REPUBLIC OF TURKEY
YILDIZ TECHNICAL UNIVERSITY
GRADUATE SCHOOL OF SCIENCE AND ENGINEERING

# EFFECT OF HEXAGONAL BORON NITRIDE ON ORGANIC/INORGANIC HYBRID POLYMER COATINGS FOR ALUMINIUM

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Mehmet KARADAĞ

Signature

*Dedicated to my family,*

*And my nation*

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# LIST OF SYMBOLS

| | |
|---|---|
| R | Alkoxide Group |
| ° | Angle Degree |
| °C | Celcius |
| cm | Centimeter |
| eV | Electronvolt |
| g | Gram |
| GPa | Giga Pascal |
| h | Hour |
| K | Kelvin |
| kV | Kilovolt |
| M | Metal |
| $\mu$m | Micrometer |
| mm | Milimeter |
| min | Minute |
| g/mol | Molar mass |
| N | Newton |
| n | Number |
| x | Ordinary number |
| y | Ordinary number |
| % | Per Cent |
| P | Polimer |
| pH | Power of Hydrogen |
| RT | Room Temperature |
| rpm | Round per Minute |
| s | Second |
| T | Temperature |
| $cm^{-1}$ | Wave number |

# LIST OF ABBREVIATIONS

| | |
|---|---|
| ASTM | American Society for Testing and Materials |
| BN | Boron Nitride |
| C-BN | Cubic Boron Nitride |
| C.S | Colloidal Silica |
| CVD | Chemical Vapour Deposition |
| FTIR | Fourier-transform Infrared Spectroscopy |
| HBN | Hexagonal Boron Nitride |
| IPA | Isopropyl Alcohol |
| MTMS | Methyltrimethoxysilane |
| $MoS_2$ | Molybdenium disulfide |
| PEEK | Polyether Ether Ketone |
| PVA | Polyvinyl Alcohol |
| PVD | Physical Vapour Deposition |
| SEM | Scanning Electron Microscopy |
| TEOS | Tetraethyl Orthosilicate |
| USD | United States Dollar |
| W-BN | Wurtzite Boron Nitride |
| $WS_2$ | Wolfram disulfide |

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# ABSTRACT

## Effect of Hexagonal Boron Nitride on Organic / Inorganic Hybrid Polymer Coatings for Aluminium

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Master of Science Thesis

Supervisor: Assoc. Prof. Dr. Buğra ÇİÇEK

Various coatings have been developed for metal substrates so as to reasons such as preventing corrosion in metals and increasing thermal and tribological properties. One of these coating types is organic/inorganic hybrid coatings. These coatings, which are produced by forming a polymer matrix, can sometimes gain different properties by using ceramic powders as an additive in some cases.

Ceramic powders are usually added to the polymer matrix to improve the desired properties or to impart an inherent property to the coating.

Hexagonal boron nitride (h-BN), which has many different properties, is one of the ceramic materials whose usage area is increasing day by day. h-BN, the polymorph of boron nitride compound with hexagonal crystal structure, is a ceramic in which boron and nitrogen atoms come together in a hexagonal arrangement and the layers are connected to each other by weak Van der Waals bonds.

H-BN, which can show a high lubricating property thanks to the friction coefficient that decreases with the breaking of weak Van der Waals bonds, is also a ceramic that stands out with its chemical inertness, high electrical insulation and low thermal expansion coefficient. In addition, h-BN is the lightest known ceramic material in the world.

In this study, organic/inorganic hybrid coatings were developed by adding h-BN as a filler in a polymeric matrix. Many parameters such as hardness, friction coefficient and hydrophobicity were investigated to determine the properties of coatings produced by the sol-gel method.

As a result of the studies and analyzes, it has been clearly demonstrated that h-BN improves the properties of organic/inorganic coatings and is a promising ceramic filler material especially for areas where low friction coefficient and low water contact angle are required.

**Keywords:** Hexagonal boron nitride, organic/inorganic hybrid coatings, sol-gel, friction coefficient

# ÖZET

## Alüminyum için Organik / İnorganik Hibrit Polimer Kaplamalarda Hegzagonal Bor Nitrürün Etkisi

Mehmet KARADAĞ

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Metallerde meydana gelen korozyonu önlemek, termal ve tribolojik özellikleri artırmak gibi sebeplerle metal susbtratlar için çeşitli kaplamalar geliştirilmiştir. Bu kaplama çeşitlerinden birisi de organik/inorganik hibrit kaplamalardır. Bir polimer matris oluşturularak üretilen bu kaplamalar bazen birtakım seramik tozlarında katkı maddesi olarak kullanılması ile farklı özellikler kazanabilir.

Seramik tozları genellikle istenen özellikleri geliştirmek veya kendilerinde olan bir özelliği kaplamaya kazandırmak için polimer matrise eklenir.

Birçok farklı özelliği barındıran hegzagonal bor nitrür (h-BN) gün geçtikçe kullanım alanı artan seramik malzemelerden bir tanesidir. Bor nitrür bileşiğinin hegzagonal kristal yapısına sahip polimorfu olan h-BN bor ve nitrojen atomlarının altıgen dizilime biraraya geldiği ve katmanlarının zayıf Van der Waals bağları ile birbirine bağlı olduğu bir seramiktir.

Zayıf Van der Waals bağlarının kırılması ile azalan sürtünme katsayısı sayesinde yüksek bir yağlayıcılık özelliği gösterebilen h-BN aynı zamanda kimyasal inertlik, yüksek elektrik yalıtkanlığı ve düşük termal genleşme kat sayısı ile öne çıkan bir seramiktir. Ayrıca h-BN dünyadaki bilinen en hafif seramik malzemedir.

Bu çalışmada organik/inorganik hibrit kaplamalar polimerik bir matris içeriisne h-BN'ün dolgu malzemesi olarak eklenmesi ile geliştirilmiştir. Sol-jel yöntemi ile üretilen kaplamaların özelliklerinin tayini için sertlik, sürtünme katsayısı ve hidrofobiklik gibi birçok parametre incelenmiştir.

Yapılan çalışmalar ve analizler sonucunda h-BN'nin organik/inorganik kaplamaların özelliklerini iyileştirdiği, ve özellikle düşük sürtünme katsayısı ve düşük su temas açısına ihtiyaç duyulan alanlar için umut vaat eden bir seramik dolgu malzemesi olduğu açıkça ortaya konmuştur.

**Anahtar Kelimeler:** Hegzagonal bor nitrür, organik/inorganik hibrit kaplamalar, sol-jel, sürtünme katsayısı

# 1
# INTRODUCTION

## 1.1 Literature Review

Today, metal materials are frequently used in industry and daily life. However, the surface properties of the metal used may not always be at the desired level. For this reason, many metal coating methods have been developed. Electrodeposition, chemical vapor deposition, physical vapor deposition and sol-gel methods are just some of them.

Organic/inorganic hybrid coatings are also widely used in metal coatings for many reasons such as preventing metals from corrosion [1,2], increasing the thermal [3] and tribological [4] properties of the metals. Generally, organic/inorganic hybrid coatings produced by the sol-gel process adhere to the metal substrate by forming chemical bonds with the metal substrate through inorganic sols. These coatings produced from polymer sols can also gain different properties by adding additives to the polymer matrix [5].

Sol-gel process is a very suitable production method for organic/inorganic hybrid coatings produced by mixing organic polymers or organoalkoxysilanes and alkoxides. The sol-gel method is ideal for producing coatings with a controllable composition and microstructure. Sol-gel, which is a production method based on M(OR)n hydrolysis and condensation of metal alkoxides, stands out with its low cost and simple procedure. The formation of M-O-P and M-O-Si bonds is very important for the adhesion of the coating to the metal substrate [5]. Organosilanes, which are relatively environmentally friendly chemicals, are one of the reasons why they are preferred for use in coatings produced by the sol-gel method, because they can strengthen the adhesion at the interface between metal and coating. Today, silicon-based sol-gel chemistry is more advanced than other metal-organic-based precursors [3].

Adding ceramic additives to the polymer matrix is a very common method to impart desired properties to organic/inorganic hybrid coatings. Ceramic materials such as $Al_2O_3$, $TiO_2$, $ZrO_2$ and $SiO_2$ have been used as fillers in polymeric coatings [6,7]. Hexagonal boron nitride (h-BN) is one of these ceramic materials.

One of the crystal forms of boron nitride, h-BN has a hexagonal crystal structure. Other polymorphs of BN are cubic boron nitride (c-BN) and wurtzite boron nitride (w-BN) [9,11]. Synthetically produced BN is produced by the combination of boron and nitrogen atoms. This ceramic, which is not found in nature, has found application areas in many sectors of industry in recent years.

In the periodic table, boron is in III-A and nitrogen is in V-A group. The compounds formed by these elements, which are adjacent to the carbon in the IV-A group, also show similar properties with the carbon compounds. For example, c-BN is the hardest known material after diamond. Besides, h-BN also has high tribological lubrication properties like graphite. This is because BN compounds are isoelectronic and isostructural with carbon compounds [9-12].

H-BN has a layered structural arrangement. Boron and nitrogen atoms are connected to each other by strong covalent bonds. However, there are weak Van der Waals bonds between the layers. The breaking of these bonds allows h-BN to show high lubrication properties and reduce the friction coefficient of the medium, just like graphite [13-16].

However, h-BN offers high chemical inertness and electrical insulation. It also has high electrical insulator. h-BN has high chemical resistance, which cannot be wetted by most metals, glass and salt melts. The lightest known ceramic in the world, h-BN, stands out with its low thermal expansion and low dielectric constant [17-22].

When the literature is examined, it can be seen that recently, h-BN coatings have been developed by methods such as magnetron sputtering and chemical vapor deposition (CVD) to protect metals from corrosion and reduce the friction coefficient [23]. Han et al. showed how effective h-BN is against corrosion with a study they have done. In another study, Li et al. observed that h-BN coatings developed using a single layer of h-BN significantly reduced the friction coefficient [24]. However, these techniques have many disadvantages such as the use of expensive equipment, high vacuum requirement and the presence of toxic substances used in the processes.

Alternatively, cheaper and easier methods have been tried. Husain et al. have produced PVA/h-BN mixed coatings to prevent corrosion on metals in marine environments [25]. In another study, an increase in the thermal conductivity of copper was observed in the coatings produced by doping h-BN into the epoxy resin [26].

H-BN has also been used as a filler in organic polymer matrices and epoxy resins in many different studies. Sombatsompop et al. used h-BN as an additive in poly(ether-ether-ketone (PEEK) and hoped to improve the tribological performance of PEEK. As a result of the analysis, the use of h-BN as a filler in PEEK coatings resulted in an improvement in the wear and friction coefficients has been demonstrated [27].

In another study, Fang et al. also investigated the effects of c-BN and h-BN fillers on the tribological properties of epoxy resin in epoxy coatings. As a result of the study, it was clearly understood that h-BN filled epoxy coatings have better wear and lower friction coefficients [28].

Therewithal, there are many other articles reporting successful tribological studies on polymer/h-BN composite coatings [29-32]. There are also studies where silane/h-BN composite coatings are produced to take advantage of the corrosion resistance and thermal properties of h-BN [33-35]. However, these studies are few in number and there are only a few studies on the use of h-BN in organic/inorganic coatings and the tribological properties of silane/h-BN composite coatings.

## 1.2 Objective of the Thesis

The first objective of the study is to reduce the friction coefficient of organic/inorganic coatings by doping h-BN. h-BN is a material that stands out with its low friction coefficient. In terms of the ease of coating production and application, organic/inorganic coatings are a very suitable coating method for metals. It is aimed to expand the tribological usage areas of h-BN doped organic/inorganic hybrid coatings by reducing the friction coefficients of these coatings.

The second objective of the study is to investigate whether the h-BN coating has a negative effect on the adhesion of the coatings to the substrate. The homogeneity of the doped materials and their agglomeration potential can affect the adhesion of the coating to the substrate. It is aimed to ensure the best adhesion of the coating to the substrate with as high homogeneity and low agglomeration as possible.

## 1.3 Hypothesis

The friction coefficients of organic/inorganic coatings are high for some application areas. For this reason, although they are coatings that can be produced with very cheap and simple methods, their use in some areas is restricted. In order to solve this problem, the coefficients of friction need to be reduced. It has been suggested that the friction coefficients of these hybrid coatings can be reduced by doping the h-BN ceramic particles.

In addition, h-BN is a non-wettable material. It is predicted that the hydrophobicity of h-BN doped organic/inorganic hybrid coatings will also increase and their wettability will decrease. In this way, it is thought that the use of these coatings as mold release agents will increase, in the metal casting sectors, especially.

Another prediction is that with the applied coating process, the h-BN particles will disperse sufficiently in the solution and will not form agglomerations at the same time. Thus, it is foreseen that there will be no problem in the adhesion of the coating to the substrate.

# 2

# METAL SURFACE COATINGS

Today, many items, devices and tools that we use in industry and in daily life are either completely made of metal parts or contain more or less metal parts. Metals are widely used due to their many physical and mechanical properties, especially their high hardness, strength, electrical and thermal conductivity. However, the desired property on the surface of the material may differ from the surface properties of the base metal, depending on the area of use. For this reason, many different coating methods have been developed for metal surfaces in the industry today. These coatings can be classified according to their materials, usage areas and application methods.

Considering the application methods, physical vapor deposition (PVD), chemical vapor deposition (CVD), electrochemical deposition, plasma spraying and sol-gel process can be counted as the most common coating types on metal surfaces.

## 2.1 Coating Methods Applied to Metal Surfaces

### 2.1.1 Physical vapor deposition (PVD)

Physical vapor deposition is a kind of vacuum deposition method. The method is based on two basic physical processes, sputtering and evaporation. The PVD method is performed in four steps. First, the coating material is evaporated by a high-energy source such as an electron beam or ions. This vapor is then transported to the substrate to be coated. In the third stage, the transported atoms react with a suitable reactive gas (oxygen, nitrogen, methane, etc.). Finally, the process is completed when the coating is deposited on the substrate surface.

Like all processes, the PVD process has some advantages and disadvantages. Advantages are that the produced coating can have more advanced properties than the substrate, can be used on some organic and all inorganic materials, and is an environmentally friendly application. However, the problems encountered in coating complex shapes, low output despite high cost, and complexity of the process are the disadvantages of the PVD method. Methods such as evaporative deposition, ion plating, pulsed laser deposition, and sputter deposition are the most commonly used PVD processes.

### 2.1.2 Chemical Vapor Deposition (CVD)

Chemical vapor deposition method is one of the most preferred methods among thin film coating methods. It is a process typically carried out under vacuum [36]. Since it is a process that is usually carried out between 500-1100 °C, it can be called a process that requires medium temperature. It is a very useful method as high quality and low cost coatings can be obtained with the CVD method.

The CVD process is a process based on the production of coating by chemical reactions with other gases entering the process so that the organometallic or halide compounds to be deposited on the substrate can form a stable coating on the substrate. The CVD method can be applied to a wide range of materials, from turbine blades to refractory materials. CVD method is also divided into some sub-techniques in itself. Some of these are atmospheric-pressure CVD, low-pressure CVD, ultrahigh vacuum CVD, plasma-enhanced CVD techniques [36].

### 2.1.3 Electrochemical Deposition

Electrochemical deposition is the process of depositing conductive and semiconductor materials on generally conductive substrate surfaces using a redox reaction under an electric field. In this method, cations of the target material are reduced from the electrolyte using electric current and the surface of the electrode is coated. A platinum anode is immersed in the electrolyte. The task of this counter electrode is to complete the circuit by leaving electrons in the electrolyte. The ability to produce thin conductive films at $\mu$ levels with the electrochemical deposition method makes this method very attractive.

Coatings produced by electrochemical deposition are often used in printed circuits, creating reflective surfaces and surface restoration of worn parts. In recent years, with the developments in microsystems, microelectronics and optics, an increase in the quality and properties required from coatings is desired. At the same time, coatings used in corrosive environments and tribological applications have started to be produced with higher quality. There are many different types of parameters in electrochemical deposition processes. The most important of these are temperature, pH, and current density.

### 2.1.4 Sol-gel Method

Sol-gel process is a chemical production method consisting of the formation of an inorganic colloidal suspension (sol) and then the gelation of this suspension to produce materials with a three-dimensional network structure. Sol-gel process is a chemical process used in synthesizing inorganic materials such as glass and ceramics. The method was first used by the French chemist J.J Ebelmen. Ebelmen succeeded in synthesizing uranium oxide using hydroxide with this method [37].

Precursors for synthesizing colloidal sols consist of organometallic compounds surrounded by reactive functional groups. Metal alkoxides such as alkoxysilanes (tetramethoxysilane and tetraethoxysilane), aluminates, titanates, zirconates, and borates are most commonly used in the sol-gel process. Sol-gels can be in the form of films, particles, fibers, aerogels and dense materials at the micro and nanoscale after a heat treatment. Sol-gel products are initially amorphous, so crystalline sol-gel products can be obtained using appropriate heat treatments. Until the 1950s, R.Roy et al. synthesized ceramic oxides with this method and made sol-gel silicate powders popular in the markets. The production process of low bulk density silica produced by hydrolysis of tetraethoxysilane (TEOS) was patented in 1971. In the 1980s, however, the sol-gel method was frequently used in many research and applications, and organic-inorganic hybrid materials began to be synthesized with this method [37]. Today, sol-gel technology attracts great attention in fields such as ceramics, polymer chemistry, organic and inorganic chemistry Figure 2.1 shows the sol-gel process routes. It is also an indispensable method in the preparation of organic-inorganic hybrid materials.

Since the sol-gel process is a process in which the properties of the material to be produced can be controlled, it can be preferred in the production of a wide variety of materials such as powders, thin film coatings, membranes, fibers, glass and ceramics. Glass and ceramics are produced by drying the gel poured into a mold. Even ceramic fiber production can be done by controlling the viscosity of the sol. It is possible to coat many complex shaped materials with the sol-gel method, which has many advantages compared to other coating methods. In addition, the sol-gel method stands out with its advantages such as low process temperature, production of porous and high-purity products.

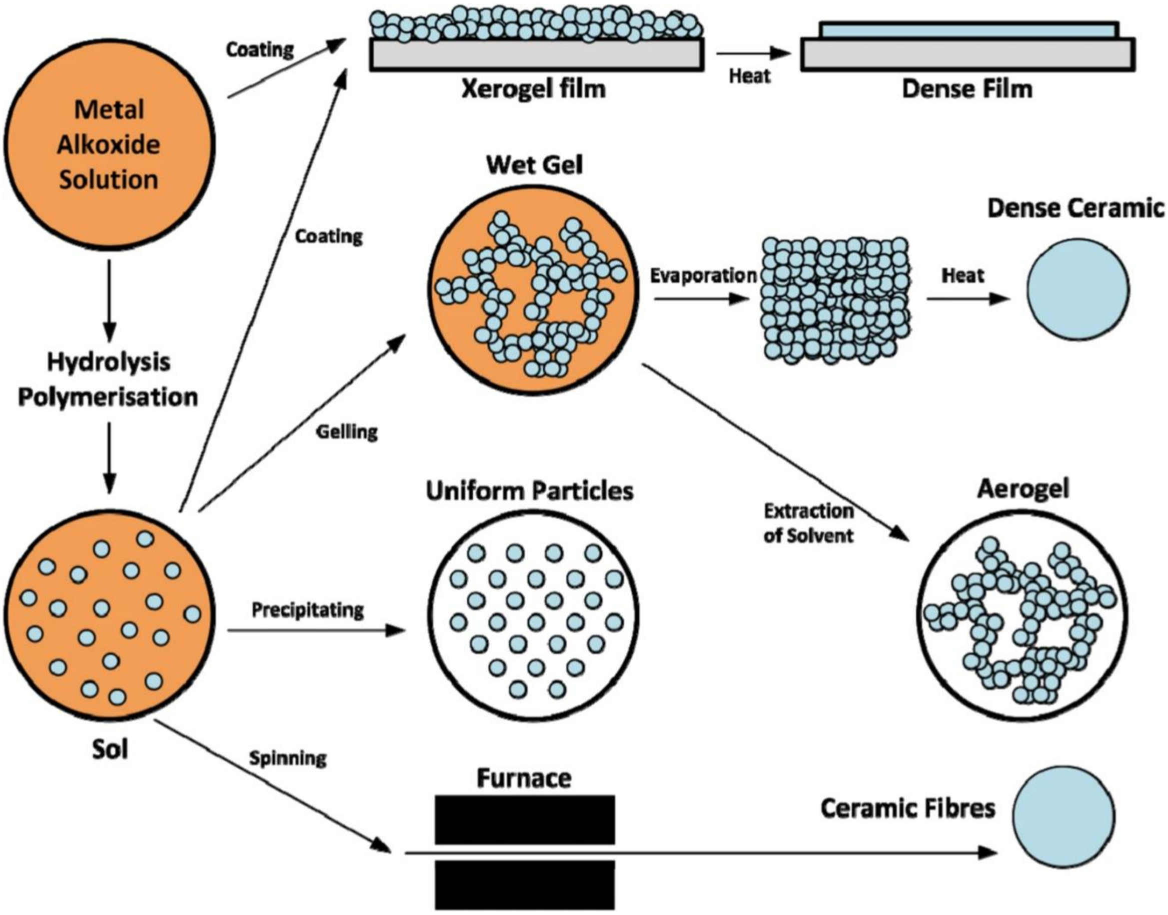


**Figure 2.1** Sol-gel process routes [38]

### 2.1.4.1 Sol-gel Synthesis

The sol-gel process is basically based on two steps. These steps are called hydrolysis and condensation. It is aimed to produce hydroxyl and residual alkoxyl groups together with the hydrolysis of metal alkoxides in the hydrolysis stage. After hydrolysis, polymerization is carried out together with the condensation process to produce a three-dimensional network structure. After these processes, the produced network is passed through some extra processes.

As a result of aging, drying and calcination processes applied to the web, products with different shapes and properties emerge [39].

The most preferred starting reagents (precursor) in sol-gel processes are alkoxides. The general formula of alkoxides is $M_x(OR)_y$. In this formula, the element represented by the letter M and R is the alkoxide group. The number of valence electrons of the element is represented by the letter y. Transition metals have low electronegativity. This means they are electrophilic. Due to their electrophilic properties, transition metals show less stability against hydrolysis, condensation and other nucleophilic reactions.

There are many reasons why the use of alkoxides in sol-gel processes is preferred [39]. Alkoxides are widely used because of the following advantages they provide:

i. Easy to purify: Alkoxides can be distilled to obtain high purity products.
ii. High diversity: There are many different types of alkoxides and they offer quite a few options for obtaining the desired reactivity.
iii. Easy controllability: Hydrolysis and polycondensation processes of alkoxides can be easily controlled.
iv. Suitability for mixed use: Allowing different alkoxides to be used together to determine the quality, homogeneity and stoichiometry of the final products.

### 2.1.4.2 Sol-gel Precursors

Sol-gel chemistry is generally based on the hydrolysis and condensation of metal oxides. However, hydrated metals are also used. Most of the alkoxide-based initiators used in sol-gel processes consist of transition group (Ti, Zr) or p-block (Al, Si) elements. The most important point here is that alkoxide can be prepared in different varieties in accordance with the nature of the metal forming the alkoxide [40].

In sol-gel chemistry, the nature of the initiator and the resulting product depend on many different parameters. One of these parameters is the electronegativity difference between oxygen and metal [40]. For this factor, the ionic character of the M-O bond can be estimated using the partial charge model developed by

Livage et al. Thus, it can be determined how this electronegativity difference may affect the process [41]. Another factor is the electron donating/withdrawal relationship between alkyl/aryl chains and alkoxy groups. These two factors have a direct effect on the gel structure as they affect especially the hydrolysis and condensation chemistry and thus the polymerization. In addition to these factors, volatility and viscosity are also physical parameters that affect the suitability of alkoxides for sol-gel chemistry. Since these parameters have an effect on the viscosity of the solution, that is, the sol, they can also change the stoichiometry and process conditions.

#### 2.1.4.3 Solvent

In the sol-gel method, a medium is needed for the reactions to take place. The components that generates this environment are solvents. Solvents may also be required to homogenize the mixture at the start of the reactions. Properties such as polarity, viscosity and dipole moment of the solvent directly affect the reaction and the final product. The polarity of the solvent is important for the precursor with which it will be used. While polar solvents are used for polar precursors, nonpolar solvents should be used for nonpolar ones. In addition, water is required for hydrolysis to occur, and together with the solvent, water is one of the main components that generate the liquid medium in the sol-gel process.

In sol-gel processes, the liquid medium of the system is usually a mixture of alcohols, water and catalysts. Acids are generally used as catalysts. Evaporation is a phenomenon that needs to be addressed separately as it is directly related to the solvent properties. If evaporation is rapid, cracks, deteriorations, and fractures may be observed in the final product. Evaporation rate also directly affects processes such as agglomeration and condensation that may occur in the system.

#### 2.1.4.4 Catalyst

Acid or base catalysts can be used in sol-gel processes. The reaction mechanisms of these catalysts are quite different from each other. The pH values required for hydrolysis are also very important. At pH 7, hydrolysis is at minimum speed. For condensation, around pH 4.5 shows the lowest limit. Conditions where the pH is less than 5 are preferred for hydrolysis. Hydrolysis and condensation must proceed in equilibrium. Because the rate of consumption of monomers and small oligomers released with hydrolysis by condensation is very important. Fluoride ions and hydroxide ions create similar conditions. The rate of disintegration and re-dissolution of Si-O-Si particles is higher at high pH. While $H^+$ ions determine the condensation rate in conditions where the pH is less than 2, the rate is affected proportionally to the concentration of OH- ions at higher pH ranges. For this reason, the presence of a suitable catalyst is very important in order to determine the rate of the reactions correctly and to provide a healthy hydrolysis-condensation balance.

## 2.2 Organic/Inorganic Hybrid Coatings

It is very important to apply some coatings to metals in order to protect the metals that are used frequently in daily life and all industrial areas where metals are used, especially in the construction, manufacturing, aviation and chemical sectors, and to show better surface properties. First of all, it is desired that the coatings be inert and adhere tightly to the metal substrate [42].

Organic/inorganic hybrid coatings, in which the sol-gel process is frequently utilized, are primarily used to prevent corrosion, friction and wear, as well as to improve the thermal and mechanical properties of metallic surfaces. These coatings form chemical bonds to metal through inorganic sols, thereby increasing the coating's adhesion to metal. Different types of organic polymers or other organic/inorganic substances can also be added to the content of the coating to achieve extra properties [5].

Hybrid coatings are produced from sol formed by mixing organic polymers or organoalkoxysilanes and alkoxides. Sol-gel processes are ideal for producing coatings with a controllable composition and microstructure. Sol-gel process, which is a low-cost and simple method, is based on the M(OR)n hydrolysis and condensation of metal alkoxides. The formation of M-O-P and M-O-Si chemical bonds is very important for the sol-gel layer to have a strong interaction with the metal surface and to show good adhesion performance [5].

Organosilanes improve adhesion at the metal/coating interface. In addition, being relatively environmentally friendly chemicals is one of the reasons why organosilanes are preferred. Today, silicon-based sol-gel chemistry is more advanced than other metal-organic-based precursors [2].

### 2.2.1 Effect of Inorganic Components

The inorganic sol has several major functions. These can be listed as follows:

i. Increasing adhesion between metals and hybrid coating
ii. To act as an adhesion promoter in metal pretreatments
iii. Improving polymer performance in hybrid coatings

Although conventional polymer coatings are mechanically flexible and robust, they have very poor abrasion and thermal resistance. Inorganic sols provide better adhesion between metallic substrate and organic coatings. However, low oxygen diffusion and good mechanical properties are other advantages [2]. In hybrid coating systems produced with sol-gel, van der Waals bonds are first formed between films and metal surfaces. As the films dry, these bonds become stable covalent bonds. Organosilane sols and OH groups react in the formation of hybrid coatings with the sol-gel process. The most critical bond in the connection of the coating to the metal surfaces is the Si-O-M connection.

Another advantage of inorganic sols besides enhancing the adhesion with the metal substrate is that it improves the performance of the polymer. Namely; a film prepared from pure phenolic resol has high crack-forming potential, while a hybrid phenolic resol coating prepared with TEOS is crack-free. Inorganic sols also improve the hardness of the coating.

### 2.2.2 Effect of Organic Components

Inorganic coatings have some disadvantages. The most important of these are the difficulty of obtaining thick coatings without cracks and the formation of porous structures in pure inorganic films. These disadvantages are eliminated by adding organic groups to inorganic sol-gel coatings [2].

In terms of corrosion, these disadvantages cause inorganic films to go beyond being weak physical barriers that cannot provide adequate corrosive protection. Organic components eliminate these disadvantages in two ways. One of them is defect healing and the other is the incorporation of organic components into the structure of inorganic sol-gel films. With organic components, the permeability of inorganic coatings is reduced and generally eliminates defects. For this reason, organic/inorganic hybrid coatings are developed.

However, when organic groups are mixed with inorganic oxides, they lower the surface tension. The essential properties of organic compounds and the organic/inorganic component ratios in hybrid coatings also have very strong effects on the corrosion resistance of hybrid coatings. In addition, while organic components increase the thickness of the coating, they also reduce the curing temperature [3].

Increasing the concentration of organic compounds in hybrid coatings results in the formation of thicker films. However, the high concentration of organic compounds also makes it difficult for the inorganic sol to adhere to the substrate and form a strong bond. For this reason, the concentration balance of organic/inorganic components is very important in hybrid coating production.

# 3
# BORON NITRIDE

Boron nitride is a chemical compound which is produced synthetically and is not found in nature under normal conditions. Boron nitride compounds containing equal amounts of boron and nitrogen atoms can have many different structures due to the special bonding properties of boron and nitrogen atoms. Boron nitride polymorphs are called Hexagonal boron nitride (h-BN), cubic boron nitride (c-BN), and wurtzite boron nitride (w-BN). In the periodic table, boron is in the group III-A and nitrogen is in the group V-A thus, they are adjacent elements to carbon. Due to this adjacence, BN compounds have similar properties with carbon compounds. For example, hexagonal boron nitride shows similar properties to graphite and is called white graphite. Likewise, c-BN has similar properties to diamond. h-BN is very soft and has good lubrication properties due to its low coefficient of friction, but c-BN is the hardest known material after diamond.

## 3.1 Cubic form (c-BN)

Cubic boron nitride is the material with the highest hardness after diamond. In addition, it is a unique material that is widely used in many different fields with its wide band gap, high thermal conductivity, high electrical resistance and chemical inertness. The physical and chemical properties of C-BN and the comparison of these properties with diamond are shown in the Table 3.1 [43].

Since C-BN is the hardest material after diamond, it is used in many areas that require high wear resistance. It is a widely preferred material especially in the production of manufacturing tools and hard protective coatings. However, unlike diamond, c-BN, which is a chemically inert material in an oxygen atmosphere, stands out in this respect. C-BN, which can maintain its chemical inertness even at high temperatures (up to 1573 K), can be used especially in environments requiring contact with ferrous metals.

**Table 3.1** Comparison between c-BN and diamond according to the characteristics [43]

| **Properties** | **c-BN** | **Diamond** |
|---|---|---|
| Density (g/cm$^3$) | 3.48 | 3.52 |
| Bandgap (eV) | 6.4 | 5.5 |
| Dielectric Constant | 4.5 | 5.58 |
| Microhardness (GPa) | 75-90 | 80-120 |
| Bulk Modulus (GPa) | 367 | 435 |

C-BN, which is chemically inert even at high temperatures to iron, cobalt and nickel, where diamond is not used due to its high affinity, is a very suitable material for tool applications in machine tools where ferrous metals are processed. In addition, c-BN is widely used as a protective coating in optical element coatings because it is transparency in wide band gaps.

## 3.2 Wurtzite Boron Nitride

Wurtzite boron nitride (w-BN) is another crystal form of boron nitride. It was first produced synthetically in the 1960s. Its superior properties and potential applications are remarkable. It is a very popular material due to its hardness close to diamond and can replace diamond in some application areas. Besides, w-BN is a promising material for electronic devices with its high thermal conductivity, wide band gap and superior self-polarization properties.

The w-BN produced from hexagonal boron nitride (h-BN) under high pressure tends to return to the h-BN phase after the pressure is released. The most common method of producing W-BN is the compression method of h-BN, which can produce only $\mu$-sized w-BN particles. It is very difficult to synthesize bulk crystals of W-BN. This is because the semi-stable high-pressure phases cannot be stabilized efficiently [44].

## 3.3 Hexagonal Boron Nitride

### 3.3.1 Properties of Hexagonal Boron Nitride

Hexagonal boron nitride is called white graphite because of its crystalline structure that is in a hexagonal layered structure like graphite and has graphite-like properties. While the boron and nitrogen atoms that generate h-BN are bonded with strong covalent bonds and the layers are held together by weak van der Waals forces. Having different bonding types in both directions causes many properties of h-BN to show anisotropy. Although the B-N bonds forming the planes have dominant covalent bonds, they exhibit partial ionic behavior due to the high electronegativity difference between them (2.04 for B, 3.04 for N). Figure 3.1 shows crystal structure of h-BN and give information about the distance between atoms and layers. Compared to graphite in terms of electrical conductivity, h-BN shows less conductivity and has higher mechanical stiffness due to the increased interaction between its layers. The higher electronegativity of nitrogen than boron leads to the presence of the $\pi$-electron in nitrogen, so h-BN is an electrical insulator with a wide bandgap. Table 3.2 shows the characteristics of h-BN.

**Table 3.2** Characteristics of h-BN [15]

| **Properties** | **Values** |
|---|---|
| Density (g/cm$^3$) | 2.27 |
| Melting Point (°C) | ~ 3000 |
| Coefficient of Friction (N) | 0.15-0.70 |
| Stability Temperature (°C) | 1000 (in air) |

h-BN is a highly stable ceramic, thus it is stable up to 1000 °C in air, 1400 °C under vacuum and can be used up to 2800 °C in inert atmosphere. The advanced properties of h-BN such as high thermal stability, high hardness, high thermal conductivity and high corrosion resistance make it a sought-after material for many structural and electronic applications. Especially due to its low coefficient of friction, h-BN powders and films are widely used in many applications that require lubricating properties. However, it can be used in liquid in the production of dispersions with lubricating properties as well. h-BN is one step ahead when compared to graphite when it is used as a lubricant in oxidizing atmospheres up to 900 °C and at extremely low temperatures.

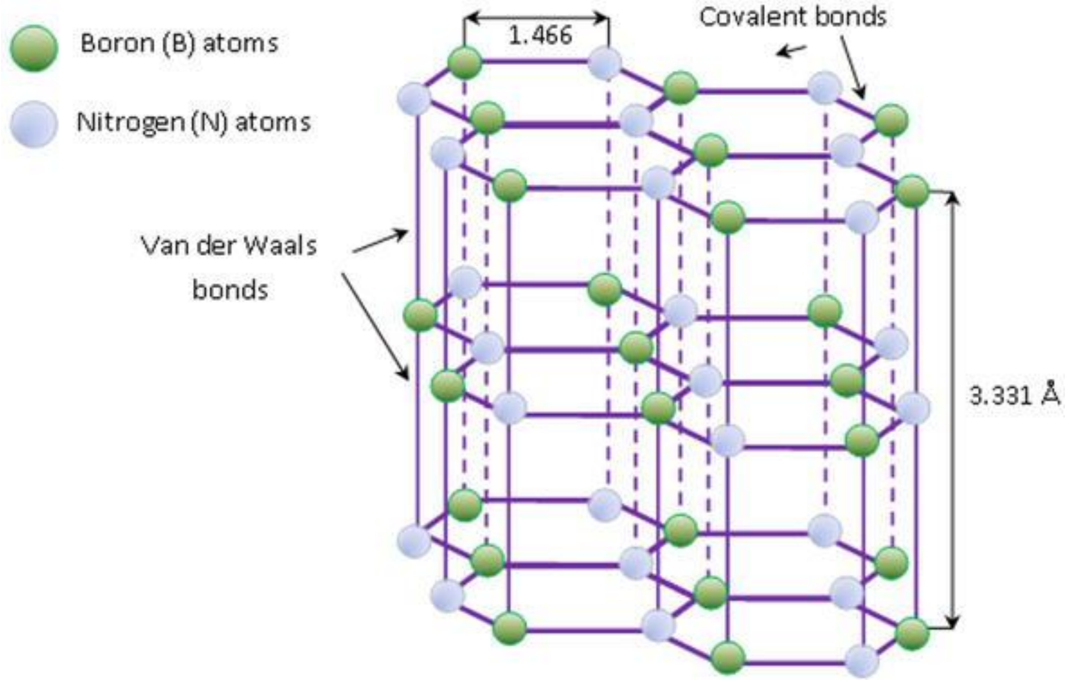


**Figure 3.1** The crystal structure of h-BN [45]

In addition, h-BN is a very suitable material for various applications in the electronics industry due to its high insulating and dielectric properties as well as high thermal conductivity. It has a dielectric strength approximately 4 times higher than alumina and it can be considered as a good insulator with this feature.

Due to its high lubricating properties, h-BN is used as a mold release agent in metal casting applications, as well as added to anti-wear oils as an additive. h-BN, which stands out from other electrical insulators due to its high thermal conductivity and low thermal expansion, is preferred as a load leakage barrier for electronic devices and equipment thanks to these features. Another feature of h-BN can be indicated that it does not react with molten metals and does not get wet. In this way, pyrolytic h-BN can be used in crucibles, linings and covers of heating elements. Besides, it is a very suitable material to increase the corrosion resistance of the tools in addition to benefiting from its lubricating property in order to prevent the wear of the manufacturing tools used in the steel and iron industry.

### 3.3.2 Synthesis of h-BN

Boron nitride is a synthetically produced ceramic material and is not found inherently in nature. BN was first synthesized by Balmain in 1842. This synthesis was based on the reaction of boric acid with potassium cyanide. However, due to the fact that this synthesis method had some technical difficulties and the used materials are high cost, it was only in the 1950s that BN became a commercial product [15].

Today, three main methods are used for the production of h-BN on an industrial scale[15,53]. Figure 3.2 shows boron nitride production processes schematically. These methods are the reaction of boric acid with ammonia [15], the carbothermic method [46], and the reaction of nitrogenous compounds such as urea or melamine in boron-containing materials such as boric acid [55].

It is estimated that the h-BN market in the world is approximately 700 million USD. The main producers and users are the USA, China, Japan and Germany.

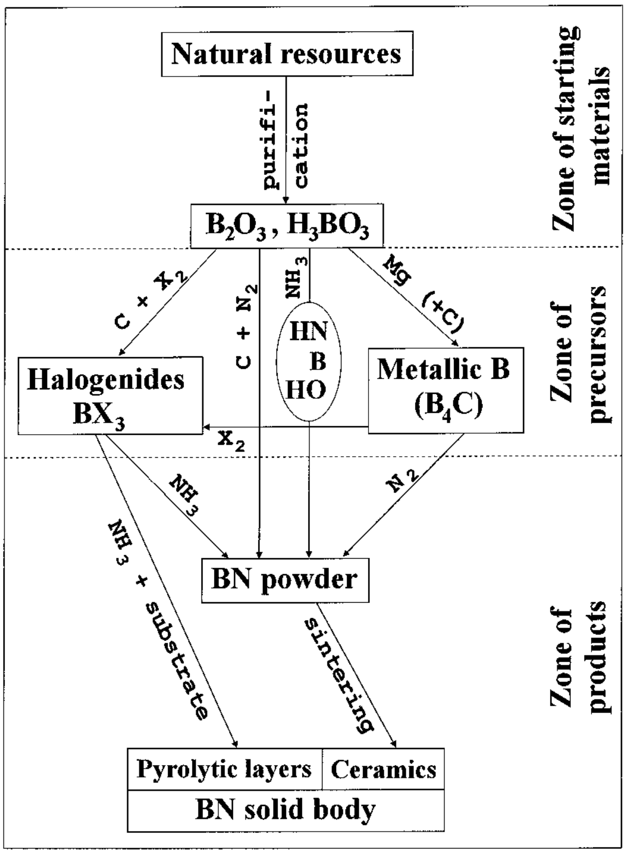


**Figure 3.2** Boron nitride production processes [49]

#### 3.3.2.1 Reaction of Boric Acid or Boric Oxide with Ammonia

This reaction occurs when boric acid and ammonia react in the presence of an inert carrier. These carriers are usually calcium phosphate ($Ca_3(PO_4)_2$) or $CaCO_3$. These reactions, which do not require very high temperatures, are usually carried out above 900 °C. Carrier particles allow the reaction to take place quickly. The boric acid solution wets the carrier particles, allowing to increase the surface area required for the reaction. If the carrier is absent, the reaction will occur rather slowly, since the boric acid solution has a very low surface area. After the reaction, the carrier is leached and removed using dilute acid solution.

The synthesized BN has an amorphous structure. This is because the reaction takes place at a low temperature. In addition, the product contains oxygen impurities. A second process is required to bring the product to a hexagonal structure and to remove oxygen impurities. As a result of this process, which is carried out at 1500 °C under nitrogen gas and h-BN is obtained [47]. In the equation below, the boron nitride production reaction is roughly seen as the reactants and the products released as a result of the reaction.

$$H_3BO_3 + NH_3 = BN + 3\ H_2O \tag{3.1}$$

#### 3.3.2.2 Reaction of Boric Acid with Nitrogen-Containing Organic Substances

Another important method in the production of h-BN is the synthesis of boric acid or alkali borates by reacting them with nitrogen-containing organic compounds such as urea, melamine, amides, cyanides and cyanamides [55] . The reaction of boric acid with urea is shown in the equation below.

$$B_2O_3 + CO(NH_2)_2 = 2\ BN + CO_2 + 2\ H_2O \tag{3.2}$$

In this method, the starting materials are first mixed at 300 °C and pre-reacted. Then, the reactions continue above 900 °C in a nitrogen atmosphere. They are removed from the environment by removing oxygen impurities and by washing with methanol or dilute acid solution at temperatures above 1500 °C with unreacted material. Following all these, a crystallization process is performed [15].

While investigating the method of producing h-BN by reacting boric acid with nitrogenous organic compounds, the effects of many different catalysts on the reactions were investigated. CaCO3 was used in one of these studies. CaCO3 was added to the initial mixture formed by melamine and boric acid and it was fired at 1800-2100 °C. As a result of the studies, it has been reported that h-BN powder with high crystallinity and low specific surface area can be produced with this method. The advantages of large grain size and high crystallinity are improved lubrication, electrical insulation and stability at high temperatures [46].

In another study, Hubacek et al. investigated the effect of copper on h-BN crystallization. Copper nitrate was used during the studies. The data obtained in experiments in which turbostatic boron nitride (t-BN) was kept under nitrogen atmosphere at 1950-2150 °C show that the grain size and crystallinity of h-BN improved significantly. As a result, it has been shown that copper improves the crystal growth of h-BN [50].

#### 3.3.2.3 Carbothermic Method

The carbothermic synthesis method is the most widely used industrial method in h-BN production [46]. Carbothermic reduction processes are processes commonly used to produce compounds such as carbides, borides, and nitrides. To produce the desired nitrides, nitriding can be applied by performing the processes in a nitrogen atmosphere during carbothermic reduction [43]. Carbothermic reactions have several advantages over melamothermic reactions. The most important of these is that by-products such as CO, which are released as a result of carbothermic reactions, are in gaseous state and are easier to remove from the system during processes. On the other hand, ,n melamothermic reactions, leaching is often required to remove metal oxides that occur as a by-product.

In this method, boric acid is reduced with carbon in the presence of pure nitrogen gas. The process is carried out at temperatures above 1200 °C [51].

Many studies have been carried out to investigate the mechanism of production of h-BN by carbothermic reduction reaction. One of these studies belongs to Pikalov [50]. As a result of Pikalov's study, he thought that the reduction nitriding steps occurred separately in the formation of h-BN. According to this claim, boric acid is first reduced by carbon to form boron carbide as a by-product.

$$B_2O_3 + 7\,C = B_4C + 6\,CO \tag{3.3}$$

The formation of h-BN then occurs as a result of the reaction of boron carbide and boric acid in the presence of nitrogen.

$$3\,B_4C + B_2O_3 + 7\,N_2 = 14\,BN + 3\,CO \tag{3.4}$$

The demand for h-BN in industry is increasing. The most sought after properties are high lubricity and high thermal stability. In order to have these properties, boron nitride must have large grain sizes and high crystallinity. The two boron nitride synthesis methods described earlier require very high production temperatures and the particle size of the resulting product is also very small. For this reason, it becomes very important to increase the reaction rate and particle size in h-BN production. Many studies are carried out for this purpose. Bartnitskaya et al. investigated the effect of adding $Li_2CO_3$ on h-BN synthesis in a study they conducted. As a result of this study, they showed that the addition of $LiCO_3$ increased the crystallinity of h-BN and had a positive effect on the synthesis of h-BN with the desired properties [41,59]. In another study, Çamurlu et al. investigated the addition of $CaCO_3$ in h-BN production. As a result of the experiments, they determined that the optimum amount of $CaCO_3$ to be added is 10% by weight. It was observed that the h-BN particles produced by the addition of $CaCO_3$ had larger dimensions. At the same time, as a result of processes using $CaCO_3$ addition, 50% higher amount of h-BN production was observed compared to processes without $CaCO_3$ [52,54].

The effects of alkaline earth oxides and carbonates, which are easily available due to their low costs, on the carbothermic synthesis of h-BN have been investigated by many different studies [55].

# 4

# EXPERIMENTAL STUDIES

## 4.1 Materials

Within the scope of this study, necessary experiments were carried out with the aim of producing an organic/inorganic hybrid coating with h-BN filling. The effect of the change in h-BN ratios on the properties of the coating was investigated in the coatings produced using the sol-gel method.

The materials to be used in the experiments were selected in accordance with the sol-gel process. These materials and their amounts that are used in coatings are shown in Table 4.1.

**Table 4.1** Materials and their amounts in coatings

| Materials | Molar Mass (g/mol) | Amount (g) |
|---|---|---|
| MTMS | 136,22 | 28 |
| CS | 60,08 | 15,02 |
| Water | 18 | 9,25 |
| IPA | 60,1 | 12,02 |
| Acetic Acid | 60,052 | 1,6 |

One of the two main materials that make up the sol is methyltrimethoxysilane (MTMS, $C_4H_{12}O_3Si$). The main task of MTMS obtained from Wacker company in the process is to provide adhesion with the metal surface. Colloidal silica, another silica-based product, was also used to complete the polymer matrix.

While 70% of the colloidal silica used is water, 30% is composed of silica particles. Colloidal silica from AkzoNobel reacted with MTMS to form the polymeric structure of the coating. However, colloidal silica also provided other benefits, such as increased surface film hardness and greater adhesion.

The catalyst used to accelerate the chemical reactions of the process is acetic acid. The concentration of the acid taken from the company Isolab is 99%. Strong acids are used as catalysts to accelerate polymerization in sol-gel processes. Isopropanol (IPA) was preferred to adjust the viscosity of the solution and to provide a solvent environment for the chemicals to react. The IPA used in the experiments was purchased from Shell Chemicals.

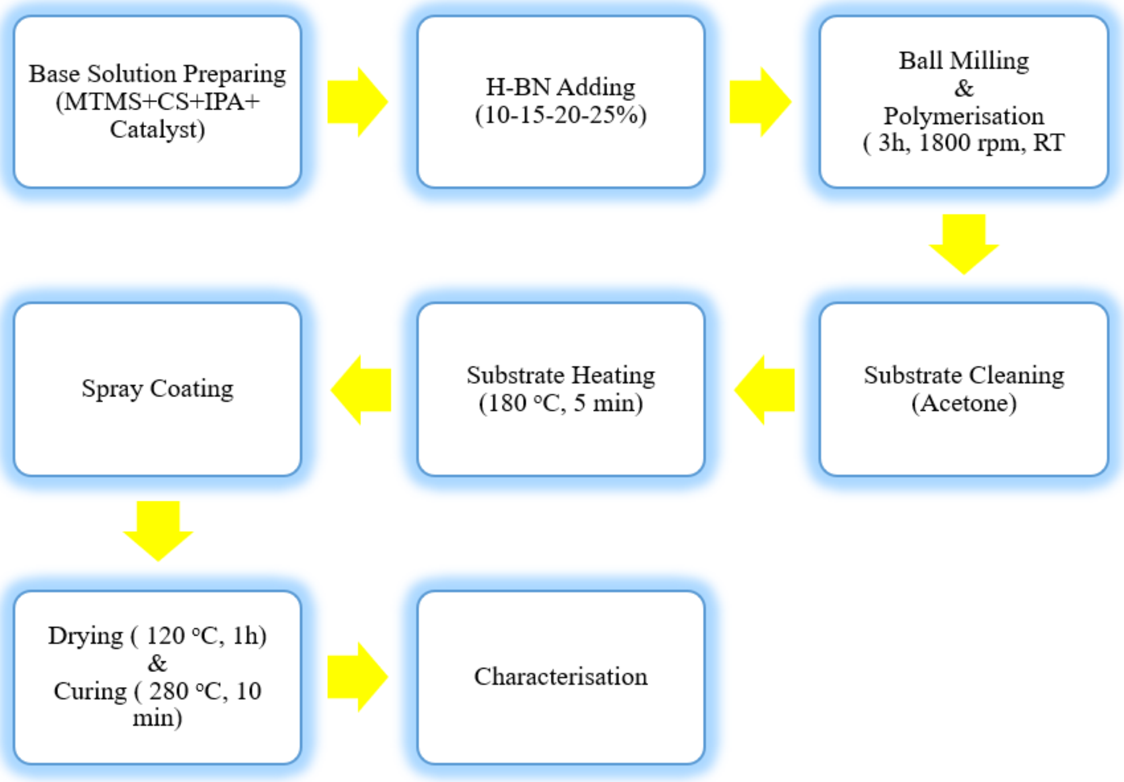


**Figure 4.1** The basic illustration of coating preparation and coating processes

In accordance with the main purpose of the study, h-BN powders were also added to the solution. These h-BN powders added to the solutions at different rates are labeled H.C Starck. The average particle size of these powders, which have 99% purity, is 10 $\mu$m.

In addition to all these listed materials, the aluminum plates on which the coatings are produced are also among the test materials. Coatings were applied to these 1050 aluminum alloy 10 cm*20 cm*1 cm aluminum plates and the necessary tests and analyzes were carried out while the coatings were on these plates.

## 4.2 Coating Process

Firstly, the solution to form the coating was prepared. MTMS, and Colloidal silica were sequentially added to the mixer to form the polymer matrix. For proper polymerization, it is necessary to adjust the pH of the solution. For this, acetic acid was added. Then, isopropanol was added to the solution to control the solution viscosity. All these additions were performed without any time in between by sequencing colloidal silica, acetic acid, MTMS and IPA. After the solution liquids were added, h-BN was added to the solution in a weight appropriate to the amount of h-BN to be used in the coating. h-BN powders were added by calculating 10-15-20% and 25% of the total weight of the materials forming the coating. Zirconia balls were used to grind h-BN powders. This grinding process, which was carried out simultaneously with the polymerization, continued with the polymerization at 1800 rpm for 3 hours at room temperature. Figure 4.1 demonstrates the steps of solution preparation and coating process.

After 3 hours, the solution was removed from the mixer and the aluminum plates were coated. The plates were cleaned with acetone before coating and preheated at 180 °C for 5 minutes before starting the coating process. Preheating has a positive effect on the adhesion of coatings. It can be seen that the solution of coating in the Figure 4.2 and Figure 4.3 shows the oven that used drying and curing processes.

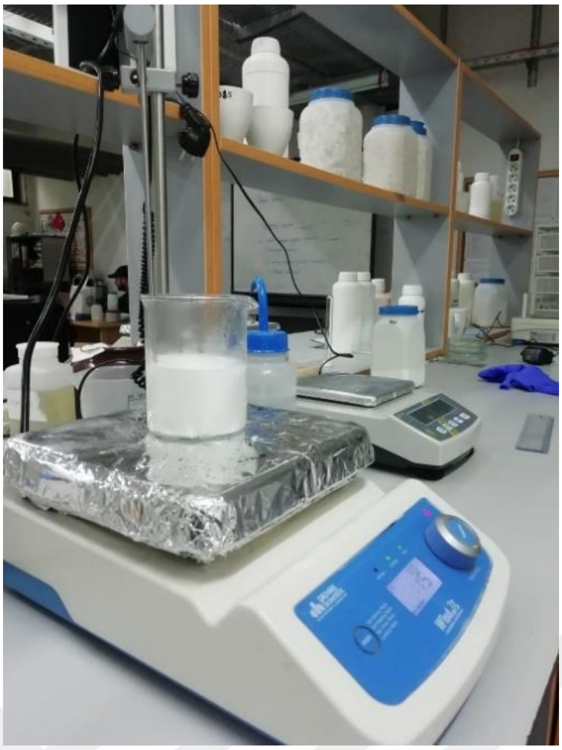


**Figure 4.2** The coating solution and stirring equipment

The plates were then coated by spray coating method at room temperature. After the coating process, the plates were dried at 120 °C for 1 hour and at 280 °C for 10 minutes. The coated samples were left in an air atmosphere at room temperature for 12 hours before the characterization processes.

**Figure 4.3** Electro-mag M 5040 P oven

# 5

# CHARACTERIZATION STUDIES

## 5.1 Chemical Analysis

Various test methods have been applied to investigate the properties of coatings. Fourier Transform Infrared Spectroscopy (FTIR) studies of solutions before and after coating were performed using a PerkinElmer Spectrum Two FTIR instrument. This device can be seen at Figure 5.1 below. With this analysis, it was investigated whether the expected reactions took place in the solution and whether the coating adhered to the substrate after the coating application.

**Figure 5.1** PerkinElmer Spectrum Two FTIR instrument

## 5.2 Hydrophobicity

The relationship between the hydrophobicity of the thin films and the h-BN content was investigated using a Biolin Scientific ThetaLite101 contact angle measuring instrument which is showed in Figure 5.2. For this test, water drops with an average radius of 5 mm and deionized water were used. Measurements were made for each thin film for 10 seconds and 3 times with 1 second intervals, and the average results were taken into account. h-BN is a hydrophobic material and with this analysis, it was investigated whether it could impart its hydrophobicity to the organic/inorganic hybrid coating.

**Figure 5.2** Biolin Scientific ThetaLite101 contact angle measuring instrument

## 5.3 Surface Morphology

Surface morphology was observed by scanning electron microscopy (SEM) using Phenom Pro X (Desktop SEM). The distribution of h-BN particles in the coating was investigated under 15 kV voltage.

## 5.4 Coefficient of Friction

Ball on disc method was used to examine the friction coefficients of the coatings. In this method, in which the friction coefficients are determined using the CSM tribometer device, the friction coefficients are measured at different time intervals. Measurements were performed under 1N and a duration time of 26 minutes per 2500 rounds of sample.

## 5.5 Hardness and Adhesion

Pencil hardness and ASTM D3359 adhesion test methods were applied to measure the hardness and adhesion properties of thin films.

# 6

# RESULTS AND DISCUSSIONS

## 6.1 Hydrophobicity

In general, there are two main factors on which the wettability of a surface depends. These factors are chemical composition and microstructural geometry. For this reason, there are two ways to create non-wetting surfaces with high contact angles. One of these ways is the chemical functionalization of the surface with materials with low surface free energy and the other is the creation of micro or nano scale roughness on the surface. This can be explained by the superior hydrophobicity of nanostructured h-BN films, despite the fact that h-BN coatings without nanostructural features are hydrophilic surfaces.

Many hydrophobic and superhydrophobic coatings have been developed so far. These coatings are produced using organic materials with low surface free energy such as silicone-based hydrocarbons, fluorinated polymers and fluorohydrocarbons. However, most of these materials cannot be applied in harsh environments, especially at high temperatures. h-BN, on the other hand, can play a role in solving this problem with its high thermal stability and melting temperature.

However, hydrophobic coatings can be used in many fields such as optics, microelectronics, photoelectricity and biomedicine. The production of nanostructured surfaces is very valuable for these fields [56]. Hydrophobic films to be produced from materials with high hydrophobic nanoparticles such as h-BN will be very useful for modern science and technology.

Although the hydrophobicity and wettability of h-BN are promising for many application areas, some difficulties encountered in the production of high quality h-BN films make it difficult to work on these films. So far, the wettability of h-BN has generally focused on vertical h-BN nanosheets and compact h-BN nanotube films. Although the water contact angle of h-BN films is theoretically estimated as 86°, due to the problems encountered in coating methods such as pulsed laser deposition and magnetron sputtering, very low contact angles of 50° can be encountered in applications made with these methods. The absence of normal dipoles in the polar B-N bonds ensures that the h-BN surfaces have a wettability comparable to graphene [57].

Hexagonal boron nitride is a material known with its hydrophobic structure. It does not get wet not only with water but also with molten metals. Due to this feature, it is used as a mold release agent in casting processes [58]. The effects of h-BN on the hydrophobicity of the coatings produced within the scope of this study were also investigated. This characterization process has been given importance in order to identify possible application areas where coatings can be used. The contact angle of the liquid with the surface is very important in the measurement of hydrophobicity. In this test with water, surfaces with a contact angle of $h > 90°$ are said to be hydrophobic [59].

The hydrophobicity of the produced coatings was investigated by a water contact angle measurement test. The contact angles of all these coatings with different amounts of h-BN were measured with the same method and compared. Deionized water drops with an average radius of 5 mm were used for this test. The measurements were repeated three times at 1 s intervals, with a measurement of 10 s for each thin film, and the average results were taken into account.

Hydrophobicity interacts with two main factors. These elements are surface energy and roughness [60]. All coatings produced within the scope of the study have exactly the same composition, except for the h-BN ratios they contain, and the production processes are exactly the same. For this reason, the fact that the coatings have different degrees of hydrophobicity from each other can be directly related to their h-BN content.

H-BN has a hydrophobic structure due to its low surface energy [61]. As the h-BN ratio increases in the produced hybrid coatings, it can be said that the hydrophobicity increases, as h-BN reduces the surface energy of the coating. In addition, it can be thought that the h-BN ratio increases, the roughness of the powders will increase and this will increase the contact angle.

As seen in Figure 6.1, the hydrophobicity of the coatings increased as the h-BN ratio increased. The lowest contact angle (89.5) is at 10%, where the h-BN ratio is the lowest, while the highest contact angle (114.75°) is at 25%, where the h-BN ratio is the highest. However, it is also seen that the most dramatic increase in the contact angle occurred when the h-BN ratio increased from 20% to 25%.

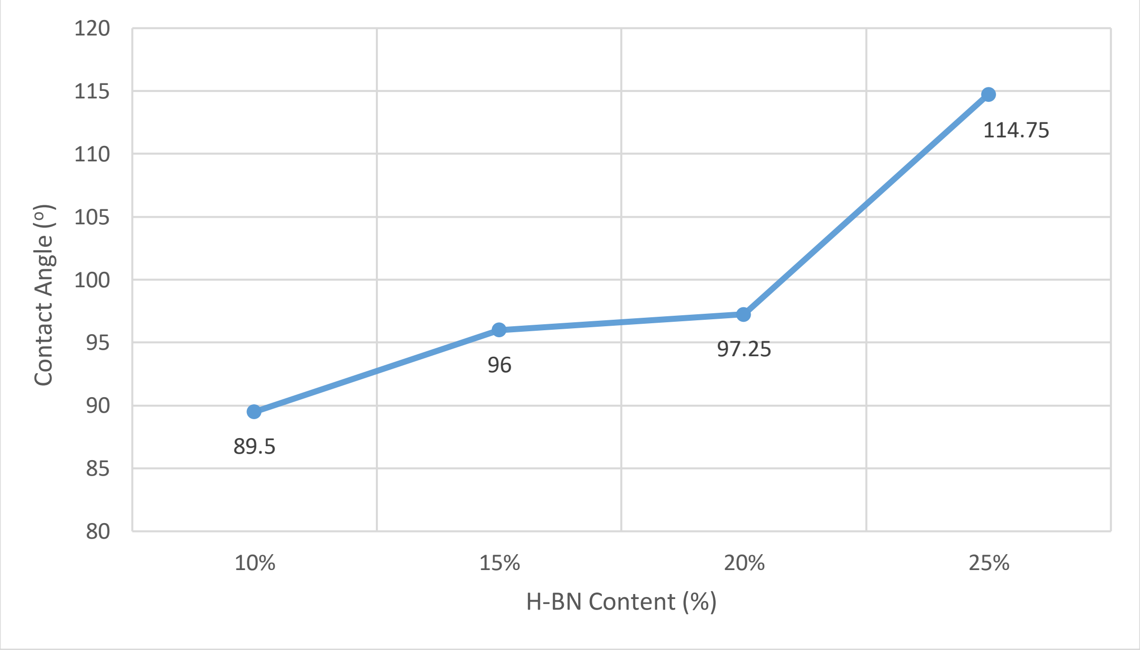


**Figure 6.1** Correlation plot between contact angle and h-BN content

## 6.2 FTIR Analysis of Coating Matrix

Conversion of Si-OR- and Si-OH containing compounds to siloxane compounds is the main chemical principle behind silica-based sol-gel processes [25-27]. In order to obtain a stable gel, the number of silanol (Si-OH) and alkoxy (Si-OR) groups should be minimized while the number of siloxane (Si-O-Si) bonds should be maximized. The realization of all these processes is based on only two basic steps. These steps are called hydrolysis and condensation. Hydrolysis and condensation, which are the basic steps of the sol-gel process, can be described by the following three equations.

$$\text{Si-OR} + H_2O = \text{Si-OH} + \text{ROH (Hydrolysis)} \tag{6.1}$$

$$\text{Si-OH} + \text{Si-OR} = \text{Si-O-Si} + \text{ROH (Condensation)} \tag{6.2}$$

$$\text{Si-OH} + \text{Si} = \text{Si-O-Si} + H_2O \text{ (Condensation)} \tag{6.3}$$

Figure 6.2 shows the hydrolysis of MTMS, the first step of the reactions involved in this study.

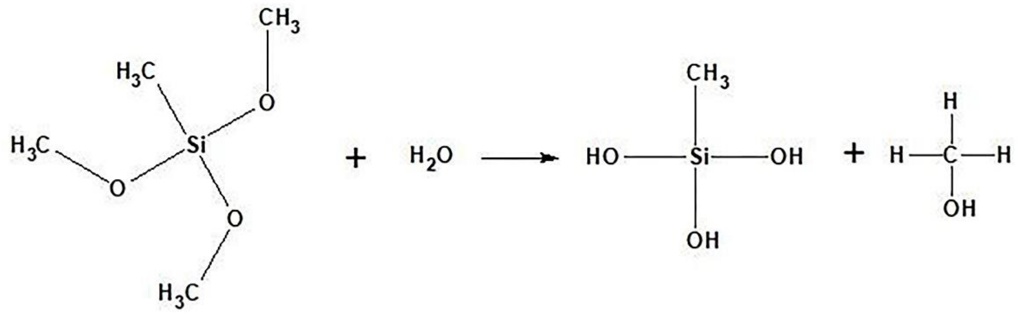


**Figure 6.2** Hydrolysis of MTMS

Previously, Si-OR groups must show hydrolysis reactions in order to form Si-OH groups required for condensation in alkoxide-based systems. Reactive groups must be formed in the first step of the reactions. However, later on, the formation of Si-O-Si bonds with condensation occurs with the release of water or alcohol [29,30].

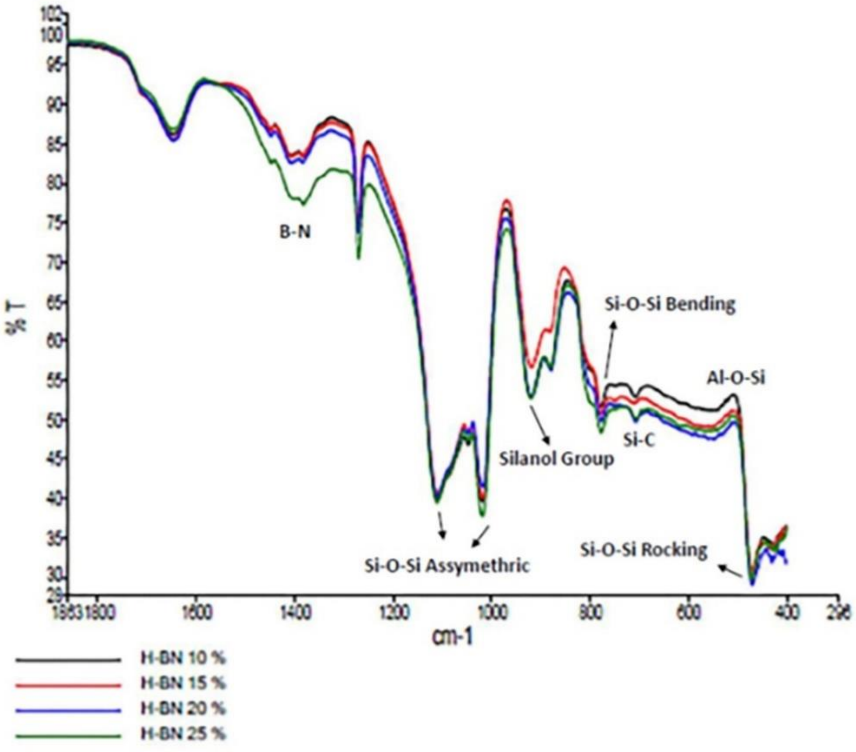


**Figure 6.3** FTIR curves of the coatings with different amount of h-BN

Hydrolysis is the name of the process in which water breaks down into $H^+$ and $OH^-$ ions, as well as the materials it reacts with. Hydrolysis can also be considered as the breakdown of a chemical bond that releases water [59,64,68]. Condensation is a chemical process in which two molecules react to form a larger molecule. The reaction usually produces a by-product such as $H_2O$ or HCl. Condensation processes consisting of chain condensation reactions are called polymerization [64,65].

In this study, thin film coatings with different h-BN ratios were produced and characterization processes were carried out. It has been tried to find out whether the thin film coatings formed by FTIR analysis adhere to the substrate surface at a high degree and whether the hydrolysis and condensation processes that are expected to occur during the production of the film coatings take place. FTIR analysis produces peaks at different wavelengths as seen in Figure 6.3. Firstly, by looking at the literature studies, it is tried to find the bonds in the sample according to the wavelengths at which these peaks occur. Figure 6.3 shows the peaks and wavelengths of thin-film coatings produced according to different amounts of h-BN. As seen in the figure, all the peaks show parallelism. From this, it is understood that the expected reactions occur in all processes and the thin film coatings show the same behavior in terms of adhesion to the substrate.

Chemical bonds, changes in bonds and properties of bonds were investigated by analyzing thin film coatings solutions produced using h-BN, MTMS, colloidal silica, acetic acid and isopropanol and coating samples obtained after the coatings were cured at 120 °C.

The overlapping of the curves shows the consistency of the solutions and also reveals that the differences in different h-BN ratios in the solutions have no effect on the reactions. The most important bonding mechanism in sol-gel coatings is Si-O-Si bonds. The formation of these bonds proves the successful production of polymer chains. In the FTIR analysis, two different peaks are seen at 1050 $cm^{-1}$ and the accompanying 1150 $cm^{-1}$. These peaks indicate Si-O-Si asymmetric stretching mode bonds [63]. Peaks of different modes of Si-O-Si bonds occur at different wavelengths. There are Si-O-Si bending mod bonds at

800 cm$^{-1}$. The peak at 480 cm$^{-1}$ indicates the rocking vibration of Si-O-Si bonds [70,71].

The FTIR analysis plot in Figure 6.3 shows the existence of many other links. For example, the peak point around 850-900 cm$^{-1}$ indicates the presence of silanol groups [66]. However, the intensity of this peak is low. Si-C bonds are also one of the very important bond types. The peak seen at wavelengths of about 750 cm$^{-1}$ indicates the presence of these bonds [67].

However, the peak at a wavelength of 1376 cm$^{-1}$ is also very important. This peak indicates the bond between boron and nitrogen atoms. The presence of this bond is very important in order to show the h-BN powders maintain their stability in thin-film matrices [51].

In addition, one of the bonds expected to be seen in the FTIR analysis is Al-O-Si bonds. This type of bond is critical because, it provides evidence of adhesion of the thin film to the aluminum substrate. When the FTIR analyzes of the samples taken from the coated aluminum plates were performed, the presence of these bonds in each h-BN ratio was shown. Al-O-Si bonds have a peak at a wavelength of 521 cm$^{-1}$ [68]. As seen in Figure 6.3 in all samples taken, peaks were obtained at this wavelength and it was proved that thin film coatings adhered to aluminum substrates with the presence of Al-O-Si bonds.

## 6.3 SEM Analysis

In order to examine the surface morphology of thin film coatings and to investigate the distribution of h-BN powders in the matrix, the coatings were examined by SEM device. Figures below shows SEM images of four different coatings with different h-BN contents. There are no defects or crack formation that were observed in the naked eye examinations of the coatings. However, for a detailed examination, SEM analysis was performed and some defects in the form of cracks and pores were observed in the coatings. The yellow signs at the figures are indicated agglomerations, pores and cracks.

Figure 6.4 shows the SEM analysis image of the thin film with 10 % h-BN content. As seen in the figure, there are some pores on the film surface. In addition, silica and h-BN particles from colloidal silica formed agglomerations. These agglomerations negatively affected the homogeneity of the h-BN particles dispersed in the matrix. It can be said that the pores seen in the thin film coating may have occurred due to the inhomogeneity of the h-BN particles and the evaporation of the solvent during curing.

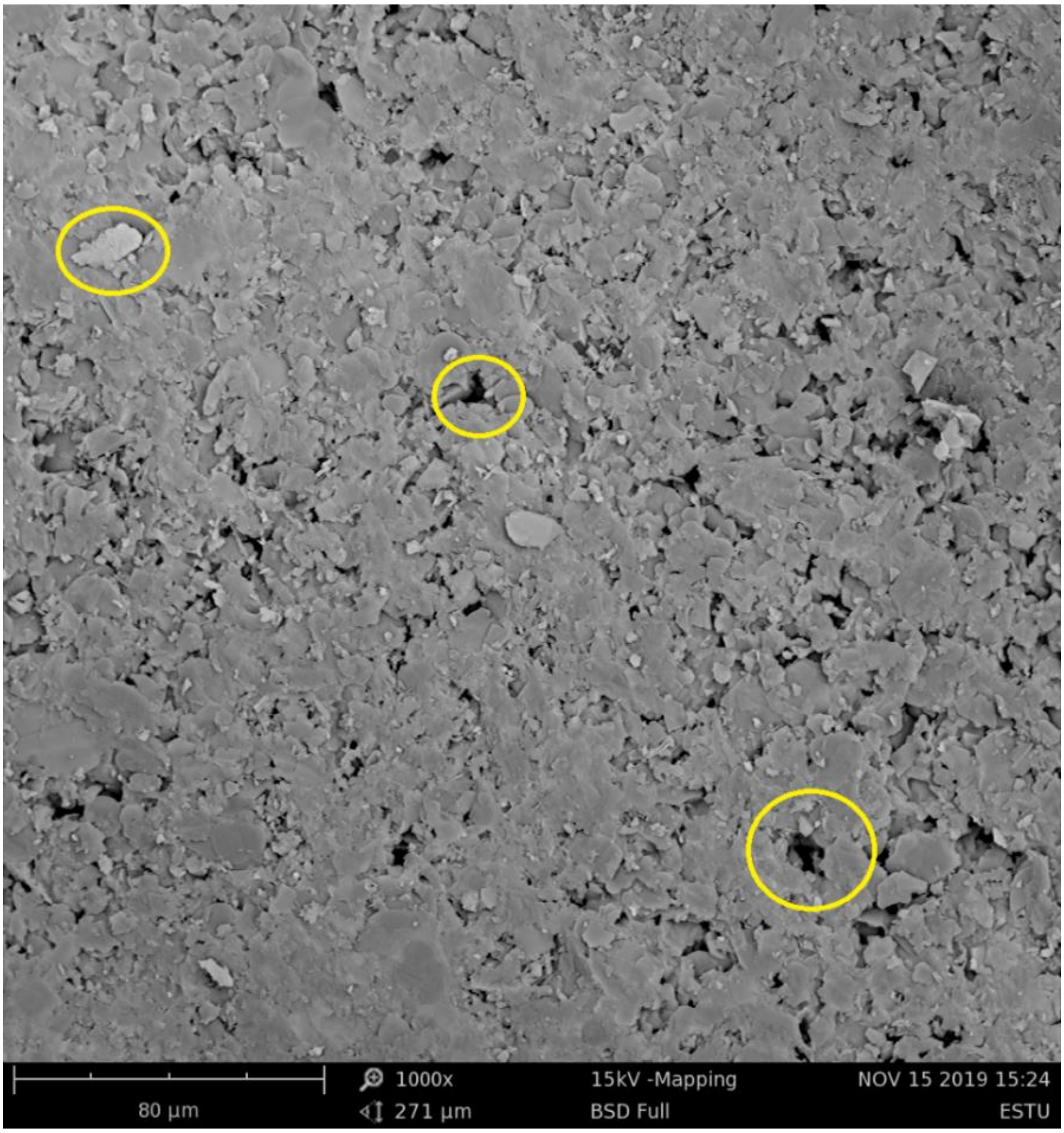


**Figure 6.4** The SEM image of 10 % h-BN ratio coating

As seen in the analysis results, the surface of the thin film coating with 15% h-BN content seems smoother. Figure 6.5 is the SEM image of this film. Cracks on the coating are clearly visible in the SEM analysis. Despite this, it can be said that the film with 15% h-BN content has less pores and agglomerations than the film with 10% h-BN content, and the resulting agglomerations and pores are reduced in size.

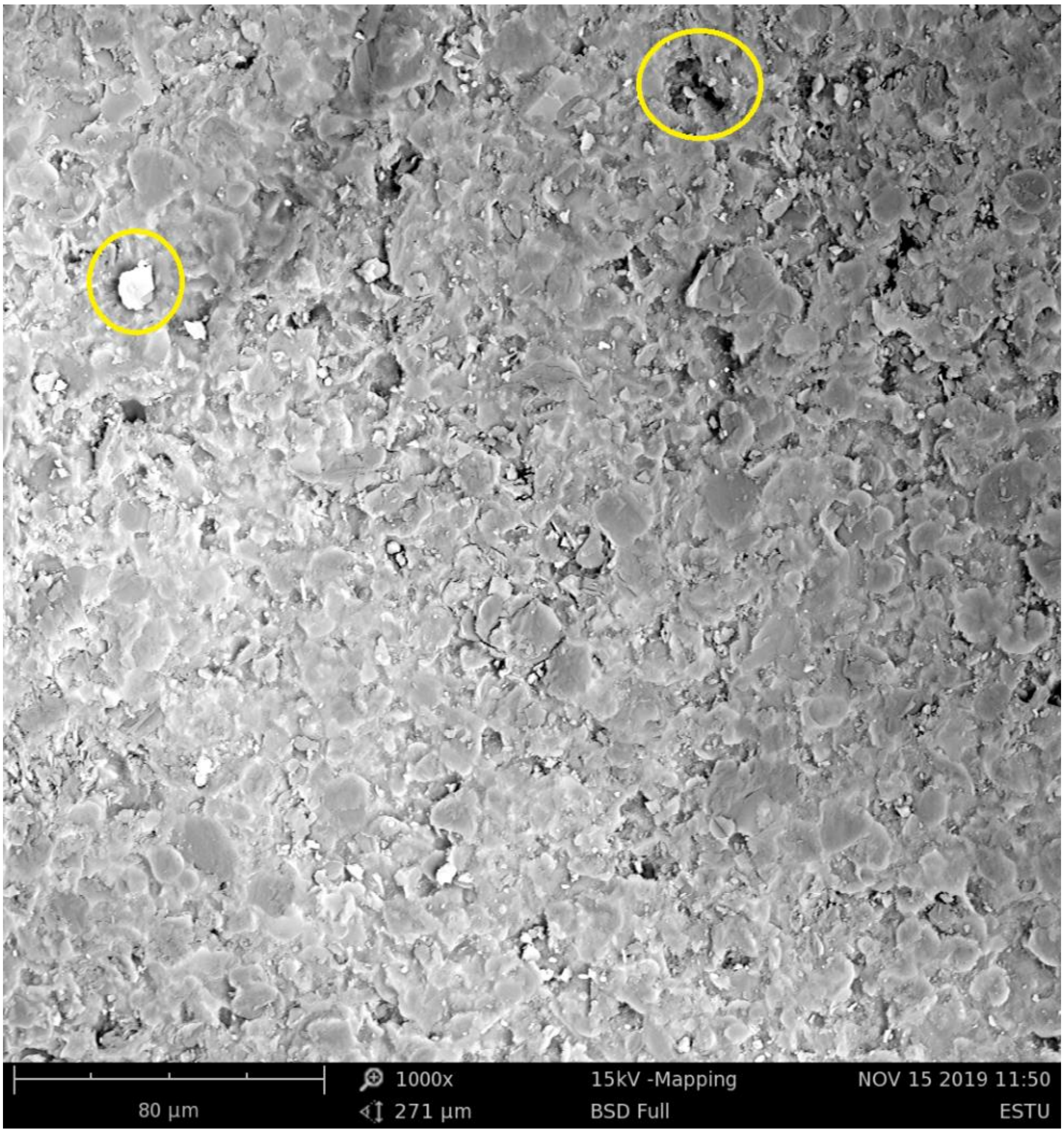


**Figure 6.5** The SEM image of 15 % h-BN ratio coating

Figure 6.6 shows the SEM analysis image of the thin-film coating with 20% h-BN. There are no cracks in the coating as seen in the figure. However, few pores and agglomerations are observed. However, these are very few compared to coatings containing 10% and 15% h-BN in number and density. This clearly shows that a smoother surface morphology is observed in coatings with an increased h-BN ratio. As a matter of fact, the results of SEM analysis of the coating with 25% h-BN ratio are even better.

Although there is no significant difference in pore sizes and amounts between thin films with 20% and 25% h-BN ratio, it is seen that there is a decrease in agglomerations. However, it is clear that the thin film with 25% h-BN content has a more uniform surface morphology as shown in Figure 6.7.

**Figure 6.6** The SEM image of 20 % h-BN ratio coating

Various amounts and sizes of pores and agglomeration were observed in all the coatings examined. However, although the thickness of the films remained constant with the increase of the h-BN ratio, there was a noticeable decrease in both the number and size of the pores and the agglomerations.

From this point of view, it can be concluded that increasing the h-BN content reduces agglomeration and porosity and increases homogeneity. The reason for this phenomenon is the effect of h-BN on the adhesion of thin films to the aluminum substrate. As will be mentioned later, it was observed that the coating adhered to the substrate with the presence of h-BN particles, and the coating without h-BN could not adhere to the substrate. It can be said that the heat resistance of H-BN is higher than that of the polymer matrix, allowing the coatings to adhere to the substrate without deterioration. Thus, the coating matrix has a better phase stability and agglomeration does not occur in the h-BN particles. As a result, higher homogeneity and a smoother surface morphology are obtained.

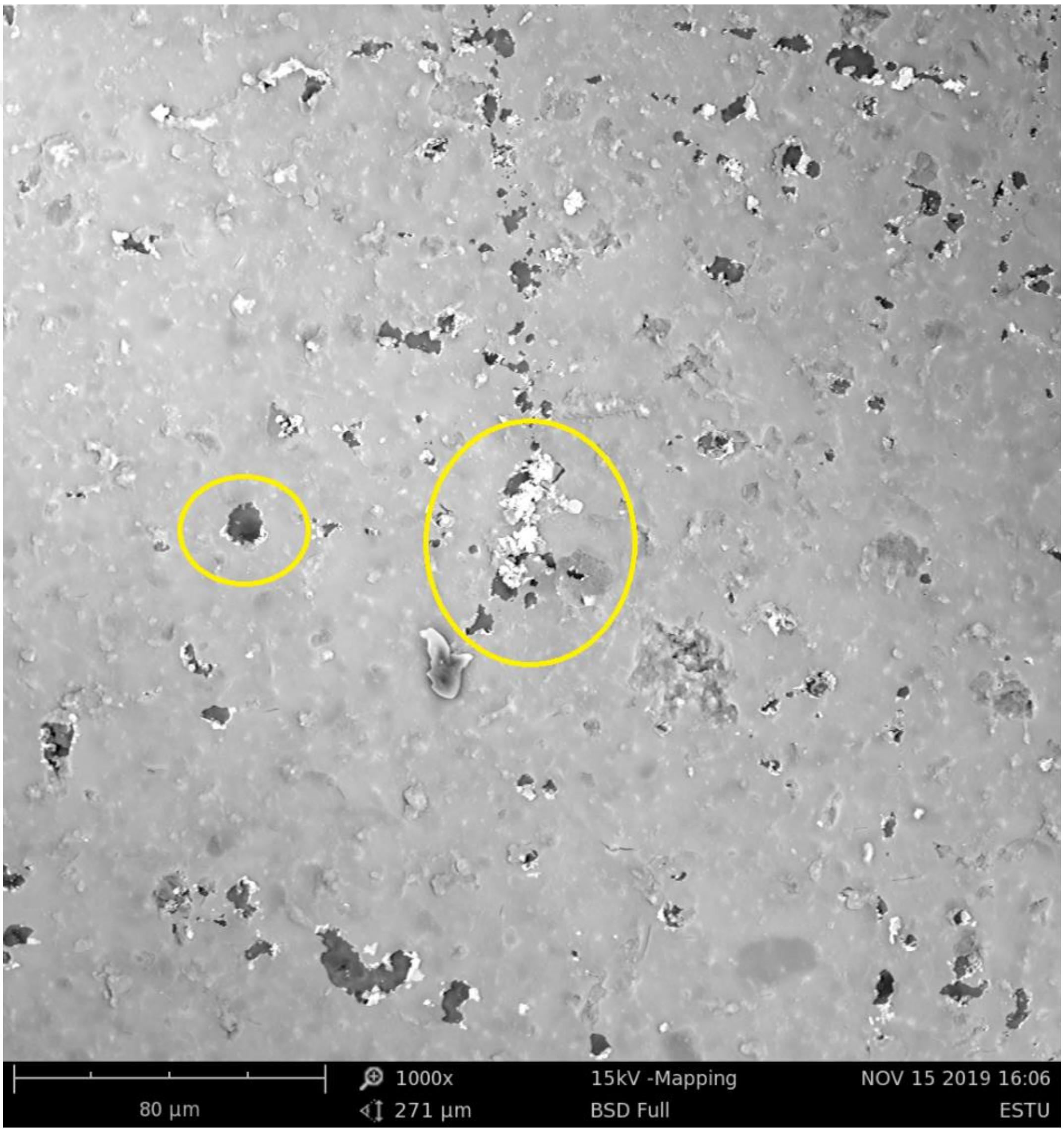


**Figure 6.7** The SEM image of 25 % h-BN ratio coating

## 6.4 Frictional Force

Friction is a resistance to motion occurring at the contact interface between two layers, while wear is the loss of volume that occurs at the contact surfaces as a reflection of this repeated frictional motion. Factors affecting friction include surface forces, material properties, contact hardness and surface geometry.

The friction coefficient, which means the ratio of the friction coefficient to the normal load, has values ranging from 0.001 to 10. Friction coefficients of less than 0.001 are usually produced using hydrodynamic or elastohydrodynamic lubrication mechanisms.

Due to the properties of the contact materials, significant physical and mechanical effects can be observed on the parts exposed to friction. For example, brittle contact materials can cause easy breakage. For this reason, the material properties of metals and coatings become very important. In order to understand the behavior of contact materials that do not contain liquid film, some factors need to be known [69]:

i. Deformation mode of roughness on interacting surfaces
ii. Critical shear strength of the contact interface
iii. Fracture mode of contact roughness
iv. Chemical reactions caused by friction on contact surfaces

On the other hand, tribological failures such as friction and resulting wear are important problems for industrial activities. They cause unnecessary economic costs due to the damage they cause to work tools and machine parts and increased energy consumption. Many different ways have been tried to solve this problem. One of these solutions is ceramic-based coatings. There are many types of ceramic coatings developed to minimize tribological effects. The most used materials for this purpose are Molybdenum disulfide ($MoS_2$), tungsten disulfide ($WS_2$) and graphite [76-78].

However, these materials also have some disadvantages. For example, the high chemical activity of $MoS_2$ against oxygen brings the risk of oxidation in humid environments where this ceramic is used. Oxidation weakens the lubricating ability of the coating [73]. Although $WS_2$ has higher oxidation resistance than $MoS_2$, it is also superior in terms of thermal stability. It can operate up to temperatures around 650 °C. However, $WS_2$ is a very soft material, and therefore the enlargement of the contact area becomes inevitable in tribological applications. With the enlargement of the contact area, wear occurs.

Another material frequently used in tribological applications is graphite, which has a layered structure such as $MoS_2$. Graphite with weak Van der Waals bonds between its layers is a very good lubricant. Graphite, which is an excellent lubricant, needs a gaseous environment to show this feature. In addition, graphite leaves dirt and black color in humid environments.

Due to these difficulties, alternative solution methods are sought for use in tribological fields. One of these solution methods is the development of coatings containing h-BN, which has the same atomic structure as graphite and has higher thermal stability, comes to the fore in this sense.

Hexagonal boron nitride has a low coefficient of friction and thus has a high lubricating effect. It shows these properties by breaking the weak Van der Waals bonds that connect the hexagonal layers [22]. One of the main motivations of the experiments and studies carried out in this thesis is to investigate the effects of the h-BN ratios in the thin film coatings produced by the sol-gel method on the friction coefficient of the films. For this reason, the friction coefficients of thin-film coatings with 10-15-20% and 25% h-BN content, which were mentioned previously, were examined one by one. Tests using a ball on disc tribometer were carried out under 1 N load at a rate of 26 minutes per 2500 rounds of sample.

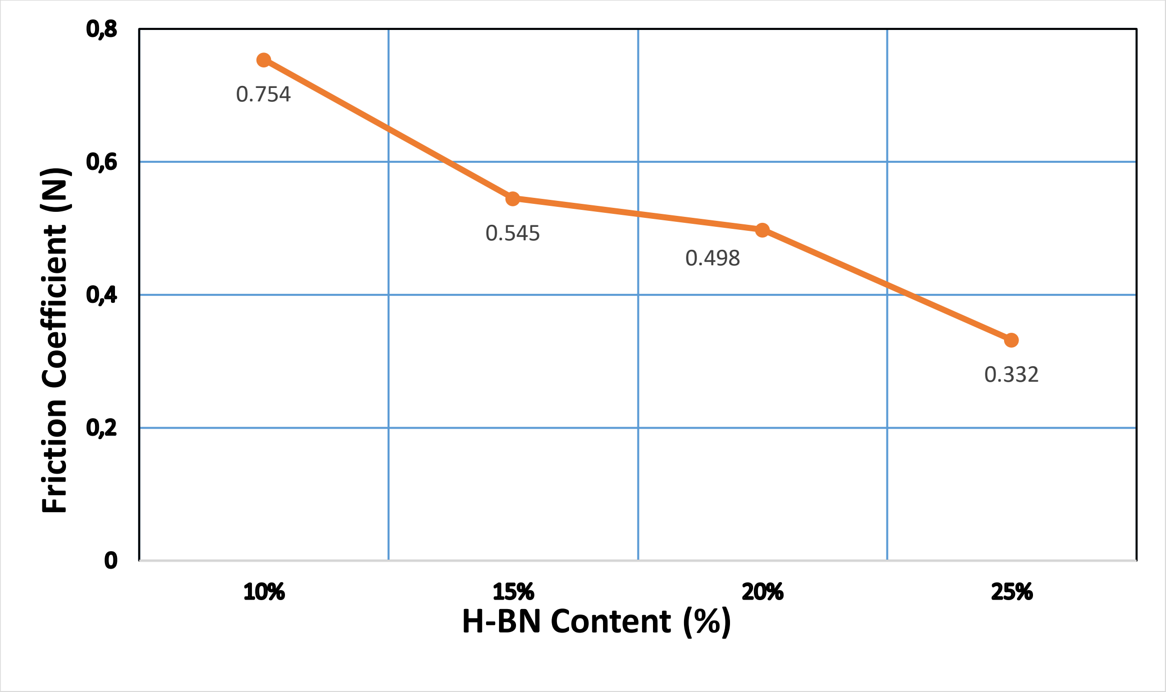


**Figure 6.8** Correlation of h-BN contents and the friction coefficients of the coatings

Figure 6.8 shows the effects of h-BN contents on the friction coefficients of thin films. It is clearly seen that the friction coefficient decreases with the increase of h-BN content. The friction coefficient reached its minimum value at 25% h-BN content. The difference between the coefficients of friction between the two h-BN content ratios was greatest between 10% and 15% in the two consecutive ratios. Between these two ratios, a decrease of 27.7% was observed in the coefficient of friction. On the other hand, the proportional decrease in friction coefficient between 15% and 20% shows the minimum decrease with 8.6%.

There are many publications on polymer/h-BN composite coatings in the literature. According to the results obtained in these publications, h-BN is quite successful in reducing the coefficient of friction. When the results obtained within the scope of the thesis are examined, the compatibility with the mentioned publications draws attention and it is clearly seen that the h-BN additive is very important in reducing the friction coefficient in polymer matrix thin film coatings [27,30].

The other materials used in the production of thin film coatings have an effect on the determination of friction coefficients, not only h-BN does. However, since the proportions of these materials are equal in all coatings, it is not important to consider them when comparing. On the other hand, the homogeneity of the h-BN content in the matrix is quite effective on the friction coefficients. The reason for this is that homogeneity affects the lubricating property significantly by directly affecting the breaking possibilities of Van der Waals bonds [79]. These bonds must be subjected to friction to break, and homogeneity causes more h-BN particles to face friction.

When the SEM images are examined, it can be seen that the homogeneity increased as the h-BN content increased. It was expected that this would have a positive effect on the reduction of the friction coefficient, and as a matter of fact, this was realized. However, the coating thicknesses of the thin films were 50 $\mu$m, but the dimensions of the h-BN particles were about 10 $\mu$m. For this reason, the h-BN particles remained embedded in the film matrix. However, in order to increase the contact between the friction surface and the h-BN particles and to benefit more from the lubricating properties of the h-BN particles, the particles should have been closer to the surface. A better uniformity or thinner film coating can help lower the coefficient of friction more economically, rather than increasing the h-BN ratio in the matrix. Figure 6.9 shows the friction coefficient values of the film coatings depending on time.

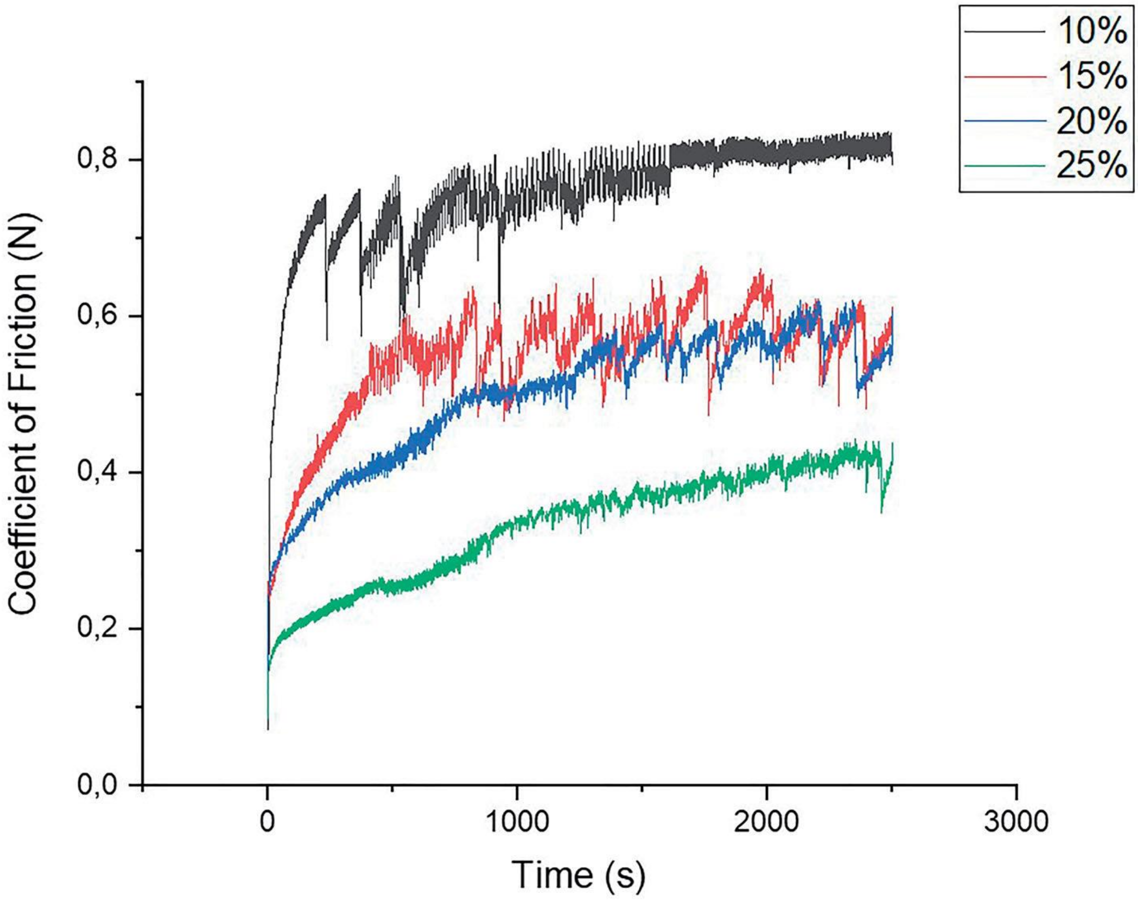
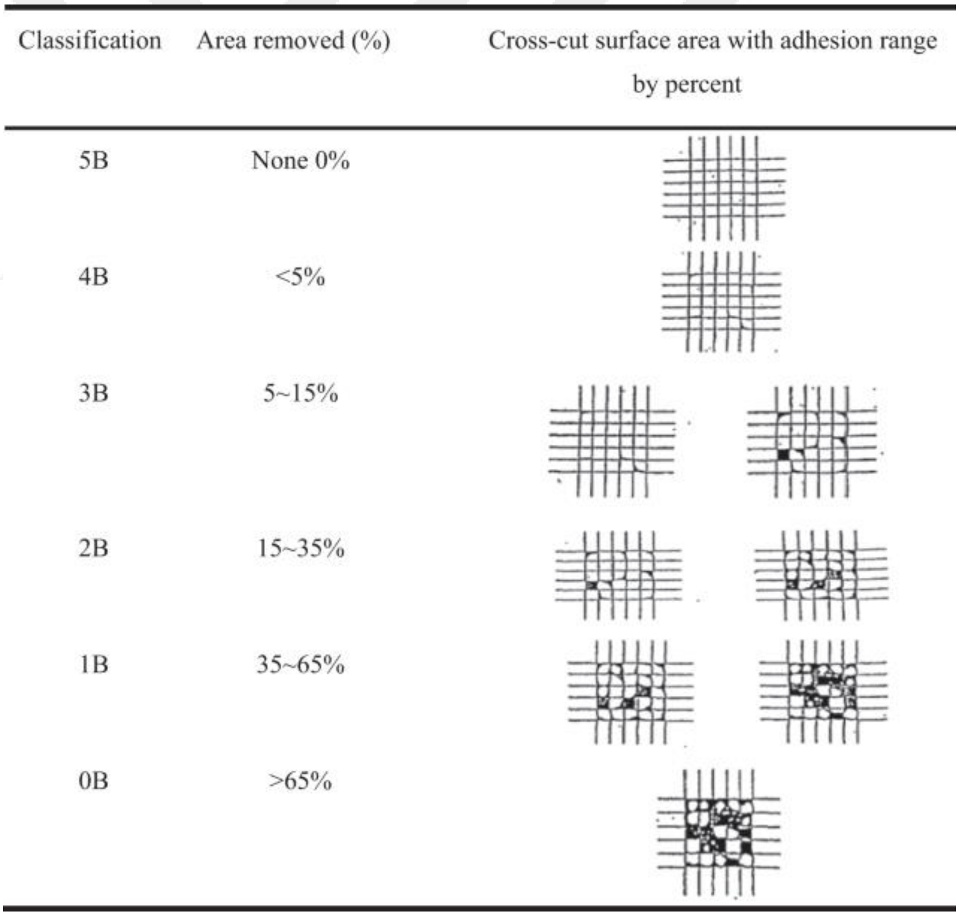


**Figure 6.9** Friction coefficients of coatings over time

When looking at the results of the time-dependent coefficient of friction, several points appeared to consider. First of all, the friction coefficient at the zero point where the test starts for all coatings is very close to zero. However, as time passed, an increase in friction coefficients was observed. The increase in h-BN content decreased the friction coefficient and increased the lubricity. However, after the breakable bonds were broken, the test device encountered the colloidal silica suspension and silica particles in the polymer matrix. Thus, the friction coefficient measurement results increased with time.

## 6.5 Hardness and Adhesion

Thin film coatings applied to aluminum substrates were obtained by sol-gel method and cured at 280 °C. The properties of the coatings such as thickness, pencil hardness and adhesion were examined by applying the necessary tests. Pencil test was performed to determine the surface hardness of the films. Pencil test is a method in which the hardness of coatings is determined by using pencils of different hardness. The same test was applied to all coatings with different h-BN content under the same conditions. The hardness of the pencils is between 1H and 10H. 10H is the hardest pencil. The results were the same in all coatings. Although they have different h-BN ratios, it has been observed that all coatings have 8H hardness values. In the literature, some publications have been found that h-BN coatings increase the hardness [27,30]. However, the opposite of these results is also true. Wang et al. in a study on poly (phenyl p-hydroxybenzoate)/polytetrafluoroethylene composites filled with h-BN particles, they showed that h-BN had no effect on hardness. In this study, in which the effect of H-BN content on the coefficient of friction was clearly demonstrated, it was also stated that there was no difference in hardness values between coatings with different h-BN content [32].



| Classification | Area removed (%) | Cross-cut surface area with adhesion range by percent |
|---|---|---|
| 5B | None 0% | |
| 4B | <5% | |
| 3B | 5~15% | |
| 2B | 15~35% | |
| 1B | 35~65% | |
| 0B | >65% | |

**Figure 6.10** ASTM D3359 Adhesion test method classification

Another tested property of thin-film coatings is adhesion. Adhesion was evaluated according to the ASTM D3359 adhesion test method. Coatings that do not show any peeling according to this test are classified as 5B. According to the amount of peeling that occurs in the coatings, the coatings are divided into 0-1-2-3-4B. According to the test results, it was determined that all the coatings obtained in this study had the same value and they had a 5B value. The Figure 6.10 shows the classification of adhesion levels and acceptance criterions for each level. This figure also demonstrate the example images about peelings of coatings.

Thereupon, another sample was prepared and tested in order to determine the effect of h-BN particles on adhesion. This sample was produced according to exactly the same procedure as previous film coatings. It does not contain only h-BN particles. However, it was determined that the sample did not show any adhesion after drying at 120 °C, which is a natural step of the process. This result shows that the h-BN particles affect and increase the adhesion between the coating and the aluminum substrate. All tested coatings had thicknesses in the 40-50 $\mu$m range.

## 6.6 Conclusion and Recommendations

In this study, it was investigated how h-BN additive effects on organic/inorganic hybrid coatings, which have been widely used in metal coatings in recent years. It is aimed to observe the differences between the thin film coatings by changing the h-BN contents.

Theoretically, it was thought that with the increase of the h-BN ratio, h-BN would transfer its unique characteristic properties to the coatings. As a result of the analysis, it was seen that the expectations were confirmed. Hydrophobicity and low friction coefficient, which are the two most characteristic features of h-BN, have also shown themselves in organic/inorganic hybrid coatings. As the h-BN ratio increases, the further development of these properties in the coatings reveals the clear link between h-BN and these properties.

Another issue is the bonding of the coatings to the substrate. It is also examined whether the addition of h-BN additive to the solution will increase the probability that the molecules that will bond with the substrate will not be able to reach the solution substrate. The increase in the h-BN ratio did not have any negative effect on the adhesion when looking at the FTIR analysis. On the contrary, the coating that was tried to be coated on the substrate without h-BN did not adhere to the substrate. The presence of h-BN allowed the organic/inorganic coatings to bond to the substrate. In addition, as the h-BN ratio increased, a better surface morphology was obtained, homogeneity increased and agglomeration decreased. However, the hardness was not affected by the h-BN content.

All these results show that the use of h-BN as an additive in organic/inorganic coatings developed for metal coatings is extremely suitable. However, experimental studies can be continued at higher h-BN ratios. However, reducing the size of the h-BN particles can also contribute to better results. By thinning the thickness of the produced coatings, the development of the properties can also be examined by ensuring that the h-BN particles are more dense on the surface.

# REFERENCES

[1] M. L. Zheludkevich, I. M. Salvado, and M. G. S. Ferreira, “Sol-gel coatings for corrosion protection of metals,” *J. Mater. Chem.*, vol. 15, no. 48, pp. 5099–5111, 2005, doi: 10.1039/b419153f.

[2] S. Zheng and J. Li, “Inorganic-organic sol gel hybrid coatings for corrosion protection of metals,” *J. Sol-Gel Sci. Technol.*, vol. 54, no. 2, pp. 174–187, 2010, doi: 10.1007/s10971-010-2173-1.

[3] S. Rahoui, V. Turq, and J. P. Bonino, “Effect of thermal treatment on mechanical and tribological properties of hybrid coatings deposited by sol-gel route on stainless steel,” *Surf. Coatings Technol.*, vol. 235, pp. 15–23, 2013, doi: 10.1016/j.surfcoat.2013.07.008.

[4] J. Ballarre, D. A. López, and A. L. Cavalieri, “Frictional and adhesive behavior of organic-inorganic hybrid coatings on surgical grade stainless steel using nano-scratching technique,” *Wear*, vol. 266, no. 11–12, pp. 1165–1170, 2009, doi: 10.1016/j.wear.2009.03.029.

[5] S. O. Pehkonen and S. Yuan, “Inorganic-Organic Hybrid Coatings,” *Interface Sci. Technol.*, vol. 23, pp. 115–132, 2018, doi: 10.1016/B978-0-12-813584-6.00005-3.

[6] M. Zaharescu *et al.*, “SiO2 based hybrid inorganic-organic films doped with TiO2-CeO2 nanoparticles for corrosion protection of AA2024 and Mg-AZ31B alloys,” *Corros. Sci.*, vol. 51, no. 9, pp. 1998–2005, 2009, doi: 10.1016/j.corsci.2009.05.022.

[7] F. Andreatta *et al.*, “Development and industrial scale-up of $ZrO_2$ coatings and hybrid organic-inorganic coatings used as pre-treatments before painting aluminium alloys,” *Prog. Org. Coatings*, vol. 72, no. 1–2, pp. 3–14, 2011, doi: 10.1016/j.porgcoat.2011.01.011.

[8] A. R. Simbar, A. Shanaghi, H. Moradi, and P. K. Chu, “Corrosion behavior of functionally graded and self-healing nanostructured $TiO_2$–$Al_2O_3$ - Benzotriazole coatings deposited on AA 2024-T3 by the sol-gel method,” *Mater. Chem. Phys.*, vol. 240, 2020, doi: 10.1016/j.matchemphys.2019.122233.

[9] W. Zhao, W. Zhao, Z. Huang, G. Liu, and B. Wu, “Tribological performances of epoxy resin composite coatings using hexagonal boron nitride and cubic boron nitride nanoparticles as additives,” *Chem. Phys. Lett.*, vol. 732, no. July, p. 136646, 2019, doi: 10.1016/j.cplett.2019.136646.

[10] G. R. Bhimanapati, N. R. Glavin, and J. A. Robinson, “2D Boron nitride,” Semiconductors and Semimetals, vol. 95, pp. 101–147, 2016.

[11] D. W. Palmer, “Electronic Energy Levels in Group-III Nitrides,” *Compr. Semicond. Sci. Technol.*, vol. 1–6, pp. 390–447, 2011, doi: 10.1016/B978-0-44-453153-7.00114-0.

[12] J. Zhang, Y. Yang, and J. Lou, “Investigation of hexagonal boron nitride as an atomically thin corrosion passivation coating in aqueous solution,” *Nanotechnology*, vol. 27, no. 36, pp. 1–6, 2016, doi: 10.1088/0957-4484/27/36/364004.

[13] Z. R. Robinson, S. W. Schmucker, K. M. McCreary, and E. D. Cobas, *Chemical Vapor Deposition of Two-Dimensional Crystals*, Second Edi., vol. 3. Elsevier B.V., 2015.

[14] Y. Kimura, T. Wakabayashi, K. Okada, T. Wada, and H. Nishikawa, “Boron nitride as a lubricant additive,” *Wear*, vol. 232, no. 2, pp. 199–206, 1999, doi: 10.1016/S0043-1648(99)00146-5.

[15] R. Haubner, M. Wilhelm, R. Weissenbacher, and B. Lux, “Boron Nitrides — Properties, Synthesis and Applications,” vol. 102, pp. 1–45, 2002, doi: 10.1007/3-540-45623-6_1.

[16] W. T. Hsiao, C. Y. Su, T. S. Huang, and W. H. Liao, “The microstructural characteristics and mechanical properties of Ni-Al/h-BN coatings deposited using plasma spraying,” *J. Alloys Compd.*, vol. 509, no. 32, pp. 8239–8245, 2011, doi: 10.1016/j.jallcom.2011.05.095.

[17] Z. Liu *et al.*, “Ultrathin higherature oxidation-resistant coatings of hexagonal boron nitride,” *Nat. Commun.*, vol. 4, no. May, pp. 1–8, 2013, doi: 10.1038/ncomms3541.

[18] L. Song *et al.*, “Large scale growth and characterization of atomic hexagonal boron nitride layers,” *Nano Lett.*, vol. 10, no. 8, pp. 3209–3215, 2010, doi: 10.1021/nl1022139.

[19] B. Zhong *et al.*, “The effects of the hexagonal boron nitride nanoflake properties on the thermal conductivity of hexagonal boron nitride nanoflake/silicone rubber composites,” *Compos. Part A Appl. Sci. Manuf.*, vol. 127, no. August, 2019, doi: 10.1016/j.compositesa.2019.105629.

[20] R. S. Pease, “An X-ray study of boron nitride,” *Acta Crystallogr.*, vol. 5, no. 3, pp. 356–361, 1952, doi: 10.1107/s0365110x52001064.

[21] S. P. S. Arya and A. D’Amico, “Preparation, properties and applications of boron nitride thin films,” *Thin Solid Films*, vol. 157, no. 2, pp. 267–282, 1988, doi: 10.1016/0040-6090(88)90008-9.

[22] A. Lipp, K. A. Schwetz, and K. Hunold, “Hexagonal boron nitride: Fabrication, properties and applications,” *J. Eur. Ceram. Soc.*, vol. 5, no. 1, pp. 3–9, 1989, doi: 10.1016/0955-2219(89)90003-4.

[23] P. Sutter, J. Lahiri, P. Zahl, B. Wang, and E. Sutter, “Scalable synthesis of uniform few-layer hexagonal boron nitride dielectric films,” *Nano Lett.*, vol. 13, no. 1, pp. 276–281, 2013, doi: 10.1021/nl304080y.

[24] X. Li, J. Yin, J. Zhou, and W. Guo, “Large area hexagonal boron nitride monolayer as efficient atomically thick insulating coating against friction and oxidation,” *Nanotechnology*, vol. 25, no. 10, 2014, doi: 10.1088/0957-4484/25/10/105701.

[25] E. Husain, T. N. Narayanan, J. J. Taha-Tijerina, S. Vinod, R. Vajtai, and P.

M. Ajayan, “Marine corrosion protective coatings of hexagonal boron nitride thin films on stainless steel,” *ACS Appl. Mater. Interfaces*, vol. 5, no. 10, pp. 4129–4135, 2013, doi: 10.1021/am400016y.

[26] I. Jang *et al.*, “Enhancement of thermal conductivity of BN/epoxy composite through surface modification with silane coupling agents,” *Colloids Surfaces A Physicochem. Eng. Asp.*, vol. 518, pp. 64–72, 2017, doi: 10.1016/j.colsurfa.2017.01.011.

[27] J. Tharajak, T. Palathai, and N. Sombatsompop, “Recommendations for h-BN loading and service temperature to achieve low friction coefficient and wear rate for thermal-sprayed PEEK coatings,” *Surf. Coatings Technol.*, vol. 321, pp. 477–483, 2017, doi: 10.1016/j.surfcoat.2017.05.022.

[28] J. Yu, W. Zhao, Y. Wu, D. Wang, and R. Feng, “Tribological properties of epoxy composite coatings reinforced with functionalized C-BN and H-BN nanofillers,” *Appl. Surf. Sci.*, vol. 434, pp. 1311–1320, 2018, doi: 10.1016/j.apsusc.2017.11.204.

[29] A. K. Kadiyala and J. Bijwe, “Surface lubrication of graphite fabric reinforced epoxy composites with nano- and micro-sized hexagonal boron nitride,” *Wear*, vol. 301, no. 1–2, pp. 802–809, 2013, doi: 10.1016/j.wear.2012.11.069.

[30] J. Tharajak, T. Palathai, and N. Sombatsompop, “Morphological and physical properties and friction/wear behavior of h-BN filled PEEK composite coatings,” *Surf. Coatings Technol.*, vol. 273, no. 1, pp. 20–29, 2015, doi: 10.1016/j.surfcoat.2015.03.030.

[31] M. Yang *et al.*, “Influence of air-plasma treatment and hexagonal boron nitride as filler on the high temperature tribological behaviors of hybrid PTFE/Nomex fabric/phenolic composite,” *Eur. Polym. J.*, vol. 67, pp. 143–151, 2015, doi: 10.1016/j.eurpolymj.2015.03.027.

[32] S. Wang, Q. Li, S. Zhang, and L. Pan, “Tribological behavior of poly (phenyl p-hydroxybenzoate)/polytetrafluoroethylene composites filled with hexagonal boron nitride under dry sliding condition,” *Mater. Des.*, vol. 43, pp. 507–512, 2013, doi: 10.1016/j.matdes.2012.07.048.

[33] H. Fang, S. L. Bai, and C. P. Wong, “‘White graphene’ – hexagonal boron nitride based polymeric composites and their application in thermal management,” *Compos. Commun.*, vol. 2, no. October, pp. 19–24, 2016, doi: 10.1016/j.coco.2016.10.002.

[34] S. Al-Saadi, P. C. Banerjee, M. R. Anisur, and R. K. Singh Raman, “Hexagonal boron nitride impregnated silane composite coating for corrosion resistance of magnesium alloys for temporary bioimplant applications,” *Metals (Basel).*, vol. 7, no. 12, 2017, doi: 10.3390/met7120518.

[35] M. Muhammad *et al.*, “Enhancing the corrosion resistance of Q235 mild steel by incorporating poly(dopamine) modified h-BN nanosheets on zinc phosphate-silane coating,” *Surf. Coatings Technol.*, vol. 390, no. November 2019, 2020, doi: 10.1016/j.surfcoat.2020.125682.

[36] A. Behera, P. Mallick, and S. S. Mohapatra, “Nanocoatings for anticorrosion,” *Corros. Prot. Nanoscale*, pp. 227–243, 2020, doi: 10.1016/b978-0-12-819359-4.00013-1.

[37] S. S. Pathak and A. S. Khanna, “Sol-gel nanocoatings for corrosion protection,” *Corros. Prot. Control Using Nanomater.*, pp. 304–329, 2012, doi: 10.1016/B978-1-84569-949-9.50012-5.

[38] P. Innocenzi, “Understanding sol–gel transition through a picture. A short tutorial,” *J. Sol-Gel Sci. Technol.*, vol. 94, no. 3, pp. 544–550, 2020, doi: 10.1007/s10971-020-05243-w.

[39] C. J. Brinker and G. W. Scherer, “Introduction,” *Sol-Gel Sci.*, pp. xvi–18, 1990, doi: 10.1016/b978-0-08-057103-4.50006-4.

[40] A. E. Danks, S. R. Hall, and Z. Schnepp, “The evolution of ‘sol-gel’ chemistry as a technique for materials synthesis,” *Mater. Horizons*, vol. 3, no. 2, pp. 91–112, 2016, doi: 10.1039/c5mh00260e.

[41] J. Livage, M. Henry, and C. Sanchez, “Sol-gel chemistry of transition metal oxides,” *Prog. Solid State Chem.*, vol. 18, no. 4, pp. 259–341, 1988, doi: 10.1016/0079-6786(88)90005-2.

[42] M. Barletta, A. Gisario, M. Puopolo, and S. Vesco, “Scratch, wear and corrosion resistant organic inorganic hybrid materials for metals protection and barrier,” *Mater. Des.*, vol. 69, pp. 130–140, 2015, doi: 10.1016/j.matdes.2014.12.048.

[43] X. Zhang and J. Meng, “Recent progress of Boron nitrides,” Ultra-Wide Bandgap Semiconductor Materials, pp. 347–419, 2019.

[44] C. Chen *et al.*, “Stabilizing the metastable superhard material wurtzite boron nitride by three-dimensional networks of planar defects,” *Proc. Natl. Acad. Sci. U. S. A.*, vol. 166, no. 23, pp. 11181–11186, 2019, doi: 10.1073/pnas.1902820116.

[45] M. Jedrzejczak-Silicka, M. Trukawka, K. Piotrowska, and E. Mijowska, “Few-Layered Hexagonal Boron Nitride: Functionalization, Nanocomposites, and Physicochemical and Biological Properties,” *Biochem. Toxicol. - Heavy Met. Nanomater.*, pp. 1–18, 2020, doi: 10.5772/intechopen.90528.

[46] R. T. Paine and C. K. Narula, “Synthetic Routes to Boron Nitride,” *Chem. Rev.*, vol. 90, no. 1, pp. 73–91, 1990, doi: 10.1021/cr00099a004.

[47] T. E. Oconnor, “Synthesis of boron nitride,” *J. Am. Chem. Soc.*, vol. 84, no. 9, pp. 1753–1754, 1962, doi: 10.1021/ja00868a065.

[48] J. Thomas, “Crystalline Turbostatic Boron Nitride Powder and Method,” vol. 1, no. 12, 2001.

[49] M. Hubáček and M. Ueki, “Chemical reactions in hexagonal boron nitride system,” *J. Solid State Chem.*, vol. 123, no. 2, pp. 215–222, 1996, doi: 10.1006/jssc.1996.0171.

[50] M. Hubáček and T. Sató, “The effect of copper on the crystallization of

hexagonal boron nitride," *J. Mater. Sci.*, vol. 32, no. 12, pp. 3293–3297, 1997, doi: 10.1023/A:1018635709062.

[51] J. Duan, R. Xue, Y. Xu, and C. Sun, "Low temperature synthesis of h-BN nanoflakes," *Mater. Lett.*, vol. 62, no. 19, pp. 3355–3357, 2008, doi: 10.1016/j.matlet.2008.03.007.

[52] R. Asmatulu, "Nanocoatings for Corrosion Protection of aerospace alloys," Corrosion Protection and Control Using Nanomaterials, pp. 357–374, 2012.

[53] D. Wang and G. P. Bierwagen, "Sol-gel coatings on metals for corrosion protection," *Prog. Org. Coatings*, vol. 64, no. 4, pp. 327–338, 2009, doi: 10.1016/j.porgcoat.2008.08.010.

[54] M. Guglielmi, "Sol-gel science," *Materials Chemistry and Physics*, vol. 26, no. 2. pp. 211–212, 1990, doi: 10.1016/0254-0584(90)90039-d.

[55] H. E. Çamurlu, Y. Topkaya, and N. Sevinç, "Catalytic effect of alkaline earth oxides on carbothermic formation of hexagonal boron nitride," *Ceram. Int.*, vol. 35, no. 6, pp. 2271–2275, 2009, doi: 10.1016/j.ceramint.2008.12.005.

[56] A. Pakdel, C. Zhi, Y. Bando, T. Nakayama, and D. Golberg, "Boron nitride nanosheet coatings with controllable water repellency," *ACS Nano*, vol. 5, no. 8, pp. 6507–6515, 2011, doi: 10.1021/nn201838w.

[57] X. Li, H. Qiu, X. Liu, J. Yin, and W. Guo, "Wettability of Supported Monolayer Hexagonal Boron Nitride in Air," *Adv. Funct. Mater.*, vol. 27, no. 19, 2017, doi: 10.1002/adfm.201603181.

[58] A. Wilk, P. Rutkowski, D. Zientara, and M. M. Bućko, "Aluminium oxynitride-hexagonal boron nitride composites with anisotropic properties," *J. Eur. Ceram. Soc.*, vol. 36, no. 8, pp. 2087–2092, 2016, doi: 10.1016/j.jeurceramsoc.2016.02.029.

[59] K. Y. Law, "Water-surface interactions and definitions for hydrophilicity, hydrophobicity and superhydrophobicity," *Pure Appl. Chem.*, vol. 87, no. 8, pp. 759–765, 2015, doi: 10.1515/pac-2014-1206.

[60] A. Owais, M. Khaled, and B. S. Yilbas, "Hydrophobicity and surface finish," *Compr. Mater. Finish.*, vol. 3–3, pp. 137–148, 2017, doi: 10.1016/B978-0-12-803581-8.09172-4.

[61] A. D. Aliev *et al.*, "Superhydrophobic coatings based on boron nitride nanotubes: The mechanism of superhydrophobicity and self-regeneration of highly hydrophobic properties," *Nanotechnologies Russ.*, vol. 6, no. 11–12, pp. 723–732, 2011, doi: 10.1134/S1995078011060024.

[62] R. K. Suleiman, "Improved mechanical and anticorrosion properties of metal oxide-loaded hybrid sol–gel coatings for mild steel in a saline medium," *J. Adhes. Sci. Technol.*, vol. 0, no. 0, pp. 1–16, 2019, doi: 10.1080/01694243.2019.1707583.

[63] D. K. Sarkar, D. Brassard, M. A. E. Khakani, and L. Ouellet, "Dielectric properties of sol-gel derived high-k titanium silicate thin films," *Thin Solid*

*Films*, vol. 515, no. 11, pp. 4788–4793, 2007, doi: 10.1016/j.tsf.2006.11.155.

[64] J.-D. Brassard, D. K. Sarkar, and J. Perron, “Fluorine Based Superhydrophobic Coatings,” *Appl. Sci.*, vol. 2, no. 2, pp. 453–464, 2012, doi: 10.3390/app2020453.

[65] X. Cui, J. Liu, H. Liu, and G. Wu, “Enhanced interfacial strength and mechanical properties of carbon fiber composites by introducing functionalized silica nanoparticles into the interface,” *J. Adhes. Sci. Technol.*, vol. 33, no. 5, pp. 479–492, 2019, doi: 10.1080/01694243.2018.1543634.

[66] K. A. Yasakau, J. Carneiro, M. L. Zheludkevich, and M. G. S. Ferreira, “Influence of sol-gel process parameters on the protection properties of sol-gel coatings applied on AA2024,” *Surf. Coatings Technol.*, vol. 246, pp. 6–16, 2014, doi: 10.1016/j.surfcoat.2014.02.038.

[67] G. Chernev *et al.*, “Sol-gel silica hybrid biomaterials for application in biodegradation of toxic compounds,” *J. Sol-Gel Sci. Technol.*, vol. 58, no. 3, pp. 619–624, 2011, doi: 10.1007/s10971-011-2436-5.

[68] Y. Guo *et al.*, “Sol-gel synthesis of new ZnFe2O4/Na-bentonite composites for simultaneous oxidation of RhB and reduction of Cr(VI) under visible light irradiation,” *J. Alloys Compd.*, vol. 781, no. Vi, pp. 1101–1109, 2019, doi: 10.1016/j.jallcom.2018.12.050.

[69] K. Kato, “Friction and wear of passive metals and coatings,” *Tribocorrosion Passiv. Met. Coatings*, pp. 65–99, 2011, doi: 10.1533/9780857093738.1.65.

[70] K. Holmberg and A. Erdemir, “Influence of tribology on global energy consumption, costs and emissions,” *Friction*, vol. 5, no. 3, pp. 263–284, 2017, doi: 10.1007/s40544-017-0183-5.

[71] J. P. Ewen, D. M. Heyes, and D. Dini, “Advances in nonequilibrium molecular dynamics simulations of lubricants and additives,” *Friction*, vol. 6, no. 4, pp. 349–386, 2018, doi: 10.1007/s40544-018-0207-9.

[72] H. Tsuji *et al.*, “Factors controlling dissolved 137Cs concentrations in east Japanese Rivers,” *Sci. Total Environ.*, vol. 697, p. 134093, 2019, doi: 10.1016/j.scitotenv.2019.134093.

[73] W. Dai, X. Li, L. Wu, and Q. Wang, “Structure and properties of molybdenum-disulfide/amorphous carbon composited coatings deposited by co-sputtering method,” *Diam. Relat. Mater.*, vol. 101, 2020, doi: 10.1016/j.diamond.2019.107643.

[74] F. Gustavsson and S. Jacobson, “Diverse mechanisms of friction induced self-organisation into a low-friction material - An overview of $WS_2$ tribofilm formation,” *Tribol. Int.*, vol. 101, pp. 340–347, 2016, doi: 10.1016/j.triboint.2016.04.029.

[75] O. A. Gali, R. R. N. Tamtam, and A. R. Riahi, “The tribological evaluation of graphene oxide and tungsten disulfide spray coatings during elevated

temperature sliding contact of aluminum-on-steel," *Surf. Coatings Technol.*, vol. 357, no. October 2018, pp. 604–618, 2019, doi: 10.1016/j.surfcoat.2018.10.031.

[76] B. Podgornik, F. Kafexhiu, T. Kosec, J. Jerina, and M. Kalin, "Friction and anti-galling properties of hexagonal boron nitride (h-BN) in aluminium forming," *Wear*, vol. 388–389, no. August 2016, pp. 2–8, 2017, doi: 10.1016/j.wear.2017.04.026.

[77] W. Qi, P. Huang, X. Chen, J. Jin, and J. Luo, "Achieving controllable friction of ultrafine-grained graphite HPG510 by tailoring the interfacial nanostructures," *Appl. Surf. Sci.*, vol. 512, no. October 2019, p. 145731, 2020, doi: 10.1016/j.apsusc.2020.145731.

[78] W. Zhao, W. Zhao, Z. Huang, G. Liu, and B. Wu, "Tribological performances of epoxy resin composite coatings using hexagonal boron nitride and cubic boron nitride nanoparticles as additives," *Chem. Phys. Lett.*, vol. 732, p. 136646, 2019, doi: 10.1016/j.cplett.2019.136646.

[79] G. Mittal, K. Y. Rhee, and S. J. Park, "Processing and characterization of PMMA/PI composites reinforced with surface functionalized hexagonal boron nitride," *Appl. Surf. Sci.*, vol. 415, pp. 49–54, 2017, doi: 10.1016/j.apsusc.2016.10.029.

# PUBLICATIONS FROM THE THESIS

## Papers

M. Karadağ, O. Karaahmet, B. Çiçek, and M. İ. Usta, “Effect of hexagonal boron nitride on the coefficient of frictions of organic-inorganic hybrid polymer thin films for metal surface coatings,” Journal of Adhesion Science and Technology, vol. 34, no. 20, pp. 2200–2215, 2020.