MARMARA UNIVERSITY
INSTITUTE FOR GRADUATE STUDIES
IN PURE AND APPLIED SCIENCES

SYNTHESIS AND CHARACTERIZATION OF NOVEL POLYIMIDE FOR HYDROPHOBIC COATING

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MASTER THESIS

Department of Metallurgical and Materials Engineering

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Thesis CO- Supervisor

Assistant Prof. Dr. Mustafa ÇAKIR

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MARMARA UNIVERSITY
FEN BİLİMLERİ ENSTİTÜSÜ

HİDROFOB KAPLAMA AMAÇLI YENİ POLİİMİDLERİN SENTEZİ VE KARAKTERİZASYONU

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ÖZET

HİDROFOB KAPLAMA AMAÇLI YENİ POLİİMİDLERİN SENTEZİ VE KARAKTERİZASYONU

Günümüzde yüksek sıcaklık kararlılığına sahip, hidrofob, aşınma dirençli ve düşük yalıtkanlık sabitine sahip özellikteki kaplamalar mikroelektronik sistemlerinde, endüstride taşıyıcı bantlar gibi geniş uygulama alanlarında ön plana çıkmaktadır. Yüksek sıcaklık kararlılığı için aromatik poliimidler harika adaylardır. Ancak endüstride yaygın olarak kullanılan aromatik polimidlerde su ve yağ iticiliği, kısmen yüksek yalıtkanlık sabiti, aşınma direnci ve düşük saydamlık konularında bazı eksiklikler gözlemlenmektedir. Bu durumun üstesinden gelmek için flor katkılı poliimidler mikroelektronik ve fotoelektronik endüstrisindeki görüntü ekranlarındaki filmler, devre kartları, fotodirenç ve yalıtkanlık film, yüksek sıcaklığa dayanıklı ve yapışkanlık göstermeyen matrisler gibi uygulamalarda ön plana çıkmaktadır. Aynı zamanda termal kararlılığı çok daha fazla geliştirmek için yeni poliimidlerin sentezinde naftalen grubu kullanılmaktadır fakat florlanmış poliimidlere kıyasen hidrofobluk ciddi seviyede düşmektedir. Bu çalışmada sentezlenen poliimidler hidrofob, iyi aşınma direnci ve harika termal kararlılık sağlamaktadır. Aynı zamanda bu poliimidler dekoratif bir görünüm, parlaklık seviyesi yüksek, saydam bir görünüm ve alt katman ile çok iyi adhezyon özellikleri göstermektedirler. Bu poliimidler aluminyum üzerine termal imidizasyon yöntemi ile kaplanmıştır. Kaplanan numuneler üzerinde çapraz kesme deneyi, parlaklık testi, kalem sertlik, taber aşınma testleri ve statik temas açısı ölçümleri yapılmıştır. Termal özellikler ise DSC ve TGA ile analiz edilmiştir. Kaplamaların yüzey morfolojileri SEM ile görüntülenmiş ve numuneler FT-IR ile onaylanmıştır.

Sonuç olarak, bu çalışmada polimer zincirlerinin yüzde biri uzun florokarbon monomerleri sonlanmış, naftalen grupları ile kopolimerize edilmiş, hidrofob ve yüksek termal kararlılığa sahip poliimid kaplamaların elde edilmesi sağlanmıştır. Bu yeni poliimid kaplamaların özellikleri ile zincir sonlarına uzun florokarbon monomerleri bağlanmayan poliimid kaplamaların özellikleri karşılaştırılmıştır.

Ocak 2017 Emre AKIN

ABSTRACT

SYNTHESIS AND CHARACTERIZATION OF NOVEL POLYIMIDE FOR HYDROPHOBIC COATING

Nowadays coatings having high temperature stability, hydrophobicity, abrasion resistance and low dielectric constant come into prominence for applications in microelectronics and carrier systems such as wafers, conveyor belts. For high temperature stability, aromatic polyimides are excellent candidates. However, there are some constraints about aromatic polyimides widely used in industry, such as water and oil repellency, relatively high dielectric constants, abrasion resistance and low transparency. For that reason, fluorinated aromatic polyimides have come into prominence for applications in the microelectronic and photoelectronic industries as circuit boards, matrices having high temperature stability and low stickness. Also, naphthalene groups are used in synthesising of novel polyimides for obtaining more improved thermal stability but hydrophobicity significantly decrease when compare to fluorinated polyimides.

Those novel polyimides synthesised provide coating surfaces on aluminum with hydrophobic property, high abrasion resistance and excellent thermal stability. At the same time they exhibit decorative visual, transparency and very good adhesion properties. Coating results were characterized by cross cut, gloss 60°, pencil hardness, taber abrasion tests and contact angle measurements. Thermal properties were analyzed by DSC and TGA. Surface morphologies of coatings were characterized by SEM and these samples were confirmed by FT-IR.

In conclusion, in this study it was achieved that synthesis of polyimide coatings terminated with long fluorocarbon monomers (1 % of all chains) and copolymerized with naphthalene groups for obtaining hydrophobic property and excellent thermal stability. Finally, these novel polyimides coatings were compared with those without long fluorocarbons monomers.

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SYMBOLS

C=C : Carbon Group

C=O : Carbonyl Group

C-N : Imide Group

N-H : Amid Group

$\mathbf{M_n}$: Number Average Molecular Weight

$\mathbf{K_{eq}}$: Equilibrium Constant

$\mathbf{M_w}$: Mass Average Molecular Weight

OH : Hydroxyl Group

$\mathbf{T_g}$: Glass Transition Temperature

$\mathbf{T_m}$: Melting Degree

γ_{vl} : Gas-Liquid Surface Tension

γ_{vs} : Gas-Solid Surface Tension

γ_{ls} : Liquid-Solid Surface Tension

θc : Contact Angle

γ : Surface Tension

$\mathbf{f_s}$: Liquid/Solid Surface Area

$\mathbf{f_v}$: Liquid/Vapor Contact Area

$\mathbf{f_{av}}$: Functionality Average

χ_p [a] : Pauling Electronegativity

$\mathbf{r_{vdW}(A^o)}$ [c] : Van der Waals Radius

α_v : Atomic Polarizability

pKa : Negative Decadic Logarithm of the Ionization Constant (K_a) of an Acid

ABBREVIATIONS

AFM : Atomic Force Microscope

Al : Aluminum

CA : Contact Angle

COOH : Carboxylic Acid Groups

CTE : Coefficient of Thermal Expansion

Cr : Chromium

Cu : Copper

DADPS : Diaminodiphenylsulfone

DMAC : Dimethylacetamide

DMF : Dimethylformamide

DP : Degree of Polymerization

DSC : Differential Scanning Calorimeter

F : Mole Fractions of Monomers

FT-IR : Fourier Transform Infrared Spectroscopy

FDA : Hexafluoroisopropylidene Diphthalic Anhydride

GPC : Gel Permeation Chromatography

IP : Ionization Potential

LALLS : Low Angle Laser Light Scattering

M· : Radical Monomer

MEK : Methyl Ethyl Ketone

NMP : N-Methyl-2-Pyrrolidone

NTDA : Naphthalenetetracarboxylic Dianhydride

ODA : Oxydianiline

P : The Extent of the Reaction

P_c : The Critical Extent of Polymerization

PAA : Polyamic acid

PAE : Polyamic ester

PFOA : Perfluorooctylamine

PI : Polyimide

PIQ : Polyimideisoindoloquinazolinedione

PMR **:** Polymerization of Monomeric Reactants

PMDA **:** Benzenetetracarboxylic Dianhydride

SEM **:** Scanning Electron Microscope

Si **:** Silicon

TGA **:** Thermogravimetric Analysis

THF **:** Tetrahydrofuran

Ti **:** Titanium

UV **:** Ultraviolet

Zn **:** Zinc

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1. INTRODUCTION

1.1. Purpose

Properties of aromatic polyimides such as high glass transition temperature, excellent electrical, thermal and mechanical stability, dimensional stability and chemical resistance have been attractive considerably for widespread engineering applicability. Polyimides and their copolymers may be successfully used in different industrial segments because of their structural characteristics. Nowadays industry needs coatings having very high temperature stability and hydrophobic property. On the other hand aluminum and alloys are used in large tonnages in chemical processing, transportation, aviation nuclear power and fossil fuel power plants, petroleum production and refining, construction and metal-processing equipment. Also, these synthesised polyimides can be used for oxide surfaces. Therefore, coatings are generally applied for hydrophobic and oleo-phobic property beside their high heat resistance.

1.2. Literature Survey

1.2.1. Hydrophobic - Heat Resistance Coatings

Nowadays, industry needs multifunctional coatings due to the improved technology in which materials are used in harsh environment. Multifunctional coatings require heat resistance, water-repellency (hydrophobic), oil-repellency (oleophobic), good mechanical resistance and wear resistance. Heat resistance polymer coatings generally is required as aromatic polyimides in industry. The polyimides are used in various applications such as adhesives, fibers, wire-coating enamels and resin matrices for composites and films [1,2]. Especially, aromatic polyimides having excellent thermal stability, high mechanical, chemical and electrical properties [3, 4].

Due to fluorine atoms addition into polymer coatings, which gain low surface energy and hydrophobicity. On the other hand the structures having fluorine bonds have excellent properties such as chemical resistance, thermal stability and wear resistance [5]. Fluorinated monomers tend to move towards surfaces and form highly ordered layers. They behave like completely fluorinated polymers. Hence surface energy significantly decreases and water and oil repellency surfaces can be obtained beside heat resistance. At the same time while fluorine chain grow longer hydrophobicity increase for that reason long perfluorinate substituted structures come into prominence [6].

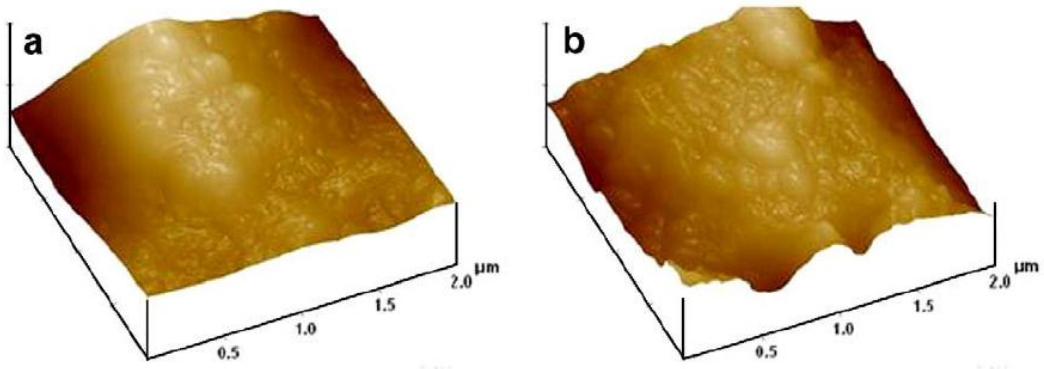


Figure 1.1 3D images in AFM of a) smooth cast film b) treated cotton fiber [7]

Static wettability of a solid surface can be evaluated by the contact angle measurement. If the surface is flat and chemically homogeneous the classical Young's equation is used. In Young's equation the contact angle is determined by surface energy of the solid substrate.

$$\cos \theta c = (\gamma_{sv} - \gamma_{sl})/\gamma_{lv} \quad (1.1)$$

where, ϒ is the surface tension, and sv (a liquid–air interfaces), sl (a solid–liquid) and lv(liquid-vapor).

There is one another equation from Cassie and Baxter for rough surfaces. Air is trapped under the liquid and the equation for rough surfaces determined as 1.2.

$$\cos \theta c = f_s \cos \theta c - f_v \quad (1.2)$$

Where f_s means the liquid/solid contact region and f_s is the liquid/vapor contact region. Hence the contact angles are determined by two factors that are surface free energy and surface geometrical structure (fs and fv). In literature two hyper-branched polymers terminated fluorocarbons are compared with each other that includes different backbones, different length of fluorocarbons chains and different surfaces as treated and smooth. It is observed that the hyperbranched-polymers terminated longer fluorocarbons and treated surfaces belong to high contact angles than shorter fluorocarbons chains and smooth surfaces. These surfaces belong to high hydrophobicity and excellent oil repellency and extremely low surface energies (13.67–24.49 mJ/m^2). Hydrophobicity depends on only terminated fluorocarbons chain length different hyperbranched backbones exhibited same property. In addition to fluorocarbons chain length treated surfaces increase the static contact angle significantly in range of 21.24-22.06 mJ/m^2. Hence surface roughness gain excellent oil repellency to the surface [8].

To improve heat resistance more than conventional aromatic polyimides, naphthalene groups can be used due to their structure. Because of the rigid, planar structure of naphthalene group polymers can provide more improved thermal stability. Naphthalene groups also have low moisture absorption when compared to polymers without fluorine. But fluoropolymers have lower moisture than polymers when they incorporate with naphthalene groups. Polyimides belong to naphthalene groups also have noticeable low dielectric constant as fluorinated polyimides. Due to the planar structure of naphthalene groups coefficient of thermal expansion becomes low [6].

1.3. Step-Growth Polymerization

The molecular weight of the polymer chain occurs slowly and the process proceeds from one reaction mechanism. The process does not involve in the initiation, propagation, and termination steps of chain-growth polymerization. At least equal molar amounts of two different di-functional monomers are necessary to obtain high molecular weight polymer. The functional groups on the monomers react with each other. Thus, reacted two monomers occur a dimer. The dimer can react with another monomer, dimer, trimmer or larger molecules to produce oligomer chains and finally high molecular weight polymer chains. This process proceeds at the same reaction rate for long period of time. While two mono-functional groups occurs a very low molecular weight, the reaction of two difunctional groups can produce a high molecular weight polymer. On the other hand, a single difunctional monomer can also produce a high molecular weight polymer. Table 1.1 shows the properties of both the step-growth and chain-growth polymerization.

Table 1.1 Step-Growth versus Chain-Growth Polymerization [9]

Reactions	One Reaction Mechanism at the Same Ratio	Initiation, Propagation, and Termination Reaction Mechanism at the Different Ratio
Polymer Growth	Slow and Random Growth	The Growth Reaction Terminated by One Unit
Polymer Molecular Weight	Steadily Molecular weight increase High conversion for high molecular weight polymer.	Immediate High Molecular Weight Polymer.
Composition of the Polymerization Reaction	Broad Polymer Weight Distribution, High Polymer Dispersivity Index	Low Polymer Dispersivity Index, Very Close Molecular Weight Distribution

1.3.1. The Essential Factors for Obtaining High Molecular Weight Polymer

In the step growth polymerization three important requirements are necessary for obtaining a high molecular weight linear polymer. Firstly, a perfect stoichiometric balance must be obtained involving, first, the two difunctional monomers that must be incorporated by flawless stoichiometrically. On the other hand, a single difunctional monomer can also produce high molecular weight polymer, for instance, aminocaproic acid. So that the system should have an internal balance. Second, the purity of the monomers is so important for high molecular weight polymer. In the case that aminocaproic acid is not enough purity, n-pentylamine, the decarboxylation product take place. As a result of that internal balance disappears. The presence monocarboxylic acid in adipic also causes to a stoichiometric imbalance. These monofunctional monomers terminate the polymer chains and the reaction ends up.

Third, the polymerization reaction must not be affected by side reactions and must have little or no side reactions to obtain high molecular weight polymer. There are four reaction mechanism generally used in the synthesis of step-growth polymers to provide high yield and low cost. These are an isocyanate reacting with an alcohol or amine, ester changing/s contact, amidation, Schotten Baumann reaction .

These requirements as given above are implemented to get high molecular weight linear polymer from the difunctional monomer. When the functionality of monomer is larger than two, these requirements are not implemented because of the cross-linked or highly branched structure.

1.3.2. Molecular Weight Distribution of Linear Step-Growth Polymers

In step-growth polymerization broad molecular weight distribution is occurred and molecular weight distribution can be calculated by considering the probability that is symbolized as P. It means that the probability of a single functional grup reacted at a given time t. The probability of unreacted functional group is symbolized as (1-P).

When considered as below;

- (x - 1) reacted functional groups and one unreacted end group in polymer
- For single monomer, the probability of reacted group is P, and so the total probability of x-1 reacted group is defined as P^{x-1}
- The probability for a single unreacted group is symbolized as (1 – P)

Hence the probability of finding an x-mer, reacted mer, if very high molecular weight polymer belongs to only one polymer chain produced, the formula of P^{x-1} would be used. Otherwise, $P^{x-1}(1 - P)$ is used for the product number is bigger than only one chain.

In the case of the polymer specimen has N molecules, the x-mer fraction (the fraction of molecules that are x-mers) is showed by equation 1.3

$$N_x = NP^{x-1}(1 - P) \quad (1.3)$$

Molecules (monomers) at the start are symbolized N_o, by using $N = N_o(1 - P)$ relation equation (1.4) occurs ;

$$N_x = N_0(1 - P)^2 \, P^{x-1} \quad (1.4)$$

1.3.3. Three-Dimensional Network Step-Growth Polymers

Bakelite is known as one of the first industrial polymers. This polymer has a crosslinked network structure which is provided by the reaction of phenol (a trifunctional monomer) with formaldehyde. Phenol has a trifunctional monomer and formaldehyde has a two functional monomer. The process is achieved by heating and cross-linked network is obtained during heating for a certain time. One another of the most known polymer is polyester resin which can be provided by the reaction of glycerin with phthalic anhydride. When the addition of longer chain diols is provided , a hard and brittle polyester material is obtained. During the polymerization after a certain time the fluid resin convert to an insoluble or a gel and swellable material. That polymerization degree can be relatively low but after that value the average becomes infinite.

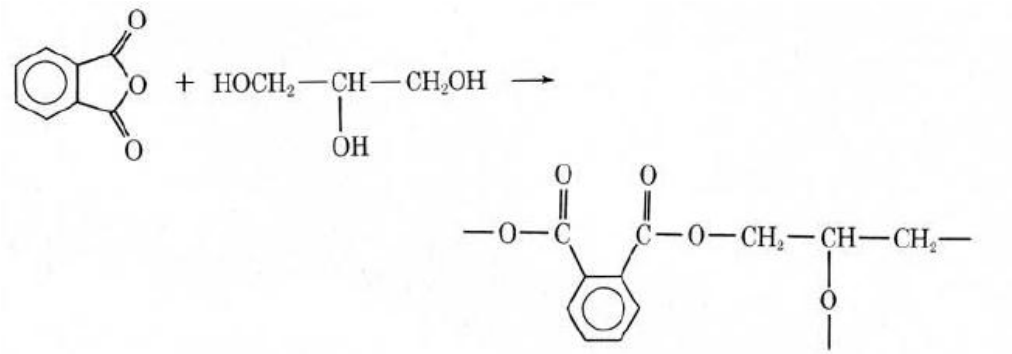


Figure 1.2 Three dimensional network polymerization [1]

The reaction extent, P, can be calculated from equation 1.5 at the certain DP to obtain enough gelation or molecular weight. The symbol of f is the average of functionality. DP continues infinitely large when the gelation occurs and equation 1.6 takes place.

$$P = \frac{2}{f_{av}} - \frac{2}{DPf_{av}} \quad (1.5)$$

P symbolize reaction extent and f presents the average of functionality.

$$P_{av} = \frac{2}{f_{av}} \quad (1.6)$$

The critical extent of polymerization, P_C, is the value at the time of occurring of gelation. For instance gelation was provided in 83.3 % of polymerization rate; f_{av}, = 12/15) [9-11].

1.4. Types of Copolymerization

In step-growth polymerization copolymerization is provided in random when the kinds of the monomers were incorporated into the other difunctional compounds at the same time. But in chain-growth polymerization the reactivity of the monomer radicals causes different types of copolymerization types.

The ratios of occurrence and consumption of these radical monomers are same. The equation 1.7 illustrates the ratio of conversion from $M_1\cdot$ to $M_2\cdot$ equals to the conversion from $M_2\cdot$ to $M_1\cdot$.

$k_{21}[M_2\cdot][M_1]=k_{12}[M_1\cdot][M_2]$ (1.7)

The ratios of consumption of radical monomers M_1 and M_2 are showed by equation 1.8 and equation 1.9

$$\frac{-d[M_1]}{\mathrm{dt}} = k_{11}[M_1\cdot][M_1] + k_{21}[M_2\cdot][M_1] \quad (1.8)$$

$$\frac{-d[M_2]}{\mathrm{dt}} = k_{12}[M_1\cdot][M_2] + k_{22}[M_2\cdot][M_1] \quad (1.9)$$

The radicals of M_1 or M_2 are eliminated by equation 1.7 The equation 1.8 can be divided by equation 1.9 for obtaining equation 1.10

$$\frac{d[M_1]}{d[M_2]} = \frac{[M_1]}{[M_2]}\frac{r_1[M_2] + [M_2]}{[M_1] + r_2[M_2]} \quad (1.10)$$

The symbols of r_1 and r_2 were defined as the reaction activity of the radical monomer with the other monomer. The equation 1.7 can be showed by considering the reactivity ratios and r_1 and r_2 are the rates of the reactivities of the monomers that defined as the equation 1.11

$r_1=k_{11}/k_{12}$ (1.11)
$r_2=k_{22}/k_{21}$

$F_1= 1\text{-}F_2 = d[M_1]/d([M_1]+ [M_2])$ (1.12)

Equation 1.11 shows the equation of copolymer product. The symbols of F_1 and F_2 are the mole fractions of monomers of M_1 and M_2 at any instant during growing the polymer chain at the equation 1.12

$$f_1 = 1 - f_2 = \frac{[M_1]}{[M_1] + [M_2]} \quad (1.13)$$

By using equations 1.12 and 1.13 it can be obtained the equations 1.14

$$F_1 = \frac{r_1 {f_1}^2 + f_1 f_2}{r_1 {f_1}^2 + 2 f_1 f_2 + r_2 {f_2}^2} \quad (1.14)$$

The quantity $r_1 r_2$ represents copolymer composition on the chain which includes the reaction of the monomer-monomer and the cross reactions of the monomers. As a result of these equations, copolymerization can be categorized according to the quantity of $r_1 r_2$ such as the unity, less than unity or greater than unity [12].

1.4.1. Ideal copolymerization

$r_1 r_2 = 1$, then

$r_1 = 1/r_2$ or $k_{11}/k_{12} = k_{21}/k_{22}$ (1.15)

$$\frac{k_{11} k_{22}}{k_{12} k_{21}} = r_1 r_2 \quad (1.16)$$

The equation 1.17 can be obtained from the equation 1.10 and 1.15 for ideal copolymerization.

$$\frac{d[M_1]}{d[M_2]} = \frac{r_1 [M_1]}{[M_2]} \quad (1.17)$$

$$F_1 = \frac{r_1 f_1}{f_1 (r_1 - 1) + 1} = \frac{r_1 f_1}{r_1 f_1 + f_2} \quad (1.18)$$

In the ideal copolymerization, each radical monomer has equal reactivity for joining each other. During growing the chains the end group on the chain are changed but that event does not affects the ratio of chain growing. So the probability of the addition of an M_1 unit to the end of M_2 unit equals to the probability of the addition of M_1 unit or M_2 unit to the end of the other monomers. In consequence of these reactions, the sequence of monomer units on growed chains take place randomly in an ideal copolymer. To sum up, determining of an ideal copolymer composition are related with the feed composition and

the re-activities of monomers. For ideal copolymerization r_1r_2 equals approximately 1 that monomers react with each other randomly. These situations are provided by two methods or ways.

Method 1: In this way, the reactivities of the monomers are different from each other such as $r_1 > 1$ and $r_2 < 1$ or $r1 < 1$ and $r_2 > 1$. Moreover, one of the monomer radicals is more active than the other radical monomer. Eventually, the more reactive monomer is located larger area on the growed chain the less reactive monomer and the squence of the monomers are also random on the growed chain. But there is an important experience that increasing in the difference of the reactivities becomes the process more difficult for the addition of high amount monomers on the chain.

Method 2: Because of the reactivity of monomers ($r_1 = r_2 = 1$) the composition of the copolymer only affected by feeding of the monomers. At the same feeding composition the monomers are totally aligned at random along the growed chain.

The copolymer equation occurs as the equation 1.19. The symbol of f is defined as feeding composition and F_1 is also defined as fraction of the monomer of 1.

$$F_1 = \frac{f_1 \mathrm{f}}{f_1 + f_2} = f_1 \qquad (1.19)$$

1.4.2. Alternating copolymerization

As the rates of monomer reactivity ($r_1 = r_2$) equal to approximately 0 (or $r_1r_2 = 0$), each monomer radical only reacts with the other monomer because the probability on the reaction of monomer itself equals to approximately 0. As a result of these reactions, the monomer units are aligned alternately along the growed chain irrespective of the feed composition. In this case the copolymer equation can be eliminated to equation 1.20

$$\frac{d[M_1]}{d[M_2]} = 1 \qquad (1.20)$$

or $F_1 = 0.5$

When the perfect alternation that both r_1 and r_2 are zero occurred polymerization proceeds until the one of the radical monomer is consumed and the process stops. Moreover, if the amount of the unity r_1r_2 approaches zero, then alternation reaction takes place largely in the polymerization process. Approaching to 0 for the unity of r_1r_2 affects the polymerization level very highly and increases the amounts of both monomers along the polymer chain.

1.4.3. Block copolymerization

For occurring the block copolymerization both r_1 and r_2 must be greater than unity thus each radical monomer would react with its own monomer. Unless a chance reaction occurs the same type of monomers proceed to join along the chain. Thus same long type of monomer units occurs along the polymer chain that is defined as block copolymer. When r_1 and r_2 approaches ∞ , both monomer radicals occurs homopolymer chains. But this type polymerization is not available in the life. In the case of approaching to 1 of the unity of r_1r_2, the amount of r_1r_2 almost always less than 1 [12].

1.5. Hydrophobic Surfaces

Hydrophobic is the word, which come from the ancient Greek means to hate water. On the other hand Hydrophilic means to desire the water. Then these all surfaces are classified according to contact angles with water. The angles between solid surfaces and liquid are characterized by contact angle. If the contact angle is less than 90° then the liquid wets the surface. Otherwise the contact angle is larger than 90° the surface cannot be wetted by the liquid. Thus the water drop spread over the surface is defined as hydrophilic. Otherwise the water drop in sphere shape forms on the hydrophobic surface. Moreover the condition of the water drop totally spreading on the surface is defined as super hydrophilic and the condition of the total spherical water drop on the surface is defined as super hydrophobic. The most important affecting factors of contact angle are surface energy and roughness. As long as the surface energy decreases, hydrophobic and oleophobic properties increase. The increase of surface roughness also causes to increase the hydrophobic and oleo phobic properties [13].

1.5.1. Surface Tension and Free Surface Energy Relation

An atom into any same liquid is affected in balance by the adjacent atoms thus a balance occurs in molecular movement and the distance between the atoms becomes equal and constant. However, the relation between the atoms is different at the surface of the liquid. The atoms at the surface of the liquid contacts with the gas molecules. For that reason the forces between the atoms becomes imbalance. Thus the distances between the atoms decreases on the surfaces and the excess of energy comes out. Due to the excess of energy the surface behaves as a coating of membrane and that event is defined as surface tension. Furthermore, this is the amount of work required to increase in the unit of surface area at

the constant temperature and pressure infinitely. The work which, takes all molecules in the sample from the dense area to the surface to increase the surface area as 1 m^2 is defined as free surface energy. The free surface energy is symbolized as " γ " and the unity is mN/m. Surface energy is also available for solid surface and the interfaces between various phases [14].

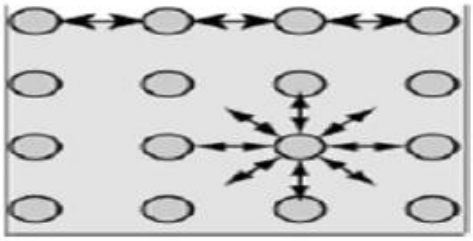


Figure 1.3 The interactions of the molecules in liquid [15]

The molecules in solid phase protect their own location and there is no replacing of the atoms each other as the atoms in liquid phase. The atoms and the molecules in solid phase behave in the condition of the vibration at the their own location with difference of the atoms in liquid phase. Figure 1.3 shows the interactions of molecules in liquid [15]. The atoms in liquid phase can minimized their surface energies without the outside effects. Moreover, the solid phases does not have take a shape as the liquid phase but that result does not mean to have surface tension in the solid phases. The surface tension of solid phases cannot be measured directly.

The contact angle measured on the solid phase reflects the thermodynamic of the interactions between liquid and solid phases. It can be utilized by these datas for calculating the surface energy of the solid phase. As a result of this, water drops are occurred on the solid surface and contact angle are measured [16].

Some experiments were conducted on various surfaces having low surface tension and measured the contact angles of these surfaces. As a result of these experiments they found some surface tension results and determined the critical surface tension. Furthermore, the only liquids having less than the critical surface tension sprang over the surface. The liquids having larger tension than the critical surface tension took spherical shape over the surface. Consequently, while wettable surfaces have high surface energy, nonwettable surfaces have low surface energy [17].

Water has high surface energy due to the hydrogen bonds (72.75 mN/m 20°C) Fluorocarbons have very low critical surface energy as 15 mN/m or less than it. That low

critical surface energy provides excellent hydrophobic and oleophobic properties. Table 1.2 shows critical surface tensions of the samples have various surface contents [17].

Table 1.2 Critical Surface Tensions of Fluorocarbons

Surface Contents	**Critical Surface Tensions (mN/m) at 20°C**	**Surface Contents**	**Critical Surface Tensions (mN/m) at 20°C**
$-CF_3$	6	$-CF_2-CFH-$	20
$-CF_2H$	15	$-CH_3$	22
$-CF_2-CF_3$	17	$-CH_2-$	31
$-CF_2-$	18	$-CCl_2-CH_2-$	43

1.5.2. Contact Angle

Contact angle is measured by occurring a liquid drop on a smooth and horizontal surface. An angle is occurred between solid surface and liquid phase due to the contact. That angle is defined as contact angle. The shape of water drop is related with surface roughness and physical and chemical properties of the solid sample [18].

The relation of surface tension and contact angle are showed in the equation 1.21

$$\cos \theta c = (\gamma_{sv} - \gamma_{sl})/\gamma_{lv} \quad (1.21)$$

θ c : Contact angle ; Υ_{sl}:liquid-solid surface tension ; Υ_{lv}:liquid-vapor surface tension ; Υ_{sv} : solid-vapor surface tension

Solid surfaces are characterized as low and high surface energy. Water drop occurs a smooth and homogeneous film on the surfaces with high energy. In that condition the contact angle becomes 0 and the surface is totally wetted by the drop. Thus that surface is defined as hydrophilic. On the other hand if the solid surface has low energy then the drop take spherical shape and separated drops occur on the surface. In that case the contact angle is larger than 90° and the surface is hydrophobic. In theory, if a solid surface belonged to totally smooth, homogeneous and non-wettable then the contact angle value would be 180°. However, in practice all these conditions cannot be provided because of the gravitation. For that reason, the contact angle obtained is always less than 180° [18].

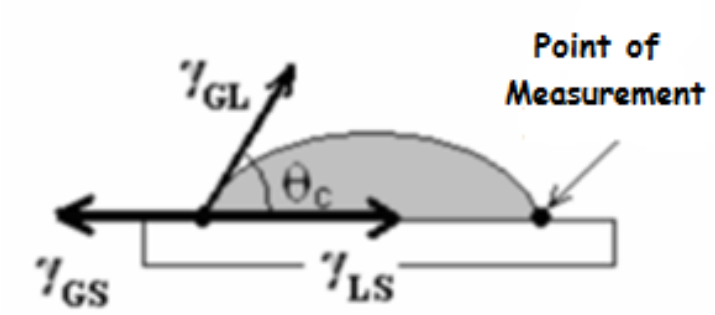


Figure 1.4 The determining of the Contact Angle (θ c) [18]

Experimental mechanism is given in Figure 1.4 for measuring the contact angle. By using a charged coupled device camera the deionized water drop photo is taken. The measurement result is transferred to a computer for monitoring [18].

1.5.3. The Factors Affect to Hydrophobic Properties

1.5.3.1. Surface Roughness

Increase in surface roughness results in increasing hydrophobic properties. That route is one of the most common applications. There are high amount of micro grooves on the rough surface as given in Figure 1.5. Air moves through these grooves on the surface and was restrained in these grooves. Due to the surface tension the liquid cannot move through the grooves on the surface. Thus the attraction between the liquid and the solid becomes so lower because of low contact surface area.

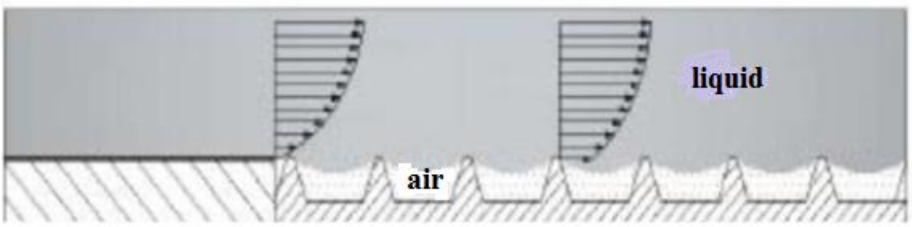


Figure 1.5 View of rough and smooth surfaces [11]

For smooth surfaces or the surfaces without any roughness, Young's Equation can be utilized. If the surface have any roughness then the contact angle was affected. When the contact angle is higher than 90° the surface shows a hydrophobic property. Furthermore the surface roughness increases the contact angle and becomes hydrophobic character. If the contact angle is higher than 90° then the increase of the surface roughness rises the contact angle. On the other hand in case of the situation of the contact angle lower than

90° the surface roughness decreases. If the droplet size is smaller than the surface roughness then the contact angle is not affected [19].

There are various routes in literature for occurring roughness on the surface.

These are;

• The Addition of Particles in Micro or Nano Size (SiO_2, ZnO, Al_2O_3, TiO_2)

• Lithography (Printing method)

• Electro spinning

• Electrochemical Reaction and Participating Method

• Solution Casting

• Chemical Abrasion

• Sol-Gel Route [20]

1.5.3.2. The Size of Drop

Contact angle changes with the droplet size and decreases by obtaining low droplet size [21].

1.5.3.3. The Chemical Heterogeneity on the Surface

The complexity on contact angle on a smooth polymer surface depends on chemical heterogeneity on the surfaces. In that situation that flowable surface becomes metastable phase. Due to the high difference between energy barriers and contact angle exhibited an increase for providing a balance [21].

1.5.3.4. Molecular Orientation

The cause of hysteresis in polar structure, the delay of the reaction in case of any effect, is derived from hydrogen bonding. In that structure surface configuration change the medium. But this is not only factor for changing of the surface structure.

At the same time, donating and accepting of electrons affect the surface properties of polymers [21].

1.5.3.5. Contamination

During coating process polymer surfaces subjected to contamination. Before contact angle test measurements surfaces must be cleaned by a solution which the polymer surface does not dissolve [21].

1.6. Preparation of Hydrophobic and Oleophobic Coatings

In recent years there are so much studies in literature about preparing hydrophobic surfaces. The chemicals used for gaining hydrophobic and oleophobic character hold the liquids on the solid surface without any dispersivity. The chemicals used for hydrophobic surfaces require to increase surface roughness or decrease surface energy [22].

Johnson and Dettre [23] obtained surfaces belong to various roughness rates by blasting wax on the smooth glass surface. Then these specimens were exposed to various heating application and is obtained smooth surfaces.

Despite to the fact that roughness is one parameter, it was observed clustering between 100 μm and 10 μm. Static contact angle values of these surfaces were 105° [24].Figure 1.6 shows contact angle dependency on changing surface roughness.

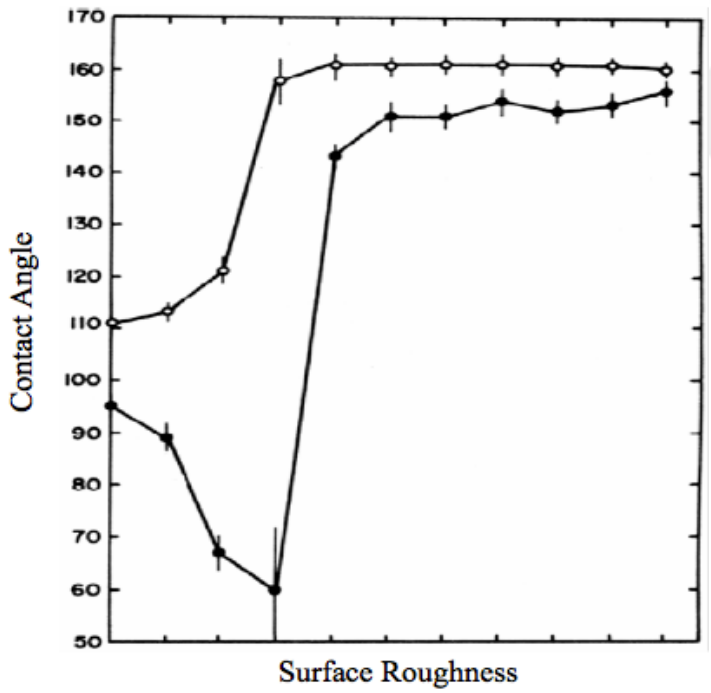


Figure 1.6 Advancing (o) and decreasing (●) contact angles depending on changing the surface roughness factor [25]

In order to increase hydrophobic character, there are various materials such as some items occurring resin and water repelling, oil acid and chromylcloride complex, zirconium paraphine emulsion and coupling agents containing silicon.

Fluorocarbons, which belong to low surface energy, are generally used for increasing hydrophobic and oleophobic character [26].

Fluoroalkyl groups (R_f) are found on coating surfaces thereby decreasing the surface energy. Hence by decreasing surface energy the surface hydrophobic and oleophobic character instead of fluorocarbons coatings containing branched alkyl groups only belong to hydrophobic character [27]. It is well known that there are two method to increase contact angle ;Chemical method and geometrical method.

Chemical method apply as changing surface chemistry to obtain materials having low surface energy. For example -CF_3 containing surfaces have low surface energy. Because, fluorine belong to low atomic radius and the highest electronegativity among all atoms. For that reason fluorine forms a very stable covalent bonding with carbon and low surface energy occur. On the other hand the surface energy increases while hydrogen and carbon elements replace with fluorine elements. The surface energies of these functional groups are lined up such as -CF_3< -CF_2H < -CF_2-< -CH_3< -CH_2-. The lowest surface energy is obtained by -CF_3 has hexagonal structure. However, the surface energy obtained by that method is considerable high.

For this reason it is advised that dual structures having micro and nano sizes. Geometric method works as increasing surface area and roughness to increase hydrophobic character [27].

1.6.1. Oil Acid and Chromyl Chloride Complex

That method is used to obtain hydrophobic character for military uniforms and cloths. However, chromium causes environmental pollution.

1.6.2. Zirconium Paraffin Emulsion

The water repellent surfaces were obtained by paraphine emulsions. That emulsion does not contain emulgator and prepared with special equipment. In order to obtain durable hydrophobic character the process must be applied in slightly acidic medium. This situation is necessary for water repelling process[27].

Paraphine emulsion containing zirconium or aluminium compounds have already sold and used widely in industry. These products exhibit more durable and effective hydrophobic character. Zirconium paraphine products are more widely used than aluminum ones because of the sufficient durability [27].

1.6.3. Coupling Agents Containing Silicon

In recent years one of widely used hydrophobic character compounds is alcoxy silane. By

hydrolyzing alcoxy silane, silanols are occurred. Then the silanols are easily condensed for occurring organosiloxane.

As these materials expose to heating condensation is occured more effectively. This is also thermal curing. Alcoxy silanes used for water repelling is classified in monomethyl, dimetyl and trimetyl. Thus these methyl groups provide hydrophobic character [27].

1.6.4. Fluorocarbons

Fluorocarbons are determined as the compounds containing one or more fluor elements bearing on a carbon element.

Volatility and density of these compounds are higher than hydrocarbons and these compounds have high physical and chemical properties.

It is known that the compounds containing fluorine element belong to good heat resistance and flammability. The properties of the compounds exhibit change due to the amount of fluorine. The low amount of fluorine in the compounds provides the products more suitable for using in pharmacy and dying industry [28].

Hydrophobic surfaces were obtained by bonding of alkyl and fluoroalkyl groups to the various molecule structures. These fluoropolymers are observed in two categories for gaining hydrophobic and oleophobic character.

These are;

1. Fluoropolymers containing only C-F bonding on the backbone
2. Fluoropolymers containing flourine and chloride or hydrogen elements and less C-F bonding

Despite the fact that flourocarbons are expensive water repelling material they are widely used due to the repelling of oil and contaminants. This property exhibits increase by longer chain length. Especially, the density is much more than hydrocarbons. Fluorocarbons have excellent heat resistance. It differs from hydrocarbon and silicones because of the repelling of oil and contaminants. That situation is related to low surface tension [29].

Although fluorocarbons became popular after 1989 the cost of the fluorocarbons is high. When it is used with auxiliary chemicals the concentration of the fluorocarbons decrease. Therefore the cost exhibits a serious decrease. Especially, fluorine containing monomers or oligomers are widely used for the coating applications in recent years.

The advantages of fluorine content for coating applications are given below [17]:

- Low friction coefficient

- Repelling of oil and contamination
- Excellent chemical and thermal stability
- Low reactive index
- Atmospheric resistance
- Low dielectric constant

1.7. Fluoropolymers

When fluorocarbons have repeating units these are defined as fluoropolymers. Because of their excellent properties such as chemical stability, thermal stability, low friction coefficient, nonadhesive nature antifouling, oil and water repellency, fluoropolymers were in demand for coating applications [30, 31]. Due to the low polarize ability fluoropolmers belong to low intermolecular force and low surface tension [23]. This is useful property in surface coatings for corrosion protection. It is well known that oxygen and water are necessary to initiate corrosion and water works as electrolyte in atmospheric corrosion. Water has excellent electrical conductivity, dissolving ability of ionic groups, O_2, SO_2, etc. in the atmosphere. For this reason it exhibits very efficient corrosion medium.

Polymers work as protective barrier coatings. Polar groups such as ester, amide and hydroxyl etc. on coating surfaces are attractive groups for water thereby holding the moisture or condensed water from atmosphere on the surface. Wettability of the surface can be decreased and protective barrier life span can be increased for reducing the interactions. Water is prevented from reaching the metallic surface in two ways: first, non-wetting of the surfaces and secondly the molecular absorption of water through polymer surface is low [32].

There are some available polymers perfluorinated in the main chain or side chain in literature [33-35]. Their lowest surface tensions were located between 10 and 13 mN/m [36]. Internal phase separation of perfluorinated groups of the side chains lead to highly ordered surfaces hence the concentration of CF_3 increase on the top layer of the surfaces.

The backbone of the polymer substituted fluorinated side chain belong to higher mechanical stability along with unique surface properties of the fluorine compounds. Shafrin and Zisman [37] state that the wettability basically is explained by the unique properties of the structures and packing of the surface atoms affected by the solid surface atoms.

A great deal of perflourinated groups that attached in main chain and side chain have been

commercialized worldwide in recent year. Also, we know that fluorine has small atomic radius and high electronegativity. Furthermore it is the largest atom among all atoms hence bonding covalently with carbon atom as very stable to occur low surface tension for coating surfaces [38]. As a result of these modification contact angle value can increase up to approximately 120° for smooth CF_3-terminated surfaces [26, 39, 40]. On the other hand fluorine containing hydrophobic coating having non-adhesive properties because of the very weak van der Waals forces. For this reasons it is necessary to copolymerized with another structures to eliminate that deficiency. The controlling of the surfaces of polymer films is important factor for applications. Incorporation of fluorine atoms into the polymer backbone and side chains can be processed by various methods regarding to occur non-wettable surface and decrease surface tensions [41-47]. Hence for obtaining these results various synthetic polymerization techniques can be used [48, 49]. By various linking units that can be occurred fluorinated chains in main backbone or side chain which have different architecture [43-47,50]. Furthermore, polymer architecture affects the surface properties of the coatings thereby providing the control of the fluorine atoms distribution.
There are three different routes for introducing the fluorinated groups into polymers:

- Occurring fluorinated groups in main backbone
- Termination of polymer backbone by fluorinated chains
- Addition of fluorinated groups as side chains to polymer backbone

1.7.1. Fluorine Containing Coatings

Fluorine containing polymers are also considerable materials for coating applications along with engineering plastics and high-tech elastomers due to unique properties such as chemical resistance, hydrophobic and oleophobic properties and low friction coefficient [51]. These coatings are classified in two ways such as thermoplastic and thermosetting-based coatings [52]. Some examples of thermoplastic-based coatings are used in industry such as poly (vinylidene fluoride) (*e.g.* Kynar from Atochem), poly (vinyl fluoride) (*e.g.* Tedlar from DuPont) and poly (tetrafluoroethylene) (*e.g.* Teflon from DuPont).
The properties of these thermoplastic fluorinated polymers depend on the distribution of fluorine along the chain and the content of the fluorine. The increase of the fluorine content exhibit high solvent resistance, weatherability, chemical and thermal stability.
Thermosetting fluorinated binders can be classified into two ways. First, chlorotrifluoroethylene and various modified vinyl ethers can be thought as alternated

copolymerization that Lumiflon from Asahi Glass Co. commercialize, these groups incorporate in the polymers and improve the coating performance. Furthermore, an acid-functionalized ether can be used to improve the resin reactivity for adhesion of the substrate. At the same time hydroxy-functionalized vinyl ethers can occur crosslinking by reaction with cross linkable moieties. The second major of fluorine-containing thermosetting binders Fluorobase from Ausimont.

These polymers are derivatives of perfluoroethers which have molecular weights in a range of $1000 < M_n < 4000$ g/mol. However, there are some problems about synthesising and cost of the fluorinated problems. For that reason application area of these polymers is limited.

1.7.2. Effect of Fluorination

Fluorine atoms effect the physical properties and chemical reactivity of organic molecules seriously. Also, polymer chains are influenced by substituted fluorine atoms on the chain. When the nature of the C-F bond considered about fluorination that brought different properties to the polymer chain [53].

As a result of this, the properties of fluorine atom are given in Table 1.3 due to the effect of the fluorination to the polymer. Also, it can be made compare with the other elements (Table 1.3).

Table 1.3 Atomic Properties

Atom	χ_p [a]	**IP (kcal mol $^{-1}$)[a]**	α_v (A^{o3})[b]	r_{vdW} (A^o)[c]
H	2.20	313.6	0.667	1.20
F	3.98	401.6	0.557	1.47
Cl	3.16	299.0	2.18	1.75
Br	2.96	272.4	3.05	1.85
I	2.66	241.2	4.70	1.98
C	2.55	240.5	1.76	1.70
N	3.04	335.1	1.10	1.55
O	3.44	314.0	0.82	1.52

χ_p [a] : Pauling electronegativity, IP, first ionization potential

α_v : Atomic polarizability

r_{vdW} (A^o)[c] : Van der Waals radius

1.7.3. C-F and C-C Bonds

Fluorine is the first member of halogen group besides the most electronegative element among all atoms. The bond arrangement of the halogen group of fluorine atom consists of three electron cone pairs and an interatomic σ bond. But fluorine is the smallest halogen and the most electronegative element thereby strongly bonding with nucleus by the tree electron pairs. For this reason the energy of the electrons becomes low. On the other hand the effect of fluorine atom bonded in organic molecules becomes different. When considering the covalent bonding of the carbon and fluorine it is well known that these elements belong to same period. As a result of that excellent match occurs between the orbitals due to (2s, 2p) of carbon and the orbitals (2s, 2p) of fluorine. Then the high electronegativity of fluorine present that element always attracting force relative to carbon and the interatomic carbon is always polarized influentially. Also, the partial ionic nature of C-F bond strengthens it compared to any C-X bond [53].

When it is observed the strength of C-F bond on different structure the energies vary from 109.9 kcal mol^{-1} for CH_3F to 130.5 kcal mol^{-1} for CF_4.About that result various researchers have present a bond regulation related with the stability. (2 in Figure 1.7) due to back-donation (3 in Figure 1.7) of the electron density from an $F_{p\pi}$ cone pair through the σC-F antibonding orbital [54]. This event is defined as negative hyper conjugation that is observed in C-F bonds next to some functional groups [55]. Wiberg and Rablen [56] explain the strength of C-F bond by the electrostatic effects because of the electronegativity of fluorine. This effect also increases the strength of the C-C bond in the series of fluorinated ethane (-CF_3-CF_3-). This bond is stronger than the CH_3-CH_3 bond that the difference of energy is approximately 10 kcal mol [57].

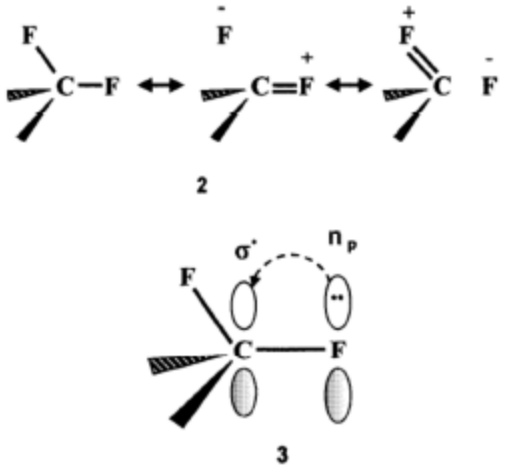


Figure 1.7 C-F Bond Orientation [58]

Likewise, the strength of the C-C bond along PTFE chain is higher than that of PE [58].When the situation of branching of the polymer chain, the (C-C) bond dissociation energy value of perfluoroalkanes changes due to the steric hinderance. While the van der Waals radii of the H atom and F atom does not change by branching of the chains CH_3- and CF_3- groups reduce the strength of C-C bond in branched perfluoroalkanes. Actually, the equivalent hemisphere volumes of the CH_3 group is 16.8 Å and 42.6 Å for the CF_3 groups [59]. Finally, microstructural arrangements must be avoided to increase steric hindrance around the C-C bond along the main chain for fluorinated polymers and perfluorinated polymers.

1.8. Polyimides

Polyimides are one of engineering polymers that defined as functional group CO-NR2 in molecules. These groups are called imide. The interaction between nitrogen atoms and carbonyl groups causes high chemical and moisture resistance. At the same time the type of hydrocarbon such as aliphatic and aromatic and functional groups such as Cl, F, NO2, and OCH3 affect seriously the physical properties.

Polyimides are synthesised by step growth polymerization and generated from the derivatives of both aliphatic and aromatic dianhydrides and diamines. A heterocyclic imide is given in Figure 1.8

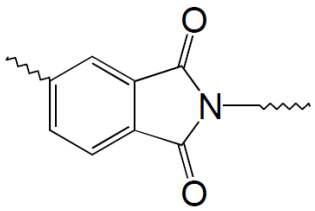


Figure 1.8 A Heterocyclic Imide Bonding [60]

On the other hand polyimides have outstanding thermal stability and very good mechanical strength. Different polyimide structures cause innovative materials for various application areas such as aerospace, microelectronics, automotive and packaging industries.

1.8.1. Classification of Polyimides

Polyimides can be divided in two ways according to aromatic and aliphatic structures such as Linear, Cyclic (Aromatic main chain, Aliphatic-Aromatic main chain) as shown in Figure 1.9, Figure 1.10 and Figure 1.11.

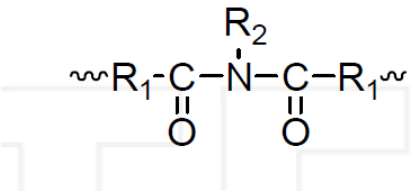


Figure 1.9 A Linear Imide Bonding [61]

Aromatic polyimides are used much more than aliphatic polyimides due to their thermal and mechanical properties but aliphatic polyimides are also potential materials for biomedical applications and engineering.

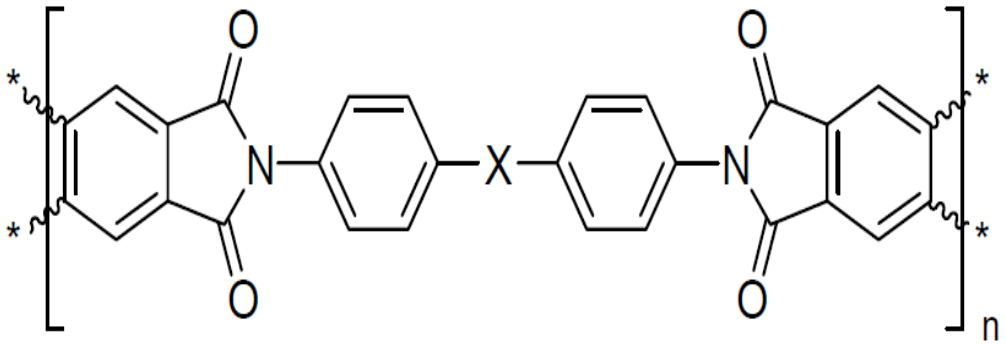


Figure 1.10 An Aromatic Main Chain [62]

1.8.2. Synthesising of Polyimides

Synthesizing methods of polyimides has facilitated for high performance applications. The prevalent methods are submitted in this section. A side-chain imide groups given in Figure 1.12.

1.8.2.1. Synthesising of Polyimide in Two Step Method

In polyimide synthesising two step method is generally used that polyamic acid behave as precursor (PAA) followed by forming aromatic imide ring at elevated temperatures. That method is also defined as classical method.

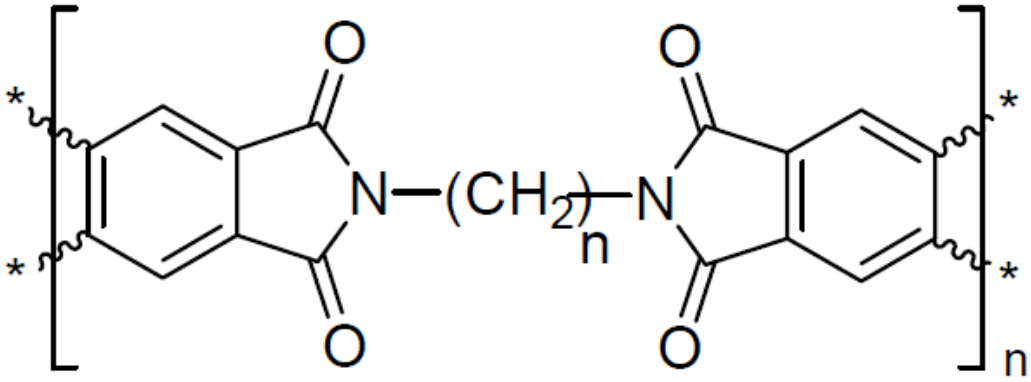


Figure 1.11 An Aliphatic-Aromatic Main Chain [63]

1.8.2.2. Formation Poly (Amic acids) and Monomer Reactivity

Polyamic acid is occurred by difunctional anhydride and amine reaction by polar aprotic solvent. This reaction continues as nucleophilic substitution that amine attacks one of the carbonyl carbons in anhydride groups. Imide groups replace with carboxylate functionality (Figure 1.13) There are three points determining of the magnitude of PAA molecular weight and its stability towards the other reactants such as reactivity, concentration and

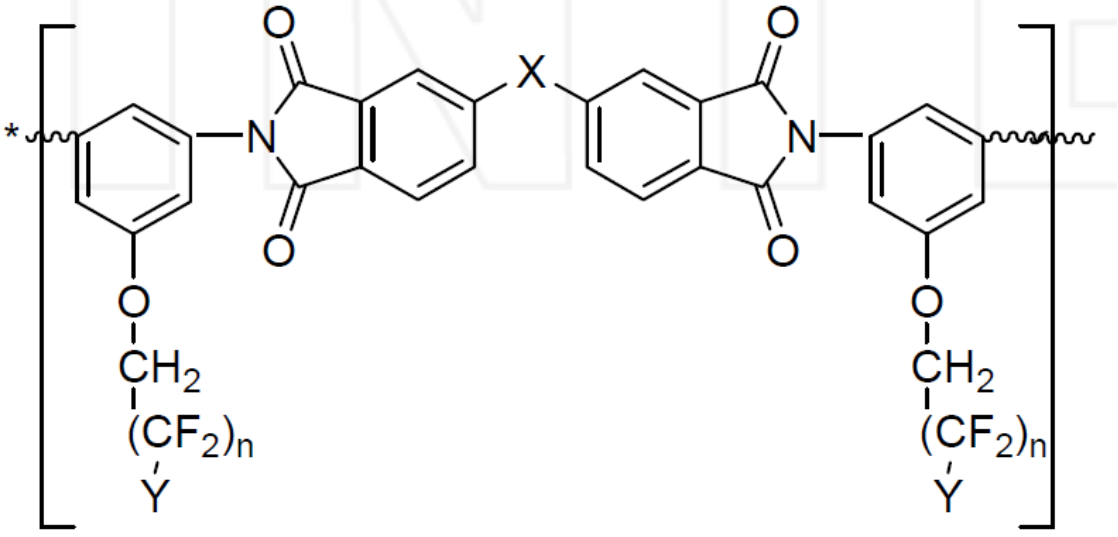


Figure 1.12 A Side-Chain [60]

the type of solvent. Common dianhydrides and diamines are shown in Figure 1.14. Di anhydride exhibits electrophilic character and its reactivity can be explained electron affinity (E_a) (Figure 1.15), hence dianhydride having the highest electron affinity means the greatest electrophilicity. Furthermore, the dianhydride having the greatest electrophilicity firstly desires to react with a given nucleophile [61]. Figure 1.15 gives the Eas of dianhydrides and PMDA belongs obviously highest electron affinity compared to BTDA, BPDA, ODPA. That difference is derived from electronic environment of the anhydride carbonyl groups of BTDA, BPDA and ODPA. When it is observed in detail, BTDA belongs to a bridge on electron withdrawing carbonyl group. For that reason the anhydride carbons exhibit more positive environment thereby becoming easier the nucleophilic attack. ODPA has an oxygen atom, which is bridged to carbonyl groups of the anhydride. Furthermore an oxygen atom desires to donate electron hence the affinity of carbons on carbonyl group decrease and reactivity with the nucleophile becomes poorer. The third one, the affinity of BPDA is observed between BTDA and ODPA because of the either withdrawing or donating of electron density. BPDA does not have bridging functionality.

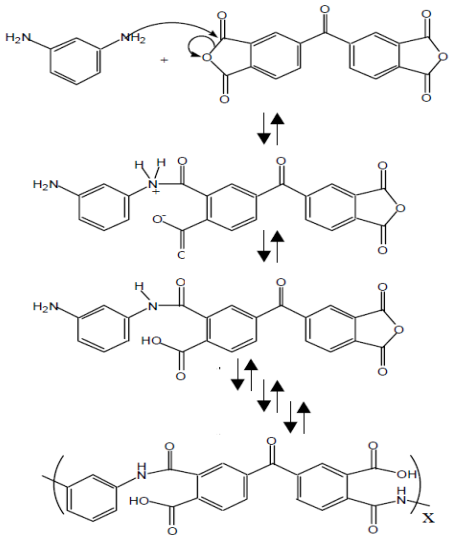


Figure 1.13 Formation of Polyamicacid by Nuclephilic Reaction of Dianhydrides and Diamines [64]

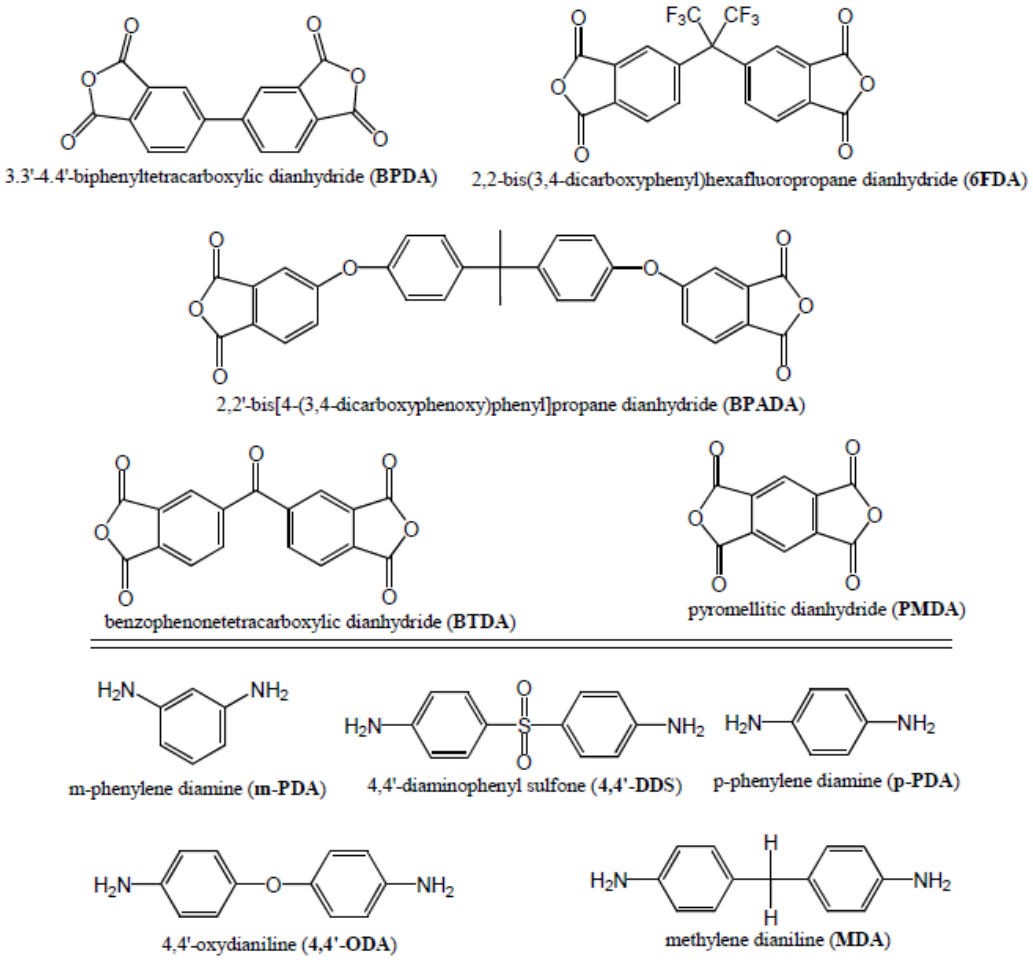


Figure 1.14 Common Dianhydrides and Diamines [65]

Also, the bonding of the electron withdrawing and donating bridges as para- or ortho-to the anhydride carbonyl influences the affinity greatly.

Reactivity of the diamine was obtained towards phthalic anhydride and is associated with pKa (Table 2.0), thus the higher pKa diamine content the faster it reacts with the anhydride. For instance, diaminobenzophenone is a diamine belong to a withdrawing group thereby decreasing nucleophilicity.

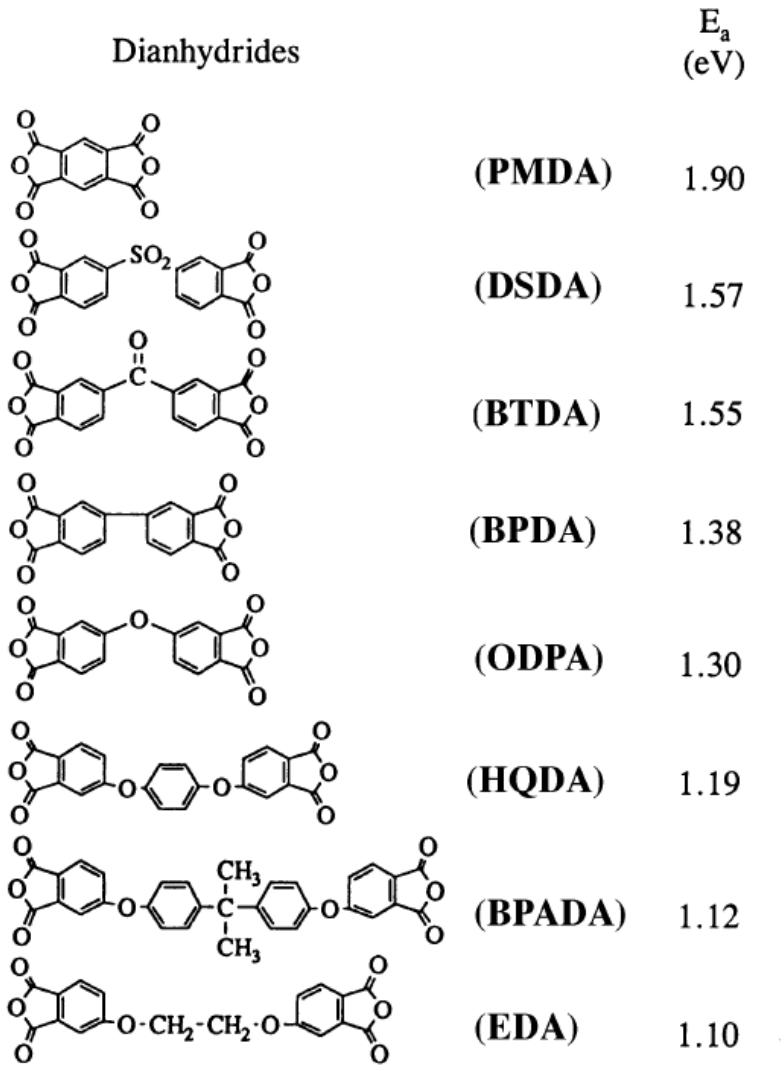


Figure 1.15 Electron Affinity of Representative Aromatic Dianhydrides [65]

While diamines and dianhydrides have high reactivity which have tendency to high molecular weight, the low reactivity of diamines and dianhydrides causes low molecular weight polymers. Furthermore, molecular weight of polymers can be calculated by 1/(1-p) (p = degree of polymerization) in case of the constant time. Common diamines with PMDA are given in Figure 1.16.

Consequently, the basicity of diamine and the electron affinity of anhydride affect seriously the rate of PAA formation. On the other hand the solvent used for the reaction influences the rate of PAA formation. When more basic aprotic solvent is used the reaction improve such as NMP, DMAc, Acetonitrile, and THF. The sequences of these solvents are given according to the degree of basicity. The rate of solvent/reagents can be

considered as 4:1 ratio of DMAC or NMP to occur the most efficient complexation with the repeating units of PAAs during the polymerization (Figure 1.17) In case of the aprotic solvent which has not enough basicity not belonging enough basic it can be occurred auto accelerating of the reaction due to the formation of strong acid. As a result of this the possibility of occurring high molecular weight polymer decreased seriously and the product can not be obtained as desired [1]. Some diamines exhibit weak basicity such as 4,4'- diaminodiphenylsulfones, thereby reacting slowly with anhydrides in DMAc but by using THF solvent high molecular weight and fast reaction can easily be obtained. This situation can be explained in two ways.

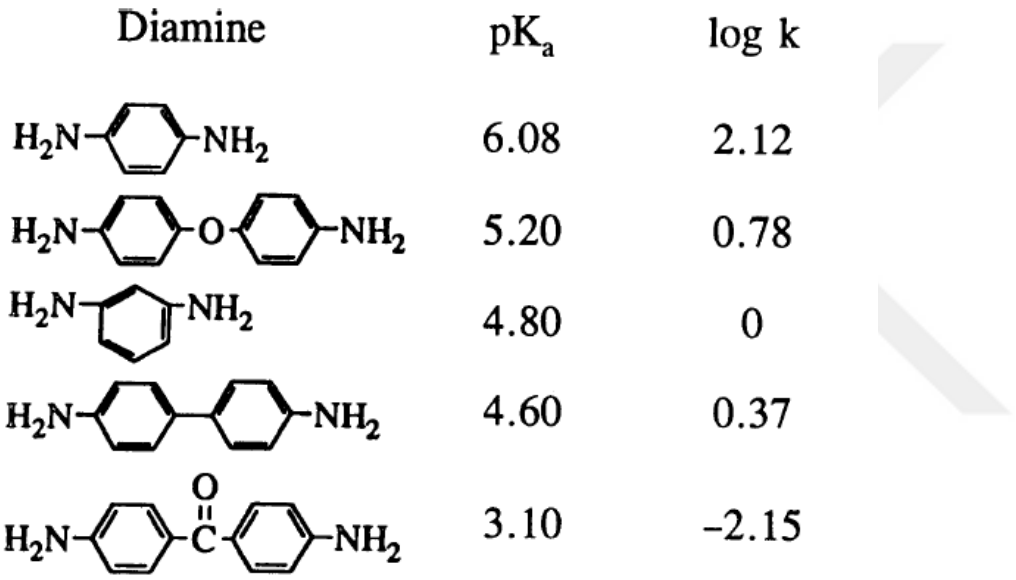


Figure 1.16 Reaction Activity of Common Diamines with PMDA [66]

One of them may be the interaction between THF and the amine that causes to increase the basicity of the amine. The second possibility, THF does not have enough basicity to correspond to protons donating from the acid for the formation of carboxylate. For that reason reaction may be transferred into reverse.

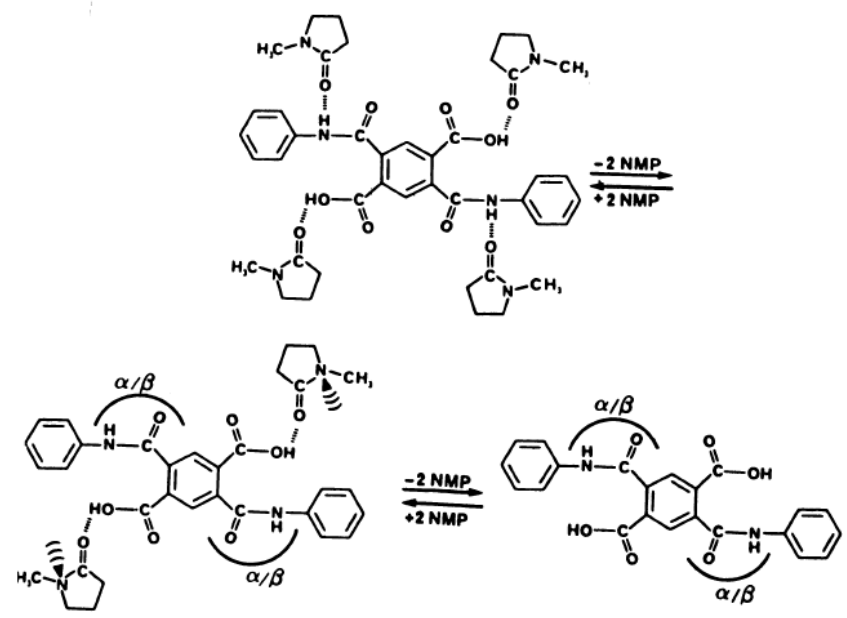


Figure 1.17 Interaction of NMP with amic acids [67]

It is very essential to remove moistures or water from monomers and during the process water or moisture must be taken from the system for enabling well-defined high molecular weight polymer. Otherwise water reacts with the dianhydrides and occurs diacids that can react very slowly with that diamines. For this reason that drying the monomers and distilling the solvents are important factors to obtain a well-defined molecular weight polymer. In case of the presence of water during the process the reverse reaction is stimulated. When the temperature of PAA is at elevated temperature the cyclization process, imidization, starts to take part. Then water is occurred during the cyclization and if the water is not taken from the process it causes to chain hydrolysis by hydrolytic scission of the amide link.

Consequently, it can be mentioned about three method to enable the cyclization of PAA such as heating the PAA in solution, casting film and chemical inducing by incorporating of the dehydrating reagents.

1.8.2.3. Effect of Solvents in Polyimide Synthesising

In the past it was only known that monomer concentration effects the molecular weight of PAA but then it was discovered that the sequence of the addition of the monomers effects seriously the molecular weight of PAA. For example when the solid dianhydrides are

added into the diamines solution and highest molecular weight is obtained. The more it is prevented from the side reactions the more high molecular weight is obtained [2].

During reaction of aromatic dianhydrides with water and impurities but they reacts with diamines considerably faster than water and impurities. On the other hand the solid mode of dianhydride leads to high molecular weight that the possibility of reaction with water and impurities decrease.

The low amount of the solvent decreases the impurities and facilitate the high molecular weight and the slight increasing of the amount of the dianhydride in stoichiometrically increase the molecular weight [3]. Also, the dissolution of solid dianhydride depends on monomer concentration. The monomer reactivity and solubility of dianhydride also influence polymerization type. Low reactivity and solubility causes to diffusion controlled polymerization like solid-liquid interfacial polymerization. At the beginning polymerization occurs at the high degree until consuming the dianhydrides and balance is obtained.

Researchers were awared of decreasing molecular weight of the PAA when the polymer was stored in solution after polymerization [2]. That situation can be derived from the hydrolysis of the amic acids. On the other hand the reaction propagation may be reversed. The few such reaction decreases dramatically the molecular weight of the PAA.

In synthesising PAA solvents have very important factor and common polar amide solvents are used such as NMP, DMAc, DMF. While the reagents used for the formation of PAA belong to weak basicity value, the product exhibit a strong acidic property. Moreover diamines present low basicity and dianhydrides have non-aprotic property. The product (PAA), and the dipolar aprotic solvent (DMF, DMAC, NMP and TMU) exhibit a very strong interaction that the result of this interaction is exothermic and promote to propagate this reaction. Hence the higher the basicity the solvent has the faster reaction occurs. For example, phthalic anhydride reacted with 4-phenoxyaniline was provided by the solvents such as THF, acetonitrile, DMAC. In consequence of these attempts the reaction rates were determined that THF is the weakest while DMAC is the highest [3].

1.8.2.4. The Effect of Side Reactions on Synthesising of Polyimides

During polymerization of PAA while the process continues along the main chain, side reactions can also involve in the polymerization process. Due to this side reactions undesired product can be occurred and prevent the chain propagation. For this reason the molecular weight (M_w and M_n) of polymerization decreases dramatically and affect the

polydispersity of the final polymer. The higher the molecular weight polymer exist the less side reaction occurs. At the same time if one side-reaction occurs the propagation would be as reverse and effect the molecular weight and regenerate dianhydrides and diamines .

This intermolecular acidolysis causes the formation of anhydride due to the pendant carboxylic groups at the ortho positions. That reaction is reversible but does not affect the molecular weight. On the other hand when an amine reacts with benzoic dianhydride that is an acylation reaction, an irreversible reaction occurs. But it was mentioned that the former reversible reaction of the formation of anhydride by the pendant carboxylic groups at the ortho positions does not affect the molecular weight due to the fact that the equilibrium constant (K_{eq}) magnitude still remains very high. Hence the repeating units of the polymer would be 300.X_n values of the poly (amic acids) generally varied from 25 to 275. Those ranges mean to a M_n in the range of 10,000 to 100,000 [4].

One of the important side reactions is the interaction of dianhydride and water. The reaction of dianhydride and water occurs as considerably fast but the reaction of the amines and anhydrides is faster. Even so, the final product becomes so low molecular weight polymer. As long as removing the water from the solution the process remains the monomer stoichiometry. At the same time the reaction rate of water with anhydride provides enhanced property. On the other hand there is little speculation that in case of the acid-base interaction of polar aprotic solvent and the ortho-dicarboxylic group low molecular weight polymer becomes due to high stabilization of ortho-dicarboxylic group.

There are some arguments from the above-discussed factors;

- During the process firstly the amine is dissolved and the dianhydride is incorporated into the solution due to avoiding from the anhydride-water reaction. By the way that the reaction of the existing water and the dianhydride is slower than the amine and the dianhydride.
- In synthesising PAA the high degree concentration of monomers are demanded
- The addition of a slight excess of dianhydride has advantageous to obtain higher molecular weights due to the reaction sensivity of dianhydride.

After for a long time water can be occurred in poly(amic acid) solution at ambient temperatures because of very slow of the reaction of poly (amic acid) to polyimide. Water is also defined as impurity and the other impurities can be solvent impurities such as monofunctional amines that can be found in the amide solvent. These solvent affect can

be dramatic for progression of the chain. These monofunctional impurities remove the balance of the reaction and change of the monomer stoichiometry. For that reason the polymer chains end up with monofunctional amines. Some authors speculate that isoimide can be occurred as another side reaction by the cyclic conversion of the o-carboxycarboxamide groups. It was mentioned about the excess of dianhydride can be used for higher molecules but can cause several damaging side reactions. That situation is generally applied for using of PMDA because of the high reactivity of PMDA. Normally, excess dianhydrides react with amic acids and cause to the formation of imide and diacid. Hence at the end of chain only the ortho-dicarboxylic acid group is found and the chain ends up [5].

1.8.3.Cyclization of Polyamic Acid by Thermal Imidization

Thermal imidization is widely used that polyamicacid precursor is transformed into polyimide at the elevated temperature. That process is favored in the application of film or coating. First, polyamicacid films are casted on the substrates and any thermal cycle is applied varied from 100°C to 350°C.Another subject that is not known exactly is to obtain 100% imidization of the poly amic acids. In literature and applications thermal imidization is applied as kinds of thermal cycles and it can be explained as two ways.

1) Slowly heating of the product between 250°C and 350°C.That heating process depends on the magnitude of glass transition temperature of the polyimide.

2) Another cycle is the heating of polyamic acid ; at 100°C for one hour, at 200°C for one hour and at 300°C for one hour and cooling slowly to the room temperature from 300°C.

Thermal imidization belong to complicating factors during the process such as along with the types of thermal cycling, the amount of solvent, the type and amount of chemical reagents. At the same time these factors determine the degree of imidization. At the initial and intermediate level of the process polyamic acid becomes a very viscous liquid. The solvent amount becomes important during the imidization at last level. On the other hand, dipolar amide solvents are more useful and by these type solvents the imidization process continues faster due to various reasons such as;

1) By proper solvent cyclizing of the polyamic acid becomes easier due to the conformation of the amic acid groups.

2) Solvents have plasticizing effect by increasing the mobility.

3) The amide solvent basicity enables to corresponding hydrogen atoms from amic acid groups that prevent side reaction [28].

The simple kinetic equation of the imidization reaction cannot explain the all process because of the various reactions of the chemicals and changing dynamic physical properties such as solvation, chain mobility, diffusion rate and acidity.

At the beginning of polymerization rate is very high due to the solvent amount and shorter chain. Because these factors increase the chain mobility. However, the reaction rate becomes slower than initial stage at the later stage because of the decreasing solvent amount, becoming the T_g of the product close to reaction temperature. Increasing of the T_g reduces the chain mobility. Another subject is that imidization rate depends on the conformation of the amic acid groups by rotation of added chain and strong bound of the solvent molecules [68].

1.8.3.1. Determination of the Degree of Imidization

Despite of the limited sensitivity of infrared spectroscopy it is still widely used to determine the imidization degree. The bands of the imidization occurs around 1780 cm^{-1} (C=O, asymmetrical stretching), 1380 cm^{-1} (C-N, stretching) and 725 cm^{-1} (C=O, bending).The overlapping of 1720 cm^{-1} (C=O, symmetrical stretching) with strong carboxylic acid band (1700 cm^{-1}, C=O) of the poly(amic acid) is observed. On the other hands some bands of unreacted anhydrides around 720 cm^{-1} and 1780 cm^{-1} can overlap the bands of imide around 725 cm^{-1} and 1780 imide bands. For polyamic acid the bands occur at around 1700 cm^{-1} 1550 cm^{-1} (C=N-H) , 3200-3300 cm^{-1} (N-H), (C=O, carbonyl bonds), 2800-3200 cm^{-1} (OH, hydroxyl) and 1660 cm^{-1} (C=O). Hydroxyl peaks are generally showed broadly.

1.8.3.2. The Factors of Effecting Mechanical Properties of Polyimide During Cyclization of Polyamic Acid

Mechanical properties change dramatically when polyamic acid transform to polyimide [69]. The size of the change of mechanical properties depends on the molecular weight of the PAA. When it is observed that the inherent viscosity of polymer films exhibiting less than 0.2 occurred as brittle and the change of the brittleness of the film was not observed after the curing cycle. Inherent viscosities varied from 0.2 to 1.0 of PAA liquid generated tough and creasable films but these films become brittle between 150°C and 200°C then above 275°C creasable films were again obtained. Finally inherent viscosities greater than

1.0 for PAA liquid produced creasable and tough films and these properties did not change during the curing cycle. All the various film properties are derived from molecular weight changing. In the vicinity of 100°C some anhydride and amine groups can regenerate then the chains are broken. Hence a fluctuation on molecular weight can occur and causes to decrease molecular weight. At elevated temperatures the terminal functional groups easily react and molecular weight increases.

1.8.4. Chemical Imidization Method in Polyimide Synthesising of the Polyamic acids

That imidization is used for molding powders. It requires low energy but involve in dangerous reagents. For this reason it is not used widely in industry. The process involve in the reactions of carboxylic acid of dianhydrides and tertiary amine at room temperatures. Anhydride, pyridine and triethylamine are common reagents for chemical imidization [48]. An anhydride is occurred by nucleophilic attack of tertiary amine. The occurred polyimide can be insoluble and precipitates out. The precipitation can also come true before the cyclization of the amic acid groups. A final treatment is needed to complete the imidization by heating up to approximately 300°C ($>T_g$) and remove the solvent from the product. It was called the reverse propagation in thermal imidization. In case of the chemical imidization that situation does not occur. Hence the molecular weight of the product does not exhibit any change. Also, mechanical properties does not show any decrease.

These are advantageous of the chemical imidization. However, the possibility of the presence of isoimides is higher than the thermal imidization [49].

1.8.5. One Step Solution Method of Synthesizing Polyimide

In order to enable to apply this technique the final product can be soluble in organic solvent. The process works at 180°C-220°C that the boiling temperatures of the mixture of the monomers. The imidization occurs immediately beside the generation of water due to an azeotrope along with the solvent and reaction is distilled. For that reaction the common solvents are widely used such as dipolar amide, m-cresol. The amounts of amic acid groups are so low at any time and these groups transform to polyimides very rapidly. At the same time polyimides can transform to anhydrides and amines very rapidly as reverse propagation. Generally, the high temperature solution process requires some catalyst such as zinc salts of carboxylic acids, tertiary amines, quinoline and alkali metals. At the same time dianhydrides and diamines become more reactive due to that method. On the other

hand high degree crystallinity is obtained compared to the two-step processes. The reason of that situation can be derived from increasing solubility due to the solvent medium [50].

1.8.6. Polyimides Properties and Characterization

1.8.6.1. Molecular Weight and Functional Group Analysis

It is well known that some of the important factors in polymer science change plenty of properties such as accurate control of functional reactive groups, the distribution of molecular weight and the magnitude of molecular weight. One another factor is polydispersities that influence seriously the mechanical and thermal properties of polymers. When compared two kinds of polymers belong to same molecular weight, mechanical and thermal properties of the polymers can be different due to the polydispersities. Moreover, polymer crystallization and crosslinking side reactions can occured due to specific functional groups. Molecular weight changes a plenty of properties of polymers hence it is very important parameter in polymer science. In order to measure the molecular weight solubility is important parameter because molecular weight is determined by solution techniques. Due to the insoluble structure the molecular weight of many polyimides cannot be determined. Polyimides belong to high crystallinity, network formation or chain rigidity. When this is the case that PAAs belong to hydrolytic instability due to the carboxylic amide linkage of the PAAs. And then molecular weight is determined by procedures applied carefully. But the procedure of soluble polyimides is simpler.

There are several different methods for determining molecular weight. One of them is solution viscosity that may be the easiest method. Unfortunately, molecular weight distribution cannot be determined in this method. Determining of the molecular weight distribution requires additional techniques for this. Gel permeation chromatography (GPC) is the most improved and widely used technique that consists of the determination of the molecular weights, molecular weight distribution and viscosity. Independent of chemical and architecture properties polymers belongs to same hydrodynamic volume passing through a same column. The determining of molecular weight and viscosity and is provided by using that parameter. In order to form calibration curve in GPC method monodisperse polystyrene samples are widely used have various molar weight. Hence the molecular weights are determined relative to those of polystyrene standards. The GPC must be integrated with viscosity detector for absolute molecular weight value. Mobile phases were obtained for polyimides such as tetrahydrofuran, chloroform, N-

methylpyrrolidone (NMP) with 0.06M LiBr. On the other hand high molecular weight peaks were eliminated by P_2O_5 and the addition of lithium bromide.

Functional group analysis by titration is attractive technique for measuring molecular weight. In this technique the specific functional reactive group concentration is determined in the polymer solution. Also, comparing to the reactions after and before the presence of the end groups can be measured and the imidization degree can be calculated.

Apart from these methods in order to determine the molecular weight of the polymers membrane osmometry (for Mn), low angle laser light scattering (LALLS) (for Mw) light scattering (for Mw), are used [51].

1.8.6.2. Structural Characterization

Various methods are widely used for elucidating the transformation of organic molecules groups such as UV spectroscopies, 19F, 13C, 1H and 15N NMR spectroscopies, Fourier transform infrared (FT-IR) and Raman spectroscopies. For example, polyimides are generally occurred from PAA formation and several alterations are produced during this transformation.

By using FT-IR method functional groups are generally determined and the imide, anhydride, isoimide and amic acid groups is examined among the absorptions peaks. Figure 1.18 shows all characteristic peaks of these structures.

Despite of the fact that a plenty of structural information are determined by FT-IR, small amount of amic acid groups can not be determined by that method. Because FT-IR does not has enough low sensitivity. For that reason NMR can also be used for perfect observation. FT-IR and NMR can complete each other. In $_1$H NMR method imidization can be explained by signal intensities of COOH protons. Also, $_{13}$C NMR spectroscopy can also used for understanding of thermal and chemical imidization [52].

1.8.6.3. Thermal Properties

The glass transition temperature is defined as relaxation points that polymer start to move as segmental motion along the backbone. That temperature is a bound between rubbery plateaus and the glassy. The factors of effecting of T_g can be emphasized such as the hydrogen bonding, the magnitude of chain packing, electrostatic and ionic interactions, the stiffness of chain. These factors are defined as intermolecular effects. The chain stiffness is the most important affect that changes the T_g. T_g can be determined by Differential Scanning Calorymeter (DSC) which is generally utilized method by observing as function

of the temperature. Furthermore it can be also observed a second order transition at around T_g.

	Absorption band (cm^-1)	Intensity	Origin
Aromatic imides	1780	s	C=O asym. Stretch
	1720	vs	C=O sym. Stretch
	1380	s	C-N stretch
	725		C=O bending
Isoimides	1795-1820	s	Iminolactone
	1700	m	Iminolactone
	921-934	vs	Iminolactone
Amic acids	2900-3200	m	COOH and NH(2)
	1710	s	C=O (COOH)
	1660 amide I	s	C=O (CONH)
	1550 amide II	m	C-NH
Anhydrides	1820	m	C=O
	1780	s	C=O
	720	s	C=O
Amines	3200 two bands	w	NH(2) sym. Structure (v(s))
			NH(2) asym. Structure (v(as))
			v(s) = 345.53 + 0.876*v(as)

vs, very strong; s, strong; m, medium; w, weak

Figure 1.18 Characteristic peaks related with imides [70-72]

Figure 1.18 exhibits the absorptions peaks of polymers containing BTDA and various diamines. The T_g is increased by diamines belong to different bridge groups due to the chain stiffness. The diamines belong to methylene-bridged show easy rotation property in the bridge groups hence the T_g becomes lower than the carbonyl bridging group in diamines. Because the carbonyl bridging group in diamines does not belong easy rotation property and the T_g and chain rigidity increases. One another group is the flexible ether-linked diamine that exhibits low T_g as methylene-bridged groups because of the easy rotation. Chain rigidity is changed by single bond and double bond. The sulfone groups belong to electron withdrawing properties that cause the T_g increase. This SO_2 functionality is the out-of-plane and decrease chain packing. Double bond between the bridging and aryl groups causes the increase of T_g for that system.

Bell et. al.[74] reported the catenation of diamines that ortho, para and meta linked systems changes the T_g of the structure. Meta linked systems have low T_g values compared

to ortho and para systems. For example benzophenone diamine that has orto and para linkage exhibit strong dipolar property hence the flexibility of the chain decreases.

One another property is thermal stability that is measured by thermogravimetric analysis (TGA). That method that observe the weight loss depending on the changing of the temperature is applied by under dynamic conditions (10 ^{o}C/min) or isothermal conditions in air or nitrogen. The 5% weight loss of aromatic polyimides is generally over 500 ^{o}C. And it can be also decreased chemical groups such as aliphatic groups and benzylic protons; hydroxyl groups ect. [7].

1.8.6.4. Insolubility/Infusibility

Due to the crosslinks some polyimides become insoluble during the imidization in some cases. In addition to this charge transfer complexes, semicrystallinity and rigid macromolecules can also become the polyimides insoluble.

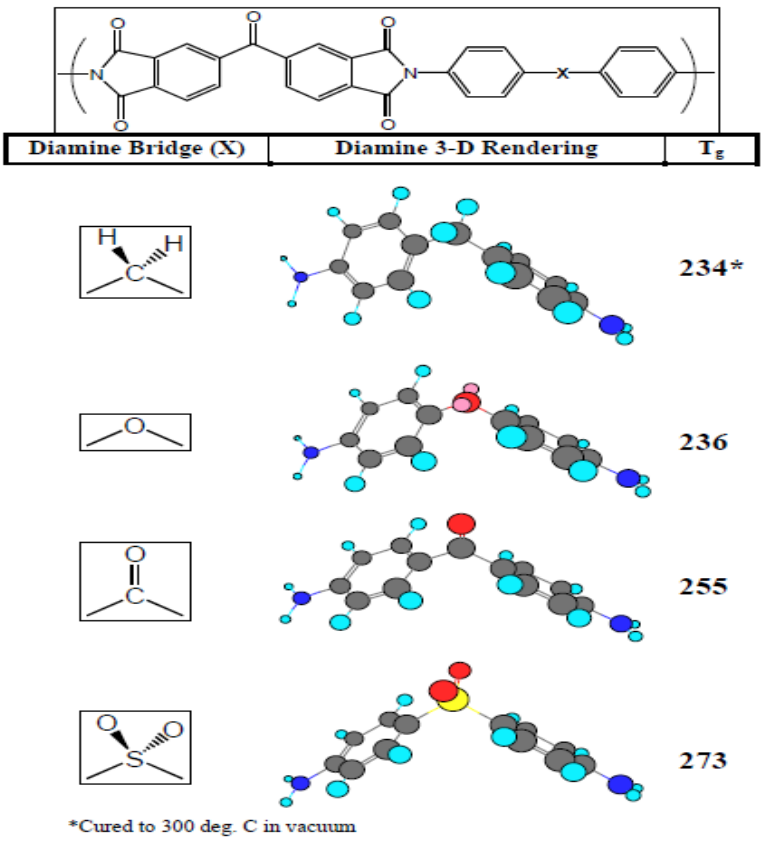
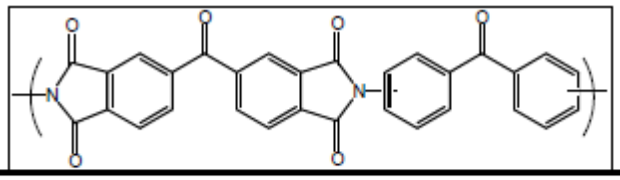


Figure 1.19 The Effect on the Glass Transition Temperature of Some Common Groups Between Diamine Functions [73]



Diamine Catenation	T_g (°C)
2,2'	285
3,3'	232
4,4'	290

Figure 1.20 Bonding Direction Effect of Diamines and Dianhydres on the Glass Transition Temperature [74]

These insoluble polyimides become soluble in concentrated sulfuric acid. In order to increase solubility some ways can be conducted such as ; placing polar groups as pendant or along the polymer backbone chain, bridging or pendant bulky moieties, catenation of the molecules as ortho and meta [53]. Figure 1.19 shows the reagents of polyimide increasing the solubility of the structures. Bonding direction effects of diamines and dyanhydrides on Tg was shown in Figure 1.20. Different structures of some common diamines and dianhdrides were presented in Figure 1.21.

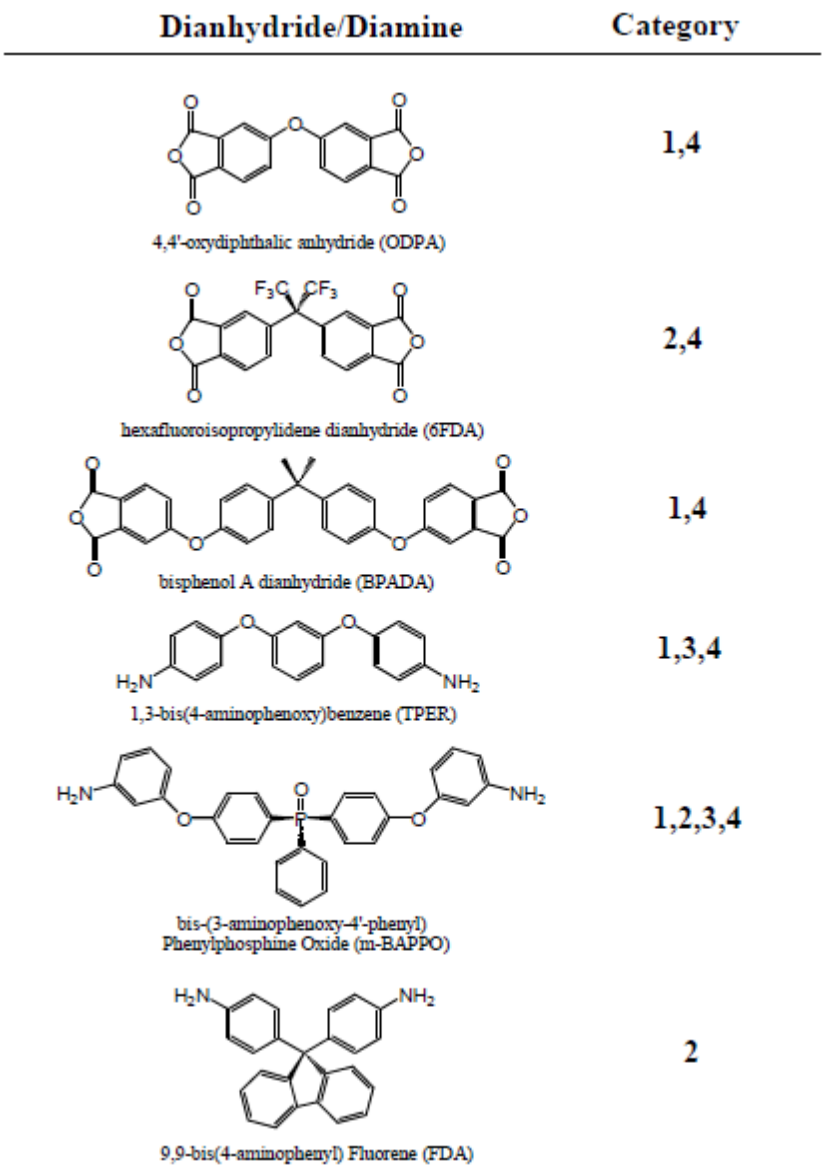


Figure 1.21 Different Structures of Some Common Diamines and Dianhydrides [73]

1.9. Polyimide Applications

1.9.1. Polyimides in Electronics

Polymers have been used in plenty of areas for example electronic areas. Polyimides in electronic areas can be utilized for wafer fabrication, chip packaging, adhesion, and assembly. It is well known that polyimides belong to excellent properties at high temperatures and it is very beneficial polymer that used for wafer manufacturing due to corrosion protection, high temperature stability and spin-coated on substrates. Polyimides also exhibit insulating properties for metal-polymer and polymer-polymer substrates. One another property is thermal expansion coefficient (CTE). In coating applications CTE

property is important and the difference of metal-substrate. For that reason polyimides can be designed as the most proper related to metal substrate. Figure 1.22 shows the relation of CTE of various metals, ceramics and organic polymers. Due to the minimizing of the CTE the possibility of the occurring stress by applying thermal cycling that can cause the failure. Polyimides are also used as photoresist in wafer fabrication. Photosensitive polyimides can be used in electrical and electronic devices to transmit the electrical current in submicron pattern. Hence the cost and steps of the process can be minimized by the polyimides have photosensitive property. The light is applied to the photosensitive polyimide and causes crosslinking and scission. Those changes affects as either increasing solubility or becoming insoluble. The light decreasing the solubility the polymer is defined as negatively imaged. Otherwise the light increasing the solubility it is defined as positively [54, 55] Figure 1.23 shows photosensitive polyamic acids that are exposed by light and convert to polyimide. Also, the exposed part of the polymer is cross-linked and provides insolubility. The other part of the polyimide which is unexposed part can remain soluble and remove by a proper solvent.

Negative imaging photosensitive polyimide exhibits so low shrinkage during the curing process. On the other hand due to the cleavage of the backbone and changing the polarity of side moieties causes positive-photoresist polyimides can become more soluble.

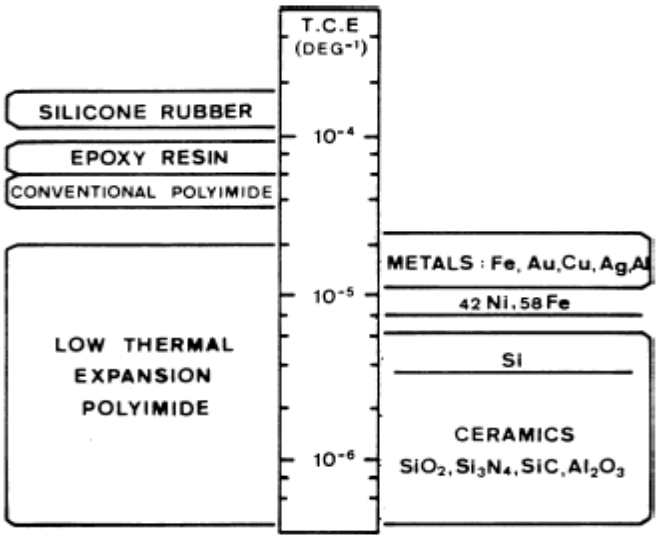


Figure 1.22 Thermal Expansion Coefficient of Some Ceramics, Metals and Organic Polymers [75]

The solubility difference of the silylated and non-silylated polyimide is available. Hence the polyimides exposing to hydrolysis by photoacid-generating molecule and the polyimides containing non-silylated polyimide can be selectively produced.

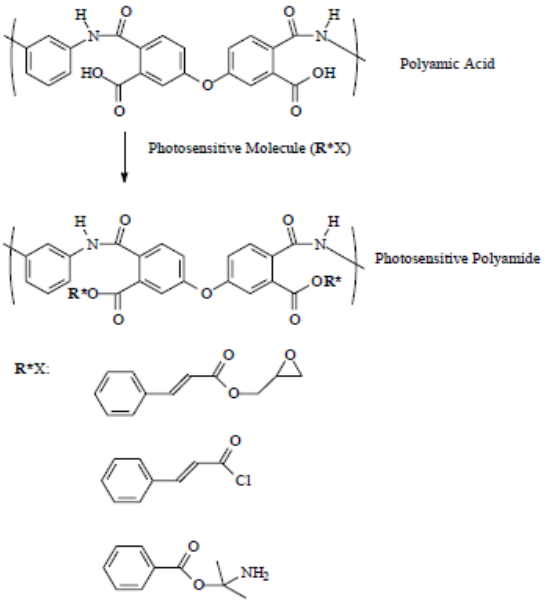


Figure 1.23 Photosensitive Polyimide Revealing Negative-Imaging [76]

1.9.2. Polyimides as Optical Waveguides

Optical waveguides have some benefits that allow the transport of multiple signals without any effect and prevent the electromagnetic interference. The other methods are freestanding and embedded waveguides. Ion Beam etching techniques and photolithography techniques are conventional techniques that coated a polymer on a substrate in specific pattern. The role of the pattern allows the light transmission on demanded polymer structure. The advance methods UV lithography is used in embedded waveguides and occurs a pattern on polymer coating by changing chemical structure. Hence the selective diffusion is provided by this method.

Waveguide materials for thermoplastics are required more properties. One example is typical flip-chip configuration is showed in Figure 1.24 that this joining method is using up to 360°C and the active chip area overlaps the substrate. The process of patternable is applied between C_4 connections.

Polyimides are ideal to optoelectronic materials that belong to high thermal stability, high decompositon temperature and good dimensional stability. Thermal imidization from PAA to polyimides causes large optical losses. Microvoids are occurred by PAA cyclization to polyimide and the removal of solvent that causes different densities fluctuations and light scattering. For decreasing optical loss full imidization is most important. For that reason thermal imidization may not be appropriate for waveguides. By chemical imidization full imidization can be provided but soluble polyimide must be occurred. The polyimides in full cyclized were occurred by the addition of 6F and 3F groups. These groups are bulk groups and become the polyimide more soluble due to the preventing the chain ordering and transfer complexes also they exhibit high T_g [56,57].

1.9.3. Polyimides in Aerospace

Technology has been growing and industry has been demanded advanced materials and polymers. Polyimides are one of engineering materials and modified polyimides belonging to advanced properties which have been improved in a plenty of industries. One of these industries is aerospace industry that requires advanced polyimides for several conditions due to their advantages.

It was mentioned about excellent properties of polyimides such as very high heat resistance, great adhesion property towards a plenty of substrates, great chemical resistance and very good mechanical properties; flexural modulus and compressive strength. In high temperature applications polyimides can be exposed to high loads. For that reason they also have excellent dimensional stability.

It is well known that phosphorus moieties increase the thermal stability, TGA char yields and fire retardancy property in air. It was discovered that the fire retardancy property, increasing the solubility and adhesion to titanium when incorporated the bis (*m*-amino phenoxy) triphenylphosphine oxide [57].

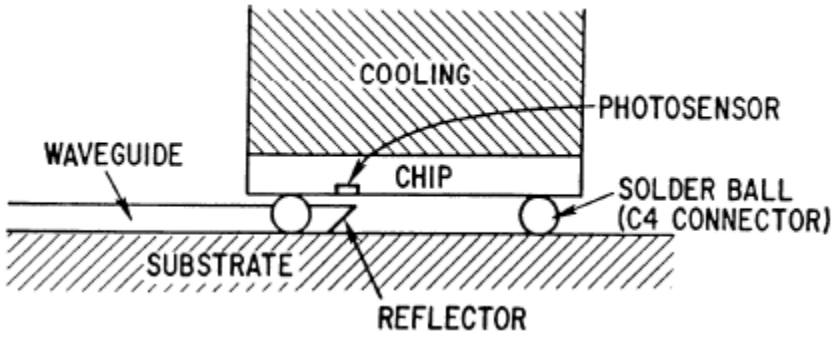


Figure 1.24 Flip-Chip Configuration Waveguide [77]

Polyimides have been also used in composites in aerospace application that belong to very good fatigue and corrosion resistance, good aerodynamic properties, low fabrication and repair costs compared to the mechanically fastened assemblies. In composite implementation the using of resin materials is very good at increasing wettability. For example polyimides have been used as the resin material for carbon fibers. In these processes polyimide can be introduced as oligomer for better wettability. These oligomer groups show low viscosity and form crosslinking bonding at high temperatures. Figure 1.25 exhibits the commercial examples about this subject. For example PMR-15 is obtained as polyimide composite that includes in oligomers end-capped with nadic anhydride belonging to low molecular weight. These materials occur crosslinking at 250 ^{o}C-300 ^{o}C due to the nadic anhydride. Unfortunately these materials contain solvent and these solvents remove from the composite. Hence these solvents cause voids in the laminates. But if the oligomers terminated acetylene, phenylacetylene, and phenylethynyl are used in composites which the voids are not formed [57, 58].

1.9.3. Polyimide Adhesives in Aerospace and Microelectronics

There must be several chemical interactions for creating adhesive bonding. They can be listed as below [58];

1. Hooking or Mechanical locking: Adhesion can be formed by trace of the fracture.
2. Acid-Base Theory; Acid-base interactions affects the adhesion strength.

Monomers	Unsaturated end cap	Examples
methylenedianiline, benzophenone dianhydride	nadic imide	PMR-15 LARC-13
methylenedianiline, maleic anhydride	maleimide	Kerimid 601
methylenedianiline, benzophenone dianhydride	phenylacetylene	ATPI Thermid
m-phenylene, bisphenol A dianhydride	phenylethynyl[52,157]	

Figure 1.25 Curable Polyimides for Aerospace Applications [78, 79]

3. Diffusion Theory: Interpenetrating network can be occurred beyond the interface as interphase area.
4. Surface Properties: Excellent wetting can cause very good adhesion in this section
5. Chemical bonding: Covalent bonding causes very good strength
6. Weak Boundary Layer Mechanism: This type interaction is related to cohesive energy.

One of these mechanisms is not only used for adhesion but one mode may be dominant and these criteria causes to affect the adhesive strength. Chemical bonding is the most demanded interaction for good adhesion of polymer/substrate interface. Because the chemical bonding is much less than Van der Waals forces and hydrogen bonding to disturbed by water, heat and chemicals.

It is important that surface must be prepared to create desired chemical interactions. If the contaminant adsorptions can be minimized the adhesion property will be excellent and bond durability will be great. Hence preparing the surface prior to application is necessary. There are several application types for preparing the surfaces ranging from physical effects to chemical methods such as a pumice scrubber, reactive ion etching and chemical modification.

In terms of polyimides adhesion characteristics which can be classified in three categories. The first class is self-adhesives with metals on Cu, Cr and Al substrates that amorphous polyimides can be attached in that section. The second one is semi-crystalline polyimides that bond to reactive metals (Al, Cr) [80,65].

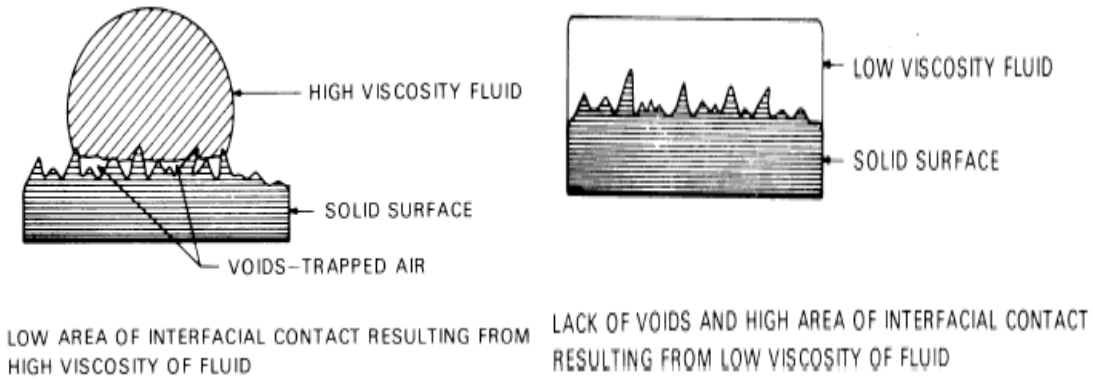


Figure 1.26 The relation of viscosity of a fluid on substrate [81]

Also, marginal self-adhesion can be observed in some semi crystalline polyimides. It was reported that the curing effect polyimide/polyimide adhesion. While fully cured two polyimides heated at 400°C (ODA/PMDA) exhibit weak adhesion property, the adhesion property between a polyimide cured completely with another polyimide cured incompletely (200°C) is considerably strong. The relation of viscosity of a fluid on substrate was given in Figure 1.26.

When compared the inter-diffusion region of two adhesion areas of polyimides the fully cured/incompletely cured laminate is higher (47nm vs. 30nm) [82].

Third class of polyimides is thermosetting resin that belongs to low molecular weights. The polyimides that the chains ended with curable groups exhibit good wettability and bond to metals, ceramics and each other.

The adhesive strength can be measured by kinds of method that include in many geometries and test configurations. In these methods it is utilized by stress distribution between adhesive joints having non-uniform property [60]. For transferring the loads between two adheres structural adhesive can be used as bonding agent. These structural adhesives are used in aerospace applications that are required to withstand static and dynamic forces. The parts of missiles for flight require superior properties that have ability for heating up to 500ºC in a few minutes. Also, the civil transport flights must withstand high speed, temperatures ranging from 177ºC to 232ºC and more than 50,000 hours [63].

According to these superior properties polyimides become prominent for using aerospace applications. In this context polymers having to these superior properties are defined as space-age polymers. Polymerization of monomeric reactants (PMR) is used for these applications that includes in nadic anhydride endgroups. Nadic anhydride end groups come prominent in aerospace. But these resins have some constrains about occurring of

cyclopentadiene during the thermal crosslinking and volatiles causing the voids that reduce the long term adhesion. On the other hand polyimides oligomers belong acetylene, phenylacetylene, phenylmaleimide or phenylethynyl reactive end groups can be considered instead of PMR resins. The advantages of these materials can be listed as the ability of fully cyclization, not forming volatiles during thermally cross-linked, good adhesion with metals. Good adhesion behavior is demanded between polyimide-polyimide and polyimide-metal interfaces in microelectronic devices. Printed circuit boards and multichip packages are common examples for these materials. This application is used by two-step thermal imidization on a substrate to form thin layer. Polyamic ester (PAE) is also used as precursor to produce the polyimide beside polyamic acid (PAA). There are kinds of reactions during the process that include also loss of water, residual solvent and the other volatiles. The adhesive behavior is so complex that chemical and physical changes are not obtained as expected. Residual stress seriously affects the adhesion strength due to difference of thermal expansion coefficient between the film and substrate and loss of volatiles. These cause the adhesive failure. Also, process parameters affect the adhesion property and bonding stability such as temperature and humidity. It is well known that the adhesion of polyimides can easily be canceled by water absorption. On the other hand aminosilanes have been used to develop the interfacial adhesion properties.

Photoimageable polyimides cure completely was studied and compared with a PAA [46].

2. MATERIALS AND METHOD

2.1. Substrate Material

2.1.1. Aluminum Sheets

Coatings were applied to 50x50 mm and 100x100 mm square shaped aluminum sheets with a thickness of 2mm that purchased from Formlaser Ltd. Şti.

2.2. Chemical Materials

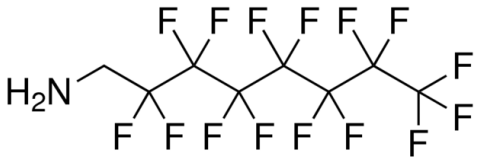
2.2.1. 1H, 1H-Perfluorooctylamine

Manufacturer: ABCR

Mol. formula : $C_8H_4F_{15}N$

Mol. Weight: 399.10 g/mol

Structural Formula :



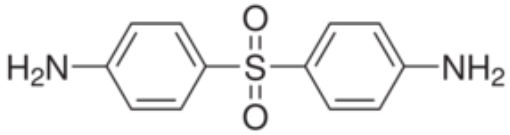
2.2.2. 4-Aminophenylsulfone

Manufacturer: Aldrich Chemical

Linear Formula: $(H_2NC_6H_4)_2SO_2$)

Molecular Weight: 248.30 g/mol

Structural Formula:



2.2.3. 4,4 - (Hexafluoroisopropylidene)diphthalic Anhydride

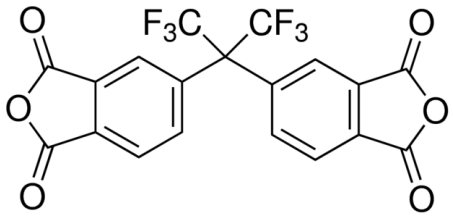
Manufacturer: Aldrich Chemical

CAS Number:1107-00-2

Linear Formula: $C_{19}H_6F_6O_6$

Molecular Weight: 444.24 g/mol

Structural Formula:



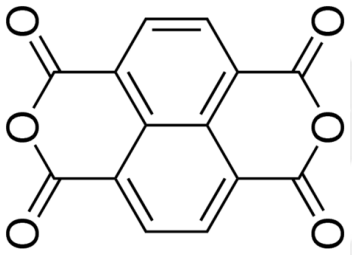
2.2.4. 1,4,5,8-Naphthalenetetracarboxylic Dianhydride

Manufacturer: Aldrich Chemical

Linear Formula: $C_{14}H_4O_6$

Molecular Weight: 268.18 g/mol

Structural Formula:



2.2.5. Dimethylacetamide

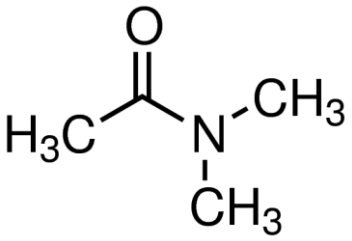
Manufacturer: Aldrich Chemical

Molecular Formula: $CH_3CON(CH_3)_2$

Molecular Weight: 87.12 g/ mol

Purity: 99. 8%

Structure Formula:



Used without any processing.

2.2.6. N-Methyl-2-pyrrolidone

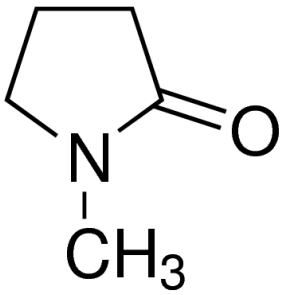
Manufacturer: Aldrich Chemical

Molecular Formula: C_5H_9NO

Molecule Weight: 99.33 g/mol

Purity: 99. 5%

Structure Formula:



Used without any processing.

2.2.7. Acetone

It was used for cleaning the substrates before the coatings.

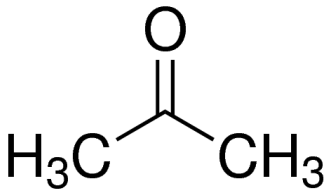
Manufacturer: Aldrich Chemical

Molecular Formula: C_3H_6O

Molecule Weight: 58. 08 g/mol

Purity: 97. 5%

Structure Formula:



2.3. Experimental Equipment

2.3.1. FT-IR Spectrophotometer

Shimadzu brand 8300 model FT-IR Spectrophotometer device was used.

2.3.2. Applicator

200 mils wire wound applicator was used for coatings to obtain homogeneous and equal thickness on the surfaces as shown in Figure 2.2



Figure 2.1 Applicator

2.3.3. Dean-Stark Apparatus

That apparatus was used during the synthesis of poly amic acid and it was used to prevent hydrolyzing and losing the solvent.

2.3.4. Scanning Electron Microscope (SEM)

SEM device belong to Carl Zeiss Ultra Plus FESEM with X-Ray elemental diffraction spectrometer was used to observe morphologic features of polyimides coatings.

2.3.5. Differential Scanning Calorimetry (DSC)

HITACHI DSC7000X equipment was used for analysis of the polyimides coatings. The analysis were applied from 40°C up to 500 ^{o}C with a heating rate of 10 ^{o}C/min under an N_2 atmosphere.

2.3.6. Thermal Gravimetric Analysis (TGA)

HITACHI TGA STA 7300 model was used for analysis of the polyimides coatings. That equipment was used with heating rate of 10°C/min from 30 to 900°C under nitrogen atmosphere.

2.3.7. TABER® Rotary Platform Abrasion Tester

Abrasion test of polyimides coatings on aluminum sheets were applied by a Taber 5135

rotary platform abrasion tester using CS10 Calibrade® wheels which was shown in Figure 2.2



Figure 2.2 Taber 5135 rotary platform abraser model abraser tester

2.3.8. Cross-Cut Adhesion Tester

BYK Gardner cross-cut device was used for adhesion test which was given in Figure 2.3 Also, Tesa® adhesive tape was used to evaluate the adhesion effect.

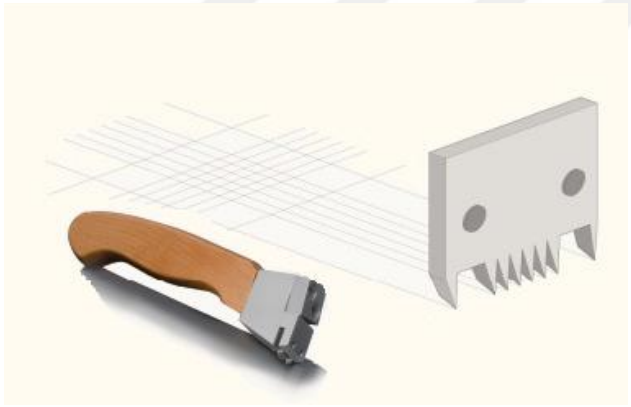


Figure 2.3 BYK cross-cut adhesion testing device

2.3.9. Hardness Test (Pencil Hardness)

In order to measure the hardness of polyimides coatings pencil hardness test was applied from 6B to 6H by using different pencils.

2.3.10. Gloss 60° Test

60° Gloss was applied to evaluate the brightness value of the coatings which was shown in Figure 2.4



Figure 2.4 Gloss 60° measurement device

2.2.11. Contact Angle Measurement

PG-X2 device was used for measuring the contact angle of the polyimides coatings on aluminum substrates which was shown in Figure 2.5



Figure 2.5 PG-X2 contact angle measurement device

2.2.12. Teflon Mold

Teflon Mold with a dimension of 50 mm length x 1 mm depth x 10 mm width were used for shaping polyimides free films which was depicted in Figure 2.6.

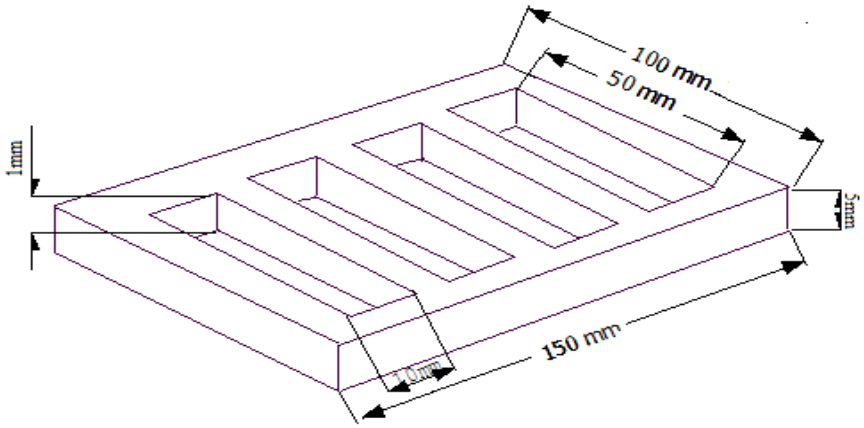


Figure 2.6 Teflon mold for obtaining free films

2.2.13. Instron Furnace

Instron electric heating furnace which operates up to 350 C^o was used for thermal imidization of PAAs on aluminum substrates. Picture of Instron furnace was shown in Figure 2.7.



Figure 2.7 Instron Furnace for Thermal Imidization of Coatings

3. RESULTS AND DISCUSSION

3.1. Decontamination of the Surfaces of Aluminum Sheets

Aluminum sheets were cleaned by acetone to remove the contamination and impurities to provide good adhesion property between substrate and polyimides. After that the sheets were dried and prepared to coating application.

3.2. Preparing of Polyimide Coatings

3.2.1. Synthesising of PAAs

Two different materials were synthesised as polyimide coatings with 1 % PFOA and without 1 % PFOA. Hence PFOA was bonded to two ends of polyimide chains. On the other hand 6FDA and NTDA were used to synthesised copolyimides in various ratio as anhydrides which is shown in Table 3.1.

Table 3.1 The Coating Formulations

The Samples	6FDA Ratio %	NTDA Ratio %	The Existence of %1 PFOA	The Samples	6FDA Ratio %	NTDA Ratio %	The Existence of %1 PFOA
PI0	0	100	not-avaliable	PIF0	0	100	avaliable
PI20	20	80	not-avaliable	PIF20	20	80	avaliable
PI40	40	60	not-avaliable	PIF40	40	60	avaliable
PI60	60	40	not-avaliable	PIF60	60	40	avaliable
PI80	80	20	not-avaliable	PIF80	80	20	avaliable
PI100	100	0	not-avaliable	PIF100	100	0	avaliable

In PAA synthesising, first DADPS was added into a 100 mL three-necked flask that fitted with a thermometer pocket and a magnetic stirrer.

A part of DMAC solvent was added to the flask to solve DADPS and stirring for one hour. After the solving the DADPS, NTDA and/or 6FDA were added to the flask to synthesis PAAs. At the same time the other part of DMAC and NMP were dropped to the flask slowly. DMAC and NMP were used as solvent in 4:1 ratio. DADPS and anhydrides were calculated in stoichiometric ratio. However, DADPS was calculated as 1 % less than the stoichiometric ratio of the anhydrides for the polyimides with PFOA (PIFs). Hence 1% of the polyimide chains were terminated the anhydrides for reacting with PFOA. But this imbalance of stoichiometric ratio can cause to lower molecular weight. Also, the increase of the ratio of NTDA decreases molecular weight of polyamic acid (PAA) and polyimides due to the insoluble structure of NTDA. For that reason incorporating the fluorine structures and heating PAAs up to 80°C for two days eliminated the drawbacks relating to the synthesis of polynaphtalimide (PNI) having sufficiently high molecular weight and good solubility [83]. But that was not sufficient for PI0 and PIF0 because these samples were not dissolved and subsided.

For PIFs (Polyimides with 1% PFOA): After adding anhydrides to the flask, diamine and anhydrides were firstly stirred for one day at room temperature in nitrogen atmosphere. Then the solution was taken to dean-stark apparatus to dissolve the solution stirring at 80 ^{o}C in the flask in nitrogen atmosphere. Because the structure of NTDA decreases the solubility of the PAAs. After dissolving the solution at 80°C the solution was again cooled down to room temperature. PFOA was added to the flask to react with the anhydrides and stirred for one day at room temperature and then the PAA solution with PFOA was finally taken to dean-stark apparatus to stir at 80°C for one day to increase the reaction rate of PFOA with anhydrides. PFOA belong to long linear fluorocarbons chain that becomes the rate of reaction low in room temperature [84].

For PIs (Polyimides without 1% PFOA): After adding anhydrides to the flask, diamine and anhydrides firstly were stirred for one day at room temperature in nitrogen and then the solution was taken to dean-stark apparatus in nitrogen for one day at 80 ^{o}C for dissolving the solution. The solution was dissolved. In order to obtain in same conditions of all samples after the dean-stark apparatus at 80°C the solution was taken to room temperature to stir for one day and then it was finally taken to dean-stark at 80°C.

3.2.2. Thermal Imidization of PAAs

After the synthesising the PAAs, all solutions were spread on the aluminum substrates by wire wound applicator. Then the aluminum sheets were heated in different ways. According to the literature there are two different thermal imidization methods reported. These are;

a) 100 ^{o}C for 1 hour; 200 ^{o}C for 1 hour; 300°C for 1 hour
b) Gradually heating up to 300- 350°C

Firstly, a method was employed for thermal imidization. But after applying of that method macro fractures were observed on the coating for all samples. On the other hand while the ratio of NTDA increased the brittleness becomes higher. It was deduced that molecular weight becomes lower while the ratio of NTDA increase [83].

In second method, thermal imidization was achieved successfully. We obtained a successful conclusion. Heating rate of the process was 10°C/min. Thermal imidization includes in a little dwelling time up to 350°C. There were no macro fractures observed on coating surfaces. On the other hand the process was applied by heating at 1°C/min but there were many fractures observed on coating surfaces. First the PIFs were heated at 1°C/min from room temperatures and the fractures started to occur on the coatings close to 80°C. Another process was applied under vacuum and it was observed that the distances between the fractures increased. Hence the number of fractures decreased due to the vacuum. Even so the most proper heating process for all samples was performed by heating to first 80°C for 30 min and then consequent heating up to 200°C and 300°C for 15 minute then finally last step was completed with 350°C for 1,5 hour by heating with 10°C/min.



Figure 3.1 PIF80 sample on aluminum by heating with 1°C/min under vacuum

For PIs: Thermal imidization was started with 80°C for 30 min and then followed heating up to 200°C and 300°C for 30-minute finally last step was completed with 350°C for 1 hour. After the last step the oven was stopped and the samples were cooled in oven. That process was successful for PI100, PI80 and PI60 but same thermal imidization heating process for PI40, PI20 and PI0 was unsuccessful. Because of the increasing the ratio of NTDA molecular weight of PAAs may decreased. Also, NTDA reveals T_g of the polyimides so higher for that reason the process should include in adequate high heating rate and it should also contain less number of dwelling line and low dwelling time [83, 84].

For that reason the thermal imidization process were adjusted for all samples as 80°C for 30 min and then followed by further heating up to 200°C and 300°C for 15 minute, finally last step was completed with 350°C for 1.5 hour. Only PI0 coating was observed as very brittle like powder because of low molecular weight and insoluble structure of PNI. The polyimides consisting of naphthalene groups without any ether groups, substituted groups or fluorine groups have low solubility and low molecular weight. In order to solve that problem the PAAs consisting of naphthalene groups has been stirred at 80 ^{o}C but that solution has not been solved exactly. Polyimides synthesised in this way (stirring at 80°C) has still low molecular weight. In literature one pot method, high heating solution process has been used for polyimides containing naphthalene groups with catalyst for obtaining high molecular weight [84].

Another thermal imidization process was applied for all samples at 80°C for 5 min and then further heating up to 300°C for 15-minutes finally last step was completed with

350°C for 1 hour and 45 min. But in this process bubbles and cracking occurred for PI100 and PI80.

PIFs in this heating process did not give same effect. An accomplished coating was obtained for PIFs in this heating process due to the probability of low molecular weight or the space volume deriving from long fluorocarbons chains at the ends of the polyimides chains [83]. Polyimide chains terminated by PFOA in PIFs was shown in Figure 3.2.

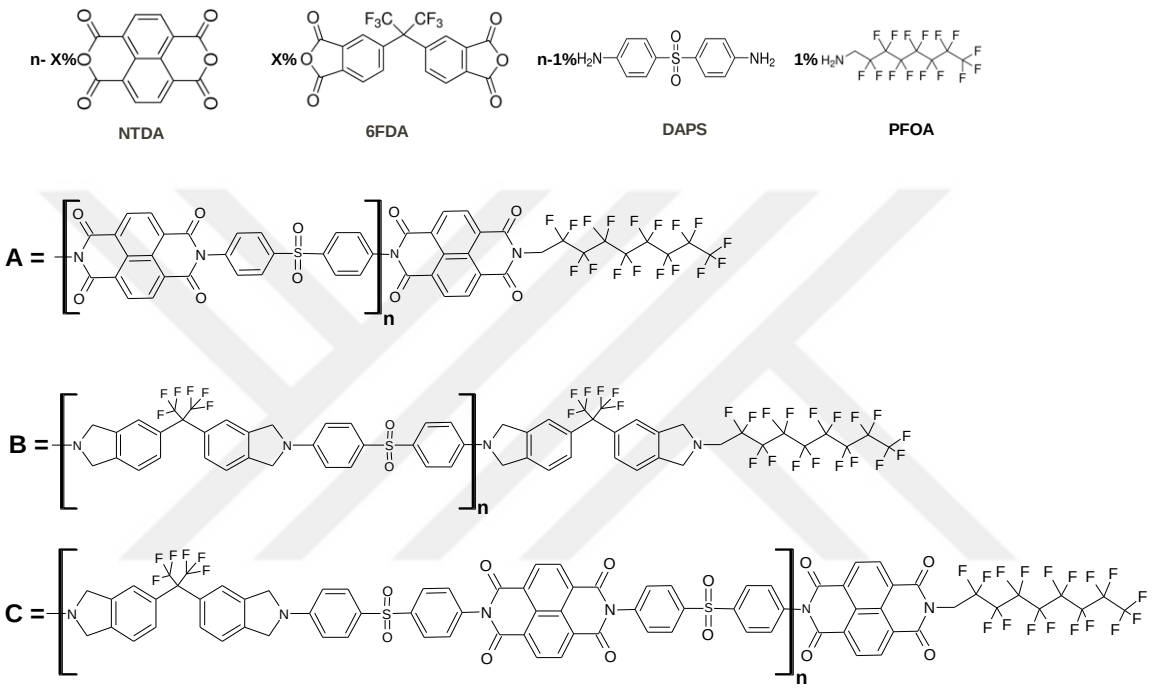


Figure 3.2 Polyimide chains terminated PFOA in PIFs

For PIFs: As PIFs, thermal imidization was started with heating up to 80 ^{o}C for 30 min and then further heating up to 200 ^{o}C for 30 minute finally last step was completed with 300°C and 350 ^{o}C for 1 hour. However that heating process was unsuccessful for all samples. At this heating process there were macro fractures observed on the coatings and the quantities of these fractures increase with the ratio of NTDA because of the lower molecular weight. Moreover PIFs have more brittleness than PIs because of the imbalance of stoichiometric ratio that the diamines was calculated 1 % less than anhydrides in PIFs. That imbalance between diamines and anhydrides cause to low molecular weight. Hence brittle coatings could easily occur. On the other hand the temperatures close to 100 ^{o}C and between 100 ^{o}C and 200 ^{o}C polymerization may get reverse and molecular weight may decrease [7, 69]. Hence thermal imidization was adjusted as first at 80 ^{o}C for 30 min and

then further heating up to 200 ^{o}C and 300 ^{o}C for 15 minutes finally last step was completed at 350 ^{o}C for 1.5 hour as shown in Figure 3.3.

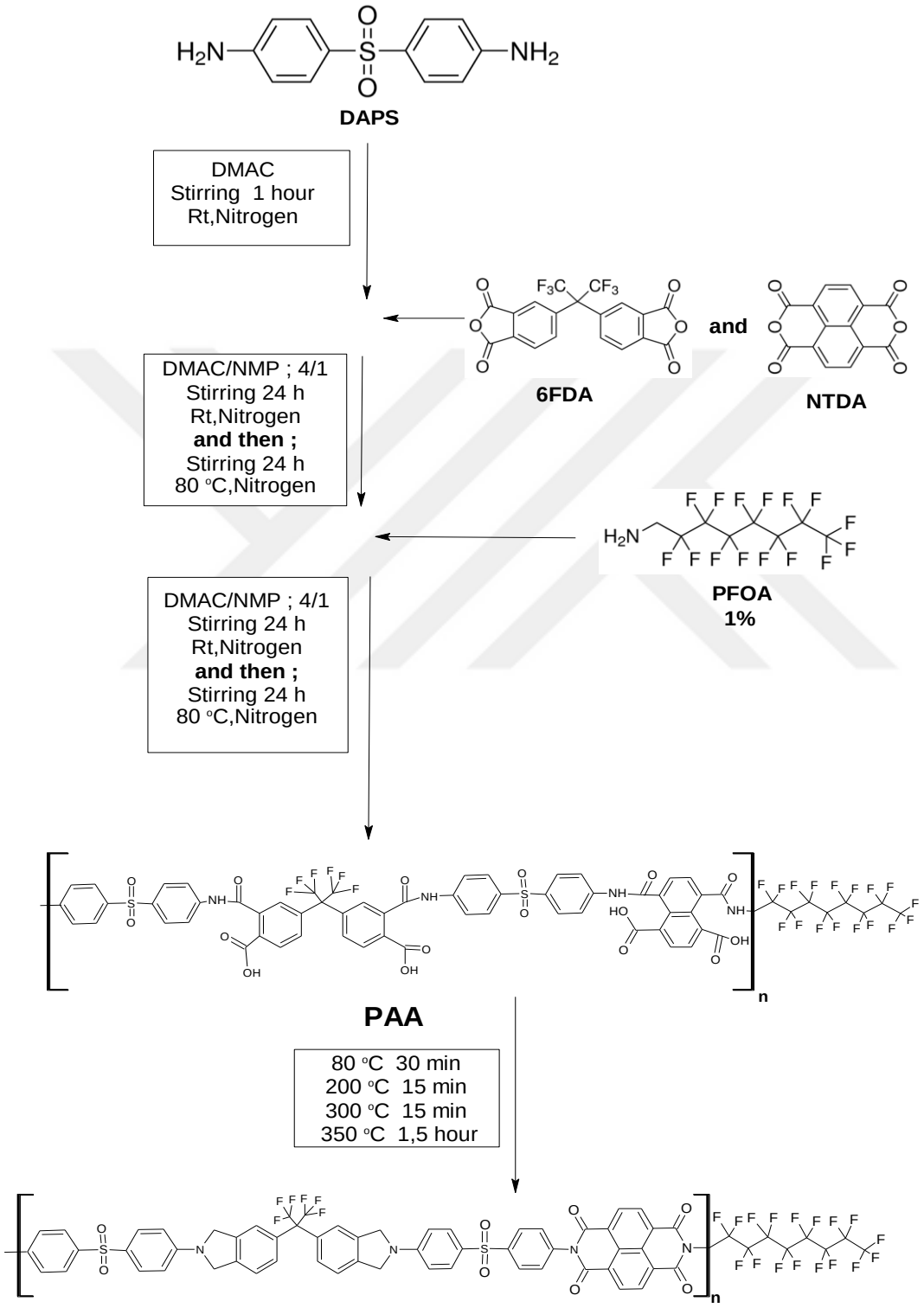


Figure 3.3 The process of synthesising of PIF copolyimides

These heating process gives the best values for all samples. PIF0 was the most brittle coating and exhibited a powder behavior on aluminum substrate.

Table 3.2 Preparations of Coating Formulations

Code of Samples	6FDA (g)	NTDA (g)	DADPS (g)	The Samples	6FDA (g)	NTDA (g)	DADPS (%99,g)	PFOA (%1,g)
PI0	0	2.7001	2.5	PIF0	0	2.7001	2.4875	0.0351
PI20	0.8945	2.1601	2.5	PIF20	0.8945	2.1601	2.4875	0.0351
PI40	1.7891	1.6200	2.5	PIF40	1.7891	1.6200	2.4875	0.0351
PI60	2.6837	1.0800	2.5	PIF60	2.6837	1.0800	2.4875	0.0351
PI80	3.5783	0.5400	2.5	PIF80	3.5783	0.5400	2.4875	0.0351
PI100	4.4729	0	2.5	PIF100	4.4729	0	2.4875	0.0351

The colour of all samples became lighter by the increase of the ratio of 6FDA shown in Figure 3.4.

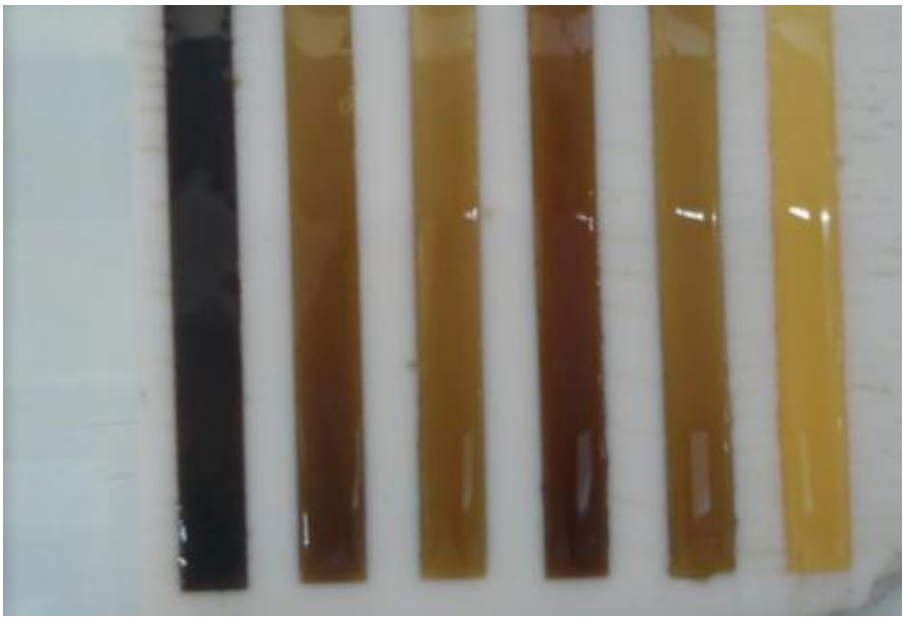


Figure 3.4 PAAs without PFOA in teflon mold before forming PI films

On the other hand PIFs reveals more transparency than PIs because of the long fluorocarbons chain (PFOA).

3.3. Characterizations and Tests Applied on Coatings and Free Films

All PAAs were spread on aluminum substrates by 200 mils wire wound applicator. Before spreading aluminum substrates were cleaned by acetone. And these substrates were heated at a heating rate of 10°C/min. These substrates were started to heat 80°C for 30 min and then by further heating up to 200°C and 300 ^{o}C for 15 minute, finally last step was completed at 350°C for 1.5 hour as shown in Figure 3.5 Also, free films were prepared in teflon mold in same process with coatings.

3.3.1. Cross-Cut Test (Adhesion Test)

Cross-cut test was applied according to ASTM D–3359 standards. Three replicated samples was produced for each test.

3.3.2. Gloss 60° Test

Gloss 60° was measured according to ASTM D-2457 standards. Three replicated samples was produced for each test.

3.3.3. Taber Abrasive Test

Taber abrasive test was performed according to ASTM D-4060 standards. Three replicated samples was produced for each test.

3.3.4. Pencil Hardness Test

Pencil hardness test was carried out according to ASTM D-3363 standards. Three replicated samples was produced for each test.

3.3.5. Contact Angle Measurement

Contact angle test was measured according to ASTM D-7334 standards. Three replicated samples was produced for each test.

3.3.6. Differential Scanning Calorimeter (DSC)

In order to determine temperature and heat flow differential scanning calorimeter was used in constant pressure. DSC characterization is a function of absorption of heat changing and temperature. That test was applied with 10°C/min heating rate up to 500°C to determine transitions of polyimides. Generally DSC has been used for observing physical changes

such as glass transition temperature.

3.3.7. Scanning Electron Microscope (SEM)

The coatings surface morphologies were characterized by Carl Zeiss Ultra Plus FESEM device.

3.3.8. Thermal Gravimetric Analyses (TGA)

Thermogravimetric analyses (TGA) of polyimide films were performed using a PerkinElmer Thermogravimetric analyzer HITACHI model. Samples were run from 30 to 900 ^{o}C with heating rate of 10°C/min under nitrogen atmosphere.

3.3.9. Fourier Transformation Infrared Spectroscopy (FT-IR)

Formation of PAAs and PIs were confirmed by FT-IR. PAAs before cyclization to PIFs and PIFs absorptions were given in Figure 3.5 and 3.6.

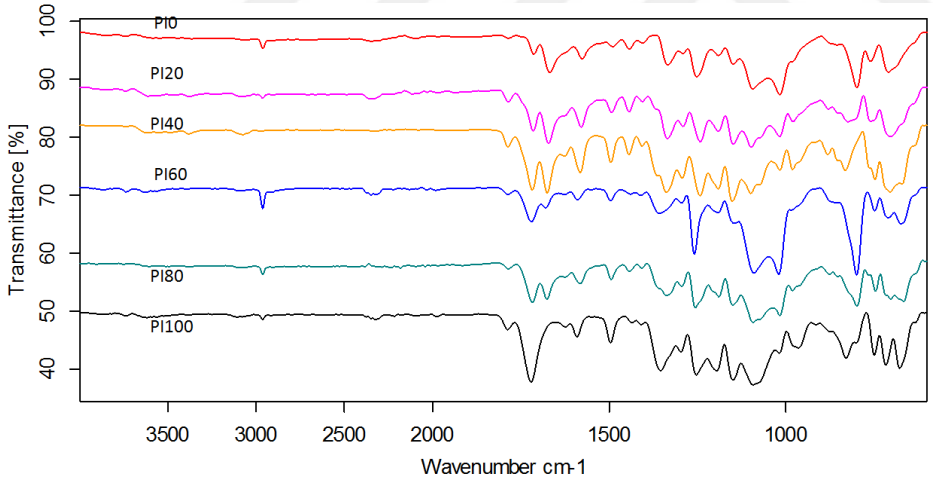


Figure 3.5 The FT-IR spectrums of the PIs

Figure 3.5 and 3.6 demonstrate the characteristics absorptions of the polyimides synthesised. The peaks of C=O symmetric stretching vibration at around 1785 cm^{-1} and C =O asymmetric stretching vibration at around 1718 cm^{-1} were observed. C=O symmetric stretching vibration in range of 1668-1680 cm^{-1} was also observed due to the availability of the NTDA. C–N stretching vibrations were observed in range of 1335 cm^{-1} (0 wt. %) - 1358 cm^{-1} (100 wt.%) [85, 57]. C-F bands were observed between 1300 and 1100 cm^{-1} [7].

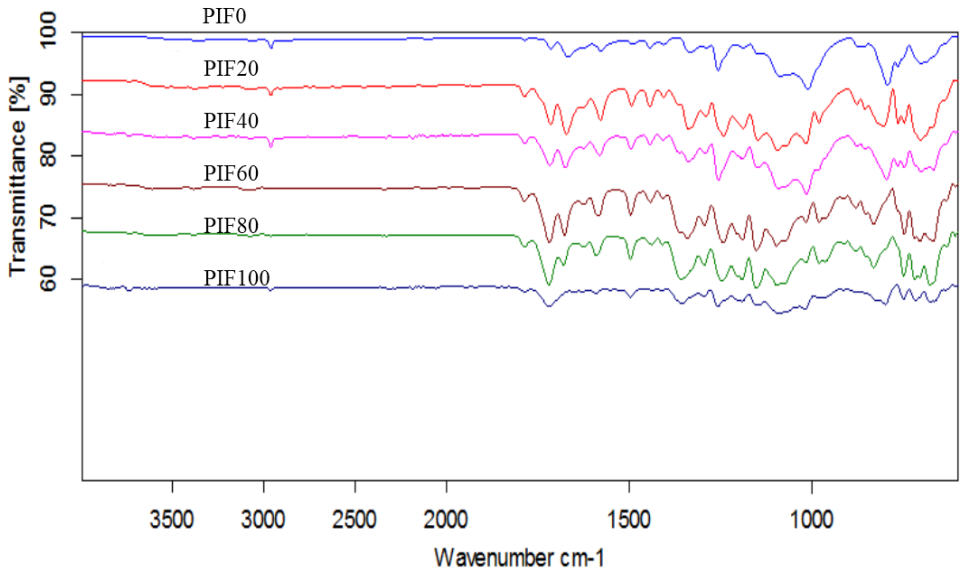


Figure 3.6 The FT-IR spectrums of PIFs

3.3.10. Shoxlet Extraction

Shoxlet was applied for obtaining the gel content of the polyimide coatings. After the thermal imidization of the coatings the parts were taken in shoxlet nest and acetone solvent was poured into the nest. That implementation was continued for 8 hours. The parts that not dissolved were taken in vacuum oven for 10 hours (10^{-1} mmHg, 40°C). After the volatilization completed the weight of the parts were measured. These residue parts indicated the % gel content of the polyimides according to first weight of the parts.

3.4. Thermal and Physical Test Results of Coatings and Free Films

3.4.1. Cross Cut Test

Tests were performed according to standard D-3359 on cross-cutted surface of which results were shown below in Table 3.3. It was observed that coatings showed different characteristic.

Crosscut tests were implemented to identify adhesion properties of the coatings. The values were ranged from 5B to 0B.While 5B presented the best adhesion property 0B presented the poorest adhesion value. As shown in Table 3.3, the coatings exhibited good adhesion on aluminum plates, varied between 5 and 3. As the fluorine percent increased or the NTDA percent decreased, cross cut adhesion increased due to low surface energy of

fluorine. In literature PIs having sufficiently high molecular weight exhibits tough and creasable coating and films while brittle films and coating generally show low molecular weight. 0 % and 20 % of PIs and PIFs exhibited less adhesion property as shown in Table 3.3.It is probably that it could be derived from low molecular weight [7].

Table 3.3 Cross Cut Test Results

PIs %	ASTM CLASS	PIFs %	ASTM CLASS
0	3B	0	3B
20	4B	20	4B
40	5B	40	5B
60	5B	60	5B
80	5B	80	5B
100	5B	100	5B

Also, due to the low friction coefficient of high fluorine content the samples having high fluorine ratio exhibited good resistance to scratch and good adhesion properties as illustrated in Figure 3.7 despite to low adhesion properties of fluorine structures in literature [86, 87]

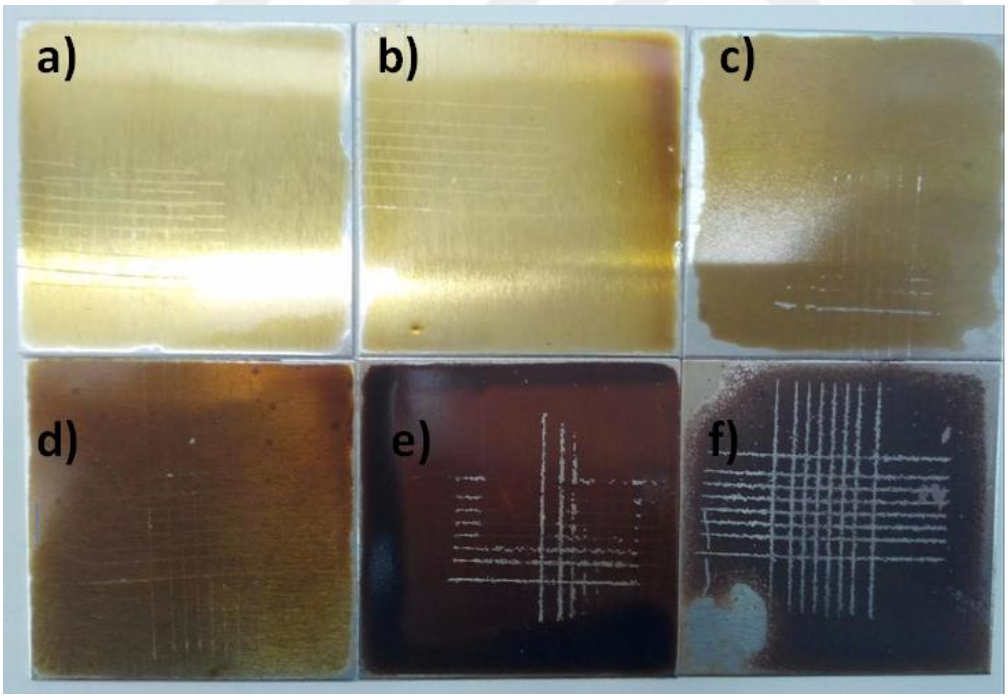


Figure 3.7 The coating samples on aluminum sheets of PIFs after the cross cut adhesion

3.4.2. Gloss 60° Test

Brightness measurement was applied with light reflection. The reflection has a sharp light beam. That beam reflects from uniform and smooth surfaces. Gloss is an important

property for many coating applications. Surface roughness affected the reflection of the light significantly. On the other hand refractive index of materials is also important for gloss values [69, 83]. Gloss test results were given in Table 3.4 and Figure 3.9. Also, the mechanism of gloss test were given in Figure 3.8.

Table 3.4 Gloss Test Results

PIFs %	Gloss 60° Value	PIs %	Gloss 60 ^{o} Value
0	14	0	13
20	99	20	98
40	134	40	122
60	155	60	124
80	172	80	125
100	184	100	126

Metals cannot be measured by the angle due to the high density but polymer coatings can be easily measured. Also, there are different angle methods available for various polymers. For example gloss 85 ° have been used for matte surfaces.

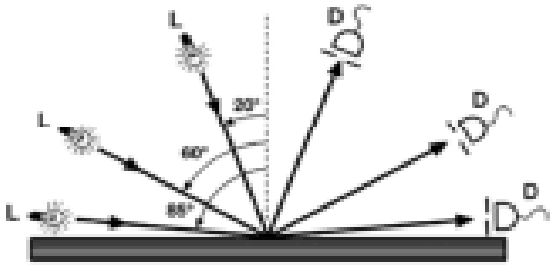


Figure 3.8 Conventional glossmeter L, lamp; and D, detector

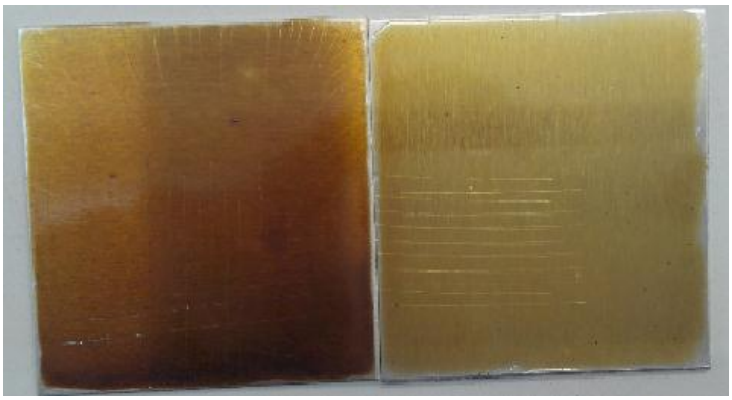


Figure 3.9 The colour difference between PI100 and PIF100 after cross-cut test

As can be seen from Table 3.4, the gloss of the coatings increased with the increase of 6FDA or the decrease of NTDA. Gloss values of PIF and PI coatings containing 6FDA were much higher than 0%, the coatings containing NDTA exhibited so matte surface. This may be explained by roughness. It can be said that PI0 and PIF0 are hard to use in any application areas for the applications required high brightness. PI0 and PIF0 samples were not dissolved. After the coating application the viscous and undissolved PAA liquid transformed into a coating like powder that contains many cracks and high roughness. For that reason the gloss values of PI0 and PIF0 exhibited low gloss values. On the other hand the gloss values of PIFs exhibited higher gloss values than the values of PIs. Hence PFOA increased the gloss values and the highest gloss value reached up to 184°. While the gloss value of PIF100 exhibited 184 the gloss value of PI100 exhibited 126.It can be deduced that PFOA provides more decorative coating.

3.4.3. Taber Abrasion Test

Abrasion resistance was measured by Taber abraser model CS10 abrasive device for ranging from 250 to 1000 cycles under 250 g weight and with 72 rpm. As shown in Table 3.5, while the ratio of 6FDA increases, coatings reveal higher abrasion resistance due to the friction coefficient of fluorine structures.

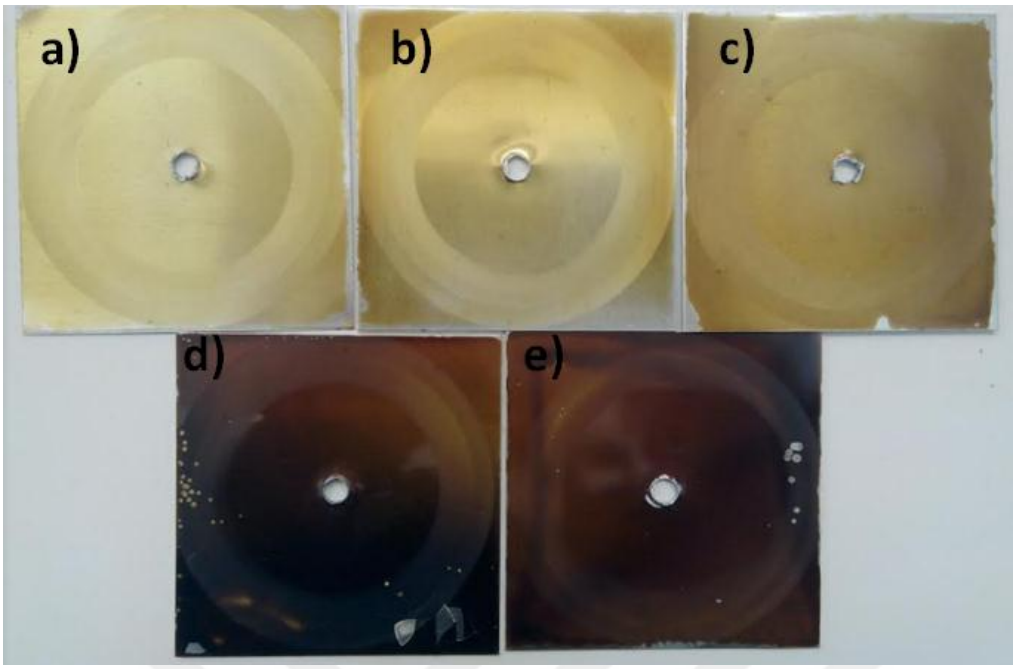


Figure 3.10 PIF coatings after taber abrasion test

PIFs contains 1 % PFOA besides the different ratios of 6FDA.Therefore we expect higher abrasion resistance for PIFs than PIs at same ratio of 6FDA is expected due to the long fluorocarbon chain. Figure 3.10 shows PIF coatings after Taber abrasion test. On the other hand it was observed that the increase of the ratio of 6FDA increased the abrasion resistance for both PIs and PIFs due to the fluorine structures. Hence 6FDA and long fluorocarbons chain at the end of the polyimide chains increased the abrasion resistance due to the low friction coefficient. It can also be observed that the increase of the ratio of NTDA generated more brittle coating and less adhesion property shown in Table 3.5. That brittleness may be derived from low molecular weight and rigid structure due to very poor solubility of naphthalene groups in polymer backbones [7, 85, 69].

Table 3.5 Taber mass loss of polyimide coatings in different distances

The Samples	250 cycles	500 cycles	750 cycles	1000 cycles
PIF0	Not-Avaliable			
PI0	Not-Avaliable			
PIF20	7.3 mg	12.6 mg	16.8 mg	20.9 mg
PI20	8.9 mg	15.1 mg	23.6 mg	30 mg
PIF40	6.6 mg	10.2 mg	15.4 mg	19.3 mg
PI40	7.2 mg	12.8 mg	17.4 mg	22.7 mg
PIF60	3.7 mg	6.5 mg	9.3 mg	11.8 mg
PI60	5.6 mg	10.4 mg	15.4 mg	20 mg
PIF80	2 mg	3.7 mg	6.2 mg	8.6 mg
PI80	2.1 mg	6.4 mg	10 mg	13.5 mg
PIF100	0.4 mg	1.2 mg	2.2 mg	3.1 mg
PI100	0.5 mg	1.8 mg	3.7 mg	5.4 mg

As shown in Table 3.5 mass losses of the coatings were measured by Taber abraser model CS10 abrasive device for 250, 500, 750 and 1000 cycles. Excellent values were obtained for all coatings except PI0 and PIF0. Successful coatings could not be obtained for PI0 and PIF0 due to the rough and cracking on the surfaces. It was probably that polynaphthalimides have very poor solubility in common solvents [83]. Figure 3.11 exhibits the PI0 coating after and before the taber abrassion test for 250 cycles. Also, Figure 3.10 shows the PIFs coatings after taber abrasion test.

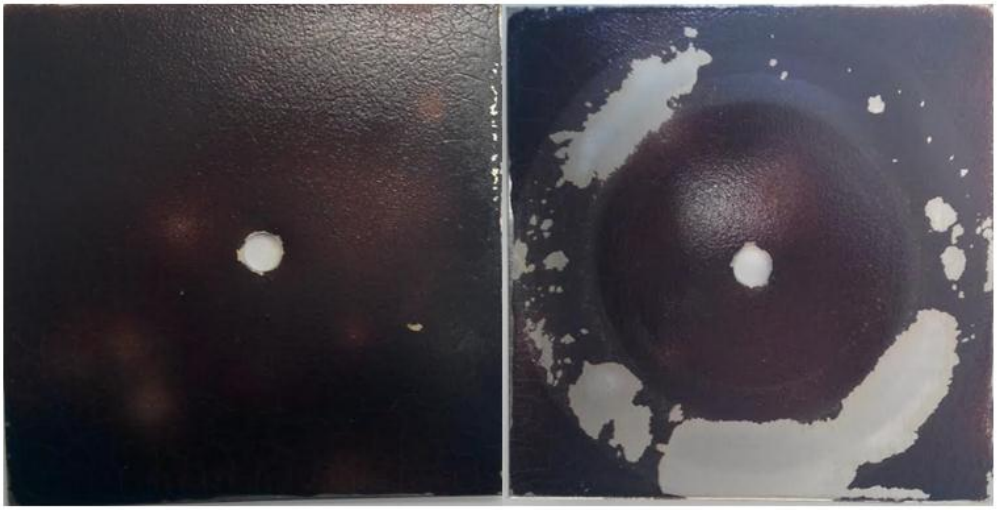


Figure 3.11 The surface of PI0 coating before and after the taber abrasion test for 250 cycles.

1 % PFOA affected the abrasion resistance of the coatings due to the long fluorocarbons chains. When PIF coatings compared to PI coatings mass losses of PIF coatings seemed lower than PI coatings for all ratio of the samples as shown in Figure 3.12.

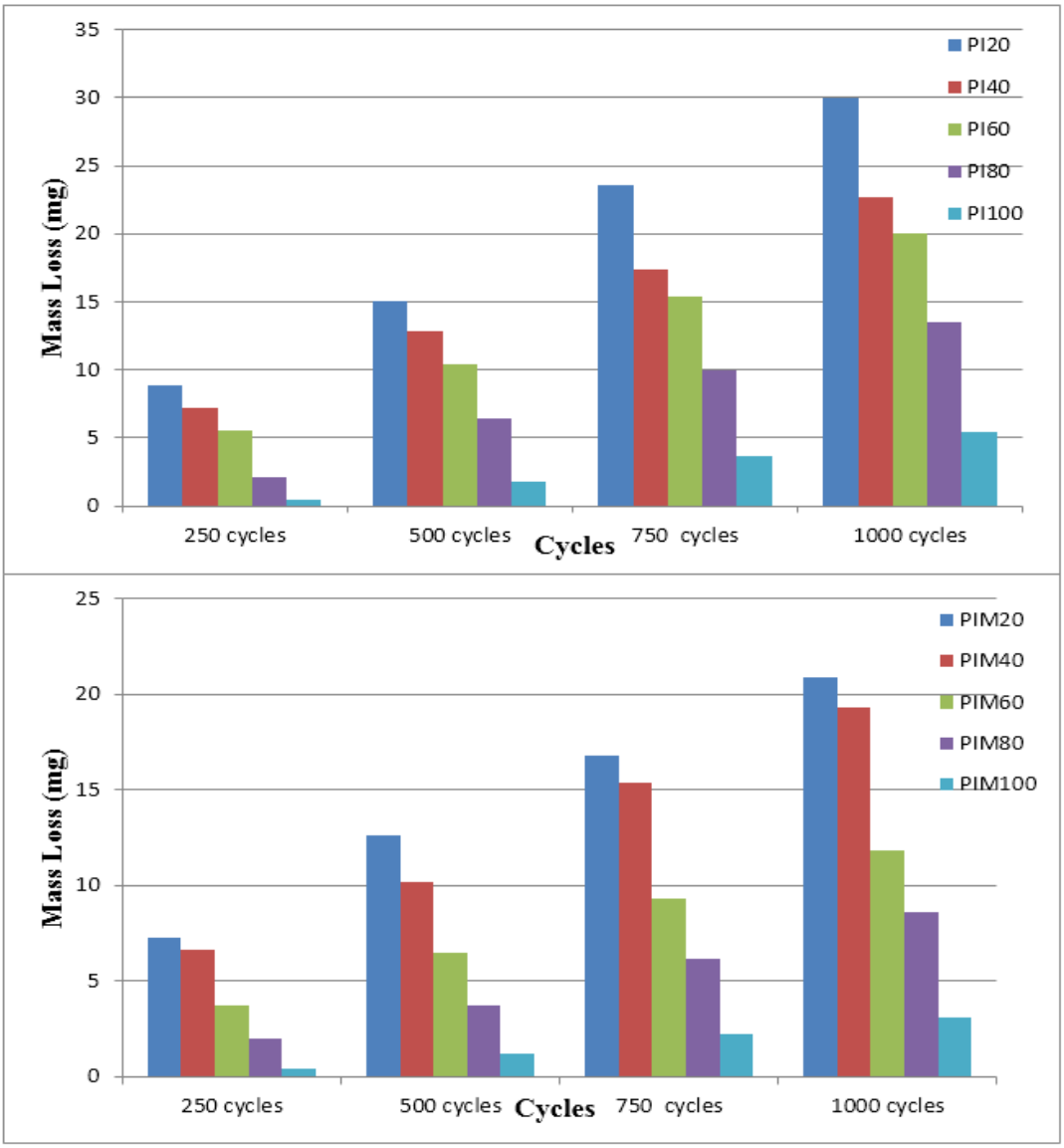


Figure 3.12 Mass loss of PI and PIF coatings by using Taber abraser model CS10 abrasive device

3.4.4. Contact Angle Test

Contact angle value is very important factor for preventing the degradation of materials. For that reason hydrophobicity has been demanded factor in most applications. The degree of hydrophobicity increased with increase in fluorine ratio. Figure 3.13 and 3.14 show sketches of the contact angle measured by a goniometer.

The higher contact angle values exhibit the more hydrophobic character on the surfaces. The surface energy was also measured directly by the contact angle goniometer. While surface energy decreased, hydrophobic character increased due to the fluorine content. The high fluorination degree provides a high hydrophobicity for the PIs [84]. Hydrophobic

properties of PIF and PI coatings were depicted in Table 3.6.

Table 3.6 Hydrophobic Properties of PIF and PI coatings

PIFs %	Contact Angle (^{0})	Surface Energy (mj/mm^2)	PIs %	Contact Angle (^{o})	Surface Energy (mj/mm^2)
0	63	42	0	55	46
20	83	35	20	72	39
40	85	34	40	75	38
60	91	32	60	79	36
80	83	35	80	76	37
100	83	35	100	75	37

When PI coatings compared with PIF coatings the difference of contact angles can be observed. While PIF0 reveals 14 % higher contact angle than PI0, PIF20,40 and 60 exhibited more hydrophobicity as approximately 15 % than PI20, 40 and 60.Morever PIF 80 and 100 exhibited also more hydrophobic character than PI80 and 100 but the increase of the hydrophobicity ratio decreased to 9 %.

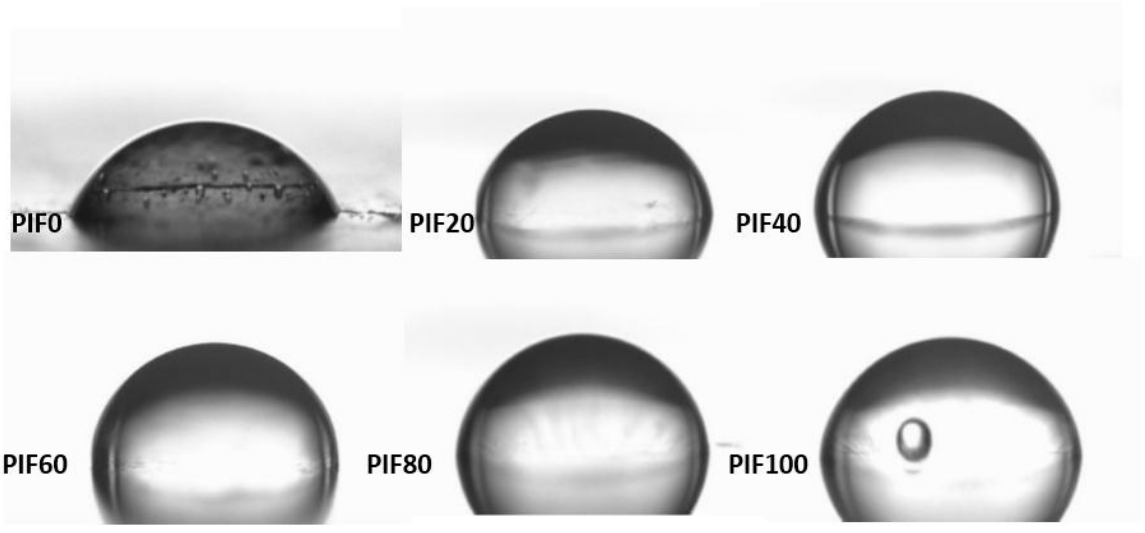


Figure 3.13 Contact Angle Measurement of PIF coatings

The hydrophobicity of PIF and PI coatings showed an increase up to 60 % 6FDA and then a slightly decrease was observed. It was expected that the contact angle would be increase up to 100 % in 6FDA but the values of the contact angles decreased. Moreover PIF60 and PI60 exhibited the highest contact angle values. It was probably that crackings were

occurred on the coating surfaces due to the increase of the fluorine content [88].

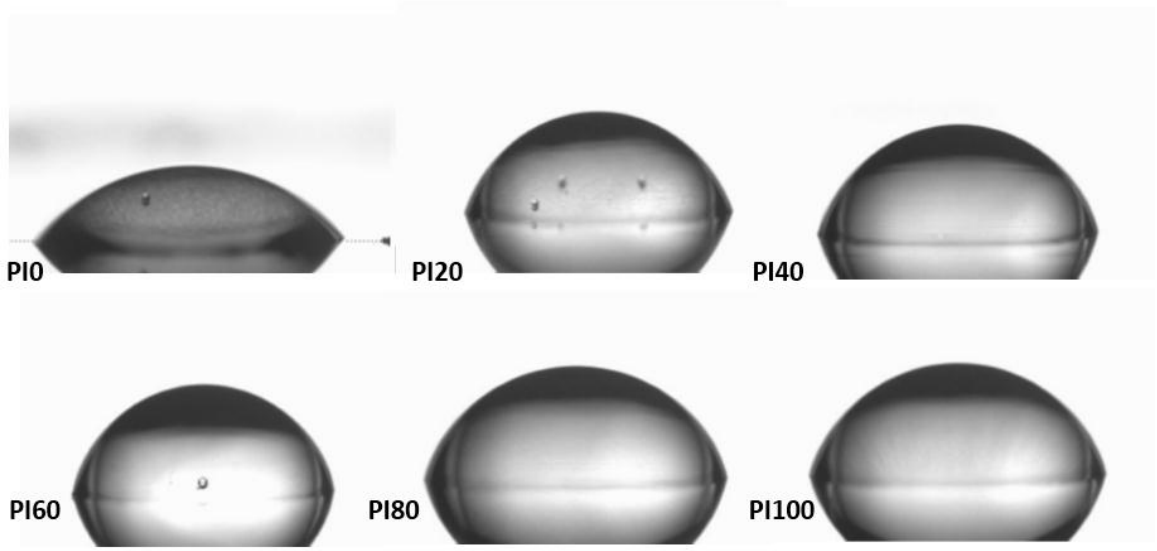


Figure 3.14 Contact Angle Measurement of PI coatings

3.4.5. Pencil Hardness Test

Results of pencil hardness test of PIs and PIFs coatings are shown in Table 3.7.

Table 3.7 Pencil Hardness Test Results

PIFs %	Result	PIs %	Result
0	1H	0	1H
20	5H	20	5H
40	6H	40	6H
60	6H	60	6H
80	6H	80	6H
100	6H	100	6H

It was observed that the pencil scratch hardness of the all coatings was between 5H and 6H except PI0 and PIF0.While fluorine ratio was increased resistance to scratch increased because of the low friction coefficient of fluor atoms [69, 86].

3.4.6. Shoxlet Extraction

The gel content of the synthesised polyimides were given in Table 3.8 and measured as higher than 99.6 %. Hence the level of non-reacted monomers was observed as negligible in polyimide structures.

Table 3.8 Gel content of Hybrid Structure

Ratio % PIFs	0	20	40	60	80	100
Insoluble Ratio % PIFs	99.9	99.8	99.8	99.7	99.7	99.6
Insoluble Ratio%	99.8	99.8	99.7	99.7	99.6	99.6

3.4.7. SEM Images

Surface morphologies of PIF80 and PIF100 were characterized by SEM. These are shown in Figure 3.15.It is known that fluorine content increases the hydrophobicity. In this study the contact angles of the coatings having higher ratio than 60 % exhibited a decrease as shown in Table 3.6.It is probably that this decrease in hydrophobicity is derived from microcrackings on the surfaces. M., Uyanik et. al. [88] reported that the polyimide coatings containing high fluorine content did not exhibit an increase in hydrophobicity due to the possibility of crackings on the surfaces. Microcrackings were observed on the surfaces PIF80 and PIF100 as shown in Figure 3.15.PIF100 presents more micro cracking than PIF80.

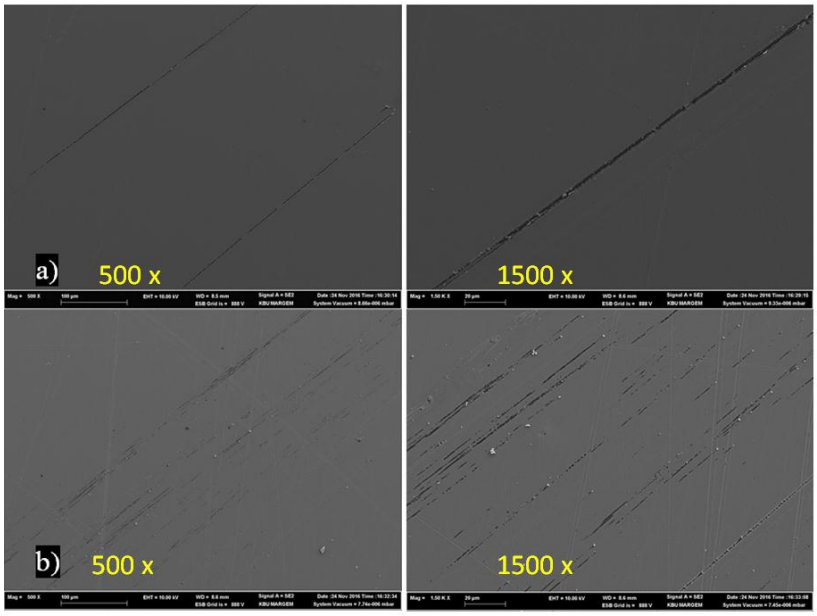


Figure 3.15 Surface morphologies of a) PIF80 and b) PIF100

3.4.8. DSC Results

DSC thermal characterization was applied from 30°C to 500°C with 10°C/minute heating rate under N_2 atmosphere.

DSC curves for PIFs and PIs are shown below in Figure 3.16 and Figure 3.17. Also, datas of these curves are given in Table 3.9.

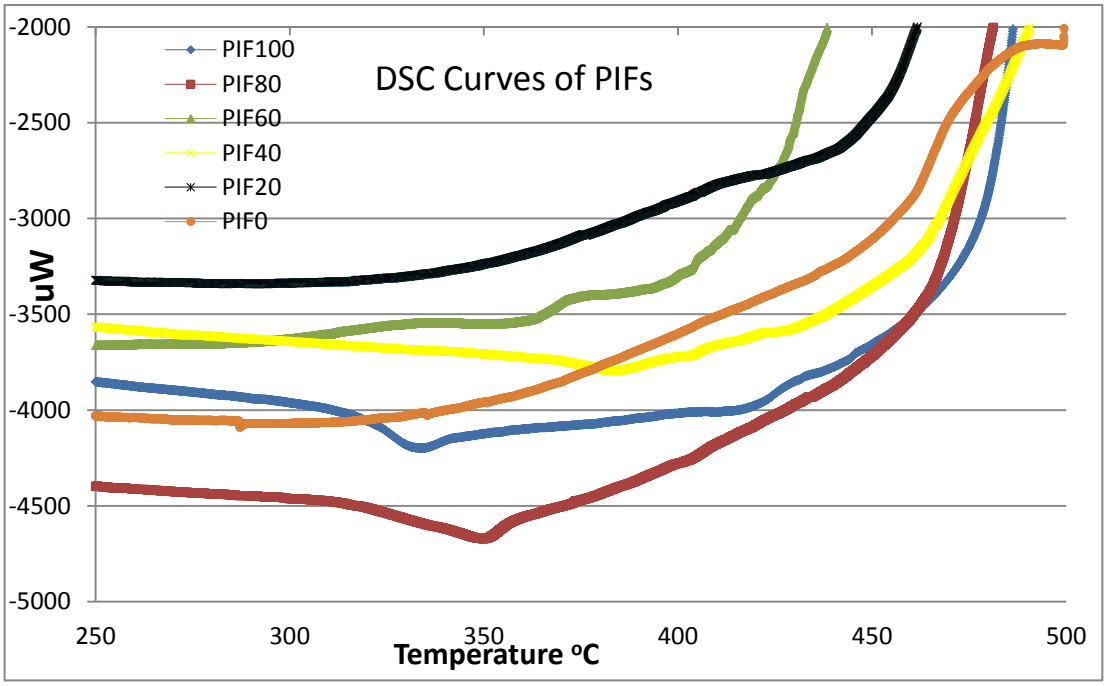


Figure 3.16 DSC analysis results of PIFs

It can be easily seen from these results that the ratio of fluorine structures in polymer backbone like 6FDA and PFOA decreased the Tg value of the polyimides coatings and all Tg values exhibited higher than 330°C. CF_3 groups and PFOA long fluorocarbon chain decrease the packing of the chains and interactions between polymer chains due to the increasing solubility. Also, fluorine structures increase the free volume of the polymers [83,89]. E., Çakmakçı et al. [89] emphasized the increasing of T_g due to the rigid structure of PMDA. Also, Chin-Ping Yang et al. [83] reported that the polyimides having naphtalimide segments belong to higher T_g value than polyimides synthesised from PMDA due to the interchain electronic structure and more rigid character.

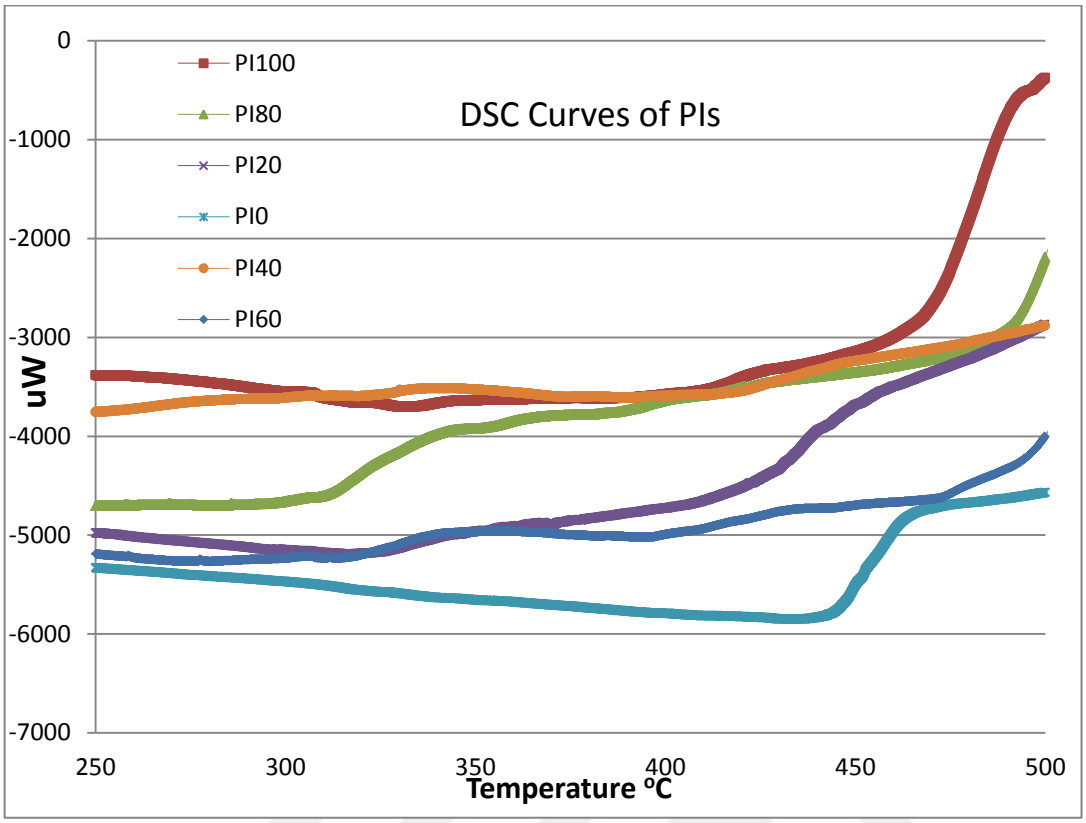


Figure 3.17 DSC analysis results of PIs

On the other hand it can be clearly observed that the increase of naphthalene groups rises the T_g. Hence the samples having high NTDA ratio exhibit high chain to chain charge transfer interactions and high chain stiffness [83,6]. Any distinct glass transition temperature could not exhibit below 450 ^oC for 0 % of PIFs and PIs as reported in Shafiq ur Rehman et al.'s study [90].

Table 3.9 DSC Test Results

PIFs %	Glass Transition Temperature (T_g)	PIs %	Glass Transition Temperature (T_g)
0	-	**0**	-
20	423	**20**	431
40	381	**40**	416
60	357	**60**	395
80	348	**80**	381
100	330	**100**	330

Also, that PIFs exhibited more distinct T_g than PIs as shown as 3.17 and 3.18 because of the PFOA that have long fluorocarbons chain. Hence PIFs has more amorphous structure than PIs.

3.4.9. TGA Results

TGA analysis was applied to the samples from 30°C to 900°C with heating rate of 10°C/min under nitrogen atmosphere.

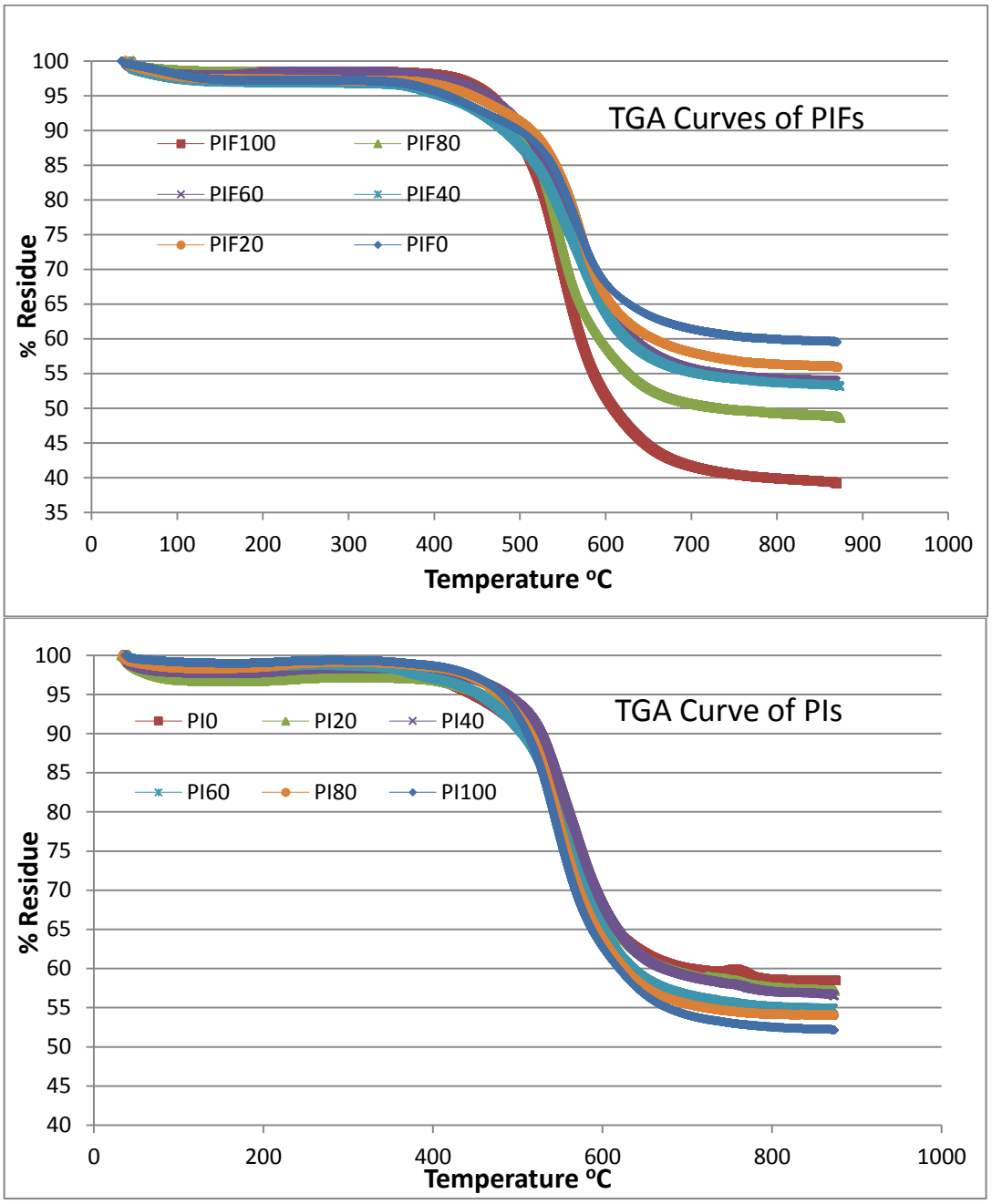


Figure 3.18 TGA curves of PIF and PI coatings

Various naphthalene groups and CF_3 substituted aromatic groups has been used for improving thermal properties of polyimides [6,83]. It is known that polyimides contain various ratios of NTDA and 6FDA which has been shown in Figure 3.18.While the ratio of NTDA increase, char yields increase as shown in Figure 3.18. The char yield of PIF0 exhibits 60 % value while the char yield of PIF100 exhibits 40 % value. First decomposition temperature T_{onset} value exhibits increasing tendency while the ratio of 6FDA increase.

Table 3.10 TGA results of Polyimide Coatings

Code of Samples (%)	**First decomposition Temperature (T_{onset},^oC)**	**10 % Weight-decomposition Temperature (T_{d10},^oC)**	**Char Yield at 900^oC (%)**
PIF0	375	508	60
PIF20	408	517	56
PIF40	410	490	57
PIF60	435	518	55
PIF80	450	518	49
PIF100	460	500	40
PI0	375	513	59
PI20	409	525	57
PI40	432	535	54
PI60	435	518	55
PI80	451	524	54
PI100	460	518	52

T_{onset} values of PIF and PI coatings are varied from 375°C – 460°C as shown in Table 3.10. It is very well known that naphthalene groups and fluorine structures in polyimide backbones improve the thermal stability. According to TGA results, NTDA and 6FDA contents reveals great thermal stability. While NTDA is more efficient to develop the char yields, 6FDA is more efficient to develop the first decomposition temperature. When the TGA of PIFs results compared with PIs results, the trends of TGA curves is very similar.

Hence the increase of 6FDA content increase the first decomposition temperature while the increase of NTDA content increase the char yield. Furthermore, the first decomposition temperatures of PIs and PIFs are very close each other. But the char yields of PIFs decrease to 40 % while the char yields of PIs decrease to 52 %. These kind of reduction and increase in thermal stability and char yield could result from diffusion transition.

4. CONCLUSIONS

In this thesis it was aimed to accomplish a hydrophobic and heat resistant coating for aluminum and reactive metal oxide substrates. Coating compositions were prepared as 0%, 20%, 40%, 60%, 80%, 100% on weight % basis according to the rate of 6FDA for PIFs and PIs and then coated aluminum sheets by wire wound applicator. Thermal properties of coatings were determined by TGA and DSC.

All coating samples exhibited higher Tg than 330 ^{o}C and PIFs have more distinct Tg curves due to the existence of PFOA. Also, the rate of the NTDA increased Tg value and the samples having high rate of NTDA did not show a distinct Tg curves . TGA results of the coatings exhibited high thermal properties. While the increase of NTDA ratio increased the char yield values, the increase of 6FDA ratio increased the T_{onset} values. PFOA content almost never changed the first decomposition temperatures but the char yields of PIFs showed more decrease than PIs. Static contact angles of water on the airside surface of the coated samples were measured at room temperature using a contact angle goniometer and hydrophobicity of the coatings was determined. The highest contact angle value was obtained for PIF60 as 91°.PIFs exhibited more hydrophobic values than PIs due to the existence of PFOA. Also, the rate of 6FDA increased the contact angle. However, contact angle values showed a decrease for 80 % and 100%. This was probably derived from micro crackings on the surfaces. Figure 3.15 shows the microcrackings on the coating surfaces of PIF80 and PIF100 in SEM micrograph. PIF100 have more crackings than PIF80 as shown SEM micrograph in Figure 3.15. Abrasion resistance were measured by TABER abrasion method for 250, 500, 750 and 1000 cycles. PIFs exhibited more abrasion resistance than PIs due to the PFOA content. Also, the ratio of 6FDA increased the abrasion resistance. The other physical properties such as pencil hardness, cross cut adhesion property, gloss 60° were also measured for PIF and PI coatings. Cross cut values were varied from 3B to 5B.While the rate of 6FDA increased adhesion property exhibited excellent performance by contrast with the adhesion property of fluorine structures in literature. On the other hand 1 % PFOA did not affect the cross cut adhesion property. Brightness was measured by gloss 60°. This property seems very suitable for decorative coatings. PIF coatings showed higher gloss values than PI coatings and the rate of 6FDA increased the gloss value. The highest gloss 60° value was obtained for PIF100 as 184.The pencil hardness of the coatings exhibited very good performance except 0 %. This test measured the resistance to scratch and the flourine ratio increased this resistance due to its low friction coefficient.

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