BIO, THERMAL AND PHOTO DEGRADATION OF POLYMER THIN FILMS FROM RENEWABLE RESOURCES

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ABSTRACT

This research is focused on the resistance to bio, thermal and photo-degradation of polymer thin films from renewable resources based on virgin and waste vegetable cooking oil from Small and Medium Industries (SMIs). Vegetable and waste vegetable oil polymers were grouped as virgin oil polymer (VOP) and waste oil polymer (WOP) thin film. The thin films were prepared by adding bio-monomer with an appropriate amount of 4, 4'-methylen-bis-(phenylisocyanate) (MDI). Percentage weight loss of VOP thin film in compost soil burial test was significantly greater than those in peat soil burial test. For 200 days degradation in compost soil, weight loss for VOP and WOP were 68.32% and 28.78%, meanwhile for peat soil burial test were 44.52% and 24.56% respectively. As the temperature and the exposure time increased, the carbonyl index (CI) via infra-red also increases for both WOP and VOP at given temperature and 600 minutes from initial value of WOP is 0.296 to 0.427, meanwhile the initial value for VOP is 0.417 to 0.44 respectively. This is due to the number of chain scissions that occur in the polymer thin films associated with the scission of the (-NHCO-O-) for both WOP and VOP. It was observed that the size of the peaks for Thermal Gravimetric Analysis (TGA) is correlated with the amount of hard and soft segment at 325°C and 431°C respectively. The ductility disappears and the strength and strain at rupture strongly decrease at over 35% upon equatorial exposure. The active participant of OH group with isocyanate was lead to the creation of more stress point, thus, lower energy needed for WOP thin films to bring to failure. As a conclusion, WOP thin films were resistance to bio and thermal degradation with the lowest value of weight loss and CI. However, WOP thin films were affected by photo-degradation where the occurrence of surface damage, which in turn enhances the degradation of these mechanical parameters.
CHAPTER 1

INTRODUCTION

1.1 Research background

Recent years have witnessed an increasing demand on natural products in industrial applications for environmental issues, waste disposal, and depletion of non-renewable resources.

Renewable resources can provide an interesting sustainable platform to substitute partially, and to some extent totally, petroleum-based polymers through the design of bio-based polymers that can compete or even surpass the existing petroleum-based materials on a cost-performance basis with high eco-friendliness values. It is well known that polymer thin films derived from renewable resources having intermolecular (-NHCO-O-) bonds which susceptible to microbial deterioration. There are many reports on the degradation of polymer by microorganisms, especially by fungi such as Aspergillus niger, Penicillium citrinum and Pseudomonas aeruginosa.
Plant oils are now being considered as the most important renewable raw materials for the production of bio-based polymer materials (M, Rus. A. Z., 2010). Polylactic acid (PLA) a biodegradable polymer derived from lactic acid which is one form of vegetable-based bioplastic. This material biodegrades quickly under composting conditions and does not leave toxic residue (Shah, A. A., Hasan, et al., 2008). When oxygen is available, aerobic microorganisms are mostly responsible for destruction of complex materials, with microbial biomass, carbon dioxide, and water as the final products.

The development of bio polymers using monomers from natural resources provides a new direction to develop biodegradable polymers from renewable resources. In this research, virgin and waste oil monomer (polyol or epoxy) are further polymerized or ‘cured’ to high molecular weight solid polymer thin films. The curing process involves addition of cross-linking agent such as methylene-4, 4’ diphenyldiisocyanate (MDI), which allows the polyl group to form a (-NHCO-O-) (M, Rus. A. Z., 2010). Polymeric isocyanates (such as polymeric MDI) are extremely thermally stable and produce thermally stable polymer thin films. Polymer made with an aromatic isocyanate will turn yellow on exposure to UV light or heat. The yellowing is caused by oxidation reaction in the backbone of the polymer. Irradiation modifies physical and chemical characteristics of polymer surface and results in rapid colour change and degradation (Rosu, D., Rosu, L. & Cascaval, C. N., 2009).

Polymer thin films from renewable resources have a number of excellent properties due to the hydrophobic nature of triglycerides. The repeating unit in polymer is the (-NHCO-O-) linkage produced from the reaction of an isocyanate (–N=C=O) with an alcohol (–OH). On the other hand, these materials have relatively low thermal stability, primarily due to the presence of (-NHCO-O-) bonds. The onset of (-NHCO-O-) bond dissociation is somewhere between 150 and 220 °C, depending on the type of substituents, on the isocyanate and polylol side. Saturated hydrocarbons are known to have relatively good thermal and thermo-oxidative resistance compared to polyether and polyester polyols derived from petrochemicals (Monteavaro, L. L., 2005). In typical polymer, hydrogen bonds are formed between hard segments via –NH groups.
in (-NHCO-O-) linkages and between hard and soft segments via –NH and soft segment ether or carbonyl groups (Pattanayak, A & Jana, S.C., 2005).

Others than bio and thermal degradation, photo-degradation polymer thin films from renewable resources also studied upon equatorial weathering exposure. Wide variety of polymeric materials absorbs solar UV radiation and undergo photo-oxidative and thermo oxidative reactions that result in the degradation of these polymer thin films. Data on wave-length sensitivity of polymer thin films exposed to different UV sources showed that radiation with wavelengths of about 400 nm affects drastically the mechanical properties of thin films. However, radiation with shorter wave lengths less than 280 nm can initiate the formation of free radicals. It has been also indicated that visible radiation (400-700 nm) accelerates polymer degradation by heating and enhances excitation of chromophores; and that infrared radiation (700-2500 nm) accelerates thermal oxidation.

Many works of research literature on polymers deal with the issue of controlling photo-degradation to ensure reliable lifetimes of such materials under outdoor exposure conditions (Salem, M. A., Farouk, H. & Kashif, I., 2002) Changes in the mechanical performances of polymer from renewable resources have also been reported after some thermal treatments. For instance, the stress-strain properties were found to be very sensitive to thermal ageing: elongation at break and tensile strength decreased during exposure to heat, mainly due to crosslinking or chain scission, depending on the temperature range.

Generally, the degradation rate of polymeric materials depends to a great extent on the nature of the material and environmental aggressiveness to which they are exposed. It is well established that the degradation of polymer, exposed to heat and/or UV-light, involves thermo- and/or photo-oxidation. These reactions lead to the build-up of a variety of oxygen containing groups such as different carbonyl compounds. Upon equatorial weathering exposure, tensile thin films polymer underwent visual inspection and mechanical testing to determine their load carrying capability. The mechanical testing exposed thin films were compared with unexposed tensile thin films to determine the extent of degradation and the performance of thin films.
1.2 Problem statement

Petroleum-based synthetic polymers are widely used in modern society.

These synthetic polymers are, however, often not environmentally friendly because they typically do not undergo the process of biodegradation and, of course, are dependent on a limited petroleum resource. The common biodegradable synthetic polymers include novel aliphatic polyesters, such as poly (e-caprolactone) (PCL), poly (b-methyl-d-valerolactone), polylactide, and their copolymers. Scientists are therefore investigating opportunities to prevent economic losses and inevitable crisis of lowered standard of living as a result of oil shortages in the future.

The stability of polymer from renewable resources has been a major area of research. It is now clear that there are number of factors affecting the stability and degradation of polymer. Polymer thin films prepared from plant oils have a number of excellent properties due to the hydrophobic nature of triglycerides. On the other hand, these materials have relatively low thermal stability, primarily due to the presence of (-NHCO-O-) bonds. The thermal degradation of (-NHCO-O-) based on 4,4'-methylenbis-(phenylisocyanate) (MDI) and polyl was shown that the (-NHCO-O-) undergoes degradation at elevated temperature. Thermal stability of polymer from renewable resources has been thoroughly investigated by many researchers and various degradation mechanisms have been proposed to explain the experimental results that give the most stable materials.

Polymer photo-degradation and stabilization is an extensive field of study. It is well established that photo-oxidation reactions play an important role in degradation process of the UV-irradiated polymeric materials, and the controlling mechanisms. One of the particular disadvantages of polymer from renewable resources is their extreme sensitivity to light, in particular to UV light. This is a major limitation which relates to their use as outdoor applications. It is known that polymer undergo significant structural changes upon exposure to UV radiation, which cause deterioration in their physical and mechanical properties (Rosu, D., Rosu, L. & Cascaval, C. N., 2009). The physicochemical changes which occur during photo-oxidative reactions are characterized by an increase in the concentration of the oxygen-containing groups such
as peroxides, hydroperoxides and also the ketonic carbonyl groups. However, crosslinking and chain scission processes occurring during photo-oxidation in polymer are believed to be sources of great importance in causing changes in the mechanical properties of this polymer.

1.3 Research aim

The primary aim of the research is to study the degradation of bio, thermal and photo-oxidation degradation of VOP and WOP thin films from renewable resources.

The key aim of the research is to use the polymer from oil palm for a variety of reasons such as biodegradable and stability upon thermal and weathering exposure for extended periods.

1.4 Research objective

(i) To study the thermal degradation of polymer thin films from renewable resources by the formation of carbonyl index (CI) by Fourier transform infra-red (FT-IR) and thermal decomposition mechanism by Thermo gravimetric analysis (TGA).

(ii) To study the bio-degradation of polymer thin films upon treatment with peat and compost soil medium which indicates by percentage of weight loss, visual observations, optical microscopy and change of pH soil medium by pH measurement.

(iii) To expose polymer tensile thin films upon equatorial induced degradation for photo-oxidation degradation study and mechanical property.
1.5 Research scope

The research scope is to study the degradation of polymer thin films from renewable resources.

An international test method applied to perform soil burial test in the laboratory standard according to EN ISO 846:1997 for bio degradation study of polymeric materials due to its simplicity and similarity to real field conditions of waste disposal. Evaluation of gravimetric weight loss is a reliable evidence to estimate the extent to which degradation takes place in the buried films. The biodegradability of the buried VOP and WOP thin films can be examined in a quantitative manner by studying changes in chemical constitution with the aid of techniques like Fourier transform infrared spectroscopy (FTI-R) as well as changes in the surface morphology by optical microscopy (OM).

Thermal oxidative degradation of polymer from renewable resources at different temperatures was studied by Fourier transform infrared (FT-IR) spectroscopy and Thermo gravimetric analysis (TGA) in order to understand the effect based on different types of polymer which is virgin oil polymer (VOP) and waste oil polymer (WOP) thin films. Fourier-transform infrared spectroscopy (FT-IR) is commonly used for investigation of polymer from renewable resources upon thermal degradation in order to follow the mechanical and structural changes of WOP thin films as a result of photo degradation upon equatorial exposure. Mechanical properties of tensile WOP thin films according to ASTM D882 Standard test was used for tensile properties of thin plastic sheeting. Studies of bio, thermal and photo degradation of polymer thin films were observed by their physical, chemical and mechanical changes upon degradation. Another polymeric materials were compared to polymer from renewable materials for discussion.
CHAPTER 2

LITERATURE REVIEW

2.1 Background of polymers

Polyethylene, polypropylene, polystyrene, polyethylene terephthalate, and polyvinyl chloride are all derived from petrochemical feedstocks.

The utilization of fossil fuels in the manufacture of plastics accounts for about 7% of worldwide oil and gas. These resources will arguably be depleted within the next one hundred years, and the peak in global oil production as estimated by some will occur within the next few decades (Williams, C. K & Hillmyer, M. A., 2008). With time, stability and durability of plastics have been improved continuously, and hence this group of materials is now considered as a synonym for materials being resistant to many environmental influences. At present all the raw materials are derived from petrochemicals, and the toxicity and volatility of starting materials such as formaldehyde require careful environmental, health and safety monitoring. But there could soon be a new, greener alternative on the market based on a new generation of ‘bio-resins’-thermoset resins derived principally from vegetable oils such as rapeseed (Shah, A. et al., 2008).
Synthetic plastics are extensively used in packaging of products like food, pharmaceuticals, cosmetics, detergents and chemicals. Approximately 30% of the plastics are used worldwide for packaging applications. The most widely used plastics used in packaging are polyethylene (LDPE, MDPE, HDPE and LLDPE), polypropylene (PP), polystyrene (PS), polyvinyl chloride (PVC), polyurethane (PUR), poly (ethylene terephthalate) (PET), poly (butylene terephthalate) (PBT) and nylon (Figure 2.1).

![Chemical structures of plastics](image)

Figure 2.1: Structures of conventional petrochemical plastics polyethylene (PE), polyvinyl chloride (PVC), polypropylene (PP), polystyrene (PS), polyethylene terephthalate (PET), polyurethane (PU).
Figure 2.2: Structure of polymers produced by bacteria using plant materials. (a) Polylactic acid (PLA), (b) Polyhydroxybutyrate (PHB) and (c) Polyhydroxybutyrate/valerate (PHBV).

Figure 2.2 shows the structure of the PL, PHB and PHBV polymer. (A) PLA is produced by bacteria of the genus *Lactobacillus*, and often D-glucose (maize dextrose) is the carbon source. It is a high-molecular-mass polymer (>1 MDa) that can be used for films and moulded. (b) PHB and (c) PHBV are in the class of PHAs that naturally occur in many bacteria as carbon reserves. Typically, highly refined sources of glucose derived from plants are used in batch-fed bacterial cultures; however, use of industrial wastewater and plant oils have also shown promise for PHA production through fermentation.
2.2 **Renewable resource**

Large amount of plastic waste generated by industries poses serious environmental problems which may require up to hundred years for total degradation (Mantia, F. P. L & Moreale, M., 2008).

An approach to decrease the solid waste is to substitute conventional material with biodegradable raw materials to reduce costs and to enhance the degradation of the final product. By renewable resources is meant agricultural products mainly from five principal crops: soybean, oil palm, rapeseed, sunflower and coconut where the materials are synthesized by sunlight. Many researchers have provided overviews of various partially and completely biodegradable resins and composites. Among various cellulose, protein and starch based materials, soy protein has been studied extensively as a potential replacement for petroleum-based products due to its low cost, easy availability and biodegradability.

The respect of the environment is a capital point in a sustainable development context. We should act in this way to preserve fossil resources and reduce the pollution of the Earth. The fabrication of industrial products must consume less energy and the raw materials must be in priority renewable resources, in particular from agricultural origins. Currently, two approaches are explored to minimize the impact of polymers on the environment:

(i) The design of polymeric materials for long duration (e.g. aeronautic devices, construction materials, coatings and containers), these materials must combine unalterability and be fashioned preferentially from renewable resources (e.g. plant oil in thermoset, wood fiber in composites materials). This kind of materials for industrial interest and low environmental impact is not within the aim of this review due to a minor biodegradability.

(ii) Technological innovations designed for the production of polymers for short duration (e.g. disposable packages, agricultural mulches, horticultural pots, etc.) must have the intention of fast biodegradability. Most biodegradable polymers belong to thermoplastics (e.g. poly(lactic acid), poly(hydroxyalkanoate), poly(vinyl alcohol)) or
plants polymers (e.g. cellulose and starch). Thermoplastics from polyolefins are not biodegradable, even if some of them have prooxidant additives making them photo and/or thermodegradable Lucas, N., et al., (2008).

As an effort to develop polymers with high modulus and strength, more polymerizable functional groups are introduced onto the triglyceride molecules, resulting in high cross-linked network. The high cross-link density leads to polymers with high glass transition temperature, high modulus and high strength. However, with increasing cross-link density, the flexible character of the fatty acid chains changes as the mobility decreases, making them very brittle with poor resistance to crack initiation and propagation (Lu, J. & Wool, R. P., 2008).
2.3 Vegetable oil derived polymers

Vegetable oils are one of the cheapest and most abundant, annually renewable natural resources available in large quantities from various oilseeds, and are now being used in an increasing number of industrial applications. Vegetable oils, such as soybean oil, palm oil, and rapeseed oil, are extracted primarily from the seeds of oilseed plants and have a wide variety of applications: as foods, fuels (biofuels), lubricants, paints, cosmetics, pharmaceuticals, plasticizers, and construction materials. They are also attractive monomers for polymer chemistry due to their natural abundance and reactive functionality. In recent years, there has been a growing trend in using vegetable oils as raw materials in resin production. Among the advantages are:

(i) The vegetable oils are renewable in perpetuity,
(ii) Products derived from natural oils and fats are more readily biodegradable than the corresponding products made from petroleum and hence their impact on the environment is less, and
(iii) The long fatty acid chains of vegetable oils impart desirable flexibility and toughness to otherwise brittle resin systems such as epoxy, urethane and polyester resins.

However, their use as monomers presents challenges due to their heterogeneous and variable structures. Indeed, it can be expensive to separate and extract the different triglycerides present because the oils are typically expressed in low concentrations and the composition of particular oil can vary seasonally. The key chemical building blocks of vegetable oils are triglycerides: triesters of glycerin and fatty acids as shown in Figure 2.3. Of the five commonly occurring fatty acids, two are saturated (palmitic and stearic) and three are unsaturated (oleic, linoleic, and linolenic) (Williams, C. K, et. al., 2008).
Figure 2.3: The structure of triglycerides and the five most common fatty acid substituents for vegetable oils.

Vegetable oils are one of the most abundant biological sources and important raw materials for the production of bio-based polyurethanes because of their numerous advantages: low toxicity, inherent biodegradability, and high purity. As a result of the hydrophobic nature of triglycerides, vegetable oils produce polyurethanes that have excellent chemical and physical properties such as enhanced hydrolytic tendencies, high tensile strength and elongation, high tear strength, and thermal stability (Oprea S., 2010). On the other hand, these materials have relatively low thermal stability, primarily due to the presence of urethane bonds. The onset of urethane bond dissociation is somewhere between 150 and 220 °C, depending on the type of substituents, on the isocyanate and polyol side. Saturated hydrocarbons are known to have relatively good thermal and thermo-oxidative resistance compared to polyether and polyester polyols derived from petrochemicals (Monteavaro, L. L., 2005).

In recent years, extensive work has been done to develop polymers with triglycerides of fatty acids as the main component. Triglycerides contain several reactive positions that are amenable to chemical reactions: ester groups, C=C double bonds,
allylic positions and the α-position of ester groups. These can be used to polymerize triglycerides directly or to modify the triglyceride structure with polymerizable groups to obtain thermosets. Raw materials from vegetable oils are important sources for green polyols. As a matter of fact, vegetable oils have a number of excellent properties which could be utilized in producing valuable polymeric materials such as epoxy, polyesteramide, alkyd and polyurethane in addition to their many applications in other areas. Other traditional seeds such as linseed, soybean, amaranth, castor, sunflower kernels, cashew nut, and karanja have been used or still under development for the synthesis of different kinds polymeric resin (Velayuthama, T. S., 2009).

2.4 Waste cooking oil

As used herein, the term "waste cooking oil" includes any vegetable oil (e.g., soybean oil, peanut oil, sunflower oil, linseed oil, coconut oil, cottonseed oil, canola oil, corn oil, safflower oil, walnut oil, castor oil, tung oil, etc.), animal fat (e.g., lard, fish oil, poultry fat, tallow, etc.), or byproduct or combination thereof that has been heated to a high temperature and/or used in the preparation of food or other products.

Traditionally, these waste oils were used as an additive to animal feed. However, many harmful compounds are produced during the frying of vegetable oils. The European Union (EU), aware of this problem, banned the use of waste cooking oils in the composition of animal feed in 2002. Most of the toxic compounds in the waste cooking oil are oxidation products from fatty acids, especially from polyunsaturated fatty acids (Bautista, L. F., Vicente, G., 2009). Waste cooking oil can pose a pollution hazard if not handled properly. To prevent pollution of waterways and clogging of private and municipal drain systems, restaurants and other food preparation facilities typically save the waste cooking oil and employ sewage traps to filter grease out of waste water streams. Yellow and brown grease (also commonly referred to as trap grease, sewage grease, or black grease) are two forms of waste cooking oil that are readily available in bulk quantities. Yellow grease is of a slightly higher quality than
brown grease and typically has a free fatty acid (FFA) content of between about 4 and 15 weight percent, while brown grease typically has a FFA content of up to about 60 weight percent.

Wang, Y., (2007) studied that waste cooking oils (WCO), which contain large amounts of free fatty acids produced in restaurants, are collected by the environmental protection agency in the main cities of China and should be disposed in a suitable way. Most restaurants, especially fast food restaurants, use commercial deep frying units to cook food items such as, for example, french fries, chicken, or fish by submerging the food items in hot cooking oil. The cooking oil (typically vegetable oil) has a limited shelf life, as it degrades and becomes contaminated by pieces of food as well as water and fats released from food during the cooking process. As a result, the cooking oil is changed on a regular basis.

2.5 Polymer derives from renewable resources

The most well-known and widely used renewable biodegradable polymers are those from polysaccharides. The principal polysaccharides of interest to polymer chemists are starches and cellulose, both of which are polymers of glucose. In addition to these, fibers, polylactic acid (PLA), and triacylglycerols of oils are of particular interest for the development of biodegradable industrial polymers.

2.5.1 Starch

Starch is the most common polymer found in plants. Large amounts of starch can be obtained from tubers such as potatoes, from cereals such as rice, and from seeds such as corn. The starch-filled polyethylene films become porous after the extraction of starch. This porous film can then be readily invaded by micro-organisms and rapidly saturated
with oxygen, thereby increasing polymer degradation by biological and oxidative methods.

Studies on the thermal degradation of starch reported that thermal reactions for starch start around 300 °C with thermal condensation between hydroxyl groups of starch chains to form ether segments and liberation of water molecules and other small molecular species. The starch structure disintegrated after heating to 400 °C, and above that temperature a highly crosslinked system was formed similar to thermally crosslinked phenol/benzene/furfuryl resins. Thereafter, the thermal reactions of the system followed similar reaction pathways as phenol–formaldehyde or furfuryl resins undergoing thermal crosslinking and decomposition at increased temperatures (Narine, S. S. & Kong, X., 2005).

2.5.2 Cellulose

Cellulose is the most abundantly occurring natural bio-polymer. Cellulose is a linear, unbranched homopolysaccharide. It resembles amylose, which is the primary polymeric constituent of starch.

Cellulose is now receiving greater attention from polymer chemists because of the easy manner in which it undergoes biodegradation by certain micro-organisms. Cellulose esters represent a class of polymers that have excellent physical properties and are relatively low-cost materials with high market potential. The structure of cellulose acetate is shown in Figure 2.4.

![Figure 2.4: Structure of cellulose (Pielichowski, K and Njuguna, J., 2005).](image-url)
2.5.3 Fibers

In addition to starch and cellulose, a wide variety of organic materials have significant commercial importance to the plastic industry.

Fibers, among these, are being currently used as fillers and reinforcing agents in plastic materials. The primary advantages of using renewable lignocelluloses fibers as additives in polymers are:

(i) Have low densities
(ii) Are low-cost materials
(iii) Have a nonabrasive nature
(iv) Provide high filling levels
(v) Require low-energy consumption
(vi) Have high specific properties
(vii) Are biodegradable and environmentally friendly
(viii) Have wide varieties available throughout the world

2.5.4 Polylactic acid (PLA)

Polylactic acid is not a new polymer. It belongs to the family of aliphatic polyesters commonly made from -hydroxy acids, which can be synthesized via two major routes. One method involves the removal of water using solvent, under conditions of high temperature and pressure. The polymer yielded using this method may be coupled with isocyanates, epoxides, or peroxides to produce a variety of other polymers.
2.5.5 Triacylglycerol oils

It has been reported above that low-cost biodegradable polymers can be prepared by using polysaccharides, fibers, and polylactic acid.

In addition to these renewable resources, naturally occurring triacylglycerol (TAG) oils are also significant starting materials for the production of biodegradable polymers. Vegetable oils are abundant and widely available; they are relatively low cost materials and offer a possibility of biodegradation. They consist of triglyceride molecules that are esters of glycerol and fatty acids, predominantly unsaturated fatty acids. These triglycerides present many reactive sites able to be reacted in order to obtain a product for the polymer industry. Polymer prepared from vegetable oils has a number of excellent properties due to the hydrophobic nature of triglycerides. On the other hand; these materials have relatively low thermal stability, primarily due to the presence of urethane bonds (Monteavaro, L. L., 2005).

Plant oils mainly consist of triacylglycerols (TAGs), which can be processed into high-value biochemicals for various industries. In polymer applications, the conversion of oilseed crops into bioplastics could be a sustainable alternative which could compete with plastics obtained from petroleum chemicals. It has been already shown that polyurethane (PU) produced using vegetable oils such as soybean oil present some excellent properties such as enhanced hydrolytic and thermal stability (Bouzidi, L., Kong, X. & Narine, S., 2007).

2.6 Methylene-4, 4'-diphenyldiisocyanate (MDI) as a curing agent

Isocyanates are the derivatives of isocyanic acid (H-N=C=O).

The functionality of the isocyanate (-N=C=O) group is highly reactive toward proton-bearing nucleophiles, and the reaction of isocyanate usually proceeds with addition to the carbon-nitrogen bond. The reactions of isocyanates fall into two main categories: (1) active hydrogen donor, and (2) nonactive hydrogen reaction. The more significant of these is the first category, where isocyanates react with polyols, which
Involves reaction with active hydrogen. The second category of reactions involving nonactive hydrogen reactions usually leads to cycloaddition products and linearly polymerized products. Figure 2.5 show some examples of diisocyanates: toluene diisocyanate (TDI), hexamethylene diisocyanate (HMDI), and cyclohexane diisocyanate (CHDI). The reactivity of isocyanates depends on their chemical structures. Aromatic isocyanates are usually more reactive than their aliphatic counterparts (Narine, S. S. & Kong, X., 2006). Polymeric isocyanates (such as polymeric MDI) are extremely thermally stable and produce thermally stable polymer.

Polyurethane (PU) prepared from a polyoxypropylene triol, Pluracol TP-440, and four different isocyanates followed the thermal stability order: HDI < 2, 4-TDI < dianisidine diisocyanate (DADI) < polymeric MDI. MDI-based PU also possess considerably higher tensile strength compared to others, which are prepared from other isocyanates. However, it is more flexible probably due to the presence of methylene linkages between the aromatic rings. The effect of isocyanates on the crystallinity and thermal stability of PU revealed that PU prepared from aralkyl diisocyanates like XDI had the best thermal stability. The PU synthesized from aromatic diisocyanates such as TDI or MDI had worse thermal stability, than those from XDI. However PU prepared from MDI had a better thermal stability than those based on TDI owing to its better crystallinity. It has also been observed that polyurethanes prepared from aromatic diisocyanates turns yellow on exposure to UV light. This can be prevented using aliphatic diisocynates or aromatic diisocyanates in which the NCO group is not attached directly to the benzene ring.

Figure 2.5: Chemical structure of aromatic and aliphatic diisocyanates in PU chemistry.
2.7 Thin films of polymeric materials

During outdoor exposure, polymers degrade chemically due to the action of short wavelength UV rays present in the solar spectrum.

The service-life of polymers in outdoor applications becomes limited due to weathering. The weathering leads to a loss of physical properties in polymers. This loss is caused by scission of bonds randomly in the polymer chain resulting in the formation of free-radicals, which migrate along the chain. The tensile properties of polymer from renewable resources (including elongation at break) are measured following the EN ISO 527-3 or its equivalent ASTM D 882, which are suited for films less than 0.25 mm in thickness. The mechanical properties (tensile strength and elongation at break) were determined according to a standard test method that has been frequently used in the literature for the characterization of strength and flexibility of free polymeric films. Mechanical properties such as tensile strength and percent elongation at break are determined to characterize polymeric films for their abrasion resistance and flexibility, respectively.

These two values of polymeric thin films can be classified as shown in Table 2.1. This classification, however, is not based on absolute values for the two parameters tensile strength and elongation but has to be seen as a relative comparison between different polymeric films. Hard and tough films have properties suited best for the intended application as drug delivery systems for the skin: they are flexible enough to follow the movements of the skin without breaking but at the same time they show an increased strength to prevent abrasion of the film caused for example by contact with clothing.

Table 2.1: Classification of polymeric thin films (Schroeder, I. Z., Franke, P., 2007)

<table>
<thead>
<tr>
<th>Tensile strength</th>
<th>Elongation at break</th>
<th>Film description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Low</td>
<td>Low</td>
<td>Soft and weak</td>
</tr>
<tr>
<td>Low</td>
<td>High</td>
<td>Soft and tough</td>
</tr>
<tr>
<td>High</td>
<td>Low</td>
<td>Hard and brittle</td>
</tr>
<tr>
<td>High</td>
<td>High</td>
<td>Hard and tough</td>
</tr>
</tbody>
</table>
Table 2.2: Mechanical properties of different polymeric thin films that had displayed sufficient strength and flexibility on human skin in vivo; evaluation criterion: integrity on skin after 18 h; rating 1: complete film, no cracks, no flaking; mean value (±SD).

<table>
<thead>
<tr>
<th>Trade name</th>
<th>Polymer</th>
<th>Tensile strength (N/mm²)</th>
<th>Elongation at break (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dynam X®</td>
<td>Polyurethane-14 and AMP-acrylates Copolymer</td>
<td>12.2 (±1.0)</td>
<td>323.4 (± 42.1)</td>
</tr>
<tr>
<td>Eudragit® RL PO</td>
<td>Ammonio methacrylate copolymer</td>
<td>1.0 (±0.1)</td>
<td>798.4 (±93.9)</td>
</tr>
<tr>
<td>Klucel® LF</td>
<td>Hydroxypropylcellulose</td>
<td>5.0 (±0.3)</td>
<td>131.4 (±5.8)</td>
</tr>
</tbody>
</table>

Based on this observation it was expected that all three formulations formed films with similar mechanical properties, most probably thin films classifiable as hard and tough behaviour. The upper half of Table 2.2 shows the results for tensile strength and percent elongation at break for the three tested films. Surprisingly, the results for the three films revealed considerable differences. While the Eudragit® RL PO film showed a high elongation with a low tensile strength (rather soft and tough), the Klucel® LF film displayed a low elongation with medium tensile strength (fairly soft and weak in comparison to the Eudragit® RL PO film). Only the third film, the DynamX® formulation, could be classified as hard due to its comparatively high tensile strength. Concerning the elongation this film was weaker than the Eudragit® RL PO film but tougher than the Klucel® LF film. The similar strength and flexibility of these three films observed on living skin was apparently not reflected in the results of the in vitro experiments (Schroeder, I. Z., Franke, P. 2007).
2.8 Degradation of polymers

Degradation of polymers includes all the changes in the chemical structure and physical properties of the polymers due to external chemical or physical stresses caused by chemical reactions, involving bond scissions in the backbone of the polymer that lead to materials with characteristics different from (usually worse than) those of the starting material.

Polymer degradation in broader terms includes biodegradation, pyrolysis, oxidation, and mechanical, photo- and catalytic degradation. According to their chemical structure, polymers are vulnerable to harmful effects from the environment. This includes attack by chemical deteriogens – oxygen, its active forms, humidity, harmful anthropogenic emissions and atmospheric pollutants such as nitrogen oxides, sulfur dioxide and ozone – and physical stresses such as heat, mechanical forces and radiation. Generally, degradation rate of polymeric materials depends to a great extent on the nature of the material and environmental aggressiveness to which they are exposed. It is well established that the degradation of PE, exposed to heat and/or UV-light, involves thermo- and/or photo-oxidation. These reactions lead to the build-up of a variety of oxygen containing groups such as different carbonyl compounds (Yildiz, Y., Kizilcan, N & Uyanik, N., 2006)

Partially biodegradable polymers obtained by blending biodegradable and non-biodegradable commercial polymers can effectively reduce the volume of plastic waste by partial degradation. They are more useful than completely biodegradable ones due to the economic advantages and superior properties, imparted by the commercial polymer used as a blending component (Thakore, I. M., Desai, S., Sarawade, B. D & Devi, S., 2006). Utilization of biodegradable polymers offers a solution to this problems faced by mankind. Except for petrochemical product family, which is of fossil origin, most biodegradable polymers are obtained from renewable resources or biomass. The biomass product family is agro polymers obtained from biomass by fractionation. The microorganisms and biotechnology families are polyesters, obtained, respectively by fermentation from biomass or from genetically modified plants and by synthesis from monomers obtained from biomass (Ramarad, S., 2008). Degradation has been reflected in changes of material properties such as mechanical, optical or electrical characteristics,
in crazing, cracking, erosion, discoloration, phase separation or delamination. The changes include bond scission, chemical transformation and formation of new functional groups. The degradation will either be photo, thermal or biological.

Figure 2.6: Classification of biodegradable polymers classified into four families (Ramard, D. S., 2008).

Figure 2.6 shows classification of biodegradable polymers and they are classified into four families. Except for petrochemical product family, which is of fossil origin, most biodegradable polymers are obtained from renewable resources or biomass. The biomass product family is agro polymers obtained from biomass by fractionation. The microorganisms and biotechnology families are polyesters, obtained, respectively by fermentation from biomass or from genetically modified plants and by synthesis from monomers obtained from biomass. The petrochemical products family are also polyesters but totally synthesized by petrochemical process.
2.9 Biodegradation

The term "biodegradable plastic" is defined by ASTM as "a degradable plastic in which degradation results from the action of naturally occurring microorganisms such as bacteria, fungi, and algae (Kijchavengkula, T., & Auras, R. 2006). Therefore, microorganisms are responsible for plastic biodegradability by using it as a food source. During biodegradation, carbon in polymer molecules is converted by microorganisms into biomass or humus, water, carbon residues, and carbon dioxide gas as defined by Eq. 2.1:

\[
\text{Bio-degradation}
\]

\[
\text{Polymer} + \text{O}_2 + \text{Biomass} + \text{Minerals} \rightarrow \text{CO}_2 + \text{H}_2\text{O} + \text{Biomass} + \text{Residue} \quad (2.1)
\]

Biodegradation is therefore considered as a subset of degradation, which is defined here as any physical or chemical change in a material caused by any environmental factor, including light, heat, moisture, wind, chemical conditions or biological activity. The field tests burying plastic samples in soil have been widely conducted for their biodegradation because of the similarity to actual conditions of use or disposal (Sasek, V. & Chcromcova, D., 2005).

An international test method applied to perform soil burial test in the laboratory in EN ISO 846:1997 (Itavara, M., 2002). After disposal, bio-polymers are degraded in natural environments, such as soil, active sludge, fresh water, and seawater. Many prokaryotic and eukaryotic microorganisms secrete extracellular depolymerases capable of hydrolyzing biopolymers, and utilize the resultant decomposed compounds as nutrients. Finally, the compounds can be converted into renewable resources, such as CO\textsubscript{2} and biomass (Hiraishi, T & Taguchi, S., 2009). The biodegradation of polymeric materials includes several steps and the process can stop at each stage:

(i) The combined action of microbial communities, other decomposer organisms or/and abiotic factors fragment the biodegradable materials into tiny fractions. This step is called biodeterioration.