A Study on the Thermal Degradation Resistance of Thermoplastic Polyurethane Coatings

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A STUDY ON THE THERMAL DEGRADATION RESISTANCE OF THERMOPLASTIC POLYURETHANE COATINGS

By

MONTASER MOHAMED ZAMZAM

A Thesis Submitted to the Faculty of Graduate Studies
United Arab Emirates University
In Partial Fulfillment of the Requirement for the Degree of Master of Science in Materials Science and Engineering

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TO

MY GREATEST PARENTS

AND

BELOVED WIFE
ABSTRACT

In this work, a comprehensive study of thermoplastic polyurethanes (TPUs) and the influence of the hard block content on their performance was carried out. The study comprises an extensive literature survey of the chemistry, structure and properties, and degradation and stability of TPUs, an experimental section dedicated to the materials, methodologies and instrumentations involved in the execution of the study, and a results and discussion section detailing all the findings and interpretation of the investigation.

TPU elastomers were prepared from 4,4'-diphenylmethane diisocyanate (MDI), monoethylene glycol (MEG), triethylene diamine (Dabco EG), Coil G-211 poly(ester) diol using the "one shot" melt polymerization process. The hard-segment content of polyurethane prepared in this study was in the range of 29-48 wt %. TPU samples were thermally aged in an air oven at 100°C for 7 and 14 days. The effects of the hard-segment concentration (HSC) as well as thermal aging duration on the polyurethane structure and abrasion resistance were investigated using differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), Fourier-transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM) and a rotary drum abrader.

Endothermic peaks at low temperatures (77-102°C) were identified in DSC for various samples and attributed to the distribution of hard segment crystallites with relatively short-range order. Single or multiple endothermic peaks were also observed at higher temperatures (150-181°C) and identified as the melting transition of hard segment crystallites with long-range order. The melting peak temperature was found to increase with the HSC. The thermal stability of TPU samples was investigated using TGA, which
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ABSTRACT

In this work, a comprehensive study of thermoplastic polyurethanes (TPUs) and the influence of the hard block content on their performance was carried out. The study comprises an extensive literature survey of the chemistry, structure and properties, and degradation and stability of TPUs, an experimental section dedicated to the materials, methodologies and instrumentation involved in the execution of the study, and a results and discussion section detailing all the findings and interpretation of the investigation.

TPU elastomers were prepared from 4,4'-diphenylmethane diisocyanate (MDI), monoethylene glycol (MEG), triethylene diamine (Dabco EG), Coim G-211 poly(ester) diol using the "one shot" melt polymerization process. The hard-segment content of polyurethane prepared in this study was in the range of 29-48 wt %. TPU samples were thermally aged in an air oven at 100°C for 7 and 14 days. The effects of the hard-segment concentration (SC) as well as thermal aging duration on the polyurethane structure and abrasion resistance were investigated using differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), Fourier-transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM) and a rotary drum abrader.

Endothermic peaks at low temperatures (77-102°C) were identified in DSC for various samples and attributed to the distribution of hard segment crystallites with relatively short-range order. Single or multiple endothermic peaks were also observed at higher temperatures (150-181°C) and identified as the melting transition of hard segment crystallites with long-range order. The melting peak temperature was found to increase with the HSC. The thermal stability of TPU samples was investigated using TGA, which
indicated that all samples started to decompose at temperatures well above 175°C in a distinct two-step degradation mechanism. The material loss after the first stage correlates well with the HSC. The onset temperatures of degradation also increased with the increase in HSC except for one case in which samples with 47.8% HSC started degradation at lower temperature than those with 41.5% HSC.

The abrasion resistance of the various materials to scrubbing stresses was also found to increase with the increase in HSC, which confirmed the increase in the microphase separation with the increase in the HSC. Mesoscopic morphological investigations using SEM detected an alternating hard and soft segment lamellar structure.

However, it was observed that thermal aging at 100°C for 14 days did not cause chain degradation or apparent chemical changes to the TPU samples. FTIR confirmed that no major alteration of the urethane link took place due to aging. Indeed, microphase separation has been affected due to the effect of thermal aging on the hydrogen bonding. Increasing aging duration was found to reduce phase separation and increase phase mixing of the hard and soft domains with more pronounced effect on the higher HSC samples. That was reflected in the broadening of the FTIR characteristic peak of urethane links at 1730-1710 cm⁻¹ for the aged samples. The same was also confirmed by having an increased rate of lost volume in the abrasion test with the increase of the aging duration.
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<th>Description</th>
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<tbody>
<tr>
<td>Å</td>
<td>Angstrom</td>
</tr>
<tr>
<td>ASTM</td>
<td>American Society for Testing and Materials</td>
</tr>
<tr>
<td>CO₂</td>
<td>Carbon dioxide</td>
</tr>
<tr>
<td>DFM</td>
<td>Dimethylformamide</td>
</tr>
<tr>
<td>DMAc</td>
<td>Dimethylacetamide</td>
</tr>
<tr>
<td>DSC</td>
<td>Differential Scanning Calorimetry</td>
</tr>
<tr>
<td>DSiD</td>
<td>Diphenylsilanediols</td>
</tr>
<tr>
<td>DTG</td>
<td>Differential thermogravimetric Analysis</td>
</tr>
<tr>
<td>EG</td>
<td>Expandable graphite</td>
</tr>
<tr>
<td>FTIR</td>
<td>Fourier-Transform Infrared Spectroscopy</td>
</tr>
<tr>
<td>HDI</td>
<td>Hexamethylene diisocyanate</td>
</tr>
<tr>
<td>HSC</td>
<td>Hard-segment concentration</td>
</tr>
<tr>
<td>HTPB</td>
<td>Hydroxy-terminated polybutadiene</td>
</tr>
<tr>
<td>IPDI</td>
<td>Isophorone diisocyanate</td>
</tr>
<tr>
<td>MDI</td>
<td>Diphenylmethane diisocyanate</td>
</tr>
<tr>
<td>MEG</td>
<td>Monoethylene glycol</td>
</tr>
<tr>
<td>NCO</td>
<td>Cyanate group</td>
</tr>
<tr>
<td>NDI</td>
<td>Naphthalene-diisocyanate</td>
</tr>
<tr>
<td>NH</td>
<td>Amine group</td>
</tr>
<tr>
<td>PMDI</td>
<td>Polymeric methylene diphenyl diisocyanate</td>
</tr>
<tr>
<td>P-PU</td>
<td>Phosphorus-containing polyurethanes</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Description</td>
</tr>
<tr>
<td>--------------</td>
<td>-------------</td>
</tr>
<tr>
<td>PTHF</td>
<td>Polytetrahydrofuran</td>
</tr>
<tr>
<td>PU</td>
<td>Polyurethane</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning electron microscopy</td>
</tr>
<tr>
<td>SSC</td>
<td>Soft-segment concentration</td>
</tr>
<tr>
<td>TDI</td>
<td>Toluene diisocyanate</td>
</tr>
<tr>
<td>$T_g$</td>
<td>Glass transition temperature</td>
</tr>
<tr>
<td>TGA</td>
<td>Thermogravimetric Analysis</td>
</tr>
<tr>
<td>$T_m$</td>
<td>Melting temperature</td>
</tr>
<tr>
<td>TPU</td>
<td>Thermoplastic Polyurethanes</td>
</tr>
<tr>
<td>UV</td>
<td>Ultraviolet radiation</td>
</tr>
<tr>
<td>VOC</td>
<td>Volatile organic compounds</td>
</tr>
<tr>
<td>XDI</td>
<td>m-xylene diisocyanate</td>
</tr>
</tbody>
</table>
1.1 Motivation

Thermoplastic Polyurethanes (TPUs) are an important class of thermoplastic elastomers produced by reacting diisocyanates with polyols and other chemicals. Polyurethanes, in general, range from flexible or rigid lightweight foams, to tough, stiff elastomers. This allows them to be used in a wide diversity of consumer and industrial applications such as high-performance elastomers, artificial-heart blood vessels, sealants and coatings. Typical TPU elastomers are multi-block copolymers comprised of alternating “soft” polyether or polyester segments and “hard” segments. The thermodynamic incompatibility of these segments, often combined with crystallization of either or both segments, drives their microphase separation into hard and soft phases that are, respectively, below and above their glass-transition temperatures. This microphase separation is responsible for the excellent elastomeric properties of TPUs. Polyurethanes are normally produced by reacting a polyether or polyester diol with a diisocyanate (NCO) and a chain extender in case of TPU elastomers and a cross-linker in case of rigid foams. However, a number of other ancillary chemicals and processing aids are usually required to allow sufficient control to produce useful commercial products. Catalysts, for example, are needed to allow the reaction to progress at a speed compatible with production processes. Physical cross-linking is present in these materials as a consequence of the hydrogen-bonding formation between the various urethane groups.
These hydrogen bonds are weak in nature and could form and break easily giving rise to a host of various properties for the elastomer. The main driving force for phase separation is the possibility for optimal hydrogen-bonding formation among the various hard-segment units.

Polyurethane coatings with low NCO content result in slower reactivity and/or higher flexibility. Alternatively, coatings with higher NCO content produce coatings with superior hardness. The NCO content affects directly the hard block content of the elastomeric samples. Polyurethanes with higher hard block content are stiff materials with higher hardness values whereas polyurethanes with lower hard block content are gum-like materials with lower hardness values.

TPU coatings combine fast curing and water insensitivity with exceptional mechanical properties, chemical resistance and durability. The result is good weathering and extreme abrasion resistance as compared to other coating systems such as epoxy resins, which tend to crack under impact whereas polyurethane systems tend to yield under impact. The systems are 100% solids making them compliant with the strictest environmental regulations. Due to its specific curing profile and exceptional film properties, the application of polyurethane coatings has been extended into various areas including roof coatings, pipe protection, inner pipelining and repair, freight ship liners, conveyer belts and others.

The environment and service conditions surrounding coated pipelines represent real challenge to the coating system, particularly in the UAE desert. Several factors contribute to form harsh service conditions for pipeline coating such as the so called “sabkha soil” which is sandy soil with high level of salty water contents. Ambient
temperatures may reach $50^\circ$C for the summer durations. Temperatures of the metallic exposed surface-laid pipeline may actually exceed $80^\circ$C under these conditions, depending on the pipe color, solar intensity and flow rate within the pipeline. Humidity is also unusually high and may reach 100% with an extremely high UV radiation. Therefore, these harsh environmental conditions, which prevail in this part of the world, make the study of their effects on TPU s an essential one.

1.2 Aims and Objectives

In order to test the thermal resistance of polyurethane coatings of various hardness values, several samples of different hard block content (resulting in corresponding hardness values in the range of 55-90 Shore A) are examined against thermal degradation. The thermal degradation is performed using the oven method as described by the ASTM 0573-99. The thermal behavior of the various polyurethane samples is investigated using differential scanning calorimetry (DSC). The mechanical response of the various coatings to thermal aging is determined using the abrasion test. In order to relate the mechanical performance of these materials to their physical nature and chemical structures, spectroscopic analysis using infra-red techniques and scanning electron microscopy (SEM) are performed on the thermally degraded samples.

The objectives of this investigation are as follows:

1. To perform an accelerated thermal aging on various thermoplastic polyurethane elastomers of different hard block content.
2 To investigate the effect of the hard block content on the thermal behavior of aged polyurethane elastomers using differential scanning calorimetry and thermogravimetric analysis.

3 To measure the dependence of the abrasion resistance of the various elastomers as possible coating candidates on the hard block content and thermal aging durations.

4 To study the influence of the thermal degradation on the chemical structure of polyurethane coatings using FTIR and on the morphology of the elastomers using scanning electron microscopy SEM.

1.3 Outline of the thesis

The thesis is divided into five chapters; chapter one (this chapter) presents the motivations, aims and objectives of the study. Chapter two provides literature review on the areas related to the study including TPU chemistry, structure-property relationship, thermal degradation, and coating application. The experimental part is presented in chapter three including the materials and characterization techniques. Chapter four discusses the results of the experimental part. The chapter includes two main sections, one for the effect of hard segment concentration (HSC) on the TPU properties and the other for the effect of thermal degradation on the polymer. Chapter six ends the study with conclusion and recommendations for future investigations.
CHAPTER TWO

LITERATURE REVIEW

2.1 Polyurethanes industry

2.1.1 History

Germany remained preeminent in the synthetic fiber field for 20 years since introducing the polyvinyl-chloride fibers in 1913 until 1935 when Carothers in the U.S. discovered the nyons. In 1937, Otto Bayer and coworkers at I. G. Farbenindustrie, Germany invented polyurethanes as one of the major breakthroughs in the polymer chemistry. Rink and Associates were awarded the first U.S patent on polyurethanes in 1938. DuPont and ICI incorporations soon recognized the desirable elastomeric properties of polyurethanes. The industrial scale production of polyurethane started in 1940 and subsequent market growth of these materials was seriously impacted by World War II [1]. Since 1945, there were many patents issued on the preparation of polyurethanes from the reaction of diamines and bischloroformates at low temperatures [2]. It was not until 1952, when polyisocyanate, especially toluene diisocyanate (TDI), became commercially available and noticeable improvements in polyurethane elastomers and foams began to be recognized. In 1958, Schollenberger of BFGoodrich introduced a new "virtually cross-linked" thermoplastic polyurethane elastomer. At approximately the same time, DuPont announced a Spandex fiber called Lycra, which is a polyurethane based on PTMO, 4,4'-
diphenylmethane diisocyanate (MDI) and ethylene diamine. In 1995, the world production of polyurethanes approached 8 million tons, which is about 5% of the world total consumption of plastics [1-3].

2.1.2 Polyurethanes applications

It is virtually impossible for anyone not to come in contact with a variety of polyurethanes several times during a day. It is estimated that the average family probably owns somewhere between 10 and 50 kilos of polyurethanes [4]. Because of their unique properties, polyurethanes have found a wide variety of applications especially in automotive, construction and furniture industries. In automobile industry, polyurethanes forms over 20% of the materials used to build a modern car. Typical components are dashboards, bumper covers, moldings, and fenders. In car as well as furniture industries flexible foams are used to make bedding, sofas, cushions, carpet backs and car seats. In construction industry, rigid foams are used for insulation in freezers, refrigerators and building walls and roofs. Several elastomers, coatings, adhesives and medical items are made of solid polyurethanes. Additionally, shoe manufacturers use tough elastomeric polyurethanes as shoe soles.

2.1.3 Polyurethane elastomer

The term elastomer is a definition for the material which at room temperature can be stretched repeatedly under low stress to at least twice its original length and upon immediate release of the stress will return to its approximate original length [3]. Polyurethane elastomers are an important member of the thermoplastic elastomer family. Their advantageous properties include high hardness for a given modulus, high abrasion
and chemical resistance, excellent mechanical and elastic properties, and blood and tissue compatibility [5-8].

Generally, polyurethane block copolymers are comprised of a low glass transition or low melting "soft" segment and a rigid "hard" segment, which often has a glassy Tg, or crystalline melting point well above room temperature. The soft segment is typically a polyester-, or polyether-polyol. The hard segment normally includes the connection of a diisocyanate (aromatic or aliphatic) and a low-molecular-weight diol or diamine, the chain extender. The combination of this soft polyol segment and hard segment forms an (AB)n type block copolymer. By varying the structure, molecular weight of the segments, and the ratio of the soft to the hard segments, a broad range of physical properties can be obtained. The materials can be hard and brittle, soft and tacky, or anywhere in between.

Polyurethane elastomers usually exhibit a two-phase microstructure, which arises from the chemical incompatibility between the soft and the hard segments. The hard, rigid segment segregates into a glassy or semicrystalline domain and the polyol soft segments form amorphous or rubbery matrices in which the hard segments are dispersed at varying content levels. The hard domain in this two-phase microstructure can act as a physical cross-linking point and reinforcing filler, while the soft segment behaves as a soft matrix. This microphase separation results in superior physical and mechanical properties, such as high modulus and high reversible deformation. The degree of phase separation or domain formation not only depends on the weight ratio of the hard to the soft segment, but also on the type of chain extender, the type and molecular weight of the soft segment, the hydrogen bond formation between the urethane linkages, the manufacturing process, and reaction conditions [7, 9-14].
2.2 Chemistry of polyurethane elastomers

Polyurethane elastomers are obtained by reacting three monomers: (i) a diisocyanate, (ii) a macroglycol (linear long chain polyol), and (iii) a low-molecular-weight chain extender. Thus, the structure of the polyurethane will depend on the choice of these components and their reactivity [15].

2.2.1 Isocyanates

Modern polyurethane elastomers industry is centered on the isocyanate chemistry. This organic function group is capable of a surprisingly diverse range of chemical reactions. As the foundation of the polyurethane industry, isocyanates are the most heavily produced specialty organic chemicals. Generally the name isocyanate refers to diisocyanates. However, mono-isocyanates are also commercially useful [1].

2.2.1.1 Industrial isocyanates

Organic isocyanates are commercially available in either solid or liquid formats and include aliphatic, cycloaliphatic, aromatic and heterocyclic polyisocyanate. The most important aromatic isocyanates are toluene diisocyanate (TDI), methylene diphenyl diisocyanate (MDI), polymeric methylene diphenyl diisocyanate (PMDI) and naphthalene-1,5-diisocynate (NDI). The important aliphatic isocyanates include 1,6-hexamethylene diisocyanate (HDI), and isophorone diisocyanate (IPDI) [1]. The aliphatic isocyanates or their modified forms are widely used in the coatings industry because of their high resistance to ultraviolet light and outdoor weathering conditions [16,17].
2.2.1.2 Isocyanate reactions

The reactions of isocyanates fall into two broad categories: (i) active hydrogen donors and (ii) non-active hydrogen reactions. The first category requires at least one co-reagent containing one or more hydrogen atoms that are potentially exchangeable (or labile) under the conditions of the reactions. A typical example for this category is the reaction with the hydroxyl groups of polyols. Non-active hydrogen reactions constitute the second broad category and involve breaking the susceptible carbon-nitrogen bond. Some key isocyanate reactions are detailed as follows [1,18].

Reaction with [-OH] compounds:

Isocyanate reacts with alcohols and phenols to form urethanes. Reaction with phenols is significantly slower than that with aliphatic alcohols and yields less stable urethane. Figure 2.1 illustrates the addition reaction of isocyanate with alcohol (ester or ether) to form the urethane linkage

\[ R-\text{NH} \rightleftharpoons \text{C} \rightleftharpoons \text{O} \rightarrow \text{R-} \text{NH} \rightleftharpoons \text{C} \rightleftharpoons \text{OR} \]

Figure 2.1 Urethane linkage formation

Reactions with [-NH] compounds:

Primary and secondary amines react vigorously with isocyanates to yield urea as illustrated in Figure 2.2

\[ R-\text{N} \rightleftharpoons \text{C} \rightleftharpoons \text{O} + \text{NH}_2-\text{R} \rightarrow \text{R-} \text{NH} \rightleftharpoons \text{C} \rightleftharpoons \text{NHR} \]

Figure 2.2 Urea linkage formation
Reaction with water:

The reaction between isocyanate and water is a special case of an alcohol/isocyanate reaction. As illustrated in Figure 2.3, the primary product is the carbamic acid, which is not stable and decomposes to the corresponding amine and carbon dioxide. The amine formed will then react immediately with the isocyanate group in the system and forms a urea. Thus, to obtain high molecular weight linear thermoplastic polyurethane, it is essential to completely exclude water from the reaction system.

\[
R-N=C=O + H_2O \rightarrow \begin{array}{c}
\text{R-NH-C-OH} \\
\text{R-N=CO} \\
\text{R-NH-C-NHR - CO}_2
\end{array}
\]

Figure 2.3 Reaction between water and isocyanate

Reactions with urethane linkages:

Isocyanate can react with urethane groups under moderate to vigorous reaction conditions to form allophanate as illustrated in Figure 2.4.

\[
\begin{array}{c}
\text{R-NH-C-OR'} \\
\text{R-N=CO} \\
\text{O=C-NH-R}
\end{array}
\rightarrow \begin{array}{c}
\text{R-N-C-OR'} \\
\text{O=C-NH-R}
\end{array}
\]

Figure 2.4 Reaction with urethane

Reactions with urea:

Isocyanate can also react with the urea formed from the previous reactions to form stable biuret cross-link as illustrated in Figure 2.5.
Dimerization of isocyanates:

Isocyanates can react with itself (dimerize and trimerize i.e. undergo oligomerization) as illustrated in Figure 2.6.

[Chemical structure of dimerization reaction]

Figure 2.6 Dimerization reactions of isocyanates.

The aromatic isocyanates in particular are known to undergo these reactions even in the absence of a catalyst

Trimerization of isocyanates:

Trimerization occurs with both aliphatic and aromatic isocyanates and produces tri-substituted isocyanurate which are often quite stable as illustrated in Figure 2.7

[Chemical structure of trimerization reaction]

Figure 2.7 Trimerization of isocyanates
2.2.2 Polyols

The soft segments used in polyurethane elastomers are di-hydroxy terminated long chain macroglycols with a molecular weight from 400 to 5000 g mol\(^{-1}\). They include polyethers, polyesters, polydienes or polyolefins, and polydimethylsiloxanes. Polyurethane elastomers have traditionally been made from polyether or polyester soft segments. Polyester-based urethanes have relatively good material properties whereas the thermal behavior of polyester-based urethanes is dependant upon the concentration of the ester groups in the polyester. An increase in ester group concentration usually leads to a reduced flexibility at low temperatures, higher hardness, higher modulus and a marked increase in permanent elongation. When the application requires good environmental stability, a polydiene based soft segment is a good candidate [1].

2.2.3 Chain extenders

Low molecular weight diol and diamine chain extenders play a very important role in the synthesis of polyurethanes. Polyurethane chain extenders can be categorized into two classes: aromatic diol and diamine, and the corresponding aliphatic diol and diamine. In general, polyurethanes chain extended with an aliphatic diol or diamine produce a softer material than do their aromatic chain extended counterparts. Also, diamine chain extenders are much more reactive than diol chain extenders and give properties superior to those of similar polymers prepared with the equivalent diol chain extender. This is because the hard segment (urea linkage) has a higher density of hydrogen bonding, which results in a higher \(T_g\) and higher thermal stability. Common chain extenders for polyurethane synthesis are 1,4-butandiol, 1,6-hexandiol, ethyleneglycol, ethylenediamine and 4,4’-methylenebis(2-chloroaniline).
method, the first step is to react the polyol with excess diisocyanate to form a diisocyanate terminated intermediate oligomer, i.e. a prepolymer, with a molecular weight of 1000 to 5000 g mol\(^{-1}\), depending on the polyol's molecular weight and the ratio between the two reactants. The prepolymer that is formed is normally a viscous liquid, or a low-melting-point solid, which can be easily stored. The next step is to convert this prepolymer to the final high molecular weight polyurethane by further reaction with a diol or diamine chain extender. This step is usually referred to as chain-extension.

A polyurethane structure made by the two-step method tends to be more regular than the corresponding polyurethane made by the one-step method [20]. Accordingly, the polymer chain has a more regular hard-soft-hard sequence distribution as compared to the random distribution of hard segments in the one-shot process, which leads to a narrower hard segment size distribution than in the one-shot method.
2.3 **Structure and properties of segmented TPU elastomers**

The structure and properties of segmented polyurethane have been extensively studied for more than 40 years for many different applications [21-29]. Some factors that affect the structure and properties of segmented polyurethane are discussed in the following review.

### 2.3.1 Morphology

It is evident that the morphology of a multiphase system plays an important role in determining the final properties of the polymers. The desired properties of a material can be obtained by controlling the morphology [30]. Hence, a profound knowledge of the morphology of the produced material is essential to understanding the structure-property relationships. The morphology of segmented polyurethanes is very complicated, not only because of their two-phase structure, but also because of other physical phenomena such as the crystallization and hydrogen bonding formation within both the hard and soft domains.

From a thermodynamic point of view, the incompatibility between the polar hard segment and the less polar soft segment in polyurethanes causes the heat of mixing to be positive and drives the two segments to phase separate. The degree of phase segregation between the hard and soft segments depends on the molecular weight and the interaction of hard segments with each other on one hand and with the soft segments on the other hand. For example, phase segregation is more pronounced in polybutadiene urethanes than in polyether urethanes, and is least evident in polyester
urethanes. Moreover, the interaction between the hard segments depends on the symmetry of the diisocyanate and on the selection of the chain extender (diol or diamine). A diisocyanate and a chain extender having a more symmetrical structure will enhance the formation of organized structures, and thus, more phase segregation. A urea-containing hard segment formed from low molecular weight diamine chain extender has a much more pronounced phase separation than urethane-containing hard segments because of the higher polarity of the urea hard segment. Multifunctional cross-linkers reduces the degree of phase separation due to the high cross-linking density of the reduced products, which reduces the movement of the polymeric chains necessary for high degree of phase separations [31].

The morphology of segmented polyurethanes can be studied at three different structural levels according to their size [32]. The smallest structural level is the molecular structure such as crystal structure, block sequence and sequence distribution. The second level of structure is domain structure, which has the dimension of 50-1000\(\text{Å}\). A complete description of sample morphology at this level consists of the determination of the phase volume fraction, size, shape, orientation, connectivity, and interfacial thickness as a function of segment content and sample history. The third level of morphology is spherulitic texture where the size considerations are in the micron range.

Several works have elucidated the existence of two-phase microstructure of polyurethanes [32-34], other studies were concerned with the factors that affect phase separation and/or phase mixing [35,36]. However, it is generally accepted that the two phases are not completely separated due to the presence of appreciable hydrogen
bonding between the hard and soft segments [7,12]. A schematic representation of the two phase segmented structure as adopted from Qi and Boyce [17] is illustrated in Figure 2.8.

![Diagram of domain structure in segmented copolymer]

(a) Low HSC  (b) High HSC

Figure 2.8 Representation of domain structure in segmented copolymer

Li and coworkers [38] studied the morphology of polybutadiene/BD/MDI-based polyurethanes having variable HSC. A rod-like or lamellar structure was observed for polyurethane with hard segment concentration of 42%-67%. However, when the hard segment was less than 31wt%, the hard segment phase was dispersed in the matrix of soft segments in the form of either short cylinders or spheroids.

2.3.2 Structure-Property relationship

The primary structure of a segmented polyurethane includes chemical composition, type, molecular weight and distribution of hard and soft segments, block length distribution (distribution of segment size), and degree of branching or cross-linking. These primary structures determine the secondary structure, such as three-dimensional chain orientations, crystallinity, and consequently, the morphology of the polyurethanes. Both primary and secondary structures contribute to the final properties
The primary structure can be well controlled by synthesis conditions. For example, varying the ratio of the soft and hard segments can control the composition. The distribution of segment size is also closely related to the synthetic method. The two-step prepolymer method affords a more regular structure than the one-step route. The branching and cross-linking can also be attributed to the synthetic strategy. For example, the branching and cross-linking structures formed during the synthesis of linear segmented polyurethanes are caused by the side reaction of isocyanate and urethane or urea linkage, which has been described previously.

2.3.3 Effect of diisocyanate

It has been shown that the structure and properties of the diisocyanates has a profound effect on high temperature properties. Factors such as high symmetry and rigidity in the p-phenylene diisocyanate have lead to high modulus and excellent tensile strength [39]. Reducing the bulkiness of the diisocyanate from naphthalene to 1,4-phenylene has resulted in a drop in modulus. Moreover, it has been also shown that the effect of the methyl group is remarkable and results in a large drop in modulus. This is due to the fact that the methyl substituent can seriously disrupt the symmetry and crystallizability of the diisocyanates. Nevertheless, the symmetry of MDI is sufficient to allow the preparation of a semicrystalline hard block, which is reflected by its excellent tensile strength.

Aliphatic, e.g. hexamethylene diisocyanate, or cycloaliphatic diisocyanates, e.g. hydrogenated MDI, can offer better light stability over the aromatic isocyanate. They also show an increased phase separation behavior over the corresponding aromatic.
diisocyanates. When the properties of \( \text{H}_2\text{MDI} \) elastomers were compared with those of the analogous \( \text{MDI} \) series, the aliphatic diisocyanate based elastomers generally had superior mechanical properties.

2.3.4 Effect of polyol

The mobility of the polyol affects the low-temperature properties as well as the ultimate stress values of the segmented polyurethane. Features related to the mobility of the polyols such as \( T_g \), \( T_m \) and the ability to crystallize under deformation affect to a great extent the mechanical properties. Polyol mobility depends to a large extent on the type and the molecular weight of the polyol. To prepare products with typical rubber elasticity, an average molecular weight of between 1000 and 4000 g mol\(^{-1}\) (which corresponds to a chain length of 180 and 300 Å) is desirable. [18] Higher molecular weight polyols afford materials with better tensile properties but with an increased tendency to cold-harden, which is a phenomenon caused by gradual crystallization of the flexible blocks during storage. In general, increasing the molecular weight of the soft block decreases the modulus and increases the elongation at break. Furthermore, polyether-based TPU have superior abrasion resistance to those produced from polyester diol [3].

However, polyethers usually have a lower glass transition temperature and a weaker interchain force than polyesters, which usually renders the corresponding polyurethanes with reduced mechanical properties. This is often attributed to the stronger hydrogen bonding between the NH and the ester carbonyl group than that between the NH and the ether oxygen atom.
2.3.5 Effect of chain extender

The use of chain extender affects the polyurethane properties. Without a chain extender, polyurethanes formed by directly reacting diisocyanates and polyols generally have very poor physical properties and often exhibit monophase polymer. Thus, the introduction of a chain extender permits hard-segment segregation and consequently improved mechanical properties such as an increase in the modulus and an increase in the hard-segment glass transition temperature (T_g) of the polymer. By modifying the ratio between the polyol and chain extender, polyurethanes can change from a hard, brittle thermoplastic to a rubbery elastomer as a result of the variation of the hard segment concentration (HSC) in the block copolymer.

The type of chain extender affects the polyurethane properties. For instance, when diamine is used as chain extender, better physical properties are usually obtained than if a diol is used. This can be explained by the stronger interchain interaction from the urea linkage compared to the urethane linkage produced from the reaction with diol.

2.3.6 Hydrogen bonding

The hydrogen bond is the strongest secondary chemical bond with a strength estimated to be about 20-50 kJ mol\(^{-1}\)[10]. Polyurethanes are extensively hydrogen bonded, which involves the N-H group as proton donor and the urethane carbonyl, the ester carbonyl (in polyester urethane), or the ether oxygen (in polyetherurethanes) as proton acceptor. Hydrogen bonding in polyurethanes can be readily detected and studied by IR spectroscopy. The hydrogen bonded and free N-H, urethane carbonyl C=O, urea carbonyl C=O are the peaks of interest [40,41]. Marcos-Fernandez and co-workers [42]
used FTIR techniques to investigate the hydrogen bonding characteristics of non-blown elastomers. The carbonyl (C=O) stretching region (1750 – 1600 cm\(^{-1}\)) was used to characterize the hydrogen bonding state of these elastomers by identifying the contribution of the non-associated and associated carbonyl groups to the total absorption. Five distinct peaks were identified in this region and were used to characterize the hydrogen bonding status of the urea and urethane groups. The peaks at 1730 cm\(^{-1}\) and 1710 cm\(^{-1}\) were shown to correspond to the free and bound urethane carbonyl groups, respectively. A well-defined peak at 1694 cm\(^{-1}\) was calculated to correspond to the free urea. A broad peak in the vicinity of 1690-1660 cm\(^{-1}\) was identified to correspond to single and loosely ordered hydrogen bonded urea groups where the carbonyl oxygen of one urea group is bonded to a single hydrogen atom or to two hydrogen atoms that belong to two different urea groups, respectively. The last peak was a well-defined sharp peak at 1640 cm\(^{-1}\) corresponding to the bifurcated hydrogen bonded urea groups, as the carbonyl oxygen is bonded to two hydrogen atoms of the same urea group. These assignments show that the bifurcated urea hydrogen bonding has the highest energy [43] associated with every functional group and the presence of these strong hydrogen bonds inside the hard blocks will cause their glass transition temperature to increase dramatically. Born et al., [44] calculated the length of the urea hydrogen bond versus the urethane one. Their calculations showed that the length of the urea hydrogen bond is shorter (4.63 Å) than that of a urethane hydrogen bond (5.10 Å) in clear agreement with the assumptions made earlier regarding the strength of the different hydrogen bonds.

However, a basic concern of hydrogen bonding in polyurethanes is related to its role in phase separation. If hydrogen bonds could be formed between the two phases, a
higher degree of phase mixing should be assumed. On the other hand, if hydrogen bonds are formed only within the hard segment, they may enhance crystallization and thus, phase separation \[45,46\]. The extent of hydrogen bonding, or the hydrogen-bonding index (the ratio of bonded to free urethane carbonyl group), can be influenced by structure, composition of the polyurethane as well as temperature. A polyether urethane has fewer hydrogen bonds; about half as many carbonyl groups in polyether urethane are hydrogen bonded, when compared to polyester urethane with the same hard segment content. Increasing the hard segment content will increase the hydrogen-bonding index. At room temperature, approximately 90\% of the N-H groups in the hard segment of a typical polyurethane are hydrogen bonded \[47\]. However, hydrogen bonding starts to dissociate as the temperature increases and this process can be accelerated by approaching the glass transition of the hard segments.

The effect of hydrogen bonding on the mechanical properties of polyurethane is frequently used to explain various anomalies or improved properties. However, it is difficult to isolate this effect from the effects of the chemical structure and the physical nature of the polymer. Some studies have concluded that molecular mobility is not controlled by hydrogen bonding. Instead, it is believed that a rapid increase in molecular mobility accompanying glass transition allows the hydrogen bonding to dissociate \[47\].

### 2.3.7 Hard segment concentration

Soft segment concentration (SSC) is defined as the ratio of the mass of the polyol chains without terminal hydroxyl groups to the total mass of the polyurethane and usually expressed as a percentage. The difference making 100 \% is the hard segment concentration (HSC) \[1\]. The abrasion resistance of PU is related to the ratio of HSC \[3\]. Matthew et al,
[48] indicated that in the range of very low HSC (6.3-9.0 wt %), the HSC has little effect on the morphology. Increasing the HSC increases the glass transition temperature [10-19].

2.3.8 Crystallization

Crystallization of hard and soft segments provides additional information on the behavior of polyurethanes. The crystalline form of the hard segments depends on their structure, as well as on the crystallization conditions. The linearity and close fit of polymer chains favor crystallinity, which leads to a reduction in solubility, elasticity, elongation, and flexibility, and an increase in tensile strength, melting point, and hardness [1]. It has been shown that the chain extender length affects the structure of MDI/diol hard segments. 1,4-butanediol and longer diol chain extenders were used to produce structures whose properties depended on the number of methylene groups being odd or even. A polyurethane chain extended with "even" diols adopts the lowest energy fully extended conformational states that allows maximum hydrogen bonding formation and therefore higher crystalline order. This explains why elastomers based on 1,4-butanediol and higher diols generally possess better properties. Hard segments based on these chain extenders can crystallize more easily, thus improving the quality of the phase separation [18].
2.4 Degradation and stability of segmented TPU elastomers

Degradation is a process where deterioration in the properties of the polymer takes place due to various factors and lead to a significant change in the structure and properties of the material [50]. The following section is a review on the various factors, mechanisms and influences of degradation as well as different methods of hindering the degradation.

2.4.1 Degradation of segmented polyurethanes

All polymers can be de-polymerized and polyurethanes are no exception [1].

2.4.1.1 Processes of thermal degradation

There are several ways polyurethanes can be de-polymerized chemically including hydrolysis [51,52], thermolysis, oxidation, photolysis [16,17], pyrolysis, solvolysis and biologically-induced environmental stress cracking. Halim [46] added to this list chemical, mechanochemical, and radiation-induced degradation [53], biodegradation, degradation due to weathering and finally degradation during storage.

Thermolysis reactions are those that occur due to heat. Oxidation is a reaction in which oxygen combines chemically with another substance. Oxidation can be initiated with heat (thermo-oxidation) or by light (photo-oxidation) while pyrolysis is the transformation of a substance into other substances by heat alone i.e. without oxidation [1]. Purely thermal degradation is often called thermolysis, thermolytic, or pyrolytic degradation as oxygen is not involved. In speaking of thermal aging tests, one usually has in mind thermo-oxidative deterioration, i.e., reactions induced by thermal energy in the
presence of and with the participation of oxygen but in the absence of visible and near-ultraviolet radiation [54].

2.4.1.2 Thermal degradation

The thermal degradation and stability of polyurethanes have been extensively studied because of their great importance from the scientific and industrial point of view and their wide range of applications [50, 55]. It is normally caused by heat in presence or absence of oxygen whereas the latter promotes in the increase of the rate of degradation [46]. Khatua and Das [56] stated that degradation is normally regarded as a kinetic process and there is a definite correlation between the chemical structure of a polymer and its degradation temperature. Pandy, et al, [57] reported several studies on thermal aging, photodegradation or photo-yellowing of TPEEs. Van der Ven and coworkers [58] studied the durability of polyurethane topcoats and the fact that it is dependent on a large number of factors such as polymer composition, stabilization package and the conditions during weathering processes. Yang and co-authors [59] have investigated the weathering-induced degradation processes of the coating system for aircraft coatings facing outdoor exposure continuously throughout their service life. Pandy, et al, [50] have evaluated the durability of several polymer nanocomposites under different thermal and photo-environments. Qi-Wei Lu, et al, [60] stated that thermal degradation of polyurethanes in the melt is inevitable because melting usually occurs around or beyond the stability temperature of the urethane linkages.
2.4.2 Thermal degradation mechanisms and behavior

2.4.2.1 Mechanisms of thermal degradation

It is well known that there are three general types of reactions that a urethane segment may go through during its degradation: [61] (1) dissociation to isocyanate and alcohol; (2) formation of primary amine, carbon dioxide and olefins and (3) formation of secondary amine. Three degradation pathways are presented in Figure 2.9.

In dissociation reactions, urethane linkages can dissociate into the isocyanate and polyol from which it was formed. These reactions are reversible as long as the isocyanate is not lost to side reactions [1]. The second and third reactions produce primary and secondary amines and generate CO₂, which is lost as a gas. These reactions are naturally irreversible [1]. Backbone chain scission degradation can be divided as occurring via depolymerization, random chain breaking, weak-link or preferential site degradation or some combination of these general routes. Szycher [1] explained that thermooxidative
degradation proceeds via a free radical mechanism. Heat causes a hydrogen extraction at an alpha carbon atom to the ether linkage. When subjected to oxygen addition, the radical forms peroxide radical. The peroxide radical then extracts hydrogen from the backbone to form a hydroperoxide. The hydroperoxide radical then decomposes to form an oxide radical and a hydroxyl free radical. The order of thermooxidation stability is ester > urea > urethane, i.e. urethane is the weakest link in a thermo-oxidative degradation mechanism. Free radical mechanism is also confirmed by the oxidation of polyethers. [62] e.g. polytetrahydrofuran (PTHF), which usually starts at the α-position of the ether bridge and proceeds via a hydroperoxide. This finally leads to a chain scission, thereby reducing the molecular weight and consequently worsening the overall mechanical properties of the polymer.

2.4.2.2 Stages of thermal degradation

Most literature reported that the degradation of polyurethane under thermo-oxidative conditions is either two-step or three-step [63] processes. Camino, et al, [64] indicated that the first step of degradation occurs in the temperature range 220-400°C and presents a maximal rate of weight loss at 320°C. The second step of the degradation which takes place in the temperature range 400-620°C may be attributed to the oxidation of the residual material. An additional step between 620 and 800°C is observed when expandable graphite EG is added to PU coating. In the presence of graphite, a high temperature residue is observed above 620°C. It may be suggested that this additional step is due to the heat resistance of the graphite. Other authors [55] observed also that initial degradation temperatures of polyurethane were above 200°C, with two- or three-step degradation profiles. Chuang and co-workers [65] suggested that the degradation
mechanism of a simple urethane hard segment formed by MDI and 1,4'-butanediol is a
depolycondensation process at about 210°C, followed by a complex process of
degradation. They also reported that N-monosubstituted PUs underwent quantitative
depolycondensation. In contrast, the thermal degradation of N-disubstituted PUs did not
form isocyanate and alcohol, but did form a secondary amine, an olefinic end group and
carbon dioxide. Oprea [66] described the thermal degradation of curable polymers as it
represents a complex kinetic situation arising from multiple initiation steps at random
scission sites, de-polymerization, termination, and chain transfer [61]. The last step of PU
degradation in air at high temperatures (500–600°C) corresponds to the decomposition of
the char formed in previous steps. Carbon dioxide was found to be the most abundant
product during the first step of degradation in nitrogen for both polymers, indicating
scission of the urethane bond. For the second degradation stage in nitrogen a much more
complex mixture of products was identified, most probably originating from polyol
segments.

2.4.3 Factors affecting thermal stability and degradation

Analogous to many other properties, thermal degradation of segmented
polyurethanes depends on many factors related to the monomers, reactions and structures
of the polymers as well as other factors such as presence of external stresses or
degradation accelerators. Main factors affecting thermal degradation include:

2.4.3.1 Isocyanates

Chuang, et al. [65] indicated that the initial temperature of degradation of
urethane formed from alkyl isocyanate and alkyl alcohol is about 250°C, and for that
formed from aryl isocyanate and alky alcohol is about 200°C, while urethane formed from an alky isocyanate and aryl alcohol degrades at about 180°C and that formed from aryl isocyanate and aryl alcohol degrades at about 120°C. Chattopadhyay, et al. [67] observed that at lower temperatures, polyurethanes prepared from aliphatic diisocyanates were more stable than those prepared from aromatic diisocyanates and vice versa at high temperatures. Bogumila [68] indicated that the thermal stability of 4,4'-dihexamethylene diisocyanate (SMDI)-based TPU is inferior to the MDI-based polymer.

2.4.3.2 Polyols

Herrera and co-workers [61] noticed that in the thermal degradation study of PU based on MDI and polyester and polyether polyols, polyether-based PU losses are 85% of the initial mass while polyester-based PU losses are 90%. This difference can be either due to the higher oxygen-content in polyester PU or due to the dehydration reactions of polyester PU which normally promote the formation of the char yield. However it was also reported that polyesters- and polycarbonates-based polyurethanes are by far less sensitive to thermooxidation [62]. Coutinho, et al. [55] studied the degradation profiles of some aqueous dispersion-cast films based on hydroxy-terminated polybutadiene (HTPB) and reported that increasing HTPB content led to materials with higher thermal stability. Yeong et al. [69] stated that generally, ester-based TPUs exhibit better thermal and oxidative stability than the ether-based TPUs.

2.4.3.3 Hetero-block copolymers

Lin and co-authors [70] indicated that the diphenylsilanediols (DSiD) incorporated into the main chain of the polymer improved the thermal stability of PU.
while phosphorus-containing polyurethanes (P-PU) displayed a lower thermal stability than pure PU. In terms of activation energies, the silicon-containing polyurethane has higher values than those of pure PU, which was increased with the increase in the D_{SiD} content. However, P-PU polymers' activation energies were smaller than those of pure PU, and decreased with increasing phosphorus content.

### 2.4.3.4 Submolecular structures

The onset of allophonate disassociation is around 100°C. The dissociation temperature of the biuret linkage is around 115 to 125°C. The aromatic-based urethane bond begins its thermal dissociation around 180°C while urea linkage dissociates at 160 to 200°C [1]. PU with siloxane-containing hard segments exhibited poor thermal degradation and stability [65]. Moreover, polyurethanes including urea groups had low thermal stability in the initial degradation stages [71]. It was found that the addition of flame retardant caused a decrease of the activation energy in the first stage, but an increase in the second once, which was probably due to the formation of a thermally stable structure.

### 2.4.3.5 Molecular weight

Thermal stability is generally greater at higher molecular weight, because higher molecular weights have less mobility and reach asymptotic properties that are less sensitive to scission. Such effect might be observed in thermoplastic PU, however, in cross-linked polymers, stability depends primarily on cross-link concentration rather than on the molecular weight itself [1].
2.4.3.6 Molecular flexibility and rigidity

Thermal stability tends to correlate with the molecular rigidity since chemical reactions and degradation depend on molecules normally moving and meeting one another. As this becomes more difficult with flexibility, the thermal stability is thus expected to improve.

2.4.3.7 Crystallinity

Song and coworker [63] showed that the polyurethane hard segment crystallinity decreases in the following order: MDI > XDI > TDI. The experimental results also indicated that polyurethanes synthesized from aromatic diisocyanates such as MDI and TDI had worse thermal stability than those from alkyl diisocyanates XDI. However, owing to the higher degree of hard segment crystallinity for polyurethanes from MDI, these polymers had better thermal stability than those from TDI.

2.4.3.8 Hard and soft segments

Degradation of PU in the initial stages is dominated by the type and content of hard segments [72,73]. Samples using long soft segment favored thermal stability in the first stages, and those using short soft segments showed higher stability in the second stages possibly due to the increase in the number of urethane links in the hard segments when MDI is coupled with short soft segments. In practical applications, thermal stability in the initial degradation stages is more important than in the second one. Servay, et al. [62] reported that soft segments in polyether-based polyurethanes is sensitive to thermal oxidation, however they also indicated that hard block of segmented MDI-polyester polyurethanes is susceptible to thermal oxidation when aged at 150°C in air for 77 days.
The investigation concluded that MDI units are oxidised at its central methylene group to a benzophenone derivative upon thermal aging in air, i.e., thermal degradation of thermoplastic polyurethanes affects both the soft block and the hard block. Sheng Wang and co-workers [71] also observed a two-stage thermal degradation behaviors of polyurethanes modified with flame retardant poly(bispropoxypolysphazene) under nitrogen. It has been shown that polymers with higher soft-segment concentration displayed lower initial weight loss and higher onset temperatures of degradation. [72]. The activation energy of the initial stages of degradation increased with the decrease in hard-segment length [72]. Most of the hard segments degraded in the first stage [71,74], and samples with less ordered hard segments degraded at lower temperatures [74], whereas the soft segments degraded at the later stages.

2.4.3.9 Supermolecular structure

Chapman, et al. [75] compared segmented polyurethanes with N-alkylated amides as the soft blocks to both poly(ester urethane) and poly(ether urethane) having the same hard block and concluded that poly(amide urethane) has greater thermo-oxidative stability than that of the polyether moiety possibly due to the formation of supramolecular structure resulting from the 2D bi-furcated hydrogen bonding network acting as physical cross-links of the system.

2.4.3.10 Influence of Processing

Maity and co-authors [56,76,77] have studied the effect of processing techniques on the degradation temperatures of blends of polyurethanes with two different functionally reactive elastomers and concluded that the preblended sample degraded at
lower temperatures than the preheated preblended samples for the same elastomeric ratio. Preheated preblended samples are more thermally stable due to the interchain cross-linking reaction between the two elastomers upon the heat treatment.

2.4.3.11 Other degradative factors

Feller [19] reported that the highest temperature to which a plastic material may be exposed outdoors is normally around 76°C, which does not provide sufficient thermal energy (70–90 kcal mol⁻¹) to cause bond cleavage in commercial polymers. Therefore, although temperature is important as a rate-controlling parameter in many of the degradative processes such as oxidation and hydrolysis, polymer degradation by pure thermal energy is not a critical factor in weather-ability studies. Nevertheless, Shi, et al., [52] showed that temperature has a strong effect on the kinetics of the photo-oxidation reactions of polymeric coating. Nagai and co-workers [57] also concluded that in presence of other degradative factors including UV, thermal energy and water, increase in temperature accelerates the rate of degradation reactions in weathering tests of thermoplastic polyester elastomers. Other forms and mechanisms of degradation were also reported. Oprea and Opera [17] reported that the applied or residual stresses on or within soft materials greatly increases their propensity to degrade.

2.4.4 Effect of thermal degradation on segmented TPU properties

Generally, thermal degradation has several effects on polyurethanes properties, these effects may result in any of the following changes: (1) change in the chemical structure, (2) changes occuring on the surface [78], (3) loss in polymer mechanical
properties [79]. (4) increase in molecular weight (cross-linking). (5) reduction of the molecular weight (scission). (6) generation of free radicals. (7) toxicity of products formed due to degradation [80]. (8) loss of additives and plasticizers and (9) impairment of transparency [46]. However, in spite of the large number of studies concerned with the effect of thermal degradation on the chemical structure and morphology of polyurethanes, insufficient attention has been given to the effect of degradation on the mechanical properties of segmented polyurethanes.

TPU undergo significant structural changes on weather exposure. These changes lead to deterioration in its physical and mechanical properties [17.81]. As a consequence of degradation, the resulting smaller fragments do not contribute effectively to the mechanical properties, thus the polymer becomes more brittle and vulnerable [50]. The effects of weathering tests on some mechanical properties of the precipitated and compact polyurethane films such as stress–strain, elongation and modulus were studied by Oprea and Oprea [17]. The ultimate tensile strength, strain and modulus were found to decrease with increasing of the weathering time as a result of disintegration of the hard domain. Nagai, et al. [57] reported a reduction in the weight average molecular weight with the increase of the thermal degradation period for polyether-polyester elastomer samples degraded at 100°C for 60 days. Crawford et al. [82] investigated the behavior of annealed polyurethane elastomers for 240 h at 76°C. Annealing in this case caused an increase in the onset and peak temperatures of the lower temperature transition and has resulted in a sharper transition. This suggested an improved phase separation between the hard and soft segments or improved short-range order of the hard segments. The onset temperature of the higher temperature endotherm is increased significantly as well; however, the peak
temperature is unaffected. The endothermic transitions have narrowed considerably, indicating improved order or phase separation. Shieh, et al. [69] investigated the effect of heating conditions on thermal degradations of 4,4'-diphenylmethane diisocyanate-based thermoplastic polyurethane elastomers and found that the degradation was accompanied by cross-linking and considerable discoloration. They also found that heating under air and nitrogen below 300°C lead to insignificant weight losses due to predominant cross-linking reactions, as compared with chain scission reactions. Servay, et al. [62] showed that the thermal aging of polyether-based polyurethanes caused oxidation of the soft segments which lead to chain scission, thereby reducing the molecular weight and consequently worsening the mechanical properties such as tensile strength and elongation. They also observed an increase in the glass transition temperature upon aging. The glass transition is shifted from about -10°C initially to about +39°C after 77 days at 150°C. The interesting observation is that urethane groups are found to be the same before and after aging indicating that urethane bonds are hardly destroyed by aging. The urethane groups as well as the polyester blocks remained more or less unaffected; confirming that the failure is caused by oxidation of the methylene group in the rigid phase of MDI-based TPU. Hu, and Koberstein [83] showed that upon thermal annealing of MDI-based segmented polyurethane above 191°C, estimated order-disorder transition temperature, for short time, i.e., less than an hour, the molecular weight increased rapidly as a result of the chain branching reactions, an increased microphase separation, and the decrease in the hard segment crystallinity. Annealing below this temperature resulted only in relatively small increases in the molecular weight. Oprea [66] stated that, in general, thermal degradation of polyurethanes involved an initial stage where trapped
temperature is unaffected. The endothermic transitions have narrowed considerably, indicating improved order or phase separation. Shieh, et al. [69] investigated the effect of heating conditions on thermal degradations of 4,4'-diphenylmethane diisocyanate-based thermoplastic polyurethane elastomers and found that the degradation was accompanied by cross-linking and considerable discoloration. They also found that heating under air and nitrogen below 300°C lead to insignificant weight losses due to predominant cross-linking reactions, as compared with chain scission reactions. Servay, et al. [62] showed that the thermal aging of polyether-based polyurethanes caused oxidation of the soft segments which lead to chain scission, thereby reducing the molecular weight and consequently worsening the mechanical properties such as tensile strength and elongation. They also observed an increase in the glass transition temperature upon aging. The glass transition is shifted from about -10°C initially to about +39°C after 77 days at 150°C. The interesting observation is that urethane groups are found to be the same before and after aging indicating that urethane bonds are hardly destroyed by aging. The urethane groups as well as the polyester blocks remained more or less unaffected; confirming that the failure is caused by oxidation of the methylene group in the rigid phase of MDI-based TPU. Hu, and Koberstein [83] showed that upon thermal annealing of MDI-based segmented polyurethane above 191°C, estimated order-disorder transition temperature, for short time, i.e., less than an hour, the molecular weight increased rapidly as a result of the chain branching reactions, an increased microphase separation, and the decrease in the hard segment crystallinity. Annealing below this temperature resulted only in relatively small increases in the molecular weight. Oprea [66] stated that, in general, thermal degradation of polyurethanes involved an initial stage where trapped
volatile materials are released, followed by chain scission and de-polymerization, resulting in weight loss and degradation of the mechanical properties, followed finally by a complete thermal breakdown of the chain yielding a mixture of simple hydrocarbons.

2.4.5 Hindering thermal degradation

Several methods were reported to be used in hindering and retarding thermal degradation and thus enhance the thermal stability of polyurethanes. These include selection of specialized monomers [62,65], addition of thermal stabilizers [84], use of antioxidants, [70,85] copolymerization with more thermally stable polymers [65,86] and development of nanocomposites of layered silicates [50].

Antioxidants are well-known to retard oxidative degradation. Heat, mechanical shear and UV radiation can also be responsible for the formation of free radicals which in turn act to shorten the polymer chain and increase cross-linking, both leading to deterioration in the material properties. Free radical production often begins a chain reaction. Primary antioxidants normally donate active hydrogen atoms to free radical sites thereby quenching or stopping the chain reaction. Secondary antioxidants or synergists act to decompose free radicals to more stable products. The antioxidant acts as a chain transfer agent to produce a dead polymer and a stable free radical that does not initiate chain radical degradation. Famous antioxidants are aliphatic thiols and disulfides [2]. Halim [46] added the use of "color inhibitors" such as tertiary phosphites or phosphonates which react preferentially with the oxidized residues of primary antioxidants. Luta, et al. [85] reported that hindered amine stabilizers (HAS) are known to be very effective antioxidants. The mechanism by which they act is still a matter of discussion but it is nowadays widely accepted that the amine functionality is converted to
the stable nitroxy1 radical in the very first steps of oxidation in the presence of oxygen and hydroperoxides. It is the nitroxy1 radicals that scavenge the very reactive alkyl radicals. Heat stabilizers are added to impart protection against heat-induced decomposition. Such stabilizers are essential for the material when is employed under condition where increased heat stability is needed [2].

One of the methods used to improve heat resistance of PU is the chemical modification of their structure by the introduction of thermally stable segments [87]. Recently, more attention has been given to the modification of polyurethanes by the use of heterocyclic groups such as heterocyclic imide, isocyanate, oxazolidone, triazine, and phosphazene [86]. Polyimides have received wide spread attention due to their unique properties, including an extremely high thermal stability, high mechanical strength, and good dielectric properties. Yeganeh and Shamekh [86] proved that the incorporation of imide group as hard segments in polyurethanes enhances the thermal stability of polyurethanes considerably. Simultaneously PU showed good physical and mechanical properties and at the same time, processability was preserved [86,87]. However, there are still some disadvantages in polyimide applications with respect to their brittleness and low processability [88]. Chuang, et al. [65] indicated that since thermal degradation of PUs is related to the structures of the hard and soft segments, chemical and physical processes such as incorporating aromatic imide promotes the thermal stability of typical PU. Furthermore, they also reported that many studies have improved the acid/base solvent resistance, the excellent thermal stability and the mechanical properties of polyurethane by incorporating silicone. The silicone-containing copolymers were studied extensively because of the real importance of these functional materials for the polymer
application. Wanga and Wei [89] reported that fluorinated polyurethanes (FPUs) have attracted considerable interest due to their thermal and oxidative stability in addition to low surface energies, biocompatibility, lubricity, and non-sticking behavior. The right choice of raw materials or monomers can hinder or retard thermal degradation or enhance thermal stability of polyurethanes. For instance, it is well-known that the poly(dimethylsiloxane) elastomers are considered to have very good resistance toward thermal and ultraviolet radiation, very low glass transition, good gas permeability and biocompatibility, but they exhibit rather poor mechanical properties [5].

Alternatively, some additives or blends may improve desired properties and reduce thermal stability of polyurethanes [71,90]. Wang, et al. [71] reported several attempts in which the thermal stability of polyurethanes was decreased with the addition of phosphorous flame retardants. They also reported that the addition of poly(ammonium phosphate) to PU showed accelerated thermal degradation, which was attributed to the formation of phosphoric acid that further converted the butanediol to tetrahydrofuran by dehydration.

Ray and Okamoto, in their comprehensive review on polymer/layered silicate nanocomposites [91], indicated that the incorporation of clay into the polymer matrix was found to enhance thermal stability by acting as a superior insulator and mass transport barrier to the volatile products generated during decomposition. In air, the nanocomposite exhibited a significant delay in weight loss possibly due to the mentioned barrier effect. Such conclusion was also reached by Pandey, et al. [50] who also reported that nanocomposites of more useful commodity polymers such as polyethylene and polypropylene exhibited less stability under UV light than neat polymers. In general, it is
therefore well-established that highly improved material properties could be reached by filling the polymer matrix with layered silicates, but durability of these materials for outdoor applications is still a challenge.

There are essentially two ways by which degradation could be controlled, the preventive and assertive stabilization. Preventive stabilization involves the elimination of by-products, catalyst carryover, residues and structure irregularities during the manufacturing of the polymer. Assertive stabilization involves the removal or inactivation of the degradation source in order to inhibit the polymer deterioration. Halim [46] introduced four general methods for inhibiting oxidative thermal degradation in polymers. These are (i) the use of “chain-breaking” or “primary” antioxidants such as hindered phenol which function by trapping free radicals or as labile hydrogen donors, (ii) the use of “preventive” or secondary antioxidants such as organosulfur compounds such as sulfides, thioletherdisulfides and sulfoxylates to decompose peroxides and rendering them inactive, (iii) the use of chelating agents as “deactivators” to trap and inactivate trace metal cations and (iv) the use of “color inhibitors” such as tertiary phosphites or phosphonates which react preferentially with the oxidized residues of primary antioxidants.
2.5 Polyurethane coatings

2.5.1 Types and classification

The fundamental purpose of paintings is the decoration of rough surfaces where the purpose of coatings is the protection of these surfaces. While technically these two terms may have different meanings, the terms can be considered interchangeable [2]. ASTM D16 classified the coating into five categories which are chiefly related to the curing mechanism as (i) oil modified (ii) moisture cure, (iii) blocked, (iv) prepolymer plus catalyst and (v) two-component.

Two-component systems, also known as two-package systems, are produced by reaction of isocyanates with relatively low-molecular-weight polyols to form adducts (the hardener package) of the system. The second package contains the chain extender.

A number of high performance coating systems are available in the market including waterborne [92,93], aqueous dispersions, powder coatings and high-solids coatings [94,95]. During the last decade, the competition between water-based, powder-based and high-solid coatings has intensified due to the increasingly restrictive VOC emission regulations [96]. In meeting these requirements, Renza and Bruchmann [96] introduced several approaches to formulate low-solvent or solvent-free or even super-high-solid polyurethane coatings. Solvent-free means that the system neither contains any solvent nor uses any solvent to dilute it [92]. Solvent-free methods are employed by mixing a liquid resins and a liquid hardeners together on the substrate, which cure immediately once applied. Solvent-based methods comprise solution of resin and
hardener in a solvent which is designed to evaporate once the material has been applied as a thin film.

2.5.2 Solid polyurethane coatings

The term ‘polyurethane’ is a generic term for the cured product which is formed from a chemical reaction between polyisocyanate hardener and polyol or diamine resins. The urethane coatings chemistry can be divided into three sub segments: (i) polyurethane coatings, (ii) polyurea coatings, and (iii) hybrid polyurethane/polyurea coatings [95]. The system is called polyurethane when its content of hydroxyl polyol is 80% or more while it is called polyurea if its amine or polyetheramine content is 80% or more. Between those two parameters, a coating can be considered hybrid or blend system [4]. However 100% solids polyurethane coatings are solvent-free, two-component, reaction type systems whereby the base resin and a hardener are combined as liquids just prior to application and convert to a solid film after curing [97].

Polyurethane coating can have great variety of properties ranging from very soft rubbery elastomers of linear chemical structure to rigid, ceramic-like with highly cross-linked structure [97]. Only one isocyanate group can react with one hydroxyl group so there is an ideal ratio of hardener molecules to resin molecules which will give optimum mechanical properties. Despite this fact, it is possible to vary this ratio slightly either way in order to modify the mechanical properties of the system. This is because the isocyanate hardener is also capable of cross-linking with itself in the presence of atmospheric moisture. More hardener than the optimum ratio will produce coatings which are harder, more brittle and have greater resistance to chemical attack. Less hardener will have the opposite effect: the film will be more flexible and its resistance to weathering will
Therefore it follows that a polyurethane coating can accommodate a degree of variance in the mixing ratio but not without this having some effect on the properties of the final film [97]. Unlike polyurea, polyurethane systems can be difficult to use when cured in moist conditions at low temperatures because of the affinity of the isocyanate for moisture. This may result in an inadequate cure and premature embrittlement [95].

Depending on the type of the isocyanate used, polyurethane coatings are either aromatic or aliphatic. Aliphatic polyurethanes are more expensive, but provide the best UV resistance and color stability among all types of industrial coatings and routinely used for exterior applications. Most of the solid polyurethanes available today are aromatic [98]. These are cheaper and less resistant to UV radiation compared with aliphatic polyurethanes. They may also exhibit a certain degree of color change (yellowing’) after a few days/months of UV exposure and therefore are often used for interior, lining or underground applications [98].

2.5.3 Performance of elastomeric polyurethane coatings

Several research groups [4,99] identified the various advantages of the elastomeric polyurethane coatings, which include (i) superior impact resistance, (ii) the greatest abrasion resistance among all other coatings, (iii) possess natural flexibility i.e. can withstand large movements and bends before displaying cracking, (iv) offer very good color stability, (v) offer very good gloss retention, (vi) have cold cure capability and rapid cure time, and (vii) have good chemical resistance (achieved by increasing the thickness). However, they also stated other list of disadvantages including (i) poor average tensile strength, (ii) poor cathodic disbondment resistance and (iii) poor
adherence to the steel substrate which result in inability to withstand undercutting at points of damage, and (iv) high permeability; the measure of the ability of water born chemical or gas to penetrate the coating through to the substrate.

A comparison was made by Guan [4] between the performance of elastomeric polyurethane coatings and other types of the commonly applied lining and coatings systems for piping. The results are summarized in Table 2.1

<table>
<thead>
<tr>
<th>Performance Testing</th>
<th>Reference Test</th>
<th>Solvent Amine Based Epoxy</th>
<th>100% Solids Epoxy</th>
<th>100% Solids Elastomeric Polyurethane</th>
<th>100% Solids Rigid Polyurethane</th>
</tr>
</thead>
<tbody>
<tr>
<td>Abrasion</td>
<td>ASTM D4060</td>
<td>122 mg loss</td>
<td>183 mg loss</td>
<td>15 mg loss</td>
<td>50 mg loss</td>
</tr>
<tr>
<td>Adhesion</td>
<td>ASTM D4541</td>
<td>1280 psi (8.8 Mpa)</td>
<td>925 psi (6.4 Mpa)</td>
<td>1000 psi (6.9 Mpa)</td>
<td>2000 psi (13.8 Mpa)</td>
</tr>
<tr>
<td>Cathodic Disbondment</td>
<td>ASTM G95; 3% NaCl, -1.5 volts, 30 days, 23°C</td>
<td>15 mm avg.</td>
<td>15 mm avg.</td>
<td>30 mm avg.</td>
<td>8 mm avg.</td>
</tr>
<tr>
<td>Chemical Resistance</td>
<td>ASTM D714, 1000 hours</td>
<td>Pass (20% Na2SO4, 3% NaCl, 3% H2SO4, gasoline)</td>
<td>Pass (20% Na2SO4, 3% NaCl, 3% H2SO4, gasoline)</td>
<td>Pass (20% Na2SO4, 3% NaCl, 3% H2SO4, gasoline)</td>
<td>Pass (20% Na2SO4, 3% NaCl, 3% H2SO4, gasoline)</td>
</tr>
<tr>
<td>Flexibility</td>
<td>ASTM D522</td>
<td>Failure at 180° over a 2&quot; (5.08 cm) mandrill</td>
<td>Failure at 180° over a 2&quot; (5.08 cm) mandrill</td>
<td>Pass at 180° over a 2&quot; (5.08 cm) mandrill</td>
<td>Pass at 180° over a 2&quot; (5.08 cm) mandrill</td>
</tr>
<tr>
<td>Impact Resistance</td>
<td>ASTM 014</td>
<td>38 in.lbs (4.3 J)</td>
<td>15 in.lbs (1.7 J)</td>
<td>80 in.lbs (9.0 J)</td>
<td>50 in.lbs (5.7 J)</td>
</tr>
<tr>
<td>Salt Spray Resistance</td>
<td>ASTM B 117</td>
<td>Pass at 1000 hours</td>
<td>Pass at 1000 hours</td>
<td>Pass at 1000 hours</td>
<td>Pass at 1000 hours</td>
</tr>
<tr>
<td>Water Absorption</td>
<td>ASIM D570, 50°C, 48 hours</td>
<td>2%</td>
<td>2%</td>
<td>6%</td>
<td>2%</td>
</tr>
</tbody>
</table>

2.5.4 Elastomeric polyurethane for pipe coating

A large number of different types of polymeric coatings exist addressing many end-uses. The majority of polymeric coatings would be applied for aircrafts, automotives,
architectural, boat and off-shore marine, electrical insulation, fabric, fire and heat retardant, and industrial and pipes [16]. The environment and service conditions surrounding coated pipelines represent real challenge to the coating system in particularly in some location in the Arabian Desert. Moosavi and Al-Bufalah [100] described several factors that contribute to form such harsh service conditions. The so called “sabkha soil” areas have sandy soil with very high water table; the water often reaches the desert surface, this water is extremely rich in salt and very corrosive. Ambient temperature may go up to 50°C for quite long summer seasons. Temperature of metallic, exposed surface-laid pipeline may exceed 80°C under summer conditions, depending on the pipe color, solar intensity and flow rate inside the pipeline. Humidity also is unusually high and may reach 100% in addition to a very high UV radiation. The coated pipes are further jeopardized by mechanical stresses, impact and abrasion due to soil movement, sand movement and frequent sand storms. Such environment is not only harsh for their effect on pipeline coatings, but also because of the difficulty to carry out on-site coating work such as repair or field joint coating.
CHAPTER THREE

EXPERIMENTAL

4.1 Materials

Thermoplastic polyurethane elastomers of various hard block contents used in this investigation were supplied by the first supervisor. The thermoplastic pellets were synthesized in the Polymer Laboratory; Department of Chemistry; College of Science at the UAE University as part of a separate and on-going research project [101]. The TPUs were prepared using "one shot" polymerization process, in which 4,4'-diphenylmethane diisocyanate (MDI), monoethylene glycol (MEG), Triethylene diamine (Dabco EG) acting as a catalyst and Coim G-211 poly(ester) diol were all mixed for 20 min using a mechanical stirrer running at a speed of 3000 rpm. Except for the poly(ester) diol which was purchased from COIM s.p.a, Italy, all other chemicals were supplied by Aldrich and used as is. The one-shot polymerization technique was chosen to ensure a complete random distribution of the hard domain sequence length throughout the elastomeric sample. The weight of MDI was predetermined as to ensure the complete conversion of all the reactive isocyanate and hydroxyl functional groups, i.e. index 1. After casting, the mold was then placed in an oven heated to 60°C and allowed to stand for 4 hours for

Figure 3.1 Sample of TPU pellets
complete curing. The cured samples were allowed to stand for two days at 25°C prior to testing. Figure 3.1 shows typical TPU pellets.

3.1.1 Polymer designation

Thermoplastic polyurethane elastomers of different hard block contents resulting in corresponding hardness values in the range of 55 – 90 Shore “A” were synthesized and designated as indicated in Table 3.1.

<table>
<thead>
<tr>
<th>Designation</th>
<th>Corresponding Hardness (Shore “A”)</th>
<th>Hard Segment Content (Wt %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PU55</td>
<td>55</td>
<td>29.40</td>
</tr>
<tr>
<td>PU65</td>
<td>65</td>
<td>35.67</td>
</tr>
<tr>
<td>PU80</td>
<td>80</td>
<td>41.50</td>
</tr>
<tr>
<td>PU90</td>
<td>90</td>
<td>47.76</td>
</tr>
</tbody>
</table>

3.1.2 Accelerated thermal aging

The accelerated aging treatment was performed on the synthesized TPU materials using the oven method as described in ASTM 0573-99. Specimens for aging were placed in an air oven preheated at 100°C. The aging duration began at the time the specimens were placed in the oven and continued for time intervals of 7 and 14 days at 100°C. After
aging, the specimens were removed from the oven, cooled to room temperature on a flat surface and allowed to stand for not less than 24 hours prior to further processing.

3.1.3 Test specimens designation

The test samples are designated with two alphabetical digits label “PU” and four digits numbers (typically PU6507), the first two digits numbers to the left represent the corresponding hardness value of Shore “A” (55, 65, 80 and 90) while the other two digits to the right stand for the duration of thermal aging in days (00, 07 and 14). As an example, sample PU6507 has a chemical composition that results into a hardness Shore “A” value of 65 and is thermally aged in an air oven for seven days.

3.2 Characterization Techniques

3.2.1 Fourier-Transform Infrared Spectroscopy (FTIR)

FTIR analysis was conducted to investigate the effect of thermal degradation on chemical composition and hydrogen bonding. FTIR spectra of TPU films were obtained in the transmission mode using a Nicolet FTIR Magna-IR 560 system. TPU films were prepared by spontaneous evaporation at room temperature of a diluted solution of the polyurethane in N, N-Dimethylformamide (DMF) placed on a KBr window. The spectra covered the infrared region 4000-400 cm⁻¹, the number of scans per experiments was 32 and the resolution was 4 cm⁻¹.
3.2.2 Differential Scanning Calorimetry (DSC)

DSC experiments were carried out in a Perkin-Elmer - DSC7 calorimeter to determine the endothermic transition of the hard segments of thin films of the various polyurethane samples. TPU granules were heated to 120°C and pressed between steel plates in an injection molder to form disc shaped thin films which were then spontaneously cooled to room temperature. Test specimens were taken out of the center of the thin films. Aluminum pans containing 15-20 mg of solid TPU films were scanned in the range of 50°C to 200°C under nitrogen atmosphere at a heating rate of 10°C min⁻¹ and sensitivity of 5 mcal s⁻¹. All tests were repeated twice under the same conditions.

3.2.3 Thermogravimetric Analysis (TGA)

TGA experiments were carried out to determine the degradation temperature of polyurethanes by TGA analyzer (TA Instruments – GA 2950). Heating rate of 10°C min⁻¹ was used to raise the temperature of 10-14 mg samples from room temperature up to 600°C under nitrogen purge flow rate of 50 ml min⁻¹. The precision of the temperature measurement was less than 0.5°C.

3.2.4 Abrasion resistance test

The abrasion resistance of the various materials to scrubbing stresses is measured following ASTM D5963-97a using a rotary drum abrader. The constant force applied on the sample was 10 N, and the traversed path was 40 m.
3.2.5 Scanning Electron Microscopy (SEM)

Scanning Electron Microscopy (SEM) was used to investigate the structure morphology of TPU samples. The original and thermally aged cast pellets were scanned using a fully computerized Jeol Model JSM-5600 electron microscope at electron beam energy of 10 kV. Specimens were coated with a sputtered film of gold to prevent charging.
CHAPTER FOUR

RESULTS AND DISCUSSIONS

Four different samples of thermoplastic polyurethanes (TPU) of increasing percentage of hard block content were all tested using DSC, TGA, FTIR, SEM and abrasion methods to evaluate (i) the influence of hard block content on the various thermal and abrasion resistance characteristics of these samples and (ii) the influence of the thermal aging on these materials as a function of the thermal aging duration in an air oven at 100°C. The four TPU samples namely, PU55, PU65, PU80, PU90 were all subjected to the thermal aging for 7 and 14 days durations in the oven at 100°C.

4.1 Polyurethanes with different hard block contents

4.1.1 TGA analysis

Thermogravimetric analysis (TGA) was carried out for all the samples at a heating rate of 10°C/min under nitrogen. TGA curves for non-thermally aged TPU samples with different hard block contents PU5500, PU6500, PU8000 and PU9000 are illustrated in Figure 4.1. Figure 4.2 illustrates the differential thermogravimetry (DTG) curves for the same samples.
Figure 4.1: TG A curves for TP1s with different HS contents.
Figure 4.2: DTG curves for TPUs with different HS contents.
The results indicate that degradation takes place between 165°C and 450°C for all samples however some interesting differences in the behaviors of the different samples can be observed in both the TGA and DTG curves. All samples show two-step degradation Step-I and Step-II as a common feature, similar behavior was reported and explained in the literature review [64,65]. However, the first step of degradation (Step-I) may, in some cases, combine sub-steps. Gupta and Adhikari [102] reported two sub-steps in the first degradation step of HTPB-based polyurethanes. The degradation steps as well as the sub-steps can be defined in DTG curves. This may be due to the presence of two types of hard-segments in the morphology of these samples as suggested by Gupta et al. [102]. Notably, the DTG curves have several small split peaks as illustrated in Figure 4.2, which may be attributed to bubble formation and bursting because of the volatility of the components in the degradation process [65].

The process of degradation is qualitatively characterized by a set of points on the TGA and DTG curves from heating commencement to complete polymer decomposition. Table 4.1 presents the characteristic temperatures in each stage of degradation for the tested samples. Upon heating, the sample commences the first degradation stage (Step-I) at temperature (T1on). The rate of percentage weight loss per degree centigrade reaches its maximum value (T1mw) at temperature (T1m). Step-II degradation starts at T2on, and then reaches its maximum rate value (T2mw) at temperature (T2m) till the complete decomposition temperature (Td). The weight loss after Step-I is abbreviated (w.loss1).
The TG and DTG of PU5500 and PU6500 samples have similar behavior which somewhat looks different from the behavior of PU8000 and PU9000 samples. Generally, PU5500 and PU6500 commence the first stage of degradation at lower onset temperature (T1on) with moderate rate of weight loss for longer durations. On the other side, PU8000 and PU9000 start the first stage at significantly higher onset temperature (T1on) and higher rate of weight loss for shorter duration. The same behavior is observed in Step-II for both sets of samples.

The onset temperature at each stage of degradation reflects the fact that heat destroys the backbone structure of polyurethane. TGA (Figure 4.1) and DTG (Figure 4.2) curves show that PU5500 is the first to commence degradation followed by PU6500 then PU9000 and finally PU8000. The degradation onset temperature for these samples (temperature at 1% weight loss) is 165°C, 185°C, 205°C and 235°C respectively. The rate of weight loss reaches its peak value (T1mw) in Step-I at temperature T1m 250°C, 295°C, 356°C and 363°C for PU5500, PU6500, PU8000 and PU9000 samples respectively. The

<table>
<thead>
<tr>
<th>Sample Code</th>
<th>HSC</th>
<th>T1on (°C)</th>
<th>T1m (°C)</th>
<th>T1mw (°C)</th>
<th>w.loss1 (Wt%)</th>
<th>T2on (°C)</th>
<th>T2m (°C)</th>
<th>T2mw (°C)</th>
<th>Td (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PU5500</td>
<td>29.4</td>
<td>165</td>
<td>250</td>
<td>0.41</td>
<td>33</td>
<td>350</td>
<td>400</td>
<td>0.59</td>
<td>?</td>
</tr>
<tr>
<td>PU6500</td>
<td>35.67</td>
<td>185</td>
<td>295</td>
<td>0.33</td>
<td>37</td>
<td>345</td>
<td>413</td>
<td>0.89</td>
<td>460</td>
</tr>
<tr>
<td>PU8000</td>
<td>41.5</td>
<td>235</td>
<td>356</td>
<td>0.63</td>
<td>40</td>
<td>375</td>
<td>411</td>
<td>1.31</td>
<td>435</td>
</tr>
<tr>
<td>PU9000</td>
<td>47.76</td>
<td>205</td>
<td>363</td>
<td>0.71</td>
<td>56</td>
<td>?</td>
<td>410</td>
<td>0.95</td>
<td>460</td>
</tr>
</tbody>
</table>
corresponding total weight loss at the end of first degradation step is 33%, 37%, 40% and 56% respectively for these samples.

A review of references [72] in TPU degradation suggests that the initial degradation in Step-I results primarily from the decomposition of the urethane segment to the original polyol and isocyanate while the consequent Step-II proceeds by the depolycondensation and polyol degradation mechanism. Thus, degradation in Step-I is correlated with the hard segment and degradation in Step-II is affected by the soft segment. The results of this work indicate that weight loss after Step-I degradation increases as the hard segment concentration (HSC) increases. Although values of weight loss after Step-I do not match well with HSC, they are in agreement with the general trend. The difference observed between HSC and the weight loss could be attributed to several factors such as solvent presence or coincident degradation of hard segment and soft segment at higher temperatures.

The effect of hard segment concentration on the onset degradation temperature was investigated by Zoran and coworkers [72]. They showed qualitatively that polymers with higher soft segment concentration (SSC) display lower initial weight loss and higher onset temperatures of degradation. Chuang et al. [65] reported that the thermal stability and onset temperature of degradation at the first stage increase with the SSC and with the HSC in the secondary stage. Although the results of this study are in full agreement with the above findings by Zoran et al., and Chuang et al. concerning the degradation in Step-II and also the weight loss in Step-I, they do not fully agree with their findings concerning the onset temperature in Step-I. The correlation between HSC and onset degradation temperature, therefore, requires further investigation.
It is however clear that all samples started to decompose at no less than 165°C which reflects the thermal stability of the various samples in the operating temperature range of all industrial applications.

### 4.1.2 DSC analysis

Figure 4.3 shows the DSC scans for the non-thermally aged polyurethane samples PU5500, PU6500, PU8000 and PU9000 respectively. Results show that the DSC analysis is well able to differentiate between the various TPU samples by means of their different thermal behavior. The thermal behavior curves of PU5500 and PU6500 show mainly two peaks for each plot. The first peak appears at approximately 105°C for PU5500 and 77°C for PU6500, whereas, the second one appears at approximately 149°C. Similar peaks have been explained in the literature [103,104] as being due to endothermic behavior of crystallites of the hard segment of TPU. They attributed the endothermic peaks at low temperatures to hard segment crystallites with relatively short-range order (residual hard segment). The endothermic peaks at high temperatures were attributed by disordering of hard segment crystallites with long-range order.

The thermal behavior curve of PU8000 shows a similar behavior to that of PU5500 and PU6500 except that two consequent endothermic peaks replace the single peak at high temperature. The first peak appears at approximately 78°C which is only one degree centigrade higher than the corresponding peak in PU6500, whereas, the other two consequent peaks appear at approximately 150°C and 168°C. Briber and Thomas [105] attributed similar two consequent endothermic peaks, at high temperatures, to the existence of two types of hard segment crystallites: type I and type II. The different
melting temperatures of both hard segment crystallites have been used to explain the multiple melting behavior shown in these graphs. Also, similar results have been reported by Wilkes and Yusek [6]. They speculated that the multiple endootherms are associated with various packing order in hard domains, including crystalline hard-segment domains and ordered but non-crystalline hard-segment domains.

The thermal behavior presented in Figure 4.3 for PU9000 shows a different lower temperature range behavior as compared to the other three types of the tested TPU. Several endothermic peaks appear before the melting peak. The first peak appears at approximately 102°C, whereas, the second, third, fourth and fifth peaks appear at approximately 118°C, 147°C, 154°C and 156°C, respectively. Only one melting peak appears at approximately 181°C. Similar peaks have been reported in literature [103] where the first peaks were explained by the dissolution of the hard segment microcrystals in the soft domain with increasing temperature. The fact that the curve has five endothermic peaks before the melting peak may indicate the existence of microcrystals of different sizes. Cooper and co-workers [106] and Jeffery and Russell [107] identified three hard segment associated endotherms (I, II and III). They attributed endotherms I and II to disruption of short and long range order respectively (due to the length distribution of hard segments). They attributed endotherm III to the melting of microcrystals in hard segment domain. Same endotherms (I, II, and III) were later confirmed by Ming and co-workers [108].
Figure 4.3 DSC curves for TPU s with different HS contents.
4.1.3 Abrasion test analysis

The abrasion resistance of the various materials to scrubbing stresses is measured following ASTM D5963-97a using a rotary drum abrader. The constant force applied on the sample was 10 N, and the traversed path was 40 m. This test is important since it is the objective of this study to evaluate the abrasion resistance of these thermoplastic polyurethane materials as possible coatings in the pipeline industry.

According to Okazaki, et al. [109] high abrasion resistance of polymer samples associated with the increase in the microphase separation, i.e. the filler effect, which corresponds to a decrease in the frictional force resulting from the resistance of the sample surface to the abrasive material.

The results show clearly that the increase in the hard block content has caused an increase in the abrasion resistance of the samples. This is probably due to the increase in the microphase separation between the hard blocks and the soft blocks with the increase in the hard block content. In line with this observation, Figure 4.4 represents the volume loss as a result of the abrasion test for different types of TPUs before thermal aging. It is obvious that the lost volume decreases and consequently, the abrasion resistance increases with the increase in the hard block content.
Figure 4.4 Abrasion resistance curve for TPUs with different NIS contents.
3.1.4 SEM analysis

Figure 4.5 shows SEM micrographs for the different examined TPU samples. The studied samples have HSC in the range of 29-49%. The micrographs show what is believed as alternating hard- and soft-segment lamellar microdomain structures. Thus, it is suggested that the micrographs in Figure 4.5 show two-phase microstructure. The polyol soft segment form matrices in which the hard segments are dispersed. The hard domain acts as a reinforcing filler whereas the soft segment behaves as a soft matrix. It is also observed that the micrographs of PU5500 and PU6500 samples show relatively coarse hard and soft domains. This two-phase domain gets finer as the HSC increases as shown in the micrographs of PU8000 and PU9000 samples.

A review of references in structure and morphology of TPU shows that Chen-Tsai et al. [110] indicate that meandering cylinders of the soft segment phase are present in the 74% HSC sample. An alternating plate-like structure is found in the 52% HSC sample. However, for samples of hard segment content lower than 50%, results from electron microscopy were inconclusive. In addition, Li and co-workers [38] reported that segmented polyurethanes with low HSC have a morphology of dispersed, short, hard-segment cylinders embedded in a matrix of polybutadiene soft segments. An alternating hard- and soft-segment rod-like or lamellar microdomain structure was characteristic of materials with higher HSC. The length of lamellae or rods increased with increasing hard-segment content while the width of the lamellar or rod-like microdomains remained constant. At very high HSC, a morphology having a dispersed soft-segment phase was
observed. It was also found that the shape of the dispersed soft-segment microdomains in the high hard-segment content samples was related to the details of sample preparation. Moreover, Serrano et al. [111] reported that the 75 wt% HSC sample shows a dispersed morphology of soft segment (SS) spheres in a glassy matrix of hard segment. A lamellar morphology is indicated at 55 wt% HSC while cylindrical domains of hard segment in a rubbery matrix of soft segment are believed to exist in the dilute range (< 40 wt %) of HSC. Recently, Pielichowski et al. [27] observed spherical aggregates with diameter of about 200 nm, arranged in a quasi-linear mode by SEM technique when investigated segmented MDI/HMDI-based polyurethanes with lowered flammability.

Estes et al. [41] suggest that such a domain structure exists on a microscopic scale and that the size and shape of the domains are dependent upon composition and block molecular weights. Meanwhile, Li et al. [38] indicated that length of hard domains is about 10-25 nm. However the exact nature of microphase structure of polyurethanes has yet to be clarified. Song et al. [112] observed by AFM 800 nm size spherical structure aggregates of hard domains. They also reported that some authors suggested that the microdomains can approach each other and coalesce.
Figure 4.5 SEM images for TPU s with different HS contents
4.2 Effect of thermal aging on segmented TPU

3.2.1 FTIR Spectroscopy

All the various tested samples show the FTIR spectrum of typical polyurethane elastomers. Specifically, all the samples show the major FTIR peak around 1710-1730 cm\(^{-1}\) synonymous with the urethane link (-O-CO-NH-). The influence of thermal aging on the various studied samples using FTIR technique is shown in Figures 4.6, 4.7, 4.8 and 4.9 for the PU55, PU65, PU80 and PU90 samples, respectively. The figures indicate that no major change of the urethane link took place due to the thermal aging treatment at 100°C. In particular, no FTIR peak at the mentioned range corresponding to the urethane link has disappeared from any of the spectra, which indicates that no specific dissociation or depolycondensation reactions involving the urethane links have taken place during these prolonged thermal treatments. Changes observed to the urethane link of some of the samples on heating at 100°C for prolonged durations are probably due to the dissolution of part of the hard segments into the interface region and subsequent involvement of the dissolved urethane groups in hydrogen bonding formation of various types and orientations. For example, free urethane groups (unattached urethane groups) usually appear sharply at 1730 cm\(^{-1}\) on the IR spectrum. Urethane groups linked to other urethane groups within the crystalline hard domains through specific hydrogen bonding formation appear sharply at 1710 cm\(^{-1}\) [42]. However, urethane groups linked to ester groups of the soft segments, loosely-ordered urethane groups (H-bonded urethane groups in the amorphous region), urethane groups involved in multiple hydrogen bonding formation such as urethane groups in which both of the hydrogen atom of the NH group and the
carbonate oxygen atom are both involved in hydrogen bonding formation, or urethane groups found on the edge of a hard domain with either the hydrogen atom or the carbonyl oxygen atom involved in hydrogen bonding formation will result in a peak appearing on an IR spectra somewhere between the sharp 1710 cm\(^{-1}\) and the 1730 cm\(^{-1}\) peaks. Convolution of all these in-between peaks will result into the observed broadening of the IR peak in the 1710-1730 cm\(^{-1}\) region. This behavior of broadening the 1710-1730 cm\(^{-1}\) peak upon thermal aging is shown repeatedly for the various TPU samples and is considered an indication of a slight phase mixing between parts of the hard blocks and the soft domains as more and more urethane links are engaged in hydrogen bonding formation of various types and orientations. The above observation is consistent for all TPU samples thermally treated for either one or two weeks except for the PU90 sample where a reduction in the peak height for samples treated for the full thermal duration of 14 days was observed.
Figure 4.6 FTIR spectra for PU55 samples at different aging durations
Figure 4.7 FTIR spectra for PU 65 samples at different aging durations
Figure 4.8 FTIR spectra for PU80 samples at different aging durations.
Figure 4.9 FTIR spectra for PU90 samples at different aging durations
4.2.2 TGA analysis

In order to elaborate more on the findings of the FTIR studies, which showed that no major chain degradation has taken place upon the thermal treatment of the polymeric samples, TGA were carried out for all samples before and after thermal aging. Figure 4.10, 4.11, 4.12 and 4.13 demonstrate the results of TGA and DTG for the PU55, PU65, PU80 and PU90 samples respectively.

Figure 4.10 illustrates the TGA and DTG curves for PU5500, PU5507 and PU5514. The three samples have the same HSC (29.4%) with different aging durations of 0-day (non-aged), 7-day and 14-day, respectively. The TGA-DTG curves for all samples have two distinct regions of weight loss, implying at least two stages of degradation as explained earlier. The degradation of the first stage (Stage I) and that of the second stage (Stage II) for PU5500 were around 165-350°C and 350-550°C, respectively. This is reflected in two peaks shown in the DTG curve around 250°C and 400°C. The degradation behavior of the thermally aged samples PU5507 and PU5514 was found to be more or less the same as compared to the non-aged PU5500 sample. Although the curves are not identical, no significant differences are observed as a result of the aging process. The same discussion is also valid for the other samples PU65, PU80 and PU90 with some insignificant differences. PU80 samples show ideal two-step degradation profile with high similarity between the three samples. On the other hand PU90 samples do not distinguish well between the two degradation steps. It is suggested that the interference in degradation between the HS and SS led to interference in the two degradation stages. This may have also caused the observed increase in the weight loss value of the HSC at the end of Stage-I of the degradation process.
Figure 4:10 TGA-DTG curves for PLLA samples at different annealing durations.
Figure 4.11 TGA-DTG curves for PU65 samples at different aging durations
Figure 4.12 TGA-DTG curves for PU80 samples at different aging durations
Figure 4.13 TGA: DTG curves for P1/90 samples at different annealing durations
4.2.3 DSC analysis

Figures 4.14, 4.15 and 4.16 show the effect of thermal aging on polyurethane samples PU65, PU80 and PU90, respectively. The three graphs shown in each figure illustrate the effect of thermal aging for periods of seven and fourteen days at 100°C compared to the reference non-aged samples.

Results presented in Figure 4.14 show that thermal aging didn’t affect much either the amount or the morphology of the short-range order crystallites of the PU65 samples. This is concluded as the shape and position of the first endothermic peak, at approximately 77°C, remain almost unchanged. However, long-range order crystallites tend to change in nature, by thermal aging, in a way such that their melting temperatures move towards lower values. The melting temperature of the long-range order crystallites of the hard segments, drop from approximately 149°C to approximately 145°C upon aging for seven days and to approximately 141°C upon aging for fourteen days.

The effect of thermal aging on the DSC behavior of PU80 samples is presented in Figure 4.15. Thermal aging for seven days at 100°C didn’t affect much the shape and position of the endothermic peak taking place at approximately 78°C. However, increasing the thermal period to 14 days resulted in reducing the height of this endothermic peak, indicating a decrease in the amount of this type of crystallites [42].

The effect of thermal aging for seven and fourteen days on the multiple melting peaks is shifting them towards lower temperatures. The amount of shift increases as the duration of thermal aging increases from seven to fourteen days. This can also be attributed to
changes in the morphology of the hard segment crystallites which facilitate melting at lower temperatures.

The graphs presented in Figure 4.16 show that the thermal aging affect endothermic peaks of PU90 samples at both low and high temperatures. Thermal aging at 100°C for seven days resulted in eliminating the first three endothermic peaks and reduced the temperatures at which the fourth and fifth peaks took place. The melting peak decreased in height and shifted slightly to a lower temperature. This behavior may be explained by the dissolution of the short-range order crystallites corresponding to the first three peaks and by a decrease in the amount of long-range order crystallites together with a slight change in their morphology.

Similar results can be observed when the duration of thermal aging is increased to 14 days. Slight shifts in the fourth, fifth and melting peaks together with further decrease in height of the melting peak took place. This indicates that increasing the duration of thermal aging to 14 days has reduced further the amount of the long-range order crystallites in this type of TPU.
Figure 4.14 DSC curves for PU65 samples at different aging durations
Figure 4.15 DSC curves for PU80 samples at different aging durations.
Figure 4.16 DSC curves for PU90 samples at different aging durations
4.2.4 Abrasion resistance

The abrasion resistances for the thermally aged samples were also tested with the abrader. Figure 4.17 illustrates the results of abrasion test using a rotary drum abrader in terms of lost volume for different hard segment containing TPU. The influence of the aging treatment on the TPU sample had a more profound effect on samples with HSC. This is indicative of the greater influence of the thermal aging on the high hard block content samples over the low ones. Apparently, the heat treatment has caused slightly more phase mixing in higher hard block samples over the lower ones, which is in agreement to earlier results from the FTIR study. This corresponds to a less microphase separation and higher loss of the material in an abrasion experiment as shown in Figure 4.17.

4.2.5 SEM analysis

Figures 4.18, 4.19, 4.20 and 4.21 show the micrographs for PU55, PU65, PU80 and PU90 samples respectively. Each figure contains two micrographs for the polyurethane samples without and with thermal aging. The images indicate that thermal aging for 14 days at 100°C does not affect the existence of two phase morphology. However, coarser phases can be noticed in all thermally aged samples in total agreement with earlier results from the FTIR and the abrasion studies.
Figure 4.17 Abrasion resistance of different HS contents TPUs at different thermal aging durations
Figure 4.18 SEM images for PU55 at different thermal aging durations

(a) PU5500  (b) PU5514

Figure 4.19 SEM images for PU65 at different thermal aging durations

(a) PU6500  (b) PU6514
Figure 4.20 SEM images for PU80 at different thermal aging durations

(a) PU8000  
(b) PU8014

Figure 4.21 SEM images for PU90 at different thermal aging durations

(a) PU9000  
(b) PU9014
CHAPTER FIVE

CONCLUSIONS

In order to evaluate the effect of thermal degradation on the mechanical behavior of polyurethane samples, accelerated aging method has been used in this research work and the aged samples have been subjected to various thermal, spectroscopic and mechanical characterization techniques.

Various thermoplastic polyurethanes of increasing hard block content were tested using DSC, TGA, FTIR, SEM and abrasion methods to evaluate (i) the influence of hard block content on the various thermal and abrasion resistance of these samples and (ii) the influence of the thermal aging on these materials as a function of the thermal duration in an air oven at 100°C.

All the various tested samples showed the FTIR spectrum of a typical polyurethane elastomer. It was observed that no major alteration of the urethane link took place due to the thermal aging treatment at 100°C. Thermogravimetric analysis indicated that the samples started to decompose at no less than 175°C which reflects the thermal stability of the various samples in the operating temperature range of all industrial applications. This was furthermore confirmed by the DSC study of these materials which indicated the higher thermal stability up to 150-200°C. At this temperature range, a major endothermic transition of the hard blocks was observed and identified as the melting transition of these domains. The abrasion resistance of the various materials to scrubbing stresses was also found to increase with the increase in the hard block content. High abrasion resistance of TPUs was associated
with an increase in the microphase separation, which corresponds to a decrease in the frictional force resulting from the resistance of the sample surface to the abrasive material. The results indicated that the increase in the amount of hard blocks not only created longer hard-segment domains acting as larger filler particles but also contributed to a higher degree of microphase separation. The accelerated thermal treatment of the TPU samples indicated the higher influence of the degradation treatment on the PU samples of higher hard block content, which was attributed to a less microphase separation resulting from a possible phase mixing of parts of the soft and hard domains in the TPU elastomers with high hard block content.

**Recommendations for future work**

As presented, TPU elastomeric coatings have high potential for application in the UAE and Arabian Gulf Countries due to their pronounced advantages. Unfortunately, the harsh environmental conditions set limitations on TPU coatings applications in this area of the world. In order to have proper understanding for the effect of these environmental conditions, further studies are essential on the effect of “sabkha” soil as well as sun radiation on the TPU coatings. Simulations of the degradative parameters individually and in combination with each other will help in developing suitable TPU coatings to the local market.
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الكتل الصلبية واللبنية ببعضهما كان هذا الأثر أكثر وضوحا عند زيادة HSC وقد انعكس ذلك في زيادة اتساع القمة المميزة لرابطة البورتليان في التحليل الطيفي للأشعة تحت الحمراء عند 1710-1730 سم⁻¹ في العينات التي تعرضت للتقادم الحراري. وقتماكد ذلك أيضا من زيادة حجم المادة المفقودة في تجارب مقاومة الاحتكاك عند زيادة مدة التقادم الحراري.
ملخص الأطروحه

تم في هذا البحث عمل دراسة مستتبضة عن البولي بيرثين البلاستيكي TPU وتأثير محتوائه من تدفق الحمض الغلياً على عواصفه وقد أثر تدفق الحمض الغلياً بالإضافة إلى المقتنيات العامة على مزيج متعدد للحويص الساقية في هذا المجال في نواعي الكيماوية، البنية والخصائص، التأثيرات، والألماس وكذلك الاستخدامات ثم خصص الجزء العلمي لتقييم وطرق البحث وأجهزة القياس المستخدمة في الدراسة، كما تناول جزء النتائج والمناقشات لملاحظات واستنتاجات البحث بالتصغير وخلصت الدراسة بجزء التعميم والاقتراحات.

تم تحسين البولي بيرثين البلاستيكي من داييغيل ميشان داي أيسيانات (MDI) و مونوإيثيلين (Coim G-211) و بولي استر دايول (Dabco EG) وذلك باستخدام طريقة البلمرة في خطة واحدة وبحث تم تغيير وزن الكلان في المادة لكي تتراوح في حدود 20-49% وتم ترشيح لعملية تقدم حاري في فرن هوائي عند درجة حرارة 100 مئوية لمدة 7 أيام و14 يوم.

بعد ذلك تم تأثير التغلب في نسبة تركيز تدفق الحمض الساقية في المادة الحاري في الفرن على تركيب ونسبة البولي بيرثين ومقاومته للاحتكاك باستخدام جهازي FTIR و FTIR مجهز السامال الأليكنويو SEM الأسطوانة الدورة HSC وكذلك مدة التقدم DSC للعنين المختلفة بين درجات حرارة 77 - 102 مئوية ونسبة إلى توزيع بدورات تدفق الحمض الساقية ذات التماساك السطحي نسبياً. بينما لوحظ قم انتاج حاري أحادية أو متعددة عند درجات حرارة أعلى من السابق في حدود 150 - 181 درجة مئوية ونسبة على أنها تواتر بدورات تدفق الحمض الساقية، وقد وجد أن درجه حرارة التدفق تزداد زيادة HSC عند خصص الاستقرار الحاري لمادة DSC والتحليل الموجبة التفصيلي TGA وطيفية الآثار تحت جهاز FTIR و FTIR مجهز السامال الأليكنويو SEM الحاري و FTIR مجهز السامال الأليكنويو SEM الاستطوانة الدورة HSC تبين وجود رقاقات من التقدم الساقية والليث في ترتيب تبادل مع سلسلة البوليمر أو حدوث تغير كيميائي ظاهر في عينات البولي بيرثين كما تأكد أيضاً باستخدام الإشعاع تحت الحمراء في حساسة البولي بيرثين نتيجة التقدم الحاري. "أن FTIR الأشعاء تحت الحمراء قريب تأثير النتائج العامية هيدروجيني. ومن ذلك البنى المجهزة قد تتأثر ذلك نتيجة التقدم الحاري على برنامج الهيدروجين. وقد لوحظ أن زيادة زمن التقدم الحاري تؤدي إلى انخفاض أطراف المادة المحتوية وزيادة مرج الكلان الساقية والليث بحسب ما كان هذا الأثر أكثر وضوحاً عند زيادة في زيادة اتساع القمة الرابعة البولي بيرثين في التحليل الطيفي للأشعة تحت الحمراء عند 1710 - 1730 سم^-1 في العينات التي تعرضت للتقدم الحاري ونذكر ذلك أيضاً من زيادة حجم المادة المفقودة في تجارب مقدمة الاحتكاك عند زيادة مدة التقدم الحاري.
دراسة مقاومة طلاء البولي يوريثان البلاستيكي للتقادم الحراري

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