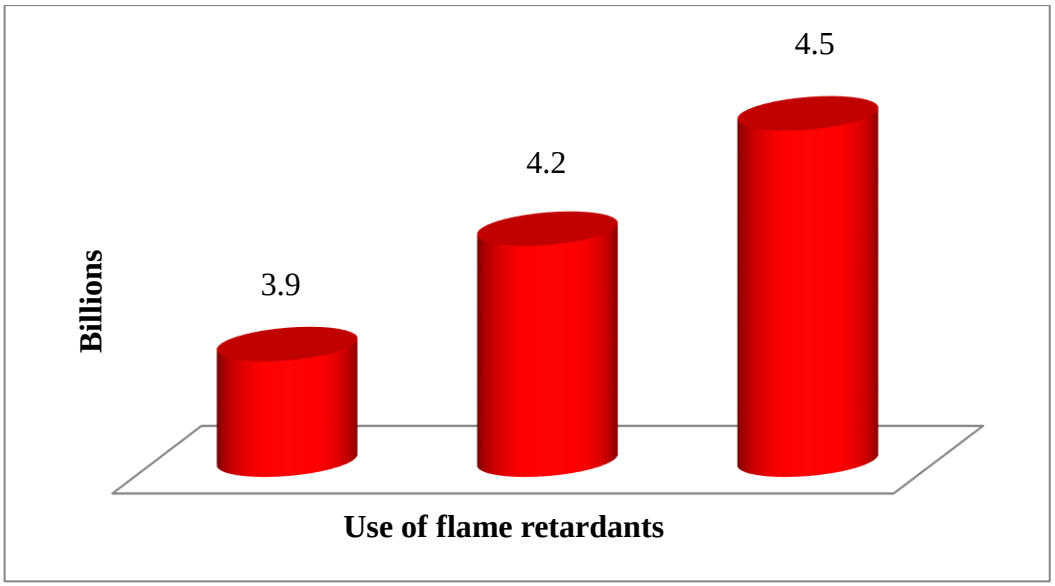


Figure 2.2 Worldwide consumption of flame-retardant chemicals and estimates 2002-2019 [29]

2.1.1. Phosphorus-Based Flame Retardants

For many polymers, both organic and inorganic phosphorus compounds exhibit flame retardant characteristics. These substances are often employed in industry as additives and reactants. Highly hydroxylated polymers like cellulose respond well to the flame-retardant properties of phosphorus-containing compounds [30].

When exposed to high temperatures, phosphoric acid is formed from the phosphorus flame retardants. The consequence is the release of water from the polymer surface or the formation of a protective layer on the polymer surface as a result of phosphoric acid's reaction with environmental carbon molecules.

Furthermore, environmental carbon molecules like char or carbonaceous materials may react with the produced phosphoric acid. A protective coating known as a "char layer" is created on the polymer's surface as a result of this reaction. The polymer behind the char layer serves as a barrier, effectively protecting it from heat and flames and restricting the spread of the fire.

The process of phosphorus flame retardants, which results in the production of phosphoric acid and the subsequent construction of a protective char layer, contributes greatly to the polymer's overall fire retardancy and improves its fire-resistant qualities.

2.1.2. Silicon-Based Flame Retardants

In recent studies, the use of silicon-based flame-retardant materials has been explored as an alternative to halogen and phosphorus-based flame retardants. Therefore, various silicon-based materials such as silicon, silica, organosilanes, and silicates have been subjected to trials [31]. Research has demonstrated that the addition of small amounts of silicone compounds to polymer materials significantly enhances their flame retardancy.

One of the most commonly used silicone-based flame retardants is polydimethylsiloxane (PDMS). When added under appropriate conditions, silicon can enhance the flame retardancy of the polymer chain, and materials can acquire flame retardant properties through the use of silicone and silica-based coatings [30].

Compared to other flame-retardant materials, silicone-based flame retardants, like PDMS, are considered to be more environmentally friendly, taking into account their potential harmful effects on the environment [31].

2.1.3. Nitrogen-Based Flame Retardants

Natural polymers like wool, silk, and leather have a resistance to burning due to the nitrogen they contain, while synthetic polymers do not have this same property. As a result, several organic compounds containing nitrogen are employed as additives to give polymers flame resistant characteristics. The main idea behind nitrogen-containing flame retardants is to slow down the combustion event by lowering the oxygen concentration in the gas phase of combustion by releasing inert gas into the atmosphere while combustion is taking place [30].

2.1.4. Boron-Based Flame Retardants

In polymers, boric acid and borate are employed as additives, particularly when combined with flame retardants made of halogens. When organic matter decomposes, boron molecules condense and stop CO or CO_2 from forming, leaving just carbon behind. In addition, it creates a barrier to stop the oxidation action of oxygen. The fact that boron-containing compounds go through endothermic dehydration and release water as a result is one of the reasons they are utilized as flame retardants [30]. The most popular boron-containing chemical is zinc borate.

2.2 Flame Retardant Polymers

2.2.1 Boron Containing Flame Retardants Polymers

Carboranes are BH and CH-based tiny trigonal structures that combine to generate polyhedral, big polymers. Compounds with an aromatic structure include the ortho, meta, and para carborane structures. (see Figure 2.1) Electronic substitution can be used to alter carboranes chemically. For instance, the C-H bond can be cleaved using n-butyllithium, which enables the insertion of different functional groups [32].

Important characteristics of these synthetic materials are their processing capabilities, strong mechanical qualities, good resistance to high temperatures, and chemical stability. When boron-based polymers are pyrolyzed in combination with other polymers, a significant quantity of carbon is produced, and the resulting carbon waste exhibits oxidation stability up to 1500°C. According to this study, a tiny quantity of carborane can give flammability stability without the necessity for a carborane to be present in every monomer unit. In order to employ them in the composite materials of space shuttles used in earth orbit, Litt and his colleagues created polymers based on poly (carborane siloxane) [33].

When the Lewis bases are contained inside the same molecule, a linear polymer can be produced. These polymers can be used to create boron carbide and boron nitride as the first building blocks. In coating technologies, it may also be utilized to boost stability, particularly against atomic oxygen.

Due to their ability to trap neutrons, boron-containing polymers are employed in a variety of industries, including the creation of ceramics, boron carbide fiber, and coatings [34].

2.2.2. Phosphorus Containing Flame Retardants Polymers

In order to provide polymers such thermosets, polycarbonates, polyesters, and polyamides with thermal stability, polyphosphonate structures are utilized [35]. Aryl polyphosphonates (ArPPN) have proven useful as flame retardants for a variety of polymer materials, including thermosets, polycarbonate, polyesters, and polyamides. This is particularly true of their satisfactory thermal stability when compared to aliphatic flame retardants and their desired flow behavior during processing of polymeric materials. Comparing aromatic polyphosphonates (ArPPN) with aliphatic polyphosphonates

(AlPPN), ArPPNs often exhibit stronger hydrolytic stability because of the hydrolysable P-O-C bond and superior thermal stability during processing and molding. ArPPN uses in flame retardants are more prevalent than others as a result [35]. (Figure 2.3) Due to its extremely reactive phosphoryl chlorides, which easily react with compounds containing hydroxy and amino groups, phenylphosphonic dichloride is a common intermediate for preparing phosphorus-containing materials in the main chain [35].

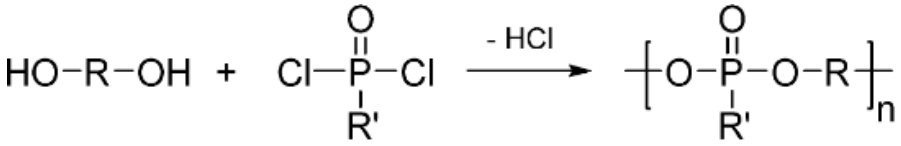


Figure 2.3 Synthesis route of main chain aromatic polyphosphonates (MC-ArPPN) [35]

Derivatives of DOPO (9,10-dihydro-9-oxa-phosphaphenthrene-10-oxide) which was produced for the first time in 1972, are now widely used in polyester fibers and electrical and electronic casting resins. By producing low molecular weight phosphorus-containing species and sequestering H and OH radicals in the flame, some researchers have proposed an explanation for the flame retardancy mechanism of DOPO and its derivatives [35].

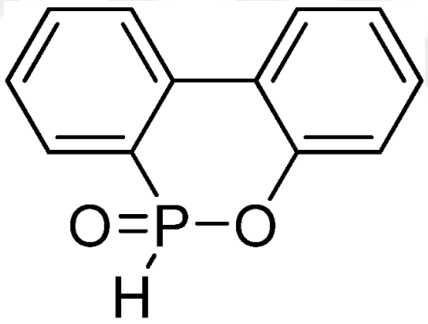


Figure 2.4 Chemical structure of 9,10-dihydro-9-oxa-phosphaphenthrene-10-oxide (DOPO) [35]

2.2.3. Silane Containing Flame Retardants Polymers

Silicones have low heat release rates (HRR), little susceptibility to heat flux from the outside, and low yields of CO release. The HRR for the majority of silicones is between 60 and 150 kW [36]. Silicones also burn slowly without producing a flame drop, and when they are pure, they don't release any harmful smoke. Based on these fire characteristics, silicones have a lot to offer applications requiring flame retardancy. PDMS has been ranked as the best polymer for use in high-temperature applications, such as electrical lines and cables. Silicones subjected to high temperatures and oxygen leave behind an inorganic silica residue, in contrast to organic polymers. Some of the essentials

for the creation of silicone-based fire retardants are provided by the shielding effects. The inclusion of filler can make silicone more flame resistant. A number of additives, including silica, calcium carbonate, wollastonite, mica, talc, kaolin, montmorillonite, carbon black, aluminum trihydrate, and magnesium dihydrate, have been employed to increase the flame retardancy of silicone [31]. According to certain studies, polycarbonate (PC), bisphenol fluorenone carbonate (BPFPC), nylon, and polyurethane can all be thermally stabilized using only PDMS. Some polymers, including polypropylene, low density polyethylene (LDPE), ethylene-methacrylic acid copolymer, PC-PDMS block copolymer, and ethylene vinyl acetate (EVA), employ PDMS loaded with flame retardants. By adding some flame-retardant components, such as phosphorus and/or nitrogen, to the structure of silicone, synergistic effects have increased flame retardancy and intumescent char production [31].

3
BORON CHEMISTRY

Boron is represented by the letter B in the periodic table. Its atom number is 5, and its atomic weight is 10,81. The periodic table's element boron is found in Group 3A and exhibits semi-metallic and semiconductive properties. The stable isotopes of boron that are found in nature are known as ^{10}B and ^{11}B. In nature, there are 19,1–20,3% of the ^{10}B isotope and 79%–81% of the ^{11}B isotope, respectively [37]. In 2016, the globe generated around 5.7 million tons (2.7 million tons based on B_2O_3) of boron. The use of boron products worldwide grew from 3,1 million tons in 2000 to 4,3 and 3,77 million tons in 2016. Industrial consumers of boron products worldwide include the glass industry (48%), agricultural (15%), ceramics (15%), cleaning and detergents (2%), and other (20%) industries [37].

Because of its capacity to absorb neutrons, boron is added in higher concentrations to steels used in the nuclear industry. Because of this characteristic, boron works well as a neutron absorber in nuclear applications. Particularly, the ^{10}B isotope, which has a natural abundance of around 20% and a large nuclear cross-section, may absorb heat neutrons produced by uranium's fission process. the stable isotope of boron 10 (^{10}B), which is highly capable of absorbing "thermal" neutrons with low energy. The resulting low energy "thermal" neutrons are collected by the ^{10}B atoms after losing energy when they enter tissue. Coolant water, shielding, and control rods are used in nuclear power reactors. Additionally, the resulting low energy "thermal" neutrons are absorbed by the ^{10}B atoms when they lose energy as they enter the tissue. High-energy alpha particles are produced as a result of the decay process, which destroy the cancer cells that have ingested enough 10B. The simplest way to define boron neutron capture therapy (BNCT) is as a hybrid radiation modality: the tumor is treated with a low-energy neutron beam that causes the fission of the ^{10}B isotope after the patient receives an inert, non-radioactive substance containing the ^{10}B isotope that preferentially targets cancer cells. A high-energy particle is released during the fission event that causes intracellular double strand DNA breakage and apoptosis [38].

Through a process known as boriding, boron is used to improve the surface hardness of steel and alloys in addition to its capacity to absorb neutrons. Boriding is the process of

introducing boron into a material's surface, increasing its hardness and resistance to wear. For components that are exposed to high temperatures and wear loads, boron composites are used, either in bulk form or as coatings. In semiconductors like silicon, germanium, and silicon carbide, borax is useful as an additive. In its ten-atom structure, boron has one valence electron absent, which results in a hole and p-type conductivity in semiconductors. Because of this quality, boron is useful for regulating the electrical characteristics of semiconductor materials.

Boron is at the formal oxidation state III in the majority of known compounds [39]. Oxides, sulfites, nitrites, and halides are a few of them. The typical formula for boron and hydrogen compounds is BxHy. These substances are not found in nature. When exposed to air, many boranes oxidize quickly, even violently. Many of the known organoboron compounds are helpful in the synthesis of organic materials. Most are made by hydroboration utilizing the straightforward borane chemistry diborane B_2H_6. The structures of boron nitrides are amazing. They have structures like those of carbon allotropes like nanotubes, graphite, and diamond. We will discuss boron nitride below section.

3.1 Boron Nitride

History of chemistry has been greatly influenced by the isoelectronic interaction between B-N and C-C bonds. Benzene's "inorganic" counterpart, borazine ($N_3B_3H_6$), has been recognized since its discovery [40]. Chemists have been led by this link to consider molecular structures and BN species [41]. Other substances with 2D and 3D structures, including hexagonal and cubic boron nitride (isoelectronically comparable to graphite and diamond) shown in Figure 3.1, have been employed in a variety of applications. [42-43]. A more recent source of inspiration was the synthesis of several intriguing novel compounds and materials, including the BN/CC analogue, BN analogs of pyrene, and fullerene-like BN hollow spheres, such as carbon nanotubes and normal boron nitride nanomesh topologies [44].

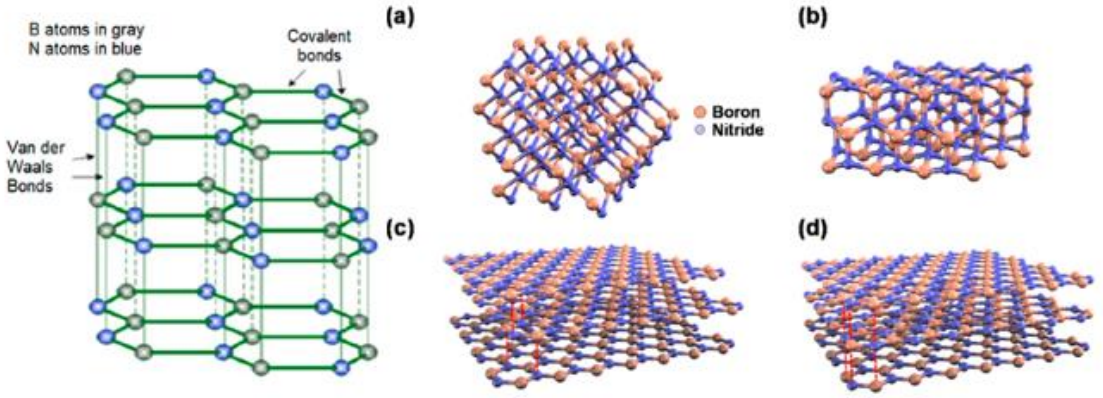


Figure 3.1 Structure of boron nitride; (a) cubic boron nitride (cBN), (b) wurtzite boron nitride (wBN), (c) rhombohedral boron nitride (rBN), and (d) hexagonal boron nitride (hBN) [45-46]

For the production of boron nitride, polyaminoboranes are used as the initial components. Depending on its structure, boron nitride exhibits unique characteristics as a non-oxide ceramic. In its cubic form (c-BN), it is the second hardest material after diamond, showcasing remarkable resistance to flames and corrosion. Hexagonal boron nitride (h-BN), resembling graphite, possesses a wide range of features include strong electrical resistance, minimal thermal expansion, resistance to thermal shock, and high thermal conductivity, non-toxicity, ease of machining, lubricity, chemical inertness, and resistance to wetting by the majority of molten metals [47-48].

Boron nitride is a versatile material that finds applications in various industries, including aerospace, automotive, electronics, semiconductors, and cosmetics [49-50]. It is created by combining ammonia (NH_3) or urea ($CO(NH_2)_2$) with hexagonal boron nitride, boron trioxide (B_2O_3), or boric acid (H_3BO_3) in a nitrogen-containing environment [51]. The reactions can be represented as follows:

$B_2O_3 + 2\ NH_3 \rightarrow 2\ BN + 3\ H_2O$ ($T = 900^oC$)

$B(OH)_3 + NH_3 \rightarrow BN + 3\ H_2O$ ($T = 900^oC$)

$B_2O_3 + CO(NH_2)_2 \rightarrow 2\ BN + CO_2 + 2\ H_2O$ ($T > 1000^oC$)

$B_2O_3 + 3\ CaB_6 + 10\ N_2 \rightarrow 20\ BN + 3\ CaO$ ($T > 1500^oC$)

The resulting boron nitride is usually in an irregular (amorphous) form, containing 92-95% BN and 5-8% B_2O_3. Additional purification processes are required to remove the remaining B_2O_3, achieving a concentration of >98% BN. Ultra-pure boron nitride can

also be obtained by evaporating boron powder in a nitrogen plasma at extremely high temperatures of 5500 °C. It is significant to state that the purification processes and the synthesis of thin films of boron nitride, such as boron trichloride and nitrogen, often involve chemical vapor deposition techniques in specific atmospheric conditions [52].

In this context, preceramic polymer materials have emerged as promising precursors and have garnered growing interest. The advantage of preceramic polymers lies in their potential for machinability, allowing for the fabrication of complex-shaped materials. With the coating technique, whether it be dipping or spraying, it is possible to achieve a uniform deposition of boron nitride onto the surface [53]. When researching in this field, borazine stands out as a dominant material in BN preceramic polymers. Derived polymers, often referred to as polyborazilenes as shown in Figure 3.2, are commonly used. However, polyborazine presents challenges due to its sensitivity, requirement of an ultra-dry solvent, and inert environment. In the past decade, polyaminoboranes have shown promise as an alternative for boron nitride production in preceramic polymers. BN offers significant advantages, as it does not require an inert environment, can dissolve in common solvents, and can achieve high molecular weight [8, 54].

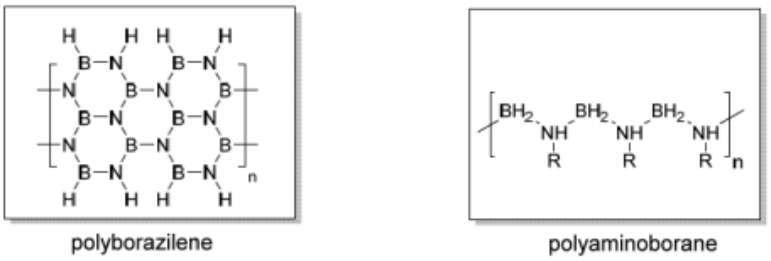


Figure 3.2 Structure of polyborazilenes and polyaminoborane

4
EXPERIMENTAL

4.1 Materials & Methods

4.1.1 Used Chemicals

MMAB(Monomethylamine borane) was purchased from Boron Specialties LLC. TEA (Triethylamine), ethylenediamine, diethyl chlorophosphate, triethylamine,

3-Aminopropyltrimethoxysilane, borane tetrahydrofuran complex, acetonitrile, hexane, sodium hydroxide 5%, deuterium chloroform, dichloromethane, tetrahydrofuran and other solvents were purchased from Aldrich. Dichloro[1,3-bis(2,4,6-trimethylphenyl)-2-imidazolidinylidene](benzylidene)(tricyclohexylphosphine)ruthenium(II) from Aldrich also used as catalyst.

4.1.2 Used Equipment and Devices

Characterization involved FT-IR spectroscopy (Perkin-Elmer, FT-IR). Yıldız Technical University's Central Laboratory used a SII Nanotechnology Brand SII6000 Exstar TG/DTA 6300 model equipment to record TGA data for thermogravimetric analysis under nitrogen and air. Nuclear magnetic resonance spectra were obtained using ^{1}H NMR (500 MHz), ^{11}B NMR (128 MHz), ^{13}C NMR (75 MHz), ^{31}P NMR and GPC data from the "Bruker-500 MHz NMR" device in the NMR Laboratory of Bezmi Alem Vakıf University Pharmaceutical Application and Research Center (ILMER). Standard TMS solvents were DMSO-d_6 and $CDCl_3$-d_6. Pyrolysis was carried out using an atmosphere-controlled tube furnace (Protherm Furnaces STF series) apparatus (Max heat capacity 1200°C) under nitrogen at 3 L/min. Physical tests (scratching, shine and hardness) were measured in Kayalar Chemistry Analysis Laboratory. Transparency and haze meter (BYK haze-gard i) were measured in Şişecam R&D center. X-Ray diffraction analysis (XRD) was measured by Istanbul Technical University. X-ray Photoelectron Spectroscopy (XPS) was analyzed by Koc University. Gel permeation chromatography (GPC) was measured by Bezmialem University. Scanning electron microscope (SEM) and Energy Dispersive X-Ray Analysis (EDX) was measured by Dow Aksa and KUYTAM (Koç University).

4.2 Synthesis of Monomers

4.2.1 Synthesis of Phosphorus-Based Amino Borane Monomer

90 ml of dichloromethane was mixed with 15 ml of ethylene diamine and 1.8 ml of triethylamine. Mixture of 6 ml of dichloromethane and 1.8 ml of diethyl chlorophosphate were added dropwise over the course of 30 minutes to an ice bath. The reaction mixture is stirred for three days. Filtration was done with filter paper and 30 ml of DCM was added to the separated fraction. In order to purify, 2x25ml distilled water and 3x30 ml 5% NaOH are used in extraction. $MgSO_4$ is used as drying agent, filtration was done, and solvent evaporated and yellow precipitate was obtained. After washing this precipitate with diethyl ether solution, color turned from yellow to white. After tetrahydrofuran-boron complex added in the synthesis of phosphorus-based amino borane precursor, which is explained detailed in below, white color persists. This residue was purified by diethyl ether again and waited at -18°C for one day.

4.2.1.1 Synthesis of Phosphorus-Based Amino Borane Precursor

Phosphorus-boron based monomer was prepared by adding 0.2 g of synthesized phosphorus-amine compound synthesized above and 2.5 ml of BH_3:THF complex in THF at -30 °C dropwise in a dry ice-acetonitrile bath under nitrogen overnight. After this, solvent evaporated and white precipitate was obtained and dried. The yield is 25%. Characterization methods employed included FTIR and NMR.

4.2.2 Synthesis of Silane-Based Amino Borane Monomer

For silane-based precursor, 1 g of 3-Aminopropyltrimethoxysilane was dissolved in THF and 5 ml of BH_3:THF complex was added dropwise to acetonitrile-dry ice bath at -30°C, then mix at room temperature for overnight. Solvent part was evaporated in a rotary-evaporator. After this step, monomer washed with 2-3 ml of diethyl ether and excessive pentane to mixture for purification, and this mixture waited for one day at -18°C. When solvent used for washing is removed, white precipitate was obtained. The product is dried in vacuum. The yield is around 33%.

4.3 Synthesis of Polymers

4.3.1 Synthesis of Methyl Functional Polyaminoboranes

0.45 g of methylaminoborane was stirred in 0.6 mL of THF under nitrogen and then cooled to 0°C. In a separate vial, 0.045 g of dichloro[1,3-bis(2,4,6-trimethylphenyl)-2-imidazolidinylidene](benzylidene)(tricyclohexylphosphine)ruthenium(II) catalyst was dissolved in 0.4 mL of THF and added to the methylaminoborane solution. After the reaction was stirred at 0°C for 20 minutes under argon atmosphere, it was brought to room temperature and stirred at this temperature for 2 hours.



Figure 4.1 Polyaminoborane powders

After adding 2-3 mL of THF to the reaction vessel at the end of the reaction, it was precipitated in excessive cold hexane-liquid nitrogen at -78°C, by adding mixture in reaction vessel to this cold hexane-liquid nitrogen mixture dropwise, filtered and then dried in vacuum. 0.170 grams (38% yield) of polymer in powder form was obtained.

4.3.2 Synthesis of Phosphorus-Functional Polyaminoboranes

Phosphorous amine-borane precursor compound reacts with catalyst, dichloro[1,3-bis(2,4,6-trimethylphenyl)-2-imidazolidinylidene](benzylidene)(tricyclohexylphosphine)ruthenium(II) with 10M THF is mixed in the presence of argon gas and at room temperature. First, temperature is dropped to 0°C with ice for half hour, and we waited to mix for two and a half hours. Temperature is dropped to -78°C with liquid nitrogen and used excess hexane to precipitate out polymer. After the filtration, brown powder residue dried under vacuum. Hexane is also used for rinsing polymers to purify them.

4.3.3 Synthesis of Silane-Functional Polyaminoboranes

In the presence of N_2 gas and at room temperature, the precursor molecule of the silane amine-borane mixed with the catalyst dichloro[1,3-bis(2,4,6-trimethylphenyl)-2-imidazolidinylidene](benzylidene)(tricyclohexylphosphine)ruthenium(II), dissolved in 10M THF. First, we used ice to lower the temperature to 0°C for 30 minutes before waiting 2.5 hours to combine. Liquid nitrogen and excessive hexane utilized to lower the temperature to -78°C, and the polymer precipitate out in this excessive hexane solution. Brown powder leftovers were vacuum-dried after filtering. Additionally, polymers can be cleaned by washing them with hexane.

4.4 Synthesis of Boron Nitride from Functionalized Polyaminoboranes

Polyaminoboranes are also used as starting materials for synthesizing boron nitride-based ceramic materials. Pyrolysis was carried out using an atmosphere-controlled tube furnace (Protherm Furnaces STF series) apparatus (Max heat capacity 1200°C) under nitrogen at 3L/min. Methyl, silane and phosphorus polyaminoboranes are pyrolyzed at 1100°C under nitrogen for two hours. Typical example indicates the boron nitride products obtained from methyl-polyaminoborane polymer (Figure 4.2)



Figure 4.2 Boron nitride obtained from polyaminoborane

4.5 Carbon Fiber Coating

Carbon fiber samples cut at 10 cm were immersed in 10% coating solutions obtained by dissolving the synthesized functional polyaminoboranes in THF. Samples immersed for 30 minutes were dried under a fume hood for 1 hour.

4.6. Glass Surface Coating

For the glass samples, 1% and 10% coating solutions were prepared according to the glass dimensions in the same process and pyrolysis was performed at 700ºC to prevent the glass from melting. However, a boron nitride layer was not sufficiently formed on the glass surface.

4.7 Wood surface Coating

For the wooden block, a 5x5 cm cut piece, methyl or silane bearing polyaminoborane were dissolved in varnish to prepare a 1% solution. Then, dropwise additions of the hardener, isocyanate, were added to this mixture. The substance was applied to the surface of the wood at intervals of five minutes using a 100-micron applicator for coating thickness. The mixture was dried in a fume hood to speed up the drying process after each application. The process of applying the mixture and drying it was repeated three times, resulting in three layers of the methyl or silane based polyaminoborane coating on the wood.

Also, the synthesized polyaminoboranes and functional polyaminoboranes powders were pyrolyzed at 1100 ºC for 2 hours under nitrogen to form boron nitride. This process was carried out with an efficiency of over 95%.

5
RESULTS AND DISCUSSION

5.1 Synthesis and Characterization of Monomers

5.1.1 Synthesis and Characterization of Phosphorus-Based Amino Borane Monomer

Ethylene diamine, dissolved in dichloromethane, reacts with diethyl chlorophosphate in ice bath for 0°C. While this reaction was taking place at 0°C, amine attached to the diethyl chlorophosphate and forms phospho-amide bond as shown in Figure 5.1. Hydrogen chloride was released while triethylamine was capturing it. After that, the unpaired electron pair of the monomer amine attacked the positive part of the boron complex, synthesizing the precursor of phosphorus-polyaminoborane in Figure 5.1. Within the scope of characterization, FTIR, ^{1}H NMR, ^{13}C NMR, ^{11}B NMR and ^{31}P NMR analyzes were performed for monomer and precursor and it was understood that the product obtained as a result of NMR analysis and detail characterization was given below.

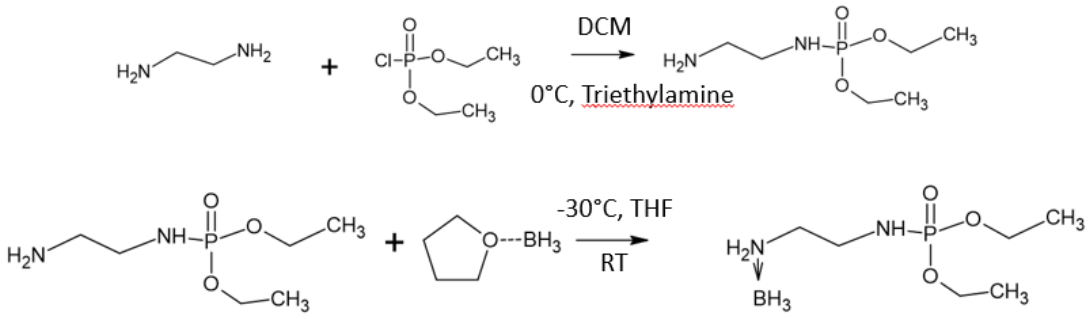


Figure 5.1 Synthesis of phosphorus-based amino borane monomer

Stretching and bending peaks for N-H are observed around 3100 cm^{-1} and 1630 cm^{-1}, respectively, at FTIR (Figure 5.2). C-H stretching peaks at 2900 cm^{-1} and bending peaks around 1465 cm^{-1} are observed, respectively. These are observed in accordance with the literature at 960 cm^{-1} and 1230 cm^{-1}, which are bound to phosphorus oxide [59].

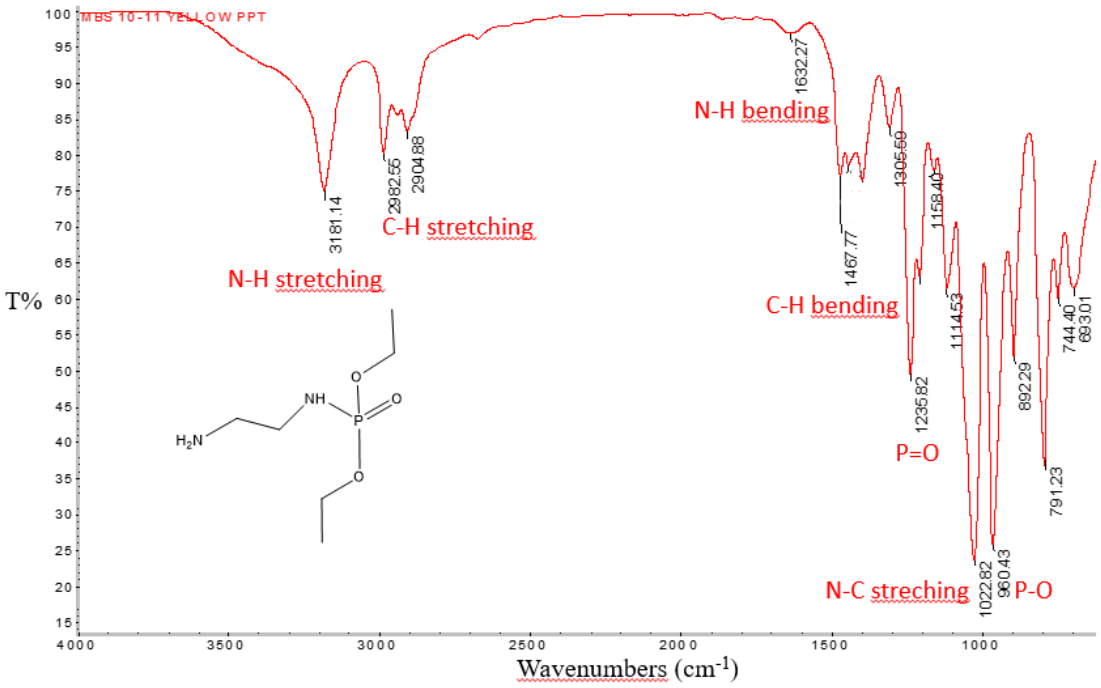


Figure 5.2 FTIR spectrum of synthesized phosphorous-amino borane monomer

When the FTIR spectrum was examined, it was observed that the boron complex was attached to the structure around 2300 cm^{-1} [60] in Figure 5.3. In the N-H group linked in FTIR, stretching peaks are seen about 3100 cm^{-1}. C-H stretching peaks were around 2900 cm^{-1} and bending peaks were around 1465 cm^{-1}. These, which are bonded to phosphorus oxide, are seen at 960 cm^{-1} and 1230 cm^{-1} in agreement with the literature [59]. In ^{31}P NMR analysis, it was observed that phosphorus was added to the structure as a single peak at 9.05 ppm [61]. Phosphorus of phosphate monoesters are present 9.05 ppm as shown in Figure 5.4.

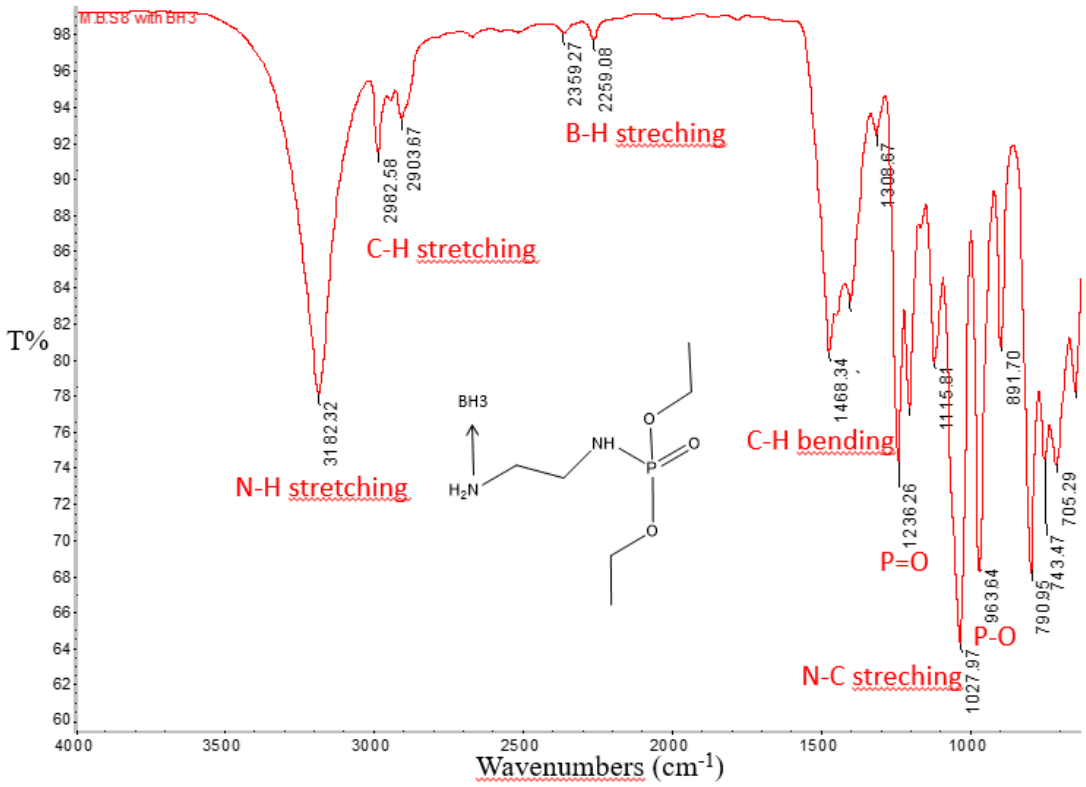


Figure 5.3 FTIR spectrum of synthesized boron-phosphorous precursor

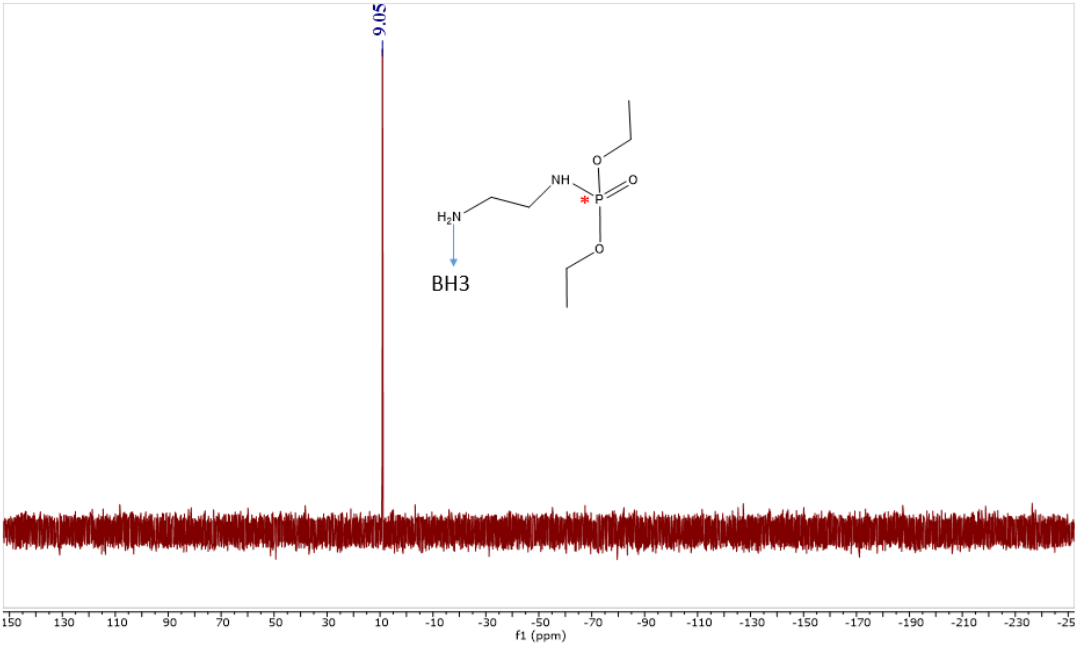


Figure 5.4 ^{31}P NMR spectrum of synthesized phosphorus-boron structure

In ^{1}H NMR analysis, hydrogen attached to boron was observed at 1.8 ppm (Figure 5.5). There are 4 and 6 integrations of CH_2 and CH_3 bound to oxygen, respectively, so it gives proton numbers of ethyl bonded to oxygen as proportion 2:3 for CH_2:CH_3. D and E are characteristic peak for CH_2. NH_2 and NH peaks have integration proportion 2:1 and they

are deshielded as around 3-3.5 ppm. Solvent peaks like $CDCl_3$ and TMS have characteristic peaks as shown in Figure 5.5. ^{13}C NMR analysis showed us that the bond between ethylenediamine and diethyl chlorophospate is established. (Figure 5.6) Carbon attached to phosphonate (C-O-P(=O)-) is observed around 60 ppm. Carbon attached to nitrogen (-CH2-NH2) are observed at 29 and 40 ppm. It was observed that it peaked at around 15 ppm due to CH_3. Although ^{11}B NMR in Figure 5.7 did not give clear peaks due to the lack of quartz tube, the presence of boron peak was observed. Amino-borane bonding's boron peak, which appears at 1 ppm, is noteworthy [55].

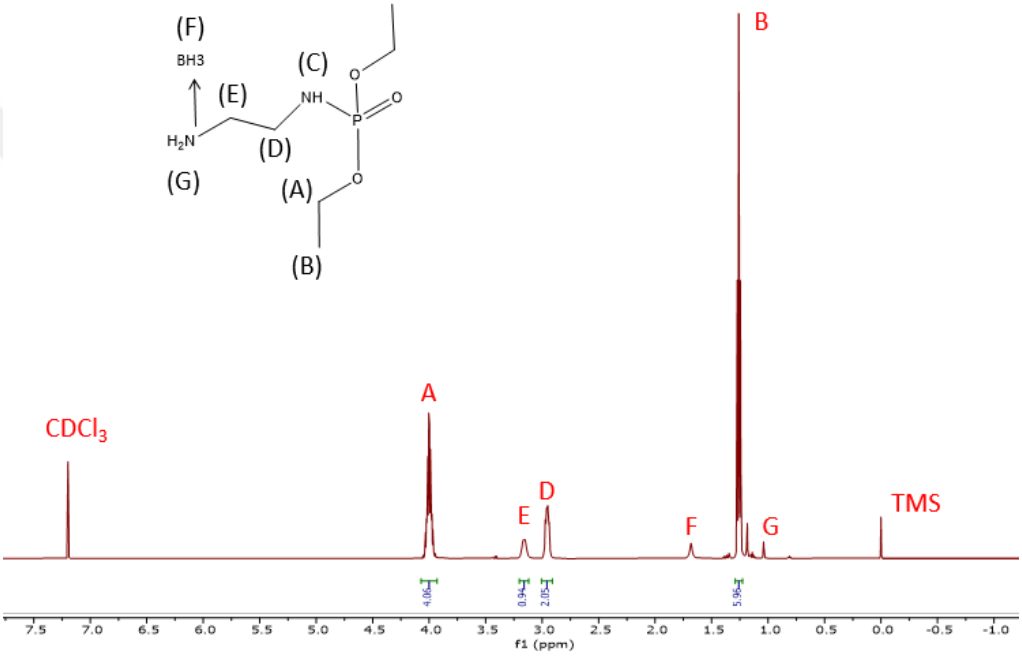


Figure 5.5 ^{1}H NMR spectrum of synthesized phosphorus-boron structure

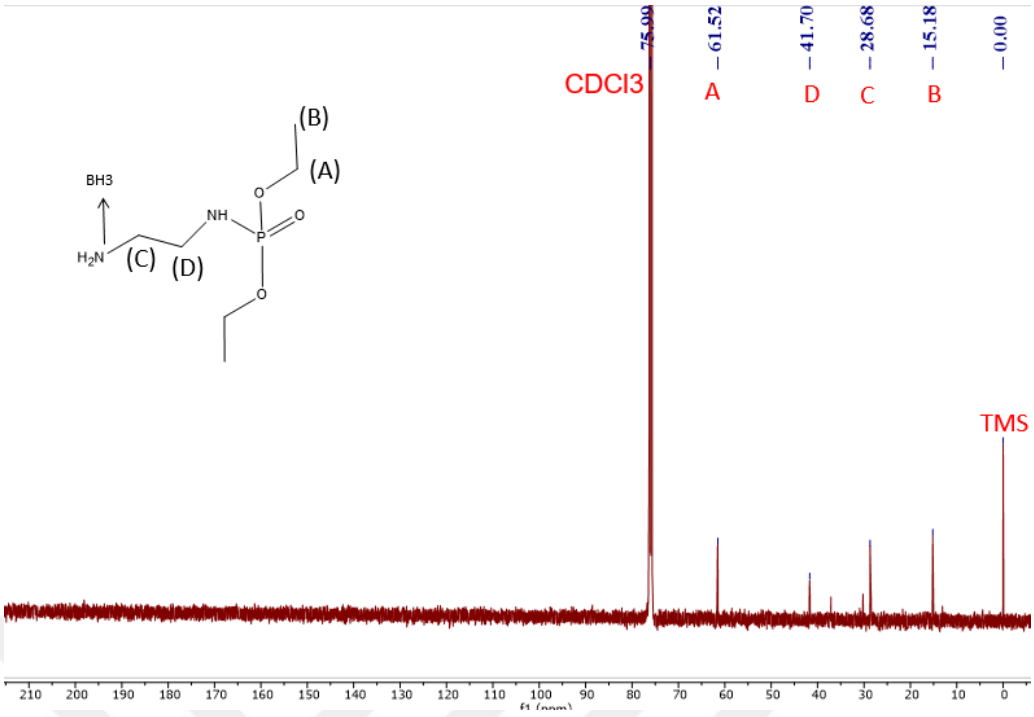


Figure 5.6 ^{13}C NMR spectrum of synthesized phosphorus-boron precursor

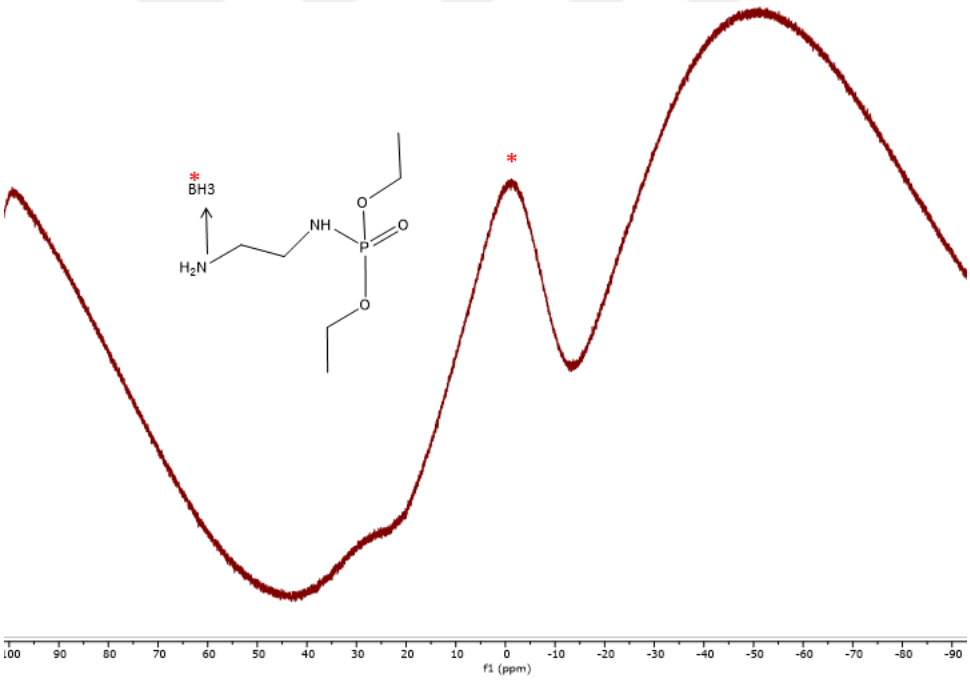


Figure 5.7 ^{11}B NMR spectrum of synthesized phosphorus-boron precursor

5.1.2 Synthesis and Characterization of Silane-Based Amino Borane Monomer

For silane-based precursor, 3-Aminopropyltrimethoxysilane, which was dissolved in THF reacts with BH_3:THF complex in acetonitrile-dry ice bath at -30°C. The unpaired electron pair of boron was attacked by the nitrogen group to cause the reaction in Figure

5.8. Impurities are removed using 2-3 ml diethyl ether and excessive pentane by waiting at -18°C overnight, and viscous white product is obtained after vacuum. It was recognized that the precursor was subject to FTIR and NMR analyses as part of the characterization process.

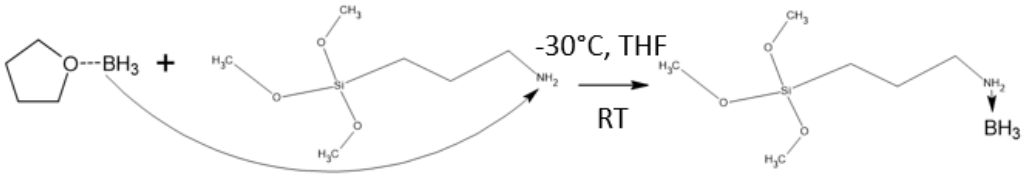


Figure 5.8 Reaction pathway for silane-polyaminoborane precursor

In FTIR characterization, in addition to the peaks of the amino-silane structure, a new peak is observed between 2305-2377 cm^{-1}, which indicates that the boron bond has been established in the boron-silane complex. N-H stretching and bending peaks are observed at 3100 cm^{-1} and 1610 cm^{-1} N-H peaks respectively. C-O stretching was observed at around 1300 cm^{-1} in Figure 5.9. The characteristic of the peaks of Si-O bond are observed as stretching at 1040 cm^{-1} which is consistent to the literature [56].

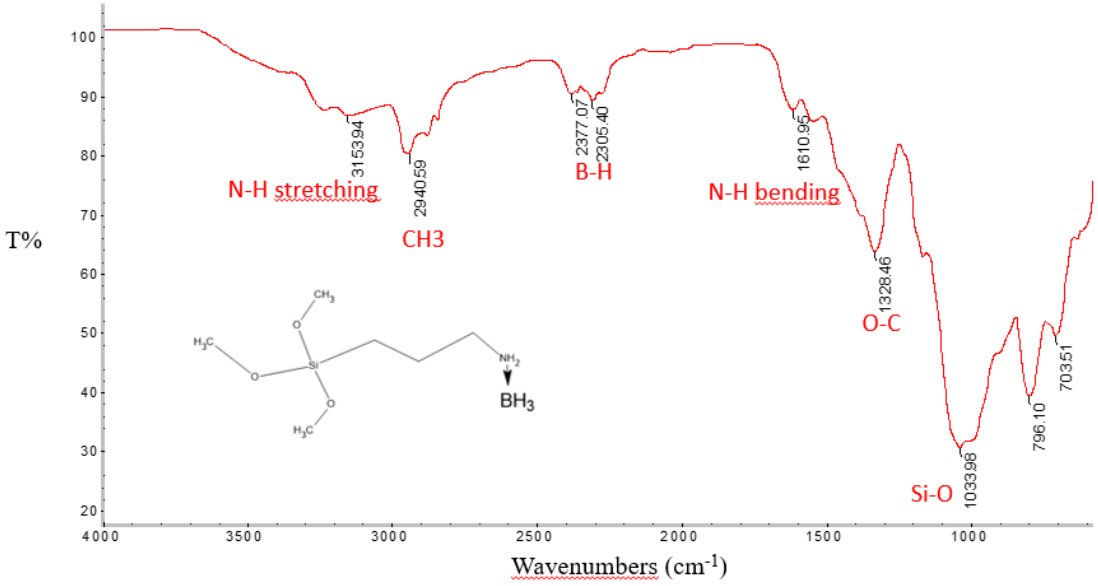


Figure 5.9 FTIR spectrum for silane-polyaminoborane precursor

^{1}H NMR also confirmed the product. Similar to the phosphorus-based monomer, a characteristic peak of hydrogen of boron bonded to nitrogen is observed at 1.5 ppm and 3.02 integration for BH_3 in Figure 5.10. It is observed that the CH_3 peak is deshielded at 3.5 ppm, the oxygen-dependent peak. It is possible to observe the peaks of the multiplet

and amino group bound to CH_2 between 1-1.5 ppm. Methylene protons attached to the Si center (Si-CH_2-) was observed at 0.65 ppm and is consistent with the literature [57].

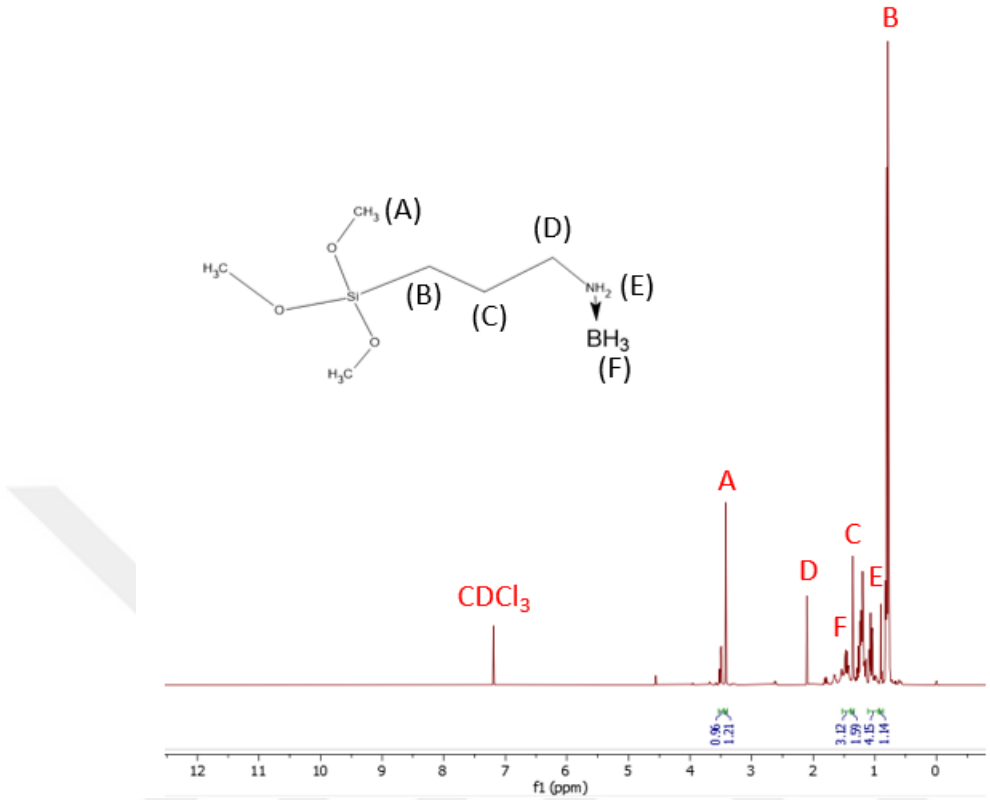


Figure 5.10 ^{1}H NMR for silane-polyaminoborane precursor

Although the ^{11}B and ^{29}Si NMR peaks are not clear due to the quartz tube, it reveals that boron and silane are in the targeted structure. However, broad B signal was observed at 1 ppm [55] in Figure 5.11. Similar to the phosphorus-borane complexes, we observe the same peak of the boron-amino structure in ^{11}B NMR. A siloxane-derived structure is observed in ^{29}Si NMR around -120 ppm in Figure 5.12 [58].

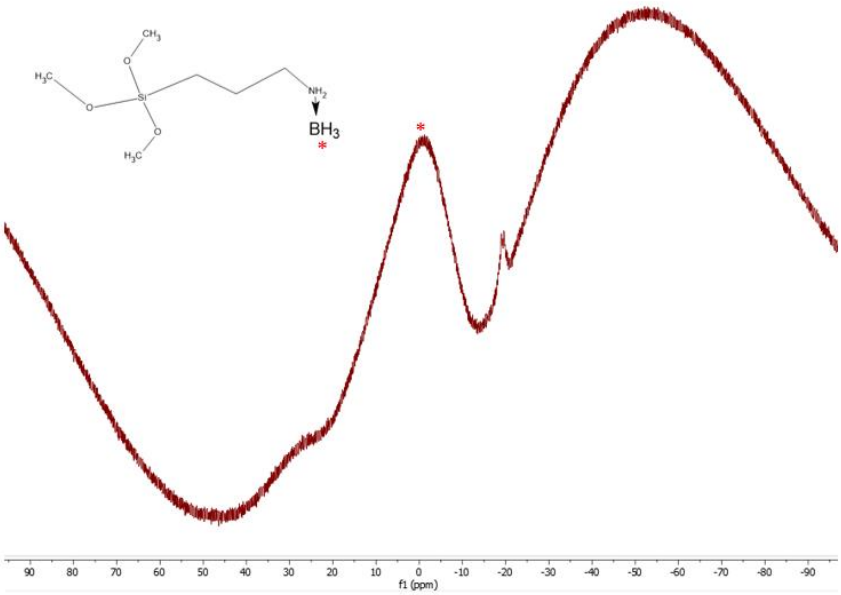


Figure 5.11 ^{11}B NMR for silane-polyaminoborane precursor

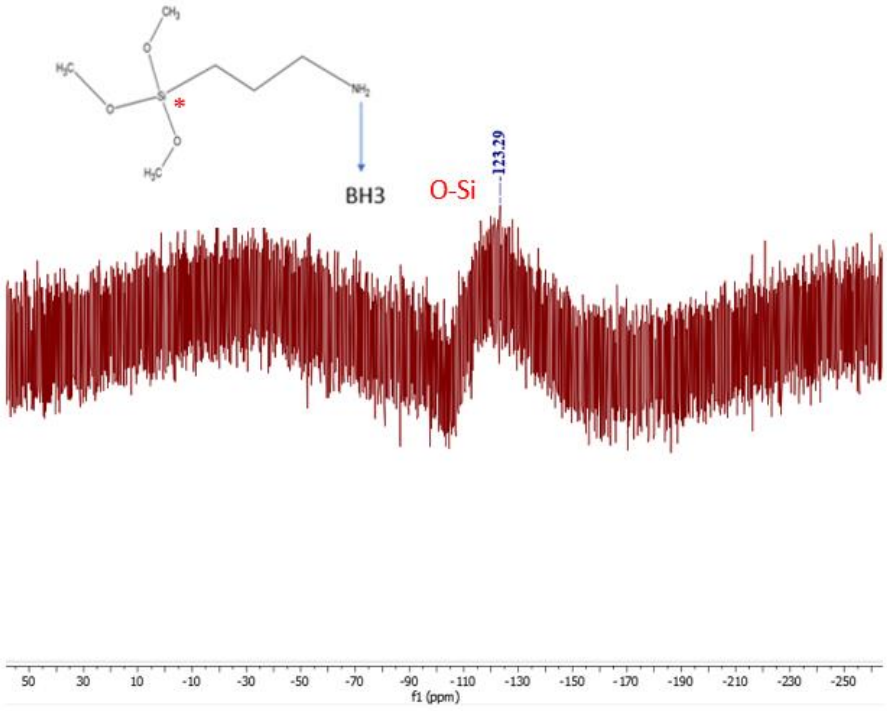


Figure 5.12 ^{29}Si NMR for silane-polyaminoborane precursor

5.2 Synthesis and Characterization of Polymers

5.2.1 Synthesis and Characterization of Methyl Substituted Polyaminoboranes

The metylaminoborane complex was dissolved in THF and polymerized with a catalyst, namely dichloro1,3-bis(2,4,6-trimethylphenyl)-2-

imidazolidinylidene(tricyclohexylphosphine)ruthenium(II), dissolved in 10M THF at 0°C under nitrogen. (Figure 5.13) At the end of the reaction, the non-polar solvent was precipitated in hexane in the reaction vessel. The brown final product was obtained with the help of unreacted non-polar solvent. In addition to FTIR, NMR, other characterization studies such as TGA, GPC, XPS were also performed.

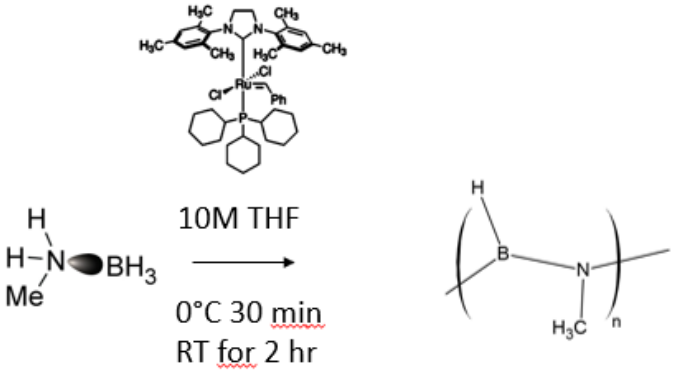


Figure 5.13 Synthesis of methyl substituted polyaminoborane

When analyzing the FTIR spectra of the polymers in Figure 5.14, the presence of boron observed at approximately 2250 cm^{-1} in Figure 5.14. The stretching and bending vibrations of the hydrogen bonded to nitrogen in the polymer structure can be observed. The stretching peaks are typically seen around 3200 cm^{-1}, while the bending peaks appear around 1600 cm^{-1} in the N-H group. In addition, stretching peaks associated with C-H bonds can be observed at approximately 2900 cm^{-1}, and bending peaks are typically seen around 1320 cm^{-1}. The stretching vibration of the C-N bond is observed around 1150 cm^{-1}. These characteristic peaks in the FTIR spectra provide information about the presence and bonding patterns of different functional groups in the polymer structure.

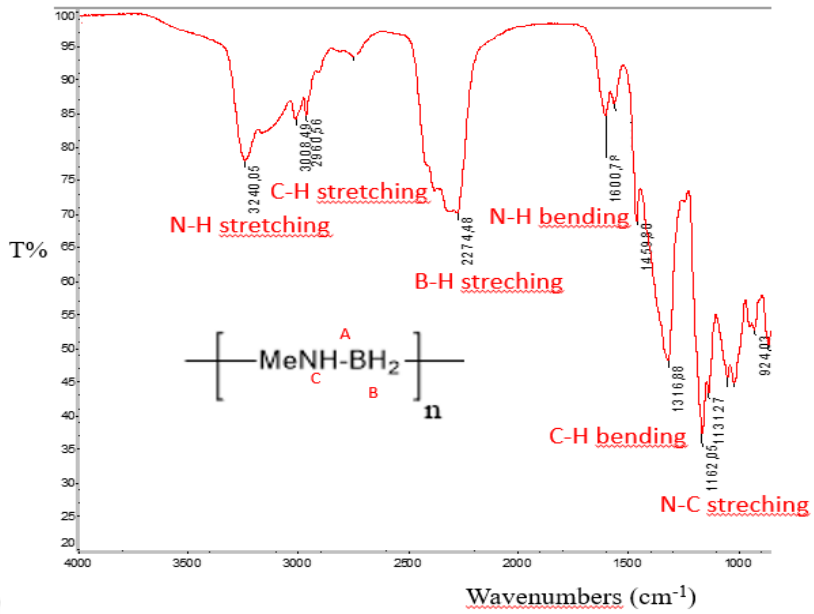


Figure 5.14 FTIR spectrum of methyl-polyaminoborane

The methyl substituted polyaminoborane synthesized from methylamine borane shows its presence at -7 ppm. The ^{11}B spectra in Figure 5.15 show the expected broad signals for methyl-polyaminoboranes are found at-7.0 ppm [55]. $BF_3.OEt_2$ used as ^{11}B reference can give peak 0 ppm as shown in Figure 5.15.

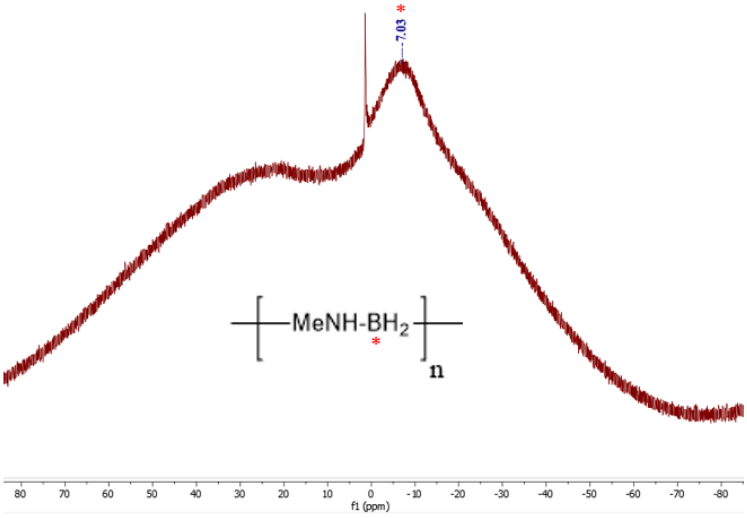


Figure 5.15 ^{11}B NMR of methyl-polyaminoborane structure

5.2.2 Synthesis and Characterization of Phosphorous Substituted Polyaminoboranes

In the presence of 10M THF (tetrahydrofuran), the precursor molecule of the phosphor amine-borane combines with a catalyst, namely dichloro1,3-bis(2,4,6-trimethylphenyl)-

2-imidazolidinylidene(tricyclohexylphosphine)ruthenium(II). After mixing the reaction mixture for 30 minutes at 0°C in a N_2 gas atmosphere, the reaction is continued for another 2.5 hours at the room temperature after workup with cold hexane brown powder is collected.

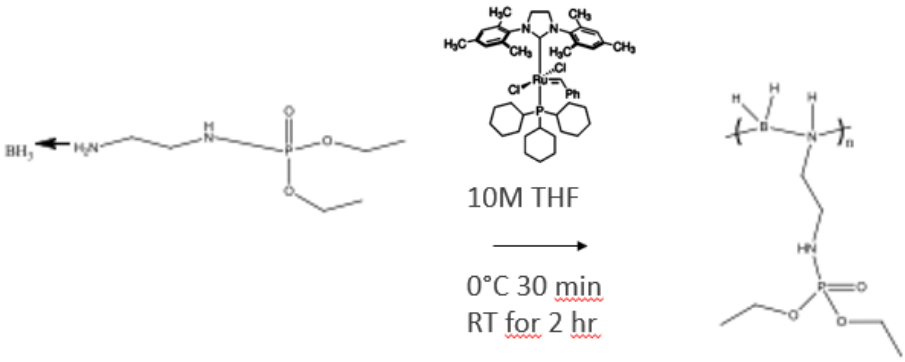


Figure 5.16 Synthesis of phosphorous substituted polyaminoborane

When analyzing the FTIR spectra of the polymers, the presence of boron observed at approximately 2370 cm^{-1} in Figure 5.17. The stretching and bending vibrations of the hydrogen bonded to nitrogen in the polymer structure can be observed. The stretching peaks are typically seen around 3270 cm^{-1}. In addition, stretching peaks associated with alkyl C-H bonds can be observed at approximately 2900 cm^{-1}. The stretching vibration of the C-N bond is observed around 1020 cm^{-1}. These characteristic peaks in the FTIR spectra provide information about the presence and bonding patterns of different functional groups in the polymer structure. Phosphorus oxide stretching are observed at 964 cm^{-1} and 1330 cm^{-1} in agreement with the literature [62]. The ^{11}B spectra in Figure 5.18 show the expected broad signals for phosphorus-polyaminoboranes are found at -7.0 ppm [55]. In ^{31}P NMR analysis, it was observed P-N peak can be seen as a single peak at-17.5 ppm [55] in Figure 5.19. The phosphor substituted polyaminoborane synthesized from phosphor-borane complexes shows its presence at -7 ppm.

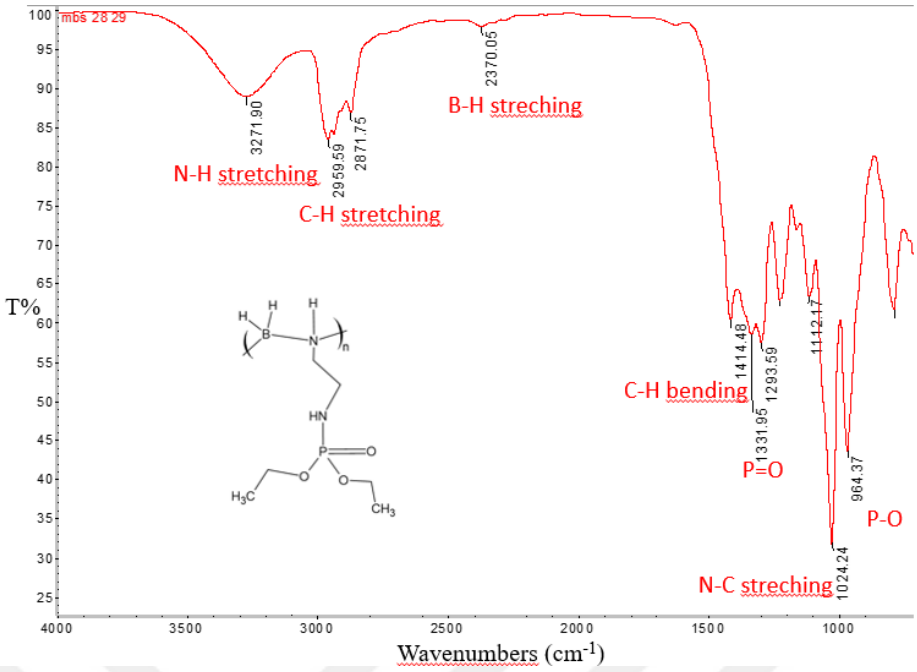


Figure 5.17 FTIR spectrum of phosphorous-based polyaminoboranes

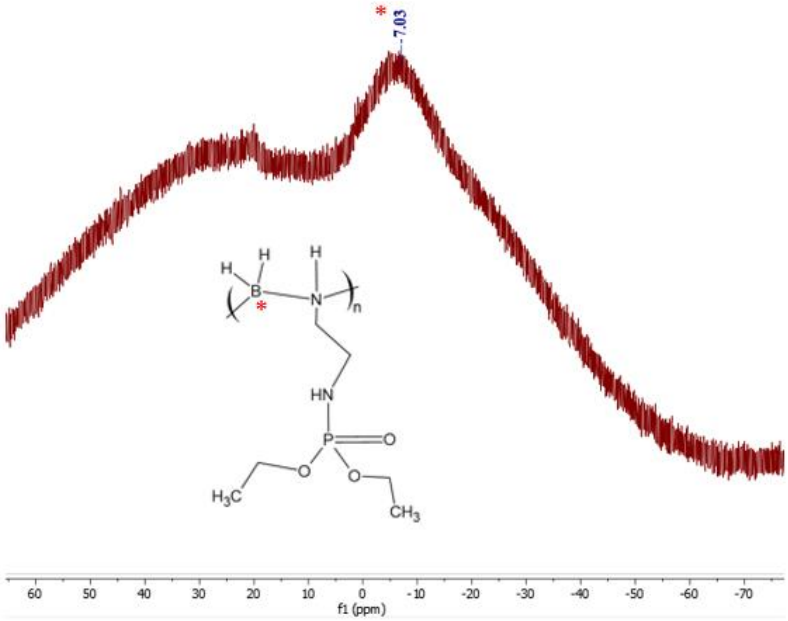


Figure 5.18 ^{11}B NMR of phosphorous-based polyaminoborane structure

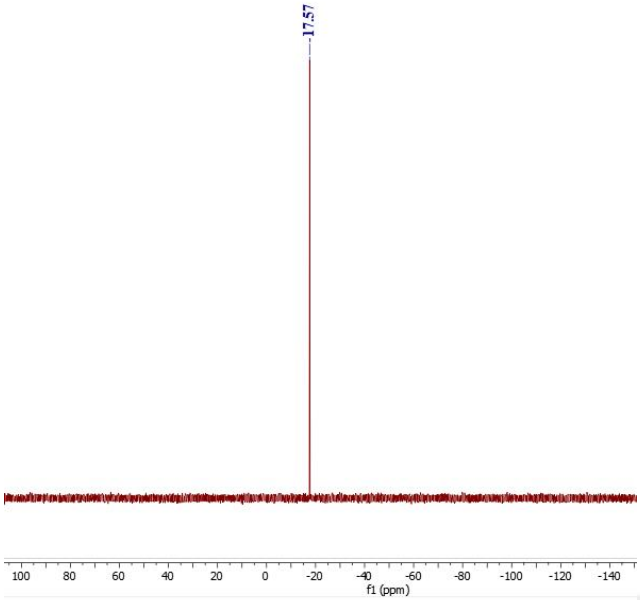


Figure 5.19 ^{31}P NMR of phosphorous-based polyaminoborane structure

5.2.3 Synthesis and Characterization of Silane Substituted Polyaminoboranes

The precursor molecule of the silane amine-borane is combined with the catalyst dichloro1,3-bis(2,4,6-trimethylphenyl)-2-imidazolidinylidene(tricyclohexylphosphine)ruthenium(II), which is dissolved in 10M THF (tetrahydrofuran), at room temperature. After workup white powder is collected. Figure 5.20 shows the synthesis of silane substituted polyaminoboranes.

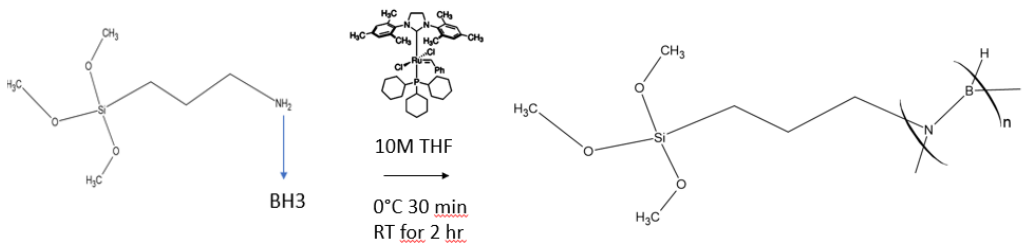


Figure 5.20 Synthesis of silane substituted polyaminoboranes

In FTIR characterization, Figure 5.21 shows that boron peak of silane-based polyaminoboranes is observed around 2300-2350 cm^{-1}, which indicates that the boron bond has been established for polyaminoboranes in the silane structure. N-H stretching and bending peaks are observed at 3200 cm^{-1} and 1600 cm^{-1} N-H peaks respectively. C-O stretching can be seen at around 1300 cm^{-1}. The characteristic of the peaks of Si-O bond are observed as stretching (1040 cm^{-1}) in similar to literature [56].

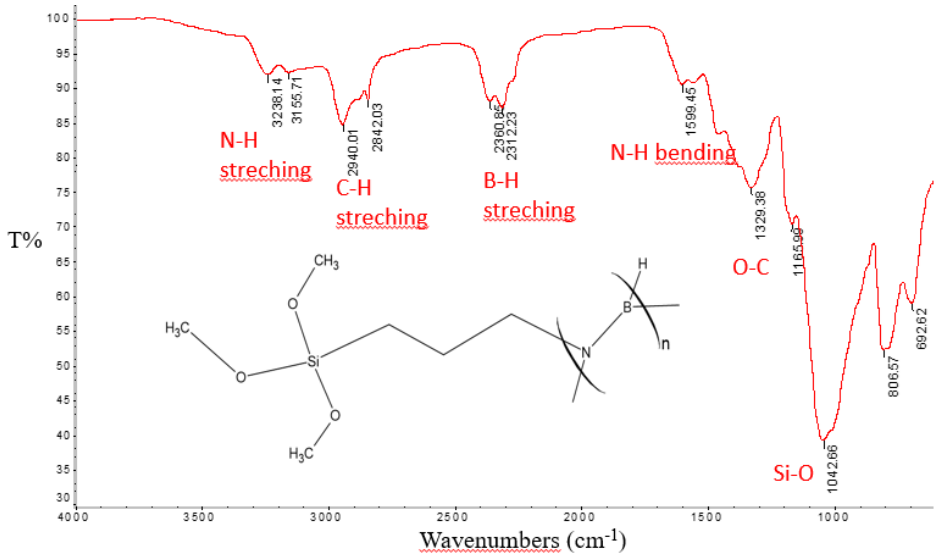


Figure 5.21 FTIR spectrum of silane-based polyaminoboranes

^{11}B NMR in Figure 5.22 and ^{29}Si NMR in Figure 5.23 reveal that silane preserve boron and silane bonds in structure of polymer. The silane substituted polyaminoborane synthesized from silane precursor shows its presence at -7 ppm. The ^{11}B spectra show the expected broad signals for silane-polyaminoboranes are found at -7.0 ppm [55]. A siloxane-derived structure is observed in ^{29}Si NMR around -120 ppm [58].

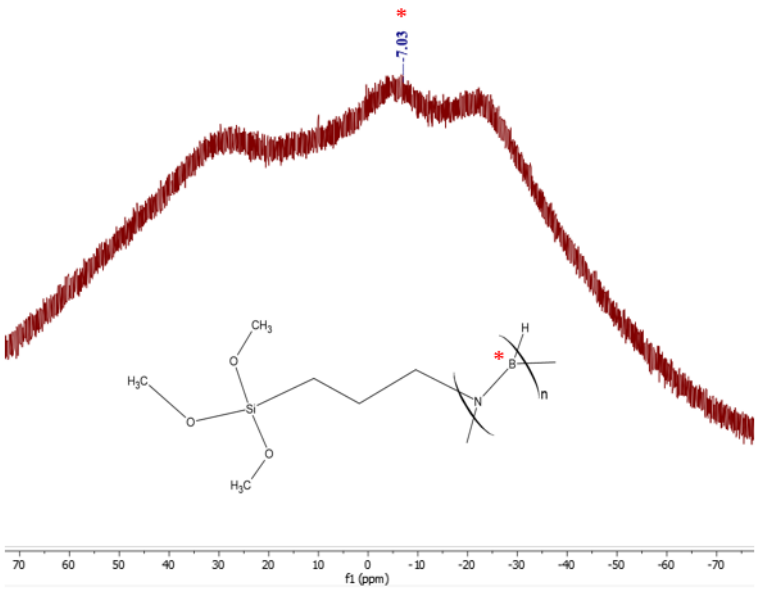


Figure 5.22 ^{11}B NMR of silane-based polyaminoborane structure

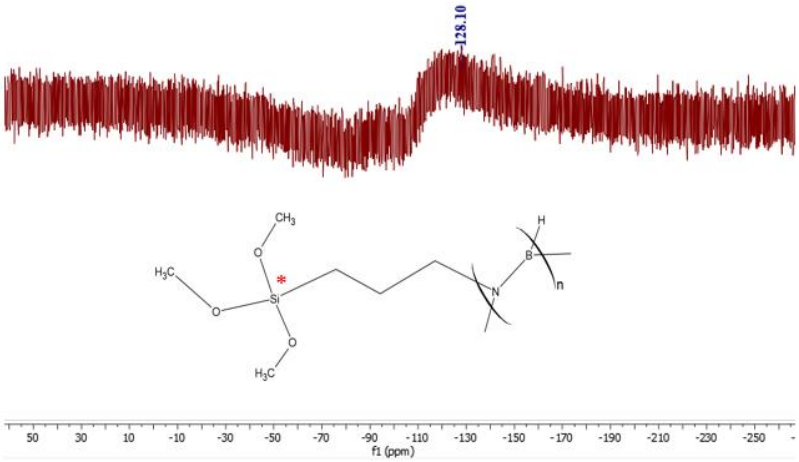


Figure 5.23 ^{29}Si NMR of silane-based polyaminoborane structure

5.2.4 Molecular Weight Distribution of Polymers

Gel permeation chromatography (GPC) was used to examine the polymer's molecular weight distribution. An aqueous mobile phase with DMF and LiCl was used for GPC. Polyethylene glycol was employed as the calibration standard. The observed and intended molecular weights differed somewhat from one another. In Table 5.1, phosphorous based polyaminoborane have highest molecular weight with 4.797×10^4 g/mol, silane based polyaminoborane and methyl-polyaminoborane follow it by 3.935×10^4 g/mol and 4.908×10^3 g/mol. Polydispersity, Đ, (M_w/M_n) is defined as the ratio of the weight-average molar mass Mw to the number-average molar mass Mn. When the Đ value is 1, it means that the monomers in the specified polymer or monodispersity are organized in equal-length chains. If the polymer has more chains than the real molecular chain, the PDI value is greater than 1. For uniform monodisperse compounds, Đ is 1, while for most macromolecules, it is more than 1. Methyl and phosphorus based polyaminoboranes homopolymers have 1.28 and 1.32 polydispersity respectively. Silane-based showed polyaminoborane broader distribution of polymer chains with a Đ value of 1.88.

Table 5.1 Molecular weight and Đ values of polyaminoborane polymers

GPC samples	Molecular weight (g/mol)	Polydispersity, Đ, (M_w/M_n)
Poly(methylaminoborane)	4.908×10^3	1.281
Silane-based polyaminoborane	3.935×10^4	1.882
Phosphorus based polyaminoborane	4.797×10^4	1.323

As can been in Figure 5.24, samples reached to detectors for almost same time. Relative scale is high for phosphorus-based polyaminoborane, which is the heaviest one.

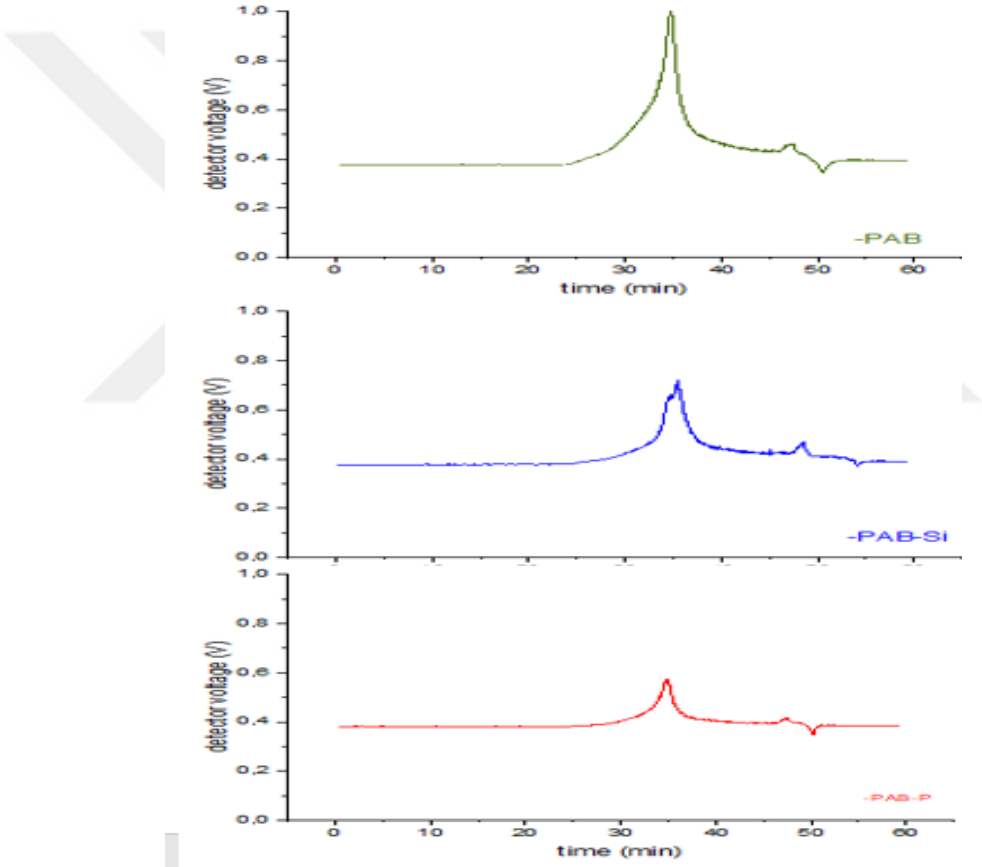


Figure 5.24 GPC spectra of poly(methylaminoborane) (PAB), silane-based polyaminoborane (PAB-Si) and phosphorus based polyaminoborane (PAB-P)

5.2.5 Thermal Properties of Polymers

Thermal gravimetric analysis (TGA) was performed to determine the char yield of the polymers, and the thermal analysis was conducted under both nitrogen and air atmospheres. The synthesized polymers exhibited a high char yield, which is a desirable

characteristic for flame retardant polymers. This property enables the polymer structure to withstand high temperatures and maintain its original integrity. TGA analysis is conducted between 200°C and 800ºC. (Figure 5.25 and Figure 5.26) While many polymers undergo structural degradation after 200°C, the synthesized polyaminoborane structures maintain their structure significantly even after 800°C in Table 5.2. Silane-based polyaminoboranes have the highest char yield (60%) under nitrogen, also they have almost same and highest char yield with methyl-polyaminoboranes (58%) under air atmosphere. For N2 atmosphere, methyl-polyaminoboranes have the least char yield (42%), but phosphorus ones have the least char yield (47%) for air atmosphere.

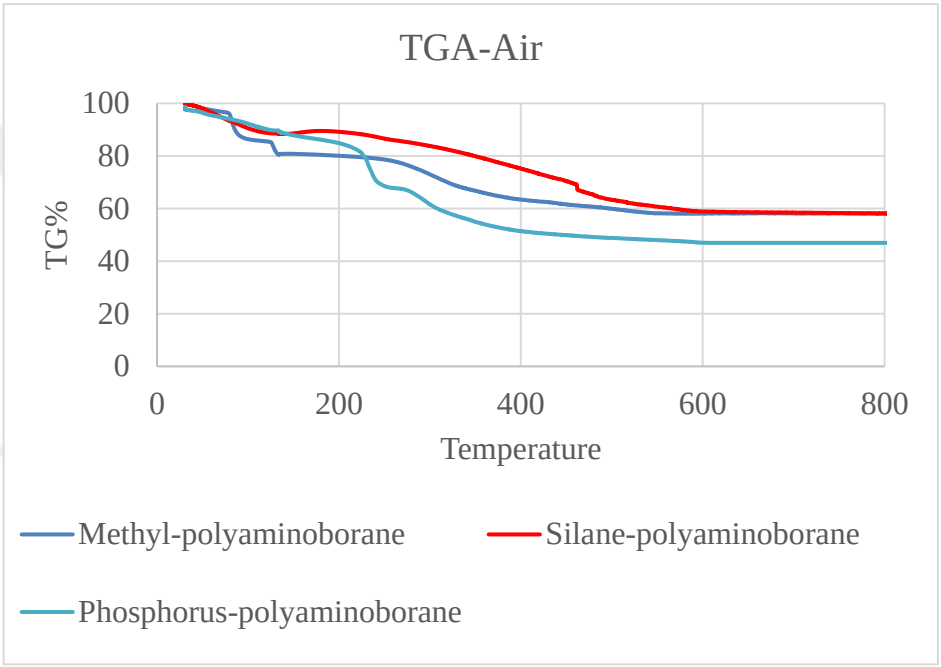


Figure 5.25 TGA under air for polyaminoborane powders

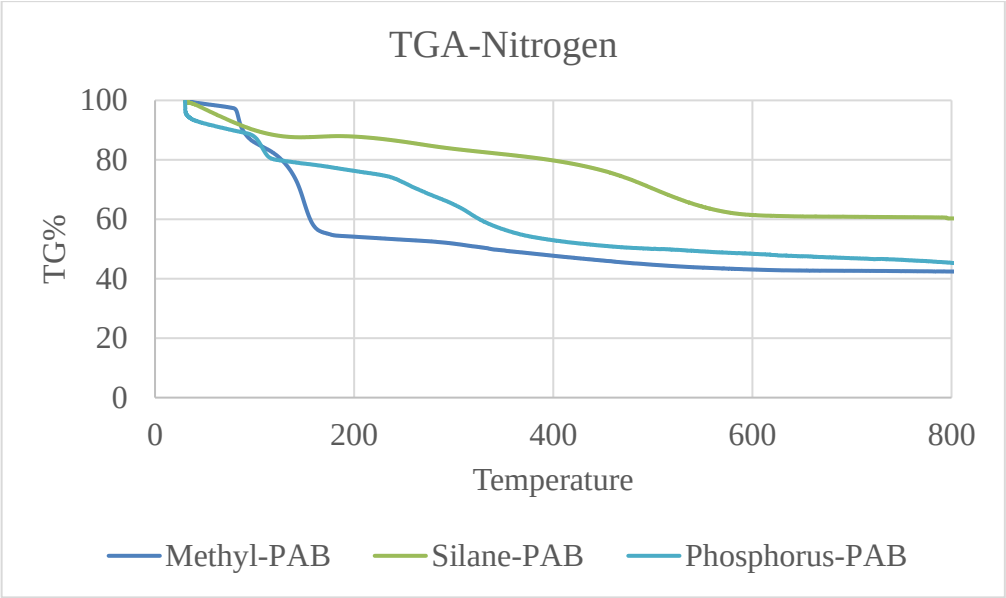


Figure 5.26 TGA under N_2 for polyaminoborane powders

Table 5.2 TGA results of synthesized polyaminoboranes under N_2 and air

	Samples	Tmax1(°C)	Tmax2(°C)	Char yield (wt%)
	Methyl-Polyaminoboranes	150	400	42.4
Nitrogen	Silane-Polyaminoboranes	263	496	60.2
	Phosphor-Polyaminoboranes	254	317	44.9
	Methyl-Polyaminoboranes	82	305	58,1
Air	Silane-Polyaminoboranes	75	462	58,0
	Phosphor-Polyaminoboranes	58	292	46,9

5.2.6 Molecular Structure of Polymers

X-ray Quantitative spectroscopic methods that rely on the photoelectric effect include photoelectron spectroscopy (XPS), which is surface-sensitive. In addition to providing details on an element's chemical state, general electrical structure, and density, it is used to identify the elements that are present in a substance or on its surface. XPS is a useful method for examining the atomic-scale composition and characteristics of materials.

For methyl-polyaminoborane, the binding energies of the N1s, B1s, C1s, and O1s on the sample surface are approximately 400, 200, 300, and 525 eV, respectively. (Figure 5.27)

The B1s spectra, which have been detected as having a B-N peak about 200 eV and a B-O peak at roughly 190 eV, are the result of certain boron atoms being hydroxide near the sample's surface [63]. N-H peak can be seen around 400 eV. Also, there is another peak around 395 eV, and this peak can be observed as N1s for B–N peak. The O1s in Figure 5.27 around 530 eV are caused by the adsorbed O2 from air.

Polymethylaminoborane powder	Atomic %
C1s Scan A	9,85
C1s Scan B	19,7
C1s Scan C	7,95
C1s Scan D	0,78
N1s Scan A	0,86
N1s Scan B	19,63
N1s Scan C	0,7
O1s Scan A	0,9
O1s Scan B	8,56
Si2p3 Scan A	1,06
P2p3 Scan A	0,06
P2p3 Scan B	0,06
B1s Scan A	23,02
B1s Scan B	6,87

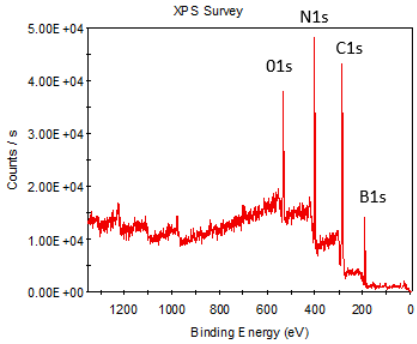


Figure 5.27 XPS analysis for methyl-polyaminoborane

The spectrum for silane-based polyaminoboranes is discovered to have three primary elements: P, Si, and N. There is just one significant peak at 400 eV in the N1s spectra for silane-based polyaminoborane, and it comes from the N-C bonds in the silane coupling agent. The peak seen about 100 eV reflects the Si-O bond, while the silane coupling agent also possesses a C-Si bond [63]. The adsorbed O_2 from air is what is responsible for the O1s in Figure 5.28 at about 530 eV. The B1s spectra, including a B-N peak at around 200 eV and a B-O peak at about 190 eV, have been identified.

Polymethylaminoborane(silane) powder	Atomic %
C1s Scan A	24,29
C1s Scan B	12,97
C1s Scan C	1,52
C1s Scan D	1,95
N1s Scan A	2,14
N1s Scan B	2,87
N1s Scan C	2,29
O1s Scan A	18,37
O1s Scan B	12,05
Si2p3 Scan A	8,52
P2p3 Scan A	0,04
B1s Scan A	12,97

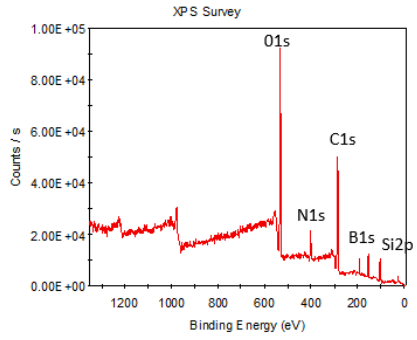


Figure 5.28 XPS analysis for silane-based polyaminoborane structure

Figure 5.29 displays XPS data for C1s, O1s, N1s, P2p, and B1s. The C-H and C-C, C-O-P groups are ascribed to the peaks in the C1s spectra detected at about 285 eV [63]. The carbonyl groups pertinent to amide groups correspond to the peak seen at 288 eV. Peaks

in the O1s spectra for the oxidized samples are located at 530 eV. The existence of the carbonyl or phosphonate functionalities can be used to explain these peaks. It is possible to classify the peak at 532 eV as C-O or P-O. The phosphonate structure of the polymer is connected to the P2p peak that was found at about 133 eV. The carbon-nitrogen bonds are responsible for the N1s peaks that were seen at 400 eV. B-N peak in the B1s spectra, located at about 200 eV.

Polymethylaminoborane(phosphor) powder	Atomic %
C1s Scan A	19,2
C1s Scan B	2,23
C1s Scan C	18,7
C1s Scan D	0,8
N1s Scan A	4,75
N1s Scan B	3,01
N1s Scan C	0,92
O1s Scan A	4,91
O1s Scan B	6,84
O1s Scan C	10,32
Si2p3 Scan A	1,6
P2p3 Scan A	5,23
B1s Scan A	4,31
B1s Scan B	8,3
B1s Scan C	8,87

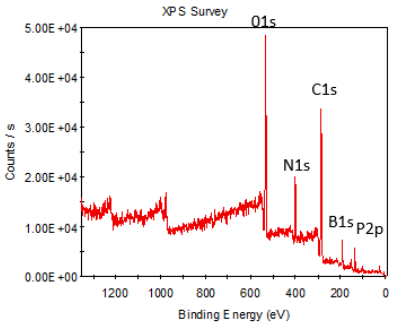


Figure 5.29 XPS analysis for phosphorous-based polyaminoborane structure

5.3 Synthesis and Characterization of Boron Nitride

For the synthesis of ceramic ceramics based on boron nitride, polyaminoboranes are necessary for starting point. Particularly, basic ingredients for the production of BN are functional polyaminoborane complexes. Functional polyaminoboranes produce various pore BN structures, each with its own set of useful features. These materials have a variety of uses, including surface coating, where they may be used to create a surface that is strong, durable, and extremely wear-resistant. To further understand the characteristics of BN-based structures produced at high temperatures, more characterization is performed.

Additionally, polyaminoboranes are employed as raw materials in the production of ceramics based on boron nitride. An atmosphere-controlled tube furnace system was used to perform pyrolysis while nitrogen flowed through at a rate of 3 L/min. Pyrolization of methyl, silane, and phosphorus bearing polyaminoboranes homopolymer series is carried out under nitrogen for two hours at 1100°C. Figure 5.30 shows the schematic synthesis procedure.

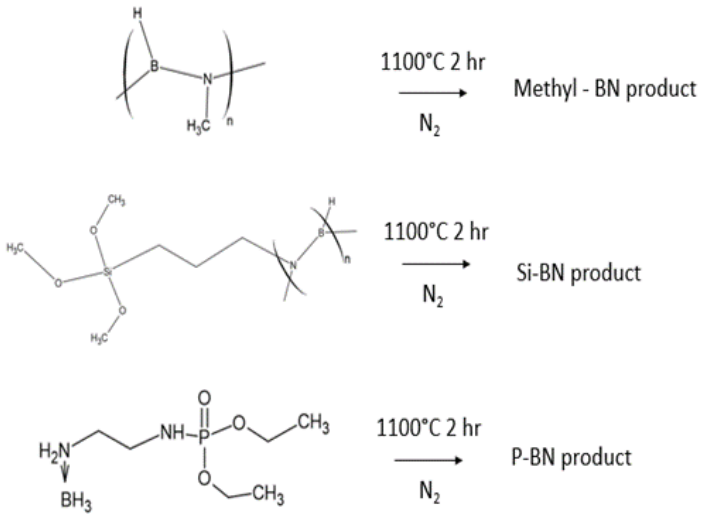


Figure 5.30 Synthesis of functional boron nitride

5.3.1 XRD analysis of Functional Boron Nitrides

As shown in the figure, the polymers and the original bulk material (BN) underwent crystalline structure characterization using X-Ray diffraction (XRD). With a noticeable and clearly defined peak at $2\theta = 29°$, the XRD patterns show a highly crystalline structure [64]. This specific peak serves as a boron nitride signature, indicating the material's presence in the sample. Methyl, silane, and phosphorous polyaminoboranes showed this diffraction peaks, this means that boron nitride structure can defined as hexagonal boron nitride. For methyl-polyaminoborane, there is peak around $2\theta = 40°$, and this defines cubic boron nitride [64]. Silane and phosphorous polyaminoboranes has amorphous B-H around $2\theta = 15°$ [65].

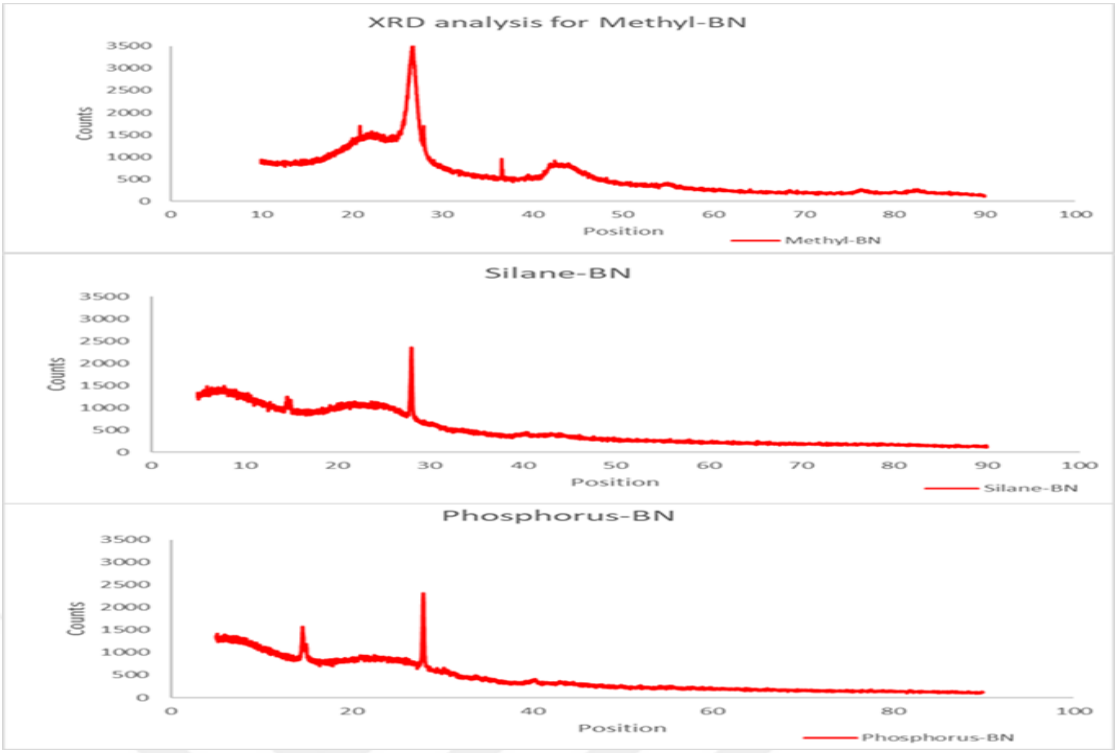


Figure 5.31 XRD analysis for functional boron nitride

5.4 Boron Nitride Coating on Carbon Fiber

While the carbon fiber was coated with functional polyaminoboranes dissolved in THF using the dipping method, a boron nitride coating was obtained on the carbon fiber while it was pyrolyzed at 1100°C. With characterization studies, its physical properties and effectiveness were revealed. Figure 5.32 and 5.33 shows the typical coating procedure.

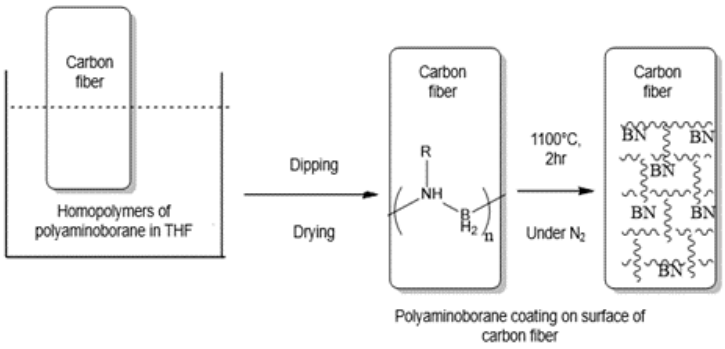


Figure 5.32 BN coating on carbon fiber

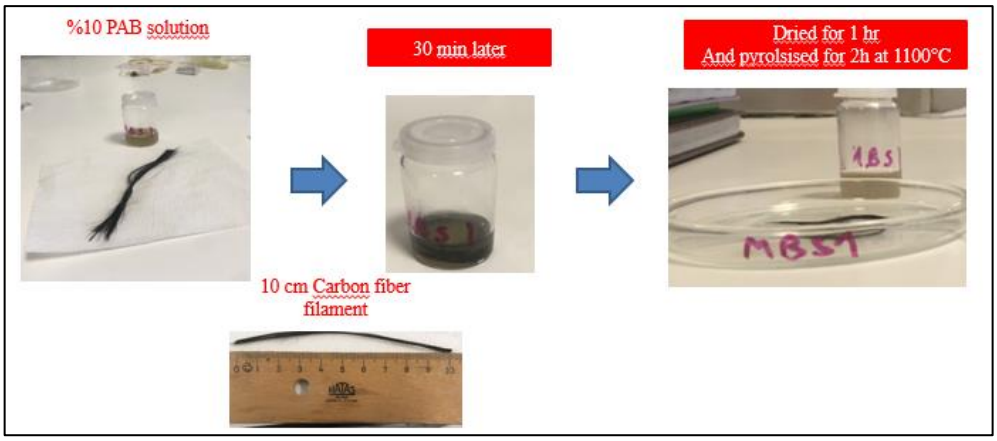


Figure 5.33 Synthesis of boron nitride from polyaminoboranes on carbon fibers

5.4.1 XPS analysis of Functional Boron Nitrides Coatings

As a result of XPS analysis, it was observed that the nitrogen ratio increased and functional bonds from silane and phosphorus were preserved thanks to the bond to boron nitride formed after pyrolysis in the structure of carbon fibers coated in boron nitride obtained from polyaminoborane. This was a factor that increased the synergistic effect. The XPS data shown in the Figure 5.34 provides information about the chemical composition of the polymer. Bare carbon fiber only has C and O bonds due to its structure. P-B-N ceramic was obtained by phosphorus bearing polyaminoborane homopolymers after pyrolysis. XPS analysis of the coated carbon fibers (Figure 5.34 and Table 5.3) shows that:

C1s spectra: Peaks at approximately 285 eV can be attributed to C-H and C-C, C-O-P groups. A peak at 288 eV corresponds to carbonyl groups, which are typically present in amide groups.

O1s spectra: Peaks at around 530 eV indicate the presence of oxygen in the oxidized samples. These peaks can be explained by the existence of carbonyl or phosphonate functionalities, suggesting the presence of C-O or P-O bonds [66].

For phosphorous-based polyaminoboranes, P2p spectra: The presence of a peak at approximately 133 eV indicates the presence of phosphorus in the polymer structure, specifically in the phosphonate groups [66].

B1s spectra: A peak at around 200 eV corresponds to the B-N bond. Another peak at approximately 190 eV corresponds to the B-O bond.

N1s spectra: Peaks at 400 eV are attributed to carbon-nitrogen (N-C) bonds.

In the case of silane-based polyaminoboranes, additional elements are observed:

Si2p spectra: A peak at approximately 100 eV indicates the presence of a Si-O bond [66].

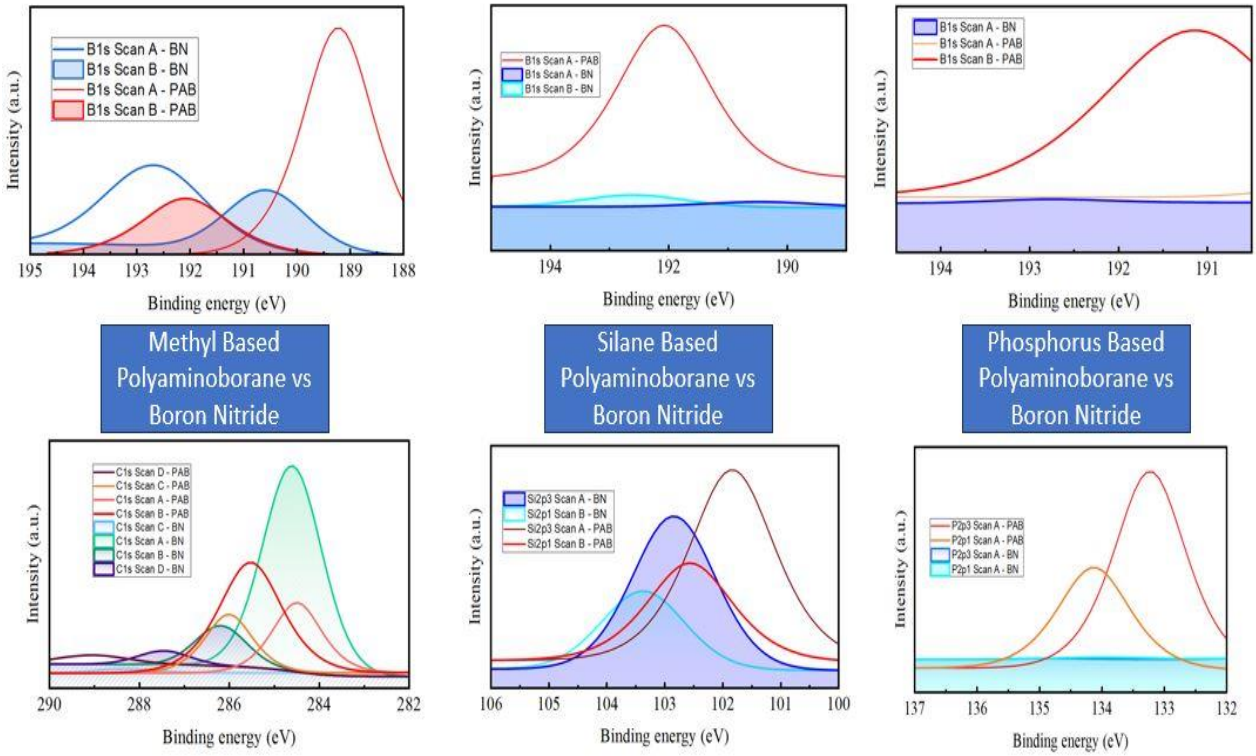


Figure 5.34 XPS analysis for bare and boron nitride coated carbon fibers

Table 5.3 Atomic distribution for BN coated carbon fibers

Reference	Atomic %		PAB	Atomic %		PABSi	Atomic %		PABP	Atomic %
C1s Scan A	45,08		C1s Scan A	46,05		C1s Scan A	47,53		C1s Scan A	42,82
C1s Scan B	9,58		C1s Scan B	4,36		C1s Scan B	7,91		C1s Scan B	6,76
C1s Scan C	4,82		C1s Scan C	6,97		C1s Scan C	6,15		C1s Scan C	7,17
C1s Scan D	2,02		C1s Scan D	4,57		C1s Scan D	3,2		C1s Scan D	5,63
C1s Scan E	2,21		C1s Scan E	1,58		C1s Scan E	2,77		C1s Scan E	1,89
N1s Scan A	2,47		N1s Scan A	3,85		N1s Scan A	2,2		N1s Scan A	4,35
N1s Scan B	0,64		N1s Scan B	3,22		N1s Scan B	2,36		N1s Scan B	1,41
O1s Scan A	2,65		N1s Scan C	1,66		N1s Scan C	0,78		N1s Scan C	1,01
O1s Scan B	20,38		O1s Scan A	2,04		O1s Scan A	3,81		O1s Scan A	4,47
Si2p3 Scan A	0,6		O1s Scan B	13,64		O1s Scan B	15,4		O1s Scan B	16,44
Si2p3 Scan B	9,18		Si2p3 Scan A	2,56		Si2p3 Scan A	6,12		Si2p3 Scan A	0,59
P2p3 Scan A	0,04		P2p3 Scan A	0,07		B1s Scan A	1,77		Si2p3 Scan B	7,08
B1s Scan A	0,34		B1s Scan A	5,15					P2p3 Scan A	0,1
			B1s Scan B	4,28					B1s Scan A	0,3

5.4.2 TGA of Functional Boron Nitrides Coatings

With the TGA, the flame retardant and strong polymer structure formed on the carbon fiber was revealed more clearly. Bare carbon fiber completely consumed at 1000°C (7,4% char residue) under nitrogen. (Figure 5.35) As shown in Table 5.4, surface coated with

methyl based polyaminoborane (gave up Methyl-BN after pyrolysis) resulted in more than 20% char yield under the same condition. S-B-N coating via pyrolysis of silane-based polyaminoborane end up with 16,2% char yield.

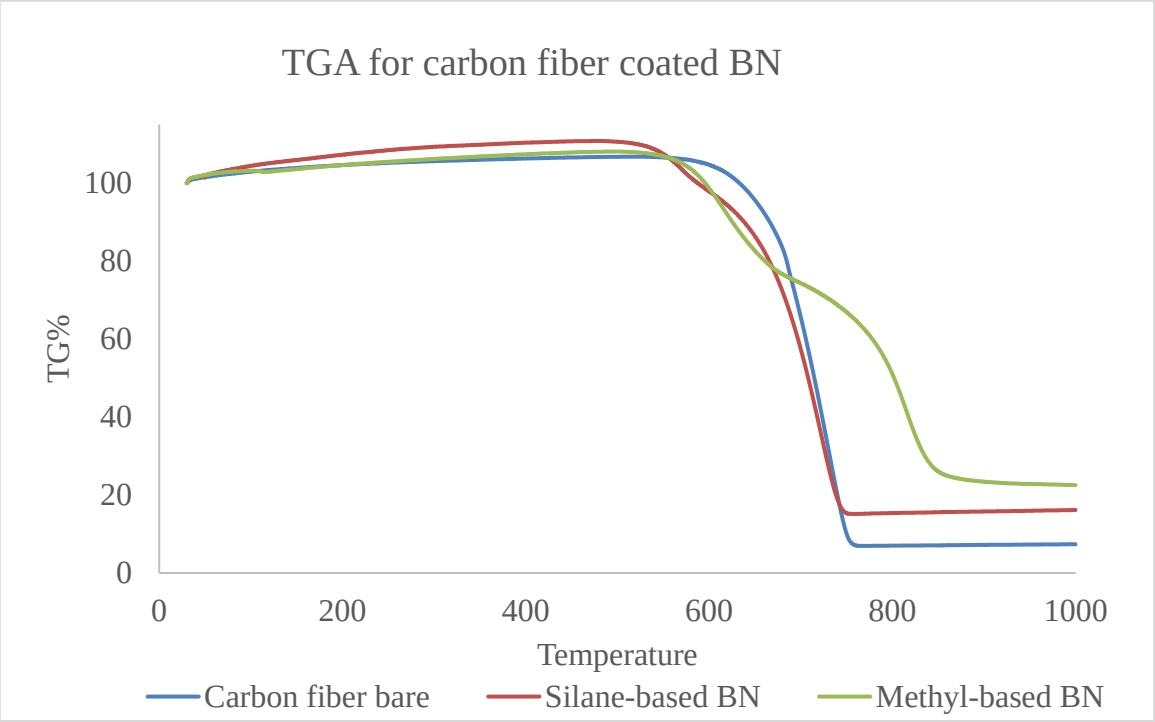


Figure 5.35 TGA analysis of boron nitride coated carbon fibers

Table 5.4 Char yield of boron nitride coatings

	Samples	Tmax1(°C)	Tmax2(°C)	Char yield (wt%)
	Carbon fiber bare	575	720	7,4
Nitrogen	Methyl-Polyaminoboranes	550	724	22,5
	Silane-Polyaminoboranes	542	773	16,2

5.4.3 SEM-EDX analysis of Functional Boron Nitrides Coatings

A concentrated electron beam is used to scan a sample's surface in an electron microscope called a scanning electron microscope, or SEM. Carbon fiber surfaces covered with coating can be observed via SEM. In line with the morphology of boron nitride, this covering gets comparatively thinner. There is a uniform coating in SEM images and no pore or broken structure was found in the images in Figure 5.36.

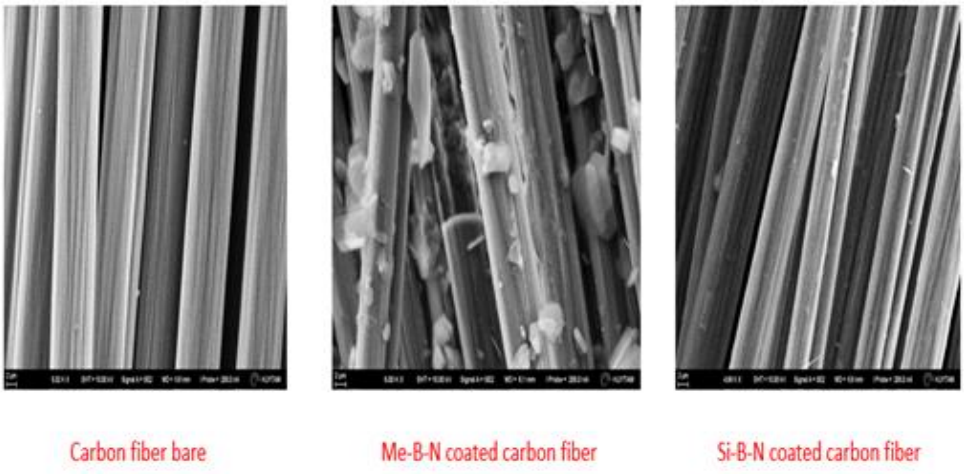


Figure 5.36 SEM images for boron nitride coated carbon fibers

An EDX analysis employing B, C, and O mapping was also performed to examine the structure of methyl-polyaminoboranes and silane-polyaminoboranes under nitrogen in Figure 5.37. Detection is based on an element's atomic number and is unable to differentiate between ionized, bound, or free atoms. The typical EDX analyzers are capable of detecting elements with atomic numbers ranging from 11 (sodium) and upwards. Therefore, Boron is hard to see and needs to be analyzed with low energy. In EDX, an electron beam is focused on the material's surface to a depth of about 1 micron; in XPS, the signal is acquired from a depth of only a few nm. These two methodologies' "depth of analysis" might result in a variation in the quantity [67].

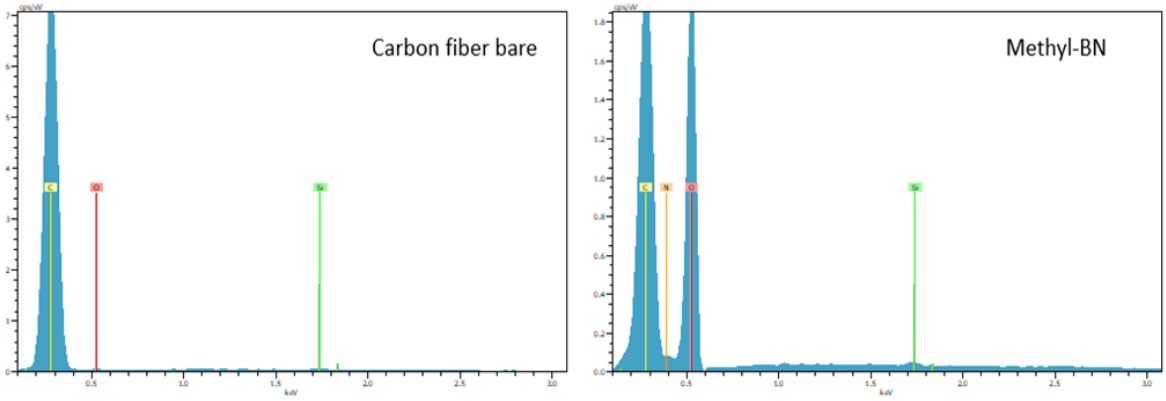


Figure 5.37 EDX mapping images for boron nitride coated carbon fiber

5.5 Polyaminoboranes Coating on Wood

For the wooden block, a 5x5 cm cut piece, methyl or silane bearing polyaminoborane were dissolved in varnish to prepare a 1% solution. The hardener, isocyanate, was then added dropwise to this mixture. For the coating application, a 100-micron applicator for thickness of coating was used to apply the mixture to the surface of the wood at five-minute intervals, instead of waiting for 1-hour intervals. This stopped the hardener from affecting how long the mixture would persist. After each application of the mixture, it was dried in a fume hood to expedite the drying process. The process of applying the mixture and drying it was repeated three times, resulting in three layers of the methyl or silane based polyaminoborane coating on the wood. Both the wood coated with the methyl or silane bearing polyaminoborane mixture and the uncoated wood were subjected to testing to compare their properties. The image clearly illustrates the stark contrast between the uncoated wood and the wood coated with polyaminoborane dissolved in varnish. When the uncoated wood was subjected to a flame from a distance of 10 cm for 10 seconds, it caught fire and burned extensively. In contrast, the wood coated with polyaminoborane dissolved in varnish remained protected from burning in Figure 5.38. Instead, a white boron oxide layer formed on the surface where the flame source made contact. The wooden surface itself did not burn, and no flames were observed. This demonstrates the fire-resistant properties of the polyaminoborane coating, which effectively prevents the ignition and burning of the wood.

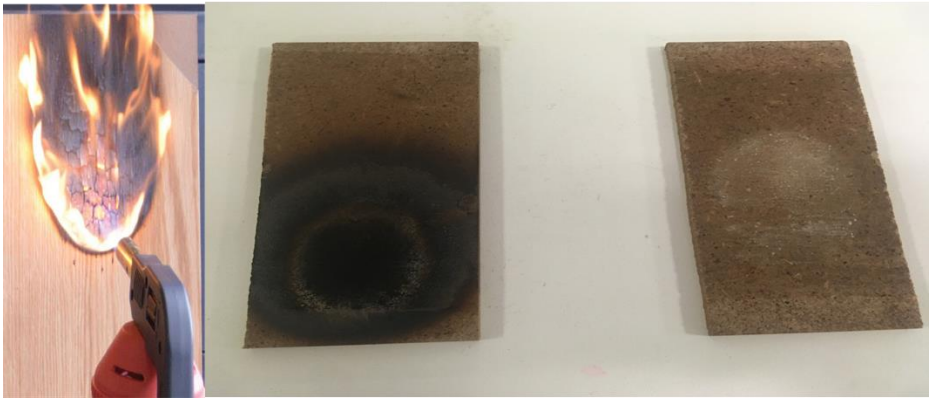


Figure 5.38 Flame retardant performance for wood

Physical properties for polyaminoborane coated wood samples was investigated by Gloss, Erichsen scratch resistance and cross-cut tests. Table 5.5 shows the analysis results.

Table 5.5 Physical properties for coated wood

Sample	Brightness (20˚,60˚,85˚) (Gloss)	Erichsen Scratch Resistance (Newton)	Adhesion Strength (Cross-cut)
MBŞ-43 Bare Wood	2,18,50 gloss	5 N	ASTM Class:5 B
MBŞ-44 PAB Wood	1,11,21 gloss	5 N	ASTM Class:5 B
MBŞ-45 PAB Si Wood	1,5,14 gloss	5,5 N	ASTM Class:5 B

Brightness is an indicator of gloss, and a high gloss is that is very shiny and reflective. Coated wood is less reflective and dull. The resistance of plastic or varnished surfaces to scratches and cuts is tested with the motorized scratch hardness tester, the Erichsen. It uses single, parallel, and cross cuts to test panels of various thicknesses. Scratch Resistance is increased in silane based polyaminoborane coating, so it gives a good opportunity for coating on wood. Paint adhesion testing is frequently used in the paint and coating industries to ascertain if the paint or coating will cling correctly to the substrates on which they are applied. As can be seen in Table 5.5, although the gloss values of silane-based polyaminoboranes decreased to 1.5.14 gloss, the anti-scratch value increased from 5N to 5.5N might be due to the silane attachment onto the surface and increasing the crosslinking density. Methyl-polyaminoborane shows a gloss value of 1,11,21, which is lower than the 2,18,50 gloss value of uncoated wood, that is, it is a more matte surface. The scratch resistance values are the same.

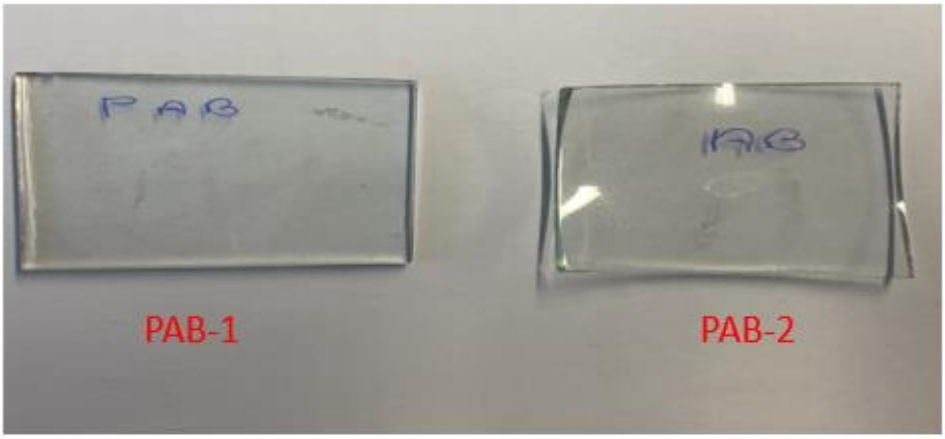
5.6 Polyaminoboranes Coating on Glass

The objective of this research is to synthesize methyl-polyaminoborane and apply it as a coating on boron nitride glass surfaces. A 1% solution of methyl-polyaminoborane in THF (tetrahydrofuran) was prepared. To coat the surfaces, a depth watch glass was used, and the reverse side of the surface to be coated was marked with a glass pen. The polyaminoborane solution was poured onto the marked area, effectively coating the upper surfaces of the glass. The coated surfaces were then left to dry for 1 hour. For the synthesis of boron nitride, the coated glass samples were subjected to a temperature of 700 °C for 3 minutes, ensuring that the polyaminoborane did not melt but instead underwent conversion to boron nitride. This method was employed for larger glass samples. For

smaller glass samples, a 1% polyaminoborane solution in THF was prepared, and a spin coater was used. The solution was poured onto the glass surface using a dropper, and the spin coater was operated under a nitrogen atmosphere. The materials coated at room temperature were sent for testing without undergoing conversion to boron nitride.

During the experiments, it was observed that the glass melted when subjected to temperatures above 1000 °C, which is the temperature required for boron nitride formation. The dip coatings procedure was applied with a concentration of 10% and the surface was also displayed the same melting behavior during a subsequent half-hour retry at 700 °C. Additionally, the formation of bubbles on the surface was observed.

To obtain better coating on glass, coatings with a reduced concentration of 1% was used. Coated glass surface was then subjected to a temperature of 700 °C for 3 minutes. We employed both the dipping method and a spin coater at room temperature to coat small glass samples. As a result, it was observed a slightly hazy structure on the glass surfaces. Figure 5.39 shows the methyl-polyaminoborane coated glass samples. Pencil hardness and transmittance (hazy) was applied for the surface characterization.



1% PAB coated glass at 700°C



1% PAB coated small glass at room temperature

Figure 5.39 Methyl-polyaminoborane coated glass samples

The quantity of light dispersed when it passes through a transparent sample is indicated by the haze measurement of that sample. Higher sample clarity indicates fewer contaminants as haze measurement values decrease. Contact angle is a wettability indicator. The intermolecular interactions between the solid and the liquid cause a drop of water to spread over the surface when it is put on a solid. The solid's wettability will be instantly apparent based on the water contact angle. The quantity of light energy that the glass absorbs, scatters, or reflects is referred to as the transmittance property of permeability. The permeability and haze values of 700 °C-treated PABs are respectively,

Bare- T: 89.7%, H: 0.41%

PAB1 (methyl bearing polyaminoborane): T: 87.9%, H: 3.49%

PAB2 (methyl bearing polyaminoborane): T: 87.2%, H: 8.31%

The contact angle values were too low to be measured, due to the super hydrophilic behavior. Pencil hardness value is 7 H (max pencil hardness 9H). The transmittance and haze values of PABs at room temperature (on thin glass) could not be measured because the glass sizes were small. It must be at least 5cmx5cm. The pencil hardness value is obtained as 3 B (pencil hardness min 9B). We can say that it is a very soft layer at room temperature.

PAB-1(methyl bearing polyaminoborane): 59.50˚

PAB-2(methyl bearing polyaminoborane)-: 54.86˚

It is observed that methyl polyaminoborane forms a soft coating at room temperature, and at high temperature (although it is not removed to the ideal degree due to the melting of the glass), the glass hardens as expected and the coating at room temperature turns into a hydrophobic glass structure and at high temperature a super hydrophilic glass structure.

These observations provide valuable insights into the behavior and characteristics of the coatings and the effects of concentration and temperature on the glass substrate. Further analysis and experimentation should be conducted to optimize the coating process and improve the clarity of the coated glass surfaces.

6
CONCLUSION

Functional polyaminoboranes have been synthesized in the scope of this research. Thus, methyl, phosphor and silane bearing polyaminoboranes' homopolymers are characterized by NMR, GPC, TGA, and FTIR analysis. TGA analysis showed that there are more than 40% char yield 800ºC for each homopolymers. Under nitrogen, silane-based polyaminoboranes have the maximum char yield (60%) while, next to methyl-polyaminoboranes, they have the highest char yield (58%) in an environment of air. Methyl-polyaminoboranes had the lowest char yield (42%) under N_2 atmosphere whereas phosphorus-containing ones have the lowest char production (47%) for air environment at 800ºC. BN synthesis was established by using these polyaminoboranes precursors using pyrolysis condition (1100ºC, 2 h). XPS, XRD and SEM-EDX analysis revealed the BN formation. Surface coating on carbon fiber, wood and glass was established by the pyrolysis of functional polyaminoboranes and formation of BN. Each surfaces showed different characteristic behavior after coating:

Wood Surface: When a 1% coating was applied to the wood surface, and a flame was applied for 10 seconds from a distance of 10 cm, no flame was observed on the coated surface. In contrast, the uncoated wood surface burned completely. Additionally, a white boron oxide layer formed on the coated wood surface instead of burning.

Glass Surface: Pyrolysis condition for glass surface has been changed due to the melting behavior of glass at 1100ºC. When the coating solution was applied to the glass surface at 700 °C, it resulted in a high hardness (7H/9H) of the coating. However, if the polyaminoboranes were not converted quantitatively into boron nitride, a softer layer was oberved. The pencil hardness value is 3 B. The transmittance and haze values of PABs at room temperature (on thin glass) could not be measured because the glass sizes were small.

Carbon Fiber: TGA analysis revealed that the boron nitride obtained from the silane- and methyl-based polyaminoborane coating on carbon fiber showed a char yield of 16,2% and 22,5 on the coated fiber. In comparison, the uncoated carbon fiber only yielded 7,4% char. This indicates that the coated fiber preserved the BN structure has better thermal resistance.

These observations highlight the effectiveness of the polyaminoborane coating in providing efficient coating properties on different surfaces, such as wood, glass, and carbon fiber.

For explanation of these observations, it can be stated that polyaminoboranes are a relatively new class of inorganic polymers that hold great promise for a wide range of applications. One of their important features is the ability to obtain boron nitride from polyaminoborane, which exhibits high thermal and flame resistance, making it self-inflammable. Polyaminoboranes allows for the synthesis of a non-oxide ceramic with unique properties depending on its crystal structure such as BN.

Cubic boron nitride, in its diamond-like form, demonstrates exceptional chemical resistance and thermal stability, earning it the distinction of being the second hardest material known after diamond. On the other hand, hexagonal boron nitride (h-BN) shares similarities with graphite but possesses important distinguishing features such as high thermal conductivity, low thermal expansion, thermal shock resistance, high electrical resistance, non-toxicity, ease of workability, slipperiness, and chemical stability.

These characteristics make boron nitride synthesized from polyaminoboranes a highly versatile material applicable in various industries, including aerospace, automotive, electronics, semiconductors, metalworking, and even cosmetics. Furthermore, it can serve as a hydrogen storage medium, piezoelectric material, and catalyst initiator in polyaminoboranes. Its solubility is high compared to many other polymers, thanks to its ability to undergo functionalization in addition to its inherent physical structure.

Despite its ability to withstand high temperatures, poly(aminoboranes) can be easily processed due to its smooth structure. With its unique structural features and potential for further development, polyaminoboranes hold great promise. Within the scope of the project, the aim is to obtain polymers with improved thermomechanical properties, good coating properties, and self-flame-retardant properties. Additionally, the neutron capture capability of boron in the polymer matrix might also contribute to the development of a multifunctional material possessing both flame retardant and neutron capture properties. Chemical and oxidative stabilities can be ruled out especially at outside of the atmosphere.

These polymers can also serve as additives to current commercial polymers. The fact that the synthesized polymers exhibit improved distribution within the applied polymer matrix

and do not release from the surface. This will set an example for the development of next-generation multifunctional surface as well.

<table>
<tr>
<td>Objective: Our project aims to synthesize functional polyaminoboranes (Me-, Si- and -P) that are resistant to extreme environments and easily applicable to materials

Description of effort:
- Synthesize functional polyaminoboranes
- Purify the resulting polymer
- Use new methods to functionalize them
- Demonstrate applications of these organic-inorganic hybrid polymers</td>
<td></td>
</tr>
<tr>
<td>Benefits of Proposed Technology:
- Our product is resistant to heat.
- It is lubricant and soluble with easy application.
- Can be applied to various materials like carbon fiber.
- Easy, processable boron nitride coating

Challenges:
- Lack of catalyst development in this synthesis, or catalysts have high costs
- Finding characterization tools for boron-based structures

Maturity of Technology:
- Homopolymers (Me, P or Si functional polyaminoboranes) are synthesized
- Trials for applications and synthesis of copolymers</td>
<td></td>
</tr>
</table>

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