

**INVESTIGATION OF HUMIDITY AND TEMPERATURE EFFECTS ON THE
ACCELERATED PHOTODEGRADATION OF POLYETHYLENE FILMSIES
USING DMA**

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**A Thesis Submitted to the Graduate School in Partial Fulfillment for the
Requirements of the Degree of Master of Science in Physics of Egerton
University**

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DECLARATION AND RECOMMENDATION

DECLARATION

This Thesis is my original work and has not been presented for any award in any university.

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RECOMMENDATION

This thesis has been submitted for examination with our approval as the candidates' supervisors.

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ABSTRACT

Polyethylene (PE) is a polymer of ethylene (ethene) used in the manufacture of packaging bags. The considerable growth in use is due to the beneficial properties it has over other alternatives. These include, extreme versatility, it is light, extreme durability, resistance to chemicals, water and impact, good hygiene properties for food packaging, excellent thermal and electrical insulation properties and relatively inexpensive. However PE disposal is a challenge, resulting in the used products littering almost every place. This creates a menace obscuring the benefits of PE to the society. Knowledge of environmental factors that can accelerate its rate of photodegradation and wavelength sensitivity of its degradation is an essential tool for effective management of its ultimate disposal. This study sought to establish presence of chromophoric sites in PE which dictates susceptibility to natural degradation in the presence of sunlight. The samples were exposed to sunlight at Egerton University Njoro area. The effects of humidity, temperature and radiation wavelength to photodegradation of flimsies were carried out. Samples were irradiated with (200-300)nm and (300-400)nm ultraviolet(UV) light ranges for two hours and exposed to environments of varying humidity and temperatures. Temperature was varied from room temperature ($\approx 24\text{ }^{\circ}\text{C}$) to 40°C and 55°C while the relative humidity (RH) was varied from room humidity (25% RH) to 40% RH and 60% RH. Dynamic mechanical analysis was done using DMA-2980 instrument to detect changes in loss factor (δ), storage (E') and loss (E'') modulus which implies degradation. This analysis was made after 50 hrs, 150hrs and 350hrs of exposure. Results show that there is a possible existence of hydroxyl, carbonyl, carboxyl, ketonic compounds or amino groups as chromophores. However UV absorption was below 62%. Hence these films were relatively unstable to sunlight UV with a 42.4% drop in storage modulus after 150 days. Irradiation of (300-400)nm UV range accelerated degradation higher than the (200-300)nm range with similar exposure conditions. Degradation was also higher at 55°C than at 40°C other conditions similar. The highest observed reduction of storage modulus (aging) of 74.6% occurred at (300-400)nm irradiation and 55°C temperature treatment. Raising humidity from 25% RH to 60% RH resulted in increase in percentage drop of storage modulus from 41% to 67%. Natural degradation of these products was low and was accelerated as expected by an initial UV irradiation and exposure to high temperature and humidity conditions. PE products should be formulated with more absorption sites. Pre-use UV irradiation especially within (300-400)nm range and enhanced moisture absorption at higher temperature should be employed to accelerate degradation to curb PE products disposal menace.

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LIST OF ABBREVIATIONS AND ACRONYMS

DMA	Dynamic Mechanical Analyzer
ESR	Electronspin Resonance
FTIR	Fourier Transform Infrared
HDPE	High Density Polyethylene
HOMO	Highest Occupied Molecular Orbital
IUPAC	International Union of Pure and Applied Chemistry
LD	Low Density Polyethylene
LLPDE	Linear Low Density Polyethylene
LUMO	Lowest Unoccupied Molecular Orbital
NEMA	National Environment Management Authority
PE	Polyethylene
PLA	Polylactic acid
PMMA	Polymethylmethacrylate (Acrylic)
POM	Polyoxymethylene
PVC	Polyvinylchloride
RH	Relative Humidity
T _g	Glass transition temperature
TA	Thermal Analysis
TSD	Thermally Stimulated Depolarization.
UHMW	Ultra High Molecular Weight Polyethylene
UV	Ultraviolet
UV-B	Ultraviolet B (315–280)nm

CHAPTER ONE INTRODUCTION

1.1 Background Information

PE flimsies are widely used in packaging (Gowariker *et al*, 1988 and Shakhashiri, 2008). The considerable growth in use (especially HDPE and LDPE) is due to the beneficial properties it has over other alternatives. These include, extreme versatility, extreme durability, resistance to chemicals, water and impact, good safety and hygiene properties for food packaging and relatively inexpensive to produce.

Around 4000 tons of LPDE are produced in Kenya every month (Shashank, 2006). Statistics also show that recycling of plastic bags is very low, it's estimated to be 1-3% (Sara *et al*, 2005). Plastic bags constitute 12% of 1500 tonnes solid waste produced daily in Nairobi alone and only 25% of it is collected (Ikiara, 2004). The recycling rates for plastic bags are extremely low due to the following factors. First, plastics are made from many different resins, and because they cannot be mixed, they must be sorted and processed separately. Most plastics also contain stabilizers and other chemicals additives that must be removed before recycling. Second, recovering individual plastic resins does not yield much material because only small amounts of any given resin are used per product. Third, the price of oil used to produce petrochemicals for making plastic resins is so low that the cost of virgin plastic resins is much lower than that of recycled resins. As a result, recycling is not economical and therefore not a simple solution to cut the created menaces (Sara *et al*, 2005). The possibility of bacterial or toxic contamination restricts the use of recycled plastics in food containers (John, 1993).

Use of PE and the unrestrained disposal of used PE products have led to continual accumulation of these products as garbage. PE products disposal problems already exist in Kenya, especially in major cities like Nairobi and Mombasa. This is evident with PE bag landfills well pronounced in urban areas and littering almost every place (Masyuko, 2006). The menace brought about, affects every aspect of human life. It also has serious environment implications (Sara *et al*, 2005). The benefits of PE to the society therefore have been obscured by the problem of their ultimate disposal.

During the Kenya budget speech for the fiscal year 2007/8 read on 14th June 2007, tax policy measures banning thin bags (20µm and below) were proposed (Kimilu, 2007). The recommended heavier bags however are expected to take much longer to degrade once they end littering environment or in garbage sites, failing to offer a lasting solution to the problem. There is a need therefore to address a balance and a need for creative and concerted management of waste disposal.

In general PE degrades naturally with time. PE photodegradation like in other polymers leads to the material deteriorating mechanical properties. This degradation results from chemical bond scission reactions that are ignited by a number of ways depending on the kind of environment the polymer is exposed to. These modes of initiation may include chemical, mechanical, thermal, photo radiation, high energy radiation and biological (Schnabel, 1981). Natural photodegradation is ignited by absorption of ultraviolet (UV) radiation reaching the earth's surface from the Sun. The process of photodegradation starts with the UV radiation absorption by the chromophoric sites. PE may have chromophoric groups as constituent additives, impurities or as defects introduced during manufacture. Over the years research has been focused on polymer photodegradation with an aim of improving their stability leading to discovery of stabilizers. Use of stabilizers has led to production of PE products that are able to withstand the harsh environmental conditions without decaying. Also during manufacture other additives are added to the product, for the manufacturer's specifications. Combination of these factors makes the prediction of rate of photodegradation of a manufactured PE product difficult. Hence there is a need to study the changes of mechanical properties Vis a Vis photodegradability of these products with an aim of accelerating degradation process.

1.2 Statement of the Problem

PE stability against degradation leads to the littering menace. Recycling alone does not provide an exhaustive solution. PE products are of short term use and do not degrade fast after use to avoid littering. No data is available, on the presence of chromophoric sites and light induced photodegradation in these PE films. Effects of temperature, humidity and wavelength on UV irradiated PE conventionally processed are unknown. It's difficult to use data obtained from pure resin to analyze photodegradation of a conventionally manufactured

PE product (with additives, impurities and defects). Hence there was a need to study these effects to the product in the market and how they can accelerate degradation.

1.3 Objectives

1.3.1 General objective

The principal objective is to determine the rate of natural degradation with an aim of determination of optimum conditions for an accelerated degradation of PE flimsies.

1.3.2 Specific Objectives

The specific objectives are;

- i. To determine the presence of chromophoric sites and natural photodegradation of PE flimsies for a four months period.
- ii. To determine the effects of temperature, to the rate of photodegradation of pre-irradiated PE flimsies at constant relative humidity.
- iii. To determine the effects of humidity, to the rate of photodegradation of pre-irradiated PE flimsies at a constant temperature.

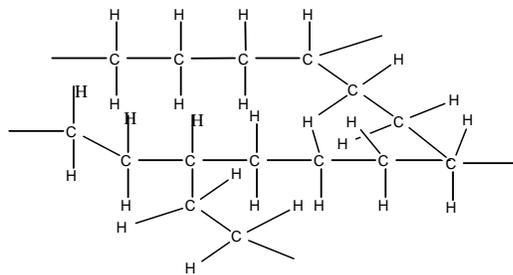
1.4 Justification of the Study

Polyethylene extensive use poses disposal challenge where recycling alone does not provide an exhaustive solution. Exploration of more ways to curb the menace is needed. This study will enable prediction of the time taken by these PE products to photodegrade. It also aims at determination of humidity and temperature optimal conditions for an accelerated degradation of pre-irradiated samples. Besides addition of this knowledge, the relevant authorities and institution like NEMA will benefit from this knowledge and use it to develop policies relating to the manufacture, use and disposal of PE.

CHAPTER TWO LITERATURE REVIEW

2.1 PE Structure and Properties.

PE is the simplest hydrocarbon monomer with the structure, $-[\text{CH}_2-\text{CH}_2]_n-$. Depending on how the monomer ethylene is polymerized the PE can be classified as high density PE (HDPE) or as low density PE (LDPE) (Sperling, 2006). Other classifications are linear low density PE LLPDE and ultra high molecular weight PE (UHMWPE) (Kroschwitz, 1990). HDPE is a hard, tough and resilient polymer of ethylene. It's formed by polymerizing ethylene at a moderate pressure (1.5-3.0) MPa using organometallic compounds. It is used in manufacture of containers such as milk bottles and laundry detergent jugs. Its 90% crystalline has a density as high as 965 kg/m^3 and melting point in the range (144 -150) °C. LDPE is a product of ethylene polymerized at elevated temperatures (190 -210) °C, high pressure (100-200) MPa and catalyzed by peroxides. Its melts at 110-125°C and is only around 40% crystalline due to high branching with density around $910\text{-}920 \text{ kg/m}^3$ (Gowariker *et al* 1988 and Shakhashiri, 2008). Most PE flimsies are made up of HDPE and LDPE with structure 2.1 (Sara *et al*, 2005).



Structure 2.1: LPDE chain branching

PE physical properties depend on molecular weight (MW), molecular weight distribution (long chain branching) and short chain branching (Billmeyer, 1984). Any alteration of the chain branching and molecular weight will lead to a significant change of the physical properties. PE exhibits viscoelastic properties, i.e. it partly behaves like an elastic material and at the same time like a viscous one.

Like other polymers, PE has two important transitions, the 1st order (thermodynamic melting) transition and the 2nd order (amorphous glass) transition. At low temperatures polymers shows glass like properties (like hardness, stiffness, transparency and brittleness). As

temperature increases the same polymer exhibits rubber like properties. This change of properties is referred as glass transition and the temperature at which it occurs is the glass transition temperature T_g . Glass transition occurs over a range of temperatures rather than at a sharp definite temperature and is recognized by many properties, the most important being the decrease in the modulus of the material by several orders of magnitudes The range of glass transition temperature for PE is (-123 to -73) $^{\circ}$ C (Malcolm, 1990).

2.2 Polyethylene UV Radiation Absorption

Electromagnetic radiation can produce a reaction, usually degradative, if the radiation has sufficient energy. Energy is related to wavelength of radiation by,

$$Energy = \frac{hc}{\lambda} \dots\dots\dots 2.1$$

where h, Planks constant, λ , wavelength and c , speed of light.

Sufficient energy for bond scission is found in ultraviolet (UV) region and shorter wavelengths. However bonds have characteristic absorption frequencies and only radiation of these frequencies can be absorbed. This energy therefore is absorbed only if it equals to the absorption frequency. On the earth’s surface UV radiation occurs in the range (300-400)nm due to filtration of smaller wavelengths by the atmosphere. Pure PE bonds like most bonds do not absorb within this range. The carbonyl group – C=O bonds are an exception; they are capable of absorbing within this range. Most polymers should therefore be stable in sunlight, however polymers usually contain carbonyl group – C=O bonds and UV reactive groups (chromophoric sites) which are incorporated accidentally during polymerization or processing. Polymers are therefore often less stable in sunlight irradiation than their structures would suggest (Dyson, 1992). Saturated compounds with bonds such as C-C, C-H and O-H like PE absorbs light at $\lambda \leq 200$ nm.

Absorption wavelength also depends on the thickness of the polymer material. Thin films absorb short wavelengths and are almost completely transparent to wavelengths longer than 320nm. Film thickness changes refractive index (wavelength dependent) of a material, consequently changing optical behavior (Yakuphanoglu *et al*, 2005). The effects of short wavelengths predominate on the surface of a material whereas the longer wavelengths interact with the bulk of the material. For example, spectra of polyester shows a shift of absorption band as the polymer thickness is changed (Kroschwitz, 1990). The expectation

was therefore that PE will interact differently with ultraviolet wavelengths of range (200-300)nm and (300-400)nm.

2.2.1 Existence of Chromophores in PE.

Virtually all plastics products are manufactured using extrusion, injection molding, or extrusion blowing. The processing of polymers using heat and high shear pressures, into useful end products introduces impurities and reaction product as chromophores that make them susceptible to photodegradation. Impurities here may include polymerization catalyst residues from processing equipments (Kroschwitz, 1990 and Global, 2008). It has been shown that PE molecules, due to structural defects or impurities, quite often contain a C=C or C-O linkage, which makes the nearby bonds susceptible to photodegradation, ignited by natural sunlight UV (290-400)nm (Gowariker, 1988).

Because of these complications, research findings on UV-induced degradation of pure polymer resins are not reliable to be used in prediction of UV-induced degradation of processed products of the same polymer. Photodegradation data generated on the actual polymer formulations used in practice, processed in the conventional manner are the most useful for degradation assessment (Global, 2008). This led to the need of this study where an already manufactured product was used.

2.3 Quantum Theory of Polymer Excitation

The lowest ground state of organic molecule is a singlet state in which electrons with opposing spin angular momenta are paired in molecular orbital. In simple nomenclature, this is shown as S_0 in Fig 2.1. Absorption of radiation energy leads to the raising of an electron from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO). This process does not change the spin of the electron making the transition and thus the excited state produced is also a singlet state, designated S_1 . Since in the excited state the pair of electrons from the original orbital is in different orbital, there are no constraints of spin angular momentum upon them and they may adopt parallel spins, resulting in a state shown as T_1 . Electrons in the singlet state experience much repulsion to one another than those in triplet state. This explains why for the same electronic configuration the triplet state is always lower in energy in relation to the corresponding singlet state. Promotion of electrons from the HOMO to other than LUMO must produce a higher energy state than S_1

(Garner and Stahl, 1983). Examples of such higher energy state are shown in Fig 2.1 as S_2 and S_3 with the corresponding triplet states shown as T_2 and T_3 . In principle any vibration level of the excited state can be formed from the ground state upon absorption. Possible de-excitation routes of a molecule excited to a specific vibration level includes; Fluorescence, phosphorescence and non-radiative fates also called vibrational relaxation. Fluorescence is a reverse process of absorption that is, removal of an electron from LUMO to HOMO with corresponding emission of a photon. This process occurs between states of the same spin. Phosphorescence results from transition from $T_1 \rightarrow S_0$. This process produces an isoenergetic level of the lower state, and collisional process are then required to take away the excess vibrational energy so produced in the ground states. This collisional vibrational relaxation is shown in Fig 2.1. These three fates compete with a much greater probability of non radiative energy dissipation processes (Canet *et al*, 2008).

The efficiency of each fate is given in terms of quantum yields. Electroluminescence studies has shown that a priori both the radiative and non radiative processes can lead to bond scission if the energy involved is very high (Canet *et al*, 2008).

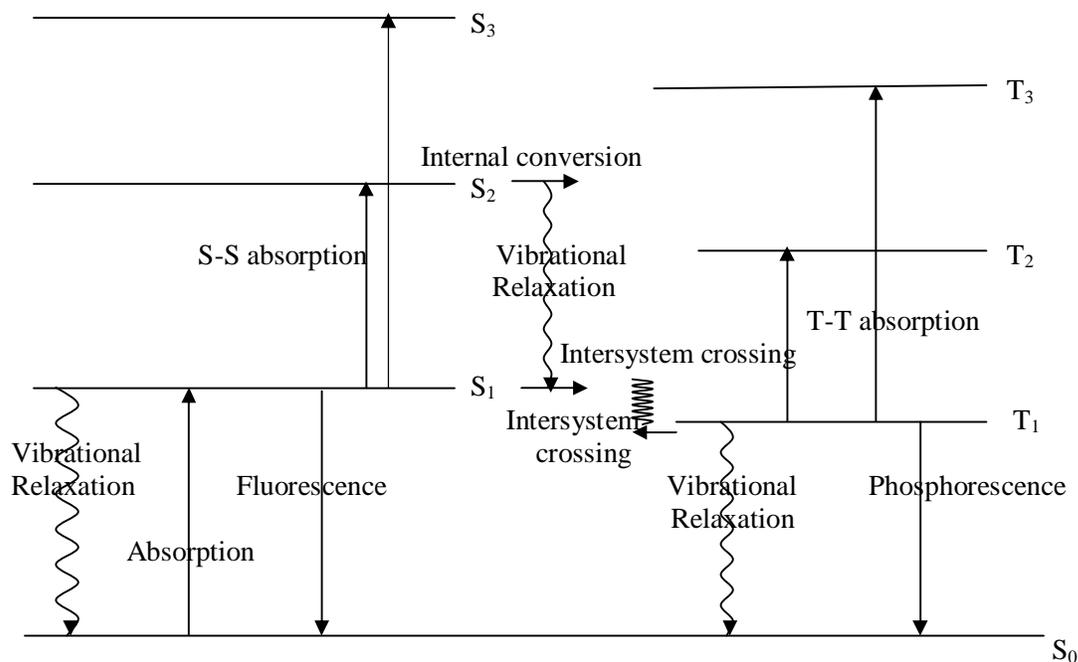
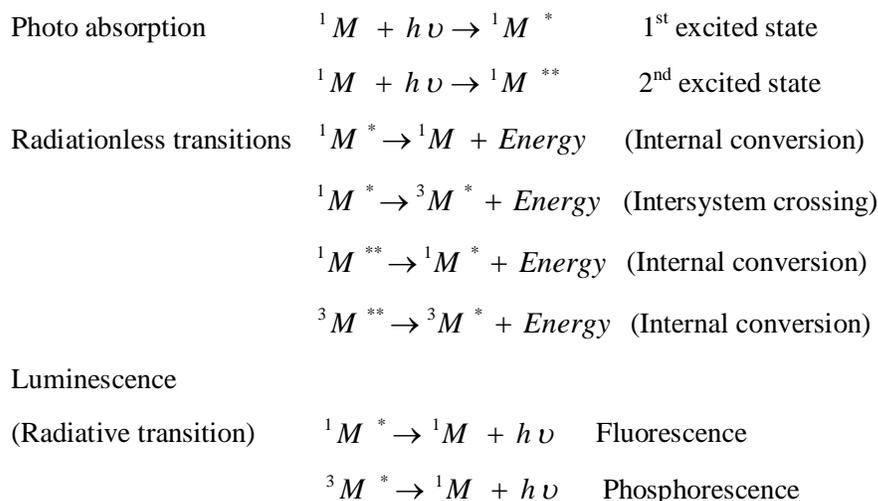


Fig 2.1 Jablonskii Energy Diagram (Garner and Stahl, 1983)

This can be represented by kinetic scheme as;



Scheme 1. Important photophysical processes

Note: Super scripts 1, 2 and 3 denote singlet, doublet and triplet states; asterisks denote excited states (Schnabel, 1981).

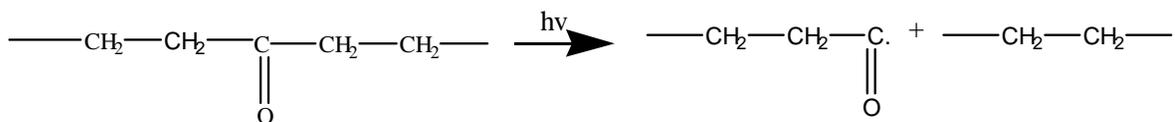
2.4 Photo Ignited Degradative Reactions in PE.

The groups C=C (as chromophores) and C-H in PE absorbs energy as shown in scheme 1, electrons are raised into higher energy levels. Carbonyl groups and conjugated C=C bonds absorb energy above $\lambda=200\text{nm}$ with absorption maxima between 200nm and 300nm. When these electrons move to lower energy states, energy is released in form of vibrational modes. If the released energies exceed the bonds dissociation energy, bond breakage occurs and radicals are created. In the simplest case these radicals might, recombine to form the original chain back. This is true if the chains are rigid and typically rigid chains containing cyclic aromatic units in the chain have high heat stability. Alternatively they can become further separated so that it is unlikely that they would recombine. Then two radicals may pick up hydrogen from adjacent chain and the radical is transferred. However, even though the chains are broken, the amount of material present remains the same i.e. there is reduction of molecular weight (MW) but not of weight. The number of chains goes up and the MW of the chain goes down. There is a reduction in the properties of the material but again total weight of the sample does not go down (Garner and Stahl, 1983). The reduction of the MW is a direct consequence of chain scission caused by photolysis. The mechanism of photolysis of

polymers however, depends mostly on the impurities present which may act as energy acceptors or donors. A carbonyl group plays an important role among all these impurities. Light absorbed by these groups can induce bond scission by either Norrish type I and type II processes. Whenever the carbonyl groups are on the polymer backbone both Norrish I and Norrish II processes cause main chain ruptures (Schnabel, 1981).

2.4.1 Norrish Type I Processes

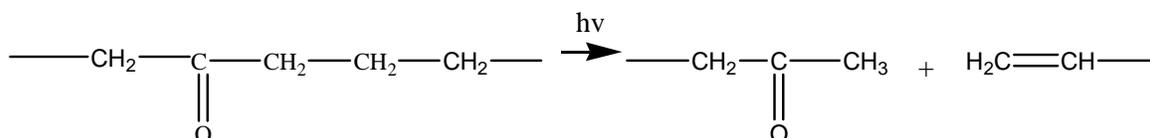
The carbonyl group interacts with the absorbed light, thus get excited to a singlet state. Through intersystem crossing a triplet state may be obtained. On cleavage of the α -carbon carbon bond from either state, two radical fragments are obtained.



These ions or radicals lifetimes, depends on diffusion rates and may be weeks or months in solids at low temperatures (Billmeyer, 1984). The expectation of this study is that photochemical degradative reactions will take place weeks or months later after irradiation of these PE products by UV radiation. The radicals formed in the Norrish type I may also undergo a process similar to step polymerization, at higher temperatures and pressures. The net effect is formation of a short branch of low molecular weight and thus loss of mechanical properties, (Garner and Stahl, 1983). Without termination of activity and further UV irradiation carboxylic acids are formed in Norrish type I process. Being photo insensitive these carboxylic acids accumulate as the end products.

2.4.2 Norrish Type II Processes

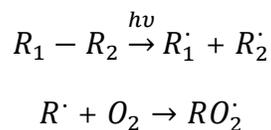
These are radical free processes. A Norrish type II reaction is the photochemical intermolecular abstraction of a γ -hydrogen (which is a hydrogen atom three carbon positions removed from the carbonyl group) by the excited carbonyl compound to produce a 1,4-biradical as a primary photoproduct (IUPAC definition).



Norrish type II leads to formation of photosensitive products with an exception of vinyl groups (Scott, 1990).

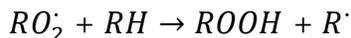
2.5 Mechanisms of Oxidative Photodegradation

Study of the loss of strength, impact resistance, and mechanical integrity of plastics exposed to UV radiation has been done. These changes in bulk mechanical properties reflect polymer chain scission (and/or cross linking) as a result of photodegradation (Global, 2008). General features of the mechanism of photodegradation in PE are a subject of discussion. The mechanism is one of thermo oxidative or photo oxidative degradation rather than of direct photolysis. Short wavelengths (highly energetic) are responsible for direct photolysis (Sec 2.4). The photo oxidative degradation of macromolecules is initiated by the absorption of light quanta by chromophoric groups and the products of thermo oxidative transformations of macromolecules (Goldade *et al*, 2004). The photo oxidative mechanism proceeds when free radicals that are formed by photo illumination react with molecular oxygen, the chemical quantum yield in presence of oxygen being rather high. Peroxides are formed according to the conventional mechanisms of autoxidation,



Electronspin Resonance (ESR) measurements in a study of long –lived free radicals in gamma – irradiated UHMWPE, PE showed changes from alkyl to peroxy radicals in air due to oxygen reaction, which did not change in vacuum (Choon *et al*, 2004).

The auto oxidative process has three important steps namely, initiation, propagation and termination. Initiation in this case is by photo irradiation and there is formation of radicals. During the propagation step peroxide radicals react with hydrogen forming hydroperoxides which decompose further with consequent chain scission (Schnabel, 1981).



The initiation process reactions are independent of temperature and cease when irradiation is removed. The secondary reactions, which includes oxidations are temperature dependent and can proceed without further irradiation (Birley *et al*, 1992). It's therefore hypothesized that initiation can be done pre- consumer use (for example during manufacture) of these short term use products. Once they are exposed to sunlight, propagation of the photodegradation take place with consequent degradation.

2.5.1 Effects of Temperature and Humidity to Degradation

Studies of Polylactic Acid (PLA) plastics, shows that their degradation is highly enhanced by increase of humidity and temperature (Kai-Lai *et al*, 2004). Increase of humidity also had an accelerating effects to the rate of degradation of biodegradable (starch added) PE films (Jakubowicz *et al*, 2006). In this study the effects of moisture and temperature on the photodegradation of PE flimsies will be investigated. While the impurity content of the PE flimsies is unknown, it is expected to influence the results.

In a study of Acrylic Melamine Coatings Photodegradation using Fourier Transform Infra Red (FTIR) technique (Ngunyen *et al*, 2000), it was shown that chain scission increased with increase of relative humidity (RH) in the exposure environment. Formaldehyde is released during hydrolysis and it acts as sensitizer thus introducing the acceleration effect to degradation. In the same study, apparent chain scission quantum yields of photodegradation processes increased from $3.0 \text{ AM}^{-1}\text{J}^{-1}$ for a dry/UV condition (0% RH) to $3.7 \text{ AM}^{-1}\text{J}^{-1}$ at 90% RH /UV condition (Ngunyen *et al*, 2000). PE flimsies being a polymer with almost similar chemical constituents and structures with these two plastics, its photodegradation is expected to be affected by these two environmental variables. Effects of these two variables are of great interests since they will determine if acceleration of photodegradation can be weather induced.

2.5.2 Degradation and Loss of Mechanical Properties.

Loss of mechanical physical properties has been associated with reduction of molecular weight (degradation). Kai-Lai *et al* (2004), in a study of degradation of Polylactic acid plastics of high molecular weight (120 to 200 Kg mol^{-1}), shows that the loss of tensile properties started when their weight-average molecular weight (MW) was in the range of 50

to 75 Kg mol^{-1} . Consequently any reaction or process that increases the rate of bond breakages automatically leads to accelerated loss of physical properties.

Loss of static mechanical properties has been used to infer aging of polymers. In such a study, changes of flexural yield strength, modulus of Elasticity and strength changes were observed in polymeric materials which included PE, PVC, PMMA and POM when aged (Kondo *et al*, 1992). Dynamic test of mechanical properties which have the advantage that the signal bears information of the mechanical properties directly has also been used though not exhaustively. In a study of aging of polymeric urinary stents, a fall of storage modulus was used to show degradation (Mouzakis *et al*, 2006). In this study measurement of storage modulus, loss modulus and loss factor was done as the PE flimsies degrade. These viscoelastic properties changes will show degradation.

2.6 Viscoelasticity, Moduli and Loss Factor Theory

Various techniques have been used to study degradation of polymers. They include IR, FTIR, X-Ray Diffraction, Thermally Stimulated Depolarization (TSD) and dynamic testing among others (Andrew, 2006). Dynamic testing is useful because the signals yield viscoelastic information directly (Mouzakis *et al*, 2006). In this study dynamic testing using the Dynamic Mechanical Analyzer (DMA) was used to monitor degradation, hence the moduli and loss factor theory will be discussed here.

Materials can be classified as viscous, elastic or viscoelastic depending on the response to applied mechanical force. A viscous flow is an irreversible bulk deformation of polymeric material associated with irreversible slippage of molecular chains past one another. If a material recovers its original shape after deformation it's said to be perfectly elastic (Bryant and Roger, 1991). Viscoelasticity is where deformation of the polymeric material is reversible but time dependent and associated with distortion of polymer chains from their equilibrium conformations through activated segment motion involving rotation about chemical bonds (Billmeyer, 1984). In linear viscoelasticity the stress amplitude is proportional to the strain amplitude at a given temperature and frequency. Thus mechanical properties measured under different condition are interrelated readily.

Consider an isotropic perfect elastic material subjected to a sinusoidal varying tensile strain ϵ at a frequency below that required to induce resonance vibrations. The deformation and hence the strain occurs in-phase with the stress (Carter, 1990).

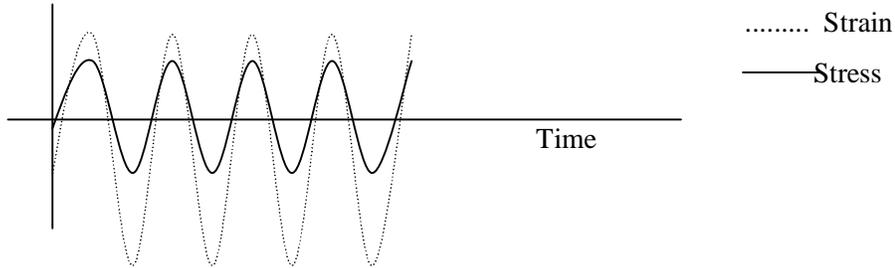


Fig 2.2 Response of an elastic material (stress in-phase with strain)

For linear viscoelastic behavior, under steady state conditions, the stress σ sustained by the sample is also sinusoidal; but the stress is out of phase with the induced strain say by an angle δ (Bryant and Roger, 1991).

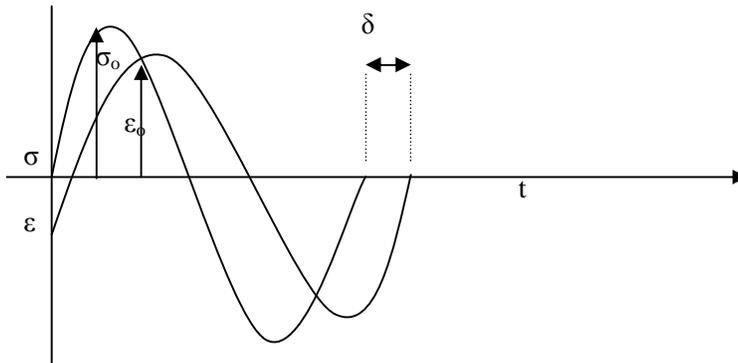


Fig 2.3; Response of a viscoelastic material (stress out of phase with strain)

Therefore

$$\epsilon = \epsilon_0 \cos \omega t \dots\dots\dots 2.2$$

$$\begin{aligned} \sigma &= \sigma_0 \cos(\omega t + \delta) \\ &= \sigma_0 \cos \delta \cos \omega t - \sigma_0 \sin \delta \sin \omega t \dots\dots\dots 2.3 \end{aligned}$$

Where ω is the angular frequency, t is time and σ_0 and ϵ_0 is the amplitudes of stress σ and strain ϵ respectively.

From equation 2.3 the stress is resolved into two components,

- i. $\sigma_0 \cos \delta$ and it's in-phase with strain,

ii. $\sigma_o \sin \delta$, which is 90° out of phase with the strain.

Therefore the material behaves partly as an elastic solid and partly as a viscous liquid, and the stress-strain relationship is written as

$$\sigma = \varepsilon_o E' \cos \omega t - \varepsilon_o E'' \sin \omega t \dots\dots\dots 2.4$$

Where the component moduli are given by,

$$E' = \frac{\sigma_o}{\varepsilon_o} \cos \delta, \text{ and}$$

$$E'' = \frac{\sigma_o}{\varepsilon_o} \sin \delta \dots\dots\dots 2.5$$

Equations 2.4 and 2.5 suggest that tensile modulus can be specified in complex form E^* .

This further implies that the strain and stress cycles are represented by the real parts of

$$\varepsilon^* = \varepsilon_o \exp i \omega t, \text{ and}$$

$$\sigma^* = \sigma_o \exp i(\omega t + \delta) \text{ respectively.}$$

Then
$$E^* = \frac{\sigma^*}{\varepsilon^*}$$

$$\begin{aligned} E^* &= \frac{\sigma_o}{\varepsilon_o} \exp i \delta \\ &= \frac{\sigma_o}{\varepsilon_o} (\cos \delta + i \sin \delta) \\ &= E' + iE'' \dots\dots\dots 2.6 \end{aligned}$$

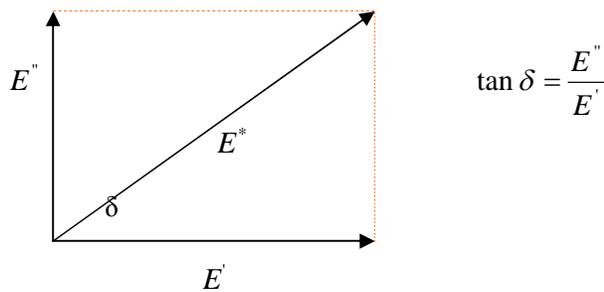


Fig 2.4 Storage (E') and Loss (E'') Moduli and $\tan \delta$

The real part of the modulus E' which is in phase with the strain is termed storage modulus since it is proportional to the peak energy stored per cycle in the material. It represents the elastic behavior of the material. The imaginary part of the modulus E'' is out of phase with the strain, is proportional to the net energy dissipated per cycle and is known as the loss

modulus. It represents the viscous part of the material response. The ratio $\frac{E''}{E'} = \tan \delta$ is termed as loss factor or damping factor. It's a dimension less quantity and is the rate of energy lost per cycle to the energy stored and hence recovered per cycle. The loss factor gives information about the samples viscous or elastic behavior. E' , E'' , and $\tan \delta$ depend on the test frequency and also on temperature, and each is used to characterize dynamic mechanical properties either at a given frequency or temperature or, preferably over a range of these variables (Sperling, 2006 and Mark, 2007) As a material degrades a change of these viscoelastic properties also changes. The changes of these properties have been used to infer about the degradation of polymeric materials (Mouzakis *et al*, 2006). PE being anisotropic has different moduli and loss factors corresponding to the different measurement directions (Bryant and Roger, 1991).

CHAPTER THREE

A Study of Chromophoric Sites Using Optical Spectrum Analyzer and Photodegradation of PE Films

Abstract

Photo-oxidative processes that lead to chain scission and chain linking in polymers play an important role in polymer degradation. Capability of radiation absorption by a polymeric material depends on the existence of chromophores. In assessment of photodegradation therefore, data obtained from a polymer material processed in conventional manner is more useful than data obtained from extrapolation of pure resin. This study reports presence of chromophores from the analysis of reflection, transmission and absorption of ultraviolet -light by PE (PE) films. Transmission, reflection and emission spectra were obtained from the Spectro 320 Optical Spectrum Analyzer. Ultraviolet radiation was obtained from fluorescent lamps and measurements made at room temperature and relative humidity of 20°C and 40%RH respectively. The study also reports on the natural degradation under solar action of these PE films. The PE samples were exposed to natural environment for 4 months (day and night). Degradation was analyzed by monitoring change of storage modulus measured by Dynamic Mechanical Analyzer instrument. These PE films showed low UV absorption of below 62% in the range (200-400)nm except at 216nm with 89% absorption. This shows that the PE films have chromophoric sites since PE bonds does not absorb UV light in the range (200-400)nm. Hence these films were relatively unstable to sunlight UV with a 42.4% drop in storage modulus after 150 days. The films took a shorter time to degrade than pure PE films. However for a desired fast degradation addition of more Chromophores absorbing in the near visible wavelengths (e.g. Aromatic compounds) should be added.

3.1 Introduction

Ultraviolet(UV) radiation with wavelength ranging from (200-400)nm, initiates oxidation degradative processes and is therefore responsible for the discoloration, weathering, loss of gloss and mechanical properties (cracking) of polymeric materials (Salem, 2001). The physiochemical 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 (Choon *et al*, 2004). Changes in the mechanical properties of PE are attributed to cross linking and chain scission processes

occurring during photo-oxidation of the material (Nguyen *et al*, 2000). In polyolefins, the effect of UV radiation on the formation of the chemical functional groups and their role in polymer chain-breaking has been reported. Sarathi *et al* (2003) studied changes in molecular weight of PE films as a function of various environmental aging. It was found that alkyl radicals ($\text{---CH}_2\text{---}^*\text{CH---CH}_3$) may be formed in Low Density PE (LDPE) films during UV-irradiation. Formation of oxy-radicals and chain breaking is also possible for wavelengths greater than 300nm (Corrales *et al*, 2001). However, UV radiation energy effects are evident when there is a probability of its absorption.

Energy is related to wavelength by the simple formula,

$$E = \frac{hc}{\lambda} ,$$

Where h, Planks constant = 6.63×10^{-34} J.s, c, speed of light = 3.0×10^8 m/s and λ , wavelength of the radiation. This gives the energy of one photon. Multiplying by Avogadro's number gives the energy for a mole of photons (Schnabel, 1981). The average bond energy of the carbon-carbon bonds along a polymer backbone is 351 kJ/mol (Ranby and Rabek, 1975). Therefore using the equation for energy and considering one mole of photons, 341nm becomes the maximum wavelength where energy is sufficient to cause chain scission or direct photolysis of the C-C backbone. Any other wavelength that is below 341nm is capable of causing main chain backbone breakages (Andrew, 2006). Table 3.1 gives the bond dissociation energies of various bonds and the energy corresponding wavelengths.

Table 3.1 Dissociation Energies of Various Bonds (Schnabel, 1981)

Bond	Dissociation energy (kJ/mol)	Corresponding wavelength λ (nm)
O - O	213	562
C - Cl	326	367
C - N	330	363
N - H	339	353
C - C	351	341
C - O	372	321
C - H	393	304
O - H	426	281
C = C	502	238

Most polymers contain only C-C, C-H, C-O, C-N, or C-Cl bonds, which were reported to require a wavelength of below 190nm for appreciable formation of free radicals and

subsequent photolysis (Hrdlovic, 2000). This is most likely due to steric effects of nearby chains, which assist in holding the bonds together by the close packing in a solid polymer, thus decreasing the rate of free radical formation (Andrew, 2006). The portion of the sunlight-spectrum that reaches the earth's surface is limited as shown in Fig 3.1.

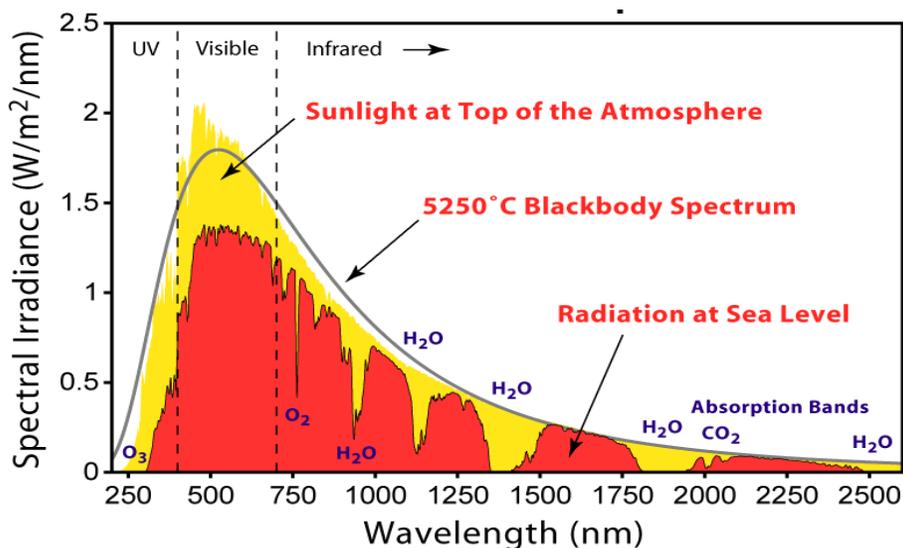


Fig 3.1: Solar Radiation Spectrum (Robert, 2009)

Most of the higher energy X-rays, gamma rays, and cosmic rays never make it through the atmosphere due to their absorption by ozone, leaving only UV, Visible, and Infra Red (IR) rays. Ozone absorption even takes care of the highest energy UV radiation, blocking radiation below 290nm. The solar energy that reaches the surface is limited to the wavelength range 290 to 2450nm. The total radiant solar energy consists of (in order of increasing energy): 37.8% IR (800-2450nm), 55.4% visible light (400-800)nm, and 6.8% UV light (290-400)nm (Ranby and Rabek, 1975).

Pure PE therefore is not expected to be susceptible to degradation under solar radiation since such lower wavelengths do not make it to the earth surface. Ultraviolet-absorbing impurities in a polymer are what enable photolysis with wavelengths greater than 290nm (Gijsman *et al*, 1999 and Hrdlovic, 2000). Thus photodegradation (photolysis and photo-oxidation) of a material is determined by the absorption characteristics of radiation in that material (Ngunyen *et al*, 2002). Polymeric materials are manufactured using extrusion, injection molding, or extrusion blowing. The processing of polymers using heat and high shear into useful end products introduces impurities and reaction products that make them susceptible to UV

radiation absorption and degradation (Gowariker *et al*, 1988, Kroschwitz, 1990 and Global, 2008). Example of such impurities includes peroxides and hydroperoxides that are always formed during processing (Billingham *et al*, 2009). As a result of these complications, extrapolation of research findings on UV-induced degradation of pure polymer resins to compounded and processed products of the same polymer, is often unreliable. UV absorption data and degradation data generated on the actual polymer formulation used in practice, processed in conventional manner is most useful for assessment of photodegradation.

Several methods can be used to determine presence of UV absorbing Chromophoric sites. These include UV spectroscopy, IR spectroscopy, and Fourier Transform Infrared (FTIR) spectroscopy among others. These methods rely on the knowledge of groups that corresponds to given absorption bands. In this study, the Optical Spectrum Analyzer (Spectro 320) is a useful tool that gives spectral analysis emission, transmission and reflection spectra. These spectra carry information that can directly infer absorbance of any radiation between 200nm-880nm by samples of different materials. The Optical Spectrum Analyzer (Spectro 320) was used to measure the transmission and reflection of UV radiation by PE. From the equation

$$A = 1 - (T + R) \dots \dots \dots 3.1$$

where A is absorption T, transmission and R the reflection all expressed as percentages gives an approximation of percentage absorption. Absorption of UV by these PE films is also discussed.

Dynamic Mechanical Analysis (DMA) offers a versatile method of analyzing polymer degradation. This analysis was done using DMA 2980 from TA instruments. The DMA analyzes the time and temperature dependence of mechanical behavior (viscoelasticity) of materials more prominent in polymers (Sperling, 2006). The various regions of polymer viscoelastic behavior are shown in Fig 3.2. Degradation caused by either chain scission or chain linking leads to the change of these intrinsic viscoelastic behaviors. These changes are well monitored using DMA Instruments to infer degradation. Increase in dynamic modulus (stiffening) is attributed to chain-linking while a decrease of dynamic modulus shows chain scission. For the special case of unconstrained uniaxial tension, the stiffness k of a sample is given by

$$k = \frac{AE}{L}$$

where A- Crosssectional area, E- Modulus , L- Length of the sample.

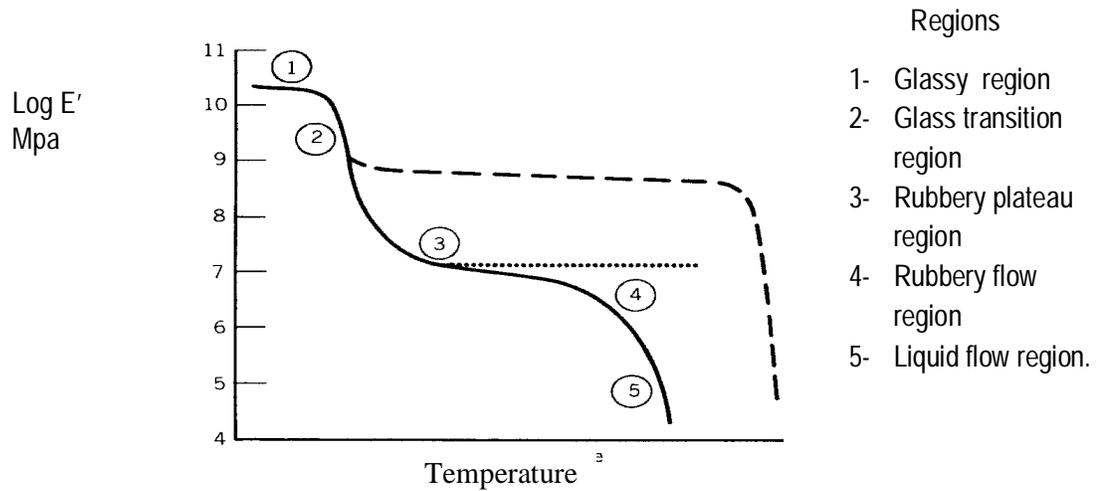


Fig.3.2: Five regions of viscoelastic behavior for a linear, amorphous polymer (Sperling, 2006)

3.2 Methodology

3.2.1 Materials

Commercial Low Density PE (LDPE) films of thicknesses 30 μ m and 80 μ m synthesized and processed by extrusion from PIL Kenya Ltd and STYROPLAST Kenya Ltd were used without any further treatment. Samples were cut into 7 cm x 4 cm for UV transmission and reflection measurements. An 8W Ultraviolet fluorescent lamp made by UVITEC (model LF-204.LS) was used. The lamp irradiates at the ranges (200-300)nm and (300-400)nm with a switch that shifts between the two ranges and provides an irradiance of 0.0475 W/m² at 242nm and 3.8590 W/m² at 360nm (measured with Optical Spectrum Analyzer-Spec 320). The temperature of the samples during UV transmission and reflection measurements was 20°C and the relative humidity was 40%.

3.2.2 Emission, Transmission and Reflection measurements

Emission of the mercury fluorescent lamps, transmission and reflection were measured using an Instruments Systems 320 Optical Spectrum Analyzer aided by SpecWin software. The instrument based on diffraction theory of light and employing solid state detectors, is able to give resolved spectra (Emission, Transmission and Reflection) of constituent wavelengths.

Fig 3.3 shows the integrating sphere with the three measuring apertures. This sphere provides the interaction of the instrument with the samples and radiations to be measured.

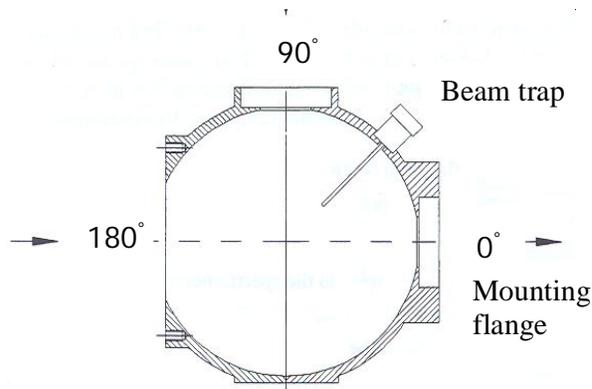


Fig. 3.3 0°, 90° and 180° Measuring Apertures of the Integrating Sphere

Fig 3.4 shows the complete arrangement for emission measurements with the emission lamps placed at the 180° measuring aperture. For the transmission measurements the samples were placed such that the UV radiation is incident at right angles. At the start of transmission measurement, a reference scan is taken without the sample. The software sets this baseline spectrum to 100%. Any other scan that follows with the sample in place is done with reference to the reference scan. The transmitted radiation is collected by the integrating sphere of the analyzer. All transmission measurements were made with the long baffle to avoid direct radiation being measured. The transmission measurements arrangement is shown in Fig 3.5.

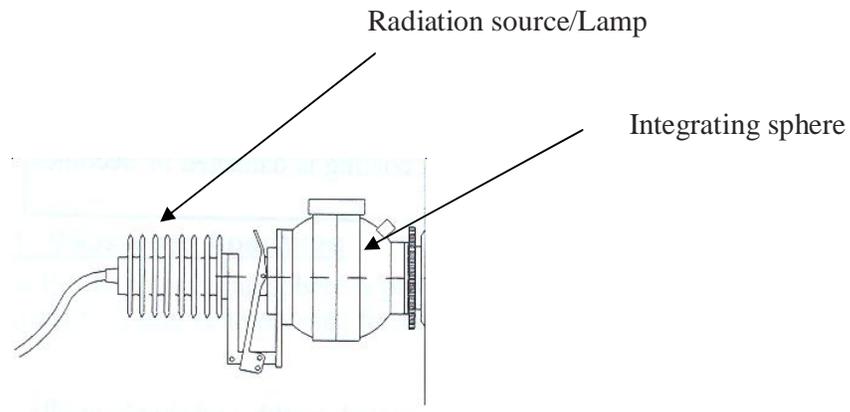


Fig 3.4: Measuring setup for Emission Measurement (Spectro 320 manual)

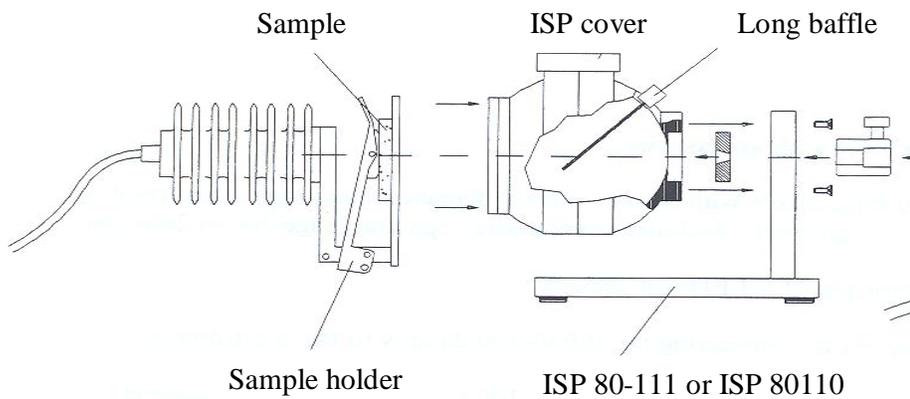


Fig.3.5: Measuring setup for Transmission Measurement (Spectro 320 manual)

Still using an integrating sphere with a short reflecting buffer, reflection of the samples was measured. The radiation source was mounted on the 90° – measuring aperture of the integrating sphere as shown in Fig 3.6. The samples were mounted on the diaphragm plate (with sample holder) which is located at the 180° – measuring aperture.

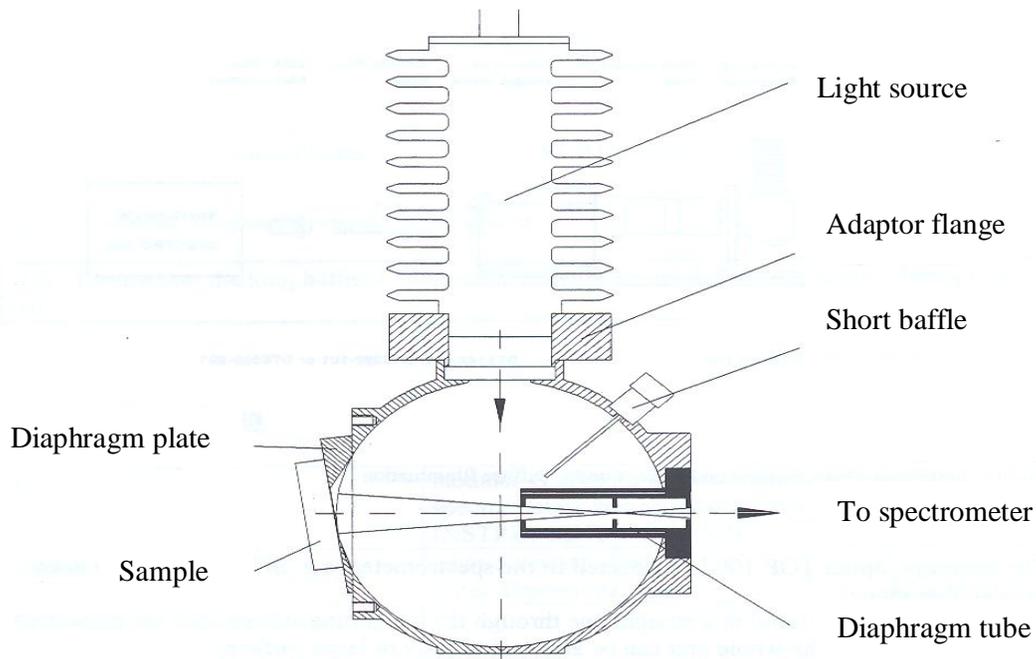


Fig 3.6: Measuring setup for Reflection Measurement (Spectro 320 manual)

3.2.3 Exposure to Sunlight

The samples were exposed to natural environment with the intention of establishing the rate of natural degradation. With sunlight being the major degrading agent, the samples were erected above the ground and then put lying horizontally to maximize solar irradiance as the sun rises and sets. The samples were tightly held using sticky tape on a carton-cutout holder to prevent them being blown by wind which could bring effects of mechanical degradation. Exposure was done for cumulative 150 days between the month of April and September the year 2009.

3.2.4 Mechanical Analysis

Measurements were carried out on the DMA model 2980 using the Tension Film clamp shown in Fig 3.7. An oscillatory stress (or strain) of a known frequency is applied to the sample clamped between the two clamps and the resulting strain (or stress) is measured by the same movable clamp. The ratio of the stress to strain gives the complex modulus (E^*) which is a measure of the material resistance to deformation. As the material ages, this quantity changes and as a result it can show the aging of a material. The storage modulus was chosen for this analysis and Multifrequency mode with a frequency of 2 Hz, amplitude of $50\mu\text{m}$ and an oscillating force of 0.01N was selected for the entire test. Tests were conducted

on i) unexposed samples then ii) samples after 70 days and iii) samples after 150 days of exposure. The DMA scan temperatures were from room temperature (25°C) to 100°C but (50-98) °C range was chosen for analysis. More information about the chains is easily obtained at this temperature range given that the polymer has molecular motions near the highest extreme (Menard, 1999). To ensure data quality, calibration of the DMA instrument preceded any measurement done. The standard samples used come with the DMA 2980 accessories. Control samples were tested for their storage modulus, loss modulus and loss factor. These measurements were used as reference to subsequent measurements of aged /treated samples.

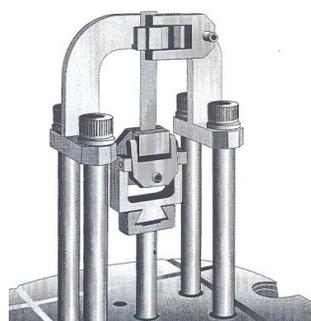
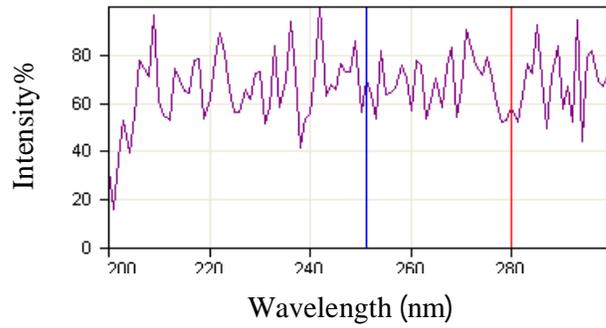


Fig. 3.7: Tension Film Clamp of DMA

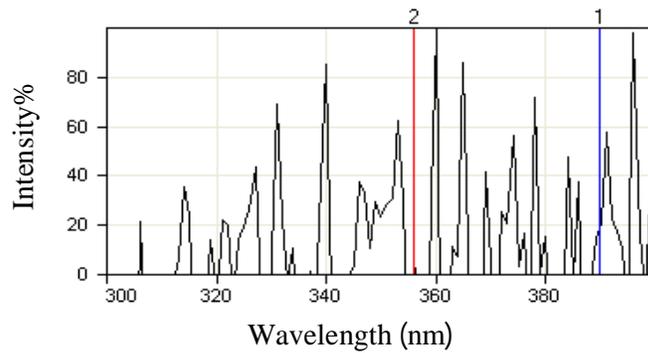
3.3 Results and Discussion

3.3.1 Emission , Reflection and Transmission

Emission of the mercury lamps is considered for comparison with solar UV that reaches the earth's surface. Fig 3.8 (a) shows emission at the range (200-300)nm. There is a maximum peak at 242nm with an irradiance of 0.0475% W/m². The (300-400)nm range emission is shown in Fig 3.8 (b) ; there exists a peak at with irradiance equal to 3.8590 W/m². The solar UV reaching earth's surface is between (290-400)nm with maximum peak of 0.5 W/m²/nm as shown in Fig 3.1. It's this radiation that is responsible for polymer degradation, as is evident by loss of mechanical strength/stiffness and discoloration. Smaller wavelengths, less than 290nm do not penetrate the ozone layer (Ranby and Rabek, 1975).



(a)



(b)

Fig 3.8: Spectral analysis at the range (a) (200 -300)nm (b) (300-400)nm

Reflection of the UV radiation by the 30 μ m PE film within the range (200-300)nm is below 20% except at 274nm and 292nm with peaks of 70% and 100% respectively as shown in Fig 3.9. Reflection is measured and read with 100% being the reference line from the spectrum analyzer. This low reflection suggests that much radiation actually enters the material film either for absorption or transmission.

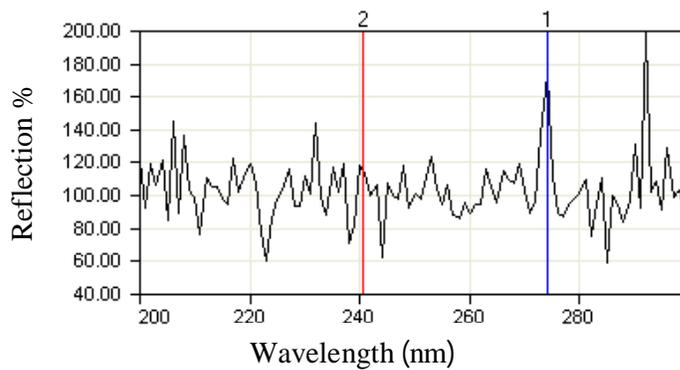


Fig 3.9: Reflection by 30 μ m PE film at (200-300)nm range

Reflection of the UV radiation by the 30 μ m PE film within the range (300-400)nm is shown in Fig 3.10.

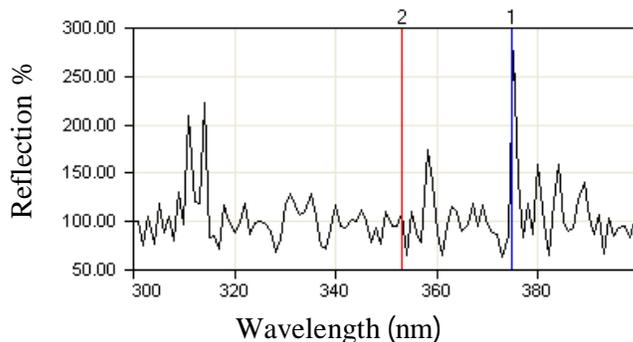


Fig 3.10: Reflection by 30 μ m PE film at (300-400)nm range

Lines between 300nm and 310nm are lowly reflected and at the same time there exists low transmission on that range. Absorption could have taken place at wavelengths at 300nm and 304nm. This may correspond to the excitation spectra of LDPE (Konar and Ghosh, 1989). There exists two reflection peaks between 315nm and 318nm where there was low transmission. The low reflectivity within the 318nm-358nm where transmission was lower than 20% except at 363nm suggests that the radiation was absorbed. This absorption is in agreement with work done on wavelength sensitivity of photodegradation where lines between 325nm and 360nm showed more degradative activity in PE than any other wavelengths (Sedac, 1998). At (200-300)nm range transmission and absorption are low except at 243nm where there is transmission maximum of above 80%. This is shown in Fig 3.11.

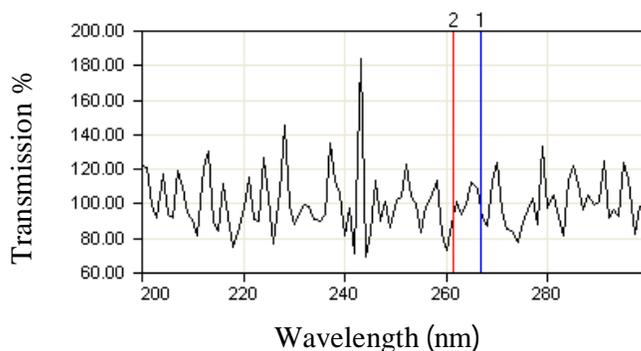


Fig 3.11: Transmission within (200– 300)nm range

The Transmission spectrum shown in Fig 3.12 has absorption of less than 20% at (300-325)nm range. There also exist transmission peaks at 327nm, (358-376)nm, 363nm with transmission of almost 80% and a single line near 397nm. It also shows a transmission of less than 20% of wavelengths between 330nm and 345nm. This could be the emission spectra or fluorescence spectra of LDPE which is normally at (330-345)nm (Konar and Ghosh, 1989 and Teyssedre *et al*, 2005).

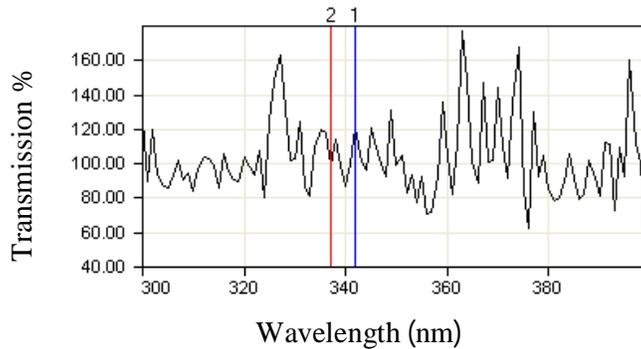


Fig 3.12: Transmission of 30 microns sample

3.3.2 Absorption

Fig 3.13 and Fig 3.14 shows the absorption percentages at ranges (200-300)nm and (300-400)nm respectively. These graphs were obtained using Excel and making use of equation 3.1. They give absorption in reference with the 100% line. Absorption was generally low especially at low wavelengths. The absorption values above 30% are shown in Table 3.2. The shaded rows show absorption at the range (200-300)nm. Many wavelengths that had absorption above 40% were at the range (300-400)nm. Normally, the chain scission quantum efficiency of solid polymers is low (Ngunyen *et al*, 2002). Expectation therefore is that the consequent degradative action will be low.

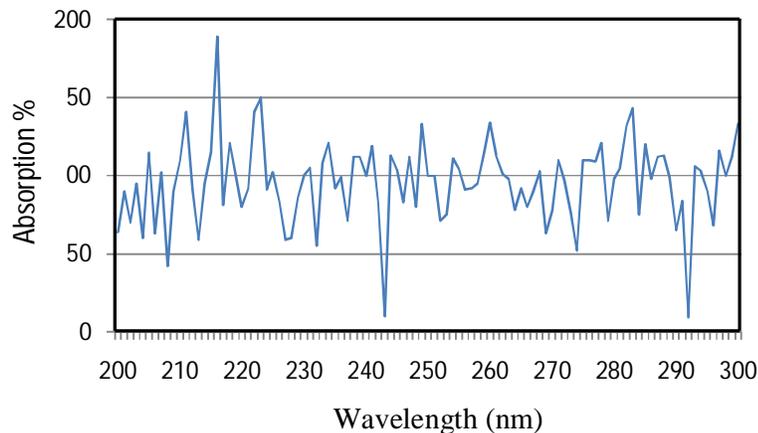


Fig 3.13: Absorption in the range (200-300)nm

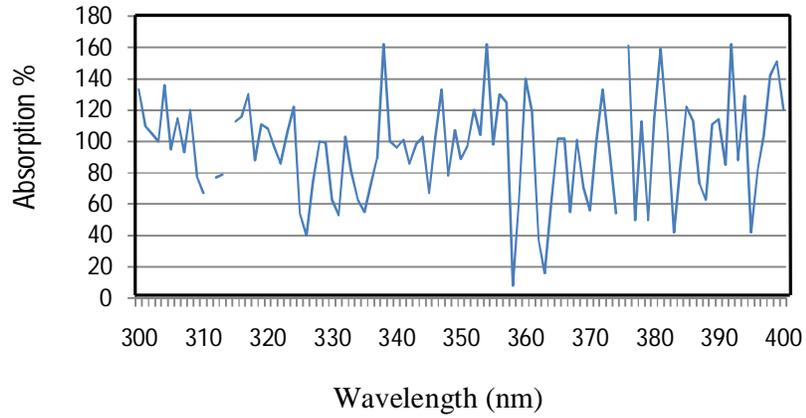


Fig 3.14: Absorption in the range (300-400)nm

Table 3.2. PE Absorption of 30% and above

Absorption %	Wavelength(nm)
30	317
32	282
33	249
33	300
33	347
33	372
34	260
36	304
40	360
41	211
41	222
42	398
43	283
50	223
51	399
59	381
61	376
62	338
62	354
62	392
89	216

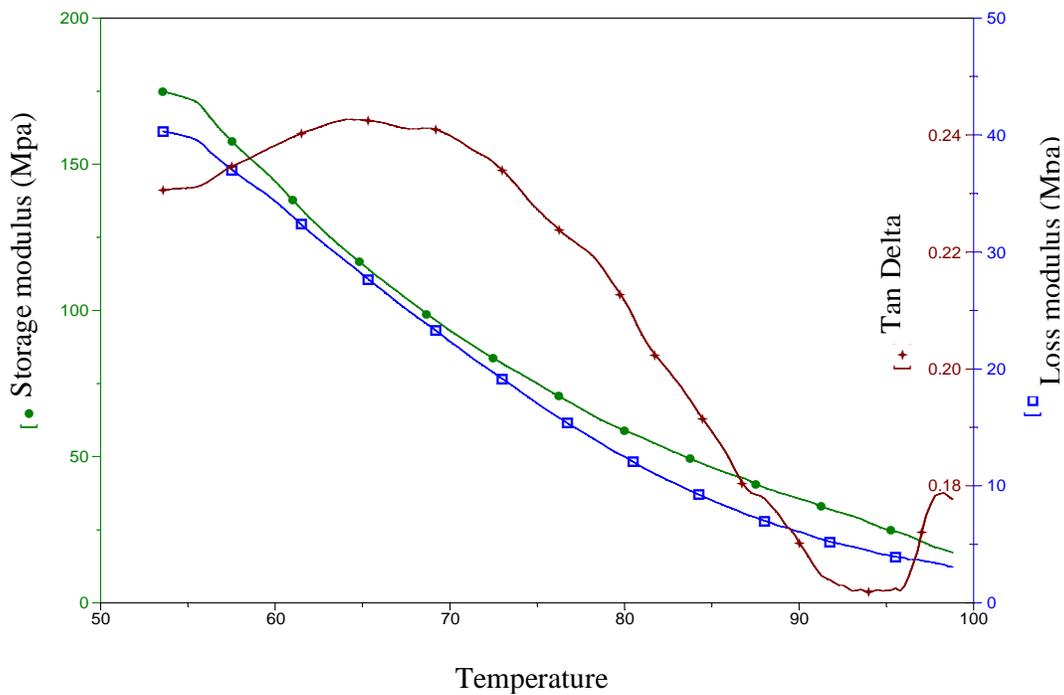
3.3.3 Mechanical Analysis for Natural Degradation

Fig 3.5 (a) and (b) shows the storage modulus, loss modulus and loss factor of the 30µm and 80µm samples respectively taken before any treatment. It can be seen therefore that the thicker sample had storage and loss moduli lower than the thinner samples. For the special case of unconstrained uniaxial tension, the stiffness k of a sample is given by

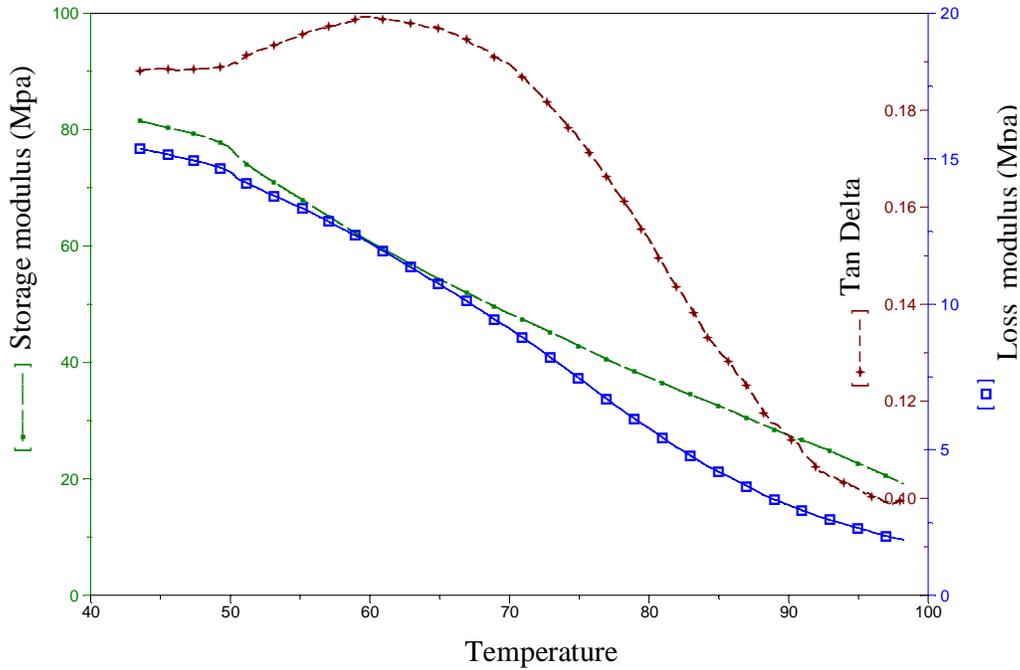
$$k = \frac{AE}{L} \dots\dots\dots 3.2$$

where A- Crossectional area, E- Modulus and L- Length of the sample.

The samples with different thicknesses have stiffness within the same range, since those with small crossectional area have higher modulus values. The slow drop of modulus confirms that the polymer is within the rubbery plateau.



(a)



3.15: DMA scan for the (a) 30 μm (b) 80 μm control PE samples

Fig 3.16 shows the drop of storage modulus as the films age for cumulative 150 days. There was a 33.6 % and 42.4 % drop in storage modulus after 70 and 150 days respectively. The standard error bars shows no significant difference between 70 and 150 days of aging. The drop of storage modulus averaged for the range (50-98) $^{\circ}\text{C}$, fits a hypothetical polynomial of order two fairly well as shown in Fig 3.17. This implies that the polymer may take much time to degrade to low modulus values. The aging of polymers follows linear Arrhenius behavior. However other studies reports non-Arrhenius behavior of polymeric materials (Celina, *et al* 2005).

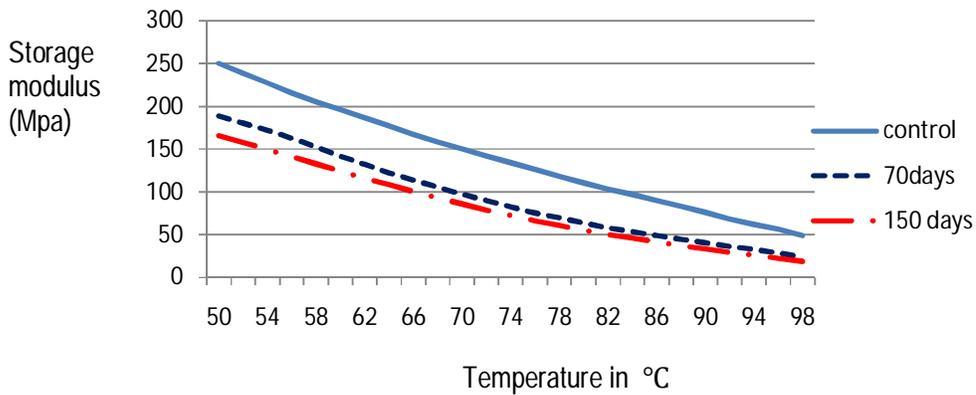


Fig 3.16. Natural aging of 30 μm PE film

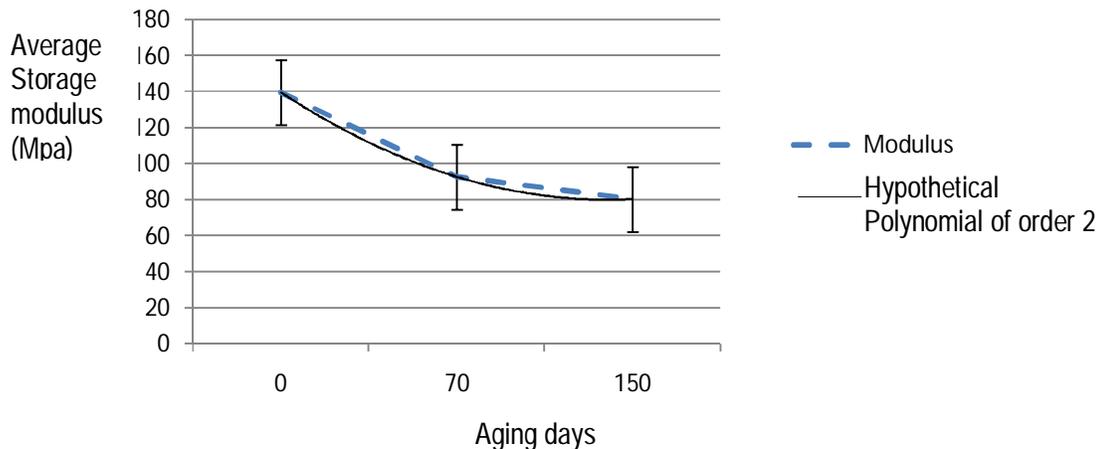


Fig 3.17. Decrease in storage modulus, with a hypothetical fitted trend

3.5 Conclusion and Recommendations

The PE films show low UV absorption of below 62%, except at 216nm where absorption is 89%. This confirms existence of “impurities” or chromophoric sites. Chromophoric sites like C=C, C=O and C-O bonds and hydroxyl groups that are known to absorb within these wavelengths ranges, are likely to be present in the PE. Expectedly therefore, these PE films should be relatively unstable to sunlight. However the rate of degradation is considerably low fitting well to a second order polynomial drop of storage modulus. For applications where there is exposure to sunlight e.g. in horticulture (for green houses), use of stabilizers is encouraged. For short term consumers e.g. food packaging, fast degradation should be encouraged by addition of Chromophores capable of near visible radiation absorption. This absorption should however be able to ignite degradation and quick fragmentation of these products that ends in landfills.

CHAPTER FOUR

A Study of Temperature and Wavelength Effects on Degradation of Photo-Irradiated PE Films Using DMA

Abstract

Plastic bags mostly made of PE (PE) cause pollution as solid wastes due to their non-degradability nature. Enhanced photo-oxidation is a possible method for an accelerated degradation. This can be achieved by ignition of a degradative process before use and disposal. This paper presents this method, where photodegradation was ignited using UV irradiation for two hours and the effects of temperature treatment analyzed. Effects of 40°C and 55°C temperatures on non-UV irradiated and UV-irradiated PE films processed under conventional methods were investigated and evaluated. Effects of UV range irradiation on degradation were deduced. Degradation was monitored by measuring storage modulus using Dynamic Mechanical Analyzer (DMA 2980 from TA Instruments). The decrease in storage modulus was 44.8 % at 55°C temperature treatment, higher than 36.5 % drop at 40°C temperature for non-irradiated samples. At the onset of degradation crosslinking in UV exposed samples, characterized by an increase in dynamic modulus (stiffening) was observed. The highest modulus increase of 22% was observed at 40°C, (300-400)nm UV exposure after 150hrs. On further exposure reduction of storage modulus followed. Temperature treatment of 55°C together with (300-400)nm UV range irradiation resulted in the highest reduction of storage modulus of 74.6% after 350hrs.

4. 1. Introduction

Generally, it is essential that PE retain its useful properties through one or more of a variety of fabrication procedures, e.g., blending, pelletizing, extrusion, blown or cast film fabrication. The final product film/ bag must have a reasonable storage and reuse life. Additionally, the customer expects to have functional bags that serve a useful purpose under a variety of circumstances. It is only at the end of the service life that the polymer must degrade in the disposal environment. This disintegration must occur in a reasonable timeframe (e.g. 3 months or 6 months), and it must not leave behind any toxic residue (ExcelPlas, 2003). Biodegradative polymers provide a possible solution to the problem with a variety of blends being introduced into the market. However, they come with high cost of production challenge and compromised physical properties when compared with fossil polymers (Sung *et al* 2002, ExcelPlas 2003 and Ojumu *et al*, 2004). Natural sunlight with ultraviolet component (290-

400nm is known to cause photodegradation of PE and other polymeric materials. This degradation nevertheless depends on light active sites (Chromophores) within the material and usually can take longer time (Teyssedre *et al*, 2005, Andrew 2006 and Canet *et al*, 2008).

Enhanced photo-oxidation can be a possible solution to accelerate the degradation of such waste. This can be achieved through addition of chromophoric sites in the product material. Addition of chromophoric sites has been successfully implemented by a South African company (ExcelPlas, 2003). The company developed an additive system that causes plastic litter to degrade rapidly into water and carbon dioxide in the outdoors under the influence of the ultraviolet (UV) portion of sunlight and the action of oxygen in the air (ExcelPlas, 2003). By introducing a prodegradant into plastic bag production, the life of the plastic bag is shortened which would ultimately reduce the build-up of litter in the environment (ExcelPlas, 2003). However these kinds of additives (prodegradant) compromise the material's desired properties (Sung *et al*, 2002 and Ojumu *et al*, 2004).

The mechanism of polymer degradation is extremely complicated, involving simultaneous formation and decomposition of hydroperoxides. Degradation is accelerated by oxygen, humidity and strain, and results in such flaws as brittleness, cracking, and fading. These factors, particularly at higher temperatures, are also well known to accelerate the rate of photodegradation of materials (Corrales *et al* 2001 and Andradý, 2003). Accelerated rate of ozone depletion in the atmosphere and related climate change is likely to increase the ambient temperature and humidity in the same regions likely to receive increased UV-B radiation (Motyakin *et al* 1999 and Andradý, 2003). These environmental factors and changes can be used to facilitate enhanced degradation of waste PE bags. To assess the accelerating effects of these changes and to reliably evaluate the degradation of materials, the wavelength sensitivity of the degradation process and the material response to various temperatures has to be known. The data needed for the purpose is not readily available for the conventionally processed PE films.

4.2. Experimental Procedures

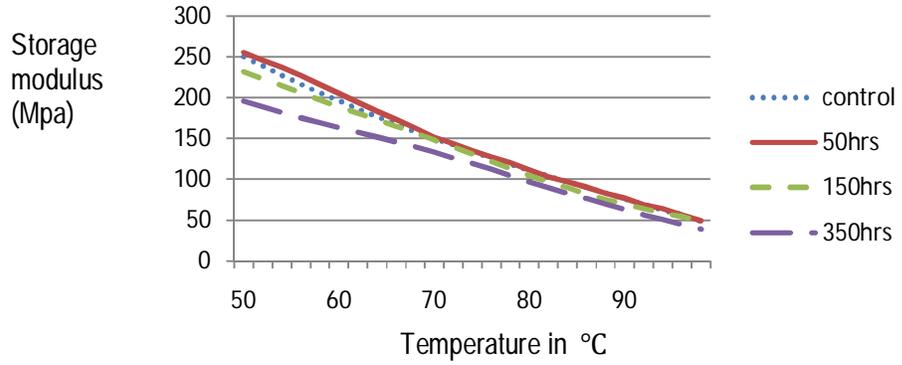
4.2.1 Sample Preparation, UV Irradiation, Temperature Treatment and Mechanical Analysis

An 8W ultraviolet fluorescent lamp, providing an irradiance of 0.0475 W/m^2 at 242nm and 3.8590 W/m^2 at 360nm (measured with Optical Spectrum Analyzer-Spec 320) with a switch that shifts between the ranges of lines was used. The samples mentioned in section 3.2.1, were cut into sizes 4cm X 8cm to fully fit within the aperture of the UV source. Control samples were locked in a dark cabinet in the laboratory at a low temperature of 10°C at night and 13°C during the day. The irradiation UV lights were of ranges (200-300)nm and (300-400)nm. The irradiated and non-irradiated samples were exposed to 55°C and 40°C in a constant relative humidity (40% RH) environment. Mechanical analysis was done using procedure in section 3.2.4.

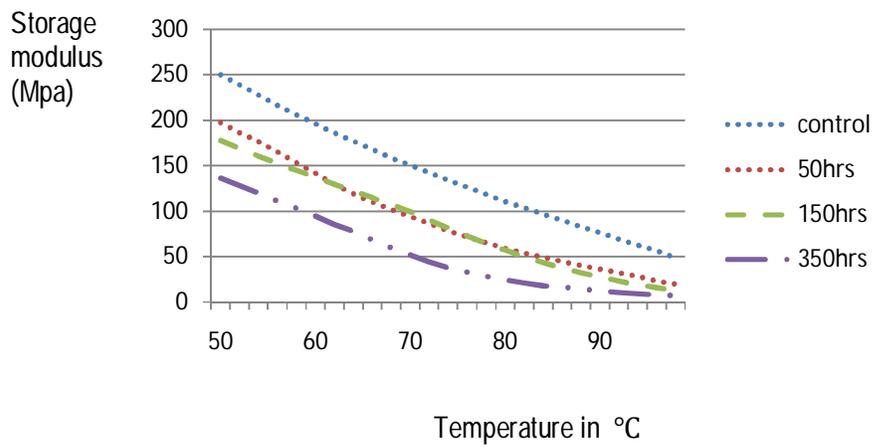
4.3 Results and Discussion

4.3.1 Un-Irradiated Samples Aging

Changes in dynamic modulus were monitored at different times of exposure for un-irradiated samples. For all the tests done a decrease in the material storage moduli with increasing scan temperature was observed. Such behavior is expected of a polymer material (Yang, 2000). Fig 4.1(a) shows un-irradiated $30\mu\text{m}$ PE sample aged at 40°C . Storage modulus did not change until after 350hrs of exposure. Fig 4.1 (b) shows a consistent decrease of modulus (stiffness) up to a cumulative 350hrs of aging at 55°C . Fig 4.2 shows the comparison of the drop of storage modulus with time of aged samples at 40°C and 55°C temperatures. The modulus values are averaged at scan temperature range 50°C to 98°C . At 55°C aging temperature the drop in storage modulus is high with a 62% drop in average storage modulus as compared to 16% drop at 40°C . Standard error bars are shown with the graphs. There is significant difference in the storage modulus as a result of aging at these two temperatures as shown by the gap between the standard error bars .



(a)



(b)

Fig 4.1 : Unirradiated 30µm PE sample aged (a) at 40°C (b) at 55°C

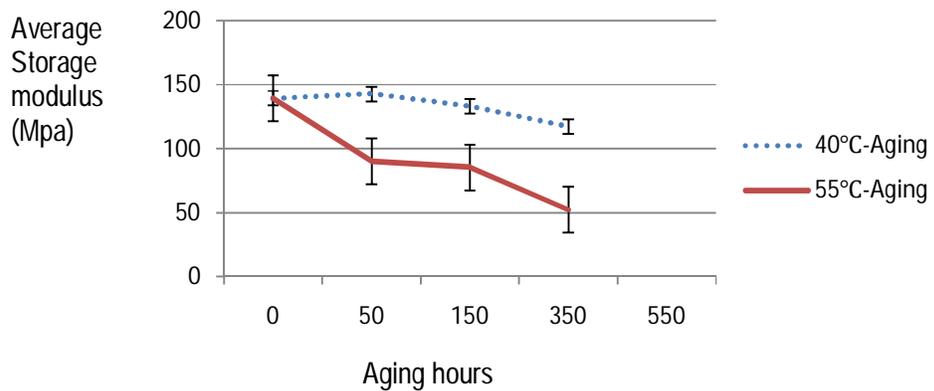
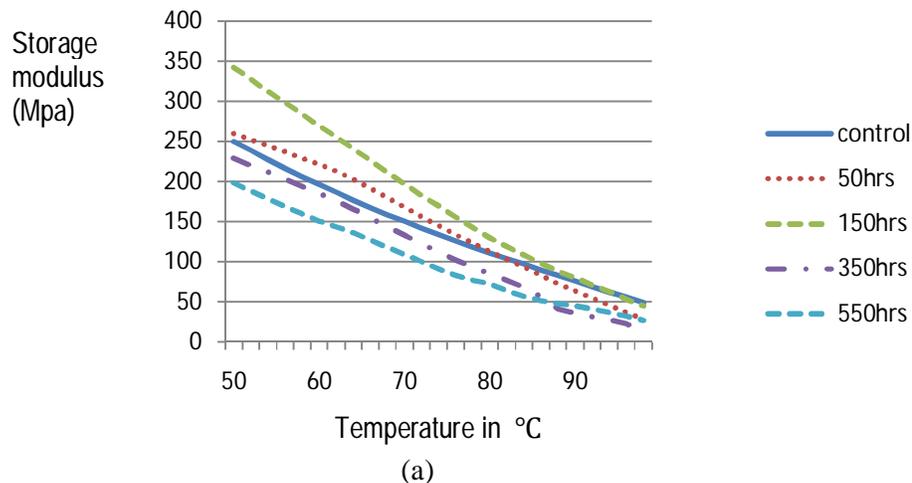
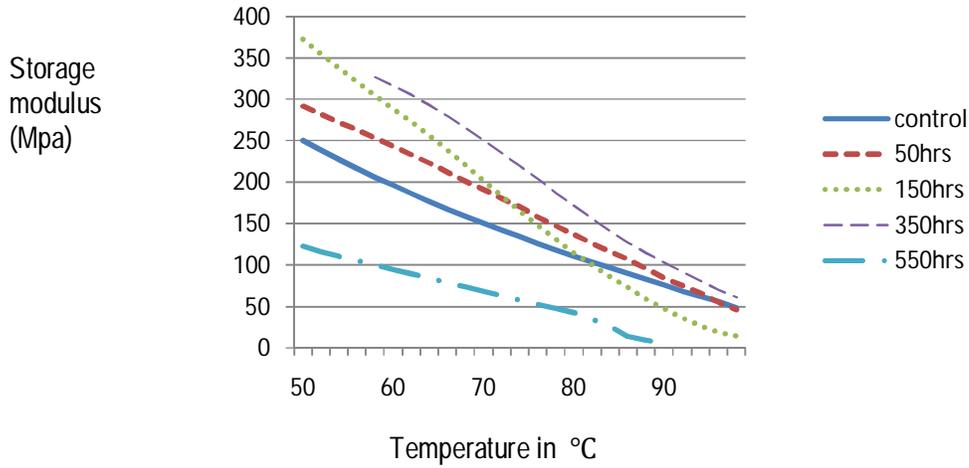


Fig.4.2: Aging at different temperatures for 30µm un-irradiated PE sample

4.3.2. Aging of Samples Irradiated at 200-300nm

There was at first a consistent increase in storage modulus followed by a huge decrease with further exposure. This increase of modulus and hence stiffness can be attributed to crosslinking of polymer chain branches (Choon *et al*, 2004 and Mouzakis *et al*, 2006). Fig 4.3 (a) and (b) shows the aging trend at 40°C and 55°C respectively. Both figures shows large gap between the highest and the lowest modulus at the onset of scan. This gap however narrows as the modulus values decreases with increase in temperature. Crosslinking process competes with the other degradation processes of macromolecules and develops during photolysis (Goldade *et al*, 2004 and Mohammad, 2007). A decrease of storage modulus was observed after 150hrs of exposure at 40°C and after 350 hrs of exposure at 55°C. This decrease of stiffness (embrittlement) is a common behavior of crosslinked polymers results from an increase of energy absorbing capacity to reach a peak, followed by a sudden decrease (Andrew,2006). This decrease in storage modulus was observed to be higher than that of un-irradiated (non crosslinked) samples. There was significant difference in change of storage modulus with (200-300)nm irradiation and exposure to 40°C and 55°C as shown in Fig 4.4. A 28% and 52% storage modulus reduction corresponding to 40°C and 55°C respectively was observed. The 55°C temperature treatment is more supportive to degradation, evidently observed by the lower modulus values. Baljit and Nisha, 2008 reported that, weathering is a degradation process, temperature dependent and will occur more rapidly at higher temperatures.





(b)
Fig 4.3: 30µm PE sample of 30µm aged (a) at 40°C (b) at 55°C

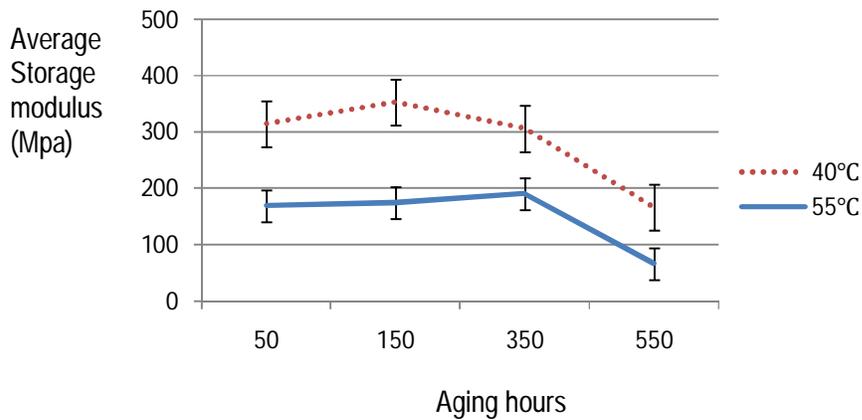


Fig 4.4. (200-300)nm irradiated samples aged at 40°C and 55°C

4.3.2. Aging of Samples Irradiated at 300-400nm

Fig 4.5 (a) and (b) shows the trend in the change of modulus at 40°C and 55°C. The most notable difference with this range exposure is the maximum storage modulus measured, which is higher than with irradiation of (200-300)nm range. The maximum average modulus values with exposure to 40°C and 55°C are 206.8 MPa and 200.3 MPa respectively with (300-400)nm irradiation. This compares to 145.9 MPa and 190.5 MPa with (200-300)nm irradiation. This could mean that (300-400)nm range lines were either absorbed more than (200-300)nm range lines or their effect of enhancing higher crosslinking is more pronounced. A comparison of changes in storage modulus of (300-400)nm irradiated samples and exposed

to 40°C and 55°C is shown in Fig 4.6. For both temperatures, the first 50 hrs of exposure show no change in the storage modulus of the samples. Subsequently both temperatures seem to be supportive of crosslinking, evidently observed by the higher values with the overlapping of the values also shown in Fig 4.6. There was an ultimate reduction of storage modulus (average) of 23.9% and 74.6% for 40°C and 55°C respectively. However there is no significant difference in aging of the polymer at these two temperatures with a (300-400)nm pre-irradiation as shown by the standard error bars overlap.

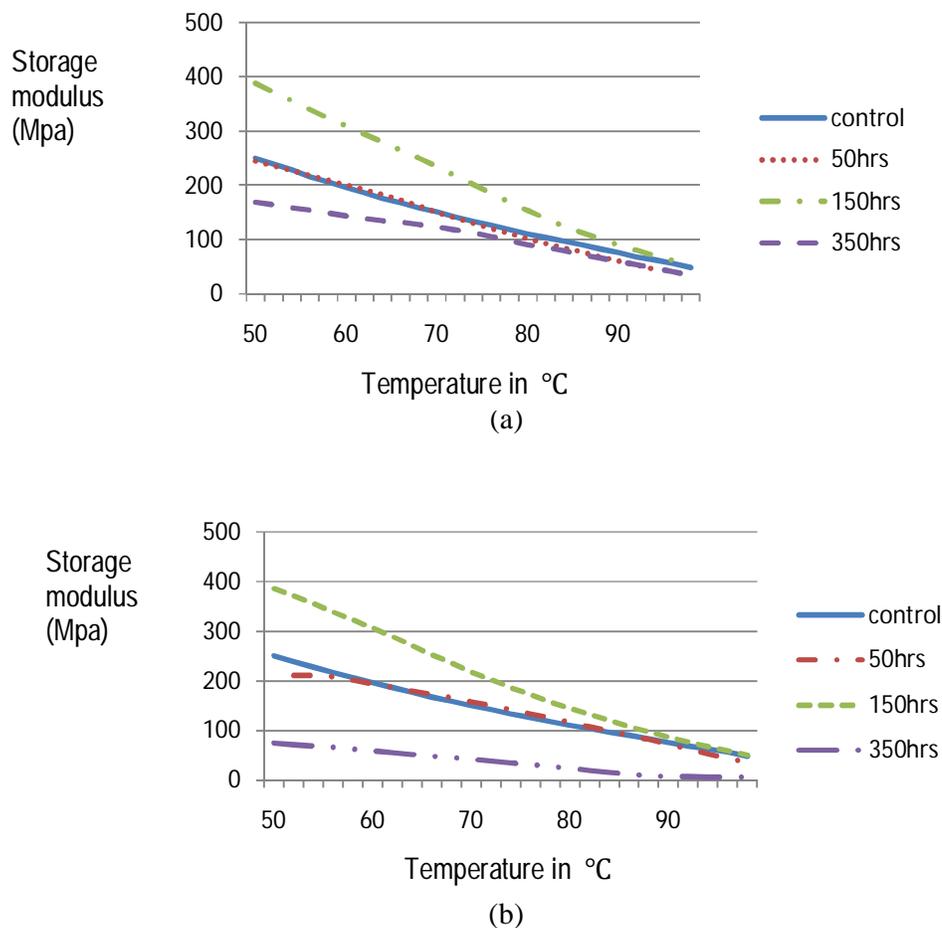


Fig 4.5: 30µm PE sample aged (a) at 40°C (b) at 55°C.

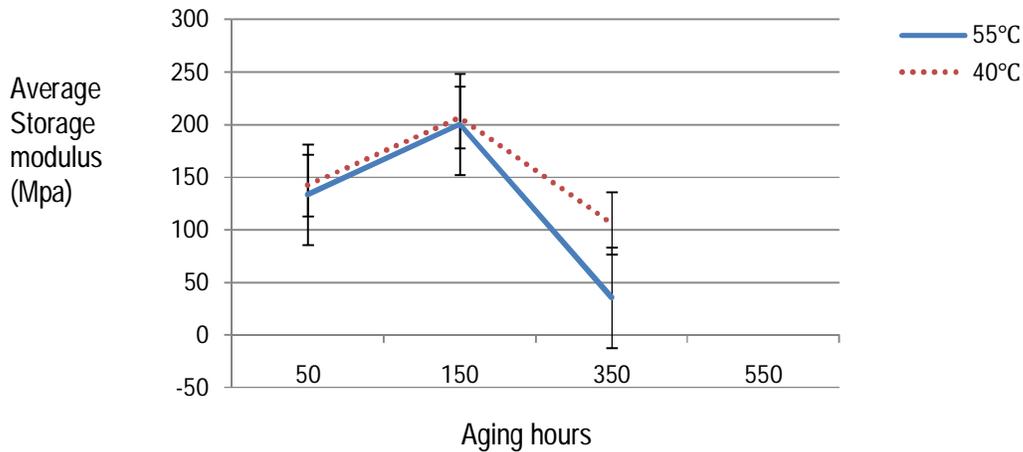
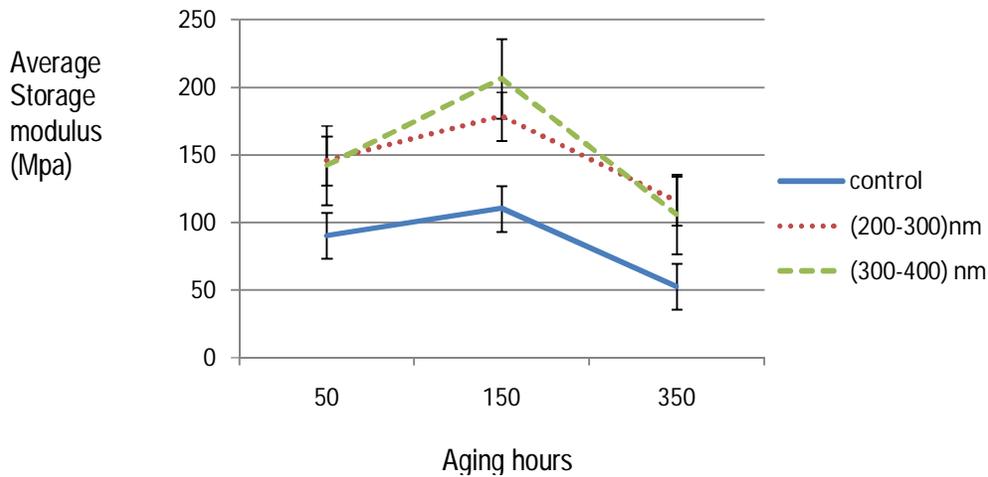


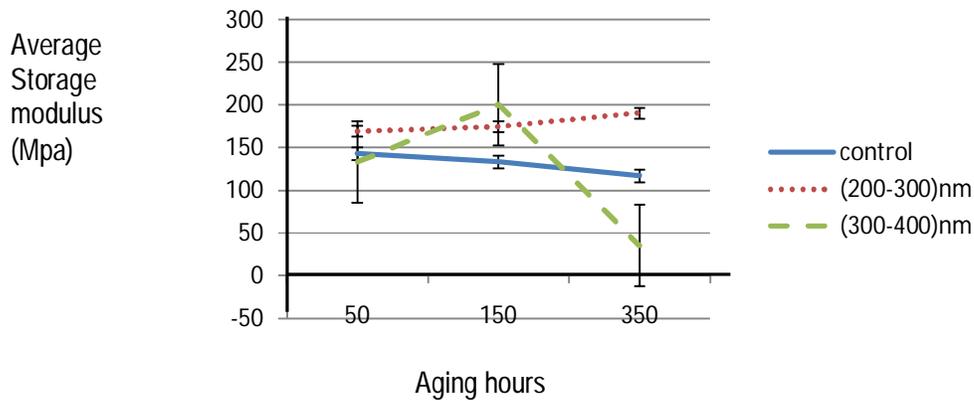
Fig 4.6: Comparison of 300nm-400nm aging at 40°C and 55°C

4.3.3. Irradiation effects to onset degradation.

The crosslinking induced by irradiation caused an increase in the time taken for reduction in storage modulus. Fig 4.7(a) shows an initial increase of storage modulus of 6% followed by 31% drop with (200-300)nm exposure after 150 hrs at 40°C. Exposure to (300-400)nm showed the highest increase of 22% followed by 74.6% decrease. Generally, irradiated samples had higher modulus values than the control (non-irradiated) samples exposed to similar conditions. At 55°C increase of storage modulus with (200-300)nm and (300-400)nm exposure was 13% and 18% respectively.



(a)



(b)

Fig.4.7: Effect of Aging time on storage modulus aging (a) at 40°C (b) at 55°C

4.4. Conclusions and recommendations

The degradation of these PE short term use products is enhanced at high temperatures with an initial UV irradiation. The highest observed reduction of storage modulus (aging) of 74.6% occurred at (300-400)nm irradiation and 55°C temperature treatment. This suggests that these PE films have chromophores absorbing within this range. This irradiation of two hours has the ability to raise the reduction in storage modulus from 62% for un-irradiated samples to 74.6%. A pre material use irradiation treatment can therefore greatly accelerate the degradation of such PE products. This accelerated degradation can reduce PE pollution to the environment. Damage to PE on solar irradiation depends on the susceptibility of the polymer to solar UV wavelength as well as the complexity of the weathering environment to which is exposed. The processing procedure is also an important factor, determining the levels of impurities as material defects, catalysts residues, additives such as coloring dyes and stabilizers. The same polymer can be compounded to have solar UV instability for short term use products. It is recommended that there should be a pre-consumer use ignition of a degradative action by UV irradiation in short term use PE products. This ensures that the product will be used while it still has its strength and degrades faster after disposal. More studies should be done to determine the effect of the degradative action and products to the consumers and also to the environment.

CHAPTER FIVE

Study of Humidity and UV Wavelength Effects on Degradation of Photo-Irradiated PE Films Using DMA

Abstract

Acceleration of the degradative processes can be achieved through moisture enhanced photolysis. This study has evaluated the effect of three Relative humidity environment (25%, 40% and 60%RH) at a constant temperature of 55°C on UV irradiated and non-irradiated samples of PE films processed under conventional ways. The wavelength sensitivity of degradation has been evaluated. Some samples were exposed to 2hrs UV radiation dose, within ranges (200-300)nm and (300-400)nm with 0.0475 W/m² and 3.8590 W/m² irradiance at 242nm and 360nm respectively. Degradation was observed at different RH inside degradation compartments. Dynamic mechanical analysis using DMA 2980 was used to measure dynamic storage modulus to monitor degradation. For non-irradiated samples change in storage modulus at the three relative humidity environments showed no profound difference after 550hrs. Irradiation of (300-400)nm range showed higher acceleration than (200-300)nm range with the highest drop in storage modulus of 67% after 550hrs. Raising humidity from 25 %RH to 40% and finally to 60 %RH resulted in an increase in percentage drop of storage modulus from 41 % to 62% and finally to 67 % respectively. A material pre-use irradiation and high moisture attraction enhancement can therefore greatly accelerate the degradation of such PE products.

5.1 Introduction

Conventional PE is still the best solution for many applications requiring tough films, because PE is cheap, easy to process and both mechanically tough and bio-inert (Sung *et al*, 2002 and Ojumu *et al*, 2004). However their degradation timescale is too long for them to be considered environmentally “friendly” and the increasing demand for such materials requires ways of converting them into mechanically weak material in short periods. The solution lies in accelerating the natural oxidative degradation of the polymers. In many applications then, the target is that the properties will deteriorate quickly at the end of the useful lifetime. Finally, upon total mechanical degradation, the residual plastic should be taken up into the bio-cycle without any negative influence on the environment (Billingham *et al*, 2009).

Degradation is a total of four processes that includes, post curing reactions, dark hydrolysis (due to Relative Humidity), photolysis and moisture-enhanced photolysis (Ngunyen *et al*, 2000). This study seeks to investigate the humidity accelerating effect on pre UV irradiated PE films processed under conventional means for local consumption. Dynamic Mechanical Analysis (DMA) method used is well explained in section 3.2.4.

5.2. Experimental Procedures

5.2.1 Sample Preparation, UV Irradiation, Temperature Treatment and Mechanical Analysis

An Ultraviolet fluorescent lamp of 8W made by UVITEC (model LF-204.LS) was used. It provides an irradiance of 0.0475 W/m^2 at 242nm and 3.8590 W/m^2 at 360nm (measured with Optical Spectrum Analyzer-Spec 320) with a switch that shifts between the range of lines was used. The samples were prepared as in section 3.2.1, cut 4 cm X 8 cm to fully fit within the aperture of the UV source. Control samples were locked in a dark cabinet in the laboratory with a low temperature of 10°C at night and 13 °C during the day. The PE samples were UV-irradiated and aged in Egerton University, Physics laboratory. The irradiation UV lights were of ranges (200-300)nm and (300-400)nm. The irradiated and non-irradiated samples were exposed to 25%, 40% and 60% RH at a constant temperature environment of 55°C. Mechanical analysis was done using procedure in section 3.2.4.

5.3. Results and Discussion

5.3.1 Un-Irradiated Samples Aging

A decrease in the material storage moduli with increasing temperature was observed for all DMA tests done. Such behavior, which arises due to increase of molecular chain slippages and movements with increase in temperature, is expected of a polymer material (Yang, 2000). Fig. 5.1 (a) shows the behavior of 30 μm sample heated at 25% RH. No appreciable change in storage modulus was observed until after a cumulative 550 hrs of exposure. Similarly for the 40% and 60% RH, the results showed slight changes as observed by the overlapping scan curves in Fig 5.1 (b) and Fig 5.1 (c). This behavior is however expected since it is assumed that for a solid polymer which underwent termination of polymerization process, there are no

free radicals to initialize large scale degradation processes. In addition steric effects deter free radical formation (Gowariker *et al*, 1988 and Andrew, 2006). Fig 5.2 shows the comparison of changes of modulus of aged samples at the three relative humidities i.e. 25 %, 40% and 60% RH. For that period of exposure no profound difference of the three relative humidity to un-irradiated films can be concluded.

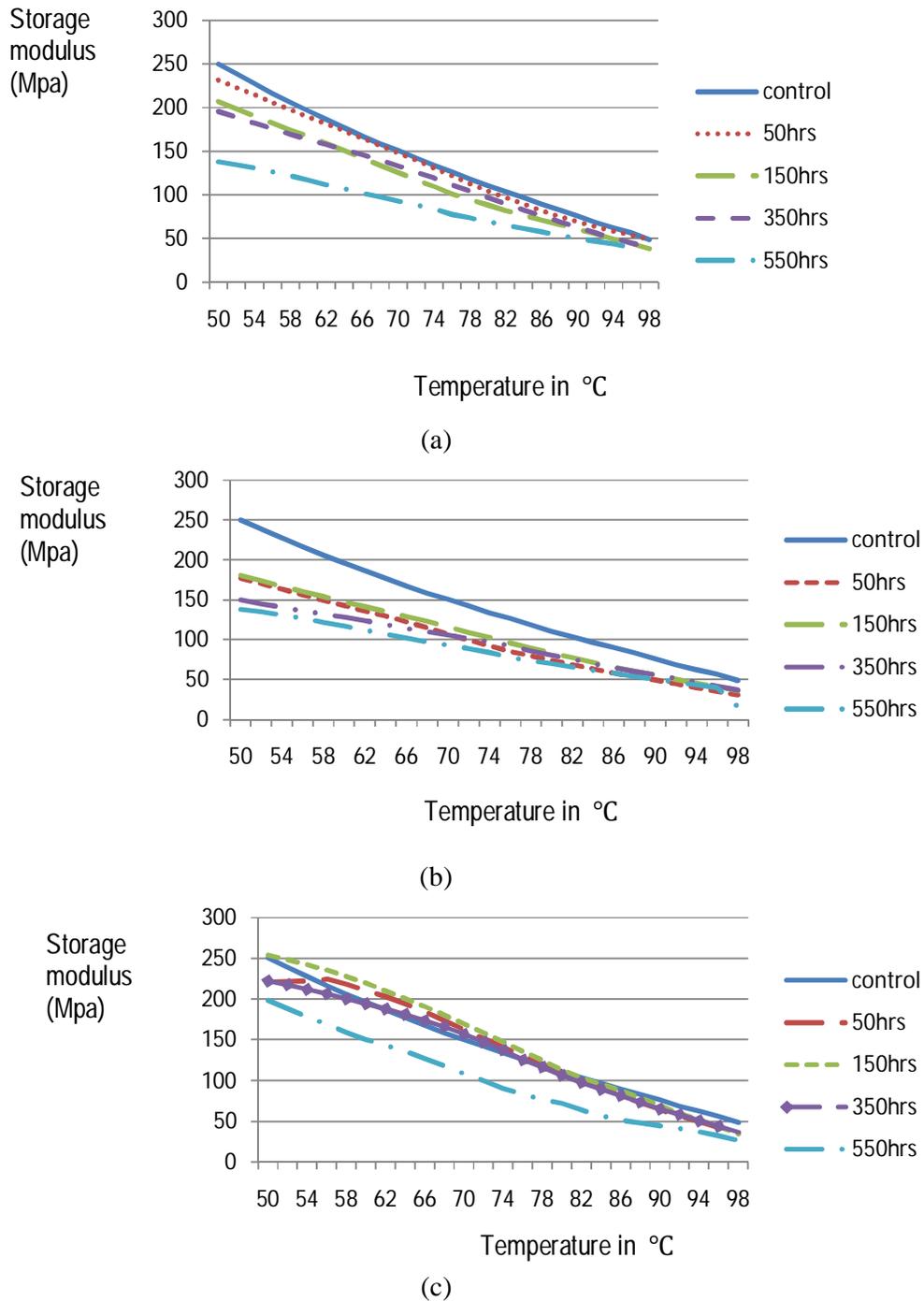


Fig 5.1: Un-irradiated 30µm sample aged (a) at 25 % RH (b) at 40% RH and (c) at 60%RH.

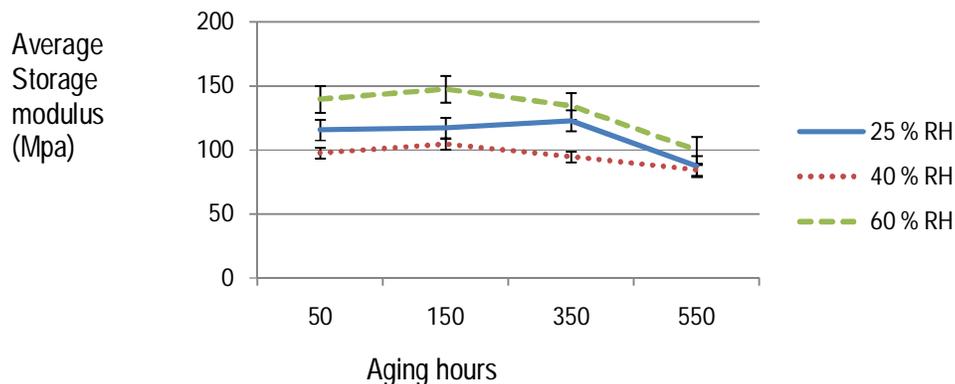
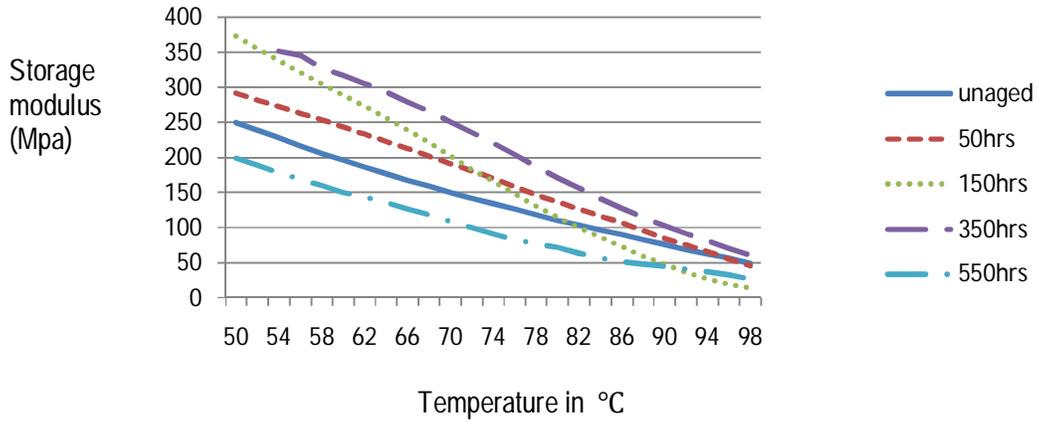


Fig.5.2: Aging at different RH for 30µm un-irradiated sample

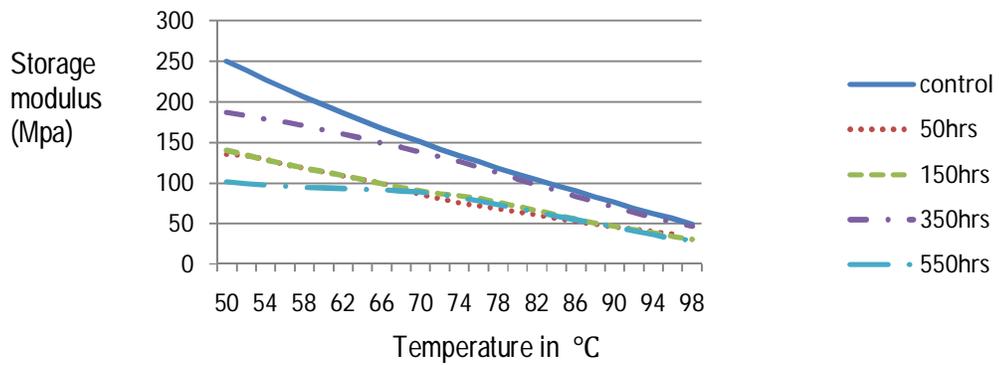
5.3.2. Aging of Samples Irradiated at (200-300)nm

At first, there was a consistent increase in storage modulus with exposure to 25 % RH after 50, 150 and 350hrs as shown in Fig 5.3 (a). This increase of modulus and hence stiffness can be attributed to crosslinking of polymer chain branches (Choon *et al*, 2004 and Mouzakis *et al*, 2006). The 2 hours UV irradiation enhanced crosslinking process characterized by an increase in their stiffness and modulus values. Crosslinking process competes with the degradation of macromolecules and develops during photolysis (Goldade *et al*, 2004 and Mohammad, 2007). However with further exposure a decrease in storage modulus after 550hrs was recorded. This decrease of stiffness (embrittlement) is a common behavior of crosslinked polymers and results from an increase of energy absorbing capacity to reach a peak, followed by a sudden decrease (Andrew, 2006). The decrease in storage modulus due to aging was observed to be larger than that of un-irradiated (non crosslinked) samples. At 40% RH and 60% RH exposure no increase of storage modulus was observed as shown in 5.3 (b) and Fig 5.3 (c). The trend is a consistent drop of the dynamic modulus. Since exposure was done in presence of atmospheric oxygen, oxidization could take place. This oxidization leads to the formation of peroxides along the polymer chains, which further induces freer radicalization and promotes chain-scission reactions (Andrew, 2006; Baljit and Nisha, 2008). Chain breakage by Norrish type II processes leads to formation of shorter chains-with low MW and hence low modulus values (Schnabel, 1981). High humidity enhances formation of hydroperoxides which are intermediary compounds formed in oxidative degradation and accelerate chain breakages. Formaldehyde is released during hydrolysis and it acts as sensitizer thus introducing the acceleration effect to degradation (Nguyen *et al*, 2000 and

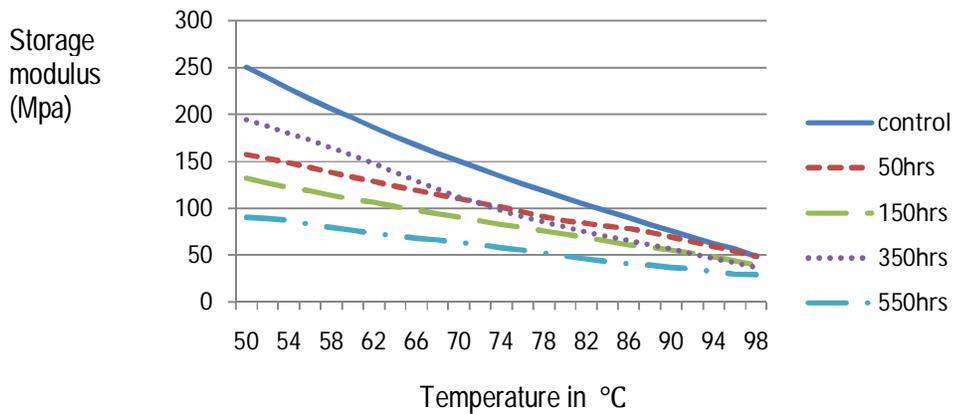
Baljit and Nisha, 2008). Hence, environs of higher RH (40% and 60% RH) favor more degradation evident by lower modulus values. This is well illustrated in Fig 5.4. However there was no significant difference in degradation with exposure to 40% and 60% RH as shown with the intersecting standard error bars.



(a)



(b)



(c)

Fig 5.3: 30µm sample of 30µm aged at (a) 25 % RH (b) 40% RH and (c) 60% RH

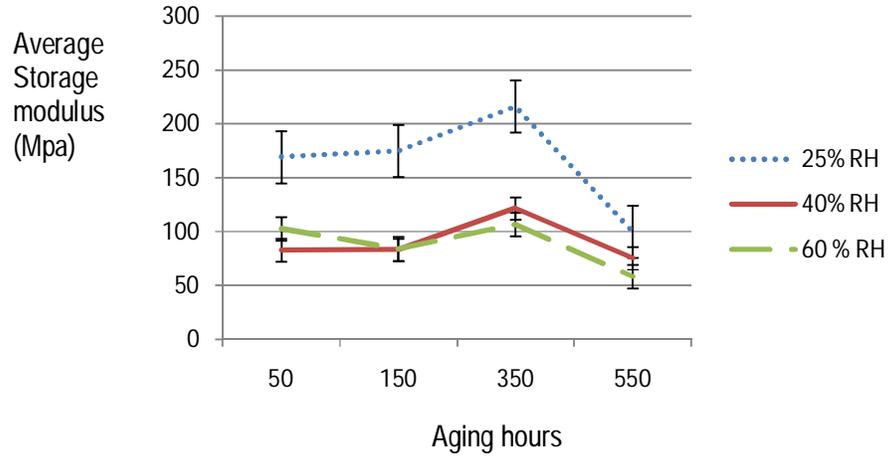
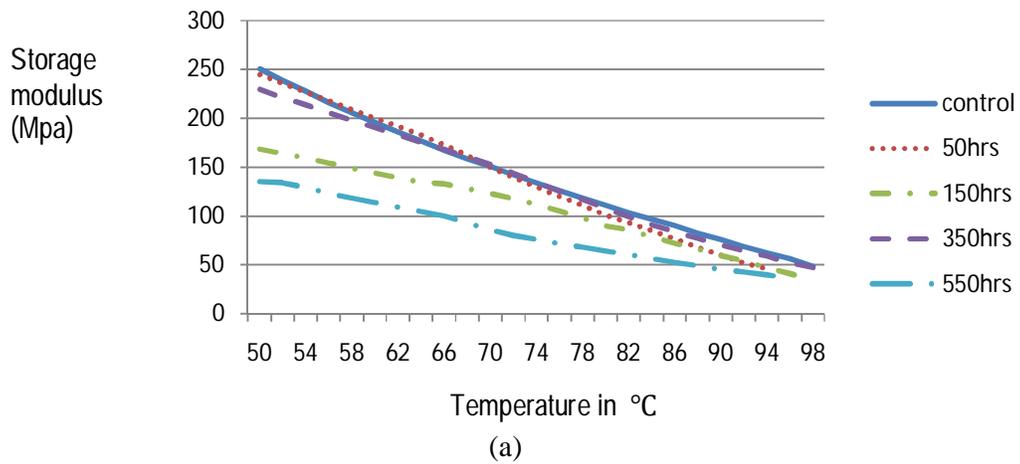
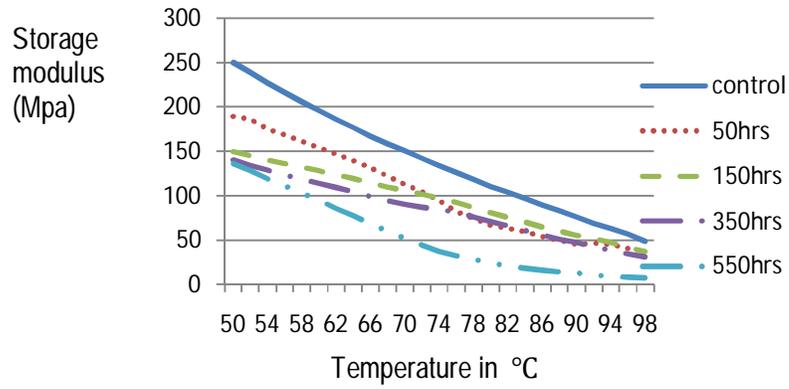


Fig.5.4: Aging Comparison of 200nm-300nm irradiated samples at 25 % RH, 40% RH, and 40% RH

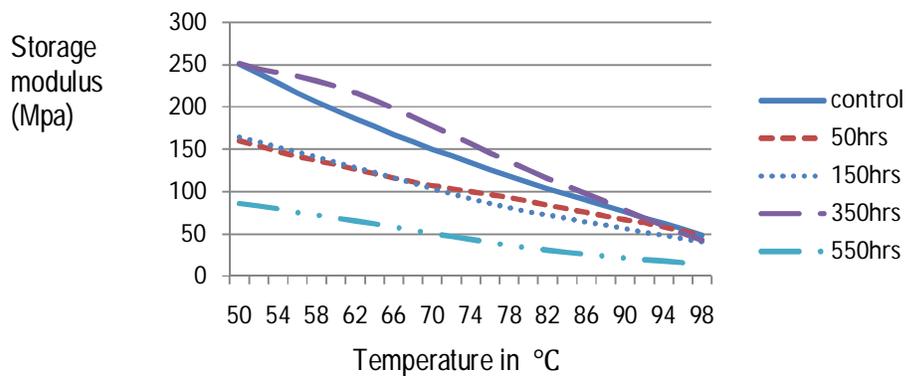
5.3.3. Aging of Samples Irradiated at 300-400nm

UV irradiation of this range exposure to 25 % RH , showed a consistent decrease in storage modulus in Fig 5.5 (a). Fig 5.5 (b) and Fig 5.5 (c) shows the modulus changes trend at 40% and 60% RH rectively.





(b)



(c)

Fig.5.5: 30µm PE sample aged at (a) 25% (b) 40% and (c) 60% RH

A comparison of changes in storage modulus of (300-400)nm irradiated samples and exposed to 25 % RH, 40% RH and 60% RH at 55°C is shown in Fig 5.6. Exposure showed similar trends of consistent increase in storage modulus average values. However there is no significant difference in exposure to 40% RH and 60% RH.

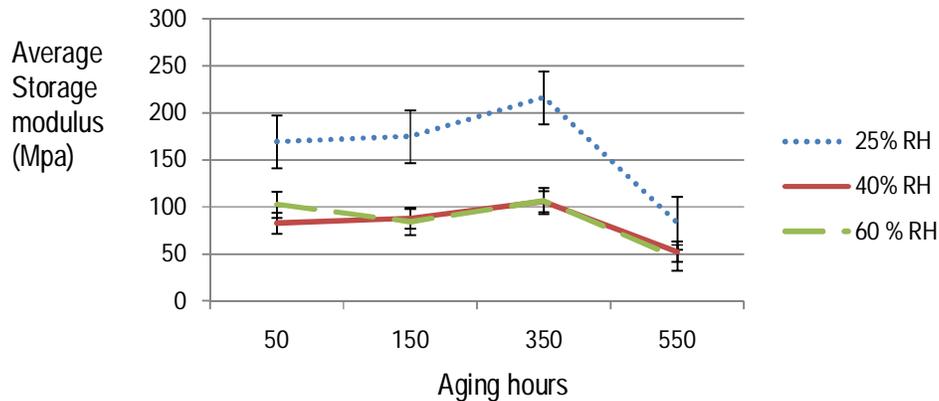
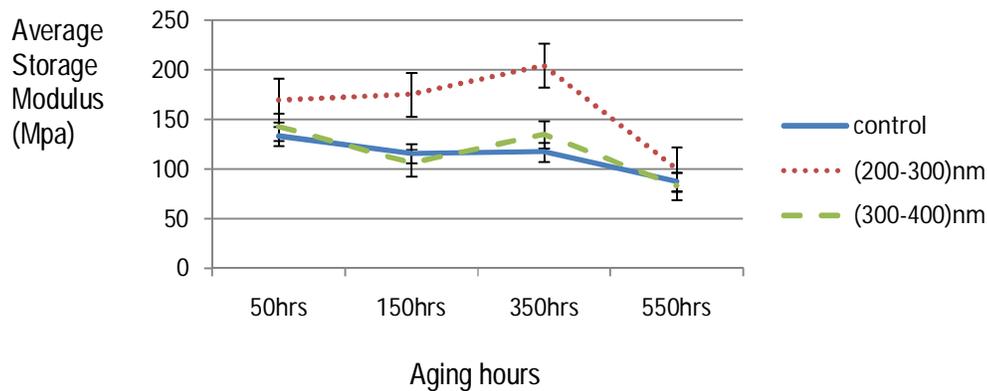


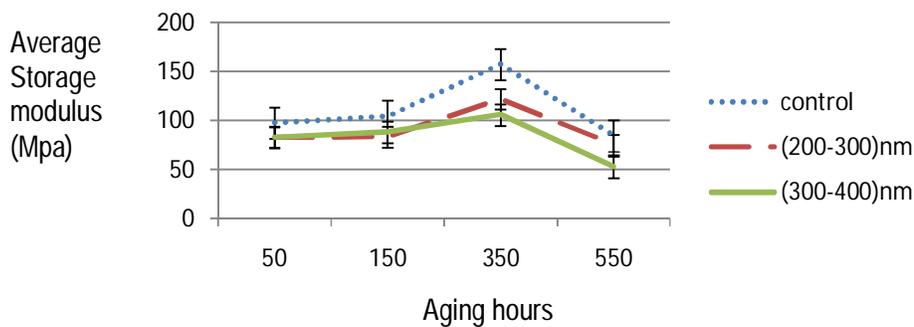
Fig. 5.6: Aging Comparison of (300-400)nm irradiated samples at 25 % RH, 40% RH, and 40% RH

5.3.4. Irradiation effects to degradation.

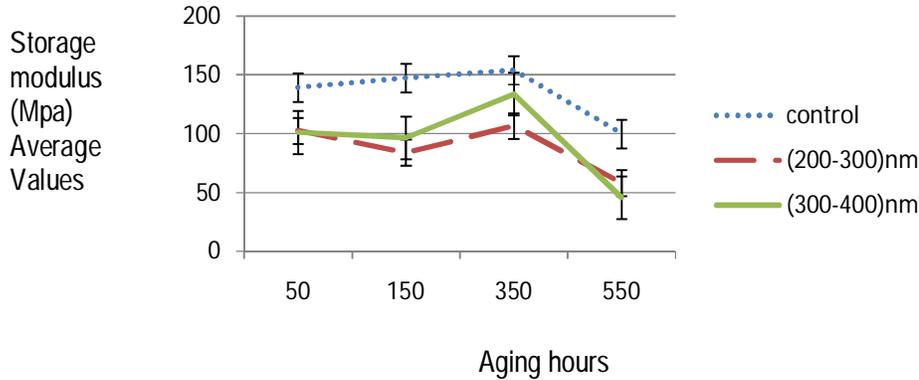
The effect of irradiation to the degradation was investigated and Fig 5.7 (a), (b) and (c), shows the difference of aging trend at 25%, 40% and 60% RH respectively. At 25% RH, a 28% and 41% drop in storage modulus was recorded with (200-300)nm and (300-400)nm irradiation respectively. At 40% RH exposure there was 46 % and 62% storage modulus drop with (200-300)nm and (300-400)nm irradiation respectively. On the other hand, at 60% RH exposure, 58% and 67% storage modulus drops were recorded with (200-300)nm and (300-400)nm irradiation respectively. At higher RH (40% and 60% RH) the storage modulus average values were below that of the control. There is no significant difference in exposure to 25 % RH compared with 40% RH and 60% RH as shown in Fig 5.7 (a) ,(b) and (c). Baljit (2008), records that temperature of the material and the presence of moisture shows a considerable synergistic effect. The presence of high humidity, particularly at the higher temperatures tends to increase the photo-damage in polymers such as thermoplastic polyester elastomer.



(a)



(b)



(c)

Fig 5.7: Effect of Irradiation on Aging at (a) 25% and (b) 40% and (c) 60% RH

5.4 Conclusions and Recommendations

Degradation of these short term products with two hour UV irradiation is enhanced at higher relative humidity. With non UV irradiation the three humidity environments did not show significant differences. Although the two wavelength ranges showed accelerated degradation, (300-400)nm shows higher acceleration than (200-300)nm range. There was 67% drop of storage modulus at 60% RH, as compared to 62% and 41% drop at 40% RH and 25%RH respectively with a pre-irradiation of the range (300-400)nm. This could mean that chromophores absorbing higher at this range are present in the material. A material pre-use irradiation can therefore greatly accelerate the degradation of such PE products. This acceleration can help in dealing with disposal problem of short term use PE products. It is recommended that there should be a pre-consumer use ignition of a degradative action by UV irradiation in short term use PE products. This ensures that the product will be used while it still has its strength and degrades faster after disposal. Moisture attraction should be enhanced in PE products. This will ensure the solar degradative action is accelerated as a result curbing disposal menace. More studies should be done to determine the effect of the degradative action on products used by the consumers and also to the environment.

CHAPTER SIX

General Discussions, Conclusions and Recommendations

6.1 Discussions

The PE films generally showed a low UV absorption of below 62%. This confirms existence of “impurities” or chromophoric sites. Chromophoric sites like C=C, C=O and C-O bonds and hydroxyl groups that are known to absorb within these wavelengths ranges, are likely to be present in the PE. As expected therefore, these PE films should be relatively unstable to sunlight. However the rate of natural photodegradation is slow, demanding a concerted effort to accelerate it. The products can be formulated to have short lifetimes after disposal. The degradation of these PE films was enhanced at high temperatures and high relative humidity exposure environs with an initial UV irradiation. The highest observed reduction of storage modulus (aging) of 74.6% occurred at (300-400)nm irradiation and 55°C temperature treatment. Although the two wavelength ranges showed accelerated degradation, (300-400)nm shows higher acceleration than (200-300)nm range. There was 67% drop of storage modulus at 60% RH, as compared to 62% and 41% drop at 40% RH and 25%RH respectively with a pre-irradiation of the range (300-400)nm. With non UV irradiation the three humidity environments did not show significant differences.

6.2 Conclusions

- The PE films and products processed here in Kenya have chromophoric sites.
- The chromophores present in the PE films have low UV absorption percentages, but absorbs relatively higher at the UV range (300-400)nm as compared with (200-300)nm range.
- As a consequent of low solar UV radiation the rate of degradation is considerably low fitting well a second order polynomial drop of storage modulus.
- Irradiation at the (300-400)nm UV range for two hours has the ability to raise the reduction in storage modulus from 62% for un-irradiated samples to 74.6% at 55°C.
- Irradiation at the (300-400)nm UV range and increase of relative humidity from 25% to 60% accelerated the drop rate of storage modulus from 41% to 67% at 55°C constant temperature.
- A material pre-use irradiation and high temperature and humidity environs can therefore greatly accelerate the degradation of such PE products.

6.3 Recommendations

For applications where there is exposure to sunlight e.g. in horticulture (for green houses), use of stabilizers is encouraged. The same films can be processed void of Chromophoric sites for those purposes. On the other hand for short term consumers e.g. food packaging, fast degradation should be encouraged by addition of more chromophores capable of near visible radiation absorption. This absorption should however be able to ignite degradation and quick fragmentation of these products that ends in landfills. Care should be taken also to ensure these chromophores do not lead to formation of toxic products further escalating the problem of environmental pollution. A pre material use UV irradiation treatment can also greatly accelerate the degradation of these PE products. This accelerated degradation can reduce PE pollution to the environment. More studies should be done to determine the effect of the degradative action and products to the consumers and also to the environment.

7.0 REFERENCES

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