DETERMINATION OF THE MECHANICAL PROPERTIES OF A BIODEGRADABLE THERMOPLASTIC – POLYLACTIC ACID AND COMPARISON WITH THOSE OF POLYETHYLENE

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DECLARATION AND RECOMMENDATION

Declaration

This research is my original work and has not been submitted for the award of a degree in any other University.

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Recommendation

This work has been presented to Graduate School with our approval as University supervisors.

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ACKNOWLEDGEMENT

ABSTRACT

Polyethylene (PE) bags have become the most widely used plastic commodity due to the fact that they are light and have good barrier properties against water and water – borne organisms. The energy requirements for their production as compared to other materials are much lower and the effluents emitted during manufacture of PE compared to paper bags (from trees) are much lower. They are however non-biodegradable and hence are one of the top environmental pollutants. Environment friendly biodegradable thermoplastics such as Polylactic acid (PLA), produced by micro organism synthesis through the fermentation of starch can replace PE. In this study, the dynamic mechanical properties of PLA and PE were compared. A4 PLA films of thickness 20 μm were obtained from Polyfilms limited. PE films of thickness 20 μm were sourced from a retail store. The Dynamic mechanical analyzer (DMA) model 2980 was used in the Multistrain mode at different amplitudes. The storage modulus of PLA was found to be 2220.000 MPa at 50°C and amplitude of 10μm. This was higher than that of PE which was found to be 232.500 MPa at the same temperature and amplitude. The glass transition temperature (T_g) of PLA was found to be 65 $^{\circ}$C against the documented T_g of PE of -78 $^{\circ}$C. At 50°C the loss tangent values of PLA was found to be 0.055 while that of PE was found to be 0.191 indicating higher dissipation of energy in PE. Analysis of the wet samples indicated a rapid loss of storage modulus of PLA while that of PE remained fairly constant. The modulus values were also found to be independent of the amplitude of the force. The densities of PE and PLA were 920 kgm^{-3} and 1249 kgm^{-3} respectively, which are close to those of PP and PS. This indicates that the properties of PE and PLA are similar, with PLA having the advantage of superior mechanical properties as well as being fully biodegradable. The replacement of PE with PLA will aid solid waste management by eliminating the need for recycling and reduce the landfill problem.

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DMA   Dynamic mechanical analyzer

GF   Geometric factor

HDPE   High density polyethylene

LDPE   Low density polyethylene

LLDPE   Linear low density polyethylene

NEMA   National Environment Management Authority

PE   Polyethylene

PHB   Polyhydroxybutyrate

PHBV   Polyhydroxybutyrate-Valerate

PHV   Polyhydroxyvalerate

PLA   Polylactic acid polymer.

PP   Polypropylene

PS   Polystyrene

Psi   Pounds per square inch

UNEP   United Nations Environment Programme

CHAPTER ONE

INTRODUCTION

1.1 Background to the Study

Environmental conservation is undoubtedly one of the top priorities in the world today. According to composters, the top contaminant in feed stocks is plastic with plastic bags being an integral part of waste collection infrastructure (Biocycle, 2008). Over 60% of plastic waste is produced by households, most of it as single use packaging (Scott, 1999).

Polyethylene (PE) is the major packaging plastic and is the main constituent of plastic waste most of which ends up in landfills. Due to the fact that PE bags are light and yet have good barrier properties against water and water – borne organisms they protect perishable commodities from the environment (Conrad, 2003). They also protect the environment from corrosive or toxic chemicals. PE is also a tough, semi-rigid plastic with a high modulus between temperatures of 188 - 409K. Compared to glass, they have superior impact resistance and resilience, resulting in reduced product losses during transport (Scott, 2009). Energy requirements for production of PE as compared to other materials such as aluminium, steel, glass and paper are much lower. Tellus institute for life cycle environmental assessment carried out a study in which the environmental impact of production and disposal of some packaging materials was compared using a monetary scale. For high density polyethylene (HDPE) it was found to be $290 per tonne, $300 per tonne for bleached paper board, $1900 per tonne for steel amongst other packaging materials (Tellus Institute, 1992).Also, the effluents emitted e.g. sulphurdioxide, oxides of nitrogen, carbon monoxide, and dust during manufacture of paper bags from trees compared to PE are much higher (Scott, 1999).

There are however major drawbacks associated with the extensive use of PE. Due to their non-biodegradability, littered PE bags result in visual pollution, cause blockage of gutters and drains and choke domestic, wild and marine animals. They also result in a reduction in agricultural productivity while providing breeding grounds for mosquitoes. At the other end of the durability scale, there is the probability of over stabilization (Scott, 1999). Environmentalists recommend a ban of PE bags saying that paper bags (from trees) are an alternative. However, according to the comparison of PE and paper bags in Table 1.1, paper bags cannot replace PE bags. Banning of

thin PE bags has actually taken place in many countries such as Kenya and China (Recycling International, 2008). In the budget speech for the fiscal year 2007/2008 read on 14th June 2007, the Kenyan Minister for Finance proposed tax policy measures banning thin plastic bags of thickness below 20 micrometers and also imposed 120% excise duty on plastic bags of 30 micrometers and above (Kimilu, 2007).

Table 1.1 A comparison of Properties of PE and Paper bags. Source: Mervyn (2004).

POLYETHYLENE BAGS	PAPER BAGS (FROM TREES)
One PE bag can carry 2- 3 times as much weight as paper bags (Greenfeet, 2009).	Cannot carry as much weight as a polyethylene bag.
Can be used to carry frozen foods and on rainy days.	Are hydrophilic.
Less fossil fuel needed in their manufacture as compared to paper bags from trees.	Paper bags use 500% more raw material to produce than PE bags. Fossil fuels used contribute to global warming (Greenfeet, 2009).
Take up less storage volume.	Are six times heavier and take up 10 times the storage volume of polyethylene bags, creating seven times more transport pollution

A suitable alternative has however not been provided. A lot of research and development is being directed towards development of environment friendly bags (Swift, 1993). Such a bag must possess all the mechanical properties of PE and disintegrate within a reasonable time frame leaving no toxic substances or visible traces. According to the American society of testing and materials (ASTM D6400-04) and the European standards (EN 13432) a compostable material should biodegrade such that Carbon is converted to Carbon (IV) Oxide to the level of 60% and 90% over a period of 180 days (EPI, 2010). In other words, it should be strong yet biodegradable. These would have to be manufactured from biopolymers. The introduction of these biopolymers will reduce the consumption of petroleum, which releases Carbon (IV) Oxide, a greenhouse emission, unburned carbon fragments and other compounds that give rise to smog and air pollution on burning. They are also compostable, aiding solid waste management

(Department of the environment, 2002). Polylactic acid (PLA) and Polyhydroxybutyrate - Valerate (PHBV) are biopolymers which can be used to manufacture thermoplastic films. In this study the mechanical properties of PLA are compared with those of PE over a temperature, amplitude and time range in order to establish whether they can replace PE for single use purposes and in the manufacture of disposable items.

1.2 Statement of the Problem

The benefits conferred on society especially in the packaging industry by the development of PE from fossil fuels have in recent years been obscured by the problem of their ultimate disposal. This is due to its non biodegradability. PE – starch blends break down in a composting environment but leave fragments of PE after breaking apart. This indicates that it is not completely converted to carbon dioxide and water. The use of fully biodegradable bags that do not contain PE would greatly reduce the pollution problem posed by PE bags. Hence there is need to carry out a study to compare the mechanical properties of PE with those of PLA to confirm whether PE can be replaced in disposable products.

1.3 Objectives

1.3.1 General Objective

The objective of this study is to determine the mechanical properties of PLA polymer using the Dynamical Mechanical Analyzer (DMA) and compare them with those of polyethylene.

1.3.2 Specific Objectives

The specific objectives are to determine and compare:-

i. The density and the stiffness of PE and PLA films.
ii. The values of storage modulus, loss modulus and the loss tangent (tan δ) of dry samples at 50°C and their variation with time and temperature using the DMA.
iii. The storage modulus of wet samples of PE and PLA under identical environmental conditions at a temperature of 50°C using the DMA.
iv. The glass transition temperatures of PE and PLA polymers.

1.4 Justification of the Study

This study of the mechanical properties of PE and PLA confirmed that indeed biodegradable bags can replace PE in single use applications and in disposable hygiene items that end up in the sewage system. This will go a long way in curbing environmental pollution by PE bags eliminating the eye sore caused by littered PE bags, reduce the blockage caused in the drainage system as well as remove the risk posed to wild and domestic animals amongst other benefits. Municipal waste managers and the tourism industry as well as the Ministry of Environment and Natural resources are amongst the main beneficiaries from this development. The manufacturers of PE films also stand to gain in that with their present infrastructure, they will be able to manufacture PLA films at a reduced cost due to the availability of the raw material. In addition, they will benefit from the reduction in the energy requirements of between 30 and 50% needed in the manufacture of PLA as compared to PE films. At the same time it will aid solid waste management with composting being a relatively easy option having eliminated the need for sorting out the biodegradable waste from the non – biodegradable one.

1.5 Scope of the Study

In this study, the mechanical properties including the storage and loss moduli, the glass transition temperature and the density of PLA and PE films were determined and compared. The PE films were sourced locally in Nakuru town while the PLA films were obtained from Polyfilms limited. The DMA at Egerton University was used from mid May to early August, 2009 as well as the one at Maseno University for two weeks from early May, 2009.

The availability of the biodegradable samples proved to be very difficult. This is due to the special conditions under which they need to be processed. There are specific bacteria as well as optimal processing conditions under which polymerization takes place, which require extensive research and long periods of time to arrive at. Due to this, the finished products had to be obtained and their mechanical properties studied. The DMA machine was also out of order for a long period of time and started working well from early May, 2009, which was very challenging. This necessitated travel to Maseno University where their machine was working. These limitations made the study quite challenging.

1.6 Limitations of the Study

The original intention of this study was to determine and compare the mechanical properties of two types of biodegradable polymers in particular PLA and PHBV with those of PE. It was however not possible to source PHBV since it was said to be under research and development stage and could therefore not be made available. It was also not possible to work at temperatures below room temperature. This led to the inability to obtain the glass transition temperature of PE, leading to the use of the expected value for comparison with that determined for PLA. The insufficient cooling of the DMA apparatus also limited the temperature range within which data was collected.

CHAPTER TWO

LITERATURE REVIEW

2.1 Development of Biodegradable Plastics

Synthetic polymers were originally developed for their durability and resistance to all forms of degradation, including biodegradation. They are also widely used because they are inexpensive. However, these same properties that make them so useful have contributed to a disposal problem. Plastics, a major proportion of which is PE, accumulate in the environment at a rate of 25 million tons per year (Yuksel and Hanife, 2000). Because of their low density, they occupy a high volume fraction of buried waste (Swift, 1992). According to a report by UNEP/Grid-arendal (2004) plastics take over one million years to biodegrade. Traditionally, PE is manufactured from nonrenewable petroleum resources, and is non biodegradable (Vaidya *et al*, 2005). It takes several centuries, between 20 and 1000 years, for efficient degradation to take place (UNEP/Grid-arendal, 2004).

Conventional disposal methods include incineration, recycling and secured landfill, which are associated with many environmental problems, such as production of dioxins. In due course the alternative strategy of sorting out biodegradable materials for composting and non-biodegradable materials for mechanical recycling and energy production emerged. However, when PE waste is recovered from litter, the energy in the form of fossil fuel utilized in collection and cleansing may be greater than that used in its manufacture from crude oil (Scott, 1999). Moreover plastic films used in packaging, more than 60% of which is LDPE or LLDPE are coloured and/or are blended making them difficult to recycle (Recycling international, 2008).

The continued depletion of landfill space and problems associated with incineration and recycling have led to the development of biodegradable polymers. Until recently little thought was given to the design of biodegradable materials for products that end up in the waste stream or as litter; but now owing to increased environmental awareness through the intervention of organizations such as UNEP and NEMA, environment friendly materials are demanded. The concept of biodegradable synthetic polymers was first proposed in the 1960's (Scott, 1999). This led to the manufacture of PE-starch blend plastics which were claimed to be biodegradable. LDPE-Starch blends are believed to be catabolized in soil but this process is slow and the

degradation period is not known with certainty (Yuksel and Hanife, 2000). Shujun carried out a study on the degradation of PE-starch films using Fourier transform infra red, weight loss percent and scanning electron microscope and found that its weight decreased by 3% in 30 days and by 4% in 60 days.

Polymer producing industries were against the idea of polymer degradability since it appeared to conflict with the basic ethos of the industry that polymers should be made as stable as possible (Query, 2008). There are localities and product types that are better suited for either incineration, recycling or burial in landfills. While there are purposes for which very stable plastic films are required for example in the horticulture industry in the establishment of greenhouses, for some purposes they are over stabilized, for example in personal hygiene items and in single use packaging where biodegradability would be desirable. Biodegradable PE bags would be favored in applications where recovery of the bags for recycling or incineration is not cost effective or is difficult, for example in the case of water-soluble polymers (Swift, 1992). Hence researchers need to design polymeric materials for much more specific end uses than in the past (Scott, 1999).

Modified natural biopolymers e.g., starch and cellulose, are the basis of 'new' biodegradable polymers. These are expected to find application in waste products that end up in the sewage systems, and may be used as replacements for traditional packaging materials. Polylactic acid (PLA) is a biodegradable polymer that has been developed by companies such as Procter & Gamble, Eastman Chemical Company, Novamont and Nature Works PLA amongst others (Biocycle, 2008).

Lactic acid is one of the most important organic acids produced by lactic acid bacteria (LAB). LAB consists of bacterial genera within the phylum Firmicutes comprised of about 20 genera. These genera include Lactococcus, Lactobacillus and Streptococcus amongst others. Lactobacillus is the largest genera comprising about 80 species. LAB can produce either l (+PLLA) or d (−PDLA), which are optically active, or a racemic mixture of lactic acid (Ajioka, 2005). The first step in the production of lactic acid involves pretreatment by gelatinization and liquefaction of cheap raw materials such as whey, molasses, starch waste, sugar beet, cane sugar

and other carbohydrate rich materials. This is followed by enzymatic saccharification to glucose. The glucose is then converted to lactic acid by Lactobacillus fermentation (Reddy *et al*, 2008).

There have however been restraints of high cost and insufficient technical performance of lactic acid produced in this way (Jones-Hulfachor, 2000). In an effort to address these restraints, researchers such as Suszkiw (2008) reveal that sugar beet can be turned into biodegradable filler material for PLA making it a cheaper alternative to petroleum-based thermoplastics. Also, PLA's former filler was corn sugar removed from the kernels. By finding ways to use starch from the entire plant, farmers would be able to sell the corn as produce and the remaining plant for plastic (Jones-Hulfachor, 2000). Amylolytic lactic acid producing bacteria have the ability to convert starchy biomass to lactic acid in single step fermentation. This will eliminate the two step process to make it economical (Reddy *et al*, 2008).

Sugar alcohol, sorbitol is used to plasticize the pulp. The pulp is reshaped into particulate matter, melted into PLA and processed through a twin-screw extruder to produce composite material for subsequent remolding. They are fully biodegradable and result in carbon savings of 30-80% compared with oil based plastic (European Environment and Packaging law weekly, 2008). PLA polymer was first used as biodegradable sutures in the 1960's (Jones-Hulfachor, 2000). PLLA is a semi crystalline polymer exhibiting high tensile strength and low elongation with high modulus. According to a polymer data sheet by Mat Base (2009), PLA has a Young's modulus of between 350 MPa and 2800 MPA and a T_g of between 45^0C and 65^0C. Its degradation period is between 18 – 24 months. It is however brittle and has a slight milkiness (Sukano News, 2005)

PLA has mainly been used in biomedical applications (Marc, 2006). It is suitable for medical products in orthopedic fixation (pins, rods, ligaments etc.), cardiovascular applications, dental applications, intestinal applications, and sutures. Other potential applications include packaging for cereals, snack foods, dairy products, food container and candy (Biocycle, 2008). PLA is degradable in soil, water or compost. When PLA is incinerated, the heat of combustion is half or less compared with conventional plastics such as PE.

Another biodegradable thermoplastic is PHBV. It is a copolymer of polyhydroxybutyrate (PHB) and polyhydroxyvalerate (PHV). PHB is made by fermentation of sugars from corn, sugar beet

or molasses and palm oil based fatty acids using bacteria such as Escherichia coli, followed by a separation that yields 85% to 95% of the polymer by weight (Fonseca, 2008). PHB has a melting temperature of 175°C and a glass transition temperature of 15°C. A PHV content of 5-20% gives a useful range of properties similar to polyolefins (Fukui, 1997).

Recent developments are geared towards genetically engineering plants to produce these polymers within leaf cells (Shah, 2008). For farmers, PHBV would become an additional agricultural commodity, creating a double crop in one plant for example in corn or soybeans. The plants would be designed to produce the PHBV plastic in the leaves only, leaving the seeds unchanged. It is one of the newest types of naturally produced biodegradable polyester. It's processing is relatively difficult and has been reported to have low elongation and very high crystallinity (Fonseca *et al*, 2008). It is however completely biodegradable and exhibits good barrier properties. PHBV is flexible and mouldable. It is insoluble in water, permeable to oxygen and is resistant to Ultraviolet radiation (UV). It could be used to produce a wide range of products, from grocery bags and soda bottles. Potential applications are film and non-woven paper packaging at costs comparable to traditional materials. When discarded, bacteria that naturally occur in the soil chew it up and turn it into water and carbon (IV) oxide (Jenkins, 2004).

2.2 Study of Mechanical Properties

The density, modulus and stiffness are an indication of the strength of a polymer. The glass transition temperature gives an indication of its flexibility as polymers are stiff and rigid below this temperature and flexible above it. The density of a polymer is a measure of the proportion of crystals within its mass (Gabriel, 2009). The crystallinity of a polymer is directly proportional to its modulus. The damping properties of a polymer are indicated by the ratio of the loss modulus (E'') to that of the storage modulus (E') i.e. $\tan \delta = \dfrac{E''}{E'}$. A study on the controlled composting of PLA found that as it degraded, there was a reduction in its mechanical strength (Weber, 2008). The DMA was used to investigate the solid state rheological behaviour of a starch-based thermoplastic aimed to be used in different biomedical applications in which case dry samples were immersed in a simulated physiological solution. The storage modulus was investigated as a

function of time and frequency. Also the damping properties were monitored. It was shown that the DMA is a suitable method to follow off-line the degradation behaviour of biomaterials for long time periods (Mano and Reis, 2004).

A study done to find internal damping and elastic stiffness of glass fibre – reinforced epoxy beams under flexural vibration found that damping and stiffness are independent of amplitude as long as the maximum strain amplitude does not exceed the threshold strain for material damage (Gibson and Plunkett, 1976). Stress – strain and torsional torque deflection curves have been used in the determination of modulus. It was found that within the temperature range -30 – $+25\,^0C$, continuously curved stress – strain curves, best described by an exponential type function permitted the determination of an initial tangent modulus. A more conventional elastic behaviour was observable below – $30\,^0C$, and a tangent modulus could be evaluated graphically. It was found that over a common temperature range, torsional and tensile techniques yielded equivalent moduli (Carey *et al*, 2009).The DMA was used in this study to investigate the mechanical properties of the polymers to establish whether the technical performance of the biodegradable polymers would measure up to that of PE.

2.3 Theory

2.3.1 Response of a Material to Stress

Polymers respond differently to mechanical stresses. Figure 2.1 illustrates the ideal behavior of a biodegradable polymer used in commercial applications. The sample must be initially strong and tough so that it can withstand the stresses imposed on it during service for example as a packaging material. Such a polymer would have a high modulus, high impact strength and low creep. A balance is however required for high rigidity and low creep usually goes with poor impact strength. It should then physically disintegrate after discard under influence of the environment and chemically transformed to carboxylic acids, alcohols, aldehydes, and hydroxyl acids normally found in nature. The bulk of the polymer is converted into biomass, carbon dioxide and water by environmental micro flora, thus completing the biological cycle (Scott, 1999).
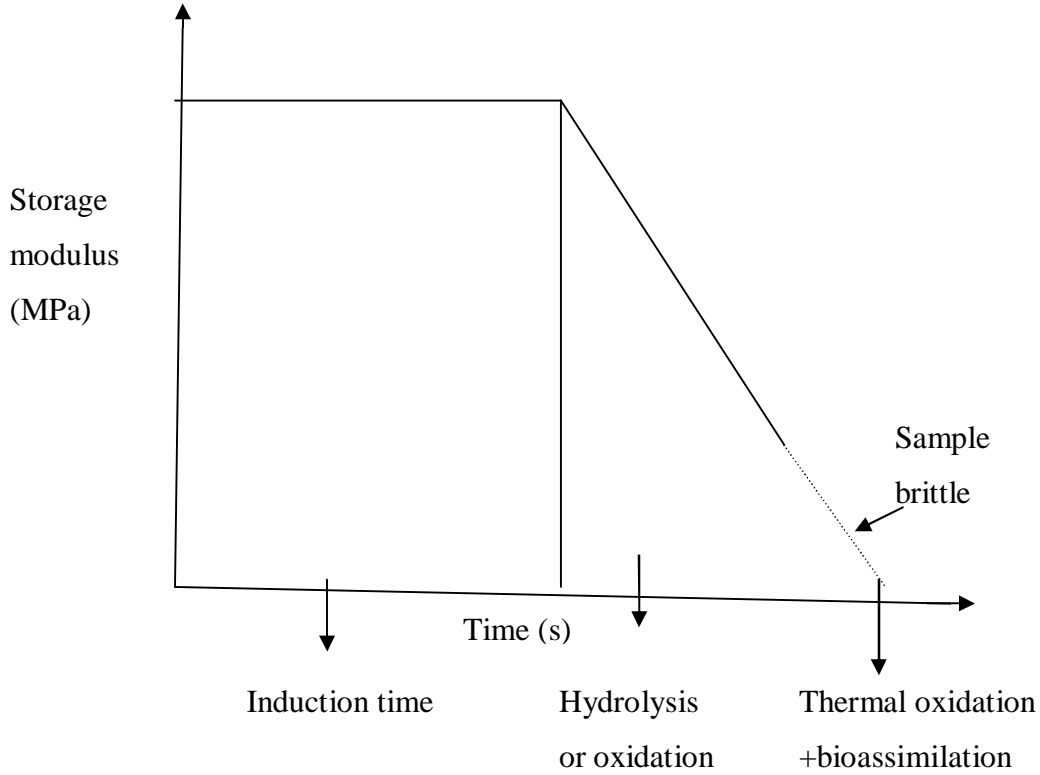
Figure 2.1 Ideal behavior of a biodegradable polymer. Source: Scott (1999)

Homogeneous, isotropic, elastic materials possess the simplest mechanical properties. Elastic deformation can be observed when such a body is subjected to simple tension, simple shear and uniform compression. Simple tension is directly proportional to the strain.

$$\sigma = E\varepsilon \qquad (2.1)$$

Where, E is the constant of proportionality known as the Young's modulus. The stress σ is a measure of the force per unit area i.e

$$\sigma = \frac{F}{A}. \qquad (2.2)$$

ε, is the strain or elongation and is defined as the extension per unit length, i.e.

$$\varepsilon = \frac{\Delta x}{x_o} \qquad (2.3)$$

E^{-1} is the tensile compliance, and is given the symbol D. By subjecting the specimen to a tensile force applied at a uniform rate and measuring the resulting deformation, a curve of the type shown in Figure 2.2 can be constructed. The tensile modulus E is obtained from the slope of portion O to L.

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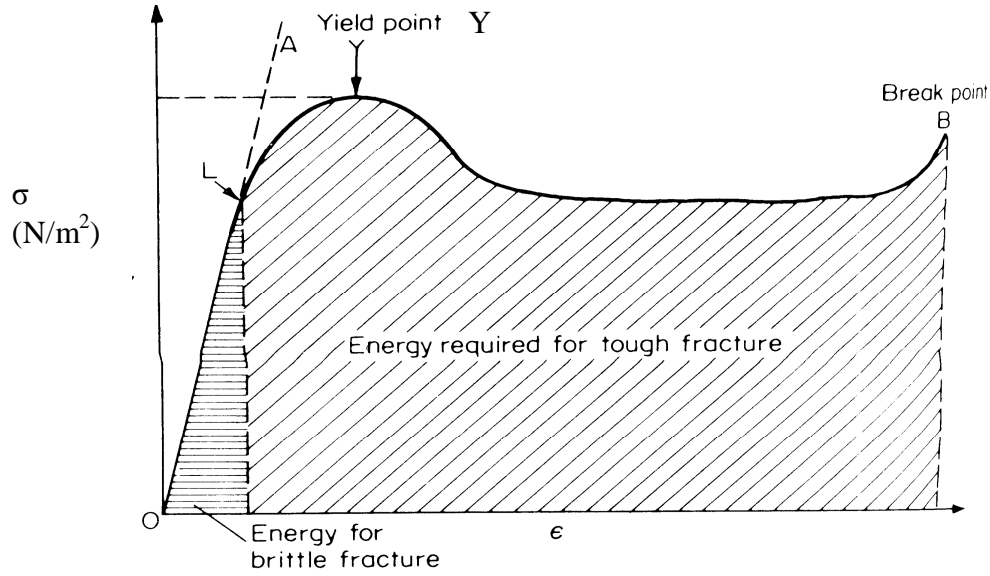
Figure 2.2: Idealized stress-strain curve of a material. Source: Cowie (1991)

The point L represents the elastic limit. The area under the curve O – L is proportional to the energy required for brittle fracture. If no fracture occurs, the curve passes through a maximum at Y, known as the yield point. Beyond this, the extensions increase until the breaking at point B. The area under this part of the curve is the energy required for tough fracture to take place. With a rise in temperature, both the rigidity and the yield strength decrease.

Stress-strain measurements provide information on the modulus, the brittleness, and the ultimate yield strengths of a polymer.

Simple shear results in shear modulus G given as

$$G = \frac{\sigma_s}{\varepsilon_s} = \left(\frac{F}{yz}\right) / \left(\frac{\Delta x}{y}\right) = \frac{F}{A \tan \theta} \qquad (2.4)$$

Where, F is the shearing force and A is the cross-sectional area.

For very small shearing strains $\tan \theta \approx \theta$ radians, hence,

$$G = \frac{F}{A \theta} \qquad (2.5)$$

G^{-1} is the shear compliance, and is given the symbol J.

Both E and G depend on the shape of the specimen and it is usually necessary to define the shape carefully for any measurement. An isotropic body is considered to possess only two independent

elastic constants. The moduli are related to each other. Table 2.1 shows a comparison of typical values of moduli for several polymeric and non-polymeric materials compared at ambient temperatures. For an isotropic body, the change in length per unit length is related to the change in width per unit of length, such that

$$V_p = \frac{\Delta y / y_o}{\Delta x / x_o} \qquad (2.6)$$

Where V_p is known as Poisson's ratio and varies from 0.5, when no volume change occurs, to about 0.2 when the volume of a material varies.

Table 2.1: Comparison of various Elastic and Shear moduli for some common materials. Source: Cowie (1991)

Material	E (GNm^{-2})	V_p	G (GNm^{-2})
Steel	220	0.28	85.9
Copper	120	0.35	44.4
Glass	60	0.23	24.4
Granite	30	0.30	15.5
Polystyrene	34	0.33	1.28
Nylon-6,6	20	-	-
Polyethylene	24	0.38	0.087
Natural Rubber	0.02	0.49	0.00067

2.3.2 Viscoelasticity

A material when subjected to stresses, may exhibit the characteristics of both a liquid and a solid and neither of the limiting laws, Hooke's Law nor Newton's laws will adequately describe its behavior. The system is then said to be in a viscoelastic state and exhibits a 'delayed elasticity'. A stress results in an instantaneous strain, which continues to increase more slowly with time. It is this delay between cause and effect, that is, the stress and strain respectively, which is fundamental to the observed viscoelastic response resulting in creep, stress relaxation and dynamic response. Polymers due to their chain like structure exhibit a viscoelastic response (Chang, 2006). A Maxwell element exhibits a dynamic response. It consists of a purely elastic

spring and a purely viscous damper connected in series (Cowie, 1991). The application of a sinusoidal stress to a Maxwell element produces a strain with the same frequency as, but out of phase with, the stress. This is illustrated in Figure 2.3 where δ is the phase angle between the stress and the strain. The strain can be described in terms of its angular frequency ω and the maximum amplitude ϵ_o using complex notation, by

$$\varepsilon^* = \varepsilon_o \exp(i\omega t) \tag{2.7}$$
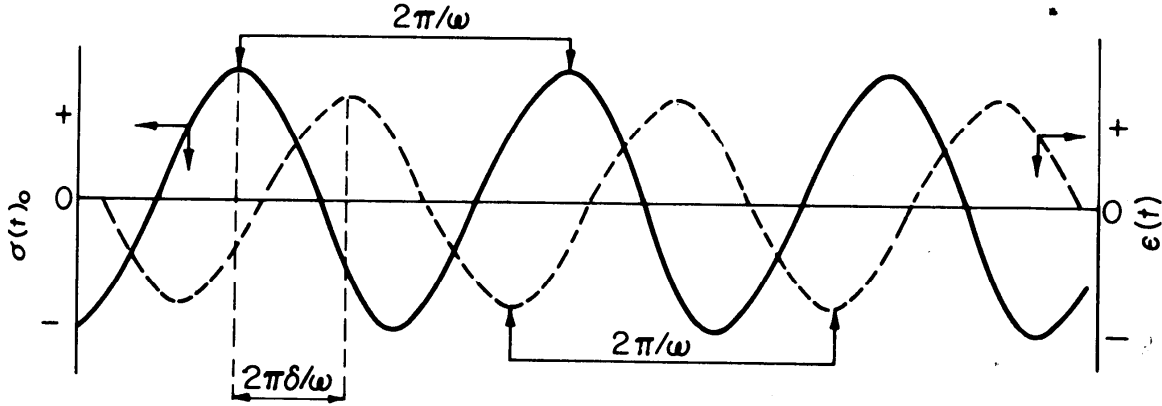
Figure 2.3: Harmonic oscillation of a Maxwell model. Source: Cowie (1991)

Where, $\omega = 2\pi v$, v is the frequency. The alternating stress and strain have the following relationship

$$\sigma^* = \varepsilon^* E^*(\omega) \tag{2.8}$$

$E^*(\omega)$, is the frequency dependent complex dynamic modulus given as

$$E^*(\omega) = E'(\omega) + iE''(\omega) \tag{2.9}$$

Where, $E'(\omega)$ is the storage modulus which measures the amount of energy stored instantaneously. $E''(\omega)$ is the loss modulus which lags behind the storage modulus and grows with time. It is defined as the ratio of the component 90° out of phase with the stress to the stress

itself. It measures the amount of energy dissipated in the material. The elastic modulus E and the dynamic modulus have the following relationship;

$$E = \left| E^* \right| \qquad (2.10)$$

hence,

$$E = \sqrt{\left(\left(E^* \right) \left(E^* \right)^* \right)} \qquad (2.11)$$

and,

$$E = \sqrt{\left(E'^2 + E''^2 \right)} \qquad (2.12)$$

Equation 2.12 shows that the elastic modulus is very close to the storage modulus. It is slightly smaller depending on the value of loss modulus.

The damping in the system or the energy loss per cycle can be measured from the "loss tangent" $\tan \delta$. This is a measure of the internal friction and is related to the complex moduli by

$$\tan \delta = \frac{E''(\omega)}{E'(\omega)} = \frac{J''(\omega)}{J'(\omega)} \qquad (2.13)$$

Viscoelastic polymers exhibit both elastic and damping behaviour. Hence if a sinusoidal stress is applied to a linear viscoelastic material, the resulting strain will also be sinusoidal, but will be out of phase when there is energy dissipation or damping in the polymer (Cowie, 1991).

To a first approximation

$$\frac{E''}{E'} = \frac{G''}{G'} \qquad (2.14)$$

The behaviour of E' and E'' reflects the onset of molecular motion in a polymer sample. Figure 2.4 illustrates the variation of E' and E'' as a function of ω, assuming only a single value for relaxation time, τ. A maximum in the loss angle is observed where

$$\omega = \frac{1}{\tau} \qquad\qquad\qquad (2.15)$$

This represents a transition point such as T_g and T_m, or some other region where significant molecular motion occurs in the sample.
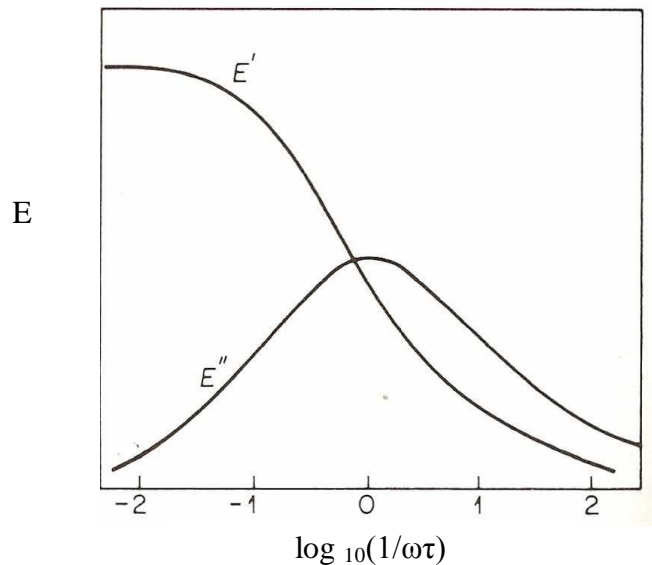
Figure 2.4: Behaviour of $E^{''}$ and $E^{'}$ as a function of ω for a system with a single relaxation time. Source: Cowie (1991)

2.3.3 Glass Transition Temperature T_g And Melting Temperature T_m

At sufficiently low temperatures all polymers are hard rigid solids. Below the glass temperature (T_g), molecular chain motion is frozen and is largely restricted to vibrations and short range rotational motion.The polymer behaves like a stiff spring storing all the available energy in stretching as potential energy, when work is performed on it and has a high modulus. The elastic modulus for glassy polymers just below the T_g is constant over a wide range of polymers having the value of approximately 3000 MPa (Sperling, 2006).

As the temperature of a polymer rises, molecular motion increases and it begins to behave like a viscous liquid if no degradation occurs. With a further rise in temperature, a transition from the glass to the rubber-like state takes place. Figure 2.5 shows the typical overall shape of a curve for the stiffness measured over a temperature range.
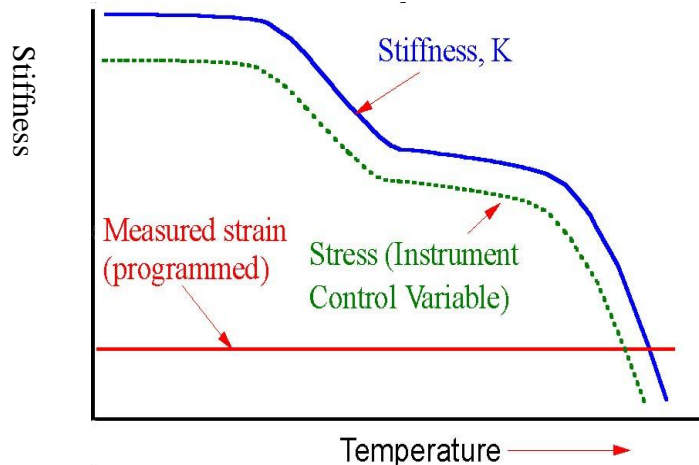
Figure 2.5: Stiffness against temperature. Source: DMA User Manual

The rapid change in stiffness indicates transitions and T_g is located within these regions. As Stiffness and Modulus are directly proportional, as per equation (2.17), a rapid decrease in modulus is also indicative of a transition and T_g is located within this region. For the loss modulus and loss tangent graphs, T_g is located at the peak of the graphs. For all polymers, T_g from the loss tangent graph occurs several degrees higher than from the loss modulus graph.

In mechanical terms the transition can be likened to the transformation of a stiff spring to a weak spring. Weak springs can only store a fraction of the potential energy that a strong spring can hold, losing the remainder as heat. The energy loss is detected as mechanical damping. When molecular motion increases to a sufficiently high level, all the chains behave like weak springs the whole time. The modulus is much lower, but so too is the damping. It passes through a maximum in the vicinity of the glass transition temperature T_g. This is illustrated by Fig. 2.4. Changes in the physical properties, such as hardness and elasticity are observed. The temperature at which T_g is observed depends largely on the chemical nature of the polymer chain. T_g has an important bearing on the potential application of a polymer. In dynamic mechanical methods for locating T_g, a rapid change in modulus is indicative of the glass transition, but the transition region is dependent on the frequency of the applied force (Cowie, 1991).

Figure 2.6 illustrates the different types of thermal responses of a polymer by following the change in specific volume, as it passes from the solid to the liquid phase. The volume change in amorphous polymers follows the curve A – D. In the region C – D the polymer is a glass, but as

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the sample is heated it passes through T_g. A continuing increase in temperature along $C - B - A$ leads to a change of the rubbery polymer to a viscous liquid.
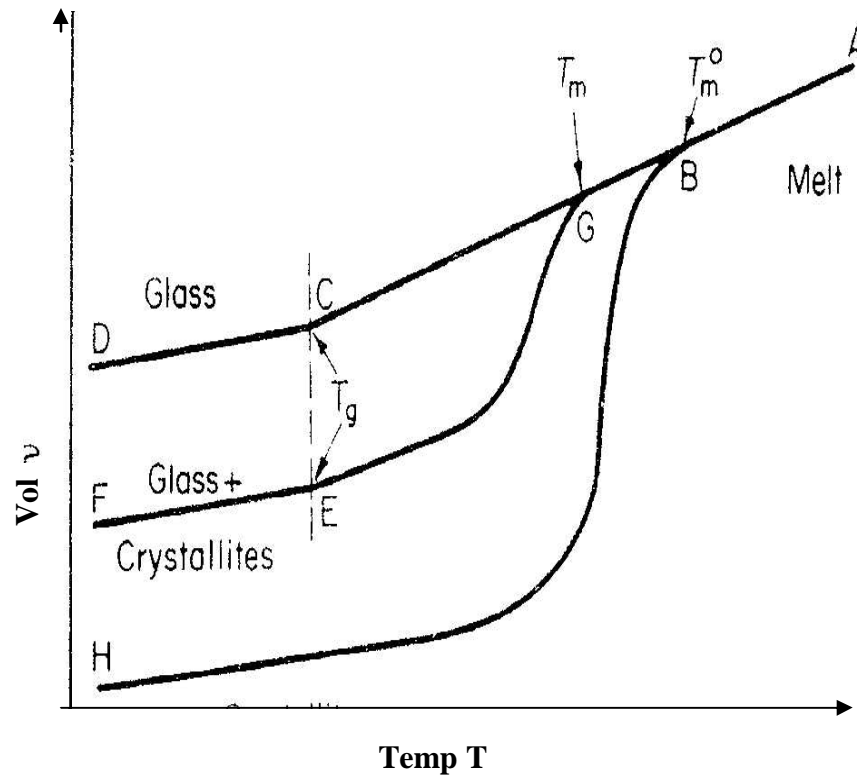
Figure 2.6: Change of specific volume *v* of a polymer with
temperature T. Source: Cowie (1991)

In a perfectly crystalline polymer, no glass transition would be observed, because of the absence of disordered chains in the sample. On heating, it follows curve $H - B - A$. At T_m^o, melting would be observed and the polymer would become a viscous liquid. Polymers contain varying proportions of ordered and disordered regions. These semi crystalline polymers usually exhibit both T_g and T_m corresponding to the ordered and disordered portions and follow curves similar to $F - E - G - A$. T_m represents a melting range, because the semi – crystalline polymer contains a spectrum of chain lengths and crystallites of various sizes with many defects and is lower than T_m^o which is the melting temperature of a perfectly crystalline polymer of high molar mass. Short range order in some regions of the solid may exist. The extent of such ordering is indicated by the degree of crystallinity of the polymer which affects the density, hardness, solubility and

heat resistance of a polymer. Table 2.2 shows how the properties of PE change as the degree of crystallinity increases.

Table 2.2: Change in mechanical properties of polyethylene with crystallinity.
Source: Cowie (1991)

CRYSTALLINITY	55%	62%	70%	77%	85%
M.P (^{o}C)	109	116	125	130	133
STIFFNESS (Psi x 10^{-3})	25	47	75	120	165
YIELD STRESS (Psi)	1700	2500	3300	4200	5100
DENSITY(g/cm3)	0.92	0.93	0.94	0.95	0.96

These test results show that the mechanical strength of the polymer increases with increased crystallinity. The properties of PE can be 'tuned' by varying the average length of the chains, making it a very versatile material with a T_g of -78 $^{\circ}C$. For example HDPE has a simple linear structure which is conducive to intermolecular interactions that lead to crystallinity.It has a density of 0.941 g/cm^3 and a T_m of between 120 and 130 ^{0}C (Theodore *et al*, 2006). Another category is LDPE which is less crystalline with a density of between 0.910 and 0.940 g/cm^3 and T_m of between 105 and 115 $^{\circ}C$ (Scott, 2009).

After the transition from the glassy to the rubbery state, typical polymers acquire modulus values of approximately 200 MPa after T_g (Sperling, 2006).

2.3.4 Stiffness

Sample stiffness K_s is defined as the force applied to the sample divided by the amplitude of deformation.

The stiffness of a material is an extrinsic property that is dependent on its geometry. The dimensions of the sample are used to compute the Geometric factor (GF), which connects the elastic modulus and the stiffness of a material as per equation 2.17. For a sample of rectangular cross-section, the geometric factor is related to the dimensions of the sample as per equation 2.16.

$$GF = \frac{Length}{Cross - \sec tional - area} \qquad (2.16)$$

2.4 DMA Analysis

There are three main experimental approaches for measuring the dynamic mechanical properties of a sample. They are:

i.   Free vibration
ii. Forced vibration – resonance
iii. Forced vibration – non-resonance

Other approaches include broadband viscoelastic spectroscopy (BVS) and resonant ultrasound spectroscopy (RUS) which can be used above and below ambient temperatures. They employ a damping mechanism at various frequencies and time ranges. (Gibson, 1976)

In this study the forced vibration – non resonance was used. This type of test can be carried out using several types of instruments. The sample is attached firmly at each end to a strain gauge; one of these is a force transducer measuring the applied sinusoidal force and the other records the sample deformation. The DMA instrument can be used for this measurement. Several clamping arrangements are available for the sample so that measurements may be made in the bending and shear or tensile, modes. For the tension film clamp, the sample is mounted as illustrated in Figure 2.7.
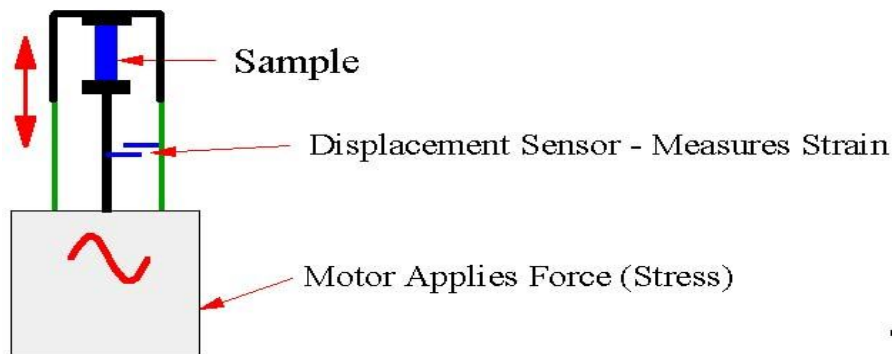

Figure 2.7: Sample mounted on the tension film clamp. Source: DMA User Manual

Dynamic mechanical analysis is a relaxation spectroscopy in which the sample is perturbed by a sinusoidal force in the form of a torque, push-pull, or a flexing mode, of angular frequency ω. Temperature can be controlled over the range 120 to 770K, either isothermally or by ramping up

and down at various fixed rates. Over a common temperature range, torsional and tensile techniques yield equivalent moduli (Carey *et al*, 2009). If the polymer is treated as a classical damped harmonic oscillator, both the elastic modulus and the damping characteristics can be obtained.

In this study, the dynamic mechanical analysis was carried out in a DMA 2980 apparatus. In order to ascertain the accuracy and precision of the measurements, a standard steel bar was used to calibrate the DMA apparatus. The storage modulus of a sample of Polyethylene teraphthalate (PET) provided by the manufacturer of the DMA apparatus was then determined and found to be 2950 Mpa. The Elastic modulus of PET lies between 2700 – 4000 Mpa. This confirmed the validity of the values obtained in this study.

The fundamental measurement of the DMA 2980 is sample stiffness K_s and the sample's modulus E_s is then calculated as follows;

$$E_s = K_s x (GF) = K_s x (\frac{L}{A}) \qquad (2.17)$$

Hence, the sample modulus is directly proportional to the sample stiffness, that is $E_s \propto K_s$. In dynamic mechanical experiments, the DMA 2980 measures the raw signals of force, amplitude of deformation, and phase angle. The drive force for this apparatus ranges between 10^{-4} N and 18 N. It uses the amplitudes to calculate the complex stiffness K* which is used with the phase angle to calculate the storage and loss stiffness ($K^{'}$ and $K^{''}$). Tan δ is the ratio of $K^{''}$ to $K^{'}$ following equations 2.13 and 2.17. The apparatus automatically calculates the GF using equation 2.16. It then calculates the storage and loss moduli by multiplying the raw stiffness measurements by the appropriate geometry factors GF using equation 2.17.

CHAPTER THREE

MATERIALS AND METHOD

3.1 Sample

The samples that were investigated in this study were PE and PLA. PLA was obtained from Polyfilms limited, who provided its specifications of thickness, biodegradability and usage. PE was obtained from a retail store in Nakuru town.

3.1.1 Sample Preparation

The DMA 2980 has amplitude, stiffness and drive force limits outside which the results would not be valid. The actual sample size was therefore determined with these limits in mind. The tension film clamp of the DMA 2980 can accommodate samples of thickness up to 2 mm.

In a dynamic experiment the amplitudes one can command are from ± 0.5 µm – 10^4 µm. For the tension film clamp, an amplitude of between 15 – 25 µm is recommended. The stiffness range of the DMA 2980 is 10^2 N/m – 10^7 N/m.
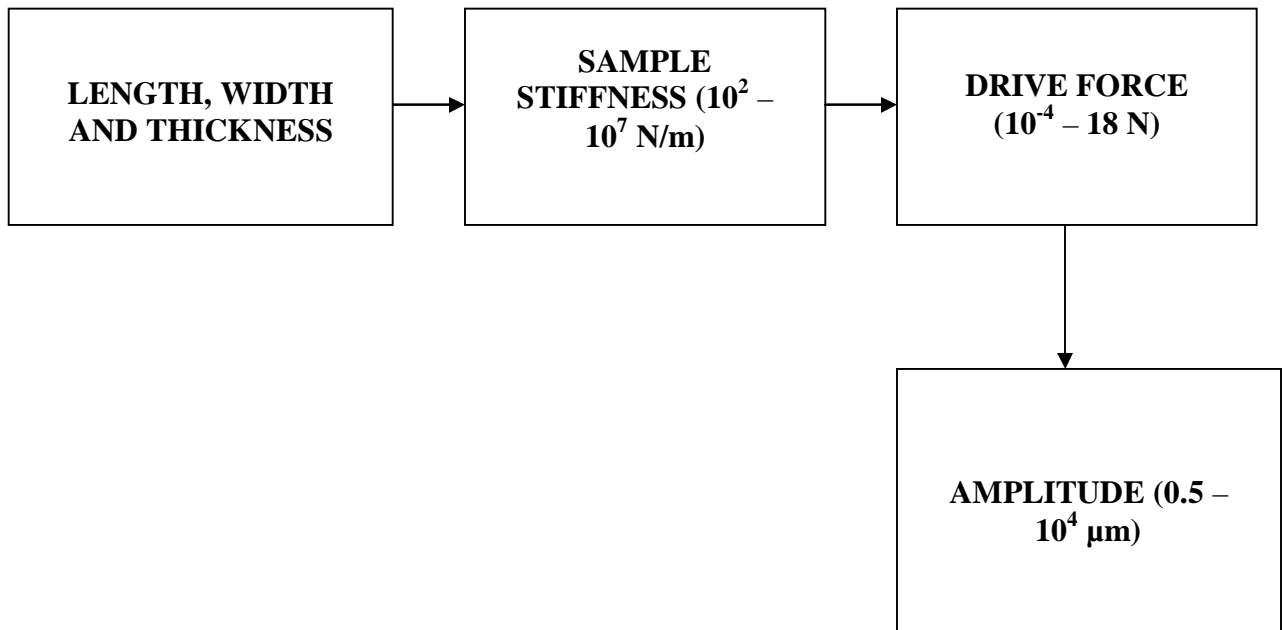

Figure 3.1: Determination of sample size. Source: DMA user manual.

 If the sample stiffness is above or below this range, the size of the sample for the clamp being used would have to be changed. For the tension film clamp, the length of sample would have to

be increased or its width and if possible thickness would have to be reduced to reduce the stiffness. These ranges of values are given in Figure 3.1. Consequently, for DMA measurements, rectangular strips of dimensions 30mm x 5mm x 0.02mm of PE and PLA were used. However, the exact length of the samples was provided by the DMA, which automatically calculated it after the samples had been clamped.

3.1.2 Determination of Sample Size

Each of the polymers studied was obtained from the same source and the samples studied were therefore identical. According to Nordgaard (2005), it is possible to draw fairly accurate conclusions based on very small samples if all samples are identical. In a study to quantify experience in sample size determination for drug analysis of seized drugs, it was found that a sample of five pills was enough to state with a high level of confidence that at least half the tablets in a presumed ecstasy seizure were genuine. In some cases it is scarcely worthwhile to repeat a measurement several times. This is because not all errors are statistical in nature and measurements such as length and mass of an object cannot be improved by repeating them many times (Felix, 1992). In such a situation, one can estimate the error by taking into account the least count or smallest division of the measuring device (Owlnet, 2010). In this study, having minimized systematic errors by calibrating the DMA, other errors were estimated by taking into account the least count. With these considerations in mind, three specimens of three samples of each polymer were measured with a frequency of three. The average values were used to determine the mean value.

3.2 Experimental Procedure
3.2.1 Determination of Density

The density of three specimens of three samples of each polymer was determined using $\rho\grave{} = m/v$, where, ρ is the density, m is the mass of a sample of volume v. The mass of the rectangular strips was determined using an electronic balance with a precision of $10^{-3} g$. The volume of the strips was determined from the dimensions of the strips which were measured using an Electronic Vanier Calipers with a precision of $10^{-4} cm$.

3.2.2 Determination of the Stiffness of the Samples

At the chosen amplitude, the stiffness of three specimens of each sample was determined from the modulus measurements taken at $50\,^{\circ}C$ .The stiffness of the samples was calculated from the modulus and GF values automatically computed by the DMA apparatus as per equation 2.17.

3.2.3 Determination of Modulus of Dry Samples

The real (storage) modulus E', imaginary (loss) modulus E'' components of the complex modulus $E^*=E' + i\ E''$ and the loss tangent (tan δ), for a specimen of each sample were recorded;

a) Against time for a fixed frequency of 1 Hz and over an amplitude range of between 10 – 20 μm.

b) At a temperature of $50\,^{\circ}C$.

3.2.4 Determination of Modulus of Wet Samples

The storage modulus of the wet samples was determined at a temperature of $50\,^{\circ}C$ using a ramp rate of $3\,^{\circ}C$ /min over the range of $40\,^{\circ}C - 80\,^{\circ}C$. The first measurement was taken on the first day before immersion in a wet mixture of green and dry leaves to encourage biodegradation. The green leaves are high in nitrogen needed to activate the heat process in compost. They also introduce the moisture needed in the process of biodegradation. The brown leaves are high in carbon and serve as the fiber for the compost. The next eighteen measurements were taken after every 6 days within 36 days.

3.2.5 Determination of the Glass Transition Temperature

The glass transition temperature of PLA was recorded. A step and hold temperature profile was programmed to obtain the absolute temperature of the transition. The recommended combination for a single-frequency temperature ramp of a frequency of 1 Hz and ramp rate of $3\,^{\circ}C$ per min was used.

CHAPTER FOUR

DATA ANALYSIS

4.1 Determination and comparison of Density and Stiffness

4.1.1 Determination of Density

a) Mass was determined using an electronic balance with a precision of $10^{-3}g$. The volume was determined from the dimensions of the rectangular film of length, width and breadth. The densities of three samples of three specimens of each of the polymers were determined. The mean value of the densities was then determined and compared. The mean was computed using

$$\bar{X} = \frac{\sum X}{n} \qquad (3.2)$$

Table 4.1: Mean density of PLA

	MASS $(g) \pm 10^{-3}g$	VOLUME $(cm^3) \pm$ $3.060 \times 10^{-2} cm^3$	DENSITY $(g/cm^3) \pm$ $6.200 \times 10^{-2} g/cm^3$
PLA 1	0.765	0.612	1.250
PLA 2	0.764	0.612	1.248
PLA 3	0.765	0.612	1.250
			$\bar{X} = \dfrac{\sum X}{n} = 1.249 \, g/cm^3$

Where $\bar{X}$ is the sample's mean density, X is the density of each specimen of a sample and n the number of samples. In PE the crystalline content determines the density of the polymer. The density of the PLA film is found to be higher than that of the PE film. This suggests higher crystallinity in PLA and therefore higher values of stiffness and elastic modulus were expected of PLA as compared with PE.

Table 4.2: Mean density of PE

	MASS $(g)\ \pm 10^{-3}\,g$	VOLUME $(cm^3)\pm$ $3.060\times10^{-2}\,cm^3$	DENSITY $(g/cm^3)\ \pm$ $4.6\times10^{-2}\,g/cm^3$
PE 1	0.564	0.612	0.921
PE 2	0.563	0.612	0.920
PE 3	0.563	0.612	0.920
			$\bar{X}=\dfrac{\sum X}{n}=$ $0.920\,g/cm^3$

4.1.2 Determination and Comparison of Stiffness

The variation of the stiffness of the samples with temperature was analyzed from the plots obtained from the DMA with the first data points taken at time $t=\dfrac{7}{Frequency}$. Since a fixed frequency of 1 Hz was used, the first data point was taken after 7 seconds. Subsequent ones were obtained at time $t=\dfrac{3}{Frequency}$. This translates to data points taken after every 3 seconds for the fixed frequency of 1 Hz. The raw signals of force and amplitude of deformation were used to determine the stiffness of the samples. The DMA produced data for modulus against temperature. Equation 2.17 was used to determine the stiffness at the different temperatures. Table 4.3 shows the corresponding stiffness values between 50 and $80\,^{\circ}C$ for PLA. Graph 4.1 was obtained for the variation of the stiffness of PLA with temperature.

Table 4.3: Variation of stiffness of PLA with temperature

| Temperature $^{\circ}C$	Storage modulus (Pa)	GF= L/A (m^{-1})	Stiffness (Nm^{-1})
50	2202000	276467	7.96
60	1882000	276467	6.81
70	862600	276467	3.12
80	163400	276467	0.59
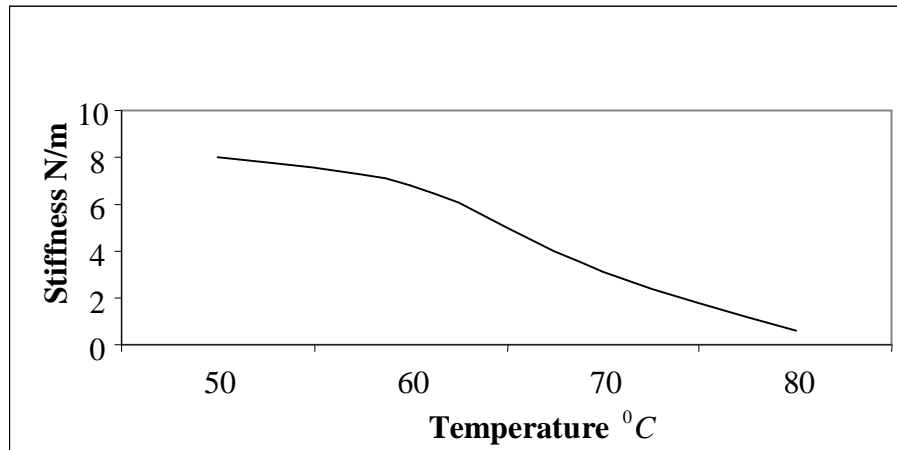
Graph 4.1: Stiffness against temperature of PLA

As the temperature increased the stiffness decreased. Between 50 and $60 °C$, the decrease was gradual. However, there was a sharp decrease in its stiffness between the temperature range 60 to $70 °C$. Between 70 and $80 °C$, the decrease was gradual once again. A sharp decrease in stiffness is indicative of a transition in which molecular rearrangements take place within the polymer. This would cause a significant change in the mechanical properties of a polymer and hence would alter its performance. A transition therefore takes place in PLA from the glass state to the rubbery state.

For PE Table 4.4 was obtained. Graph 4.2 shows the variation of the stiffness of PE with temperature.

Table 4.4: Variation of stiffness of PE with temperature

| Temperature. ($°C$)	Storage Modulus(Pa)	GF = L/A (m^{-1})	Stiffness (Nm^{-1})
50	232500	241690	1.0
60	188325	241690	0.8
70	151125	241690	0.6
80	109275	241690	0.5
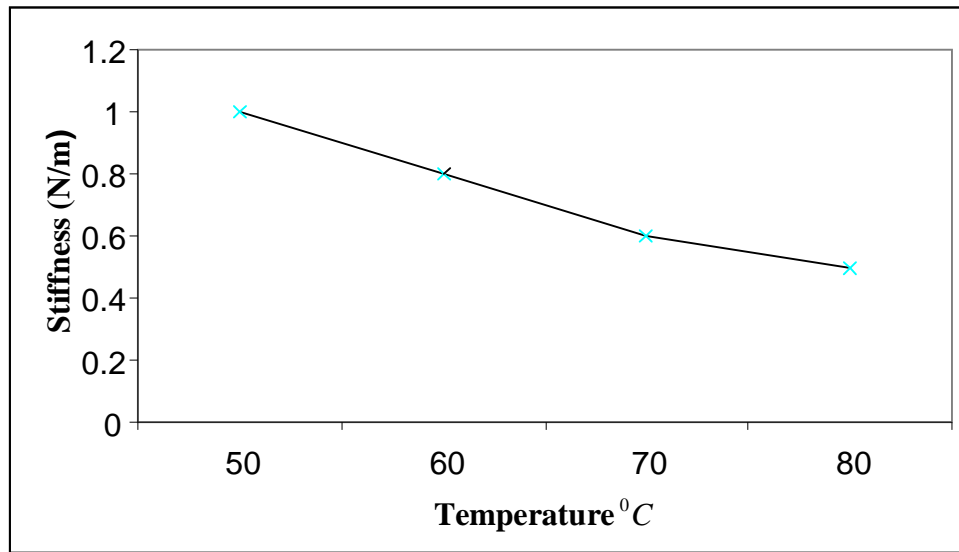
Graph 4.2: Stiffness against temperature of PE

There is a gradual decrease in the stiffness of PE within the temperature range 50 to 80 $^{\circ}C$ hence there are no significant property changes within this temperature range. Unlike PLA, there was no sharp decrease in stiffness within this temperature range. PE is already in its rubbery state and its stiffness decreases gradually indicating the absence of a transition.

4.2 Variation of the Storage Modulus of Dry Samples with Time

Storage modulus for PLA was measured against time for a fixed frequency of 1 Hz. and at amplitudes of 10, 15 and 20 μm. Graph 4.3 shows a decrease in storage modulus with time at all the amplitudes. At time t = 2 minutes the storage modulus is 2247.000, 2327.100 and 2399.400 MPa at amplitudes of 10, 15 and 20 μm respectively. These values are quite close as indicated in Graph 4.4 where the error bars overlap indicating the independence of the storage modulus on the amplitude. At time t = 8 min, at the amplitudes 10, 15 and 20 m, the storage modulus was 2135.700, 2191.400 and 2266.600 MPa respectively.
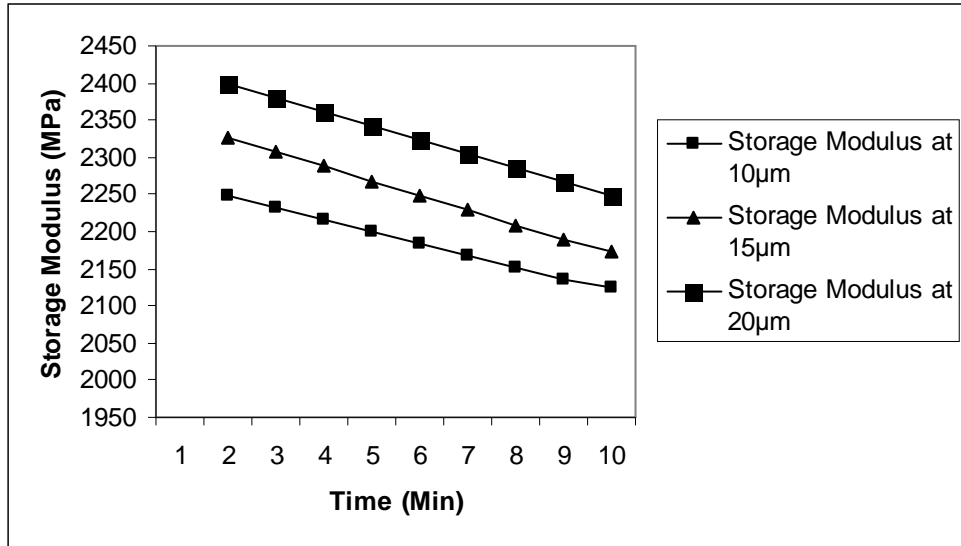
Graph 4.3: Storage modulus of PLA against time
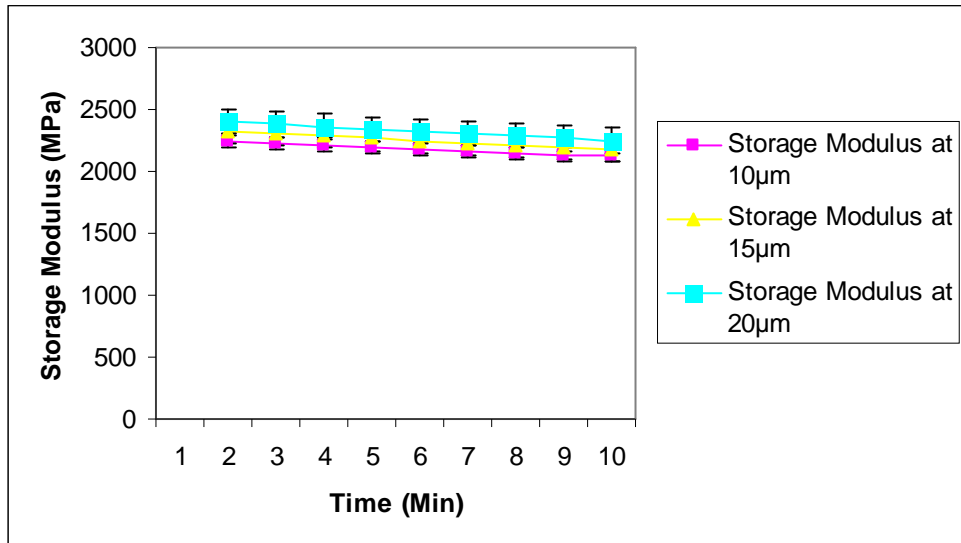
Graph 4.4 Error bars on Storage Modulus of PLA against time

This represents a 5%, 6% and 6% decrease in storage modulus within 6 minutes respectively. Graph 4.5 shows the Storage Modulus of PE remaining fairly constant with time at all the amplitudes. At time t = 2 minutes the storage modulus is 236.300, 264.090 and 296.100 MPa at amplitudes of 10, 15 and 20 µm respectively. These values are quite close as indicated on Graph 4.6, whereby the error bars overlap.
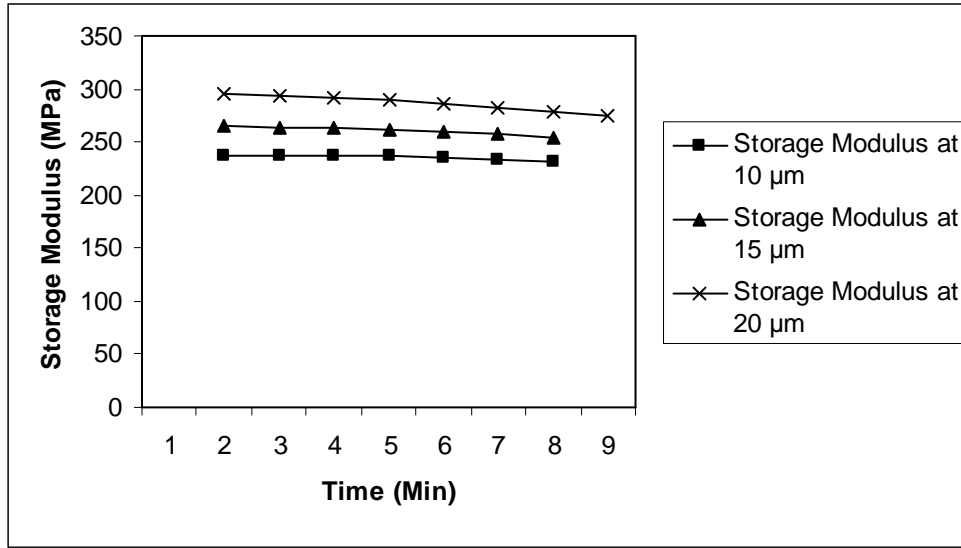
Graph 4.5: Storage modulus of PE against time
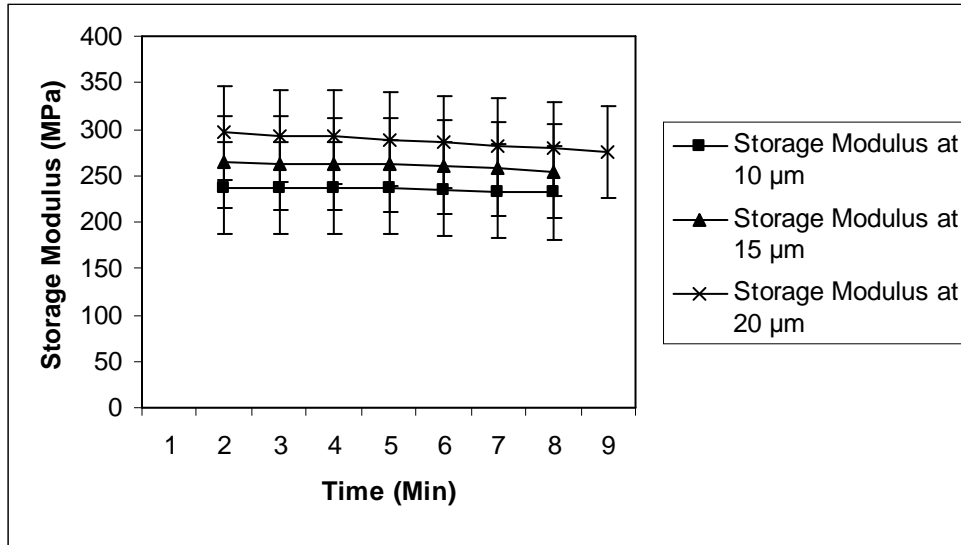
Graph 4.6: Error Bars on Storage Modulus of PE against Time

At time t = 8 min, at the amplitudes 10, 15 and 20 µm, the storage modulus was 230.840, 254.670 and 278.980 MPa respectively. This represents a 2%, 4% and 6% decrease respectively, in storage modulus within 6 minutes. This is a very slight decrease in the value of the storage modulus within this time. For amplitudes 10 and 15 µm, the storage modulus of PLA decreased more as compared to PE. A decrease of storage modulus indicates increased molecular

rearrangements leading to a transition. This causes changes in the mechanical properties of a polymer and would determine the potential uses of a polymer. The value of Storage modulus for PLA is higher than that of PE after similar time intervals. Due to the decrease in the storage modulus of PLA, a transition is expected from the glass to the rubbery state. The gradual decrease of the storage modulus of PE indicates the absence of a transition. The potential uses into which PLA could be put into should therefore take into account the softening of PLA unlike PE which retains its stiffness.

4.3 Variation of the Loss Modulus of Dry Samples with Time

Loss modulus was measured against time for a fixed frequency of 1 Hz. and over an amplitude range of between 10 – 20 μm. Graph 4.7 shows the variation of the loss Modulus of PLA with time.
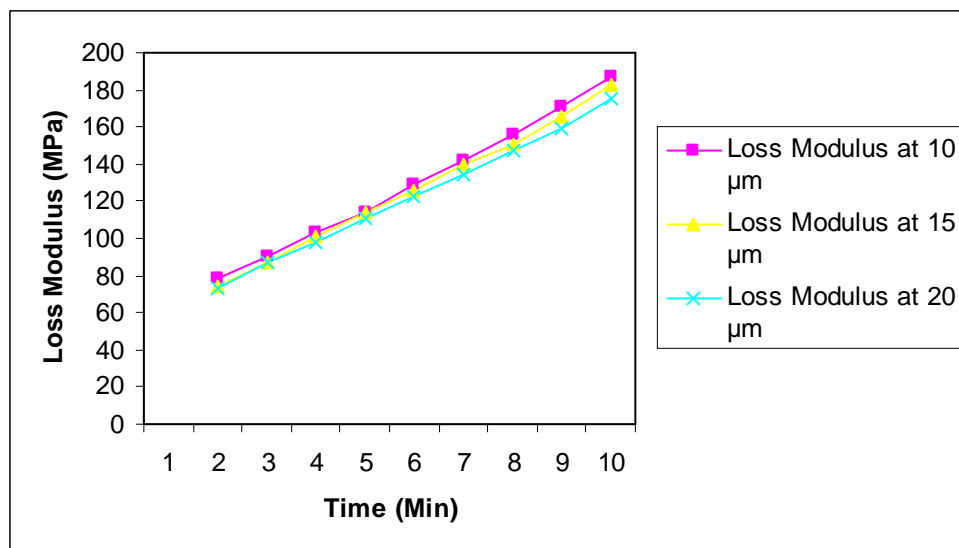
Graph 4.7: Loss Modulus of PLA against time

At time t = 2 minutes the loss modulus is 77.900, 74.200 and 72.300 MPa at amplitudes of 10, 15 and 20 μm respectively. These values are quite close despite doubling the amplitude. This confirms operation within the linear viscoelastic region.

After 8 minutes, the loss modulus increased to 156.000, 150.500 and 146.700 MPa at the amplitudes 10, 15 and 20 μm respectively. This represented approximately 100%, increase in

each case. This indicates a high increase in the dissipation of energy in PLA with time at the different oscillations
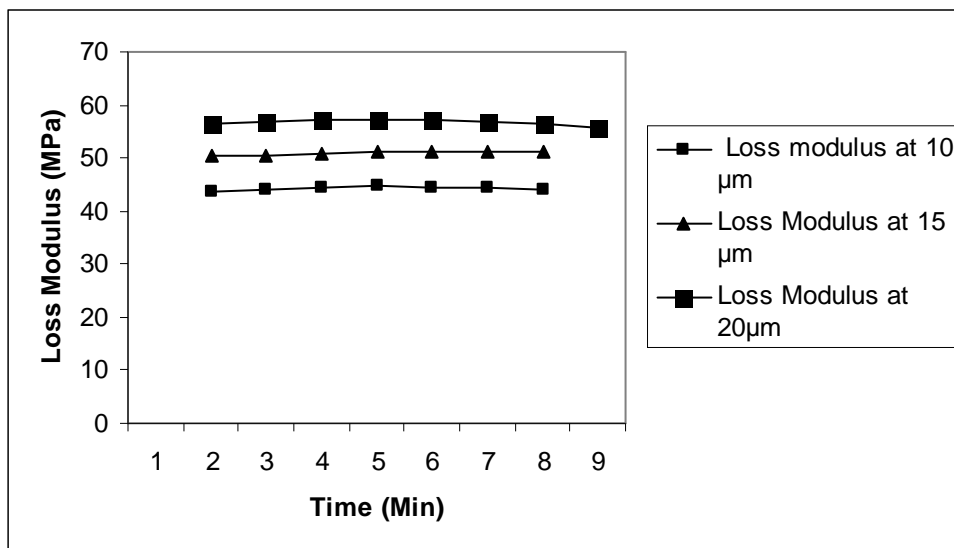
For PE, Graph 4.8 was obtained

Graph 4.8: Loss Modulus of PE against time

At time t = 2 minutes the loss modulus is 43.600 MPa, 50.200 and 56.700 MPa at amplitudes of 10, 15 and 20 µm respectively. These values are quite close despite doubling the amplitude, suggesting independence of loss modulus on amplitude. This confirms operation within the linear viscoelastic region.

After 8 minutes, the loss modulus values were 44.300 MPa, 50.800 MPa and 56.700 MPa at the amplitudes 10, 15 and 20 µm respectively. This represents a 2%, 1% and 0% increase respectively. This is a very slight change for 10 and 15 µm amplitude, indicating a very slight increase in the dissipation of energy in PE with time at the different oscillations. The value of the loss modulus of a substance is an indication of the viscous property of a material. It shows the extent to which energy would be dissipated in a material, causing it to flow. PLA has higher values of loss modulus than PE. These values also increase at a much faster rate as compared to PE with time on application of a dynamic force resulting in oscillations of different amplitudes. This shows high molecular motion in PLA suggesting that PLA is close to a transition state.

4.4 Variation of the Loss Tangent of Dry Samples with Time

The loss tangent (tan δ) was measured against time for a fixed frequency of 1 Hz and over an amplitude range of between 10 and 20 µm. Graph 4.9 shows an increase in the loss tangent of PLA with time at the different amplitudes. At time t = 2 minutes tan δ was 0.034, 0.030 and 0.030 at amplitudes of 10, 15 and 20 µm respectively.

Graph 4.9: Loss tangent of PLA against time

After 8 minutes, the loss tangent, tan δ, values were 0.073, 0.072 and 0.066 at the amplitudes 10, 15 and 20 µm respectively. This represents a 113%, 136% and 121% increase respectively. This indicates quite a high increase in the dissipation of energy in PLA with time at the different oscillations.
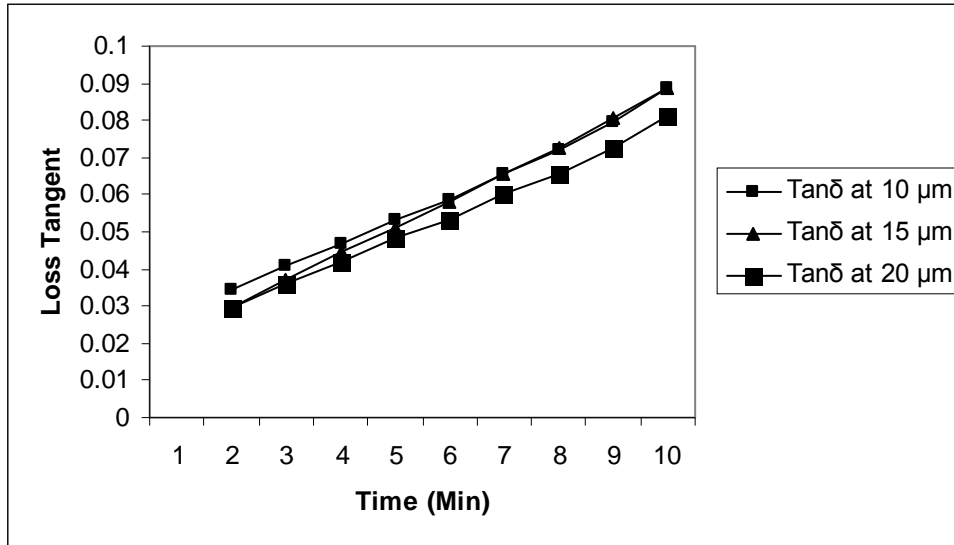
Graph 4.10 shows the variation of the loss tangent of PE with time. At time t = 2 minutes tan δ was 0.184, 0.190 and 0.191 at amplitudes of 10, 15 and 20 µm respectively. After 8 minutes, the tan δ values were 0.192, 0.201 and 0.202 at the amplitudes 10, 15 and 20 µm respectively. This represents a 4.3 %, 5.8% and 5.7% increase respectively.
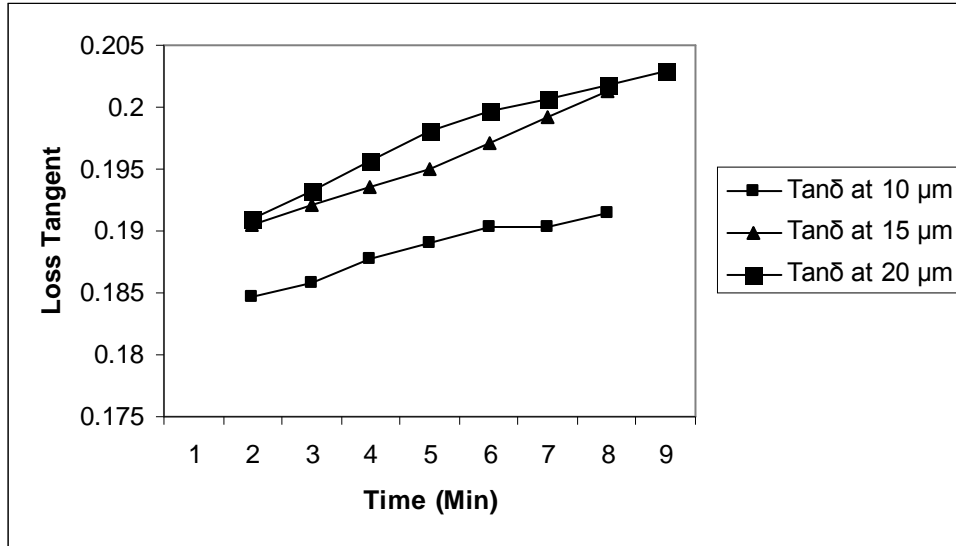
Graph 4.10: Loss tangent of PE against time

This indicates almost constant dissipation of energy in PE with time at the different oscillations. Since tan δ measures the damping in the system, it gives an indication of energy lost in a material per cycle. PLA has lower tan δ values as compared with PE. However these values increase by a great margin for PLA unlike for PE, which remain fairly constant. This indicates a change in the structure of PLA under the action of the dynamic force, resulting in higher damping.

4.5 Variation of the Storage Modulus of Dry Samples with Temperature

Storage, loss modulus and tan δ for PE and PLA were compared at $50\,^{\circ}C$. This temperature was chosen since packaging material is not commonly used at temperatures higher than $50\,^{\circ}C$. Graph 4.11 shows the variation of the Storage Modulus of both PLA and PE with temperature. The storage modulus of PLA at $50\,^{\circ}C$ and amplitude of 10 µm was found to be 2220 MPa. The storage modulus of PE was found to be 232.5 MPa at the same temperature and amplitude.

The storage modulus gives information about the elasticity of a material. According to equation 2.12 it is almost equal to the elastic modulus especially if the value of the loss modulus is low. The elastic modulus is also directly proportional to the stiffness of a material as per equation 2.17. As compared with PE, PLA is stiffer and has a much higher storage modulus at $50\,^{\circ}C$. This indicates that PLA is stronger and tougher than PE at this temperature.

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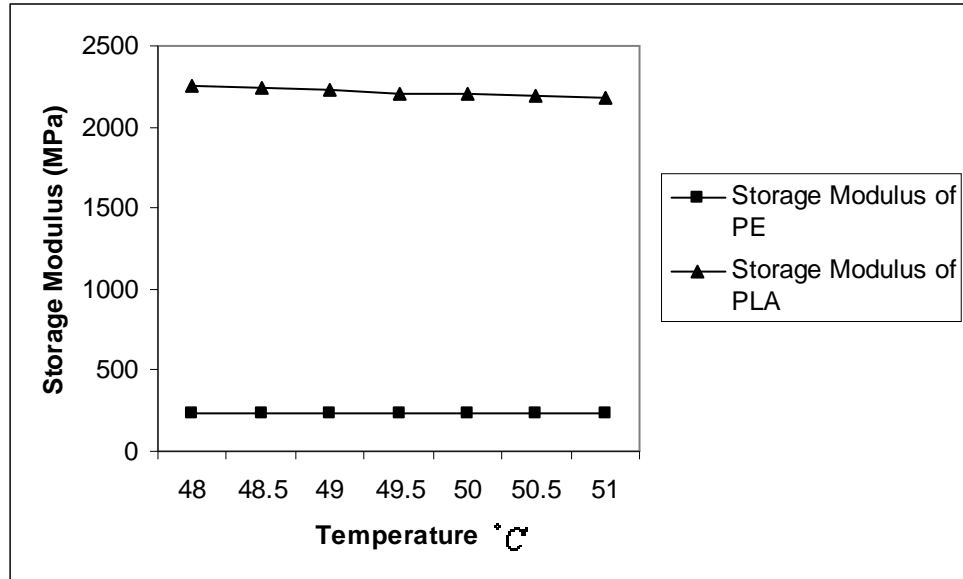
Graph 4.11: Storage Modulus of PE and PLA against Temperature

4.6 Variation of the Loss Modulus of Dry Samples with Temperature

Graph 4.12 shows the variation of loss modulus of PE and PLA with temperature.
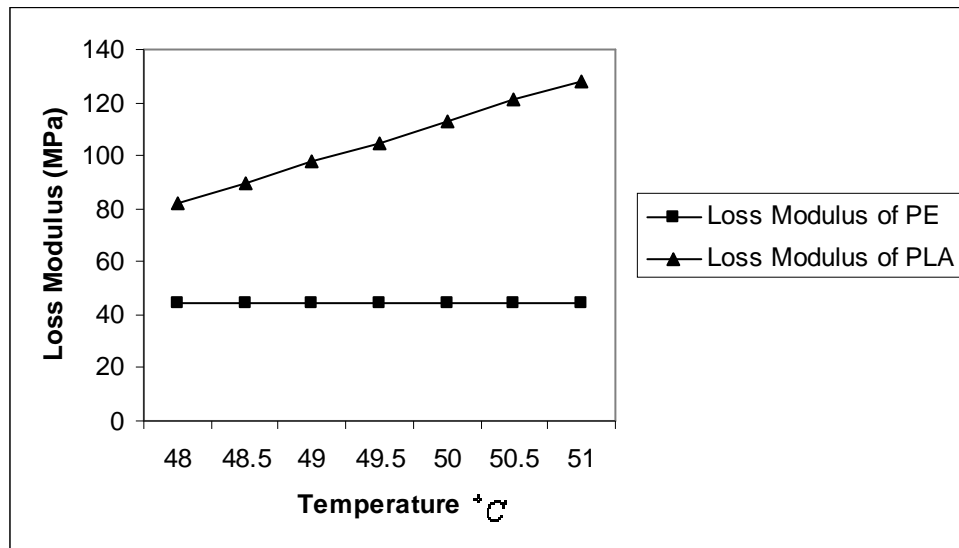
Graph 4.12: Loss Modulus of dry samples of PE and PLA against Temperature

The loss modulus for PLA was found to be 112.9 MPa at $50\,^{\circ}C$ while that of PE was found to be 44.33 MPa at the same temperature and amplitude of 10 µm. The loss modulus of PLA is found to be much higher than that of PE at $50\,^{\circ}C$. The loss modulus of PLA is found to rise steadily

with temperature unlike that of PE which reduces slightly within this particular temperature range.

4.7 Variation of the Loss Tangent of Dry Samples with Temperature

Graph 4.13 shows the variation of loss tangent with temperature for both PE and PLA. At $50\,^{\circ}C$ the tan δ value of PLA is found to be 0.055 and that of PE is found to be 0.191.

Graph 4.13: Loss Tangent of PLA and PE against temperature
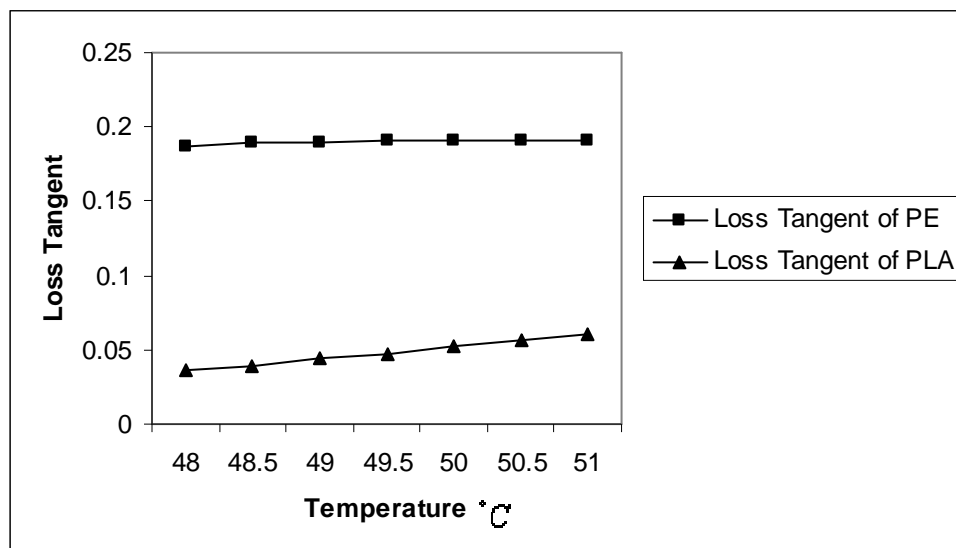
PE has a higher tan δ value than PLA at $50\,^{\circ}C$. On the application of a dynamic stress, more energy is lost per cycle in PE than in PLA since tan δ is the ratio of the loss modulus to the storage modulus.

4.8 Modulus of Wet Samples

After the determination of the modulus of the dry samples, the samples were immersed into a wet mixture of dry and green leaves to encourage biodegradation. Biodegradation is performed by micro-organisms, mostly bacteria. These bacteria require certain conditions in order to work effectively. One of the requirements is carbon, whose microbial oxidation produces the heat required. A good source of carbon is brown and dry leaves. Nitrogen is also required in order to grow and reproduce more organisms to oxidize the carbon. Green leaves have a high Nitrogen content. Oxygen and water are required to oxidize the carbon and to maintain activity without

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causing anaerobic conditions. The storage modulus was determined at a temperature of $50\,^{\circ}C$ and amplitude of 10 µm after every 6 days for 36 days to monitor any changes. Graph 4.14 shows the variation of the Storage Modulus of PE and PLA with time and constant temperature of $50\,^{\circ}C$.
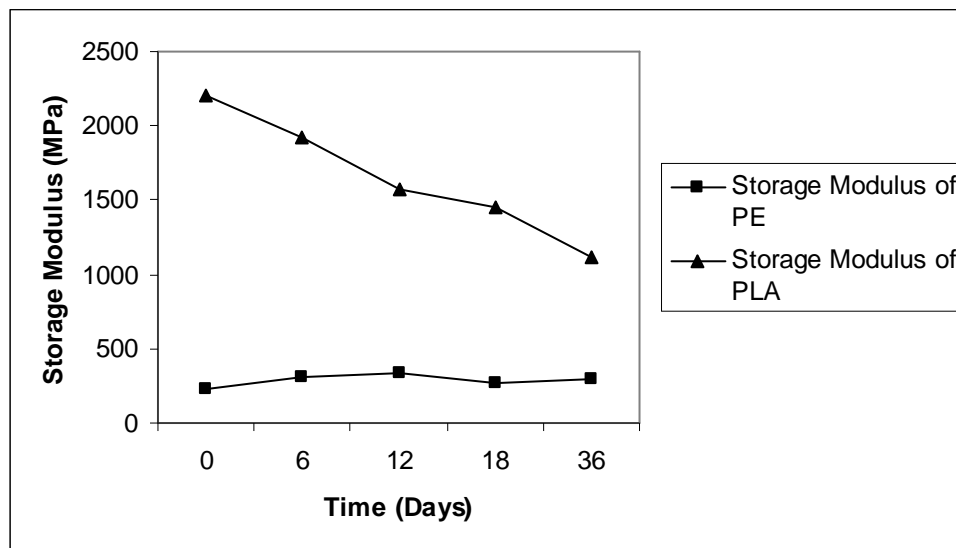
Graph 4.14: Storage Modulus of wet samples at $50\,^{0}C$ and amplitude of 10 µm

The storage modulus for PLA reduces by 49% within 36 days as compared to PE, whose storage modulus actually increases by 29% by the 36th day after an initial decline. The reduction in the storage modulus of PLA indicates deterioration in its mechanical properties. This would lead to its ultimate elimination from the environment within a comparatively reasonable time frame as compared with PE which seems to become even more stable within this time period.

4.9 Glass Transition Temperature (T_g)

The glass transition temperature (T_g) was determined from the plots of storage and loss modulus and loss tangent against temperature. It is located in regions of rapid change in modulus for storage modulus and at the peaks for the loss modulus and loss tangent graphs. It was not possible to obtain a graph that would give the T_g for PE since the apparatus would not cool below room temperature. Graph 4.15 shows the variation of storage modulus of PLA with temperature. The storage modulus of PLA decreased gradually within the temperature range of $47 - 60\,^{\circ}C$ from 2270 MPa – 1882 MPa.
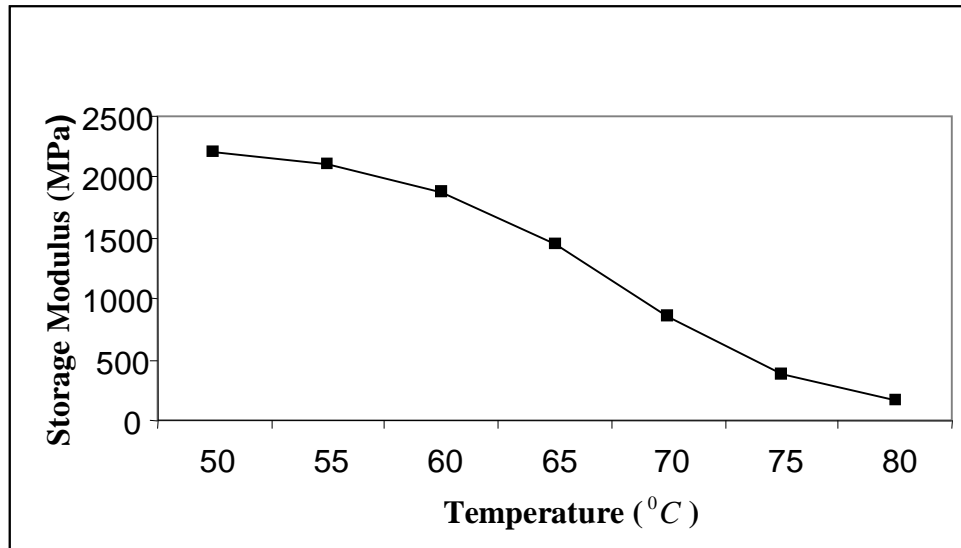
Graph 4.15: Storage modulus of PLA against temperature

Between temperatures of 60 and 76 $^\circ C$ the decrease was rapid from 1882 MPa – 285 MPa. The storage modulus then decreased between the temperatures 76 – 85 $^\circ C$ from 285 – 75 MPa. This shows that a transition takes place within the 60 - 76 $^\circ C$ temperature range. For the variation of Loss modulus with temperature, Graph 4.16 was obtained.
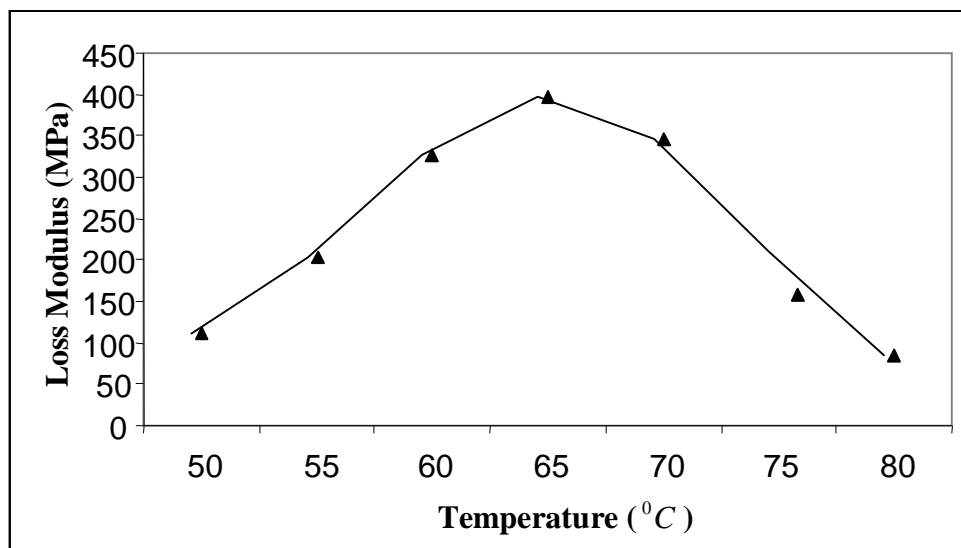
Graph 4.16: Loss modulus of PLA against temperature
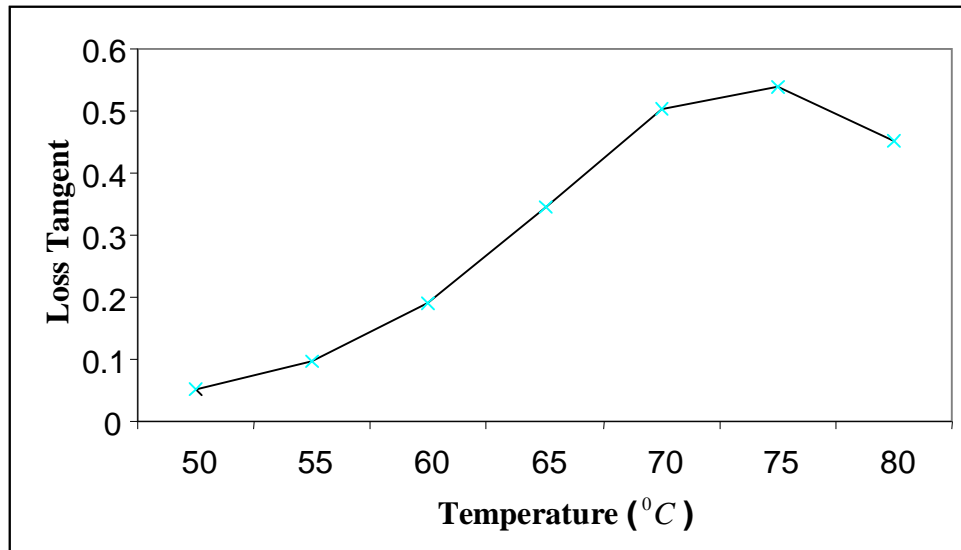
Graph 4.17: Loss Tangent of PLA against temperature

From the peak of the loss modulus graph the T_g of PLA was found to be $65\,^{\circ}C$. T_g from the variation of loss tangent with temperature occurred at $74.3\,^{\circ}C$.

Graph 4.18 shows the variation of storage and loss modulus as well as loss tangent with temperature for PLA. The loss tangent graph is slightly shifted to the right and hence gives a T_g which is slightly higher than the loss modulus graph. Also, the region within which the storage modulus decreases rapidly coincides with the region where the peaks of the loss modulus and loss tangent arise. PLA is in the glassy state below $65\,^{\circ}C$ according to the loss modulus graph and below $74.3\,^{\circ}C$ according to the loss tangent graph. It is therefore quite stiff below these temperatures. After the glass transition, its storage modulus comes down to 285 MPa at $76\,^{\circ}C$. The theoretical value for T_g of PE is $-78\,^{\circ}C$ (Lam and Geil, 2004). This explains why it is more flexible than PLA at $50\,^{\circ}C$ since it has already changed from the glass to the rubbery state. It also explains why its storage modulus is 232 MPa as this is typical of all polymers in the rubbery state.
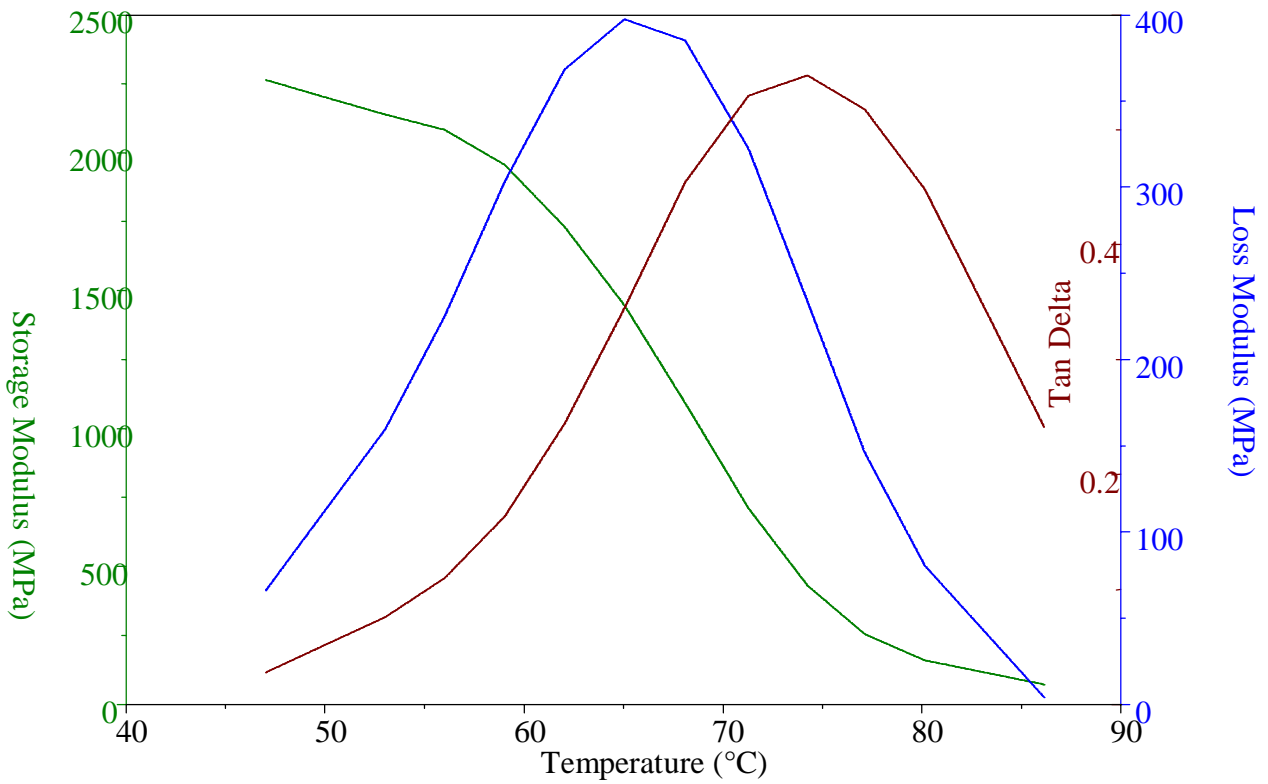
Graph 4.18: Storage and Loss modulus and loss tangent against temperature for PLA

4.10 Summary of Results

Table 4.5 shows the results arrived at from this study.

Table 4.5: Summary of results

Mechanical Property	PLA	PE
Density	$1249\,kg/m^3$	$920\,kg/m^3$
Stiffness (50^0C)	$7.960\,N/m$	$1.000\,N/m$
Storage Modulus(50^0C)	$2220.000\,MPa$	$232.500\,MPa$
Tan δ (50^0C)	0.055	0.191
Glass Transition Temperature	$65^\circ C$	$-78^\circ C$

CHAPTER FIVE

CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

The density of PLA was found to be 1249 kg/m^3 while that of PE was found to be 920 kg/m^3. PLA is therefore more crystalline than PE. Consequently the stiffness of PLA was found to be higher than that of PE at 50$^{\circ}C$. It was 7.960 N/m as compared to that of PE that was found to be 1.000 N/m. PLA is therefore stiffer than and more elastic than PE at a temperature of 50$^{\circ}C$. The stiffness of PLA however decreases with time and temperature at a faster rate than PE and would therefore exhibit property changes such as flexibility, strength and toughness during use.

The storage modulus value of PLA decreased with time and temperature while that of PE remained fairly constant. At time 2 min and amplitude of 10 µm the values were 2247 and 236.300 MPa for PLA and PE respectively. At time 8 min the values had decreased to 2135.700 and 230.840 MPa for PLA and PE respectively. The storage modulus value for PLA was found to be 2220 MPa while that of PE was 232.500 MPa at 50$^{\circ}C$. The values obtained are quite close for the different amplitudes for both PE and PLA indicating operation within the linear viscoelastic region.

The loss modulus of PLA increased at a much faster rate as compared to PE with an increase in time and temperature on the application of a dynamic force. The values were 77.900 and 43.600 MPa for PLA and PE respectively at time 2 min and amplitude of 10 µm. At time 8 min the values were 156.700 and 44.300 MPa for PLA and PE respectively at the same amplitude. At 50^{0}C, the values were 112.9 and 44.33 MPa respectively. This indicates that PLA becomes less stiff with time while PE retains its stiffness.

The damping properties of PE at 50$^{\circ}C$ are higher as compared to PLA .The tan δ values at 50$^{\circ}C$ and an amplitude of 10 µm was found to be 0.055 for PLA and 0.191 for PE. Hence, there is a higher dissipation of energy in PE as compared to PLA on the application of a dynamic force at this temperature. The damping characteristics of PE remain fairly constant with time while those of PLA increase. At time 2 min it was 0.034 and 0.191 for PLA and PE respectively. At time 8 min, it was 0.073 and 0.201 for PLA and PE respectively.

The values for the storage moduli of the wet samples of PLA and PE were 2220.000 and 232.500 MPa respectively before immersion in a composting environment. After 36 days, the values were 1114.1 and 289 MPa respectively. PLA undergoes rapid degradation as compared to PE when immersed in a wet mixture of dry and green leaves which are composting conditions. This is indicated by the decrease in the storage modulus values of the wet samples of PLA as compared to those of PE whose storage modulus values remain largely unchanged, and infact registering a slight increase.

From the loss modulus curve, the glass transition temperature of PLA occurred at $65\,^{\circ}C$ which is above room temperature ($25\,^{\circ}C$). That of PE occurs below room temperature at $-78\,^{\circ}C$. PLA is therefore less flexible than PE at $50\,^{\circ}C$. PLA is in its glassy state while PE is in its rubbery state at this temperature.

Apart from exhibiting superior mechanical properties to those of PE, PLA would biodegrade much faster after disposal in a composting environment leaving carbon (IV) oxide and water. It would therefore be a suitable packaging material for disposable products in place of PE. This would greatly reduce the pollution problem caused by PE. The following conclusions were drawn as per the objectives;

i. PLA is denser and stiffer than PE at a temperature of $50\,^{\circ}C$.

ii. The storage modulus value of PLA was found to be higher than that of PE at $50\,^{\circ}C$. The damping properties of PE at $50\,^{\circ}C$ are higher as compared to PLA at $50\,^{\circ}C$ as per the loss tangent values obtained. These properties vary with time and temperature for PLA while those of PE remain fairly constant.

iii. PLA undergoes rapid degradation as compared to PE when immersed in a wet mixture of dry and green leaves. This is indicated by the decrease in the storage modulus values of the wet samples of PLA as compared to those of PE whose storage modulus values remain largely unchanged and in fact registering a slight increase.

iv. The glass transition temperature of PLA occurs at $65\,^{\circ}C$, above room temperature ($25\,^{\circ}C$) while that of PE occurs at $-78\,^{\circ}C$, below room temperature. PLA is therefore less flexible than PE at $50\,^{\circ}C$ since it is in the glassy state while PE is in the rubbery state.

The findings of this study show that PLA can be used in place of PE for a wide range of purposes due to its superior mechanical properties. Above T_g PLA acquires a modulus similar to that of PE and is therefore a very suitable substitute for PE. The modulus of PLA reduced significantly over time after immersion in an environment that encouraged biodegradation. That of PE increased slightly and remained fairly constant. PLA would compost after use and address the pollution problem caused by PE. PLA films were found to be of superior mechanical strength as compared to PE and can replace it in single use packaging. As expected, their initial mechanical properties reduced as they biodegraded.

5.2 Recommendations for further Research

1. A study in which a wider temperature range is considered when determining the moduli of the samples would yield more information especially at much lower and higher temperatures.

2. The variation of the moduli with frequency would also give information on the behavior of the polymers at different frequencies. Other mechanical properties such as the strength and toughness of these polymers could be compared.

3. The mechanical properties of other biodegradable polymers such as PHBV could be studied and compared with those of PE and PLA. The synthesis of these biodegradable polymers could also be attempted and their mechanical properties determined.

CHAPTER SIX
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