İSTANBUL TECHNICAL UNIVERSITY ★ INSTITUTE OF SCIENCE AND TECHNOLOGY

PREPARATION OF HIGH PERFORMANCE POLYURETHANE COATING MATERIALS

M.Sc. Thesis by
Chem. & Env. Eng. Arzu HAYIRLIOĞLU

Department : Polymer Science and Technology

Programme : Polymer Science and Technology

JANUARY 2009

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Arzu HAYIRLIOĞLU
(515061002)**

Supervisor (Chairman) : Prof. Dr. İ. Ersin SERHATLI (ITU)
Members of the Examining Committee : Prof. Dr. Atilla GÜNGÖR (MU)
Prof. Dr. Ayşen ÖNEN (ITU)

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İSTANBUL TEKNİK ÜNİVERSİTESİ ★ FEN BİLİMLERİ ENSTİTÜSÜ

YÜKSEK PERFORMANS POLİÜRETAN KAPLAMA MALZEMELERİNİN HAZIRLANMASI

YÜKSEK LİSANS TEZİ
Arzu HAYIRLIOĞLU
(515061002)

Tezin Enstitüye Verildiği Tarih : 29 Aralık 2008
Tezin Savunulduğu Tarih : 22 Ocak 2009

Tez Danışmanı : Prof. Dr. İ. Ersin SERHATLI (İTÜ)
Diğer Jüri Üyeleri : Prof. Dr. Atilla GÜNGÖR (MÜ)
Prof. Dr. Ayşen ÖNEN (İTÜ)

OCAK 2009

FOREWORD

This study has been carried out in POLMAG Laboratory (Polymeric Materials Research Group), located at Faculty of Science and Letters in Istanbul Technical University.

First of all, I would like thank to my advisor Professor Dr. İ. Ersin SERHATLI, for sharing all his wide experience and great knowledge with me, for his guidance and motivation throughout this study. I am also thankful that I could be a part of his research group.

I also would like to thank to Prof. Ayşen ÖNEN her guidance, kindness and all her help,

To Prof. Dr. Atilla GÜNGÖR for all his helpfulness and generous behavior in sharing information.

Special thanks to İbrahim AKENGİN and BEMKA A.Ş. for working opportunity and help on resources.

In addition, I am thankful to all my colleagues in this research especially to Tuba ÇAKIR ÇANAK, Müfide KARAHASANOĞLU, Burcu İŞCANI and Burcu KENARLI for all their help, friendship and motivation through this study.

I would like to give my special thanks to my friends Pınar CANA, Zehra AYYILDIZ and Onur TOPUZLU for their caring, understanding, unique friendship, physical and emotional support.

Finally, I specially thank to my great family, my parents; Hatice and Sebahattin HAYIRLIOĞLU, my sisters Aslı HAYIRLIOĞLU RUBACI and Ayşe HAYIRLIOĞLU who helped me to reach these days and appreciate their huge efforts. Without their support, patience and love I could not achieve all of this.

January 2009   Arzu HAYIRLIOĞLU

                                                     Polymer Science and Technology

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ABBREVIATIONS

VOC   : Volatile Organic Component
UV   : Ultraviolet
TDI   : Tolylene Diisocyanate
MDI   : Diphenylmethane Diisocyanate
NDI   : Naphthylene 1,5-diisocyanate
HDI   : Hexamethylene Diisocyanate
IPDI   : Isophorone Diisocyanate
H$_{12}$MDI   : Bis(4-isocyanatocyclohexyl) Methane
XDI   : 1,3-xylenediisocyanate
TMXDI   : Tetramethyl-*m*-xylidene Diisocyanate
TMI   : *m*-isopropenyl-α,α.-dimethylbenzylisocyanate
TMHDI   : 2,2,5-trimethylhexane Diisocyanate
DABCO   : 1,4-diazabicylo Octane
TEA   : Triethyl Amine
PU   : Polyurethane
DETDA   : Diethyl Toluene Diamine
IPDA   : Isophorone Diamine
ASTM   : American Society for Testing Materials
PVA   : Poly (vinyl acetal)
THEIC   : Tris-(2-hydroxyethyl)-isocyanurate
PAI   : Polyamide-imide
PEI   : Polyester-imide
TFE   : Tetrafluoroethylene
FPU   : Fluorinated Polyurethane
PFPE   : Perfluoropolyether
PFAE   : Perfluoroalkylether
FT-IR   : Fourier Transform Infrared Spectroscopy
TGA   : Thermogravimetric Analysis
SEM   : Scanning Electron Microscope

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PREPARATION OF HIGH PERFORMANCE POLYURETHANE COATING MATERIALS

SUMMARY

Using blocked isocyanate is very common in polyurethane coating industry due to isocyanate's potential reaction with most of the elements in nature and its harmful effect while being free. In order to provide desired surface properties and improving environmental friendly coating materials, using modified blocked isocyanate based polyurethanes with polysiloxanated or fluorinated chemicals cause eleminate harmful materials coming from after curing and also, it provides improving in polyurethane coating material's thermal, mechanical and electrical properties. Because of their low surface energy, bio-compatibility, lubricity, thermal and oxidative stability, non-sticking behaviors of the fluorinated polyurethanes and because of their hydrophobic character ,thermal stability, bio-compatibility of polyurethanes modified by polysiloxane make them interesting.

In this study, polyurethane coating material including blocked isocyanate is mixed with additives including fluorine or polysiloxane with certain proportions, and coated firstly on glass and then wire surfaces. Thermal curing by different temperatures are observed and final coating properties are investigated.

Contact angle results coming from samples coated on glass surface, and samples' coated on copper wire surface thermal, mechanical and electrical test measurements are investigated. Because of high voltage and high speed winding, slip properties and effects of dielectric losses are important. Considering all this circumstances and results, it is observed that products with coating materials including polysiloxane modified polyurethane provide desired mechanical, thermal and electrical properties.

YÜKSEK PERFORMANS POLİÜRETAN KAPLAMA MALZEMELERİNİN HAZIRLANMASI

ÖZET

İzosiyanatın ortamda var olan pek çok madde ile reaksiyon vermesi ve serbest halde bulunduğunda zararlı olmasından dolayı poliüretan kaplama endüstrisinde bloklanmış izosiyanat kullanımı yaygındır. Bloklanmış izosiyanat ile oluşturulan poliüretanlar, istenen yüzey özelliklerinin sağlanması ve çevreye karşı duyarlı kaplamaların geliştirilmesi amacı ile florlu ve polisiloksanlı maddeler ile modifiye edilerek, kaplamaya kürlenme sonrası katılan zararlı maddeleri ortadan kaldırmakta ve poliüretan kaplama malzemesinin termal, mekanik ve elektriksel özelliklerinin arttırılması sağlanmaktadır. Florlu poliüretanlar düşük yüzey enerjileri, biyouyumlulukları, kayganlıkları, termal ve oksidatif kararlılığa sahip olmaları, yapışmama özelliklerinden dolayı ve polisiloksan ile modifiye edilmiş poliüretanlar da hidrofobik özellikleri, termal kararlılıkları ve biyouyumlu olmalarından dolayı önem taşımaktadırlar.

Bu çalışmada bloklanmış izosiyanat içeren poliüretan kaplama malzemesi belirli oranlarda florlu ve modifiye polisiloksanlı maddeler ile karıştırılarak önce cam üzerinde ve daha sonra bakır tel üzerinde farklı yüksek sıcaklıklar ile kürlenme sağlanmış ve sonuç kaplama özellikleri incelenmiştir.

Elde edilen sonuç ürünlerinden cam üzerine uygulanan numunelerin temas açısı sonuçları ile bakır tel üzerine uygulanan numunelerin termal, mekanik ve elektriksel sonuçları incelenmiştir. Ayrıca yüksek voltaj ve sarım hızlarından ötürü bakır teldeki emayenin kayganlık ve dielektrik katsayısının etkileri büyük önem taşımaktadır. Bu koşulların ve sonuçların hepsi göz önüne alındığında, polisiloksan modifiye bloklanmış poliüretan kaplama malzemesi içeren ürünlerde istenen mekanik, termal ve elektriksel özelliklerin hepsinin sağlandığı görülmüştür.

1. INTRODUCTION

There are great developments in winding wire insulation applications, which are used engine, transformers and all kind of applications in energy industry and transportation industry and also these developments are interesting in order to obtain desired surface attributes to increase the performance of polymeric coating and lower the dielectric properties without causing environmental problems. To reduce the friction of the enamel wire surface and to enable lubricity, common commercial polyurethane usage followed by adding paraffin or similar products. However, these lubricant products in solvents do not show presence uniformly and cause damage on winding of wire. Additionally, these lubricants are used together with the solvent and vaporization of the solvent during the practice cause spreading the hazardous gases to environment. As a result of this, they are applied by modifying polyurethane coating materials including blocked isocyanates with group of fluorine or polysiloxane.

In this case, properties such as low surface energy, bio-compatibility, lubricity, thermal and oxidative stability, and non-sticking behaviors of the fluorinated polyurethanes make them interesting in wide range of application area. Fluoropolymers are used especially in electronic applications because they provide low dielectric constants and dissipation factors. On the other hand, because of the hydrophobic character, thermal stability, bio-compatibility and excellent dielectric properties of polyurethanes modified by polysiloxane they are used in coating, adhesives and many other applications.

Blocked isocyanates have been much attention in polyurethane coatings because of their undesired side reactions.The –NCO groups in isocyanate are highly toxic, and it can further give reactions with the moisture and or other materials in the environment. Isocyanates are blocked by a variety of blocking agents and these agents then evaporate with solvent during curing mechanism.

In this study, after the preparation the polyurethane including blocked isocyanate modified with flourine and polysiloxane, curing method of coating and its characterization are observed. Furthermore, prepared coating materials were applied on copper wire surface and surface thermal and mechanical properties are analyzed by several devices.

2. THEORETICAL PART

2.1 Coating

Coating is known usually as a liquid material which is based on organic binders and when it is applied to a surface produces a cohesive, continuous or discontinuous film after drying. Generally, the process of application and the resultant dry film is also regarded as coating. Drying of the liquid coating is mostly carried out by different methods like evaporative means or curing by oxidative, thermal or ultraviolet light and other methods. [1,2].

Today, many objects that we use or come across in daily life are coated by different materials and as a result of usage of coating wide range of application area, the importance of coating has increased hugely during the modern period of technology. For example, electronic devices, cars, furniture, military application such as vehicles, artilleries and invisible radars and aerospace products such as aircraft, satellites and solar panels and many other things include coated materials [1].

Coatings are used because they efficiently provide desirable features to substrates, such as enhanced aesthetics, protection against environmental influences, such as greater barrier to moisture and chemicals or biological deterioration, improved resistance to weathering and surface damage through physical impact, and certain specialty characteristics such as electrostatic dissipation [3,4]. Many daily products are only made usable and thus saleable because of their surface treatment and to obtain this, relevant coating formulations, their production plant, the coating material and suitable coating process for the process must be available [5].

2.1.1 Composition and Application of Coating Material

Coatings occur in both organic and inorganic forms. Coating material can be classified by volatile matter as shown in Table 2.1. On the other hand, organic coatings are complex mixtures of chemical substances that can be grouped into four broad categories: 1. binders, 2. volatile components, 3. pigments and 4. additives [2,6].

Table 2.1: Coating Materials

Coating Material	
Non-volatile matter	Volatile matter
Pigments Fillers Film-formers Non-volatile additives	Solvents or dispersants Volatile additives

2.1.1.1 Binders

Binders adhere to a subsrate (the surface being coated) and form continuous film. Binder are polymer resin systems with varyin molecular weights. In some cases, these polymers are prepared and added to the coating before application but in other situations final polymerization takes place after the coating has been applied. Common binders are acrylics, epoxies, polyesters and urethanes [6].

2.1.1.2 Volatile Components

The majority of all coatings include volatile components and play important role of applying coatings. Volatile components are liquid materials which make the coating fluid enough for application. They evaporate during and after application. Volatile component may be in the coating formulation before application, but after evaporation it allow the solid materials to immobilize and form the thin protective film.

The volatile components were low molecular weight organic solvents that dissolved the binder components until 1945, but the term solvent mislead because since 1945 many coatings have been developed for which the binder components are not completely soluble in the volatile components. Furthermore, to reduce the VOC (Volatile Organic Component) emisions high solid containing coating material are used by reducing solvents. Also, water using and eleminating solvents is important. On the other hand, solvent take place in coating temporarily but it plays a major role in how well the film perform. Today most of the coating include at least one volatile organic component except powder coatings, certain solventless liquid coatings, radiation-curable coatings and small part of architectural coatings [6,7].

2.1.1.3 Pigments

Pigments are insoluble particles in coating materials and suspended in the binder after film formation. Generally pigments are the colorant portion of the coating material, but they have also different property like providing opacity to the coating film. Some pigments provide corrosion protection, stability in ultraviolet (UV) light or protection from mold, mildew or bacteria. Other pigments can be used for their conductive ability, texture or metallic or pearlescent appearance. Although most coatings contain pigments, there are important types of coatings that contain little or no pigment. This type of coating materials called as clear coats. Clear coats for automobiles and transparent varnishes are examples [6,7].

2.1.1.4 Additives

Additives are usually low molecular weight chemicals and are included in small quantities to modify some property of a coating but do not contribute to color. Examples are catalysts for polymerization reactions, stabilizers and flow modifiers. Non-pigment additives include stabilizers to block attacks of ultraviolet light or heat, curing additives to speed up the crosslinking reaction, co-solvents to increase viscosity, or plasticizers to improve uniform coating [6,7].

2.1.1.5 Application Methods of Coating Materials

Coatings are generally applied as multi layered systems that are composed of primer and topcoat. However, in some cases like automotive coating system this may vary from four to six layers. Each coating layer is applied to perform certain spesific functions, though its activities are influenced by other layers in the system. The overall performance of multi-coat system is affected by the interactions among different layers and the interfacial phenomenon [1,8]. Different properties of coatings are typically associated with specific parts of a coating system (Fig. 2.1) [1].
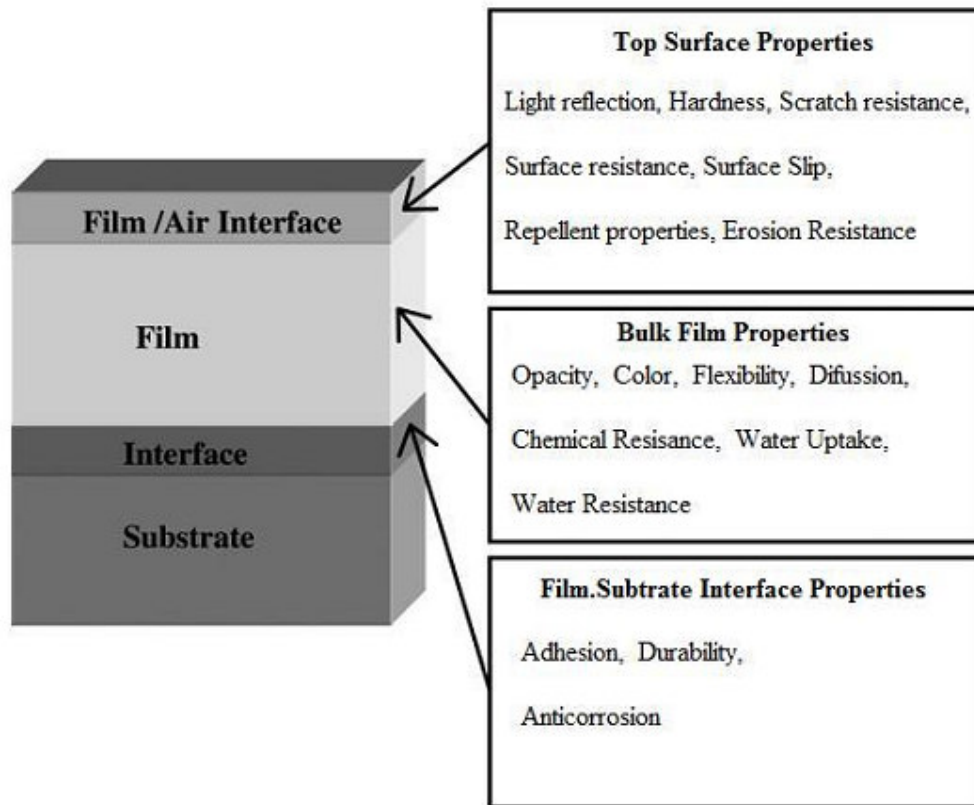
Figure 2.1 : Topographical classification of coating properties.

2.1.2 Classification and Technology of Coating

Since early years coatings are used for several purposes and after the 20th century huge innovations take place in coating technology. In 1907 the first synthetic resins, phenol-formaldehyde condensates were launched on the market and then vinyl resins, urea resins and from the 1930s, alkyd resins, acrylc resins, polyurethanes and melamine resins followed this. Epoxy resins were introduced in the late 1940s. All these developments in coating chemistry were paralleled by advanced in coating technology [2].

Coating technology provide surface protection, decorative finishes and many special functions. Protection and decoration are the two of the most important functions of coating [5]. Generally inorganic coatings are applied for protective purposes. On the other hand, organic coatings are mostly used for decorative and functional applications [1]. The object to be coated itself with its specific material and design and also application process play significant role. Quality optimization and rationalization while minimizing the impacts for humans and the environment must

be taken into account as the framework. Therefore, it can be said that coating technology is an interdisciplinary subject [5].

Coating defines as architectural coatings, product coatings, special purpose coatings and miscellaneous [6]. Organic coatings can be classified as either architectural coatings or industrial coatings [1].

Architectural coatings include paints and varnishes used to decorate and protect outside and inside of buildings. However, product coatings, also called industrial coatings, are applied in factories on products. On the other hand, special purpose coatings include industrial coatings which are applied outside a factory along with a few miscellaneous coatings. Finally, miscellaneous coatings are defined as paint removers, thinners, pigment dispersions, glazing compounds and so on [6].

2.1.2.1 Coatings for Protection and Decorative Purposes

Decorative and protective coatings are used in a variety of applications such as coatings for buildings, furniture, automobiles, large industrial structures, removable coatings, paper coatings, and specialized coatings for optical fibers and electronic components [9]. In economic terms, the most important function for coatings is surface protection, so coatings help to retain value and improve the usability properties of products and therefore, provide huge economic significance [5]. Furthermore, coatings must resist combined effects like physical and chemical effects to which objects are subjected. The interaction of sunshine, rain, heat and frost combined with emmisions from heating systems and internal combustion engines, by ozone and saline fog makes great demands on a coating's resistance and protective properties [5,6]. On the other hand, the primary role of decorative coatings is to enhance the esthetic appeal of homes, offices and other architectural structures by providing color, texture and sheen to interior and exterior surfaces [9].

2.1.2.2 Functional Coatings

Functional coating includes both decoration and protection purposes and it describes systems which possess an additional functionality besides the classical properties of a coating (i.e., decoration and protection) [10]. This functionality depend upon the actual application of a coated sustrate. Examples of functional coatings are self-cleaning, easy- to clean (anti-garffiti), antifouling, soft feel and antibacterial [1].

Besides their special properties, functional coatings must often satisfy additional requirements like nonstick cookware coatings. General expectations of functional coatings are durability, reproducibility, easy application and cost effectiveness, tailored surface morphology and environmental friendliness and functional coatings can be classified as several types depending on their functional chracteristics (Fig. 2.2). Also, functional coatings perform by means of pyhsical, mechanical, thermal and chemical properties. Chemically active functional coatings perform their activities either at film-substrate interfaces (anticorrosive coatings), in the bulk of the film (fire-retardent or intumescent coatings) or at air-film interfaces (antibacterial, self-cleaning) [1].
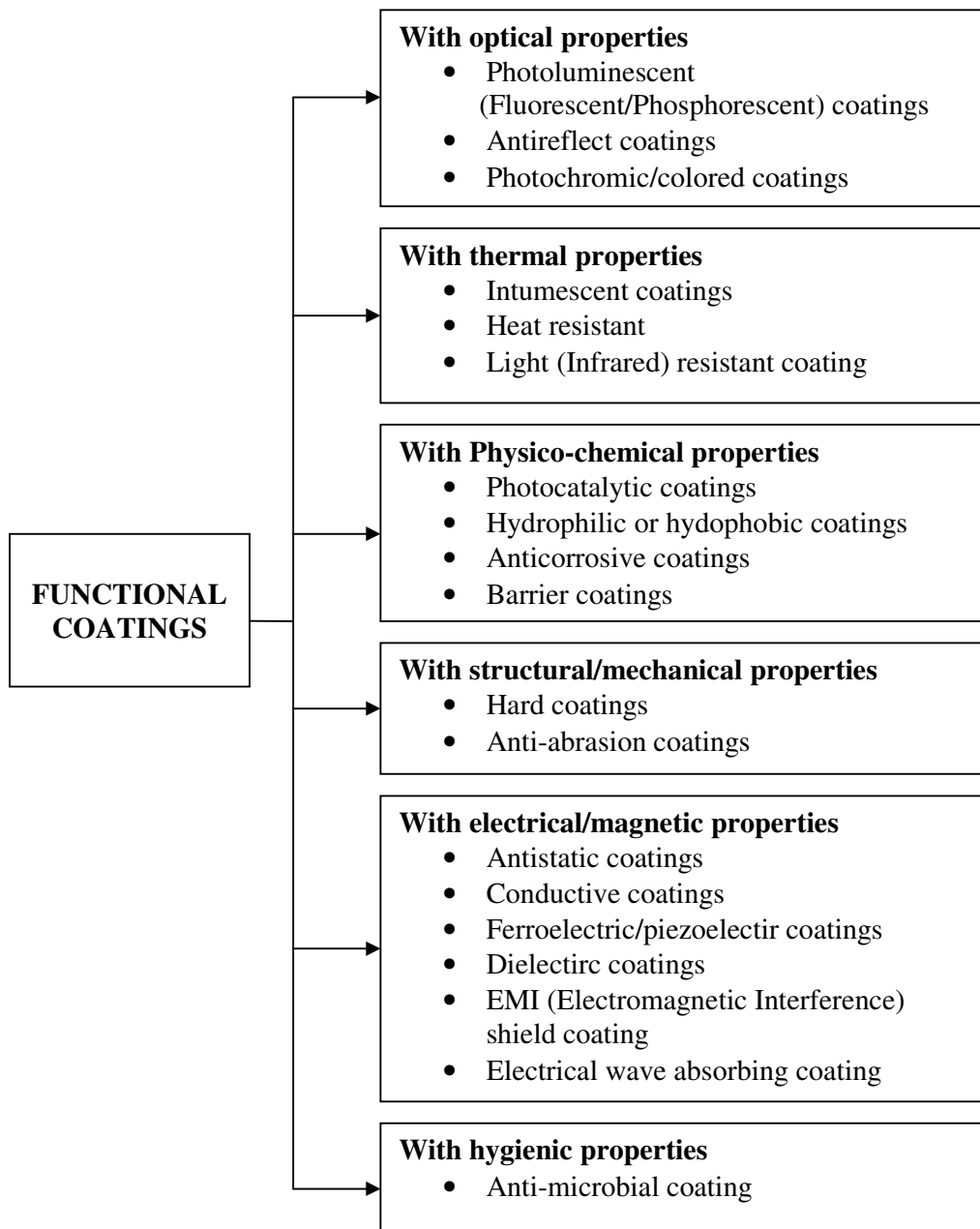
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                        ┌──────────────────────────────────────────┐
                        │ With optical properties                  │
                        │   • Photoluminescent                     │
                    ┌──→│     (Fluorescent/Phosphorescent) coatings│
                    │   │   • Antireflect coatings                 │
                    │   │   • Photochromic/colored coatings        │
                    │   └──────────────────────────────────────────┘
                    │   ┌──────────────────────────────────────────┐
                    │   │ With thermal properties                  │
                    ├──→│   • Intumescent coatings                 │
                    │   │   • Heat resistant                       │
                    │   │   • Light (Infrared) resistant coating   │
                    │   └──────────────────────────────────────────┘
                    │   ┌──────────────────────────────────────────┐
                    │   │ With Physico-chemical properties         │
                    │   │   • Photocatalytic coatings              │
  ┌────────────┐    ├──→│   • Hydrophilic or hydophobic coatings   │
  │ FUNCTIONAL │    │   │   • Anticorrosive coatings               │
  │ COATINGS   │────┤   │   • Barrier coatings                     │
  └────────────┘    │   └──────────────────────────────────────────┘
                    │   ┌──────────────────────────────────────────┐
                    │   │ With structural/mechanical properties    │
                    ├──→│   • Hard coatings                        │
                    │   │   • Anti-abrasion coatings               │
                    │   └──────────────────────────────────────────┘
                    │   ┌──────────────────────────────────────────┐
                    │   │ With electrical/magnetic properties      │
                    │   │   • Antistatic coatings                  │
                    │   │   • Conductive coatings                  │
                    ├──→│   • Ferroelectric/piezoelectir coatings  │
                    │   │   • Dielectirc coatings                  │
                    │   │   • EMI (Electromagnetic Interference)   │
                    │   │     shield coating                       │
                    │   │   • Electrical wave absorbing coating    │
                    │   └──────────────────────────────────────────┘
                    │   ┌──────────────────────────────────────────┐
                    │   │ With hygienic properties                 │
                    └──→│   • Anti-microbial coating               │
                        └──────────────────────────────────────────┘
```

Figure 2.2 : Types of functional coatings

2.1.2.3 Environmentally Friendly Coatings

Because of economic competitiveness and environmental concerns coating technologists begin to explore newer chemistry and approach to improve the efficiency of organic coatings include minimum volatile organic component (VOC). The necessity in the industries is to maintain or improve properties at a reasonable cost, while at the same time meeting the need for environmentally friendly coatings.
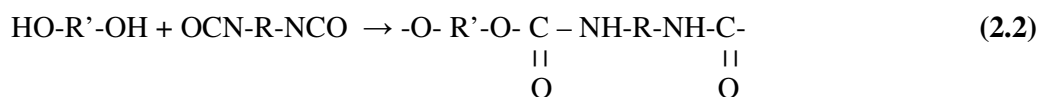
For this purpose several new technologies, such as radiation curable, waterborne and powder coatings have obtained. On the other hand, solvent borne coatings have had particular importance in the area of industrial coatings, where performance is essential. Therefore, some researchers have focused on methods to improve the solid content of the binder by utilizing relatively low molecular weight polymer that build in properties during cure through the formation of crosslink networks. The presence of crosslinks provides thermoset coatings with enhanced tensile strength, good abrasion and mar resistance as well as acid, alkali and solvent resistance, which are lack in thermoplastic coatings. During the development of new systems, numerous aspects must be considered such as the production of the coating formulation, storage of the coating, application and film formation must work with the techniques intended [3].

2.2 Polyurethanes

Polyurethanes are heterogenous polymers which are product of the reaction of isocyanates (–N=C=O) with a hydroxy compound (2.1)

$$R–NCO+HO–R'\rightarrow RNH\text{-}\underset{O}{\overset{\|}{C}}\text{–}O–R' \tag{2.1}$$

They contain the urethane linkage (RHN–C(=O)OR′) and may be considered as esters of carbamic acid or ester amides of carbonic acid. When a diisocyanate and a diol react together, linear polyurethane is obtained whilst a diisocyanate and a polyol lead to a crosslinked polymer [11]. The reaction of a diisocyanate with a diol is presented in the equation 2.2 [12]. Typical polyurethane may contain, in additon to urethane groups, aliphatic and aromatic hydrocarbon, esters, ether, amide and urea groups [13].

$$HO\text{-}R'\text{-}OH + OCN\text{-}R\text{-}NCO \rightarrow \text{-}O\text{-} R'\text{-}O\text{-} \underset{O}{\overset{\|}{C}} – NH\text{-}R\text{-}NH\text{-}\underset{O}{\overset{\|}{C}}\text{-} \tag{2.2}$$

Nearly 90 years before Bayer et al's developments, Charles-Adolphe Wurtz discovered the actions of isocyanates in 1849 [13]. Although the reaction between isocyanate and hydroxyl compounds was identified in 19th century, most of the explanation of the basic chemistry of polyurethanes was performed Otto Bayer in

Germany around 1937 [14,15]. This is followed by DuPont in United States around 1940 resulting in a series of patents on the reaction products of polyisocyanates with various glycols, alkyd resins, polyamides and polyesters. However, it was not until after World War II the commercialization and wide use of polyurethanes occured [15].

Commercially, polyurethanes are produced by exothermic reaction of molecules containing two or more isocyanate groups with polyol molecules containing two or more hydroxyl groups. Mostly few basic isocyanates and a broad range of polyols of different molecular weights and functionalities are used to produce of polyurethane materials. The first commercial applications of polyurethane, for millable elastomers, coatings and adhesives were developed between 1945 and 1947 and this followed by flexible foams in 1953 and rigid foams in 1957 [14]. Generally, polyurethane's application area is diverse types of foams (soft and rigid), soft and hard elastomers, skins, adhesives, sealants, coating for many purposes and highly crosslinked plastics [13,16].
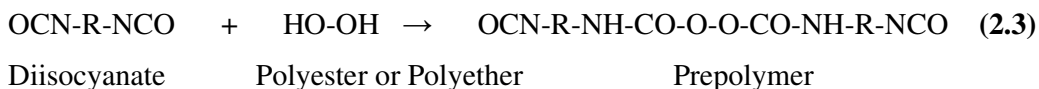
On the other hand, the raw materials for preparing polyurethanes are polyisocyanates, polyols, diamines, catalysts, additives and blocking agents. The polyisocyanates are either aliphatic or aromatic and also, polyols are either polyethers or polyesters. Initially, all comemercial applications of polyurethanes were based almost on polyester polyols but thereafter polyether polyols were introduced in 1957. Generally, polyether polyols are used to produce flexible and rigid foams and polyester polyols are used to produce elastomers, flexible foams and coatings [12,17]. Besides these compounds numbers of additives are utilized to produce polyurethanes. Aditives are catalysts, stabilizers, blowing agents, flames retardants and compounds which protect the polyurethanes against hydrolytic, thermal and oxidative degredation as well as against degradation by light [12].

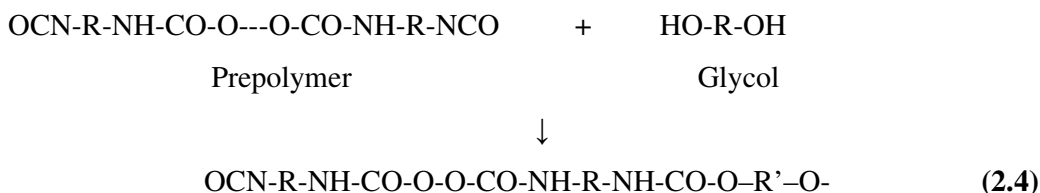### 2.2.1 Chemistry of Polyurethane

Most of polyurethanes are composed of at least three basic components like long chain polyether or polyester polyol, diisocyanate and glycol, water or diamine [12]. The basic building blocks of polyurethane resins are di- or polyisocyanates and generally a mixture of 80 percent toluene-2,4-diisocyanate and 20 percent toluene-2,6-diisocyanate are used. On the other hand, methylene bis (4-phenylisocyanate)

also referred to as p,p'-diphenylmethane diisocyanate is used as diisocyanate widely [15,18].
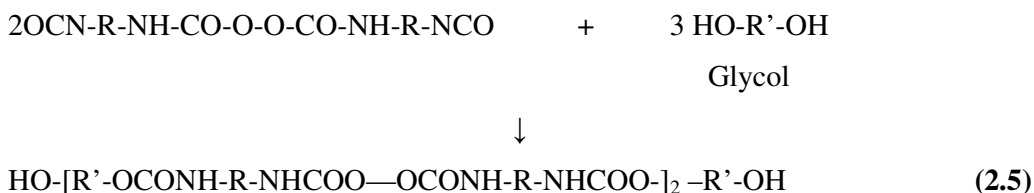
Generally, when diisocyanates react with a polyol, they form isocyanates-terminated prepolymers (2.3)

OCN-R-NCO   +   HO-OH →   OCN-R-NH-CO-O-O-CO-NH-R-NCO   **(2.3)**
Diisocyanate   Polyester or Polyether   Prepolymer

Then the prepolymer reacts with glycol to form urethane group (2.4)

OCN-R-NH-CO-O---O-CO-NH-R-NCO   +   HO-R-OH
                    Prepolymer   Glycol

↓

OCN-R-NH-CO-O-O-CO-NH-R-NH-CO-O–R'–O-   **(2.4)**

When an excess of glycol is used, a hydroxy group terminated polyurethane is obtained (2.5) [17].

2OCN-R-NH-CO-O-O-CO-NH-R-NCO   +   3 HO-R'-OH
                                                    Glycol

↓

HO-[R'-OCONH-R-NHCOO—OCONH-R-NHCOO-]$_2$ –R'-OH   **(2.5)**

High molecular weight polyurethanes can be produced by one of two low temperature condensation methods. These methods are interfacial polycondensation or solution polycondensation. In interfacial condensation, two fast reacting intermediates are dissolved in a pair of immiscible liquids. One of the liquids is generally water. The water phase contains the diamine and the other phase consists of a diacid anhydride and an organic compound. The polymerization takes place at or near the liquid interface. On the other hand, solution polycondensation is carried out in a single liquid inert to both intermediates. The liquid can be one or more organic solvents without reactive functional groups and the reaction generally starts with all the ingredients fully dissolved. The polymer may remain in solution or precipitate at any time. Both interfacial and solution polycondensation methods have been used to prepare polymers by hydrogen transfer reactions like in producing polyurethanes [17].

Depending on their structure, polyurethanes cover a broad range of properties. Besides the primary structure like chemical composition, chan length, chain stiffness, degree of branching or crosslinking, the morphology of polyurethanes is determined by the potential interaction between the polymer chains [12]. There are two fundamental types of chemistry involved in making polyurethane Firstly, phase separated structures as found in flexible foams, thermoplastic polyurethanes, elastomers, adhesives and coatings. The other one is highly crosslinked glassy amorphous material as seen in rigid foams and some composites [14].

At room temperature the higher melting polar hard segments are incompatible with the less polar soft segments and phase separation occurs. This situation takes place more easily with polyether based polyurethanes than those made from polyester polyols [14]. This immiscibility between the hard urethane segments and the soft polyol segments shows that on microscopic level polyurethanes are not structurally homogeneous. The structure may be considered as hard segment domains dispersed in a soft segment matrix. Soft segments are derived from a low T_g polyether, polyester or polyalkanediol and hard segments are derived from usually a high T_g aromatic diisocyanate chain extended with low molecular weight diol or diamine [6,11,13].

The hard segments form crystalline domains by hydrogen bonding and hard segment microphases are covalently linked with each other through the flexible soft segments (Figure 2.3). When stress is applied, the soft segments can extend between the hard segment anchors. The soft segments give the material its elasticity while the crystalline domains prevent permanent deformation of the soft segments as the polymer chains are stretched. Therefore, the elasticity and toughness of a polymer depends on the hard and soft segment percantages [13,14].
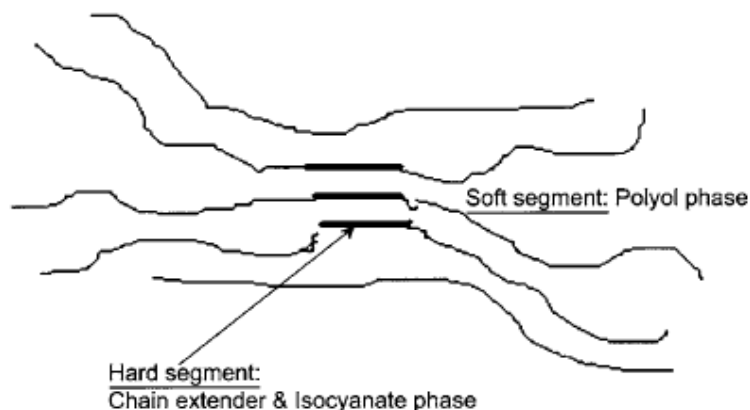
Figure 2.3 : Morphology of polyurethanes

2.2.2 Isocyanates

Isocyanates are highly reactive chemicals and create several chemically different products when combined with –OH and –NH functional groups. Isocyanates with two or more NCO groups in the molecule are needed for the formation polyurethanes. The high reactivity of isocyanate groups toward nucleophilic reagents is mainly due to the positive character of the C atom in the cumulative double bond sequence consisting of nitrogen, carbon and oxygen. The electronegativity of the oxygen and nitrogen imparts a large electrophilic character to the carbon in the isocyanate group [3,12]. The high reactivity and polarizability of the double bonds permit multiple reactions, and because of this isocyanates are widely used intermediate products [12]. The resonance forms of isocyanates are illustrated in Figure 2.4. Generally, electron withdrawing group linked with R will increase the positive charge on carbon, so increasing the reactivity of the isocyanate group towards nucleophilic attack. On the other hand, electron donating group will reduce the reactivity of isocyanate groups [14].
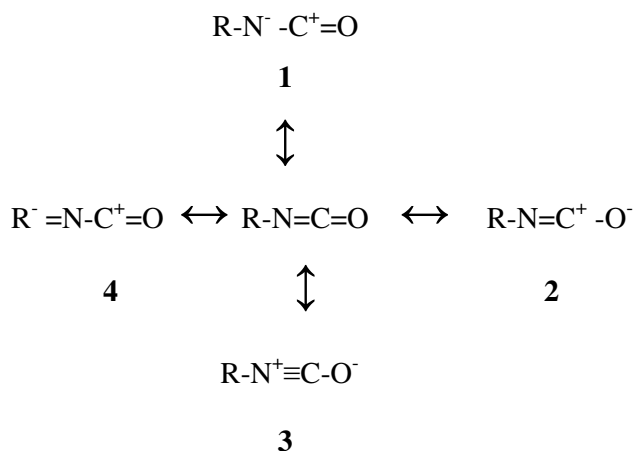
$$R\text{-}N^-\text{-}C^+\text{=}O$$

1

$\updownarrow$

$$R^-\text{=}N\text{-}C^+\text{=}O \quad \leftrightarrow \quad R\text{-}N\text{=}C\text{=}O \quad \leftrightarrow \quad R\text{-}N\text{=}C^+\text{-}O^-$$

4 $\qquad\qquad$ $\updownarrow$ $\qquad\qquad$ **2**

$$R\text{-}N^+\text{≡}C\text{-}O^-$$

3

**Figure 2.4 :** Resonance forms of isocyanates

2.2.2.1 Reactions of Isocyanates

Isocyanates react with any compounds containing hydrogen atoms which are attached to a nitrogen atom. They react with hyroxyl groups, water, amines, urea, urethane, carboxylic acid and also isocyanates react with other isocyanates [14,17]. The reaction between isocyanate and hydroxyl groups like hydroxyl terminated polyesters and polyethers is the most important reaction to produce carbamate, which is called a urethane (2.6) [13]:

R-N=C=O + R'OH ↔ R-NH-CO-OR' **(2.6)**
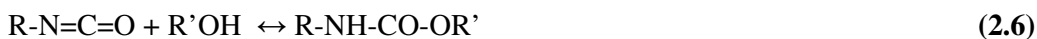
Isocyanate   Alcohol   Carbamate (Urethane)

Aliphatic primary alcohols are most reactive than secondary and tertiary alcohols due to steric reasons. Phenol reacts with isocyanate more slowly than alcohols and resulting urethane groups are readily broken to yield the original isocyanate and phenol [13,14]. The reacton of isocyanates with water produces an amine and carbon dioxide and the reaction is highly exothermic. The initial product is carbamic acid, which is an unstable compound and further breaks down into carbon dioxide and primary amine. The amine will react immediately with another isocyanate to produce urea (2.7) [6,13,14].

$$R-N=C=O + H_2O \longrightarrow \left[R-\overset{H}{\underset{}{N}}-\overset{O}{\underset{}{C}}-OH \right] \longrightarrow R-NH_2$$

(2.7)
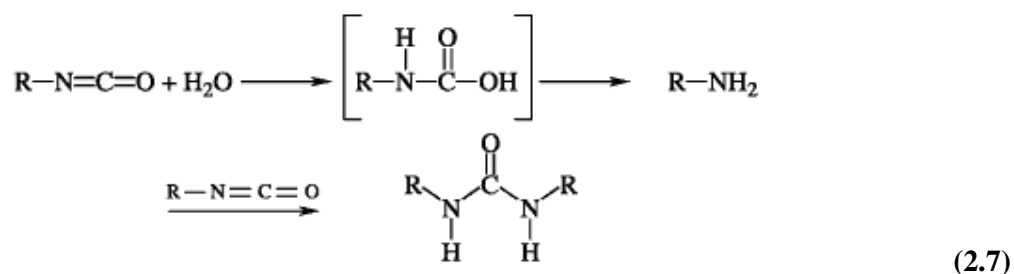
Additionally, isocyanates react with primary and secondary amines to produce urea. Primary aliphatic amines react most quickly followed by secondary aliphatic amines and aromatic amines. These conversions are exothermic and diamines are used as chain extending and curing agents in polyurethane producing (2.8) [6,13,14].


(2.8)
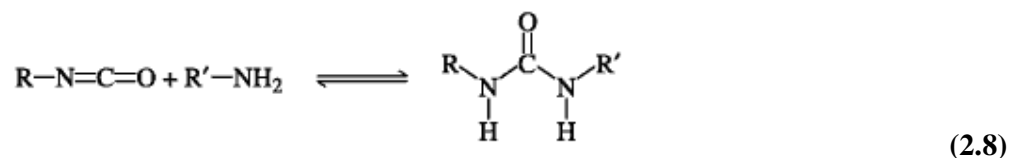
Isocyanates can react with urea to form biurets by an exothermic reaction (2.9). This reaction is faster than allophonate reaction. An allophonate group is formed as a result of the exothermic reaction of isocyanate with the active hydrogen on urethane group (2.10) [6,13,14]. Carboxylic acid reacts slowly with isocyanates to form amides and carbon dioxide (2.11).
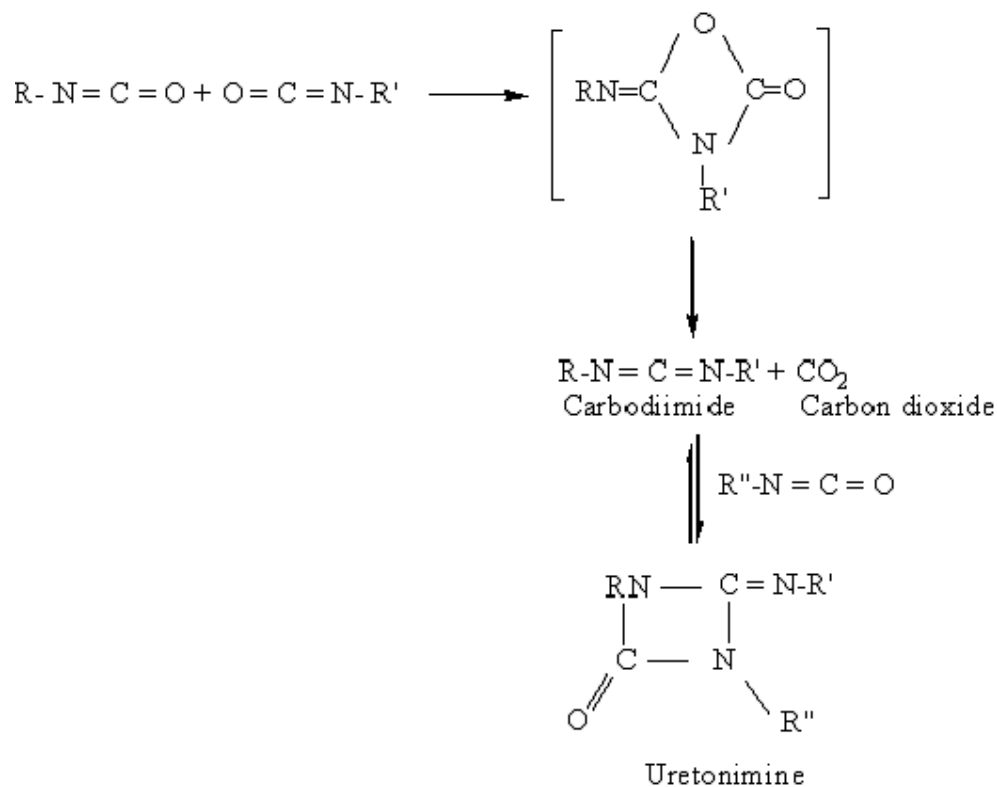

(2.9)

(2.10)

(2.11)
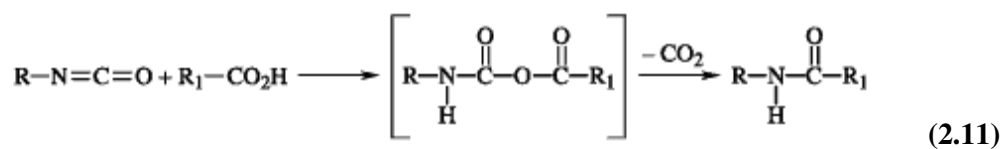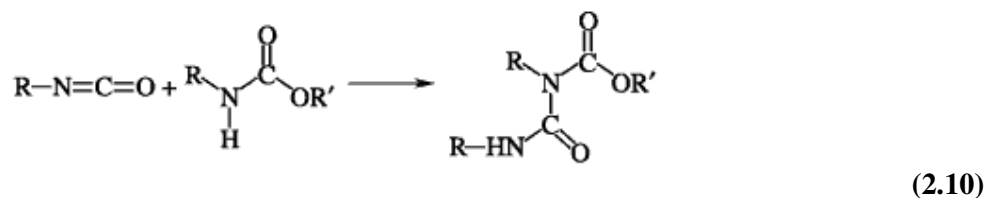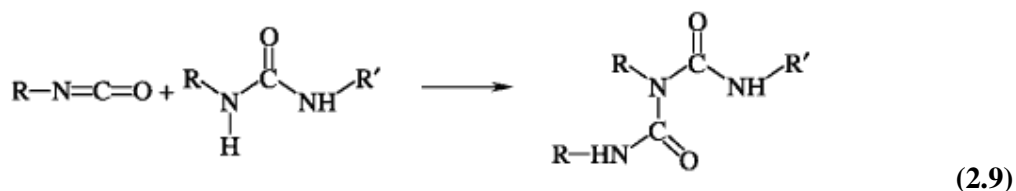
Futhermore, isocyanates react each other to form dimers (uretdiones) and trimers (isocyanurates). In dimer formation isocyanates undergo exothermic cyclo-addition

reaction resulting in a four membered ring (2.12). On the other hand, three isocyanates undergo a cylisation reaction resulting a six membered ring (2.13). Trimerisation is highly exothermic and continues until all NCO groups have reacted [6,14].

$$R\text{-}N\text{=}C\text{=}O + R'\text{-}N\text{=}C\text{=}O \rightleftharpoons$$

(2.11)

$$3\ R\text{-}N\text{=}C\text{-}O \longrightarrow$$

(2.12)
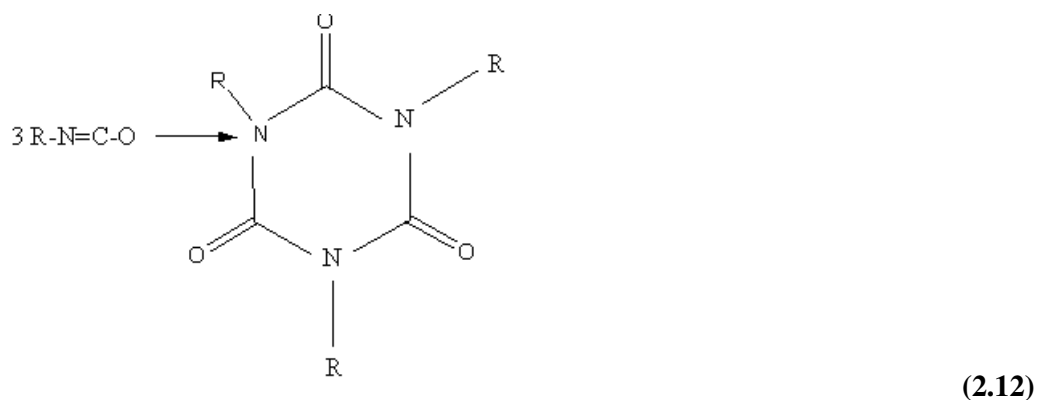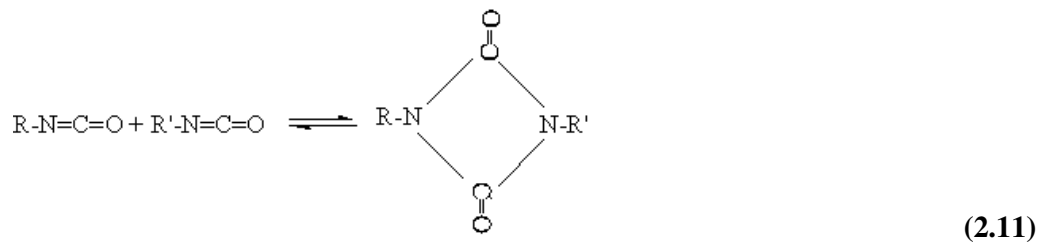
Additionally, isocyanates can react with each other at high temperature to form carbodiimides and carbodiimide can react with another isocyanate in a cyclo addition reaction forming a uretonimine (2.14) [12,14].

$$R-N=C=O + O=C=N-R' \longrightarrow \left[\begin{array}{c} O \\ RN=C \quad C=O \\ N \\ | \\ R' \end{array} \right]$$

$$\downarrow$$

$$R-N=C=N-R' + CO_2$$

Carbodiimide   Carbon dioxide

$$\Updownarrow R''-N=C=O$$

$$\begin{array}{c} RN \longrightarrow C=N-R' \\ | \qquad\qquad | \\ C \longrightarrow N \\ \| \qquad\qquad \backslash \\ O \qquad\qquad\quad R'' \end{array}$$

Uretonimine

(2.14)

2.2.2.2 Types of Isocyanates

Monoisocyanates are used as intermediates products but multifunctionally polyisocyanates is considerably more important than that. Further, diisocyanates are compounds with two isocyanate groups in the molecule and also polyisocyanates include two or more isocyanate groups. Common isocyanates used as building blocks for polyurethanes include aromatic, aliphatic or cycloaliphatic. However, aromatic polyisocyanates are economically more available. On the other hand, aliphatic isocyanates are used if their reactivity fits spesifically the polymer formation or if special properties are required. The most commonly used diisocyanates are tolylene diisocyanate (TDI) (as a mixture of isomers), diphenylmethane diisocyanate(MDI), naphthylene 1,5-diisocyanate (NDI), hexamethylene diisocyanate (HDI) and isophorone diisocyanate (IPDI) [11-13].

a) Aromatic Isocyanates

Aromatic diisocyanates are much more reactive than aliphatic isocyanates with active hydrogen compounds. One of the most common important aromatic isocyanate is tolylene diisocyanate (TDI) consisting of 80% of the 2,4-isomer and

20% of the 2,6-isomer (Figure 2.5) [13]. The isocyanate groups on 2,4-TDI have with the 4-position approximately four times the reactivity of the 2-position and about 50% more reactive than 4-position group in MDI. MDI is one of the monomers more widely used in polyurethane industry and it is preferred over TDI because it has significantly low pressure and usually high performance polymers can be produced by MDI. Pure 4-4'-MDI is a symmetrical molecule which has two aromatic isocyanate groups of equal reactivity. Also, 2,4'-MDI is an asymmetrical molecule with two aromatic isocyanates of different reactivity. 2,4'-MDI is commercially available as a mixture with the 4,4'-isomer (Figure 2.6). [12-14].
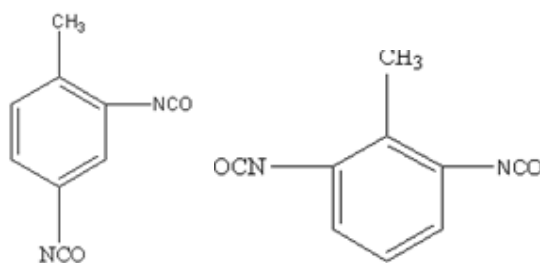

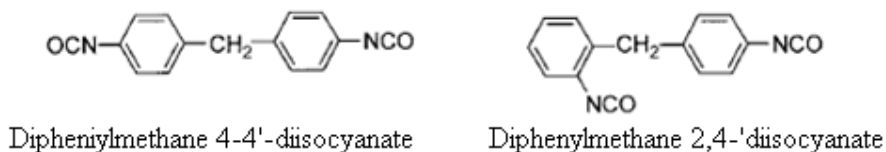
Figure 2.5 : Toluene diisocyanate isomer

Figure 2.6 : MDI monomer

b) Aliphatic Isocyanates

Generally, the major aliphatic polyisocyanates are hexamethylene diisocyanate (HDI), isophorone diisocyanate (IPDI) and bis(4-isocyanatocyclohexyl) methane (H_{12}MDI), 1,3-xylenediisocyanate (XDI), tetramethyl-*m*-xylidene diisocyanate (TMXDI), *m*-isopropenyl-α,α.-dimethylbenzylisocyanate (TMI) and 2,2,5-trimethylhexane diisocyanate (TMHDI). Aliphatic isocyanates give light stable polyurethanes, but those made with aromatic isocyanates rapidly yellow on exposure to light. Therefore, the most commonly application of aliphatic isocyanates are applications which are exposed to light such as floor coatings [6,13,14].

c) Blocked Isocyanates

Polyisocyanates are high molecular weight resins such as prepolymers, adducts and isocyanurate. Blocked isocyanates are a group of polyisocyanates. Generally, because of the high reactiviy and high toxicity of isocyanates the use of isocyanates in one component systems, polyurethane coatings and adhesives are always difficult. Because of this problem, isocyanates are used as blocked form and this is also eleminate toxic hazards coming from using some diisocyanates. Less commonly used terms to describe blocked isocyanates are "capped", "heat latent", "thermally liable", "masked", and "splitters" [16,19,20].

The highly reactive isocyanate functional group can be blocked by several methods and typical method is in which the isocyanate group is reacted with an active hydrogen or methylene compound such as malonic esters (2.15) At elevated temperatures the reaction proceed in such a way to regenerate the isocyanate and the blocking agent. Such thermal splitting is used in heat-curable systems. The regenerate isocyanate group can react with the substrate forming thermally more stable bonds [21-24].

$$R\text{-}N\text{=}C\text{=}O + B\text{-}H \longrightarrow R\text{-}NH\text{-}\underset{\underset{O}{\|}}{C}\text{–}B \qquad\qquad (2.15)$$

There are two urethane forming mechanisms by which a blocked isocyanate can react with a nucleophile. In the first reaction, also called elemination-addition reaction, the blocked isocyanate decomposes to the free isocyanate and the blocking agent. The isocyanate then reacts with a nucleophile to form final product. In other mechanism, which is called addition-elemination reaction, the nucleophile reacts with blocked isocyanate directly to yield a tetrahedral intermadiate by elemination of the blocking agent (Figure 2.7) [20,21,25].

The equilibrium is almost on the side of the blocked isocyanate at storage temperatures, but as temperature increases, the eqilibrium shifts to the right and release iscyanate to cross link with the co-reactant [6].
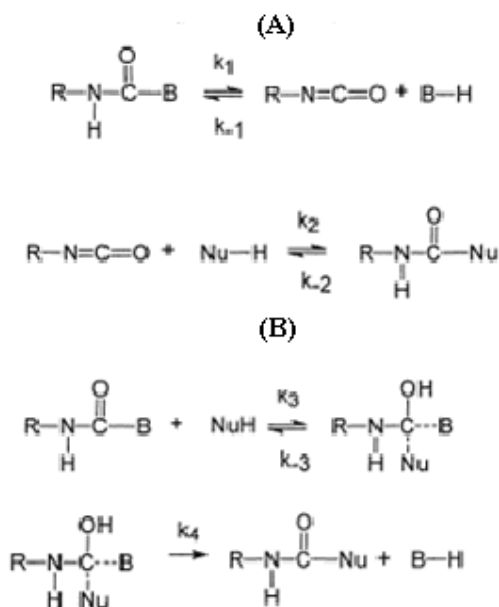
Figure 2.7 : Urethane formation mechanisms by blocked isocyanates (A-Elimination-Addition, B-Addition-Elimination)

On the other hand, heating a blocked isocyanate alone is complicated because of the possible side reactions of the isocyanate. At high temperatures, dimerization or trimerization of the isocyanate takes place or reaction with the original blocked isocyanate form allophanate or biuret [21].

Aliphatic and aromatic isocyanates can be blocked by a variety of blocking agents. Blocking agents are phenols, oximes, alcohols, caprolactam, dibutyl malonate, imidazoline, tetrahydropyrimidine, imidazole, pyrazole, etc. [3]. Amines were also used as blocking agents and thermal studies showed that the N-methylaniline toluene 2,4-diisocyanate (TDI) adduct dissociates with higher rate and at lower temperature than the diphenylamine and N-phenylnaphtylamine blocked TDI adducts [16]. Generally, crosslinking is more rapid in the presence of a nucleophile that can react rapidly with the isocyanate and the differences in reactivity depend on the structures of amines, alcohols and blocking agents [21].
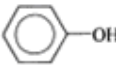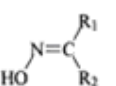
On the other hand, the deblocking temperature of the blocked isocyanate is one of the limiting factors in industrial applications. The rate and extend of deblocking reaction depend on many factors such as the structure of isocyanate and blocking agent including substituents, solvents, catalysts, temperature and thermal stability of the isocyanate blocking agent bond [16]. In general blocked aromatic isocyanates

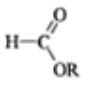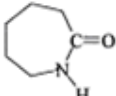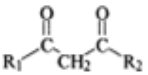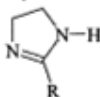deblock at lower temperatures than blocked aliphatic isocyanates. Substitution the aromatic ring to blocked isocyanate with electron withdrawing groups such as Cl, NO_2 and COOR, increase deblocking rates. However, electron donor groups, such as alkyl groups decrease deblocking rates [21]. The thermal deblocking temperature of urethane vary in the following order [12,16]:

• *n*-Alkyl–NHCOO–*n*-alkyl: 250ºC

• Aryl–NHCOO–*n*-alkyl: 200ºC

• *n*-Alkyl–NHCOO–aryl: 180ºC

• Aryl–NHCOO–aryl: 120ºC

Furthermore, the structure of blocking groups has a major effect on deblocking temperatures and curing rates of coating (Table 2.2).

Table 2.2: Some blocking agents of isocyanates

Many alcohols have been used as blocking agents and they give generally high deblocking temperatures (Figure 2.8). Phenols react more slowly with isocyanates than alcohols, however phenol blocked isocyanates deblock at lower temperatures than aliphatic urethanes, in line with the slower rate of the reverse reaction. Phenols are extensively studied for a variety of isocyanates [21,23,24]. Ortho substituted phenols are found to be better blocking agents than para substituted phenols based on the blocking temperatures (Figure 2.9) [19,21].
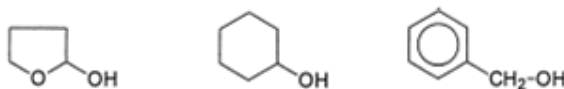
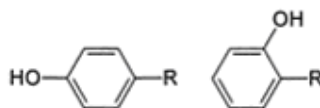**Figure 2.8 :** Hydroxy functional blocking groups

Figure 2.9 : Para and ortho substitution of phenols

On the other hand, the solubility of the blocked diisocyanate in different polyols is very important for the uniform curing of the deblocked isocyanate with them. Generally, 160ºC with 30 minutes duration is preferable [19,23].

2.2.3 Polyols

Polyols are compounds with several hydroxyl functions that react with isocyanates to form polyurethanes (Table 2.3). Common polyols contain two to eight reactive hydroxyl groups and they have average molecular weights from 200 to 10000. Accordingly, most of the polyols cannot be crystallized, distilled or sublimed. Lower molecular weight polyols, such as ethylene glycol, glycerine, butanediol, trimethylolpropane, etc., act as chain extenders or as crosslinkers. However, higher molecular weight polyols are the basis for the formation of polyurethanes. The two types of polyols are polyethers and polyesters, which are both high molecular weight materials prepared from monomers [12-14].

Because of high concentration of urethane groups the low molecular weight reactants result in hard and stiff polymers. However, using of high molecular weight polyols as the main reactants produces polymer chains with fewer urethane groups and more flexible alkyl chains. On the other hand, long chain polyols with low functionality give soft and elastomeric polyurethane, but short chain polyols of high functionality give more rigid and crosslinked polymer [13].

Table 2.3: Polyol types used in polyurethane

Hydroxyl-terminatd polyester polyols	Hydroxyl-terminated polyether polyols	Miscellaneous
Linear&lightly branched aliphatic polyester polyols	Poly(propylene oxide) polyols(PPGs) Poly(propylene oxide/ethylene oxide) copolymers	Acrylic polyols
Aromatic polyester polyols	Reinforced polyether polyols SAN/PHD/PIPA	Natural products esp castor oil
Polycaprolactones	Polytetrahydrofuran (PTHF)	Polyhydroxbutadienes
Polycarbonatepolyols	Amine-terminated polyether polyols	Fire retardant polyols
		Recylcled polyols

2.2.3.1 Polyether Polyols

Polyether polyols are produced by addition of ethylene oxide or propylene oxide to a polyhydroxy molecule in the presence of a catalyst. Addition to the ethylene oxide and propylene oxide, tetrahydrofuran is used commercially in the manufacture of polyether. Besides the limited using of ethylene oxide, propylene oxide is the most significant cyclic ether. On the other hand, tetrahydrofuran is used for the manufacture of range of speciality polyols [3,12,14].

Polyether polyols were first used in the USA but became very important for manufacture of polyurethane foam. Today, polyether polyols still have a limited importance in this application as well as in a few thermo plastic elastomers and in fibers [12].

2.2.3.2 Polyester Polyols

Polyesters polyols are compounds, which are produced generally in an equilibrium reaction of polyfunctinal corboxylic acids or anhydrides with polyfunctional alcohols and polyesters are high molecular weight substances containing the ester group (–O-CO-) as the repeating unit in the chain (2.16).

$$R\text{-}OH + R'\text{-}\underset{\underset{O}{\|}}{C}\text{-}OH \leftrightarrow R\text{-}O\text{-}\underset{\underset{O}{\|}}{C}\text{-}R + H_2O \qquad \qquad \textbf{(2.16)}$$

Because of water formation at the same time of the reaction, this reaction designated as condensation reaction. On the other hand, numerous product groups are available as starting materials for polyesters, so polyesters include so many classes of high molecular weight substances with widely different characteristics [12-14]. There are four main classes of polyester polyols:

- Linear or lightly branched aliphatic polyester polyols (mainly adipates) with terminal hydroxyl groups
- Low molecular weight aromatic polyesters for rigid foam applications
- Polycaprolactones
- Polycarbonate polyols

The outstanding abrasion resistance of polyester polyol based polyurethanes is important using in surface coating and footwear applications. Specialty polyesters such as caprolactone polyols are used to enhance performances in a wide range of applications [14].

2.2.4 Additives

Large numbers of additives are used in the manufacturing of polyurethane. First of all, catalysts are added to the reaction to take place at rapid rate and at lower temperatures. The most common used catalysts in polyurethanes are tertiary amines, especially 1,4-diazabicyclo octane (DABCO), triethyl amine (TEA). Tertiary amines promote isocyanate reactions like reaction with water, alcohols and carboxylic acids which can be occur at moderate temperature, but they are not strong enough for the reactions of isocyanates at elevated tempretaures. Synergistic effects of tin and amine catalysts are important and are widely studied because of the difference in reactivity. Typical tin catalysts are dibutyltin dilaurate and dibutyltin dimercaptide. Organometallic compounds are also used due to their complex ability with both isocyanate and hydroxyl groups. Metallic catalysts are usually employed in systems based on the slower reacting aliphatic isocyanate adducts. Further, in the absence of a storng catalyst, allophanate and biurets formation do not take place for aliphatic isocyanates [3,12-14].

Cross linking agents and chain extending agents are low molecular weight polyfunctional compounds and reactive with isocyanates and also known as curing agents. Generally, difunctional compounds are chain extenders and higher functional

compounds are cross linkers. Chain extender can be difunctional glycols, diamines or hydroxyl compounds and typical chain extender agents are shown in Table 2.4 [14]. Cross linkers have three or more functionality and are used to increase the branching or cross-linking of polyurethane networks through the formation of urethane bonds. Typical cross linkers are glycerol, trimethylolpropane and amine compounds and shown in Table 2.5 [14]. Cross linker mostly used in rigid polyurethanes, coatings and adhesives [12,14].

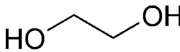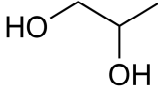**Table 2.4:** Chain extending agents
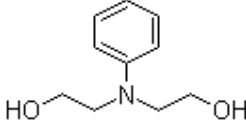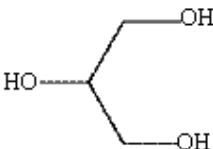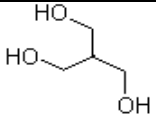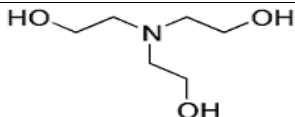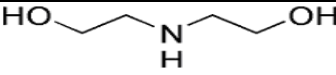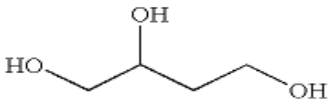
Chemical Name	Chemical Structure
Ethylene glycol	
Propylene glycol	
1,4-cyclohexanedimethanol	
Hydroquinone dihydroxyethyl ether	
Ethanolamine	
N-Phenyldiethanolamine	

Table 2.5: Cross-linking agents

Chemical Name	Chemical Structure
Glycerol	
Trimethylolpropane	
Triethanolamine	
Diethanolamine	
1,2,4-Butanetriol	

Further it may be necessary to use stabilizers, blowing agents, flame retardents, surfactants, fillers, antiaging agents, pigments, reinforcing material as well as mold relase agents, dye stuffs, biocides and blocking agents [12].

2.2.5 Types and Applications of Polyurethanes

Polyurethanes can be grouped for particular properties as foamed or solid. There are three types of significant foamed materials; low density flexible foams, low density rigid foams and high density flexible foams, generally referred to as microcellular elastomers and integral skin foams. Low density flexible foams are often used as flexible and resilient padding material and are made from a lightly cross linked polymer with an open cell macro structure. However, low density rigid foams are highly cross linked polymers and these materials offer good structural strenght and excellent thermal insulating properties. On the other hand, integral skin and microcellular elastomers are used in upholstery, vehicle trim and shoe soling.

Although foamed materials have wide range application area solid polyurethanes are used in many diverse application, like cast polyurethanes in the production of printing rollers and tyres, polyurethane elastomeric fibres in clothing, thermoplastic

polyurethanes in hose and cable sheating, footwear components and high-wear engineering applications. On the other hand, polyurethanes are also used in coatings, adhesives for film and fabric laminates. Polyurethanes are further used in automotive, furniture, construction, thermal insulation and footwear.

2.3 Polyurethane Coatings

Polyurethane coatings are products which are made from the reaction polyisocyanates with a polyol, a polyamine or with water, so polyurethane coating may contain urethane, urea, allophanate and biuret linkages. Since 1950s polyurethane coatings have grown rapidly because of the versatile chemistry and excellent properties like toughness ad abrasion resistance, flexibility, chemical resistance and good adhesion. Polyurethane (PU) coating formulations and processing techniques continuously developed as one- and two-pack systems and today, PU coatings can be found on different materials to improve their lifespan and appearance [3,14].

2.3.1 Materials in Polyurethane Coatings

As it is explained before, urethane technology developed in Germany and is formed from polyisocyanates called desmodurs and polyesters called desmophens. These polymers became popular and widely used because of their excellent properties [15].

Generally, all commercial diisocyanates are important for polyurethane coatings and there are five isocyanates which are used in coating formulations. The most widely used isocyanates in coating formulations are tolylene diisocyanate (TDI), p,p'-diphenylmethane diisocyanate (MDI) and aliphatic isocyanates; H_{12}MDI, HDI, IPDI. Aliphatic isocyanates have lower rate of reaction and form softer coating than aromatic isocyanates [12,14].

Further, there are three main types of polyols with hydroxyl values in the range 30 to 500 used in coating formulations: acrylics, polyethers and polyesters. Acrylic and polyester polyols are generally used in harder coatings with better weatherability. Polyesters can be branched or linear. While branched polyesters are resinous materials and their hardness ranges from soft to hard, the linear and slightly branched polyesters are generally softer and liquids. On the other hand, typical polyether

polyols used in coating are liquid and in comparison to polyester polyols they are more resistant to hydrolysis but resistance to oxidative degradation is lower [12,14].

Besides of isocyanates and polyols, amine compounds are also used in coating technology, especially polyoxyalkyleneamines, basically amine-tiped propylene oxide/ethylene oxide copolymers and amine-terminated chain extenders, such as diethyl toluene diamine (DETDA) or isphorone diamine (IPDA) [12,14].

On the other hand, solvents are added to the coating composition to reduce the viscosity of components and in order to improve processing and commonly they are used a mixture of at least three solvents. Solvents evaporate at different stages during film formation. They are evaporate slowly in the first stage to avoid excessive sagging and dripping, but during the final stages slow evaporation is needed to provide enough levelling and adhesion in coating. Solvents can be esters, ketones, ether-esters and olar aromatic and aliphatic solvents and they can be classified as fast, medium and tail or heavy for their boiling points:

- Fast- boiling point under 100 ºC
- Medium- boiling point 100 to 150 ºC
- Tail or heavy- boiling point greater than 150 ºC

2.3.2 Classification of Polyurethane Coatings

Polyurethanes are classified and defined as six types by American Society for Testing Materials (ASTM). These types are one-component urethane alkyds, one-component moisture-cured urethanes, one-component heat-cured urethanes, two-component catalyst cured polyurethane, two-component polyol-cured urethanes and one-component nonreactive lacquers [15,18].

One-component urethane alkyds or known as oil modified urethanes are formed by the reaction of polyisocyanates with a polyhydric alcohol ester of a vegetable fatty acid. The oil is first de-esterified to give a mixed hydroxyl ester which is further reacts with a diisocyanate to give pre-polymer resin. They cure by oxidation and are used in insulation and conformal coatings, wood, metal and marine finishes. The main feature of these coatings is their low cost and urethane alkyds are not widely used in electrical applications [15,18].

One-component moisture cured urethanes have free reactive isocyanate groups which can cross link and harden with ambient moisture. Their curing rate slower than one-component urethane alkyds and at higher temperatures and levels of humidity these systems may react fast that carbon dioxide formed causes defects, blisters and pinholes, especially with thicker coatings. Reducing the viscosity can be avoiding this problem. This type of polyurethanes is widely used steel construction, seamless floors, bowling alleys, gym floors, industrial floors and insulating coating, but they have limited usage in electronics [14,15,18].

One-part heat cured urethanes also known as oven cured systems. These are included phenol-blocked isocyanates that release the blocking agent when heated to 160ºC and regenerate the isocyanate on heating. However, other blocking agents are also used. The free blocking agent then either remains in the coating or is removed by evaporation. The unblocking temperatures vary from 100 to 200ºC. The one-part heat cured blocked isocyanates widely used for electrical and electronic applications, especially for wire insulation. Mechanism for unblocking one-part heat cured polyurethanes is shown in Figure 2.10 [14,15,18].
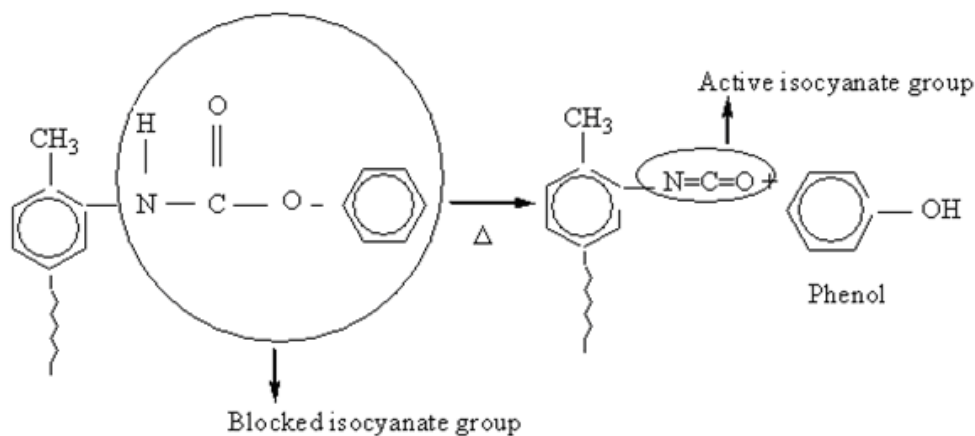

Figure 2.10 : Mechanism for unblocking one-part heat cured polyurethanes

Two-component catalyst cured urethanes consist of a prepolymer or adduct having free isocyanate as a first part and a catalyst, accelerator or cross-linking agent as the second part. This type of urethanes is used in textile finishes and floor coatings [15,18].

Two-component polyol-cured urethanes have a prepolymer or adduct having free isocyanate groups as a first part and a resin having reactive hydrogen atoms as a second part. Part one is usually a tolylene diisocyanate or polyisocyanate prepolymer and part two is hydroxyl-terminated polyesters, polyethers, polyols, castor oil and some epoxy resins. Two-component polyol-cured urethanes widely used for high-reliability electrical insulating and corrosion protective coatings [14,15].

One-part nonreactive lacquers, such as thermoplastic polyurethanes are form by reaction of isocyanates with polyesters or polyether diols and these polyurethanes are thinned with a solvent such as alcohols, methyl ethyl ketone, toluene or N-methyl-2-pyrrolidone. They are used for textile coating and topcoats for plastics [14,15,18].

Generally, polyurethanes coatings are used in industrial coatings such as automotive, aircraft, electrical insulation, electronics, textile, leather, wood products, coil coatings, appliances, metal furniture and machinery, in construction such as protection of metalwork, sealing floors and roofs, in decorative coatings such as wood varnishes and pigmented enamels [3,14].

2.3.2.1 Coating of Electrical Materials and Insulation

Coatings are used in electronic devices for environmental protection, particularly moisture protection and electrical insulation. Besides protection from moisture, coatings are used to protect from other environmental conditions such as salt atmosphere, abrasion from particles, dust and blowing sand, bioorganisms, cleaning solvent and chemicals. Electrical insulating materials insulate and also strengthen electrically conductive materials such as wires, electronic components, motors, transformer components and machine components [2,5,26].

On the other hand, electrical and electronic insulating materials are also called dielectric materials. Generally, coatings may be electrically insulative, electrically conductive or semiconductive depending on their ingredients and molecular structure. However, one of the most important functions is electrical insulation and dielectric isolation. Further, the effectiveness of a coating is defined by its insulation resistance such as volume resistivity, surface resistivity and dielectric strength. Besides these functions there are also other functions such as capacitance, conductance, dielectric constant and dissipation factor [15,18]. One of the most important one is dielectric constant which is defined as the ratio of the parallel

electrical capacitance with the material between the plates to the capacitance when a vacuum seperates the plates. Dielectric constants for insulating or protective coatings are between 2 and 8. In addition to this, low electrical constants and low dissipation factors are preferred for electrical insulation [15].

There are many requirements among desirable manufacturing of insulated electrical material like low material cost, low loss of material during its application, long shelf life and working life, inexpensive process and process equipment, non-toxic, etc. To obtain these properties lots of polymers have been used several years. Polyurethanes, which are one of the most using polymers, were among the first coatings to be used for printed wiring board electrical insulation. They are also used as potting compounds for connectors and as vibration-damping fillets for large components [15,18].

2.3.2.2 Wire Enameling

Most of the electrical machines include electric wires to conduct electric current. These wires consist of generally a metal, mainly copper due to its low resistance to electrical current. However, it is required that bare conductors not coming into contact with each other because of to force the electric current to run in a defined way. It can be achieved by leading the conductors at a distance from each other but this is hardly to use in an electrical motor or generator. Therefore, an insulating material must be used to allow the conductors to be brought into close contact, which makes the construction of machines much easier and more effective, so wire must be electrically insulated and environmentally and physically protected [15,27].

General use of liquid polymer coatings is to insulate magnet wire used in coils and windings for transformers, inductors, hermetic motors, automotive alternator stators. At the beginning, cotton, cellulose (paper) or silk are used to insulate wires. Then, since about 1900, the wrapping of winding wires has been impregnated with air drying varnishes. After 1915, varnishes based on natural resins were substituted by varnishes based on synthetic resins, like phenolic resins. By using these synthetic varnishes it is possible to cover the copper wires without the necessity to first insulate the wires with fibrous materials. In 1938, poly (vinyl acetal) (PVA) and then in 1940, polamide based varnishes are introduced. In 1950, varnishes based on polyurethane are introduced and since that day, polyurethane coated wires have used

widely. The worldwide production of wire enamelling is chemically based on 30% THEIC (tris-(2-hydroxyethyl)-isocyanurate) modified polyesterimides, 20% polyurethanes, 18% polyesters, 10% polyamideimides, 7% polyviniylformales, 4% selfbonding and 1% others [15,18,27].

Organic coatings are applied directly to copper wire which may be round, square or rectangular and wires are generally overcoated for greater toughness, higher dielectric breakdown voltage and moisture protection. It is necessary that the conductor, which is mainly copper, present a smooth, clean surface, as free as possible of oxides for production of magnet wires. If not, coatings will not have good adhesion, cause to produce pinholes and also some other defects in mechanical properties can be occurring [15,18].

a) Enameling Process and Curing Mechanism

In a traditional manner, magnet wire is made by passing copper wire through tanks containing solution of insulating enamel. On the other hand, generally enamel is applied on the wires with felt or dies which regulate the film thickness. Generally, the wire enamel is applied on thin wires by felts and on thick wires by dies. The wire with liquid enamel runs through the oven of temperatures over 400ºC, generally from 400ºC to 700ºC, so the cure time is only a few seconds or much less [2,18,28]. In this process, the viscosity of the enamel decreases due to the high temperature, but by evaporating solvents viscosity increases again. After these deblocking of the blocked isocyanate adduct occurs and by helping of the catalyst, the isocyanate cross-linked with the polyol during ongoing solvent evaporation. At this time, blocking agent diffuses to the enamel surface and evaporates with the solvents and also, high boiling solvents evaporate. After wire cools down, the process is repeated until the desired thickness of enamel is obtained; typically 6 to 20. Coatings for enameled wires frequently have two coat or multicoat structure with at least one base coat and at least one top coat [28,29].

b) Properties and Classification of Magnet Wires

There are four categories of properties of enameled wires; mechanical, thermal, electrical and chemical. Mechanical properties are the behaviour of the enameled wire under the influence of different mechanical stress. These are elongation, springiness, flexibility and adherence, and the resistance of abrasion [27]. Elongation

is the increase in length before breaking and expressed as a percentage of the original length and springiness is the recoil, measured in degrees, after the wire is wound in the form of a helical coil or bent by defined angle. Flexibility and adherence means the potential of wire to withstand stretching, winding, bending or twisting without showing cracs or loss of adhesion of the insulating film. The resistance of abrasion is the maximum force which can be substained when a needle scrapes along the wire under a progressively increasing force.

Maintaining the capacity of enamel structure and properties at high temperatures are described as thermal properties. They are heat shock, thermal endurance, cut through and high temperature failure test. Heat shock is the potential of mechanically stressed wire to withstand high temperatures and the thermal endurance describe the temperature index. Cut through is thermoplasticiy of the enamel wire at high temperature. The thermal properties are very important for the finally manufactured electrical equipment using the enamel wires [27].

Electrical properties describe the behaviour of enamel under the influence of electrical fields like electrical resistance, dielectric loss tangent and voltage like breakdown voltage and continuity of covering. Breakdown voltage is resistance of the insulating film and continuity of covering is uniformity of coating measured under a specified potential difference. Dielectric loss tangent describes steep rise of the dielectric loss showing the correct curing of the insulating film and it is very important for high voltage applications [27].

Finally, chemical properties describe the capacity of the enamel to withstand attack by chemicals and they are resistance to solvents, resistance to refrigerants, resistance to transformer oil [27].

The general wire enamel types are:
- Plain enamel
- Polyvinyl formal
- Polyurethane (PU)
- Nylon
- Epoxy
- Polyester
- Polyamide-imide (PAI)

- Polyester-amide-imide
- Polyester-imide (PEI)
- Polyimide

By the way, magnet wire is generally classified according to its thermal endurance and thermal index rating according to ASTM D2307, "Standard Test Method for Thermal Endurance of Film-Insulated Round Magnet Wire". First of all, plain enamel has adequate dielectric, physical, mechanical, and chemical resistant properties for many applications with thermal class of 105ºC. Also, polyvinyl formal, which is in class 105ºC, has high adhesion to base wire and provides excellent windability, abrasion resistance, and compatibility with most varnishes and encapsulating compunds and they are used especially oil filled transformers [15,18,27].

On the other hand, polyurethane coatings are used for magnet wire suitable for temperatures up to 130ºC and they permit soldering without striping, provide fast enameling. Nylon has limited usage as primary insulation for magnet wire and is used generally as an overcoat to improve physical, mechanical, and solvent resistant properties and epoxy-enameled wires are used generally in wet transformers. First usage of polyesters was based on glycerin, but during the 1960s this was replaced by tris-(2-hydroxtyethyl)-isocyanurate (THEIC). This tris-based polyester has a thermal rating of up to 200ºC with good solvent resistance and it is compatible with most varnishes and encaplusating compounds [15,18,27].

Furthermore, polyamide-imide and polyester-amide-imide are used in magnet wire having a thermal rating of 200ºC. The polyamide-imide contributes toughness and good windability which withstands and polyamide-imide overcoated magnet wire is suitable for used in hermetic motors. On the other hand, polyester-amide-imide insulated magnet wire is used with high-speed winding devices. Polyester-imide enameled wire is included thermal class 180 and thermal class 200 and it provides a coating with outstanding features and is suitable for high-temperature applications. Finally, polyimide-enameled wire has the highest thermal stability and it is used in applications and environments where other enameled wires would be unsuitable [15,18].

2.3.2.3 High Performance Polyurethane Coatings in Wire Enameling

Polyurethane coated wires are used mainly communication and electronic industry because they allow high enameling speed and direct soldering of the coated wire. Another feature of polyurethane insulated wire is its superior "Q" characteristics at high frequencies and humidities, which is reciprocal of the dissipation factor [15,27].

General composition of a polyurethane wire enamel includes blocked polyisocyanate adducts, a polyester polyol, catalyst, solvent and additives and the wire enamel composition is one-component [15]. The polyurethanes use salts of tin, zinc or complex mixtures of amines to accelerate the dormation of the urethane bonds. Aromatic isocyanates are used in wire enamelling, because they have higher thermal stability and higher reactivity compared to aliphatic isocyanates. As it explained before, no free monomeric isocyanates are left in polyurethane wire enamel by using blocking agent for isocyanates. Forming the blocked isocyanate adduct increases the molecular weight, the branching density and the functionality and cause to a high cross linking density on the wire with a higher hardness and chemical resistance. Further, the blocking of the free isocyanate groups with aromatic alcohols provides stable one-component formulation with long shelf life. The blocked isocyanate adduct in polyurethane wire enamel is stable in room temperature, but at elevated temperatures in the oven deblocking occurs and free isocyanate group reacts with polyester polyol to obtain stable urethane structure [14,27,28].

Besides the use of the ingredients, flow additives and dyes to color the polyurethane enameled copper wire are included in the finished enamel. The manufacturing process of enameled wires is economically and environmentally suitable but the enamels are harmful because of the solvents needed. Therefore, the manufacturers considered this situation and they developed new wire enamels with alternative solvents and alternative methods. On the other hand, in order to improve processing of the enameled wires on high-speed automatic winding machines, the surface of enameled wire is coated with a lubricant and this lubricant is generally applied to the enameled wire directly after it leaves the enameling stove. Once the solvent has evaporated it forms a coating with good sliding capacity [26,27,30].

Paraffin and waxes are generally used as lubricants and to the enameled wire from a solution having a few percent of the lubricant dissolved in solvents such as petroleum

benzene and xylene, and the solvent is subsequently evaporated. However, this not a healthy method and can cause damage on workers. Furthermore, the lubricant solution has such a low concentration and viscosity that the thickness of the lubricant coating cannot be controlled satisfactorily. Another method that has been proposed for providing enameled wires with high self-lubricating properties is to use wire enamel compositions containing synthetic resins having good lubricating properties such as polyethylene, polypropylene and polytetrafluoroethylene, silicone oil and fluorine containing surfactants. This types of chemicals are incorporated into the composition of the wire enamel and to eliminate the defects of the conventional enameled wires, it have found that a desired enameled wire can be produced by forming one or more wire enamel coatings on a conductor and a lubricating wire enamel coat on the outermost layer and migrate to a greater or lesser extent towards the enamel surface during curing [26,31].

a) Fluoropolymers in Polyurethane Coatings and Wire

Fluorocarbons and fluoropolymers are used in commercial products widely, such as nonstick coatings for cookware, construction materials, carpets, textiles, paints, electronic materials, household cleaners, personal hygiene products and non wetting biological applications [32-34]. The term fluoropolymers is the generic term and it actually includes fluorocarbons, which consist of polymers with only carbon-fluorine bonds, among the strongest known in organic chemistry and the interactions of fluorocarbons are weak due to the small size and high electronegativity of fluorine [3,18]. Polymeric materials that have low surface energy and thus low wettability and low adhesion are highly desirable in many practical applications [35]. As a consequence, fluorine-containing polymeric materials exhibit unique property combinations of low surface energy, low friction, low refractive indices, dirt repellant, biological inertness (i.e., resistant to a harsh environment), good resistance to corrosive chemicals, good stability against hydrolysis, thermal stability, low water and ion permeability, lubricity, low solubility in polar and non-polar organic solvents (being non-wettable and oleophobic, low interfacial free energy) due to substantial hydrophobicity [36,37]. Polymers with fluorinated chains are reported to be highly hydrophobic materials; the fluorinated chains segregate toward the surface, resulting in considerable decrease in surface energy [38].

Flurocarbons typically classified as two main groups: (1) polymers based on highly fluorinated monomers such as tetrafluoroethylene (TFE), hexafluoropropylene, perfluoromethyl vinyl ether, and vinylidene fluoride, and (2) chemicals and polymers containing the perfluoroalkyl group, $F(CF_2)_n$ – (n=4-18) [34]. As electronics move toward high-speed, high-frequency applications, fluoropolymers are important to electrical functions because of their low dielectric constants and dissipation factors [15].

Polyurethane is one material that could benefit from characteristic properties of fluorinated polymers [36,39]. Fluorinated polyurethanes (FPUs) are a class of new materials which also have improved properties in terms of mechanical and surface characteristic and chemical resistance and they are used also insulating for wire and cable [40].
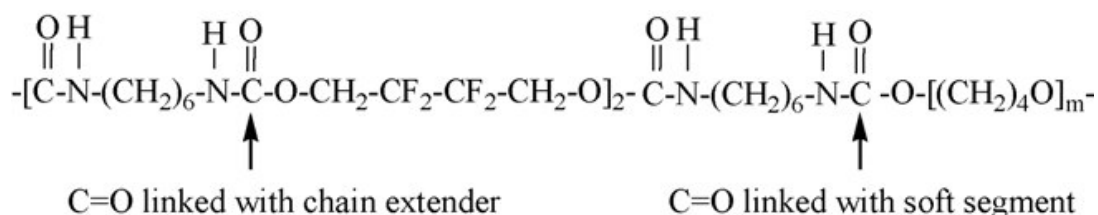
Figure 2.11 : Schematic structure of fluorinated polyurethanes

b) Siloxane in Polyurethane Coatings and Wire

Silicone resins have been available since about 1944 and unlike other polymers silicones are not entirely organic. Chemically, silicones consist of alternate Si and O atoms linked to organic sidegroups such as aliphatic or aromatic hydrocarbons and they are classified as semi-organic. The –Si-O-Si-O- backbone structure is referred as siloxane [15,18]. The general structure for linear silicone polymer is represented in Figure 2.12.
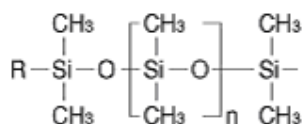
Figure 2.12 : General structure for linear silicone polymer

The polysiloxane is an important kind of materials used for coating, adhesives, impact-resistance plastics, etc. [33]. Furthermore, polysiloxane materials are well known for their hydrophobicity, biological consistency, good water repellency,

lubricity, high flexibility and excellent thermal stability, but some defects in tensile strength and adhesion property restrict their application in some areas [33,41].

The polysiloxane modification using functional polymers or compounds has become increasingly important for a wide range of application [33]. The polysiloxane modified polyurethane (Si-PU) obtained by incorporating siloxane units into the main chain of polyurethane possesses both the properties of polysiloxane and polyurethane. These properties do not only include good thermal stability, freeze resistance, hydrophobicity and insulativity, but also adequate flexibility, cohesiveness, wear resistance and surface property, and also excellent dielectric properties. However, more siloxane components are needed to improve the surface property for this main chain type of Si-PU [41].

3. EXPERIMENTAL WORK

3.1 Materials

3.1.1 Chemicals

Polyurethane Varnish (193.25 series- Altana)

It was used as it recieved.

Krytox$^®$ 103 (DuPont^{TM})

It was used as recieved. Krytox$^®$ oils are clear, colorless, fuorinated synthetic oils that are nonreactive, nonflammable, and are long-lasting. Krytox$^®$ is perfluoropolyether (PFPE) and it is also called perfluoroalkylether (PFAE). They are a series of low molecular weight and fluorine end-cap with the following chemical structure:

$$F-(CF-CF_2-O)_n-CF_2CF_3$$
$$|$$
$$CF_3$$
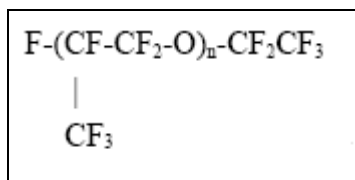
Figure 3.1 : Chemical structure of Krytox$^®$ product

Fluoroguard® (DuPont^{TM})

It was used as recieved. DuPont^{TM} Fluoroguard® polymer additives are based on a fluorinated synthetic oil and they are colorless, odorless, and chemically inert.

Baysilone$^®$ OL31 (Borchers)

It was used as recieved. Baysilone$^®$ is based on hydroxy functional polyether modified methyl polysiloxane.

Bemkay (Special Product)

It was used as recieved. Bemkay is based on hydroxyl functional polydimethylsiloxane.

3.2 Equipments

Infrared Spectroscopy (FT-IR)

Infrared spectra were recorded by Perkin-Elmer Spectrum One FT-IR Spectrometer.

Thermogravimetric Analysis (TGA)

Thermal stability of polymers was measured by Thermogravimetric Analysis (TA TGA Q50) in flowing nitrogen atmosphere at heating rate of 20 ºC / min.

Spin Coater Device

Thin films of the polymeric material were prepared on glass in SCS Spin Coater System P6700 under 1000rpm and vacuum.

Contact Angle Device

Contact angle measurements of the samples was measured by KSV CAM 200.

Enameling Machines

Coating materials were applied on wires by wire enameling machines MAG HESF 2 and 3, Aumann DLH 2, 3 and 6.

Static/Dynamic Coefficient of Friction Tester

Static and dynamic coefficients of wire enamels were recorded by Static/Dynamic Coefficient of Friction Tester (RIGON Instruments-SST5).

Heat Shock Tester

The potential of the wire to withstand temperature exposure after the wire has been streched and/ or wound or bent around a mandrel was recorded by oven at 200 ºC.

Cut-through Tester

Thermoplasticity of the enamel at high temperature was measured by Cut Through Tester PCML 3X.

Breakdown Voltage Tester

Resistance of the insulating film to an a.c. voltage with a nominal frequency was measured by High Voltage Breakdown Tester at room temperature RIGON RDT-V15 and High Voltage Breakdown Tester at high temperature RIGON SCF 96 DG.

Continuity of Insulation Tester

Uniformity of coating under specified potential difference was measured by High/Low Voltage Continuity Tester, P&F Maschinbau GmBH EFCL.

Dielectric Losses (tg δ-Tangent Delta)Tester

Dielectric losses and also correctness of the insulating film of enameled wires were measured by Tan Delta Tester Dansk TD-Series.

Solderability Tester

Solderability of the enameled wire is observed by a solder bath at 390 ± 5 ℃.

Spring Back Tester

Springback and flexibility were measured by Springback Tester MFAL21.

Automatic Elongation Tester

Elongation -the increas in length before beraking- was recorded by Automatic Elongation Tester.

Pinhole Tester

Pinhole testing was used determination of the wire insulation failure [42].

Scanning Electron Microscope

The surface topography of sample enameled wires was observed by Scanning Electron Microscope (SEM) JEOL 7000-S.

3.3 Preperation and Application of Coating Materials

In this thesis, all coating materials were prepared by polyurethane-based varnish, both in laboratory and industrial plant. Before the preparation of the coating material the varnish

was chacterized by FT-IR (Figure 4.1). Additionally, polyurethane varnish was coated on glasses by Spin Coater Device under high velocity and vacuum, and these thin films were cured at oven. After curing, contact angles of these cured films were measured.

3.3.1 Preparation of Coating Materials

3.3.1.1 Preparation of Coating Materials with Fluorinated Chemicals

All coating materials were prepared by adding fluorinated chemicals to polyurethane varnish. The solid content of the varnish was 25 % of the whole varnish and in this part, all calculations were made with considering this percentage. For this purpose, all fluorinated chemicals were added to the varnish with variety of proportions. The proportions for Krytox 103 were 0.1 % and 0.15 %, for Fluoroguard was 0.1 % and 0.15 %.

3.3.1.2 Preparation of Coating Materials with Coating Materials with Polysiloxane

The proportions for Baysilone were 0.05 %, 0.1 %, 0.15 %, 0.17 %, 0.2 % and 0.25 %, for Bemkay 0.05 %, 0.25 %, 0.5%, 0.75 %, 1 %, 1.2 % and 1.33 %. Also, the mixture of Baysilone and Fluoroguard were prepared with different proportions:

Baysilone 0.05 % + Fluoroguard 0.05%

Baysilone 0.05 % + Fluoroguard 0.1%

Baysilone 0.1 % + Fluoroguard 0.05 %

Baysilone 0.15 % + Fluoroguard 0.1 %

3.3.2 Application of Coating Materials

In laboratory, coating materials were added seperetely in different dry flasks with magnetic stirrer. After mixing coating materials were applied on glass in Spin Coater device under high velocity and vacuum. Spin coating method is a widely used coating method to achieve uniform thin films of materials, often polymers, onto the surface of a substrate by employing the concept of centrifugal force (Figure 3.2) [43].
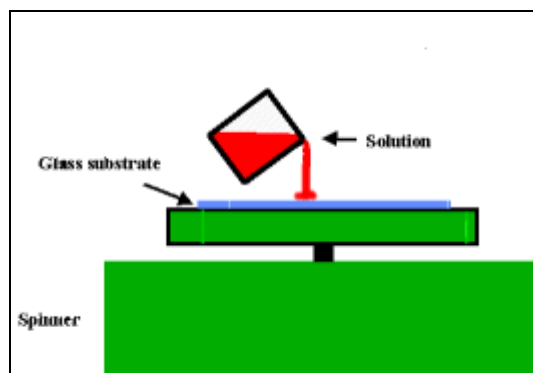
Figure 3.2 : Schematic structure of spin coating

The films were then cured in drying oven at different temperatures. After several experiments it is obtained that 4 minutes is enough for curing time. The working temperatures and proportions are shown in Table 3.1 and codes for samples are shown in Table 3.2.

Table 3.1: Working temperatures and proportions in laboratory

Component	Proportions %w/w	Temperatures ºC
Krytox® 103	0.1	160 180 200 220
Bemkay	0.05 0.25 0.5 0.75	200
Fluoroguard®	0.1	180 200 220
Baysilone®	0.05 0.1 0.15	180 200
Fluoroguard® + Baysilone®	0.05+0.05 0.1+0.05 0.05+0.1	180 200

Table 3.2: Codes for samples

Sample Name	Sample Code
Krytox 103®	FAC3
Fluoroguard®	FAG
Baysilone®	BYS
Bemkay	Bemkay

Schematic structure of curing mechanisms is showed in Figure 3.3.

Figure 3.3 : Schematic structure of mechnasim of polysiloxane modified polyurethane

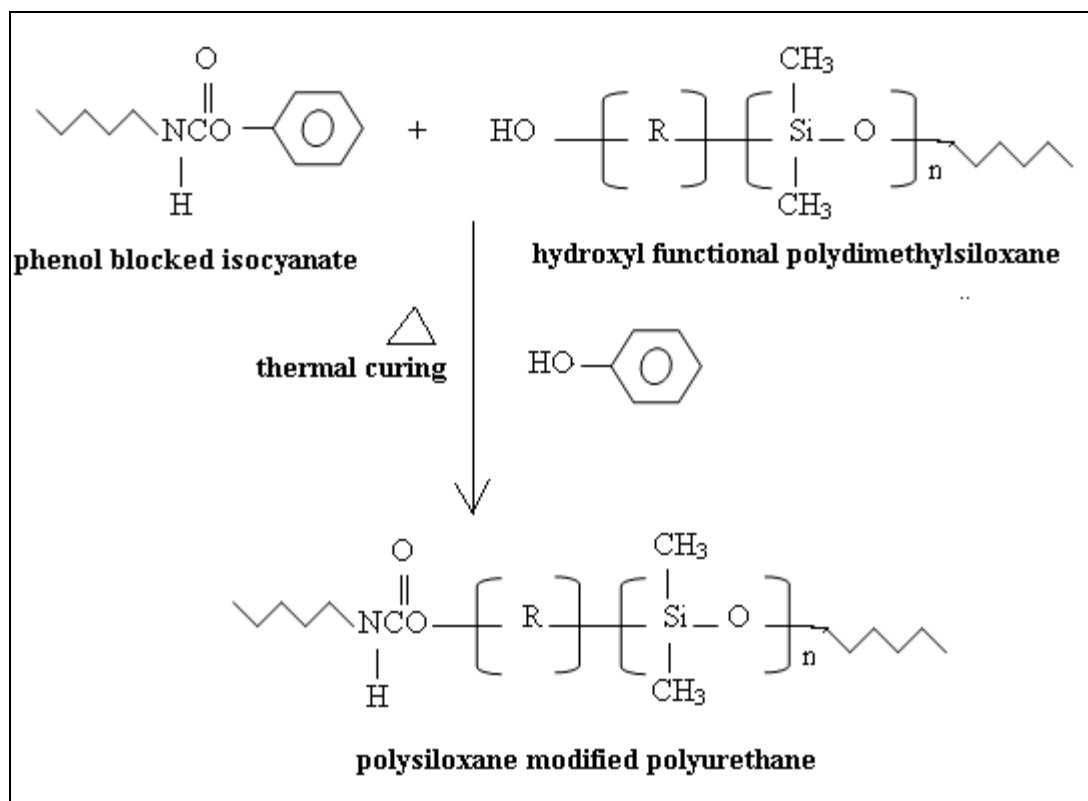In industrial plant, coatings materials were prepared in tanks fitted with mixers. First of all, all coatings materials were mixed and then passed through enameling machine. Schematic structure of enameling machine is showed in Figure 3.5.
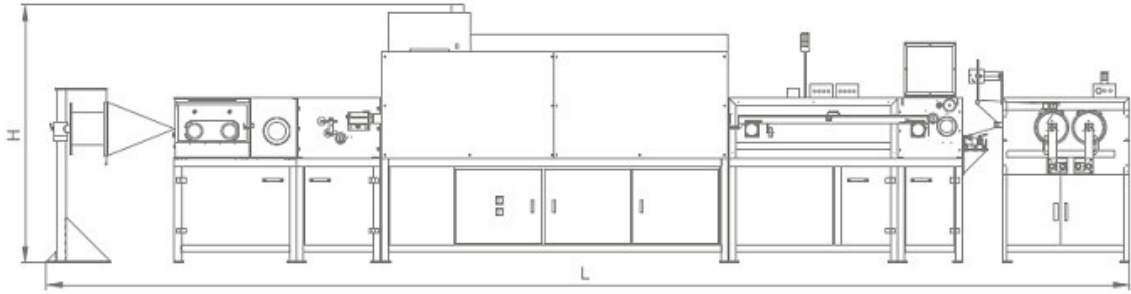
Figure 3.4 : Enameling machine structure

Polyurethane varnish were applied approxametly 18-20 layer and prepared coating materials were applied as a top coat on wires. The annealing temperature was 500-550 ºC and oven temperature of the enameling machine was 470-500ºC and speeds were 800-1000 m/min.and 700-800 m/min. for different diameters.

3.4 Analysis

Generally, FR-IR is used to analyze samples that are available either in small quantity or a small entity, and FTIR is used for qualitative identification of various functionalities [44]. In this study, FT-IR and TGA were used to chacterizing and thermal analyzing of samples. On the other hand, contact angle measurement, static/dynamic coefficient of friction test, heat shock, cut-through, continuity of insulation, dielectric losses, breakdown voltage, solderability, pinhole, spring back, elongation, SEM were used to monitor physical, mechanical, thermal and electrical properties of samples.

Contact angle was measured by producing a drop of pure water on films and it is explained by Young's equation;

$$\gamma^{sv} = \gamma^{sl} + \gamma^{lv}\cos\theta \qquad\qquad (3.1)$$

θ: contact angle

γ^{sl}: solid/liquid interfacial free energy

γ^{sv}: solid surface free energy

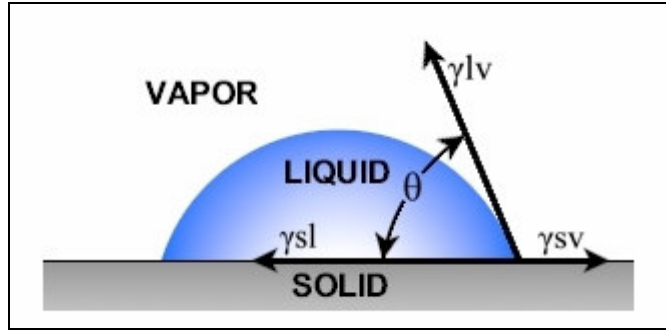γ^{lv}: liquid surface free energy

Figure 3.5 : Contact angle measurement

The hydrophobicity of a surface can be enhanced by a chemical modification that lowers the surface energy. This modification leads to an increase in the contact angle of a water drop [45].

On the other hand, the scanning electron microscope (SEM) images the sample surface by scanning it with a high energy beam of electrons and it provides an improved depth of field, higher magnification, analytical capabilities, and the benefits of image processing [46].

Further, static/dynamic coefficients of friction were recorded by the tester showed in Figure 3.7. Dynamic coefficient of friction is recorded by part B, and static coefficient of friction is recorded by Part A. In dynamic test wire specimen is pulled under a test load. The force is developed between the wire surface and the load contact surface and transferred to an appropriate measuring device. The reading in N is divided by the load in N for determination of the dynamic coefficient friction (μ_d).

$$\mu_d = Fr/Fn \tag{3.2}$$

Fr: Friction force (measured by the load cell)

Fn: Normal force (weight applied to the wire)

On the other hand, the static coefficient of friction (μ_s) is determined by measuring the inclining angle α of a plane at the moment when a block begins to slip on the tack made from the wire specimen.

$$\mu_s = \tan \alpha \tag{3.3}$$
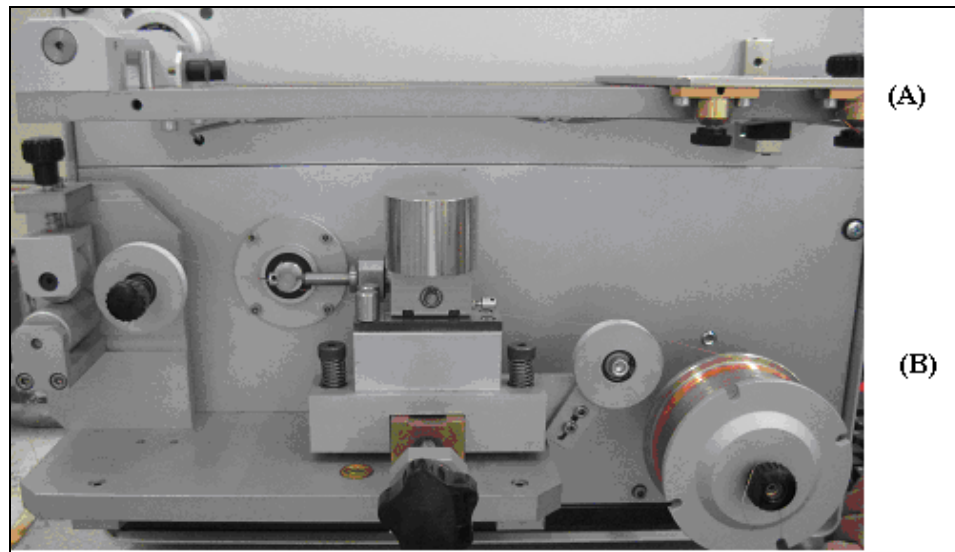
Figure 3.6 : Static/dynamic coefficient of friction tester

4. RESULTS AND DISCUSSION

In this study, we want to improve the surface, thermal and mechanical properties of copper wire enamel because of necessities in enameling industry. For this purpose, numbers of chemicals which are mentioned previously were used and polyurethane coating materials modified with fluorine and siloxane were prepared. All formulations are coated on both glass and copper wire surface and cured by means of thermal curing. After curing this samples are subjected to further thermal, mechanical and electrical tests.

4.1 Fourier Transform Infrared Spectroscopy Results

In order to obtain molecular structure of coated materials after thermal curing and polyurethane varnish, Fourier Transform Infrared Spectroscopy was used. From the FT-IR spectra (Figure 4.1) of the polyurethane varnish, the strong absorption bands at 3379 cm^{-1} for the hydroxyl group (OH streching) appear.

Figure 4.1 : FT-IR spectra of the polyurethane varnish

Furthermore, the strong absorption bands at 3023 cm^{-1} for the aromatic compounds and at 2923 cm^{-1} for the aliphatic compounds CH antisymmetrical and symmetrical streching appear due to the CH$_2$ structure in the varnish. The strong absorption band at 17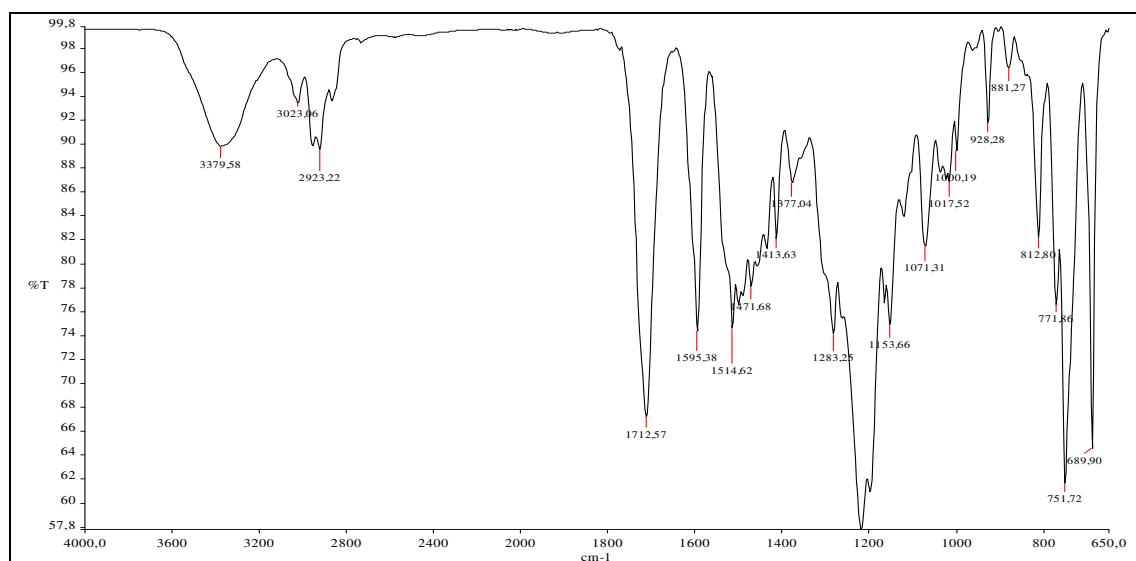12 cm^{-1} streching for the carbonyl group is obtained. The strong absorption band at 1595 cm^{-1} is the streching of C=C double bonds and at 1514 cm^{-1} from NH deformation. The peaks 1285 cm^{-1}, 1219 cm^{-1}, 1153 cm^{-1}, and 1071 cm^{-1} come from C-O-C streching, and the last part of the spectra comes from – C-H – deformation.

From the FT-IR spectra of the 1 wt % Bemkay coated film after curing for 4 minutes (Figure 4.2), strong absorption bands at 3379 cm^{-1} for the hyrdoxy group, at 3023 cm^{-1} for the aromatic compounds, and at 2923 cm^{-1} for the aliphatic compounds disappear because of the deblocking of phenolic resins after thermal curing and disappearing of them [47].
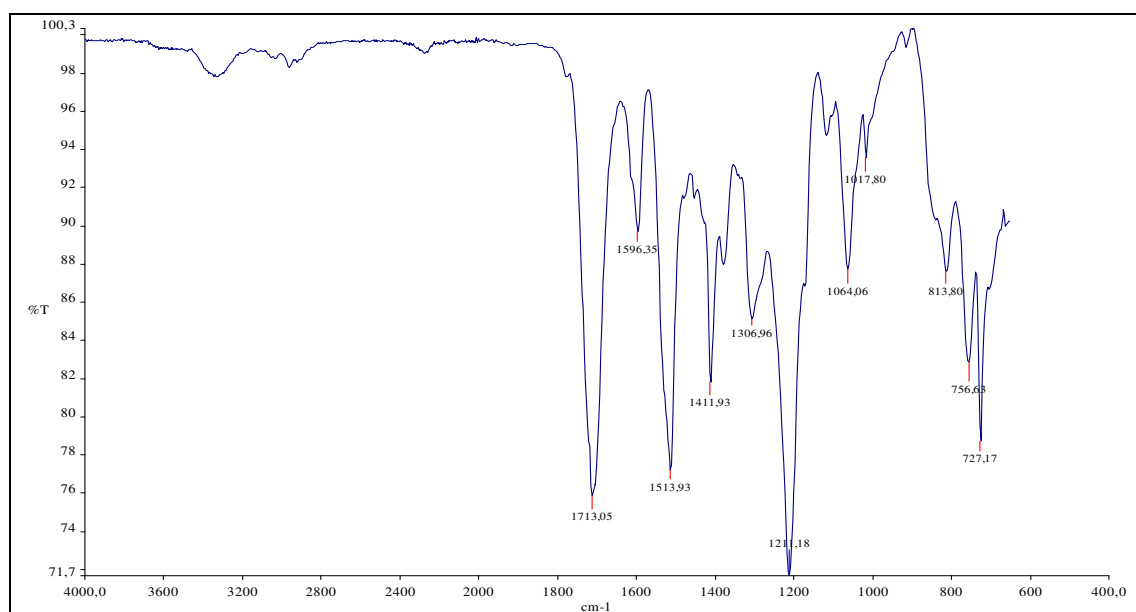
Figure 4.2 : FT-IR spectra of the coated film containing 1 wt % Bemkay compound after curing.

The strong band at 1713 cm^{-1} remains which shows the streching of C=O carbonyl groups. Also the peaks 1596 cm^{-1} and 1513 cm^{-1} remain. It can be said that the strong absorption band at 1064 cm^{-1} comes from Bemkay product which shows the Si-O-Si streching vibrations. The first absorption band of Bemkay compound (Figure 4.3) at 2931 cm^{-1} comes from C-H streching of CH$_3$ and the peak at 1454 cm^{-1} from CH$_3$

deformation of Si-CH$_3$. The 1259 cm^{-1} peak also comes from CH$_3$ symmetric deformation of Si-CH$_3$. The two peaks at 1089 cm^{-1} and 1021 cm^{-1} show the Si-O-Si streching vibrations and the last part of the spectra show the Si-C streching and CH$_3$ rocking. From the spectra of 1% Bemkay containing coating material the last part may be comes from Bemkay, but the peaks are overlapped by the peaks of varnish.
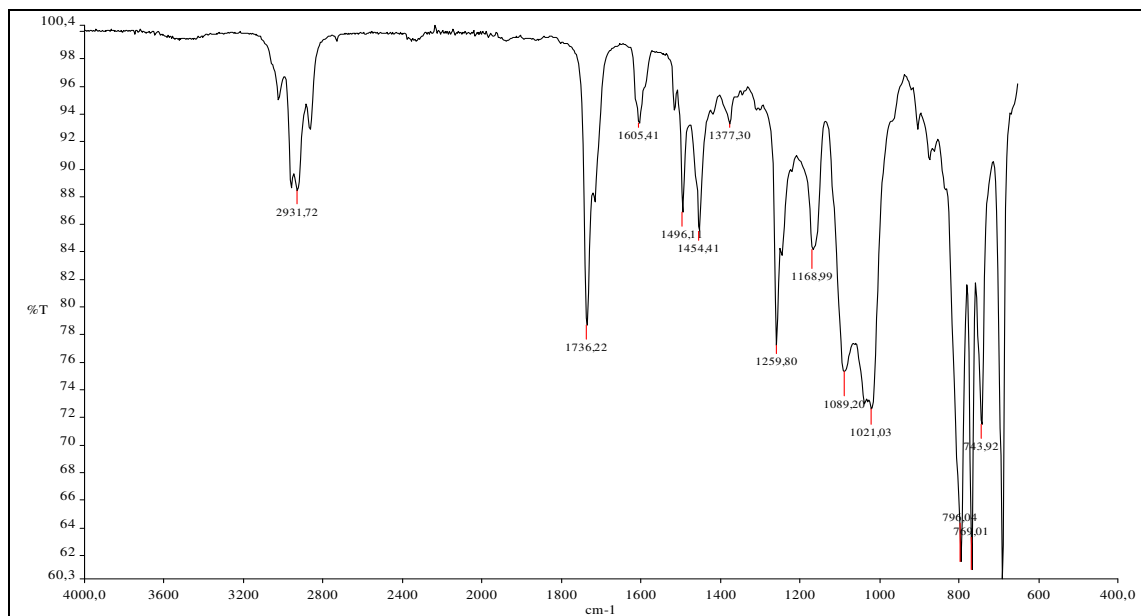
Figure 4.3 : FT-IR spectra of Bemkay compound

4.2 Thermal Analaysis of Coating Materials

Thermal stabilities of the coating materials after thermal curing were investigated by thermogravimetric analysis (TGA).

TGA was carried out in a nitrogen atmosphere at a heating rate of 20 °C/min. TGA profiles of Bemkay containing polyurethane coating materials as given in Figure 4.4 show a single stage decomposition. As it seen in TGA profiles of Bemkay containing polyurethane (PU) coating materials, the Bemkay concentration increases 1 wt % to 1.33 wt %, tempererature at 50% residue have decreased 477 ºC to 376 ºC.
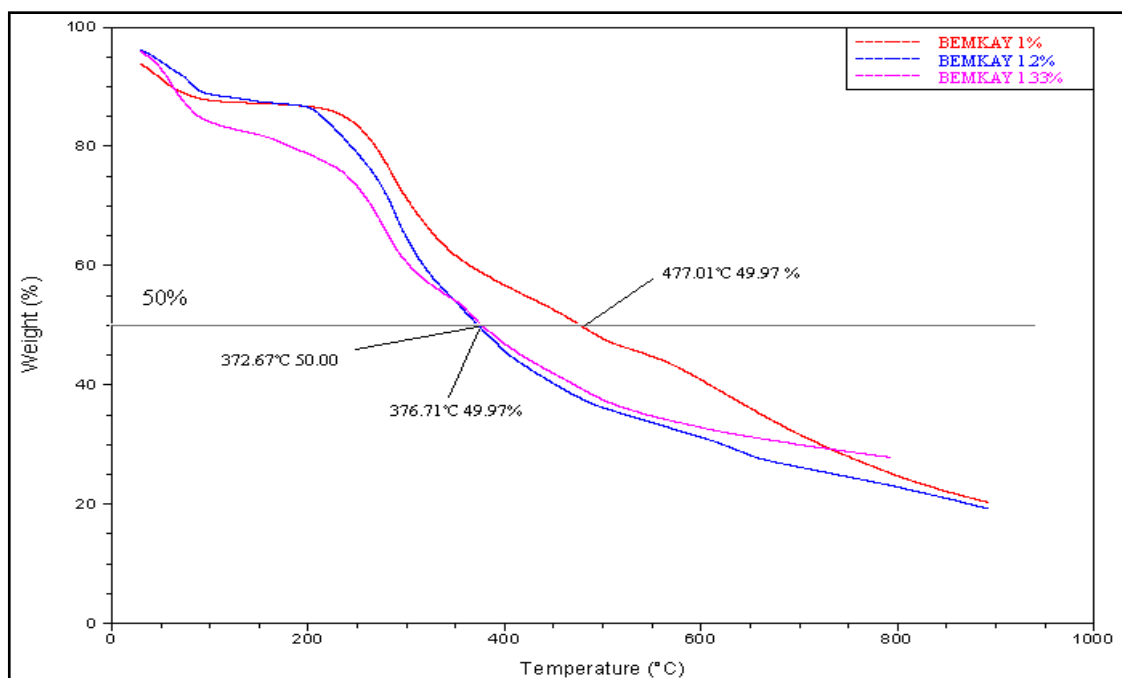
Figure 4.4 : TGA profiles of 1 wt %, 1.2 wt % and 1.3 wt % Bemkay containing polyurethane coating materials

The results show that thermal stability is decreased by Bemkay content after 0.1 wt % due to the microphase separation between hard segment and soft segment domains in polyurethane structure. However, thermal stability of films increased by Bemkay content compared to non-siloxane contaning film.

4.3 Contact Angle Measurements of Coating Materials

FAC3, FAG, BYS and Bemkay containing polyurethane coating films with variety percentage which are shown in Table 3.1 and Table 3.2 were coated onto glass surface by spin coating and were cured at stated temperatures.

Table 4.1 : Contact angle measurements of FAC3 and FAG with 0.1 wt %

Temperature (ºC)	Contact Angle Measurements (º)	
	FAC3 (0.1 wt %)	FAG (0.1 wt %)
160	88.03	-
180	89.31	82.2
200	89.5	85.8
220	89.92	87.45

The contact angle results of films containing 0.1 wt % FAG and 0.1 wt % FAC3 are given in Table 4.1 and related graph is shown at Figure 4.5.
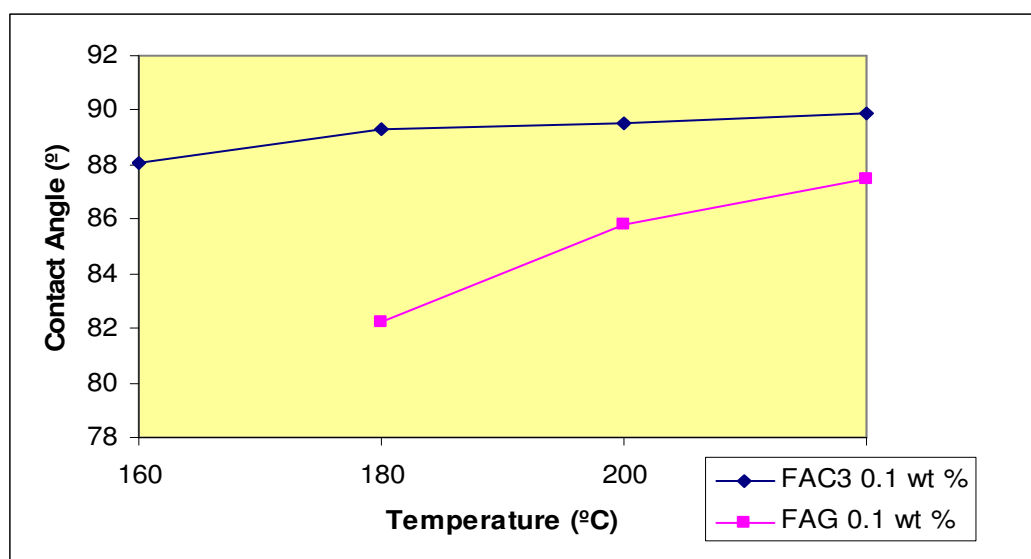
Figure 4.5 : Contact angle diagram of FAG and FAC3

As it seen from the Figure 4.5, contact angles of samples containing FAC3 0.1 wt % and FAG 0.1 wt % increases by increasing the curing temperature due to the fluorine content, but after 200 ºC there is a small changes in contact angle measurement of coated film by FAC3.

Table 4.2: Contact angle measurements of BYS and FAG+BYS containing films

Sample Name	Percentage (wt %)	Contact Angle Measurements	
		180 ºC	200 ºC
BYS	0.05	93.06	95.20
BYS	0.1	85.56	90.80
BYS	0.15	98.01	95.34
FAG+BYS	(0.05+0.05)	88.18	85.63
FAG+BYS	(0.1+0.05)	88.75	89.12
FAG+BYS	(0.05+0.1)	91.79	88.98

The contact angle results of films containing BYS with percentage 0.05 wt %, 0.1 wt % and 0.15 wt %, and BYS+FAG with different percentages are given in Table 4.2 and related graph is shown at Figure 4.6 and Figure 4.7.
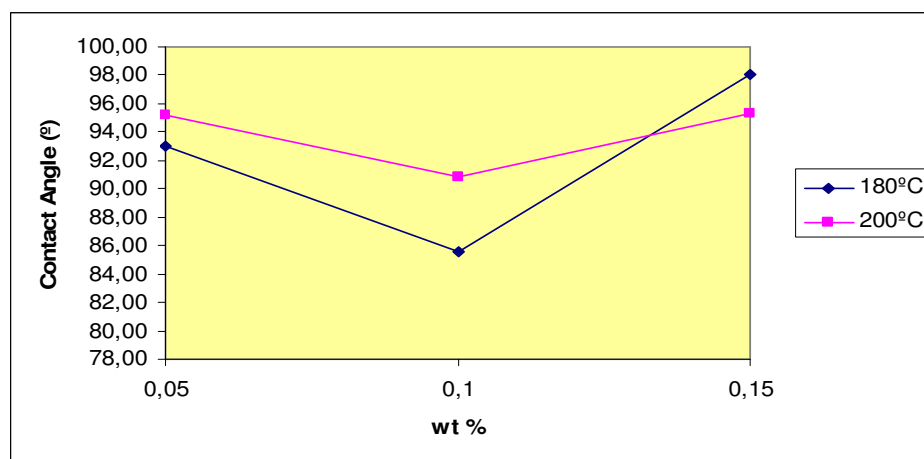
Figure 4.6 : Contact angle diagram of BYS films

As shown in Figure 4.6, contact angle values decrease with increasing BYS content but after the 0.1 wt % BYS contact angle increases with increasing BYS content, both at temperatures 180 ºC and 200 ºC. However, if temperatures are compared then it can be clearly seen that increasing temperature cause decreasing contact angle after 0.1 wt % BYS content.
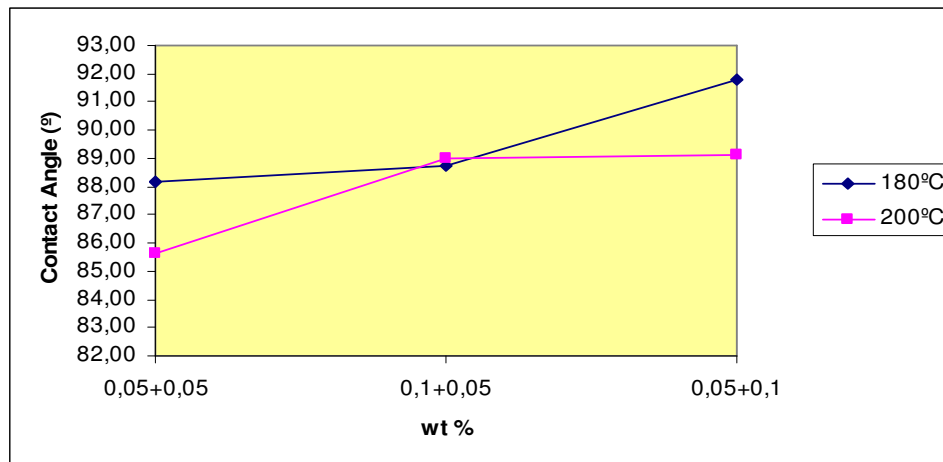
Figure 4.7 : Contact angle diagram of FAG+BYS films

As the BYS content increasing with increasing temperature from 180 ºC to 200 ºC shown in Figure 4.7, contact angle results decrease. It can be said from these figures that BYS is unsufficient at high temperatures. The reason for this is probably incompatability between polyurethane varnish and BYS, because polyurethane varnish is based on polyester imide while BYS is based on polyether.

Table 4.3: Contact angle measurements of FAC3+BYS and BEMKAY containing films

Sample Name	Percentage (wt %)	Contact Angle Measurements
		200 ºC
FAC3 + BYS	(0.05+0.05)	89.76
FAC3 + BYS	(0.1+0.05)	93.12
FAC3 + BYS	(0.05+0.1)	94.33
BEMKAY	0.05	93.83
BEMKAY	0.25	96.68
BEMKAY	0.5	98.39
BEMKAY	0.75	98.58
BEMKAY	1	98.91

The contact angle results of films containing BEMKAY with percentage 0.05 wt %, 0.25 wt %, 0.5 wt %, 0.75 wt % and 1 wt %, and FAC3+BYS with different percentages are given in Table 4.3 and related graph is shown at Figure 4.8 and Figure 4.9. It is clearly seen that contact angle measurements have decreased with increasing BYS content at 200 °C because of the incompatibility between polyurethane varnish and BYS.
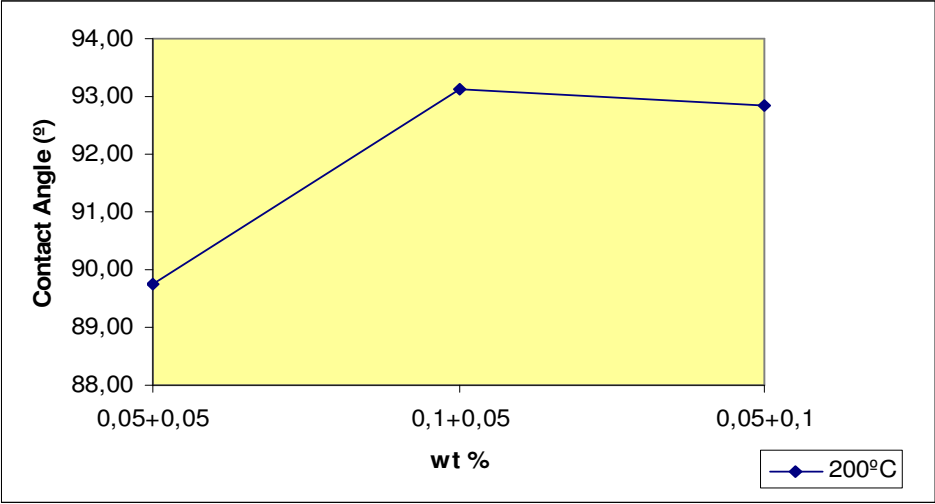
Figure 4.8 : Contact angle diagram of FAC3+BYS films

Figure 4.9 shows that contact angle measurements have increased with increasing Bemkay content due to the compatibility between polyurethane varnish and Bemkay.
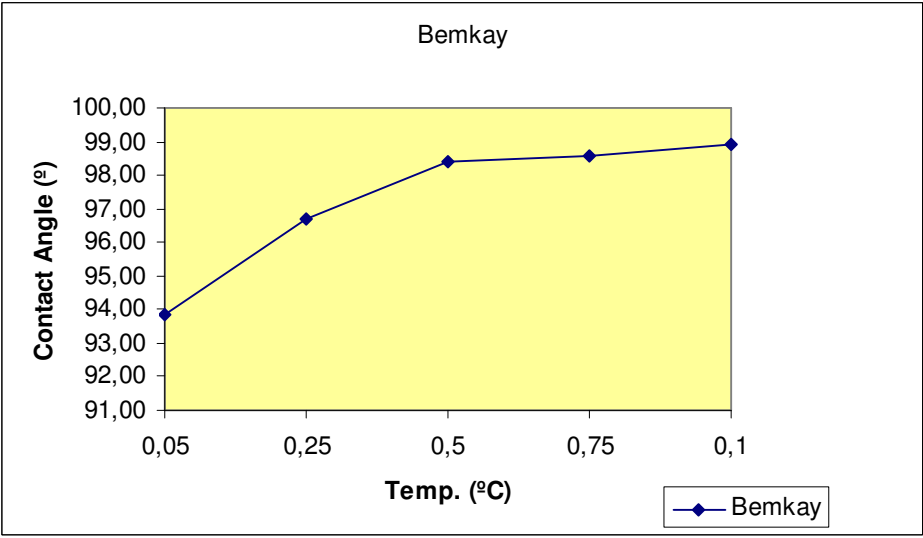
Figure 4.9 : Contact angle diagram of BEMKAY films

4.4 Static and Dynamic Coefficient of Friction Tests

Static and dynamic coefficient of friction tests were applied after winding of coated wires. Dynamic coefficient of friction test were applied all samples and results are shown in Table 4.4.

Table 4.4 : Dynamic coefficient of friction test results

Sample Name	Content (wt %)	Maximum Value	Minimum Value	Average Value
FAC3	0.1	0.242	0.154	0.201
FAC3	0.15	0.272	0.122	0.220
BYS	0.05	0.337	0.248	0.308
BYS	0.1	0.261	0.194	0.232
BYS	0.15	0.336	0.222	0.268
BYS	0.17	0.246	0.192	0.236
BYS	0.2	0.273	0.208	0.248
BYS	0.25	0.218	0.143	0.194
BYS+FAG	0.15+0.1	0.238	0.160	0.207
BEMKAY	1	0.135	0.073	0.109
BEMKAY	1.2	0.158	0.074	0.127
BEMKAY	1.33	0.173	0.138	0.164

Dynamic coefficient of friction results show that Bemkay coated wires display better surface smoothness than other coated wires. On the other hand, the roughest surfaces were obtained at wires coated by BYS. The reason for this is incompatibility between polyurethane varnish and BYS, but compatibility between PU varnish and Bemkay.

Static coefficient of friction test results of Bemkay are shown in Table 4.5.

Table 4.5: Static coefficient of friction test results

Sample Name	Content (wt %)	α	μ_s
BEMKAY	1	6.1	0.11
BEMKAY	1.2	4.7	0.08
BEMKAY	1.33	5.3	0.09

4.5 Other Tests

In order to to obtain the mechanical, electrical and thermal behaviour of enameled wires, elongation, springback, breakdown voltage, direct current resistance, heat shock, tan delta (δ), solderability and pinhole tests were applied them.

Table 4.6 : Elongation results of enameled wires

Code	Component Percentage	Diameter	Elongation
	% w/w	mm	% min
			21
BYS+FAG	(0.15+0.1)	0.185	34
FAC3	0.1	0.21	35
FAC3	0.15	0.21	36
BYS	0.25	0.2	40
BEMKAY	1.33	0.2	37
BEMKAY		0.2	41
			16
BYS	0.15	0.1	26
BYS	0.10	0.1	34
			17
BYS	0.25	0.118	33

Elongation and springback values of enameled wires are displayed in Table 4.6 and Table 4.7, and the numbers written with bold show the limit values of that wire. The results show that all wire samples which are coated by fluroinated and polysiloxated coating materials as a top coat, are suitable to the limit values.

Table 4.7 : Springback test results of enameled wires

Code	Component Percentage	Diameter	Springback
	% w/w	mm	max
			51
FAC3	0.1	0.21	40
FAC3	0.15	0.21	39
			54
BYS+FAG	(0.15+0.1)	0.185	43
BYS	0.25	0.1	34
BEMKAY	1	0.2	36
BEMKAY	1.33	0.2	36
			62
BYS	0.25	0.118	50
			64
BYS	0.15	0.1	48
BYS	0.1	0.1	43

Breakdown voltage and direct current resistance of enameled wires are shown in Table 4.8 and Table 4.9. All results are suitable to the limit values.

Table 4.8 : Breakdown voltage results of enameled wires

Code	Component Percentage	Diameter	Breakdown Voltage
	% w/w	mm	Volt
			500
BYS	0.1	0.1	4000
BYS	0.15	0.1	4800
			1500
BYS	0.25	0.118	3500
			1800
BYS+FAG	(0.15+0.1)	0.185	3700
BYS	0.25	0.2	4100
BEMKAY	1	0.2	4000
BEMKAY	1.33	0.2	5100
			1900
FAC3	0.1	0.21	4700
FAC3	0.15	0.21	5400

Table 4.9: Direct current resistance of enameled wires

Code	Component Percentage	Diameter	Direct Current Resistance
	% w/w	**mm**	**Ohm/m**
			0.4756 **0.5122**
FAC3	0.1	0.21	0.49
FAC3	0.15	0.21	0.492
			0.5236 **0.5655**
BYS	0.25	0.2	0.5327
BEMKAY	1	0.2	0.5348
BEMKAY	1.33	0.2	0.54
			0.6105 **0.6626**
BYS+FAG	(0.15+0.1)	0.185	0.635
			1.4739 **1.6597**
BYS	0.25	0.118	1.56
			2.0341 **2.3328**
BYS	0.15	0.1	2.14
BYS	0.1	0.1	2.159

Heat shock, tan delta (δ), solderability and pinhole tests results are shown in Table 4.10.

Table 4.10: Heat shock, tan. delta, solderability and pinhole tests results

Code	Component Percentage	Diameter	Heat Shock	Tan. Delta	Solderability	Pinhole
	% w/w	**mm**	**ºC**	**ºC**	**ºC**	
			200	**170** **185**	**390± 5ºC**	**10%** **max3**
FAC3	0.1	0.21	√	175	1	0
FAC3	0.15	0.21	√	175	1	0
BEMKAY	1	0.2	√	177	1	0
BEMKAY	1.33	0.2	√	176	1	0
BYS+FAG	(0.15+0.1)	0.185	√	179	1	0
BYS	0.25	0.118	√	176	1	0
BYS	0.25	0.2	√	174	1	0
BYS	0.1	0.1	√	176	1	0
				170 **190**		
BYS	0.15	0.1	√	180	1	0

4.6 Scanning Electron Microscopy

Enameled wire sample's images were obtained by scanning electron microscope with the magnifications of x200, x1000 and x5000. 1 wt %, 1.2 wt %, and 1.33 wt % Bemkay containing enameled wires surface properties are shown in Figure 4.10, Figure 4.11 and Figure 4.12.
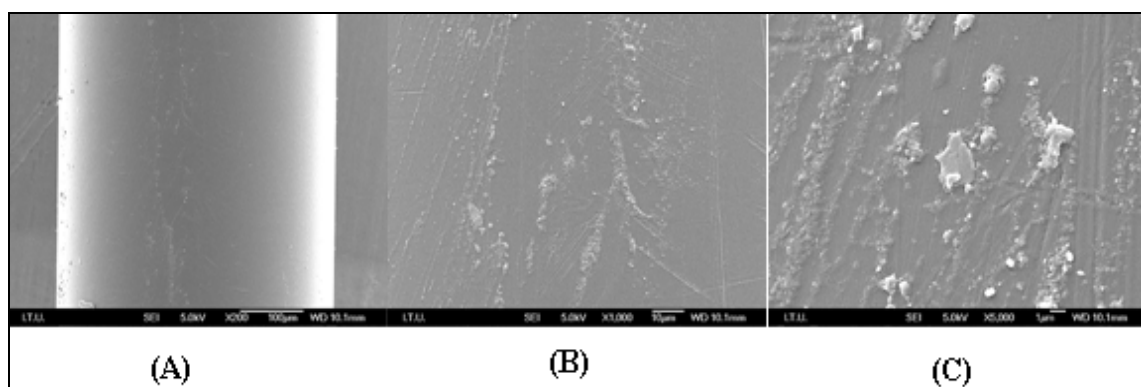

Figure 4.10 : SEM images of wire enamel with 1 wt % Bemkay-(magnifications of A-x200, B-x1000, C-x5000)

As it clearly seen from figures with magnifications x200, all wire surfaces are smooth and glossy. Hovewer, increasing the magnification shows us that (B and C) there are some deformations on the surfaces after increasing the Bemkay content.
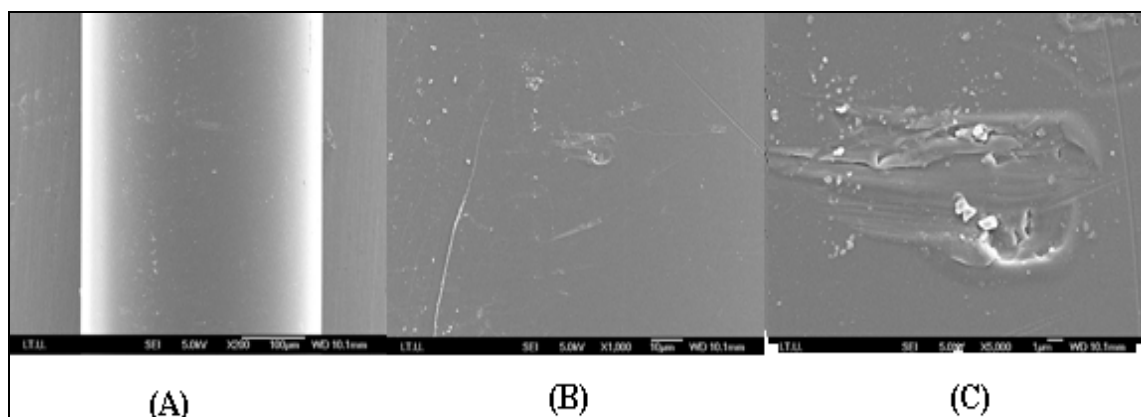

Figure 4.11 : SEM images of wire enamel with 1.2 wt % Bemkay-(magnifications of A-x200, B-x1000, C-x5000)

The deformations or particles on the wire surfaces (C) can be explained by incompatibility between hard segment and soft segment domains of polyurethane. When Bemkay content have increased from 1 wt % to 1.33%, maybe the other test results not

show great changes but deformations and surface begin to form because of these imcompatabilities between two segments.
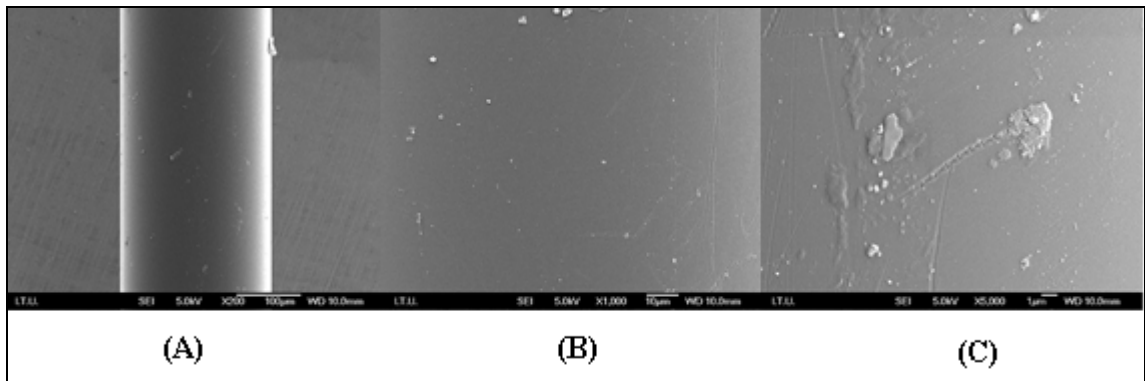

Figure 4.12 : SEM images of wire enamel with 1.33 wt % Bemkay-(magnifications of A-x200, B-x1000, C-x5000)

5. CONCLUSIONS

In this study, wire enamel compositions based two main coating materials were prepared by using additives containing fluorine and polysiloxane. Those materials were first applied on glass surfaces and samples were cured at oven by thermal curing.

Afterwards, obtained films were tested for their surface wettability by contact angle measurements. Generally, all contact angle measurements increased by increasing fluorinated or polysiloxated additive content. Coated films by polysiloxane showed greater contact angle results than fluorinated films. This may be due to, polysiloxane and polyurethane varnish connected by strong chemical bonds while fluorinated additive and polyurethane varnish formed chemical mixture.

Further, prepared coating materials were applied on copper wire surfaces, cured and winded on bonds by automatic machines at industrial plant, and mechanical, thermal and electrical tests were applied on enameled wires. Static/Dynamic coefficient of friction test results showed surface smoothness of wires coated with Bemkay containing enamel is more than wires coated with other enamel compositions. The reason for this is probably structural compatibility between polyurethane varnish and Bemkay, but imcompatibility between polyurethane varnish and other additives.

Thermal stability were analysed by TGA and its results showed that thermal stability of coating materials are increased by Bemkay content. However, after passing certain proportion of Bemkay both thermal and surface properties begin to decrease. From the SEM images some deformations begin after adding more than 1 wt % of Bemkay to enamel composition. This may be due to the microphase seperation between hard segment and soft segment domains in polyurethane structure.

Consequently, although, all materials electrical test results were suitable to limit values, wires coated with 1 wt % Bemkay showed desired surface and thermal properties.

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CURRICULUM VITA

Candidate's full name:	**Arzu HAYIRLIĞOLU**
Place and date of birth:	**İstanbul, 07.06.1983**
Permanent Address:	**Kartaltepe Mah. 13/6 Bakırköy-İST.**
Universities and Colleges attended:	**İstanbul Technical University, Polymer Science and Technology, MSc.**
	İstanbul Technical University, Chemical Engineering, Bachelor
	İstanbul Technical University, Environmental Engineering, Bachelor