ISTANBUL TECHNICAL UNIVERSITY ★ INSTITUTE OF SCIENCE AND TECHNOLOGY

PREPARATION OF FLUORINE CONTAINING POLYURATHANE COATING MATERIALS

M.Sc. Thesis by
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Department :	**Polymer Science and Technology**
Programme:	**Polymer Science and Technology**

JANUARY 2009

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JANUARY 2009

İSTANBUL TEKNİK ÜNİVERSİTESİ ★ FEN BİLİMLERİ ENSTİTÜSÜ

FLOR İÇEREN POLİÜRETAN KAPLAMA MALZEMELERİNİN HAZIRLANMASI

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OCAK 2009

FOREWORD

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

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December, 2008 Burcu İŞCANI

Polymer Science and Technology

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ABBREVIATIONS

PUs : Polyurethanes
DBTDL : Dibutyltin Dilaurate
DABCO : 1,4-diazabicyclo[2.2.2]octane
TDI : Toluene Diisocyanate
MDI : Methylene-bis-diphenyl Diisocyanate
CDI : Cyclohexane Diisocyanate
HDI : Hexamethylene Diisocyanate
IPDI : Isophorone Diisocyanate
NuH : Nucleophile
FPU : Fluorinated Polyurethane
Non-FPU : Non-Fluorinated Polyurethane
PFPE : Perfluoropolyether
PFAE : Perfluoro-alkylether
PFPAE : Perfluoropolyalkylether
F-OH : Fluorinated Mono Alcohol
TGA : Thermal Gravimetric Analysis
SEM : Scanning Electron Microscopy
SCS : Spin Coater System

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PREPARATION OF FLUORINE CONTAINING POLYURETHANE COATING MATERIALS

SUMMARY

As surface coating industry is growing rapidly in these years,studies related with synthesis of new materials are also increasing rapidly. Fluorinated polymers possess a whole range of very interesting bulk and surface properties, such as excellent environmental stability, water and oil repellency, low coefficient of friction, biocompatibility, excellent thermal stability and chemical resistance and low interfacial free energy. Polyisocyanate is one material that could benefit from characteristic properties of fluorinated polymers, as mentioned above. Fluorinated polyurethane is new class of new material. However, the high sensitivity of -NCO group towards moisture and its susceptibility to undergo undesirable side reactions makes the use of polyisocyanate with -NCO groups problematic. This problem can be overcome by blocking isocyanate groups with phenols through the formation of carbamate having a labile bond which can dissociate at an elevated temperature to regenerate -NCO functionality. Besides,using free isocyanate groups lead to various environmental and health problems. Because isocyanates are highly reactive, exposure can result in primary irritation, sensitization and hypersensitivity reactions (allergic reactions). The breathing system, the eyes and the skin are the main areas affected by exposure. So, blocked polyisocyanates are preferred for many technical, economic and environmental reasons in the coating technology.

In this thesis, the aim is to develop some formulations with blocked polyisocyanate and fluorine containing compounds to improve chemical, mechanical and surface properties.The formulated solutions are coated on glass surfaces by using Spin Coater Instrument and cured thermally to prepare further analysis.

FLOR İÇEREN POLİÜRETAN KAPLAMA MALZEMELERİNİN HAZIRLANMASI

ÖZET

Günümüzde yüzey kaplama endüstrisi hızla gelişirken yeni malzemelerin hazırlanması ile ilgili çaılşmalar da hızla artmaktadır. Florlanmış polimerler, mükemmel çevresel dayanım, su ve yağ itme, düşük sürtünme dayanımı, biyouyumluluk, mükemmel termal ve kimyasal dayanım ve düşük yüzey serbest enerjisi gibi birçok çözelti ve yüzey özelliğine sahiptirler. Poliizosiyanatlar, florlanmış polimerlerin yukarda bahsedilen karakteristik özelliklerinden yararlanabilen bir materyaldir. Florlanmış poliizosiyanatlar yeni bir sınıfı oluştururlar ancak, – NCO gruplarının neme karşı yüksek duyarlılığı ve istenmeyen yan reaksiyonlara yatkınlığı poliizosiyanat kullanımını problemli bir hale getirmektedir. Bu problem izosiyanat gruplarının fenol ile bloklanması ile aşılabilir. Fenol ile bloklanan izosiyanat grubu, düzensiz karbamat bağını oluşturur ve bu bağ yüksek sıcaklıklarda bozunarak izosiyanat grubunu yeniden meydana getirir. Bunun yanı sıra, serbest izosiyanat grubu kullanımı çeşitli çevre ve sağlık sorunlarına da yol açar. İzosiyanatların yüksek aktivitesi, birincil olarak tahriş, duyarlılık ve aşırı duyarlılık reaksiyonlarına sebep olur (alerjik reaksiyonlar).Solunum sistemi, gözler ve cilt etkilenen ana alanlardır. Bu teknik, ekonomik ve çevresel nedenlerle kaplama teknolojisinde bloklanmış poliizosiyanat kullanımı tercih edilmektedir.

Bu çalışmada, bloklanmış poliizosiyanat ve flor içeren bileşikler kullanılarak, kimyasal, mekanik ve yüzey özellikleri gelişmiş kaplama formülasyonları hazırlanmıştır. Formülasyon çözeltileri cam yüzeylere Spin Coater Cihazı ile kaplanmış ve ısı yolu ile kürlenerek ileri analizlere hazırlanmıştır.

INTRODUCTION

Polyurethanes have revealed an unusual versality; their chemistry, as well as the chemistry of related intermediates (isocyanates among them), has been enormously developed and polyurethanes have one of the widest ranges of polymer applications throughout the world: fibres, elastomers, foams, skins, adhesives, coating [1].

The use of “blocked” polyisocyanates has many advantages in the coating industry. It permits the formulation of stable one package coatings which on heating deblock and lead to the formation of the highly reactive polyisocyanate. Applications for these systems are in diversified areas such as powder coatings, electrocoating, wire coatings and in textile finishing. The nature of the blocking agent has a significant effect on the deblocking temperature of the isocyanate[2]. Typical blocking agents used include malonates, triazoles, ε-caprolactam, sulfite, phenols, ketoxime, pyrazoles and alcohols.

For alcohol blocked isocyanates the decomposition to the isocyanate is a rather high temperature reaction step. In the presence of a catalyst, alcohols are effective blocking groups for isocyanates. Transesterification reaction according to is the most likely reaction mechanism. The overall reaction rate can depend on the volatility of the alcohol[3].

For both the elimination-addition and the displacement mechanism, dibutyltin dilaurate (DBTDL) has been found to be an effective catalyst. Depending on the alcohol used non-tin metal compounds and chelates were also found to be effective catalysts[4].

Polyurethanes are time-honored solutions for protecting surfaces against chemicals, corrosion, wind, and weather. By combining polyurethane with fluorine, it is possible to improve the oleophobic and hydrophobic properties of these coatings significantly. The fluorine is incorporated into the polymer through side chains. Because it is chemically bound, it can’t be washed out, and the desired properties last a long time. Another advantage is that, despite the force of repulsion of the fluorine side chains, there are no adhesion problems on the substrates, because the perfluoroalkyl side chains remain embedded in the polymer matrix. At the interface with the air, however, the fluorine side chains protrude from the polymer surface, thereby developing their dirt and water-repellent effect. This behavior is substantiated by a statistical distribution of the fluorine in the polymer, and also on the surface of the polyurethane coating[5].

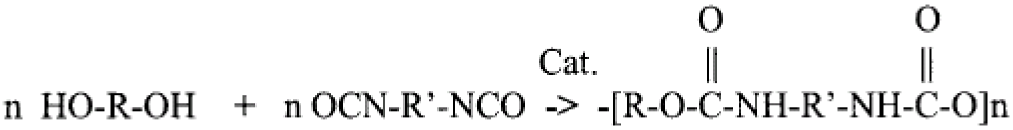
Incorporation of fluorinated moieties in polymers is carried out using different methods: (1) participation of fluorinated unit in main chain; (2) modification of polymer terminals by fluorinated derivatives; and (3) fluorination of polymer side chains. When side chain fluorinated polymer block is combined to non-fluorinated block, block copolymer is formed[6].

This thesis will concern the preparation of fluorine containing polyurethane coating materials which will contain phenol-blocked polyisocyanate and various fluorinated agents and their polymerization by heat. The aim is enhancing surface and thermal properties of polyurethane thin film by modifying with fluorinated agents. Therefore, these properties of modified and non-modified surfaces will be investigated.

2. THEORETICAL PART

2.1 Urethane And Polyurethane Chemistry

Polyurethanes (PUs) are a family of step-growth polymers made by the reaction between a diisocyanate and a diol which produces the urethane linkage NH—COO—, but no byproducts, as seen in Figure 2.1. Properties of particular representatives of this group of polymers are greatly dependent on their chemical structure. Variation of the ratio of reagents introduced into the reactions allow obtaining polymers with different concentration of elastic and rigid blocks, and different density of intermolecular hydrogen bonds[7].Thus, products with different hardness and elasticity are formed, which allows production of an assortment of materials with different mechanical properties. As a general rule , the isocyanates are hard segments that impart rigidity to the polymer. The polyol is the so-called soft segment.



$$n\ \mathrm{HO\text{-}R\text{-}OH} + n\,\mathrm{OCN\text{-}R'\text{-}NCO} \xrightarrow{\text{Cat.}} \mathrm{\text{-}[R\text{-}O\text{-}}\overset{\overset{\mathrm{O}}{\|}}{\mathrm{C}}\mathrm{\text{-}NH\text{-}R'\text{-}NH\text{-}}\overset{\overset{\mathrm{O}}{\|}}{\mathrm{C}}\mathrm{\text{-}O]}n$$

Figure 2.1 : Basic polyurethane reaction.

Besides diisocyanate and diol PUs use catalysts to accelerate the reaction of the isocyanate with the polyol. Dibutyltin dilaurate (DBTDL) is a common catalyst for urethane coupling reactions. Tin atoms coordinate to the terminal oxygen of the isocyanate group and faciliate attack by the oxygen atom of a hydroxyl group on the isocyanate carbon atom. Other catalyst include triethylenediamine (DABCO) or other lewis bases[8].

For the preparation of foams it is also necessary to use a blowing agents to create the cell structure and a surfactant to stabilize the foam during the foaming stage. In addition to these basic components a polyurethane can also contain flame retardants, pigments or colorants, antioxidants[9].

2.1.1 Isocyanates

Isocyanates, the esters of isocyanate acid, were first synthesized by Wurtz in 1848. Prominent nineteenth century scientists, such as Hofmann and Curtius, studied the chemisty of isocyanates, but it took almost a century until it was recognized that diisocyanates are ideally suited to undergo addition polymerization reaction with polyester or polyether diols to form polyurethanes[10].

Isocyanates are divided into mono- and di-isocyanates. The monoissocyanates are subdivided into alkyl and aryl isocyanates; unsaturated isocyanates; halogenated alkyl and aryl isocyanates; carbonyl, thiocarbonyl and imidoyl ispcyanates; sulphur isocyanates; phosphorus isocyanates; and inorganic isocyanates. The isocyanates are also divided into aliphatic diisocyanates and aromatic diisocyanates[10].

Common isocyanates used as building blocks for polyurethanes include aromatic and aliphatic diisocyanates. Among the diisocyanates that are commonly used in polyurethane synthesis the following sholdu be quoted:

- Toluene Diisocyanate (TDI), usually a mixture of toluene- 2,4- and toluene - 2,6 diisocyanate
- Methylene-bis-diphenyl diisocyanate (MDI)
- Cyclohexane diisocyanate (CDI)
- Hexamethylene diisocyanate (HDI)
- Isophorone Diisocyanate (IPDI)

The molecules are toluene diisocyanate (TDI) and its isomers and methylene-bis-diphenyl diisocyanate (MDI) in monomeric and polymeric forms. As a general rule, TDI makes flexible polyurethanes and MDI produces stiffer polymers [11].

Aliphatic diisocyanates are used in the manufacture of color-stable polyurethanes for coatings and elastomer applications. The major aliphatic diisocyanates are hexamethylene diisocyanate (HDI),isophorone diisocyanate (IPDI),cyclohexane diisocyanate (CDI). Using aliphatic polyisocyanates provides the following benefits to polyurethane coatings[12]:

- No yellowing
- Chemical Resistance
- Exceptional Gloss Retention

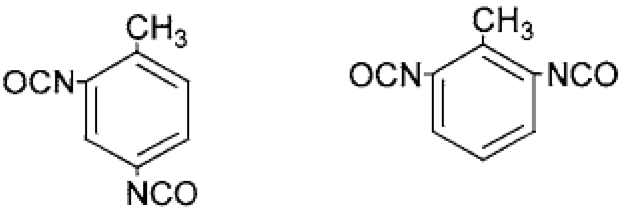
Polyurethane coatings made from aliphatic polyisocyanates are well known for their non- yellowing properties upon ageing thanks to:

- The lack of phenyl group

It makes polyurethane coatings prepared from aliphatic polyisocyanates less prone to oxidation rather than those prepared with an aromatic hardener.

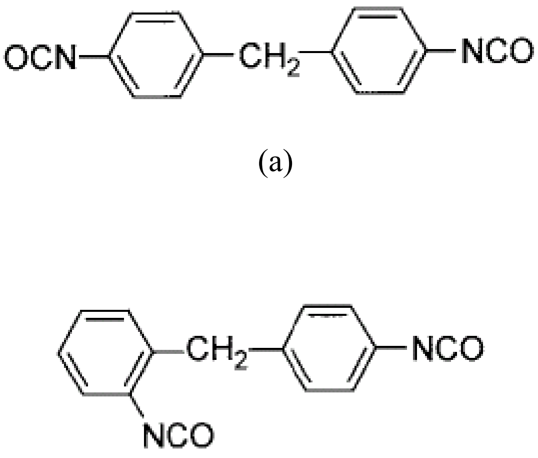
- The resistance of the urethane bond when exposed to UV light

In the majority of reactions, mainly with active hydrogen compounds, aromatic diisocyanates are much more reactive than their aliphatic equivalents[12].



2,4 isomer 2,6 isomer

Figure 2.2 : TDI isomers.



(a)

(b)

Figure 2.3 : MDI isomers. (a) Diphenyl methane 4-4’diisocyanate, (b) Diphenyl methane 2-4’diisocyanate.

Isocyanates will react with all compounds containing hydrogen atoms attached to a nitrogen atom. There are four basic reactions chemists employ to make polyurethanes. The reaction of isocyanates with hydroxyl groups to produce urethane is the primary reaction. The reaction of isocyanates with amines yields urea; and the reactions of isocyanates with urea and urethane produce biurets and allophanates, respectively[10].

2.1.1.1 Reaction of isocyanates with alcohols

Isocyanate groups react with polyfunctional active hydrogen compounds to give high molecular weight polyurethane products. The reaction is shown in Figure 2.4. One of the most important reactions of isocyanate compounds is with di- or polyfunctional hydroxyl compounds, e.g. hydroxyl terminated polyesters or polyethers. The functionality of the hydroxyl containing compound as well as of the isocyanates can be increased to three or more to form branched or cross-linked polymers. This is also affected by the steric hindrance of either the isocyanate or the active hydrogen compounds. The reaction proceeds at ambient temperatures without the use of catalysts. Reactivity is higher for primary alcohols, decreasing for secondary, tertiary, and aromatic alcohols[13].

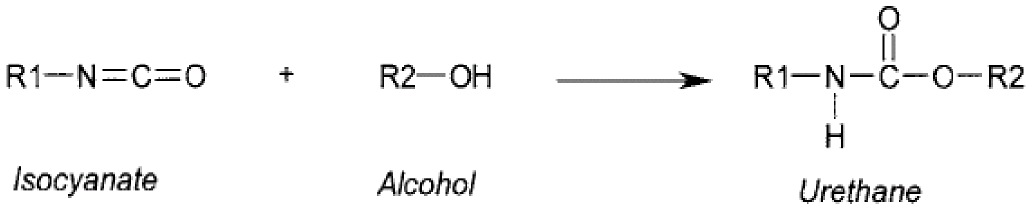


Figure 2.4 : Reaction of isocyanates with alcohols; R1 and R2 stand for an aromatic or aryl group.

2.1.1.2 Reaction of isocyanates with amines

In addition, isocyanates react with amines usually at 0-25°C yielding urea. Primary aliphatic amines react most quickly followed by secondary aliphatic amines and aromatic amines (Figs. 2.5 and 2.6.).

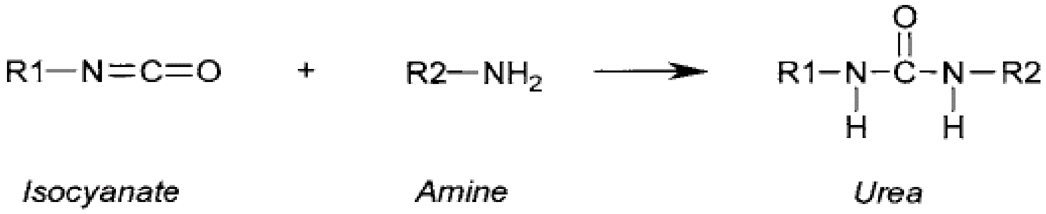


Figure 2.5 : Reaction of isocyanates with primary amines.

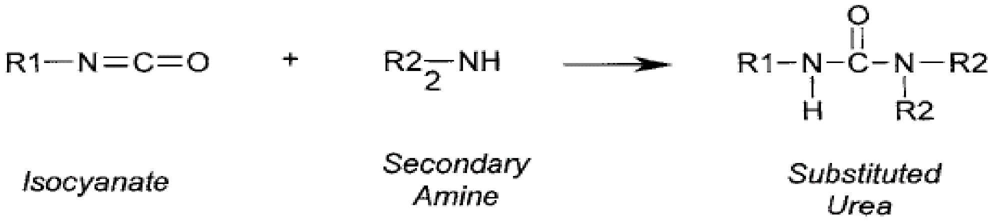


Figure 2.6 : Reaction of isocyanates with secondary amines.

2.1.1.3 Reaction of isocyanates with water

In general, isocyanates have a strong affinity to water, which makes them difficult to store. This reaction is not desirable in applications such as structural adhesives and sealants [14]. Isocyanate reacts with water giving carbamic acid, an unstable compound which spontaneously decomposes into a primary amine and carbon dioxide, together with a subsequent urea formation (Fig. 2.7.).

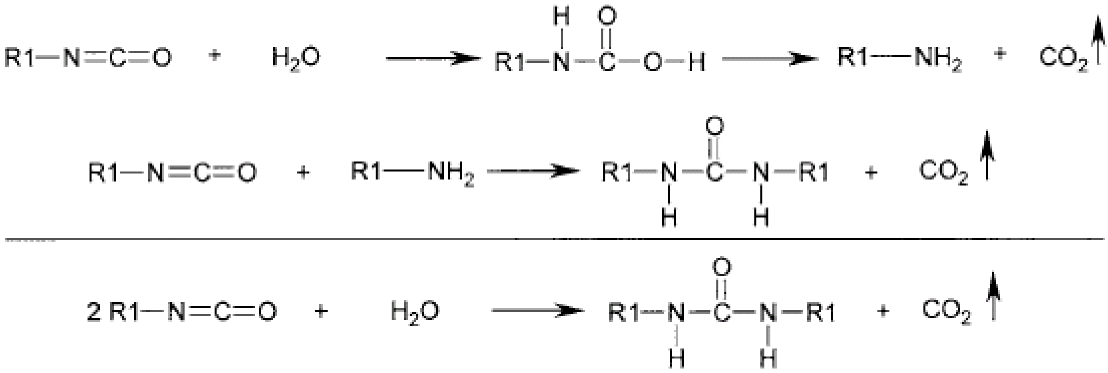


Figure 2.7 : Reaction of isocyanates with water and polyurea formation.

Initially, the water slowly reacts with the isocyanate. However, the reaction can be catalyzed with an appropriate catalyst, such as DBTDL or a morpholine tertiary amine catalyst. The isocyanate will react with water to form a carbamic acid, which is unstable and splits off carbon dioxide, to produce a terminal amine end group. This amine then reacts with more isocyanate-terminated prepolymer, as shown above, to form a polyurea[15].

2.1.1.4 Allophanate and biuret formation

Isocyanates can react, in excess conditions, with urea and urethane to produce allophanate and biuret compounds. The first reaction is quicker with a kinetic constant (K) 30 times higher for the reaction of phenyl isocyanate with urea than with urethane at the same temperature [16]. In polymers containing both urea and urethane groups in roughly the same concentrations, branching is introduced principally by biuret formation. These reactions will occur more readily at higher temperatures and it can be seen that the products, allophanates and biurets, are in equilibrium with the starting materials, isocyanates and active hydrogen compounds (Figs. 2.8. and 2.9.).

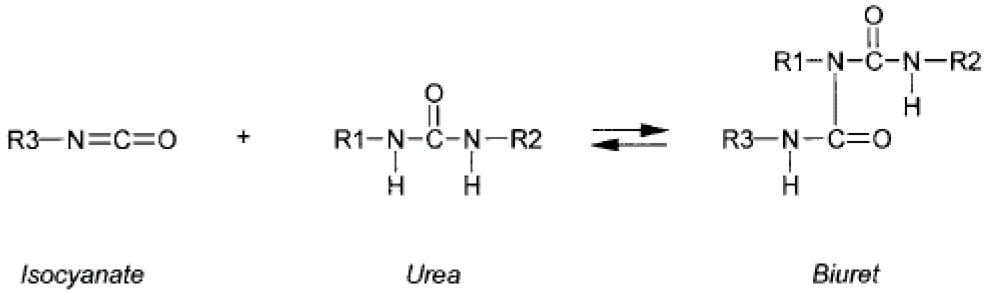


Figure 2.8 : Biuret formation.

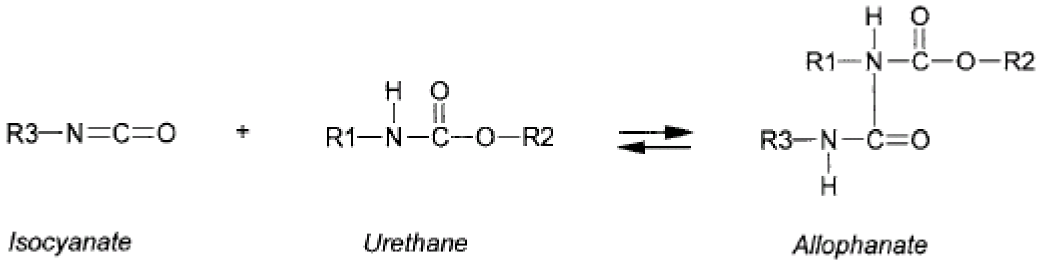


Figure 2.9 : Allophanate formation.

2.1.2 Polyols

Polyols are reactants which contains as functional groups hydroxyl groups. In urethane reactions primary hydroxyl groups, such as derived from ethylene oxide are faster reacting with an isocyanate than secondary hydroxyl groups, for example propylene oxide derived groups. Polyether polyols contain in the polymer backbone ether groups. These polyether polyols are very stable to hydrolysis under basic conditions, but can be attacked in an acidic environment. Polyether polyols are the main stay of the polyurethane market, they are used in foams, elastomers and coatings. Polyether polyols can be di-functional (diol) or they can be of higher functionality. In applications where high flexibility and elongation is required diols are used to create highly flexible and soft polyurethanes. Highly functional polyols are used in the preparation of hard or rigid polyurethanes. The products made this way are highly crosslinked and not soluble in a solvent. Besides polyether also polyester polyols are used in the preparation of polyurethanes. The ester linkage in the polyester makes the polyurethanes more sensitive to hydrolysis, but it is possible to prepare polyurethanes with improved exterior durability[17].

2.1.3 Catalysts

The most commonly used catalysts in polyurethanes are tertiary amines. As indicated earlier, there are many reactions taking place and the catalyst can be involved in any one or more of these[18]:

- The deblocking reaction, or
- the reaction of the free isocyanate with the other nucleophile, or
- an addition-elimination reaction, and/or
- side reactions.

They promote isocyanate reactions which will occur at moderate temperatures, i.e. reaction with alcohols, water, and carboxylic acids. However, the tertiary amines are not strong catalysts for the reactions of isocyanates and isocyanate derivatives at elevated temperatures [16]. Strong catalysts for these reactions are the strong bases, e.g. NaOH and NaOR.

With aromatic isocyanate resins, the formation of the urethane linkage can be promoted by a number of metals in the form of organometallics and/or salts of organic acids. Tin compounds such as DBTDL and tin (II) octoate are particularly effective, having superseded the more toxic lead equivalent components.

Synergistic effects of tin and amine catalysts are of technical importance and are widely studied principally because of the differences in reactivity. Metal catalysts are usually employed in systems based on the slower reacting aliphatic isocyanate adducts[19].

Standard cure catalysts used in polyurethane reaction are:

- Tin catalysts, Dibutyltin dilaurate (DBTDL), dibutyltin diacetate (DBTDA);
- Amines, Morpholine derivatives, tertiary amines;
- Bismuth catalysts, which are increasingly replacing mercuric catalysts.

Both blocked aromatic and aliphatic polymers use latent curatives such as ketimines and oxazolidines; however, they do have some inherent disadvantages. The use of ketimines and aldemines often produces products that have a tendency to yellow upon exposure to sunlight, and that take a longer time to achieve complete cure and retain slow evaporating ketones or aldehydes. Oxazolidine modification can also result in some yellowing and reduced chemical resistance to some acids [20].

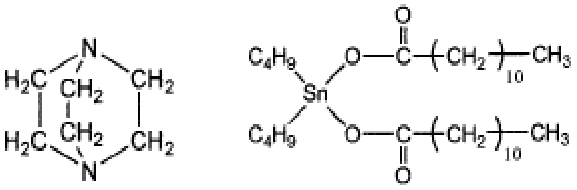

DABCO DBTDL

Figure 2.10 : Chemical structures of DABCO and DBTDL catalysts [21].

2.2 Blocked Isocyanates

Isocyanates are highly reactive precursors to amines, ureas and urethanes that are sensitive to nucleophilic reagents under both acidic and basic mediated conditions. This chemistry is extensively exploited commercially. The polyurethane industry is enormous with a wide variety of applications including elastomers, coatings, paints, adhesives, foams, furniture, footwear, construction and automotive applications[22]. The high reactivity associated with isocyanates can cause detrimental side-reactions and uncontrolled condensations leading to the formation of unworkable cross-linked materials consisting of allophanates, biurets, isocyanate dimers and trimers, as well as ‘abnormal products’ [23] that are difficult to process. In order to prevent such unwanted side-reactions it is necessary to block or ‘mask’ the isocyanate monomer as another function, which can then be converted to the active isocyanate form when required.

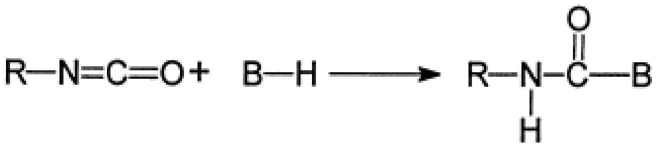
They present several advantages compared to isocyanates [24]:

- They do not react with residual moisture.

- They are more stable than the corresponding isocyanates and are consequently storage stable.
- They reduce toxic hazards associated with the handling of free isocyanates.

Blocked isocyanates are used extensively in many applications mostly for technical and economic reasons when the presence of free isocyanate must be eliminated, due to the potential toxic hazards associated with their use, and heat curing is possible. Blocked polyisocyanates are also used to crosslink both solvent-borne and water-borne resins offering a wide spectrum of possible formulations. They are blended with polyols, pigments, additives and fillers to improve flow[13]. These mixtures are stable at room temperature while at higher temperatures from 120°C to 250°C the blocking group volatilise either regenerating totally polyisocyanate functionality or remaining at least partially with the finished urethane.

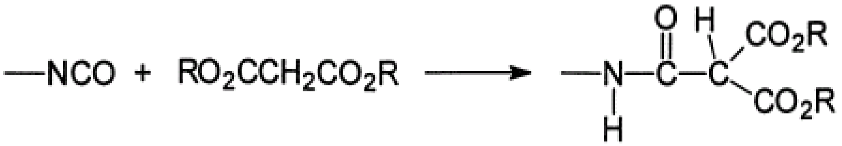
The isocyanate functional group can be ``blocked" through one of the several methods. Commonly, one thinks of a blocked isocyanate as one in which the isocyanate group is reacted with an active hydrogen compound ( Figure 2.11). Upon heating in the presence of a nucleophile, product is obtained. In some cases, ``blocked isocyanates" can be made via other routes not involving isocyanates; they are still generally called blocked isocyanates[18].



$$\mathrm{R{-}N{=}C{=}O + B{-}H \longrightarrow R{-}\underset{\underset{H}{|}}{N}{-}\overset{\overset{O}{\|}}{C}{-}B}$$

Figure 2.11 : Blocked isocyanate by reaction with active hydrogen compounds.

In the case of active methylene groups, such as those of malonic esters, the reaction product with an isocyanate is called a blocked isocyanate. This type of blocked isocyanate is produced by addition of the isocyanate to the active methylene site.



$$\mathrm{{-}NCO + RO_2CCH_2CO_2R \longrightarrow {-}\underset{\underset{H}{|}}{N}{-}\overset{\overset{O}{\|}}{C}{-}\overset{H}{C}(CO_2R)_2}$$

Figure 2.12 : Reaction of an isocyanate with a malonic ester.

However, when they react with a nucleophile, the dominant products obtained are not the urethane or urea products obtained by reaction of isocyanates.

Isocyanates can self-condense to form thermally unstable dimers (uretdiones, Figure 2.13) which regenerate isocyanate groups on heating. Products of this type are frequently referred to as self-blocked isocyanates.

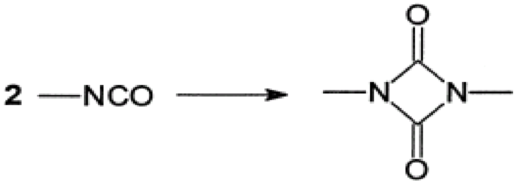


Figure 2.13 : Isocyanate dimerization, uretdione structure.

Another method of inactivating isocyanates involves encapsulating the polyisocyanate within a solid particle (Fig. 2.14); the isocyanate is liberated when the particle shell is broken down through melting or mechanical means.

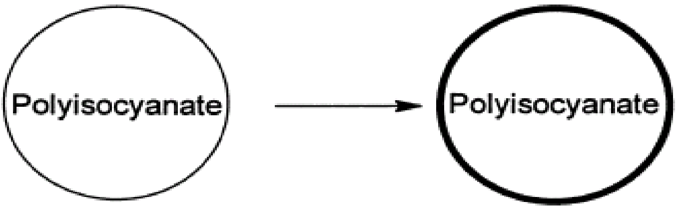


Figure 2.14 : Encapsulation of a polyisocyanate.

Kinetic studies are complicated by the fact that all, or almost all, the reactions are reversible and several side reactions are generally possible as seen in Figure 2.15. Even the simplest case of heating a blocked isocyanate alone is complicated by possible side reactions of the isocyanate. At high temperatures, there are dimerization or trimerization reactions of the isocyanate or reaction with the original blocked isocyanate to form, for example, an allophanate or biuret. These in turn can also thermally decompose through different kinetic pathways. When used with a polynucleophile, the liberated isocyanate can in addition react with the urethanes or ureas produced. In some cases, the deblocking reaction may be catalyzed by another molecule of blocked isocyanate or by the blocking agent [18].

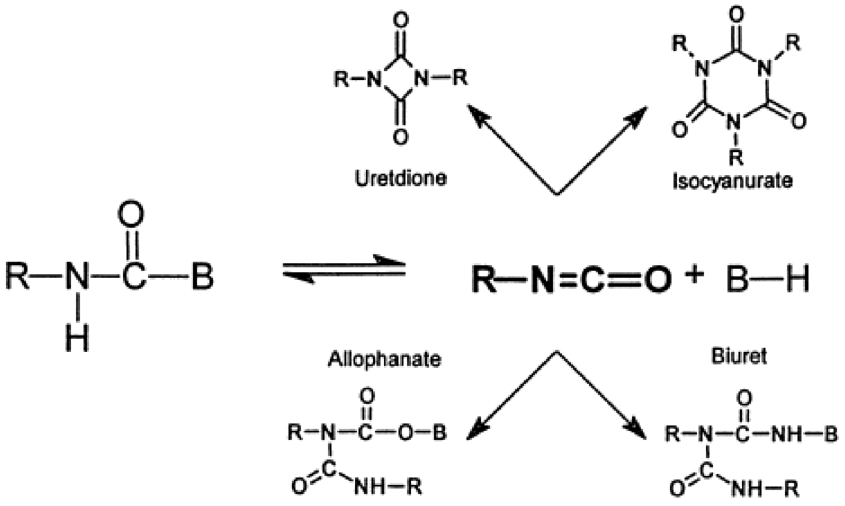


Figure 2.15 : Side reactions of isocyanates after deblocking.

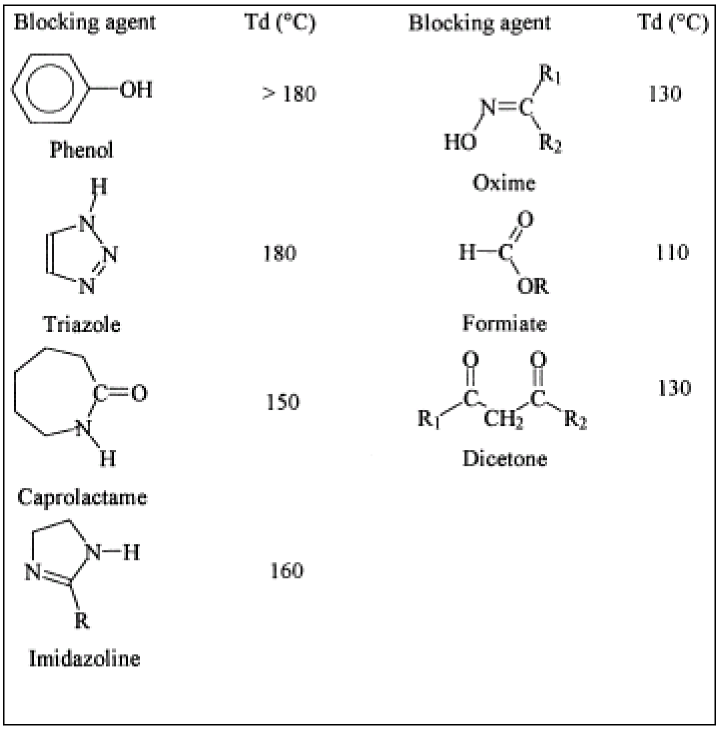
2.2.1 Factors effecting on deblocking reaction of blocked isocyanates

A blocked isocyanate is an adduct containing a comparatively weak bond formed by the reaction between an isocyanate and a compound containing an active hydrogen atom. At elevated temperatures, the reaction tends to proceed insuch a way as to regenerate the isocyanate and the blocking agent. The regenerated isocyanate could react with a co-reactant containing the hydroxyl functional groups to form urethane with thermally more stable bonds (addition-elimination mechanism (S_N2)) in section 2.2.2.)

There are several variables which affect the rate and extent of the deblocking reaction such as:

- the structure of the blocking agent and the polyisocyanate used,
- the structure of substituent,
- presence of catalysts,
- effects of solvents, and
- temperature.

The deblocking temperature of the blocked isocyanates depends on the structures of the blocking agents and structures of the isocyanates. Several compounds namely phenols, oximes, amides, imides, imidazoles, amindines and related compounds, pyrazoles, 1,2,4- triazoles, hydroxamic acid esters, and active methylene compounds have been reported as blocking agents[25]. Among these blocking agents, phenols are the most studied blocking agents because of the possibilities of introducing number of substituents on the benzene ring. Generally, the dissociation or deblocking temperatures (Td°C) of blocked polyisocyanates based on commercially utilised blocking agents decrease in the order: alcohols > e-caprolactam > phenols > methyl ethyl ketoxime > active methylene compounds[13].



Blocking agent	Td (°C)	Blocking agent	Td (°C)
Phenol	> 180	Oxime	130
Triazole	180	Formiate	110
Caprolactame	150	Dicetone	130
Imidazoline	160		

Figure 2.16: Some blocking agents and deeblocking temperatures of isocyanates.

The substituent being a strong influencing factor on the deblocking temperature of blocked isocyanates. Substitutents present in the phenolic aromatic ring with electron-withdrawing tendency decrease the deblocking temperature while electron releasing groups increase the deblocking temperature [26- 27]. The structures of isocyanates also have major effect on the deblocking temperatures; the isocyanate structure has additional effect on urethane formation reaction. In general, blocked aromatic isocyanates deblock at lower temperatures than aliphatic isocyanates.

Isocyanate structure can strongly affect the strength of the labile bond formed during the blocking reaction, and hence the deblocking temperature. If the blocked isocyanate is based on aromatic isocyanate, the aromatic ring drains the electron density of the nitrogen atom of isocyanate moiety and makes the labile bond formed between the isocyanate and blocking agent more labile. The vice versa is true for the cases of blocked isocyanates based on aliphatic isocyanates[28].

2.2.2 Urethane forming reactions from blocked isocyanates

There are two urethane forming reaction mechanisms by which a blocked isocyanate can react with a nucleophile (NuH). In the elimination-addition reaction(Figure 2.17.), the blocked isocyanate decomposes to the free isocyanate and the blocking group (BH). The isocyanate then reacts with a nucleophile to form a final product. In the addition-elimination reaction(Figure 2.18.), the nucleophile reacts directly with the blocked isocyanate to yield a tetrahedral intermediate followed by elimination of the blocking agent[25].

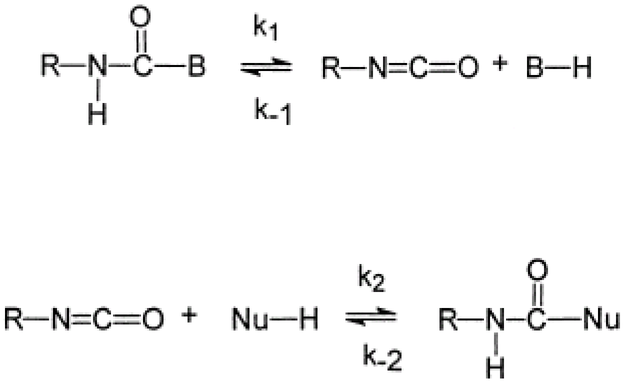


Figure 2.17 : Elimination-addition reaction.

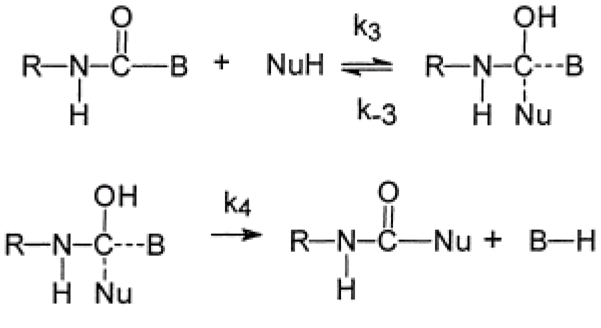


Figure 2.18 : Addition- elimination reaction.

In general, crosslinking is more rapid in the presence of a NuH that can react rapidly with the isocyanate; for example, amines react much more rapidly than alcohols. The differences in reactivity depend on the structures of the amines, alcohols, and blocking agent. Primary amines react more rapidly than secondary amines. Thus, blends of oxime blocked isocyanates and secondary amine-functional polymers increase in viscosity more slowly than those with primary amine-functional polymers [29].

During the curing process, low molecular weight blocking agents can evaporate from the film. Those that can diffuse more rapidly through the crosslinking film and volatilize more rapidly from the surface give more rapid (or lower temperature) cure than other blocking agents of the same class that diffuse and evaporate more slowly. For example, methyl, ethyl, and isopropyl alcohol blocked TMXDI and an acrylic polyol with a tin catalyst gave crosslinked films in increasing times[30].

The curing schedule required for crosslinking of blocked polyisocyanates with polynucleophiles is dependent on many variables including[18]:

- structures of the isocyanate, blocking agent, and nucleophile,
- relative rate of reaction of the nucleophile with the isocyanate compared to the reverse reaction rate of the isocyanate with the blocking agent,
- the rates of diffusion and evaporation of the blocking agent,
- polarity and hydrogen bonding potential of the reaction medium (solvents or coreactant),
- concentrations of reactive groups,
- type and concentration of catalysts,
- extent of side reactions and whether they lead to crosslinking or termination, and
- the extent of crosslinking required to achieve film proper

2.3 Fluorine-Containing Polymers

It is a widely recognized method to modify the surface and bulk properties of polymers by introducing fluorine into polymeric chains. The fluorine atoms can confer to polymers desirable properties, such as low surface energy, thermal stability, excellent dielectric properties, good chemical resistance, low water absorption, and weatherability. These characteristics of fluorine containing polymers are imparted by the highest electron negativity (4.0), the third smallest van der Waals radius (0.135 nm), low polarizability ($\alpha = 1.27 \times 10^{-24}$ cm^3) of the fluorine atom, together with the strong bonding energy (472 kJ/mol) and the weak intermolecular cohesive energy. There has been growing interest in the synthesis of polymers containing fluorine atoms in their structure[31].

The C–F bonds in organic molecules are very strong and the intermolecular interactions of the fluorocarbons are weak due to the small size and high electronegativity of fluorine. So, the presence of fluorine group, strongly affects chemical reactivity. For example, nucleophilic substitution at a fluoro- substituted carbon atom is not an easy process. The difficulty is attributed to destabilization of the transition state by fluorine and also to electrostatic repulsion between a nucleophile and the lone pair of electrons on the fluorine atoms. As a consequence, fluorine-containing polymeric materials exhibit unique property combinations of low surface energy; low friction; low refractive indices;dirt repellant; biological inertness (i.e., resistant to a harsh environment); good resistance to corrosive chemicals; good stability against hydrolysis; low water and ion permeability; low solubility in polar and non-polar organic solvents (being non-wettable and oleophobic, low interfacial free energy) due to substantial hydrophobicity. They also have remarkable resistance to flame, UV radiation, fouling agents like by marine organisms, chemicals, solvents, oxidative attack and possess excellent thermal stability [32-33]. The hydrophobic nature reflects low values of cohesive energy density and surface energy. In general, the strength of the C–F bond increases with the extent of adjacent carbon fluorination, and this means that the longer the fluoroalkyl group is, the higher its stability and hydrophobicity. Out of the list of properties mentioned above, some are bulk properties, e.g., chemical inertness, thermal stability, and lubricity, and some are surface properties such as oil, dirt and water repellence and cleanability. In many coating applications, the bulk properties of fluoro polymers such as chemical and thermal resistance are the desired properties. In these cases, the use of large quantities of fluorine throughout the coating is necessary.

However, thermoset polyurethane coatings have adequate chemical and thermal resistance and the use of fluorine-containing monomers and polymers is not a cost-effective alternative approach for structural modification. Therefore, obtaining the repellency and cleanability of a fluoropolymer would be desired with a less cost. In these cases, the surface property improvement by introducing fluorine will tailor the coating for using in aggressive environment and formulator do not need to use systems that have fluorinated groups throughout the bulk of the film. In fact, excess fluorine content throughout the film decreases the adhesive strength at the metal/ polymer interface [34]. Incorporation of fluorine into the polymer main chain or its side chains are well known methods that lead to large changes in the surface properties. This is due to the segregation of fluorinated chains toward the polymer–air interface, which results in a considerable decrease in the surface energy.

2.4 Two-Component And One-Component Polyurethane Coatings

Two-component polyurethane coatings are formulated from the list of chemical coreactants "Solventborne Coatings." As the name implies, two component coating are supplied to the end user in two separate containers, and are mixed prior to application. One container (component A) holds the polyol, catalyst, solvent, and additives (rheology control agents, etc.). The second container (component B) hold the polyisocyanates, solvent, and additives (UV Stabilizers). Each container is individually shelf stable[35].

The isocyanate/hydroxyl (NCO/OH) reaction begins as soon as the containers are combined. The mixing ratio of the components can he based either on volume or weight and is precisely calculated to achieve stoichiometry of the coreactants (NCO/OH = 1). This ratio gives a finished coating optimum mechanical performance and optimum chemical resistance.

If necessary, the NCO/OH ratio may be varied to change coating properties. If the NCO/OH ratio is less than one, some OH functionality is unreacted and the coating has increased flexibility, better adhesion to substrate, and reduced solvent and chemical resistance. If the NCO/OH ratio is greater than one, some NCO is unreacted and the coatings needs a longer time to dry and surface harden. The final product is harder, solvent and chemical resistance is increased, flexibility is decreased and adhesion to the substrate is reduced.

One-component waterborne polyurethane coatings utilize the same chemical reactants used in two-component coatings and are formulated by the same process except for three modifications: the polyisocyanate adduct is blocked; all chemical coreactants are blended into one container; and the coating must be heat cured.

Blocked polyisocyanates utilize a chemical moiety to protect the isocyanate functionality from reaction during shelf storage at room temperature. The chemical moiety blocks, or caps the isocyanate by reacting with the NC0 functional groups. With the addition of heat, the blocked isocyanate breaks apart, regenerating the isocyanate functional groups NCO at the higher temperature. After the NC0 functional group is regenerated the coating cures by the reaction of the NC0 group with the OH group (acrylic or polyester) on the polyol.

One-component coating are used in end use market that require no mixing or metering prior to applications and that have available curing ovens.

3.EXPERIMENTAL PART

3.1 Materials

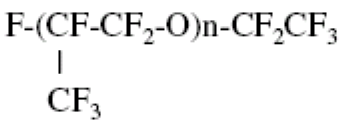
In fluorinated polyurethane (FPU) film synthesis, Voracor® CM 647 Polyol (from Dow Chemicals) , Desmodur BL 3175 SN (form Bayer Chemicals),Dibutyl Tin Dilaurate (DBTDL), Aromatic 100 (other name is Solvesso 100 from ExxonMobil Chemicals) ,Krytox® 100, Krytox® 103, Fluoroguard® (from Dupont Chemicals) and a special fluorinated mono alcohol (F-OH) were used.

Desmodur BL 3175 SN (free NCO content < % 0.2, blocked NCO content approximately 11.1%) is a type of phenol-blocked aliphatic polyisocyanate based on hexamethylene diisocyanate (HDI).Using aliphatic polyisocyanates provides to polyurethane coatings; no yellowing, chemical resistance and exceptional gloss retention[12].

Dibutyl Tin Dilaurate (DBTDL) is a organometallic tin compound that is added to allow the reaction to take place at a rapid rate and a lower temperatures.

Voracor® CM 647 Polyol contains sorbitol and propylene oxide polymer more than %30. They generate ‘soft segment ‘ of polyurethane. Sorbitol is a sugar alcohol and has six hydroxyl groups, because of its high functionality it also acts as a crosslinker in our synthesis.

Krytox® 100, Krytox® 103 and Fluoroguard® oils (from Dupont) are fluorinated synthetic oils that were used to modify the surfaces of blocked polyurethane films. All of this agents are perfluoropolyether (PFPE)—also called perfluoro-alkylether (PFAE) or perfluoropolyalkylether (PFPAE)—with the following chemical structure, where n= 10- 60:



$$\mathrm{F{-}(\underset{\underset{\displaystyle CF_3}{|}}{CF}{-}CF_2{-}O)n{-}CF_2CF_3}$$

Figure 3.1 : PFPE structure.

The polymer chain is completely saturated and contains only carbon, oxygen, and fluorine. On a weight basis, a typical oil contains 21.6% carbon, 9.4% oxygen, and 69.0% fluorine.

They have excellent color, UV, and thermal stability. Added to plastics and elastomers, they improve processing of polymers. Fluoroguard® internally lubricates to improve flow properties, processibility, throughput, uniform mixing/dispersion of ingredients, and offers many advantages over competitive process aids.

F-OH is a special type of an aromatic fluorinated mono alcohol and it was utilised as fluorine containing compound to improve and modified the surface properties of polyurethane thin films. Because of its hydroxyl functionality, it can be able to make a bond with polyisocyanate. This agent was synthesized in our laboratory by organic synthesis way and we claimed that using F-OH is more favourable when comparing the other fluorine containing compounds.

3.2 Equipments

3.2.1 Infared Analysis (IR)

Infared analysis was performed on Schimadzu 8300 spectrometer.

3.2.2 Thermogravimetrical Analysis (TGA)

Thermal gravimetrical analysis was performed on a TA TGA Q50 instrument at a heating rate 20 °C/min.

3.2.3 Contact Angle Meter

The contact angle of cured FPU films was measured by KSV CAM 100 instrument.

3.2.4 Pendulum Hardness Tester

A König Pendulum Hardness (Gardner, BYK) tester was used to measure the film hardness of the FPU films. The method used in this study described in 3.6.4.

3.2.5 Scanning Electron Microscopy (SEM)

The bulk morphology of FPU films was observed by Scanning Electron Microscopy (JEOL 7000-S).

3. 3 Preparation of Formulations

Different coating formulations including blocked polyisocyanate, polyol, solvent, dibutyl tin dilaurate and four different fluorine containng compounds were developed. Formulation compositions are shown in Table 3.1.

Table 3.1 : General formulation composition

Blocked Polyisocyanate	HDI based Aliphatic Blocked Polyisocyanate (Desmodur®)
Polyol	Propylene Oxide based Polyol (Voracor ®)
Catalyst	Dibutyl Tin Dilaurate (DBTDL)
Solvent	Aromatic 100
Fluorine-Containing Compound	Krytox® 100,Krytox® 103,Fluoroguard® and Fluorinated mono alcohol (F-OH)

To improve the surface properties of polyurethane coatings, four different fluorine-containing compounds were added to formulations at different percent; 0.1%, 0.4% and 07%. The name and percent of these fluor compounds in the formulations are shown in Table 3.2.

Table 3.2 : The name and percent of fluorine-containing compounds in FPU formulations

Sample Name	**Fluorine-Containing Compound**	**F % in bulk**
FPU- 1	Fluorinated mono alcohol (F-OH)	0.7
FPU- 2	Fluorinated mono alcohol (F-OH)	0.4
FPU- 3	Fluorinated mono alcohol (F-OH)	0.1
FPU- 4	Krytox® 100	0.1
FPU- 5	Krytox® 103	0.1
FPU- 6	Fluoroguard®	0.1

The reactions between phenol-blocked polyisocyanates and polyols lead to the formation of a urethane(carbamate) linkage via addition-elimination mechanism that described in Section 2.2.2.

The mixture of blocked polyisocyanate, polyol, DBTDL and fluorine-containing compounds were dissolved in solvent as desired content in flask at room temperature for 12 hours, according to the basic reaction showed in Fig. 3.2.

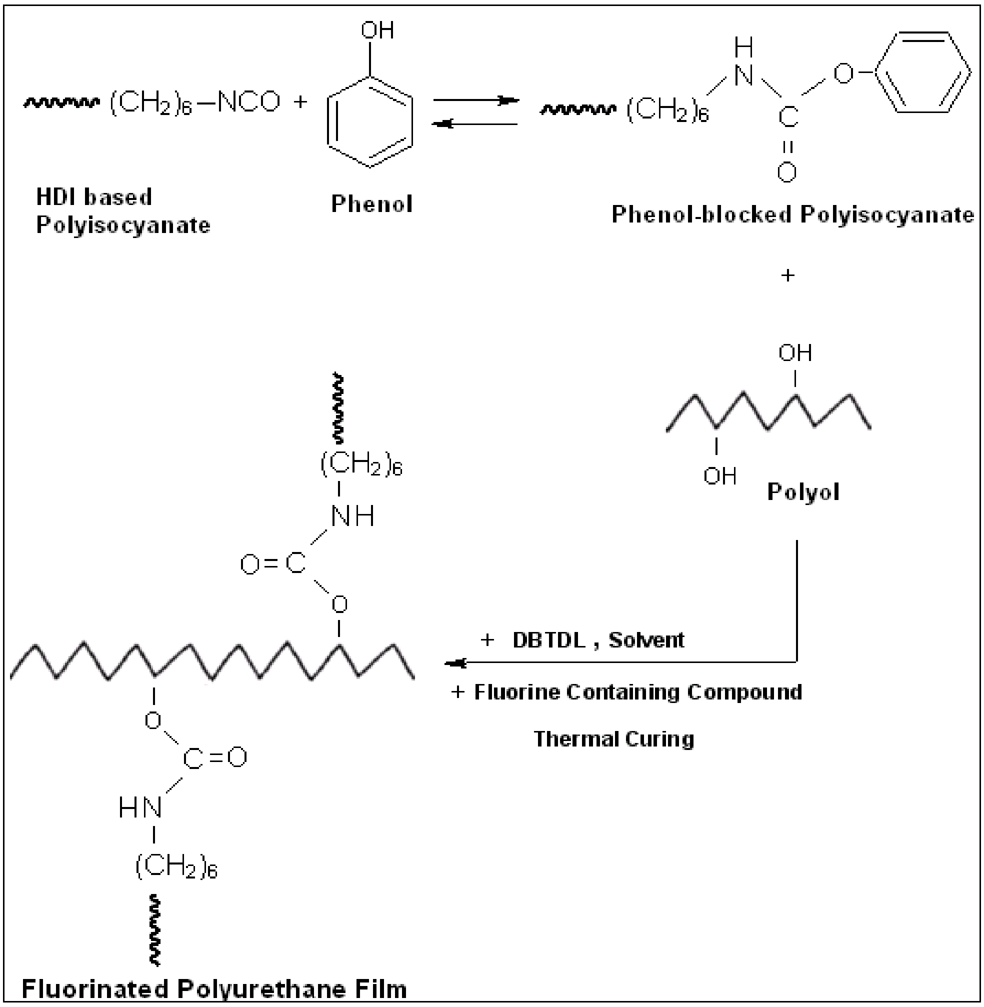


Figure 3.2: Fluorinated polyurethane film synthesis.

3.4 Application

The formulated solutions were cast onto glass substrate (5cm x 5 cm) to obtain free films using Spin Coater System (SCS Spin Coater P6700) at 1000 rpm. The glass substrates were silanated with %5 chloro trimethyl silane containing solution before use to provide cured film peeled off easily in water.

Spin coating has been used for several decades for the application of thin films. In the spin-coating process, a thin film of liquid is placed on a flat rotating substrate at high speed (typically around 3000 rpm) and the liquid film then thins under the action of spin forces and evaporation (Fig. 3.3.). The simplest models for this process use the lubrication approximation and a typical model (in dimensional form) is that of Emslie et al. [36].

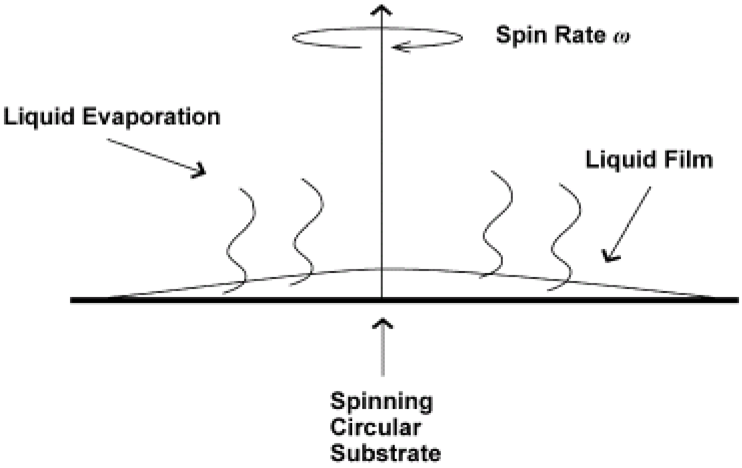


Figure 3.3 : Spin coating system.

In particular, the spin-coating process is not sensitive to the initial amount of liquid deposited on the substrate and the liquid film thickness quickly equilibrates. When the optimum configuration has been reached (i.e. , the correct distribution of solute has occurred) the spinning is stopped and the remaining solvent is allowed to evaporate off (this can be accelerated by the introduction of heating elements) and the remaining solution dries out and leaving solute adhering to the substrate[37].

3.5 Thermal Curing of Samples

For thermal curing of samples, a typical oven was used. All samples which cast onto glass subsrates were thermally polymerized with different temperatures; 140°C,170°C,180°C and 200°C.

3.6 Analysis

Following tests; Infrared Analysis (IR), Thermal Gravimetric Analysis (TGA), Pendulum Hardness, Contact Angle Measurement and Scanning Electron Microscopy (SEM) Analysis were performed to monitor thermal, morphological and film properties of FPU's.

3.6.1 Infrared Analysis

Infrared (IR) spectroscopy is one of the most common spectroscopic techniques used by organic and inorganic chemists. Simply, it is the absorption measurement of different IR frequencies by a sample positioned in the path of an IR beam. The main goal of IR spectroscopic analysis is to determine the chemical functional groups in the sample. Different functional groups absorb characteristic frequencies of IR radiation. Using various sampling accessories, IR spectrometers can accept a wide range of sample types such as gases, liquids, and solids. Thus, IR spectroscopy is an important and popular tool for structural elucidation and compound identification.

Infrared radiation spans a section of the electromagnetic spectrum having wavenumbers from roughly 13,000 to 10 cm–1, or wavelengths from 0.78 to 1000 μm. It is bound by the red end of the visible region at high frequencies and the microwave region at low frequencies.

IR absorption positions are generally presented as either wavenumbers ($\tilde{\nu}$) or wavelengths (λ). Wavenumber defines the number of waves per unit length. Thus, wavenumbers are directly proportional to frequency, as well as the energy of the IR absorption. The wavenumber unit (cm^{-1}, reciprocal centimeter) is more commonly used in modern IR instruments that are linear in the cm^{-1} scale. In the contrast, wavelengths are inversely proportional to frequencies and their associated energy. At present, the recommended unit of wavelength is μm (micrometers), but μ (micron) is used in some older literature[38].

3.6.2 Thermal Gravimetric Analysis

Thermogravimetry has become a general method for comparing the thermal stability of polymers. TGA measures the amount and rate of change in the weight of a material as a function of temperature or time in a controlled atmosphere [39]. Measurements are used primarily to determine the composition of materials and to predict their thermal stability at temperatures up to 1000°C. The technique can characterize materials that exhibit weight loss or gain due to decomposition, oxidation, or dehydration. In comparing thermal stability, it should be remembered that TGA measurements only record the loss of volatile fragments of polymers, caused by decomposition. TGA cannot detect any chemical changes or degradation of properties caused by cross-linking[40].

In this study, thermal stability was evaluated using a Q50 TGA from TA Instruments. Film samples of 5–10 mg were placed in the sample pan and heated from 25°C to 600°C under N_2 (flow rate: 40 mL/min) at an applied heating rate of 20°C /min.

During the heating period, the weight loss and temperature difference were recorded as a function of temperature. The results are given in Table 4.1.

3.6.3 Contact Angle Measurement

The determination of solid-vapor γ_{SV} and solid-liquid γ_{SL} interfacial tensions is of importance in a wide range of problems in pure and applied science. Because of the difficulties involved in measuring directly the surface tension involving a solid phase, indirect approaches are called for: Several independent approaches have been used to estimate solid surface tensions, including direct force measurements; contact angles; capillary penetration into columns of particle powder; sedimentation of particles; solidification front interaction with particles; film flotation; gradient theory; Lifshitz theory of van der Waals forces; and theory of molecular interactions. Among these methods, contact angle measurements are believed to be the simplest[41].

Contact angle measurement is easily performed by establishing the tangent (angle) of a liquid drop with a solid surface at the base. The attractiveness of using contact angles θ to estimate the solid-vapor and solid-liquid interfacial tensions is due to the relative ease with which contact angles can be measured on suitably prepared solid surfaces. It will become apparent later that this seeming simplicity is, however, very misleading.

The possibility of estimating solid surface tensions from contact angles relies on a rellation which has been recognized by Young [42] in 1805. The contact angle of a liquid drop on a solid surface is defined by the mechanical equilibrium of the drop under the action of three interfacial tensions : solid-vapor, γ_{SV}, solid-liquid, γ_{SL} , and liquid-vapor, γ_{LV} (Fig.3.4.). This equilibrium relation is known as Young's equation:

$$\gamma_{LV} \cos \theta_Y = \gamma_{SV}, - \gamma_{SL}$$

where θ is the Young contact angle, i.e. a contact angle which can be inserted into Young's equation. It will become apparent later that the experimentally accessible contact angles may or may not be equal to $\theta_{Y.}$

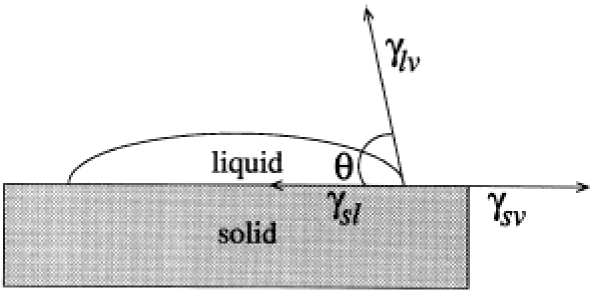


Figure 3.4 : Scheme of a sessile-drop contact angle system.

Contact angle is a well-known technique for investigating and controlling adhesion, surface treatments and cleaning, and polymer film modification. The wetting of solid substrates is a basic feature of many natural and industrial processes and contact angle is a simple, rapid, and sensitive method of characterizing the wettability of a solid surface[41].

The wettability of the film surfaces was measured using a contact angle KSV CAM100 system at ambient temperature. The equilibrium contact angles of 5μL water droplets were measured by the sessile drop method. The contact angles were measured as follows: a 5μL water droplet was placed on the sample using a syringe, and contact angle was recorded.

The water contact angle of FPU films prepared in our experiments are listed in Table 4.2.

3.6.4 Pendulum Hardness Tests

König pendulum hardness method which is frequently encountered in practice is used for measuring the hardness of the samples. The device itself consist of a pendulum, to the support of which two agate balls are attached. The pendulum is placed on the coating with the two balls 5 mm in diameter and moved 6° away from the position of rest. After releasing the 200 g pendulum the oscillations are recorded by a counter. The measure of damping is the number of oscillations or the time in seconds whic elapses until the amplitude of the pendulum has dropped from 6° to 3° [43].Pendulum hardness of the cured film was measured to determine the film hardness.

The test were applied while the cured FPU film was peeled off from the glass substrate in water. The test results are shown at Table 4.3 for all formulations, respectively.

3.6.5 Scanning Electron Microscopy (SEM)

The scanning electron microscope (SEM) is a type of electron microscope that images the sample surface by scanning it with a high-energy beam of electrons in a raster scan pattern. The electrons interact with the atoms that make up the sample producing signals that contain information about the sample's surface topography, composition and other properties such as electrical conductivity[44].

Morphologic properties of FPU films was observed in SEM analysis and SEM micrographs of fluorinated and non-fluorinated FPU films are shown in Figure 4.11.

4.RESULTS AND DISCUSSION

In this thesis, fluorine containing polyurethane coating materials are prepared. Formulations consist of blocked polyisocyanate, polyol, fluorine containing compounds, solvent and catalyst. All coating formulations are coated on glass substrates by spin coating method and cured thermally. After curing with different temperatures obtained samples are subjected to further tests.

4.1 Infrared Analysis

As mentioned before, basically two different types of fluorine-containing compounds were used to prepare FPU; Aromatic fluoro mono alcohol based (F-OH), PFPE based (Krytox® 100,Krytox® 103, Fluoroguard®). To determine the functional groups in coatings, one each example of these two types coatings were analyzed with IR spectra.

FT-IR spectrum of FPU coating prepared with F-OH as a fluorine-containing agent is shown in Figure 4.1. Blue peaks indicate the functional groups which exist in all coatings and red peaks indicate the spesific peaks.

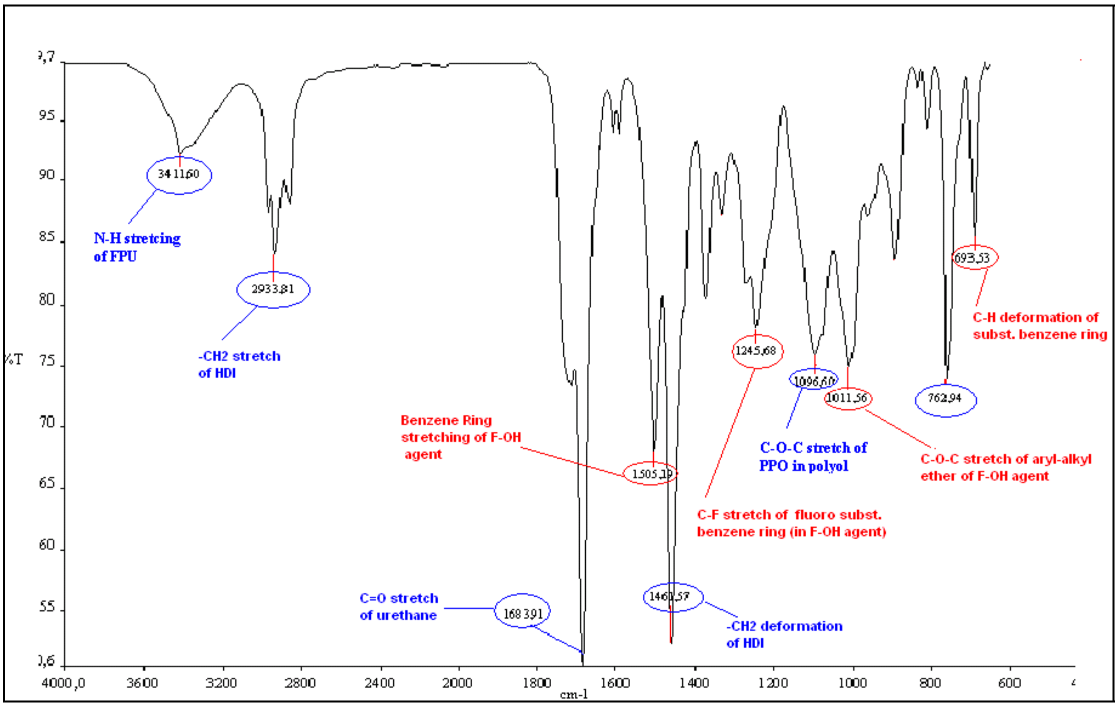


Figure 4.1 IR spectra of FPU coating prepared with F-OH.

In Figure 4.1, the IR spectra showed strong peak at 1683 cm^{-1} due to urethane carbonyls and medium peak at 3411 cm^{-1} due to N-H groups. -CH$_2$ (2933 cm^{-1}) aliphatic stretching and deformation (1460 cm^{-1}) bands of HDI are also observed. The absorption band at 1096 cm^{-1} originates from C-O-C group of PPO in our polyol structure.

In addition to these blue peaks, there are some spesific red peaks which come from F-OH compound. The peak at 1505 cm^{-1} indicates the benzene ring stretching of F-OH compound. The absorption band (1245 cm^{-1}) dealing with stretching absorption of C-F bond is also observed and proved the existance of fluorine in coating. The peak at 1011 cm^{-1} is resulted from C-O-C stretch of alkyl aryl ether structure in F-OH compound and peak at 693 cm-1 due to C-H deformation of benzene ring comes from aromatic F-OH compound.

Infrared spectra of FPU prepared with Krytox 100® as a fluorine-containing compound was shown in Figure 4.2.

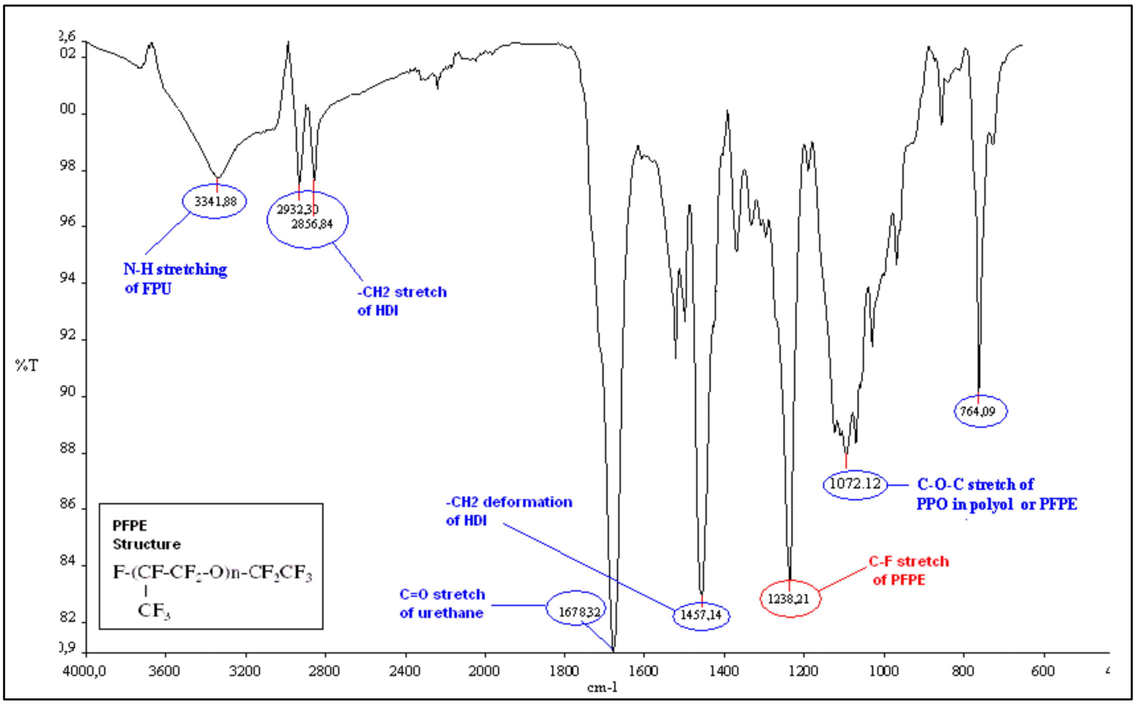


Figure 4.2 IR spectra of FPU coating prepared with Krytox 100.

In this IR spectra, blue peaks are still remaining because they come from our final urethane structure or polyurethane raw materials. However, there is a remarkable peak at 1238 cm^{-1} and indicates the C-F stretching of PFPE which is in the structure of Krytox 100® compound. Similar IR spectras are obtained for coatings which prepared with other PFPE based compounds; Krytox 103® and Fluoroguard®.

As a result of IR analysis,

- The absorption band of -NCO and -OH group are not found in both spectrums and this result also proves the synthesis of FPU.
- The characteristic peak of carbonyl stretch shows the formation of final urethane linkage.
- The band caused by the C-F bond are observed, which indicates the presence of fluorine in both types of coatings.
- From the various peaks of benzene ring, it can be said that the FPU coating which prepared by F-OH is gained aromatic properties.

4.2 Thermal Gravimetric Analysis

Thermogravimetry involves the continuous recording of mass versus temperature or time as a sample is heated in a furnace with a controlled environment. The principal applications of TGA in polymers are (1) determination of the thermal stability of polymers, (2) compositional analysis, and (3) identification of polymers from their decomposition pattern. Also, TGA curves are used to determine the kinetics of thermal decomposition of polymers and the kinetics of cure where weight loss accompanies the cure reaction[44].

TGA was carried out in a nitrogen atmosphere at a heating rate of 20°C/min for analysing thermal stabilities of the FPU's**.** Figure 4.3. and 4.4. are showed TGA curves for FPU's at the curing temperatures; 140°C and 200°C.

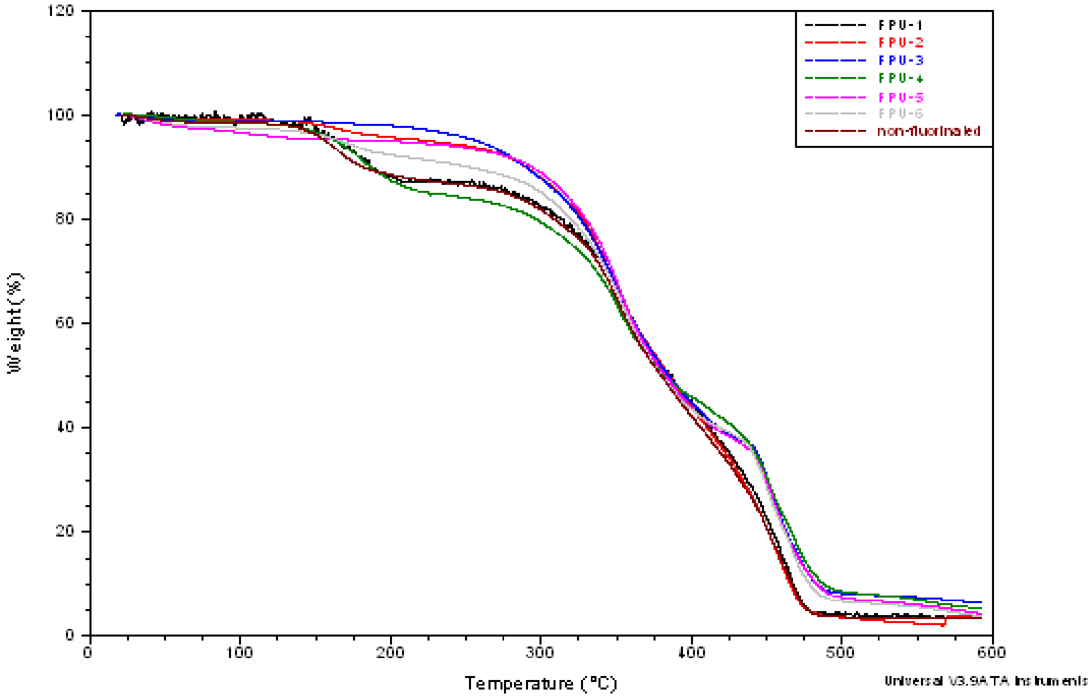


Figure 4.3: TGA thermogram of FPU films at 140°C.

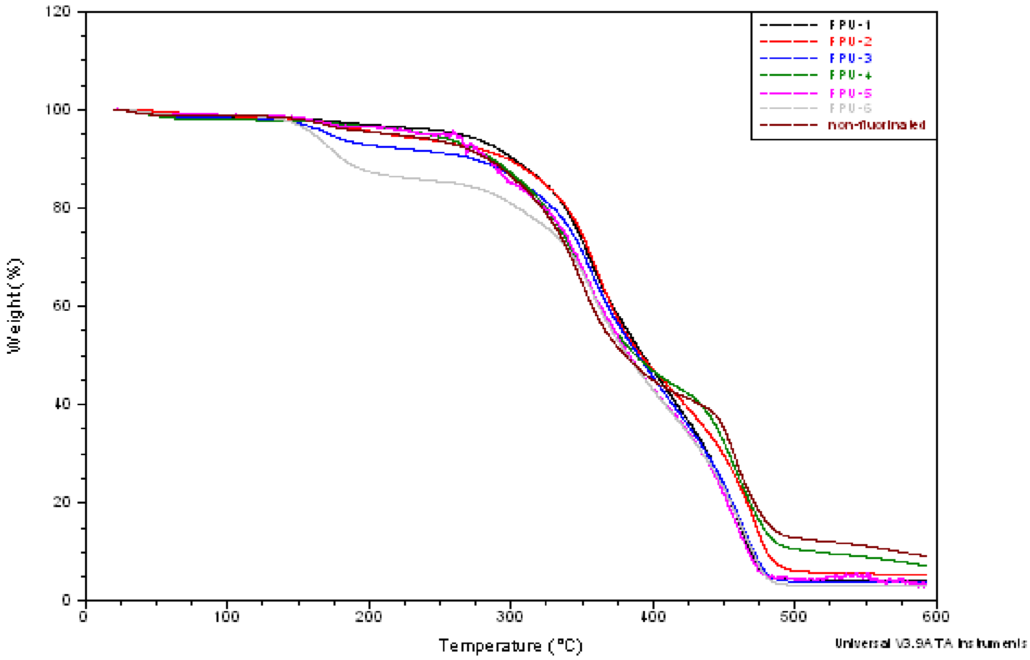


Figure 4.4: TGA thermogram of FPU films at 200°C.

The temperature at 50% residue of all FPU's are given in Table 4.1. Fluorine concentration and curing temperature directly effect the thermal stability of FPU films. As the curing temperature increases from 140°C to 200°C, the temperature at 50% residue have increased for all FPU films.

Table 4.1 : The temperatures at 50% residue of all FPU's.

Sample Name	140°C	200°C
FPU- 1	385°C (50%)	394°C (50%)
FPU- 2	385°C (50%)	392°C (50%)
FPU- 3	384°C (50%)	390°C (50%)
FPU- 4	382°C (50%)	388°C (50%)
FPU- 5	382°C (50%)	383°C (50%)
FPU- 6	379°C (50%)	382°C (50%)
Non-Fluorinated	379°C (50%)	380°C (50%)

In addition, the temperature at 50% residue of FPU-1, FPU-2 and FPU-3 were 394°C, 392°C and 390°C respectively. It means that when the fluorine concentration rises from 0.1 to 0.7 wt % , thermal stability have increased.

As a result of TGA analysis,

- Introducing the fluorine into the polyurethane chain as a soft segment, improves the thermal stability for all coatings.
- The aromatic (rigidity of benzene rings) nature of F-OH component, which used as a fluorined agent in FPU-1, FPU-2 and FPU-3, can caused higher half-decomposition temperature when comparing FPU-4,FPU-5 and FPU-6 coatings.

4.3 Contact Angle Measurement

The value of the contact angle of a liquid on a film is a direct reflection of the surface wettability. Contact angles of water were measured on glass substrates coated with six different FPU films which were cured at different temperatures. For each measurement six drops (5µL) of water was tested on the surfaces and results are tabulated in Table 4.2.

Table 4.2 : Contact angle results

Sample Name	**140°C**	**170 °C**	**180°C**	**200°C**
FPU- 1	98.0	101.7	102.1	103.3
FPU- 2	94.7	95.0	98.3	101.1
FPU- 3	94.9	95.2	98.2	99.0
FPU- 4	86.1	86.9	87.3	89.8
FPU- 5	87.0	86.7	88.8	89.2
FPU- 6	82.3	83.6	87.3	87.2
Non-fluorinated	84.2	84.5	84.7	85.7

When the FPU-1, FPU-2 and FPU-3 films were cured at 200 °C, the water contact angles increased steadily from 98° to 103° ,as the added fluorine content in the films increased from 0.1 to 0.7 wt % (Table 4.2.). These high contact angles showed clearly that the surface of the films was significantly enriched in the fluorinated species.

The contact angles on the films from F-OH, and other fluorinated species (Krytox® 100, Krytox® 103 and Fluoroguard®) showed a similar trend as the fluorine content increased, but the contact angle values of films which were prepared with Krytox® 100, Krytox 103® and Fluoroguard® were lower(Figs 4.5 to 4.8). This can be due to the chemical bond (covalent bond) between F-OH agent and polyisocyanate. Other chemicals are synthetic oils and these are not able to make a covalent bond with polyisocyanate.

Similarly, as can be seen in figures below, when the curing temperature increases 140°C to 200°C, the contact angle values of all coatings increases. As a consequence, a higher curing temperature also led to a surface enrichment of the fluorinated species.

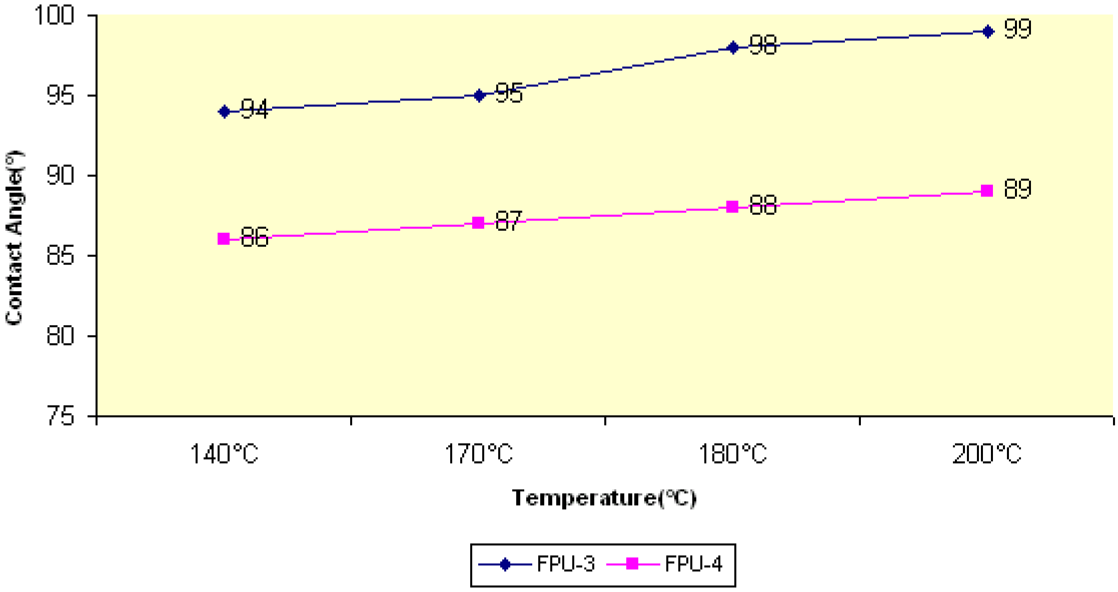


Figure 4.5 : Contact angle graph of FPU-3 and FPU-4 films.

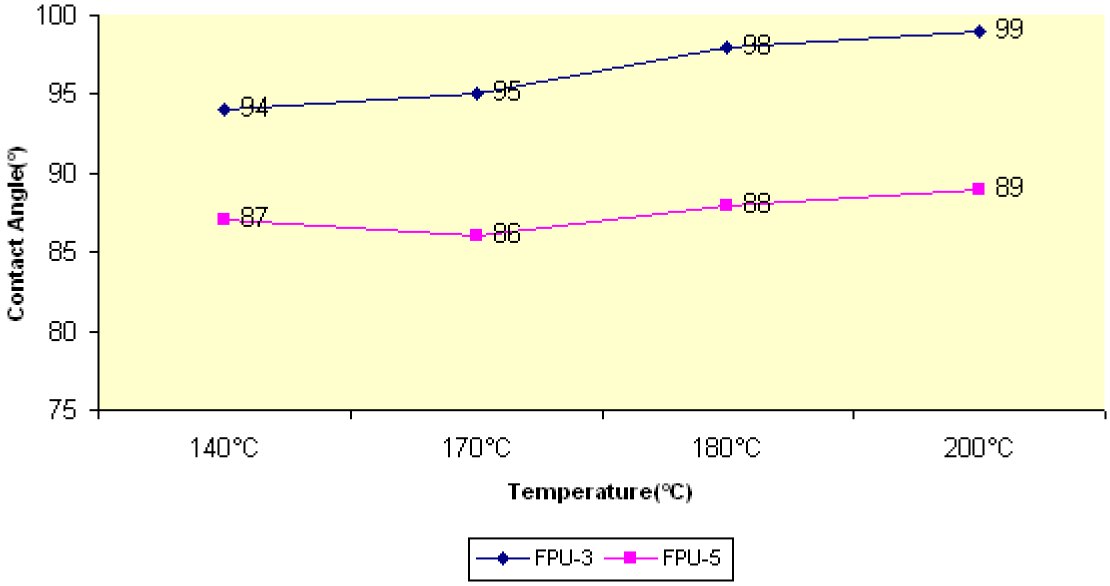


Figure 4.6 : Contact angle graph of FPU-3 and FPU-5 films.

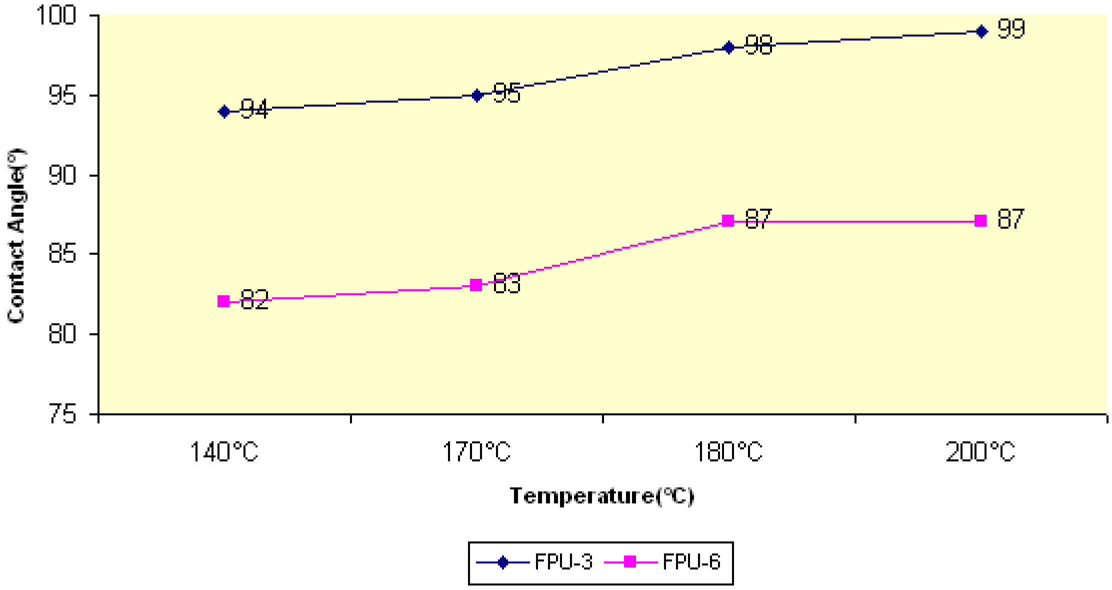


Figure 4.7 : Contact angle graph of FPU-3 and FPU-6 films.

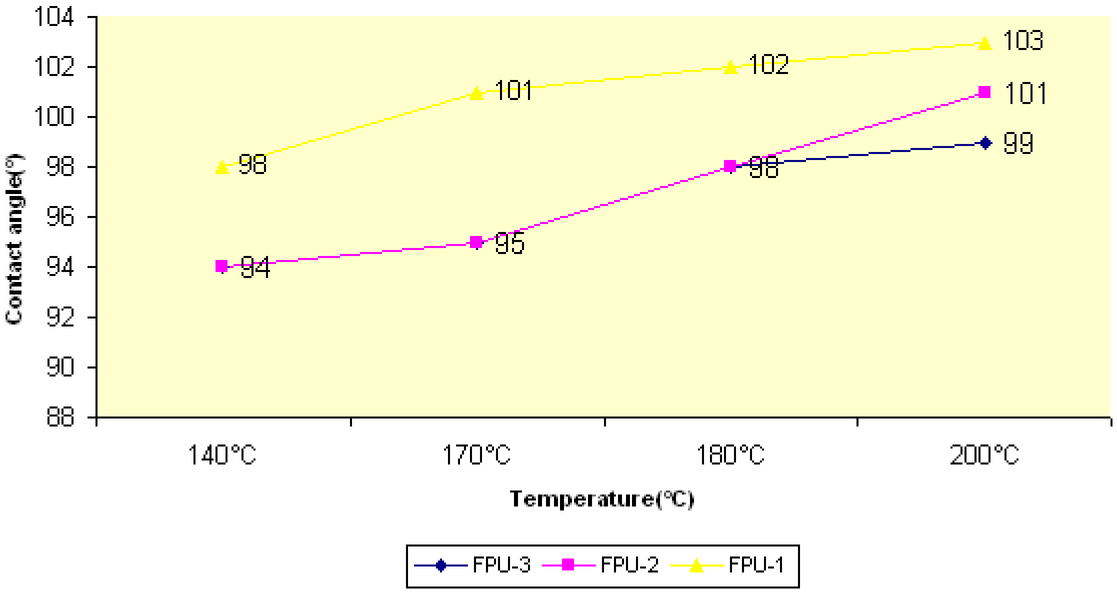


Figure 4.8 : Contact angle graph of FPU-1, FPU-2 and FPU-3 films.

As a result of contact angle measurement,

- Curing temperatures have a significant affect on the water contact angle of all coatings.
- As the adding of fluorine containing compounds increased, water contact angles increased steadily for all coatings.
- Coatings prepared with F-OH compound have higher contact angle values when compared other films implying that F-OH compound was chemically bonded to our polyurethane chain.

4.4 Pendulum Hardness Tests

König pendulum hardness tests are applied after all formulations coated glass substrate and cured with different temperatures from 140°C to 200°C.

Table 4.3 : Pendulum hardness results

Sample Name	**140°C**	**170 °C**	**180°C**	**200°C**
FPU- 1	53	57	61	63
FPU- 2	47	49	50	52
FPU- 3	41	43	46	49
FPU- 4	40	42	42	45
FPU- 5	23	28	33	35
FPU- 6	15	17	17	20
Non-fluorinated	30	32	33	40

The results are given at Table 4.3 and related graphs are shown at Figure 4.9 and Figure 4.10.

As it seen at Figure 4.9 and 4.10, pendulum hardness of samples have increased with increasing temperature from 140°C to 200°C which means as curing increases, pendulum hardness of film surfaces have increased for all formulations.

The data suggests that hardness values of F-OH containing films, named FPU-1, FPU-2 and FPU-3, increase with increasing fluorine concentration. For instance, the hardness values of 0.1%, 0.4% and 0.7% F-OH containing films at 200°C were 49, 52, 63, respectively. Similarly, for other films increasing surface hardness have observed with increasing fluorine concentration. The difference in values of pendulum hardness between F-OH containing films and other fluorinated agents (Krytox® 100,Krytox® 103 and Fluoroguard®) containing films can be due to the chemical structure of these agents. As indicated before, F-OH is a aromatic type fluorinated alcohol and it makes coating more stiffer. The nature of other fluorinated agents are perfluoropolyether and ether bond lead to coating become soften.

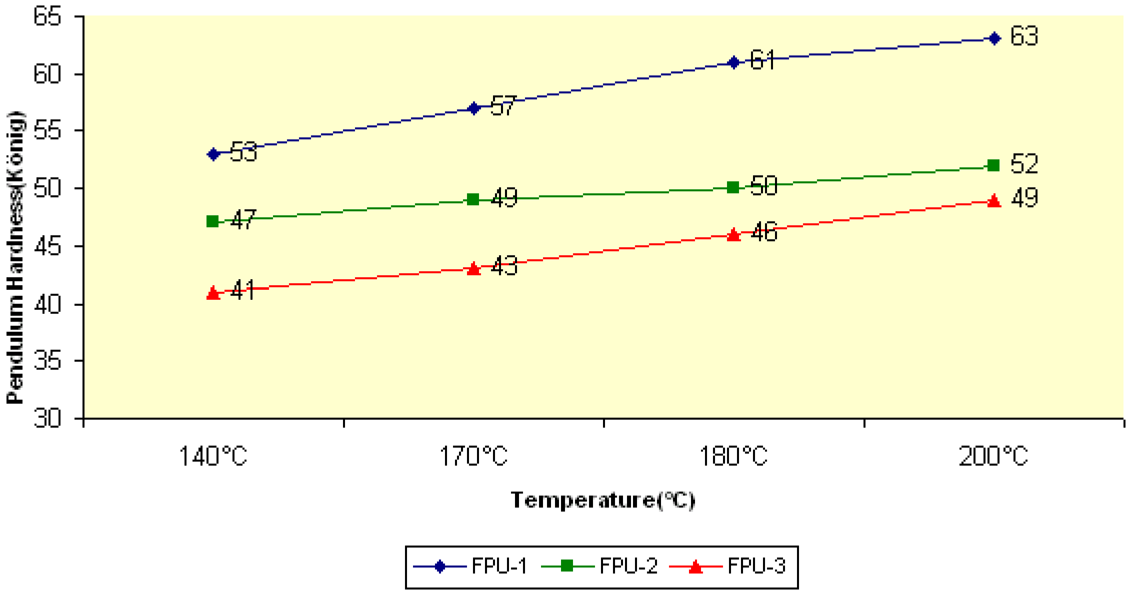


Figure 4.9 : Pendulum hardness graph of FPU-1, FPU-2 and FPU-3 films.

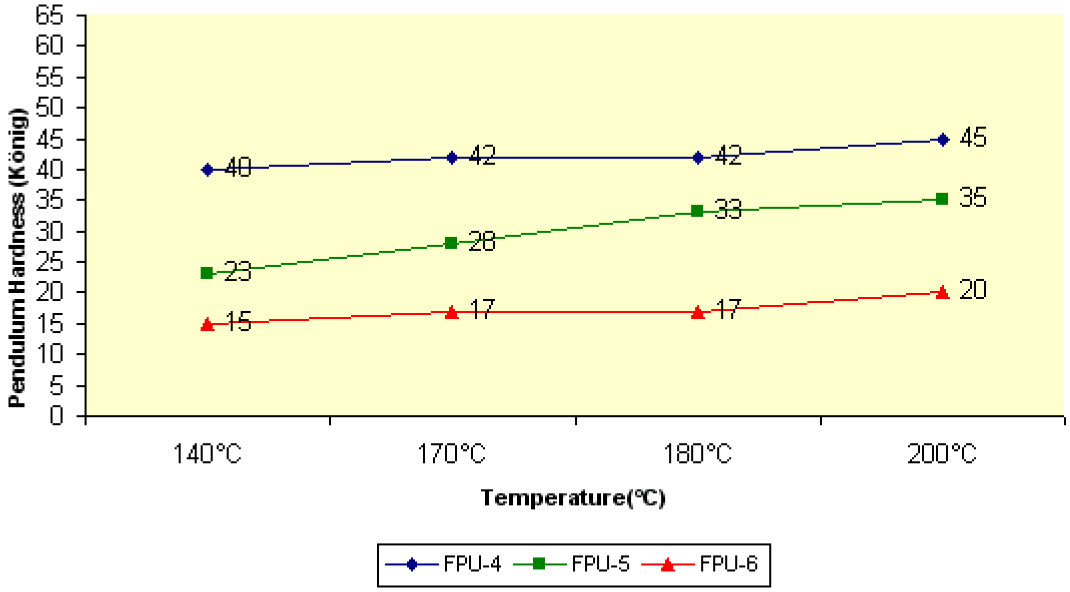


Figure 4.10 : Pendulum hardness graph of FPU-4, FPU-5 and FPU-6 films.

As a result of pendulum hardness test,

- Pendulum hardness of samples have increased with increasing temperature from 140°C to 200°C.
- Structure of fluorine containing compound used in formulations has a strong effect on the surface hardness.

- Krytox® 100,Krytox® 103 and Fluoroguard® have an ether bond and their low surface hardness results may be due to the softening effect of this ether bond.
- F-OH component is a aromatic type of fluoro alcohol so we obtained more rigid surfaces with utilising F-OH as a fluorine containing compound.

4.5 Scanning Electron Microscopy(SEM) Analysis

Scanning Electron Microscopy(SEM) was used to understand bulk morphology of fluorinated polyurethane. Until now, FPU's which prepared by F-OH as a fluorine containing compound (especially FPU-1) showed the best results in all analysis, so the SEM analysis are carried out for only this type of samples and the results are compared with non-fluorinated samples.

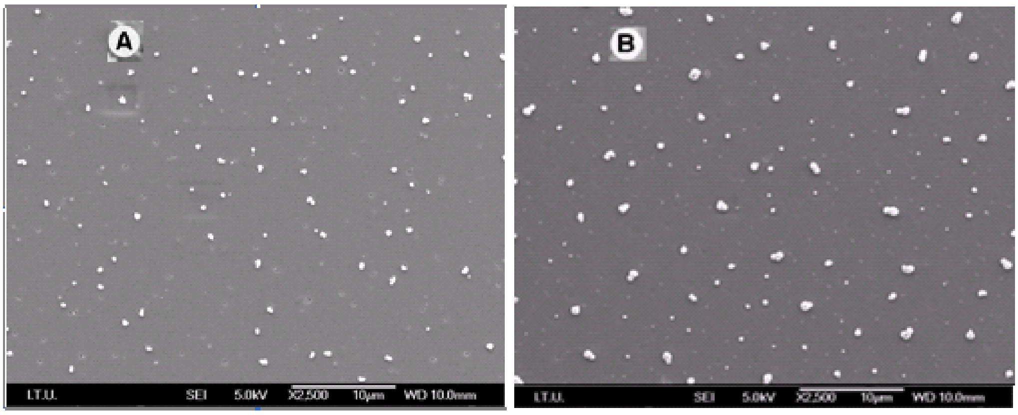


Figure 4.11 : SEM of fluorinated and non-fluorinated polyurethanes. (A) Non-fluorinated polyurethane(magnification= 2500×),(B) Fluorinated polyurethane (FPU-1, magnification= 2500×)

Figure 4.11(A) is the SEM micrograph of surface of the non-fluorinated polyurethane. It shows an equably size distribution of phase micro-domains, with so many small balls standing out. The same morphology is observed for FPU-1 [Fig. 4.11(B)] . It shows very different size of small ball from non-FPU. The macrostructure of non-FPU and FPU-1 are all regular, which suggest the being of micro-phase separation. All this is due to a higher incompatibility between fluorinated side chains soft segment, other soft segment and hard segment because of large differences in chemical structure. The dimension of the balls attributes to the different fluorine content in the FPU films. With the increasing fluorine content, the size of balls tends to increase. Similarly, the bulk structure of the fluorinated polyurethane has intensively been investigated Tonelli et al. [46] in the study of the fluorinated polyurethanes composed of 4,40-methylenebis (phenylisocyanate) (MDI), 1,4-butanediol (BDO) and perfluoropolyether (PFPE), observed that the due to the incompatibility of the fluorinated soft and the hard segments, and that synthesis methods affected the morphology and microstructure.

5. CONCLUSIONS

Six different fluorinated polyurethane coating formulations based on blocked polyisocyanates are prepared. To fluorinate the polyurethane surfaces, four different chemicals were used. One of these chemicals, named F-OH, is a special type of aromatic fluorinated mono alcohol and synthesized in our laboratory. Others (Krytox® 100, Krytox® 103 and Fluoroguard®) are synthetic fluorinated oils and generally used as a lubricant in industry.

Firstly, all formulations were applied on glass substrates and cured with temperatures between 140°C and 200°C. As a second step, obtained free films (films peeled off glass substrates in water) were tested for their, thermal, morphological and surface properties.

Infrared analysis showed absorption band of -NCO and -OH group are not found in spectrums and this result proves the synthesis of fluorinated polyurethane. In addition, the band caused by the C-F bond are observed, which indicates the presence of fluorine in all types of coatings.

Contact Angle results of cured films showed us that, the wetting contact angle for water on FPU films increases with increasing fluorine concentration, indicating improvement on the hydrophobic performance of the FPU films with fluorine incorporation. The FPU film modified with 0.7% F-OH at 200°C is the most hydrophobic surface with contact angles of 103. The chemical bonding betweeen hydroxyl functionality of F-OH and –NCO functionality of polyisocyanate can cause this higher water contact angle when comparing other fluorinated agents. Similarly, a higher curing temperature also led to a surface enrichment of the fluorinated species.

Pendulum hardness of samples have increased with increasing temperature from 140°C to 200°C which means as curing increases, pendulum hardness of film surfaces have increased for all formulations. Besides, Krytox® 100,Krytox® 103 and

Fluoroguard® have an ether bond in their chemical structure and their low surface hardness results may be due to the softening effect of ether bond.

Thermal behaviour of FPU films are determined by using TGA. According to TGA results, a slight increase in thermal stability at 50% of all FPU films with increasing cure temperature between 140°C and 200°C and increasing fluorine concentration.

SEM images of FPU films demonstrated that a higher incompatibility between fluorinated side chains soft segment, other soft segment (including polyol) and hard segment with the increasing fluorine content because of large differences in chemical structure.

Consequently, we succesfully synthesized fluorine containing polyurethane coating materials by using blocked polyisocyanate and different fluorinated agents. All results have been consistent with each other and the best results have obtained from coatings which utilise F-OH as a fluorine-containing agent. F-OH has a hydroxyl group and it was chemically bonded to our polyurethane chain when compared with the others.

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