

BIO-DEGRADATION OF POLYURETHANE BASED ON BIO-EPOXY

ASSOC. PROF. DR. ANIKA ZAFIAH BINTI MOHD RUS

Members:

**PROF. DR. DARWIN SEBAYANG
CIK SAFFIAH BINTI ABDULLAH KHIR
DR AHMAD MUJAHID BIN AHMAD ZAIDI
ENCIK MOHAMED NASRUL BIN MOHAMED HATTA**

**FUNDAMENTAL RESEARCH GRANT SCHEME (FRGS)
VOT 0556 (PHASE 1/2008)**

UNIVERSITI TUN HUSSEIN ONN MALAYSIA

ABSTRACT

This research is focused on the resistance to thermal, photo and bio-degradation of polymer thin films from renewable resources based on virgin and waste vegetable cooking oil from Industri Kecil Sederhana (IKS's). Vegetable and waste vegetable oil polymers were grouped as virgin oil polymer (VOP) and waste oil polymer (WOP) thin films were prepared by adding bio-monomer (1gm; 0.5 gm equivalent weight with polyol) with an appropriate amount of 4, 4'-methylen-bis-(phenylisocyanate) (MDI) which thickness was 110-200 μm \pm 0.01 μm . VOP and WOP thin films were tested for its resistance to thermal, photo and bio-degradation exposure for an extended period of time. The techniques utilized were principally infra-red (IR). The degradation of which upon thermal exposure was tested by measuring the change in the carbonyl index, CI for WOP and VOP thin films. Thermal exposure was measured at 50°C, 100°C, 150°C and 200°C up to 600 minutes. As the temperature and the exposure time increased, the CI also increases for both WOP and VOP at given temperature and 600 minutes from initial value of WOP is 0.296 to 0.391, 0.380, 0.413 and 0.427, meanwhile the initial value for VOP is 0.417 to 0.507, 0.45, 0.433 and 0.44 respectively. The increased in CI formation for polymer after thermal exposure is proportional to the number of chain scissions that occur in the polymer thin films associated with the scission of the (-NHCO-O-). The absorption band of carbonyl groups near 1738 cm^{-1} was broadened on increasing the heating time; also shoulders appeared on the main peaks in a range at 1805-1800 cm^{-1} . The shape of the peaks for all spectra thin films are fairly broad suggesting that more than one functional groups are formed within the carbonyl group (C=O) family such as aldehydes, ketones, acids, esters, amides and anhydrides in the range of 1805-1704 cm^{-1} . The TGA curves of the WOP and VOP display three distinct regions of weight loss. The size of the peak at higher temperature was found to be correlated with the amount of soft segment that can be attributed to the alkyl chain. It was established previously that the amount of weight loss at the lower temperature is well correlated with the amount of hard segment, suggesting that the degradation process starts in the hard segment based on the MDI component. Biodegradability of polymer thin films was measured using soil burial test according to EN ISO 846:1997. The percentage weight loss of VOP thin film in compost soil burial test was significantly greater than those in peat soil burial test. IR-changes, yellowing of tensile WOP thin films as a result of photo-degradation upon equatorial weathering were studied. As a conclusion, mechanical properties of polymer thin films for WOP and VOP can be strongly influenced by photo-oxidation upon equatorial weathering exposure. The ductility disappears and the strength and strain at rupture strongly decrease at over 35%. 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. Moreover, the occurrence of surface damage enhances the degradation of these mechanical parameters.

CONTENTS

TITLE	i
DECLARATION	ii
DEDICATION	iii
ACKNOWLEDGEMENT	iv
ABSTRACT	v
CONTENTS	vii
LIST OF TABLE	xiv
 CHAPTER 1 INTRODUCTION	
1.1 Research background	1
1.2 Problem statement	4
1.3 Research aim	5
1.4 Research objective	6
1.5 Research scope	6

CHAPTER 2 LITERATURE REVIEW

2.1	Background of polymers	8
2.2	Renewable resources	11
2.3	Vegetable oil derived polymers	13
2.4	Waste cooking oil	15
2.5	Polymer derives from renewable resources	16
2.5.1	Starch	17
2.5.2	Cellulose	18
2.5.3	Fibers	18
2.5.4	Polylactic acid (PLA)	19
2.5.5	Triacylglycerol oils	20
2.6	Methylene-4, 4'-diphenyldiisocyanate (MDI) as a curing agent	20
2.7	Thin films of polymeric materials	22
2.8	Degradation of polymers	24
2.8.1	Mechanisms of polymer degradation and erosion	28
2.9	Biodegradation	26
2.10	Thermal degradation	30
2.10.1	Thermal oxidation	31
2.10.2	Thermal stability of polymeric materials	32
2.10.3	Mechanism for thermal degradation polymer	35
2.10.4	Soft and hard segment	37
2.10.4.1	Degradation mechanism of hard and soft segment	39
2.10.4.2	Hard segment	40
2.10.4.3	Soft segment	42
2.11	Photo-oxidation degradation	42

2.11.1	Light source	43
2.11.2	Impact of ultraviolet radiation on polymers	43

CHAPTER 3

METHODOLOGY

3.1	Introduction	48
3.2	Preparation of monomer	49
3.3	Polymer thin films from renewable resources preparation	50
3.4	Biodegradability test for VOP and WOP thin films upon natural soil burial test standard according to EN ISO 846:1997	53
3.4.1	pH determination of starting peat soil and compost medium	55
3.4.2	Visual observations and optical microscopy for VOP and WOP thin films	55
3.4.3	Weight loss measurements for VOP and WOP thin films upon bio-degradation: Determination of residual polymer	56
3.4.4	Attenuated total reflectance- Fourier transform infra-red (ATR-FTIR) spectroscopy for VOP and WOP thin films upon bio-degradation	57
3.5	Thermal degradation for VOP and WOP thin films upon thermal exposure	57
3.5.1	Attenuated total reflectance- Fourier transform infra-red (ATR-FTIR) spectroscopy and thermo gravimetric analysis (TGA) for thermal degradation	57

3.6	Thermal stability of VOP and WOP thin films upon TGA	58
3.7	Mechanical properties of tensile thin film according to ASTM D882 Standard test method for tensile properties of thin plastic sheeting	59
3.8	Equatorial weathering exposure test according to ASTM D1435 Standard practice for outdoor weathering of plastics	61

CHAPTER 4

RESULTS AND DISCUSSION

4.1	Bio-degradability test for VOP and WOP thin films upon natural soil burial test according to EN ISO 846: 1997	64
4.1.1	Infrared spectroscopic (FT-IR) study for bio-degradability test for VOP and WOP thin films	72
4.1.2	Morphological changes of polymer thin films during bio-degradation by optical microscope observation	75
4.2	Thermal degradation of polymer thin films of VOP and WOP upon oven exposure	79
4.2.1	Carbonyl indices (CI) of (VOP) and (WOP) upon thermal exposure	86
4.2.2	Optical microscope for WOP thin films at 50°C, 100°C, 150°C and 200°C upon oven exposure for 600 Minutes	90
4.3	Thermal gravimetric analysis (TGA) measurements for VOP and WOP thin films from renewable resources	93
4.3.1	Weight loss kinetics of VOP and WOP thin films from renewable resources	97

4.3.2	Hard and soft segment in IR spectra of polymer thin films for VOP and WOP upon TGA	101
4.3.3	Hard segment thermal degradation spectra for WOP thin film	103
4.3.4	Soft segment thermal degradation spectra for WOP thin film	107
4.4	Mechanical properties polymer thin films upon equatorial weathering exposure	114
4.4.1	Surface damage of WOP thin films after equatorial weathering by photo-oxidation	117

CHAPTER 5

CONCLUSION	127
SUGGESTION FOR FUTURE RESEARCH WORKS	129
REFERENCES	130
APPENDIX	144

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 intramolecular (-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, F., Hameed, A. & Ahmed, S., 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 polyol 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 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 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. and 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. These results 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 (ϵ -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. They are searching for new raw materials that can be synthesized into environmentally friendly polymers so as to make available the materials needed by various industries at lower costs. These new materials are, in fact, not so new; they stem from natural agricultural sources, called "renewable resources". By definition, renewable resources are the agricultural products that are synthesized by the use of solar energy. Some examples of these resources are polysaccharides, such as cellulose and starch, and glycerol esters of fats and oils (Narine, S. S & Kong, X., 2006).

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' diphenylmethanediisocyanate and polyol 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 polymer from renewable resources.

The key objective of the research is to modify the polymer from oil palm for a variety of reasons such as biodegradable, improved processing and stability upon thermal and weathering exposure for extended periods. The increased outdoor use of plastics has created a need for a better understanding of the effect of the environment on plastics materials. The changes that can occur in a material with photo-oxidation can affect its application, performance, and lifetime; therefore, a study of this effect is very important. The unique properties of polymer from renewable resources were to produce a range of materials with varied properties to encourage industrial uptake.

1.4 Research objective

1. To study thermal degradation of polymer thin films from renewable resources indicates by the formation of carbonyl index (CI) investigated by Fourier Transform Infra-red (FT-IR).
2. To proposed thermal decomposition mechanism of polymer thin films for hard segment and soft (polyol) segment by thermogravimetric analysis (TGA).
3. 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 toxic residue of soil medium by pH measurement.
4. To prepare polymer tensile thin films with thickness not greater than 0.25 mm for mechanical properties (tensile test).
5. To expose polymer tensile thin films upon equatorial induced degradation for photo-oxidation degradation study.

1.5 Research scope

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

Soil burial method is a largely employed test method for biodegradation 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 films can be examined in a quantitative manner by studying changes in chemical

constitution with the aid of techniques like Fourier Transform Infrared spectroscopy (FTIR) 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 thermogravimetric 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). 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 polymer as a result of UV irradiation. 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).

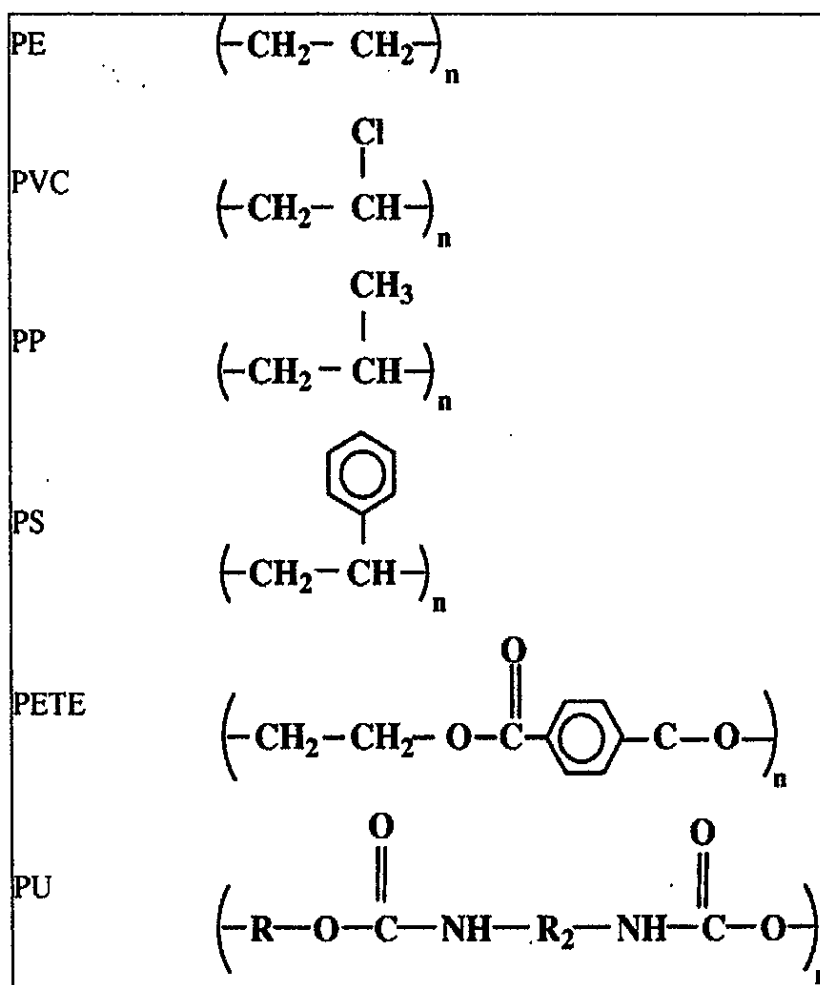
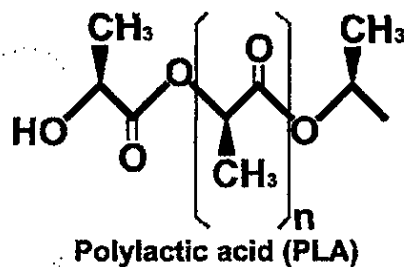
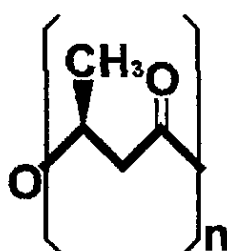


Figure 2.1: Structures of conventional petrochemical plastics polyethylene (PE), polyvinyl chloride (PVC), polypropylene (PP), polystyrene (PS), polyethylene terephthalate (PET), polyurethane (PU).

a)



b)



c)

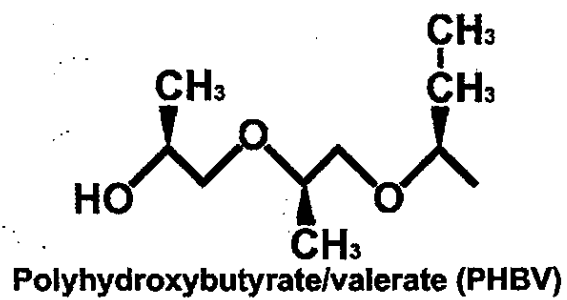


Figure 2.2: (a) - (c) Structure of polymers produced by bacteria using plant materials.

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, rapseed, 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.

Alternatively waste cooking oil is used because of their potential to substitute petrochemical derivatives. Waste cooking oil usually has large amounts of fatty acids, triglycerides, polymers and decomposition products. This residue poured down the drain, resulting in problems for waste water treatment or plants and energy loss, or it's integrated into the food chain through animal feeds, thus becoming a potential cause of health problem.

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 & Hillmyer, M. A., 2008).

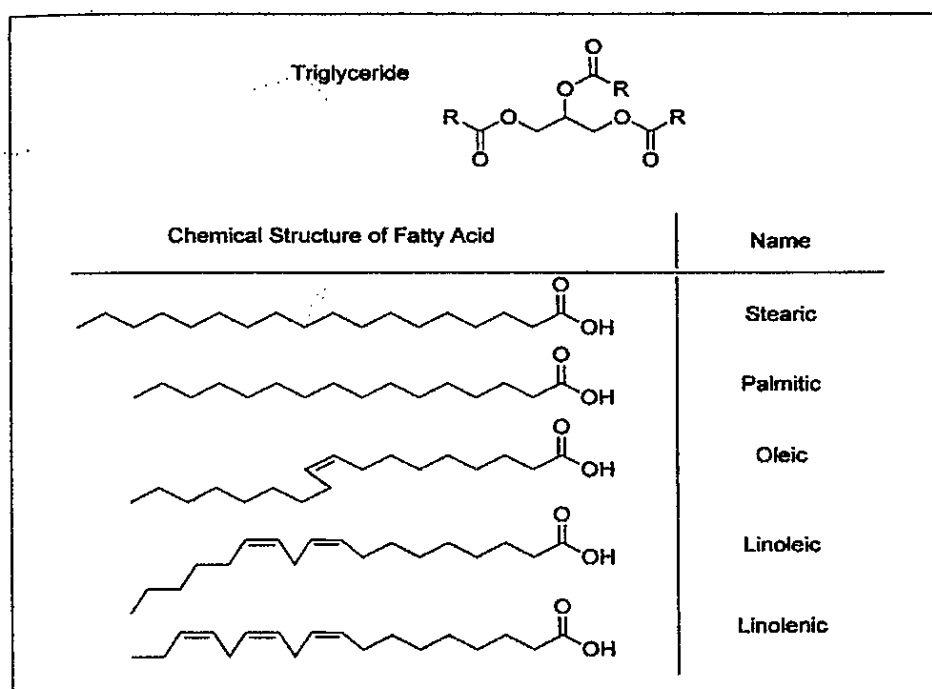


Figure 2.3: The structure of triglycerides and the five most common fatty acid substituents for vegetable oils.

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 used 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. The current supply of yellow and brown grease exceeds the demand for these feedstocks.

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 submersing 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 molecule is heavily hydrated as it contains many exposed hydroxyl groups, which form hydrogen bonds on coming into contact with water. 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. Dehydration of neighbouring hydroxyl groups in the glucose ring also occurred, resulting in the formation of C=C bonds or breakdown of the glucose ring. Increasing temperature generated aromatic rings, such as substituted benzene and furan structures with either $-\text{CH}_2-$ or $-\text{CH}_2-\text{O}-\text{CH}_2-$ as the main linkages between the aromatic groups. 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.

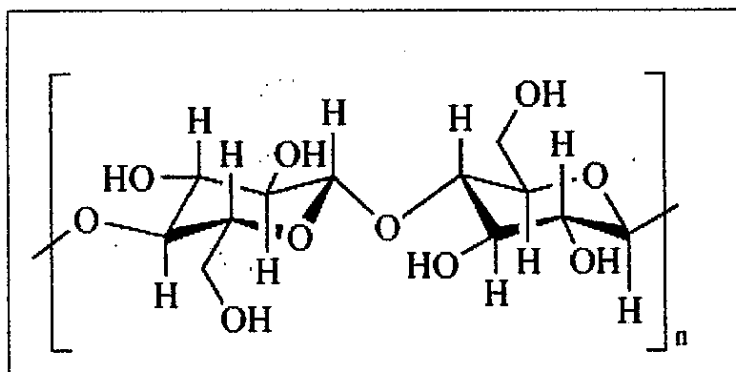


Figure 2.4: Structure of cellulose (Pielichowski, K and Njuguna, J., 2005).

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 α -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. *et al.* 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 ($-\text{N=C=O}$) 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. Some examples of diisocyanates are: 2, 4-toluene diisocyanate, 2,6-toluene diisocyanate, 1,6-hexamethylene diisocyanate, and 1,5-naphthalene diisocyanate, among others. 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.

Baumann showed that PUs 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 polyurethanes 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 polyurethanes revealed that polyurethanes prepared from aralkyl diisocyanates like XDI had the best thermal stability. The polyurethanes synthesized from aromatic diisocyanates such as TDI or MDI had worse thermal stability, than those from XDI. However polyurethanes 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 diisocyanates or aromatic diisocyanates in which the NCO group is not attached directly to the benzene ring.

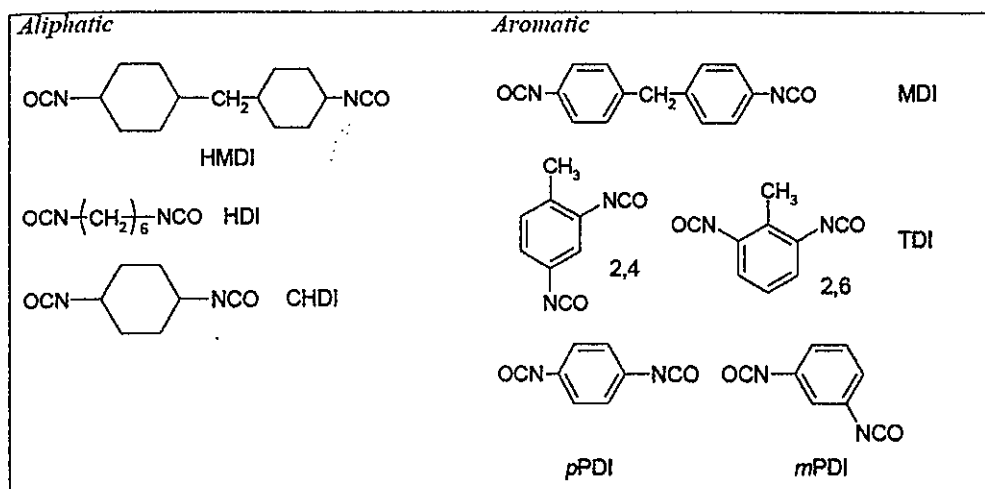


Figure 2.5: Chemical structure of aromatic and aliphatic diisocyanates in PU chemistry.

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 rapid 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).

Tensile strength	Elongation at break	Film description
Low	Low	Soft and weak
Low	High	Soft and tough
High	Low	Hard and brittle
High	High	Hard and tough

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 (\pm SD).

Trade name	Polymer	Tensile strength (N/mm ²)	Elongation at break (%)
Dynam X®	Polyurethane-14 and AMP-acrylates Copolymer	12.2 (\pm 1.0)	323.4 (\pm 42.1)
Eudragit® RL PO	Ammonio methacrylate copolymer	1.0 (\pm 0.1)	798.4 (\pm 93.9)
Klucel® LF	Hydroxypropylcellulose	5.0 (\pm 0.3)	131.4 (\pm 5.8)

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 macromolecules 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 deterogens – 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.

REFERENCES

- Arkatkar, A., Arutchelvi, J., Sudhakar, ., Bhaduri, S. & Uppara, P. V. (2009). Approaches to enhance the biodegradation of polyolefins. *The Open Environmental Engineering Journal*, 2, pp. 68-80.
- ASTM International (2002). Standard Test Method for Tensile Properties of Thin Plastic Sheeting. United States: ASTM D882-10.
- ASTM International (2002). Standard Practice for Outdoor Weathering of Plastics. United States: ASTM D 1435 – 05
- Bastarrachea, M. I. L., Kao, W. H., Cervantes, J. M. (2010). A TG/FTIR Study on The Thermal Degradation of Poly(Vinyl Pyrrolidone). *J Therm Anal Calorim*, vol. 10. 1023- 1061.
- Bastioli, C. (2005). *Handbook of Biodegradable Polymers*. Rapra Technologies. United Kingdom.

- Bautista, L. F., Vicente, G. (2009). Optimisation of FAME Production from Waste Cooking Oil for Biodiesel use. *J.Biomass and Bioenergy*, vol. 33, pp. 862- 872.
- Behjat, T., Russly, A.R., Luqman, C. A., Yus, A. Y. & Azowa, N. (2009). Effect of PEG on the biodegradability studies of kenaf cellulose -polyethylene composites. *International Food Research Journal*, vol. 16, pp. 243-247.
- Bouzidi, L., Kong, X. & Narine, S. (2007). Physical Properties of Polyurethanes Produced from Polyols from Seed Oils: I. Elastomers. *J Amer Oil Chem Soc*, vol. 84, pp. 55-63.
- Cerventes, J. M., Causich, J. V. (2006).TGA/FTIR Study on Thermal Degradation of Polymethacrylates Containing Carboxylic Groups. *Polymer Degradation and Stability*, vol 91, pp. 3312-3321.
- Chang,T. C., Shen, W. S., Chid, Y. S. & Ho, S. Y. (1995).Thermo-oxidative Degradation of Phosphoruscontaining Polyurethane. *Polymer Degradation and Stability*, vol. 49. 353-360.
- Chattopadhyay, D. K., Webster, D. C. (2006). Thermal Stability and Flame Retardancy of Polyurethanes. *Progress in Polymer Science*, vol. 3, pp. 2389-2356.