MECHANICAL, DIFFUSION AND DEGRADATION BEHAVIOUR OF POLYPROPYLENE AND CELLULOSE BLENDS

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A thesis submitted in partial fulfillment of the requirement for the award of the degree of Master of Science, in the School of Pure and Applied Sciences of Kenyatta University

OCTOBER 2013
DECLARATION

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

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DEDICATION

I dedicate this work to my parents, my dear wife Gladys and my son Parseen.
ACKNOWLEDGMENTS

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<tbody>
<tr>
<td>CL</td>
<td>Cellulose</td>
</tr>
<tr>
<td>DMA</td>
<td>Dynamic mechanical analysis</td>
</tr>
<tr>
<td>DMTA</td>
<td>Dynamic mechanical thermal analyzer</td>
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<tr>
<td>DTG</td>
<td>Differential thermal graph</td>
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<tr>
<td>DSC</td>
<td>Differential scanning calorimetry</td>
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<tr>
<td>HDPE</td>
<td>High density polyethylene</td>
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<tr>
<td>LDPE</td>
<td>Low density polyethylene</td>
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<tr>
<td>MA-EPDM</td>
<td>Maleic anhydride grafted ethylene-propylene-diene copolymer</td>
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<tr>
<td>MA-PP</td>
<td>Maleic anhydride grafted polypropylene</td>
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<tr>
<td>NFPCs</td>
<td>Natural fiber/polymer composites</td>
</tr>
<tr>
<td>OH</td>
<td>Hydroxyl</td>
</tr>
<tr>
<td>PE</td>
<td>Polyethylene</td>
</tr>
<tr>
<td>PMMA</td>
<td>Polymethylmethacrylate</td>
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<tr>
<td>PP</td>
<td>Polypropylene</td>
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<tr>
<td>PP/CL</td>
<td>Polypropylene/cellulose</td>
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<tr>
<td>PS</td>
<td>Polystyrene</td>
</tr>
<tr>
<td>PVC</td>
<td>Poly (vinyl chloride)</td>
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<tr>
<td>SEM</td>
<td>Scanning electron microscopy</td>
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<tr>
<td>SLS</td>
<td>Standard linear solid</td>
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<td>TA</td>
<td>Thermal analysis</td>
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<tr>
<td>Acronym</td>
<td>Description</td>
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<td>---------</td>
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<tr>
<td>TGA</td>
<td>Thermogravimetric analysis</td>
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<tr>
<td>UV</td>
<td>Ultra Violet</td>
</tr>
<tr>
<td>VFT</td>
<td>Vogel Fulcher Tamman</td>
</tr>
<tr>
<td>WF/PP</td>
<td>Wood-floor/polypropylene</td>
</tr>
<tr>
<td>WPCs</td>
<td>Wood plastic composites</td>
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<tr>
<td>WLF</td>
<td>William Landel Ferry</td>
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# LIST OF SYMBOLS

<table>
<thead>
<tr>
<th>Symbol</th>
<th>What the Symbol Represents</th>
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<tbody>
<tr>
<td>$\Delta E$</td>
<td>Activation energy</td>
</tr>
<tr>
<td>$\eta$</td>
<td>Dynamic Viscosity</td>
</tr>
<tr>
<td>$\varepsilon$</td>
<td>Strain</td>
</tr>
<tr>
<td>$\eta^*$</td>
<td>Shear viscosity</td>
</tr>
<tr>
<td>$\tau_0$</td>
<td>Characteristic time</td>
</tr>
<tr>
<td>A</td>
<td>Constant</td>
</tr>
<tr>
<td>B</td>
<td>Constant</td>
</tr>
<tr>
<td>$C_p$</td>
<td>Creep</td>
</tr>
<tr>
<td>CH$_2$</td>
<td>Methyl</td>
</tr>
<tr>
<td>E</td>
<td>Shear modulus</td>
</tr>
<tr>
<td>$E^*$</td>
<td>Complex modulus</td>
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<tr>
<td>$E'$</td>
<td>Storage modulus</td>
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<tr>
<td>$E''$</td>
<td>Loss modulus</td>
</tr>
<tr>
<td>$E_1$</td>
<td>Elastic modulus</td>
</tr>
<tr>
<td>$E_2$</td>
<td>Viscous modulus</td>
</tr>
<tr>
<td>$f$</td>
<td>Frequency</td>
</tr>
<tr>
<td>i</td>
<td>Different processes which contribute to the mechanical response</td>
</tr>
<tr>
<td>J</td>
<td>Creep compliance</td>
</tr>
<tr>
<td>$J^*$</td>
<td>Complex compliance</td>
</tr>
<tr>
<td>k</td>
<td>Boltzmann constant</td>
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R  Universal gas constant
S  Disappearance rate of the species
\(T_g\)  Glass transition temperature
T  Absolute temperature
\(T_0\)  Vogel temperature
\(T_m\)  Melting temperature
V  Total volume
\(V^*\)  Minimum volume
\(V_m\)  Mean volume
\(V_o\)  Occupied volume
X  Conversion factor of the decomposed compound at time \(t\)
\(\delta\)  Phase lag
\(\sigma\)  Stress
\(\sigma_d\)  Dashpot stress
\(\tau\)  Relaxation time
\(\omega\)  Angular frequency
\(\varepsilon_o\)  Amplitude
ABSTRACT

Polypropylene is one of the most important commodity polymers and is used in many areas. Its applications are often limited due to its low impact strength, Young’s modulus properties and non-biodegradability nature. Blending polypropylene with different polymers is an economic and effective way to improve these drawbacks. Polypropylene/wood flour blends have undesirable properties; they have weak structural rigidity, very low thermal stability and high diffusivity. Cellulose is linear, rigid and has a higher thermal stability and diffusivity hence effective in reinforcement of polypropylene and high density polyethylene. In this research a series of experiments have been conducted. Samples blends of polypropylene reinforced with cellulose were prepared by melt mixing followed by injection molding. The study deals with the effect of cellulose on Dynamic mechanical, creep, degradation and diffusion properties of polypropylene and its cellulose blends. Dynamic mechanical analysis was carried out in the frequency and temperature range of 1 to 30 Hz and -30 to 120 °C respectively. The effects of cellulose concentration on relaxation processes were investigated. Two relaxation processes (α and β) were observed. The α process was assigned to main chain motion while β process was a local process due to interlamellae shearing. Relaxation frequency showed overlaps with cellulose intake confirming that cellulose loading has no effect on free volume for relaxation processes, hence overlapping Vogel temperature (T_o). Vogel Fulcher Tamman (VFT) equation was used to analyze the data. Creep measurements were performed at 30, 40, 50 and 60 °C. The time for deformation and recovery of the samples were 12 minutes each. Creep deformation of the samples decreased with cellulose loading. Time temperature superposition was used to predict the long time experiment up to approximately 10^4 seconds. Shift factors obeyed the William Landel Ferry (WLF) model hence; the deformation was dependent on free volume. Thermal degradation analysis was carried out using Lindberg Blue tube furnace within a temperature range of 25 to 550 °C at a heating rate of 5 °C/min. Two decomposition stages corresponding to polypropylene and cellulose decomposition were observed. Thermal stability of the blends decreased with cellulose loading (thermal activation energy decreased from 70.0 to 40.6 kJ/mol). Broido equation was used to analyze the data. Diffusion measurements were done at room temperature and mass differences were monitored after 1, 7, 30, 60, 90 and 120 days. The test specimens were removed from the test liquid one at a time. Diffusion coefficients increased from 4.89 x 10^{-10} to 4.21 x 10^{-8} cm^2 s^{-1} with cellulose loading. Fick’s second law was used for data analysis. Biodegradation measurements were also done by burying the dried samples in soil at a depth of 20 cm behind the physics laboratory in Kenyatta University main campus. Samples were removed after 1, 7, 30, 60, 90, 120 and 150 days. The rate of biodegradation increased with cellulose intake from 20,000 to 5 years due to increase in hydrophilicity. Regression line method was used to analyze the data. Use of cellulose as a blend on polypropylene should be adopted to improves its mechanical properties and minimize environmental pollution.
CHAPTER ONE

INTRODUCTION

1.1 Background to the study

Non-biodegradable polymers have attracted much public and industrial interest because of their disposal problems. Besides solution such as incineration, recycling or re-use, non-biodegradable polymers can be entirely converted by microbial activity in a biologically active environment to biomass and biological by products. One ecologically and economically approach to overcome these limitation is to incorporate natural fibers into non-biodegradable polymers to obtain environmentally friendly composite materials called bio-composites [Alfonso and Roxana, 2003]. Ecological and economical concerns have resulted in a renewed interest towards the natural and renewable bio-resources. This is because of non-biodegradability of most commercially available plastics, which has caused many environmental problems associated with their disposal [Kim and Rhee, 2003].

Depletion of petroleum resources and escalating prices of the petroleum based polymers are added causes that have stimulated the efforts to find a better alternative. A feasible option can be provided by the combined usage of petroleum and available bio-resources. Lignocellulosic fibers are the most widely used bio-resources, and the utilization of these fibers in the production of polymeric biocomposites are attractive particularly because of the worldwide availability of plant based fibers like jax, jute, sisal, kenaf and other abundantly accessible agro-waste. These biocomposites, made by cellulose-based fibers, are biodegradable, thus causing minimal environmental pollution, and nontoxic to living
being [Khalid et al., 2009]. Polypropylene as one of the most popular industrial thermoplastics has been widely used in various industrial fields such as automotive parts, furniture and packages. However, its application as high-performance engineering plastic is limited by its poor mechanical properties, in particular at low temperatures. In the past three decades, the impact strength of polypropylene has been improved by blending it with multiple blends in order to improve its mechanical properties [Rongbo et al., 2009].

Polypropylene is one of the most important commodity polymers and is used in many areas, such as home appliances, automotive parts, construction and other important industrial applications. Polypropylene applications are often limited due to its low impact strength and Young’s modulus properties, particularly at low temperatures and high temperature loading conditions. Blending polypropylene with different polymers is an economic and effective way to improve these drawbacks [Huerta et al., 2005]. The need for non-toxic and environmentally friendly materials favors the use of natural fibers, over inorganic and synthetic fillers, as fillers in polymeric materials. Dikobe and Luyt [2009] used lignocellulosic fillers as reinforcing material in different polymer matrices. Since the pioneering work of Toyota group on the incorporation of clays in thermoplastic matrixes, the addition of different kinds of anisometric nanofillers (either plates or needles of nanometric sizes) to various thermoplastic polymers has become widespread, among these matrixes, polypropylene has been particularly studied because of its wide use. The goal is to increase its biodegradability at the same time improving its mechanical properties [Ljungberg et al., 2006]. Despite the undoubted general excellence of many polymers, there remains the need to modify and regulate the properties of any one polymer to overcome specific deficiencies and make it more suitable for a particular
application. The main reason why so much work has gone into development of modified thermoplastics rather than the creation of new polymers is largely the cost. It is very much cheaper to take existing polymers and develop composite systems based upon these, than it is to develop new polymers [Dyson, 1993].

The utilization of blends from various sources into PP has been an accepted route to achieve enhancement in material properties or cost saving possibilities, or both. These blends can be categorized as inorganic and organic. Over the past two decades, organic blends have become a strong competitor to inorganic blends due to their low densities, very low cost, non-abrasiveness, high filling levels, recyclability, biodegradability and renewable nature. The studies carried out have shown that stiffness, hardness, dimension stability and biodegradability of plastics could be improved by incorporation of these types of blends [Hattotuwa et al., 2002].

During the past two decades, cellulosic materials have been increasingly used as reinforcements of thermoplastic matrix composites. Cellulosic reinforcements offer good mechanical properties, low density, reduced health hazards and several well-known advantages, including increased biodegradability of the final materials and availability of renewable natural resources [Orden et al., 2009]. The intensive use of polymers makes it necessary to create new materials with enhanced properties while at the same time avoiding use of chemical additives in some areas such as pharmaceutical industry and medicine [Raphol et al., 2000]. Cellulose whiskers hold a particular place among the various types of anisometric nanofillers. In natural structures, they already act as reinforcing elements. Cellulose whiskers consist of slender parallel piped rods with
nanometric lateral dimensions, high aspect ratios and important surface areas, and also have a renewable character. Cellulosic whiskers have mainly been employed as fillers in several kinds of polymeric matrixes from aqueous suspension, giving rise to very strong and tough percolating networks of hydrogen whiskers [Ljungberg et al., 2006]. Environmental advantages such as biodegradability, dynamic properties such as storage modulus, loss modulus and damping behavior and thermal properties such as thermal stability and thermal expansions are very important factors that affect the quality of the final products [Fuad et al., 1994].

An abundance of acacia trees cell saps that can be readily obtained provides a new area for research and development. The presence of hydroxyl groups in cellulose creates an environment which increases the mechanical properties and biodegradability of polypropylene. Dynamic Mechanical Analysis is a sensitive technique used to characterize the mechanical responses of a material by monitoring property changes with respect to temperature or frequency of oscillation or both. Diffusion and thermal degradation measurements are also important in the study of hydrophilicity and thermal stability of polymers blends.

1.2 Statement of the research problem
Depletion of petroleum resources, poor impact strength, non-biodegradability, and minimal permeability of the petroleum based polymers are causes that have stimulated the efforts to find better alternative to enhance these properties. Most researchers have mainly concentrated on blending these polymers with woodflour, polycaprolactone or cross-linking with glutaraldehyde, but this has resulted in no much increase in their biodegradability, mechanical and permeability properties. This research has studied on
the different proportions in which polypropylene was blended with cellulose materials to improve its mechanical, permeability and degradability properties because cellulose is structurally rigid, has low thermal stability, abundant, high diffusivity and has highly polar hydroxyl groups. Upon the exploration, the dynamic mechanical and viscoelastic properties, water infusibility and degradability testing of the polypropylene/cellulose blends were investigated.

1.3 Objectives

1.3.1 Main objectives
The main objective of this research was to carry out dynamic mechanical, diffusion and degradation analysis in polypropylene/cellulose blends.

1.3.2 Specific objectives
The specific objectives were to investigate the effect of cellulose on:

(i) loss and storage moduli as well as creep and recovery processes in polypropylene/cellulose blends.

(ii) thermal degradation in polypropylene/cellulose blends.

(iii) diffusion properties in polypropylene/cellulose blends.

(iv) biodegradation of polypropylene/cellulose blends.

1.4 Rationale
Polypropylene is one of the most important commodity polymers and is used in many areas, such as home appliances, automotive parts, construction and other important industrial applications. Polypropylene materials available in the Kenyan market have been found to have poor impact toughness and are non-biodegradable. One way of
improving the mechanical, diffusion and biodegradability properties of polypropylene is by blending it with cellulose. Therefore in this regard, it was expected that the highly polar hydroxyl groups in the cellulose makes polypropylene materials to be stiffer, improves performance, reduces thermal properties, increase permeability and biodegradability rate. Dynamic mechanical analysis, creep, thermal degradation, diffusion and biodegradation measurements provides information related to the mechanical properties, dimensional analysis, stability and degradation, permeability and the rate of biodegradation of the blends.
CHAPTER TWO

LITERATURE REVIEW

2.1 Dynamic mechanical test of polypropylene

Most polymers are very durable, however, can be made to degrade photo-chemically by incorporation of carboxyl groups that absorb ultra-violet radiation to form excited states that are energetic enough to undergo bond cleavage [Gindl, 2006]. Water is considered relatively harmless; however, it can have at least three kinds of effects leading to early polymer degradation: a chemical effect, a physical effect and a photochemical effect [Shah, 1980].

Cellulose is among the simplest of the natural polymers that consist of a single repeating unit of D-glucose, linked through carbons 1 and 4 [Reddy and Yang, 2005]. Cellulose is not thermoplastic but decomposes before melting; it is insoluble in water and most other common solvents. Solution of metal complexes such as copper (II) Ammonia or copper (II) – diamine dissolve cellulose [Joel, 1995]. Cellulose ethers prepared by pretreating cellulose with base then reacting with halogen compounds are biodegradable [Bikales and Segal, 1971]. Large numbers of graft copolymers of cellulose have been prepared which need modifications of cellulosic fibers for example cellulose acetate grafted with vinyl forms a group of biodegradable cellulose [Barbut and Mittal, 1996]. The viscoelastic behavior of polypropylene is considerably affected by the presence of natural fibers. An increase in the storage (E’) modulus and reduced damping values can be observed with increasing fibre content due to reinforcing effect and interfacial adhesion between fibres and matrix [Amash and Zugenmaier, 2000]. Faucher and Schulz [1999]
investigated the stress relaxation behavior of isotactic polypropylene at temperature between -67 and 140 °C and found that a master curve could be formed.

The linear mechanical properties above the glass-rubber transition of nanocomposite film of isotactic polypropylene reinforced with natural fibers are drastically enhanced as compared to the neat polypropylene matrix [Ljungberg et al., 2006]. Empirical functions based on the Cole-Cole equation have been employed to model dynamic mechanical data obtained for isostactic polypropylene over a wide frequency range (10^{-2} – 10^{7} Hz) at temperatures between -10 °C and 50 °C. This analysis has yielded parameters characterizing the glass-rubber β-relaxation as a function of temperature [Read et al., 1988]. Guo [2006] and coworkers investigated the effects of compatibilizers including maleic anhydride grafted polypropylene (MA-PP) and maleic anhydride grafted ethylene-propylene-diene copolymer (MA-EPDM) on wood-floor/polypropylene (WF/PP) composites. Dynamic mechanical analysis showed that the loss factor of composites decreased and the storage modulus improved in the presence of MA-PP. More recently, the advent of polypropylene in-reactor alloys or so-called in-situ blends has drawn extensive scientific and industrial interests, owing to the excellent mechanical properties and relatively low cost [Rongbo et al., 2009]. Natural fibers are generally suitable to reinforce plastics (thermo sets as well as thermoplastics) since natural fibers are strong, abundant, non-abrasive, nonhazardous and inexpensive [Nayara et al., 2009].

2.2 Creep
The use of natural fibers as reinforcement of polymeric matrices has attained a great academic and commercial interest in the past decade owing to the low cost, large availability and biodegradability of the fibers. Wood fibers have low specific gravity,
high specific strength during processing. On the other hand, polypropylene is a versatile, recyclable, commodity polymer. Reinforced PP exhibits several attractive mechanical properties through an appropriate compounding of polymer and filler, allowing its use in several industrial sectors, such as automotive components, domestic appliances, frames, furniture and packaging. Because of its ease of processing a large variety of shapes can be obtained. Thus, polypropylene-wood flour composites are increasing their market share because of their low cost, good mechanical properties and environmentally friendly composites [Nunez et al., 2004]. Natural fiber/polymer composites (NFPCs) are experiencing dramatic growth in utilization because of low cost, low density, biodegradability, sound mechanical properties, water and rot resistance, dimensional stability and processing ability [Oksman and Clemons, 1998, Bledzki and Gassan, 1999].

The natural fibers used to reinforce thermoplastics mainly include wood, cotton, flax, hemp, jute, sisal and sugarcane [Wollerdorfer and Barder, 1998; Bledzki and Gassan, 1999; Mohanty et al., 2003]. The application of NFPCs in construction raised the requirements of their mechanical properties, especially their creep resistance under constant stress that commonly exists in structural building products. Creep is the deformation of a material under constant stress, dependent on time, temperature and material properties. Creep deformation can exceed the creep limit and cause product failure, especially in applications with long term loading. Understanding, evaluation and prediction of creep behaviors of NFPCs are thus of great importance for its application [Park and Balatinez, 1997]. The creep process of polymeric material can be segregated into four stages: instantaneous deformation, primary creep, secondary creep and tertiary creep. When a load is applied, the instantaneous deformation results from the elastic
deformation of a material. The instantaneous deformation is followed by the primary creep stage, during which the creep rate starts at a very high value and decreases gradually to a relatively low value. In the secondary creep stage, the viscous flow occurs and the creep rate remains constant. Finally, the creep goes into the tertiary stage with an increasing creep until creep rupture occurs [Yang et al., 2004].

2.3 Thermal degradation
Thermal degradation is a process whereby the action of heat or elevated temperature on a material causes a loss of physical, mechanical or electrical properties or all. By using apparatus as a Thermo gravimetric analyzer (TGA) in kinetic studies, the evaporation rate of product is determined and not the intrinsic chemical reaction rate, since not every broken-bond in the polymer chain leads to the evaporation of the products. Only product fragments which are small enough to evaporate will actually evaporate at a given reaction temperature and thus leads to a decrease of the polymer mass [Weterhout et al., 1997]. Natural fibers to polymer reduce drastically the amount of combustible gases and favor the formation of carbonaceous char and water. Uncontrolled incineration can produce serious air pollution, environmental problems due to the possible emission of toxic flue gases (dioxins, furans, acid gases and heavy metals) [Dimitrova et al., 2008]. Use of natural fiber reinforced polypropylene biocomposites in electrical and automotive engineering has been increasing in recent years mainly due their excellent high modulus (stiffness), which makes it possible to replace conventional materials such as glass fibers. A specific advantage of cellulose-based fibers composites over glass fiber composites, however, is the fact that they can be burned without leaving large amount of slag. On the whole, the use of cellulose-based fibers has a definite ‘green image’ [Broge, 2000].
natural fiber composite systems, dynamic properties such as damping behavior and thermal properties such as thermal stability and thermal expansions are very important factors that affect the quality of the final products. For example, the thermal deformation of the bathroom interiors can be brought on by hot vapor generated during a shower, while dashboards are affected by the high temperature inside the vehicle during summer. Moreover, the stability of these systems is very important during a fire, because these materials must bear the heat [Khalid et al., 2009].

2.4 Diffusion
Diffusion in polymers occurs by the transport of a penetrant via random molecular motion [Crank and Park, 1968]. Compared with the traditional synthetic fibers, natural fibers present lower density, less abrasiveness, lower cost, renewable and biodegradable. The main disadvantage of these natural fiber polymer composites seems to be the incompatibility between the hydrophilic natural fibers and the hydrophobic thermoplastic matrix that makes necessary the use of compatibilizers or coupling agents to improve the adhesion between the fiber and the matrix. New applications and end uses of these composites for decking, flooring, outdoor facilities and their exposure to atmosphere or contact with aqueous media have made it necessary to evaluate the water uptake characteristics of natural fiber thermoplastic composites [Mehdi et al., 2006]. Moisture diffusion in polymeric composites has shown to be governed by three different mechanisms. The first mechanism involves diffusion of water molecules inside the micro gaps between polymer chains. The second involves capillary transport into the gaps and flaws at the interfaces between fiber and the matrix. This is a result of poor wetting and impregnation during the initial manufacturing stage. The third involves transport of
microcracks in the matrix arising from the swelling of fibers (particularly in the case of natural fibre composites) [Espert et al., 2004].

Diffusion behavior of polymeric composites can be classified according to the relative mobility of the penetrant and of the polymer segments, which is related to either Fickian, non-Fickian or anomalous, and an intermediate behavior between Fickian and non-Fickian [Collings et al., 1993]. Water absorption is one of the most important characteristics of wood floor composites materials exposed to environmental conditions that determine their end use applications. [Ismael and Behzad, 2009].

2.5 Biodegradability

Biodegradation of polymers involves the following steps;

(i) Attachment of microorganisms to the surface of the polymer.
(ii) Growth of microorganisms on the surface of the polymer.
(iii) Primary degradation of the polymer.
(iv) Ultimate degradation.

Microorganisms can attach to the surface, if the polymer surface is hydrophilic. Since PP and PE have only CH₂ groups, their surfaces are hydrophobic [Arutchelvi et al., 2007]. There is a growing interest in the use of natural fibers as reinforcements for biodegradable polymers because natural fibers not only have the functional capability to substitute glass fibers that are currently used in the industry today but also have advantages such as low cost, low density and possess good affinity for polymer matrices. Fiber reinforced composites have gained importance from automotive to geotextiles sectors, where high mechanical properties and dimension stability have to be combined
with low weight. Besides their low density, they reduce abrasion of screw and barrel and the energy input for distributing them in the polymer melt. So the biodegradability of this renewable raw material is important [Dhakal et al., 2006].

Cellulose represents a renewable material with special properties as biocompatibility and in wood as a composite with lignin and hemicelluloses, long-term durable and extreme-resistant raw materials in a wide temperature range. Cellulose is produced by photosynthesis. Polymer/natural fibre composites show enhanced properties in comparison with neat polymers and offers scope for replacing composites containing glass fibres, owing to resultant advantages in weight, recyclability and ease of disposal [Peter, 2006]. The use of natural plant fibres as reinforcement in polymer composites for making low cost engineering materials has generated much interest in recent years. New environmental legislation as well as consumer pressure has forced manufacturing industries (particularly automotive, construction and packaging) to search for new materials that can substitute for conventional non-renewable reinforcing material such as glass fibre. The advantage of natural fibres over traditional glass fibres are acceptable as good specific strengths and modulus, economical viability, reduced tool wear, enhanced energy recovery and good biodegradability [Dhakal et al., 2006].

Despite the research that has been done on polypropylene and natural fibers, investigations on the mechanical, biodegradability, thermal degradation and diffusion analysis of polypropylene/cellulose from acacia cell sap are sparse. This was intended to give an insight into the mechanical, biodegradability, thermal degradation and sorption properties of polypropylene/cellulose blends.
CHAPTER THREE

THEORETICAL BACKGROUND

3.1 Introduction
This chapter describes the related fundamental theory applied in this thesis including the dynamic properties, linear viscoelasticity, and the time temperature-stress superposition principle, the behavior of creep, thermo gravimetric properties, diffusion and biodegradability of the material.

3.2 Dynamic mechanical analysis (DMA)

3.2.1 Dynamic mechanical Analysis measurement system
The DMA measurement system consists of four components:

a) Mechanically controlled displacement detector: this is the part that accurately tracks any mechanical changes occurring in the sample due to changes in temperature and time. The system detects changes in the systems resonance frequency and supplies electrical energy needed to maintain the preset amplitude. The amount of electrical energy supplied is a measure of damping properties of the material. Changes detected are expressed in terms of current, which are easily separated by a phase sensitive detector enabling the signals to be measured.

b) A linear force motor: This provides precise control of all stresses applied to the sample. The high resolution of this motor allows for reproducible force control. It supplies the sinusoidal deformation force to the material.
c) The central core rod (drive shaft): the drive shaft is the device through which all stresses are applied to the sample from the drive motor. It transfers the force from the drive motor to the clamps that hold the sample.

d) Furnace: the furnace controls the temperature of the system.

3.2.2 Linear viscoelastic properties

The stress function, which is sinusoidal, in a perfectly elastic system results in-phase with strain. However, in an ideal fluid, the stress leads the strain by 90 °C out of phase. Thus, with viscoelastic materials, the stress function is some hybrid of these responses. The stress and strain will be out of phase by some phase angle, \( \delta \). A small phase angle indicates high elasticity, while a large phase angle is associated with high viscous properties. A smaller the phase angle, indicates how closer the elastic modulus is to the complex modulus.

When a specimen is subjected to an oscillatory shear strain of angular frequency, \( \omega \), the strain is generated as shown in equation 3.1:

\[
\varepsilon(t) = \varepsilon_o \sin \omega t
\]  (3.1)

where \( \varepsilon_o \) is the amplitude.

An ideal elastic body deformation instantly follows an applied stress, and consequently, \( \sigma(t) \) will be as shown in equation 3.2:

\[
\sigma(t) = \sigma_o \sin \omega t
\]  (3.2)

For a linear viscoelastic material, the stress response is sinusoidal but out of phase with the strain by a phase angle, \( \delta \). Introducing \( \delta \), into equation 3.2 yields equation 3.3 as shown below.

\[
\sigma(t) = \sigma_o \sin(\omega t + \delta)
\]  (3.3)
In such cases the deformation (strain) lags behind the applied stress as shown in Figure 3.1.

![Figure 3.1: Stress as a function of time with dynamic (sinusoidal) loading (Strain)](image)

With ideal viscoelastic bodies, the resulting phase angle $\delta$ in the corresponding vector diagram can be assumed to be constant. From equation (3.3), $\sigma$ can be expanded as shown in equation 3.4:

$$\sigma(t) = (\sigma_o \cos \delta) \sin \omega t + (\sigma_o \sin \delta) \cos \omega t$$  \hspace{1cm} (3.4)

The stress vector consists of the sum of two components. One component, $\sigma' = \sigma_o \cos \delta$, is in phase with the strain and the other component $\sigma'' = \sigma_o \sin \delta$, is 90 $^\circ$C out of phase with strain. The relationship between stress and strain in this dynamic case can be defined as shown in equation 3.5:

$$\sigma(t) = \varepsilon_o (E' \sin \omega t + E'' \cos \omega t )$$  \hspace{1cm} (3.5)

In which the two components obtained as storage and loss moduli are expressed in equations 3.6 and 3.7 respectively.

$$E' = \frac{\sigma_o}{\varepsilon_o} \cos \delta = \text{storage modulus}$$  \hspace{1cm} (3.6)
\[ E'' = \frac{\sigma''}{\varepsilon''} \text{sin} \delta = \text{loss modulus} \quad (3.7) \]

A modulus can be assigned to each of these two components. The storage modulus, \( E' \), which is in phase with the oscillatory strain measures the rigidity and resistance to deformation of the sample. It is related to the complex modulus of rigidity \( E^* \) by equation 3.8:

\[ E' = \frac{\sigma'}{\varepsilon_0} = \frac{\sigma}{\varepsilon_0} \cos \delta = E^* \cos \delta \quad (3.8) \]

The imaginary, or loss modulus, \( E'' \), which is out 90° of phase with strain measures the energy dissipated. Loss modulus \( (E'') \) is related to the complex modulus by equation 3.9:

\[ E'' = \frac{\sigma''}{\varepsilon_0} = E^* \sin \delta \quad (3.9) \]

The complex modulus is as shown in equation 3.10:

\[ E^* = E' + iE'' \quad (3.10) \]

where: \( i^2 = -1 \)

The loss tangent is calculated simply as the tangent of the phase angle, or alternatively, as the ratio of the loss to storage moduli as shown by equation 3.11:

\[ \tan \delta = \frac{E''}{E'} \quad (3.11) \]

The loss factor spectra will quantitatively be described by a superposition of model function as shown by equation 3.12:

\[ E^*(T) = \sum_{i=1}^{2} A_i \exp \left\{ -\frac{\Delta E_i}{kT} - \frac{T^2}{T_m^2} \exp \left[ \frac{\Delta E_i}{k} \left( \frac{1}{T_m} - \frac{1}{T} \right) \right] \right\} \quad (3.12) \]
In this model function $A$ is a constant, $k$ is the Boltzmann constant, $T$ is the absolute temperature, $T_m$ is the temperature representing maximum loss modulus, $E$ is the activation energy and $i$ refers to different processes which contribute to the mechanical response. The complex, phase angle, storage and loss moduli, are illustrated by the trigonometry of a right triangle, as shown in Figure 3.2.

![Figure 3.2: Relation among dynamic and phase angle](image)

In Dynamic Mechanical Analysis testing, the storage, the loss moduli, and tangent of the phase angle are important. The loss factor, storage modulus and loss modulus vary with frequency of loading as shown in Figure 3.3.

![Figure 3.3: The complex modulus, $E^* = E' + iE''$, as a function of frequency [Ward and Hadley, 1983]](image)

At low frequency the polymer is rubber like and has a low storage modulus, which is independent of frequency. At high frequency, the polymer is glassy and the storage
modulus is again independent of frequency. In the intermediate region where the material behaves viscoelastically, the storage modulus increases with increasing frequency. As the frequency is increased it becomes more difficult for the polymer chains to respond to the applied forces and tends to remain in a frozen state. A frozen system stores more energy than a free system [Ward and Hadley, 1993]. The loss modulus is zero both at low and at high frequencies where stress and strain are in phase for the rubbery and glassy phases. In the intermediate viscoelastic region, the loss modulus increases to a maximum value then decreases. If the mechanical force applied has a low frequency compared to the transition rates in the system, establishment of a thermal equilibrium is rapid and the system can always remain in equilibrium. The system therefore encounters quasistatic conditions and observes the full relaxation strength. On the other hand when the frequency of the applied force is large compared to the transition rates, equilibrium cannot be established. The system reacts to the average strain only, which is always zero. Crossover from one regime to the other occurs at $\omega \tau \equiv 1$ [Ward and Hadley, 1983; Strobl, 1997].

For purely elastic materials, the phase angle ($\tan \delta$) equals zero, because $E''$ is zero while for purely viscous materials, the phase angle is $90^\circ$. Since $\tan \delta$ is dimensionless, it is an important parameter for describing the viscoelastic properties of materials, whereas storage and loss modulus values may be subject to change, due to different formulations, geometry or processing methods. An important aspect of DMA is assurance that the analysis is conducted within the linear viscoelastic region. The response within the linear viscoelastic region is directly proportional to the mechanical input, polymer packing is not altered and the response reflects the polymer structure and organization. When the stress/strain response becomes non-linear, the mechanical stimulus significantly alters
polymer packing. The response can then reflect other phenomena. However, the quality of DMA signal is not satisfactory at very low stress and strains; consequently, DMA is typically conducted at the highest possible stress/strain within linear viscoelastic to optimize the signal quality [Sun et al., 2007].

3.2.3 Temperature Dependence of the Relaxation Time

The temperature dependency of polymer properties is of great importance because the physical and mechanical properties of the polymers change drastically as temperature changes. It is important to study the relaxation behavior of polymers, at a particular temperature for a given time period. The temperature dependency of the relaxation time provides a way of varying the temperature to bring the relaxation process within a time scale that is readily accessible. Viscoelastic behavior at short or long time periods can be predicted by extrapolation. Changes due to temperature can be described in terms of free volume or relaxation time. At temperatures below glass transition temperature \( T_g \) local chain relaxation takes place. At these temperatures motions are hindered by close presence of other molecules. For relaxation to take place a potential barrier must be surmounted. In this region the kinetics of relaxation are better described on the basis of barrier state theories as such that the temperature dependency of the relaxation time \( \tau \) is often described by the Arrhenius equation [Sperling, 1992; Fried, 1995] as shown in equation 3.13:

\[
\tau = \tau_o \exp \left[ \frac{\Delta E}{kT} \right]
\]

where \( \tau_o \) is the pre-exponential factor, \( \Delta E \) is the activation energy, \( k \) is the Boltzmann constant and \( T \) is the absolute temperature. The Arrhenius equation is typically used to
describe viscoelastic events for the glass transitions associated with semi-crystalline polymers. Frequently it is mostly used to obtain the activation energy associated with glass transition events [Pramanick and Sain, 2006]. In contrast to local motions, relaxation times associated with secondary motions are dependent on free volume. The presence of volume allows the molecules to relax to a new configuration. The Doolittle equation gives a relation that expresses the dependency of relaxation time on the free volume as [Doolittle and Doolittle, 1957]. This can be given as shown by equation 3.14:

$$\tau = \tau_0 \exp\left(\frac{BV_0}{V - V_o}\right)$$  \hspace{1cm} (3.14)

where $V$ is the total volume, $V_o$ is the occupied volume, $B = \xi \left(\frac{V^*}{V_m}\right)$ is a constant, $V^*$ is the minimum volume required for relaxation process to take place, $V_m$ is the mean volume of the relaxing polymer segment. $\xi$ is a constant such that $0.5 < \xi < 1$. At temperature above the glass transition ($T_g$), the dependency follows the William-Landel-Ferry (WLF) law [William, 1996] as shown in equation 3.15:

$$\log\left(\frac{\tau(T)}{\tau(T_g)}\right) = \frac{C_1(T - T_g)}{C_2 + T - T_g}$$  \hspace{1cm} (3.15)

where $\tau(T)/\tau(T_g)$ is the shift factor relative to the defining temperature, $T_g$ is the defining temperature, in °C or K, which is a glass transition temperature, $C_1$ & $C_2$ are empirically determined constants and $T$ is the selected temperature, in °C or K. The values of $C_1$ and $C_2$ depend on the particular morphology or structure associated with a given sample. For amorphous materials, the best approximations for the parameters are $C_1 = 17$ and $C_2 = 56$. As the sample becomes more crystalline (for example polypropylene and polyethylene)
or cross linked (such as a vulcanized rubber), the values of $C_1$ and $C_2$ will increase, reflecting changes in the free volume and the expansion with respect to temperature. Conversely, Vogel-Fulcher-Tamman equation [Vogel, 1921] can also be used to explain temperature dependency above $T_g$ and the relationship is as shown in equation 3.16:

$$\tau = A \exp \left( \frac{B}{T - T_o} \right)$$

(3.16)

where $\tau$ is the relaxation time, $A$ and $B$ are constants depending on materials morphology and $T_o$ is ideal (Vogel) temperature which is $50 \, ^0C$ below $T_g$.

From the Figure 3.4 above, it can be seen that at high temperatures the two are approximately the same but differ significantly at lower temperatures.

### 3.3 Viscoelastic Theory

#### 3.3.1 Viscoelasticity

Polymeric materials exhibit viscous or elastic behavior in response to applied stress. If low stress is applied, elastic responses are typical in solid materials and follows Hooke’s law. This can be given by equation 3.17:
\[ E = \frac{\sigma}{\varepsilon} \]  \hspace{1cm} (3.17)

where \( \sigma \) is the stress, \( \varepsilon \) is the strain and \( E \) is the creep modulus. This Hookean behavior can also be observed in different modes of stress. The response of an elastic system to applied stress is instantaneous and completely recoverable. Viscous behavior characterizes fluids, whereby stress applied will result in a strain that increases proportionally with time until the stress is removed. This can be shown by equation 3.18 defined by Newton:

\[ \sigma = \eta \left( \frac{d\varepsilon}{dt} \right) \]  \hspace{1cm} (3.18)

where \( \sigma \) is the stress, \( \eta \) is the constant viscosity and \( \left( \frac{d\varepsilon}{dt} \right) \) is the strain rate. Due to their chain-like structures, the deformation of polymers is usually accompanied by a complex of short and long range of cooperative molecular rearrangements; therefore polymers are not perfectly elastic bodies [Cowie, 1973]. Polymers, because of their viscoelastic nature at all temperatures, display behavior during deformation that is both temperature and time dependent and both temperature and time have a similar effect on the linear viscoelastic properties. The simplest way to simulate the combined viscous and elastic behavior of a material is to use of mechanical analogies that include viscous elements (dashpots) and elastic elements (springs). Polymer molecules respond to an external force in two ways. One part of the response is instantaneous and this is referred as elastic response. All the mechanical energy put is recovered upon release of external force, and thus this part is associated with energy storage. The other part is delayed response that involves dissipation of mechanical energy into heat as in the flow of a viscous liquid. Hence
showing that viscoelastic is a combination of the two responses. In other words, viscoelasticity is a combination of viscosity and elasticity in varying amounts, meaning that polymeric system does not follow a Hookean (elastic) or viscous (flow) behavior. Various models have been proposed to explain viscoelastic behavior. These include, Kelvin-Voigt, standard linear solid (Zener) and Maxwell-Wiechert models, among others [William, 1980; Sperling, 1992; Fried, 1995]. Figure 3.5 shows a spring which represents the elastic component.

Figure 3.5: Linear spring-Elastic component

Equation 3.17 is the constitutive equation for linear spring elastic component. Figure 3.6 shows a dashpot which represents the viscous component of a viscoelastic material.

Figure 3.6: Linear dashpot-Viscous component

Equation 3.18 is the constitutive equation of linear dashpot viscous element.
3.4 Creep

Creep is the progressive deformation of a material at a constant load. First the material suffers an instantaneous elastic deformation followed by a rapid creep rate which decreases with time. The creep rate reaches a steady-state value and finally increases rapidly with time making the material to fracture. Accurate creep predictions are important especially in structural application. A counterpart to creep is stress relaxation, in which the strain is held as the constant and the stress required to maintain the strain decreases as a function of time. If a constant stress is applied to a viscoelastic material, the strain is observed to be time dependent. To quantify the effect of strain on the material, creep is normalized as creep compliance, \( J(t) \), as expressed in equation 3.19:

\[
J(t) = \frac{\varepsilon(t)}{\sigma}
\]  

(3.19)

where \( \sigma \) represents a constant applied stress and \( \varepsilon(t) \) is the time – dependent strain. For a material in its linear viscoelastic range, the creep compliance is independent of stress, whereas, the creep compliance is dependent on the stress in the nonlinear range. Long term creep compliance is one performance criteria commonly used to evaluate composite materials [Lin et al., 2004]. But contrary, if a constant strain is applied to a viscoelastic material, stress is observed to be time dependent. To quantify the effect of stress on the material, stress relaxation is normalized as stress relaxation modulus, \( G(t) \), as expressed in equation 3.20:

\[
G(t) = \frac{\sigma(t)}{\varepsilon}
\]  

(3.20)

A general illustration of viscoelastic material is shown in Figure 3.7.
From Figure 3.7, the material initially responds in an elastic manner and then in the viscous manner. It can be observed that the elastic portion recovers over an extended period of time when stress is removed. A general form of creep curve is shown in Figure 3.8.

From Figure 3.8, it can be observed that, when stress is applied to a material, there is an instantaneous extension followed by a rapid creep. This part is known as primary creep. This is followed by a steady elongation referred to as secondary creep and then an
accelerated creep leading to rupture known as tertiary creep [Nkiwane and Mukhopadhyay, 1999].

3.4.1 Standard Linear Solid Model

When a polymeric material is subjected to an abrupt force, it can be described using a Standard linear Solid Model which combines the Kelvin - Voigt Model and a Hookean spring in series as shown in Figure 3.9. The standard linear model combines a spring and a Kelvin element in series as shown in Figure 3.9.

![Figure 3.9: Standard Linear Solid model [Ward and Hadley, 1993]](image)

By considering equilibrium of stress and compatibility of strains, the governing equation for this model is expressed in equation 3.21:

\[
\eta E_1 \frac{d\varepsilon}{dt} + E_1 E_2 \varepsilon = \eta \frac{d\sigma}{dt} + (E_1 + E_2)\sigma
\]  

(3.21)

where \(E_1\) and \(E_2\) are elastic moduli and \(\eta\) is the viscosity. For a constant stress \(\sigma\), the corresponding strain \(\varepsilon\), is obtained by solving equation 3.21. Since stress is a constant,

\[
\frac{d\sigma}{dt} = 0,
\]

and equation reduces to equation 3.22:

\[
\eta E_1 \frac{d\varepsilon}{dt} + E_1 E_2 \varepsilon = (E_1 + E_2)\sigma
\]  

(3.22)

This can be rewritten as shown in equation 3.23:
\[
\frac{d\varepsilon}{dt} + \frac{E_2 \varepsilon}{\eta} = \frac{(E_1 + E_2)}{\eta E_1} \sigma
\]  
(3.23)

Noting that the equation has an integrating factor, \( e^{\frac{E_2 t}{\eta}} \), we obtain an expression for strain as expressed in equation 3.24:

\[
\varepsilon e^{\frac{E_2 t}{\eta}} = \left( E_1 + E_2 \right) \frac{\sigma}{E_1 E_2} e^{\frac{E_2 t}{\eta}} + C
\]
(3.24)

At \( t = 0 \), \( \varepsilon = \frac{\sigma_0}{E_1} + \frac{\sigma_0}{E_2} \)-substituting these values in equation 3.24 and solving for \( C \), we obtain an expression of strain as shown in equation 3.25:

\[
\varepsilon = \frac{\sigma_0}{E_1} + \frac{\sigma_0}{E_2} \left[ 1 - \exp \left( - \frac{t}{\tau} \right) \right]
\]
(3.25)

where \( \frac{\sigma_0}{E_1} \) is instantaneous elastic deformation corresponding to the spring, \( \frac{\sigma_0}{E_2} \) is delayed elastic deformation corresponding to the Kelvin element, \( \tau \) is retardation (relaxation) time. At \( t = 0 \), \( \varepsilon = \frac{\sigma_0}{E_1} \) and \( \tau = \frac{\eta}{E_2} \). This is illustrated in Figure 3.10.

Figure 3.10: Creep response of Standard linear solid model [Ward and Hadley, 1993]
The time dependences of the relaxed moduli in the creep ($C_p$) and subsequent recovery ($R$) processes at different loading levels are given by equation 3.26:

$$C_p = \frac{E_0 - E_t}{E_0} \text{ and } R = \frac{E'_0 - E'_t}{E'_0}$$

(3.26)

where $E_t$ represents the creep modulus at time $t$ seconds, $E'_t$ represents the modulus at the time $t$ in the recovery process, $E_0$ represents the original modulus in the creep process, $E'_0$ is the initial modulus in the subsequent strain recovery process at 10 s after 3600 s of creep. This work has adopted the standard linear solid model, because the model provides a good qualitative description of both creep and stress relaxation behavior of polymeric materials. The responses of this model, under both creep and stress relaxation conditions were analyzed. In this model, at any point in time, stress is directly proportional to the strain.

3.4.2 Boltzmann’s superposition principle (Complex Loading Histories)
The Boltzmann superposition principle states that the response of a material to a given load is independent of the response of the material to any load, which is already on the material. The deformation of a specimen is directly proportional to the applied stress, when all deformations are compared to equivalent times. Boltzmann proposed that:

i) The creep is a function of the entire past loading history of the specimen.

ii) Each loading step makes an independent contribution to the final contribution, so that the total deformation can be obtained by the addition of all the contributions.
It is only valid in linear viscoelastic region. Suppose the time-dependent compliance, \( J(t) \), is known from \( t_0 \) to \( t_n \), the strain, \( \varepsilon_o(t) \), for \( t_0 < t < t_n \) resulting from a constant stress, \( \sigma_o \), applied at \( t_0 = 0 \) would be given as shown in equation 3.27:

\[
\varepsilon(t) = \sigma_o [J(t-t_0)] = \sigma_o [J(t)] \tag{3.27}
\]

If there is an additional stress, \( \sigma_1 \), applied at time \( (t_1) \) the resulting strain, \( \varepsilon_1(t) \), for only itself is expressed by equation 3.28:

\[
\varepsilon_1(t) = \sigma_1 [J(t-t_1)] \tag{3.28}
\]

Therefore, if \( \sigma_0 \) and \( \sigma_1 \) act together, the total strain at \( t \) is given as shown by equation 3.29:

\[
\varepsilon(t) = \varepsilon_0(t) + \varepsilon_1(t) = \sigma_o [J(t)] + \sigma_1 [J(t-t_1)] \tag{3.29}
\]

If the material is subjected to additional stresses, \( \sigma_1, \sigma_2, \sigma_3, \ldots, \sigma_n \) after time \( t_1, t_2, t_3, \ldots, t_n \) respectively, then Boltzmann’s superposition principle states that the creep response can be predicted simply by assuming the individual responses from each stress increment as expressed by equation 3.30:

\[
\varepsilon(t) = \sigma_o [J(t)] + \sigma_1 [J(t-t_1)] + \sigma_2 [J(t-t_2)] + \sigma_3 [J(t-t_3)] + \ldots + \sigma_n [J(t-t_n)] \tag{3.30}
\]
This behavior is shown in the Figure 3.11.

![Figure 3.11: Boltzmann superposition principle; (a) applied stress history, (b) resulting strain history [Ward and Hadley, 1993]](image)

### 3.5 Time-Temperature superposition principle

#### 3.5.1 Time – Temperature stress superposition

A comprehensive creep test is prohibitively expensive and time consuming; therefore, it was necessary for methods of interpolation and extrapolation to be developed in order to make the most of limited data [Darlington and Turner, 1978]. Temperature effects are described by altering the time scale of the response for example horizontal shift as shown in Figure 3.12, according to equation 3.31:

\[
\log t - \log t_o = \log \frac{t}{t_o} = \log a_T
\]

(3.31)

where \(a_T\) is the temperature shift factor and it is positive if the curve moves to the left of the reference temperature and negative, if the curve move to the right [Cowie, 1973].
The creep compliance at two differences temperatures can be related as shown in equation 3.32:

\[ J(t, T) = J \left( \frac{t}{a_T}, T \right) \]  \hspace{1cm} (3.32)

The basis of time-temperature superposition is the free volume theory and Doolittle’s viscosity equation [Doolittle and Doolittle, 1957; Ward and Hadley, 1993; Luo et al., 2001], which is in the form shown by equation 3.33:

\[ \eta = A \exp \left( \frac{B}{f} \right) \]  \hspace{1cm} (3.33)

Taking natural logarithm of equation 3.33 yields equation 3.34:

\[ \ln \eta = \ln A + B \left( \frac{1}{f} - 1 \right) \]  \hspace{1cm} (3.34)

where \( \eta \) is the viscosity of the material, \( A \) and \( B \) are material constants and \( f \) is the free volume fraction. A linear dependence of the free volume fraction on temperature variation is given by equation 3.35:
\[ f = f_0 + \alpha_T (T - T_o) \]  
(3.35)

where \( f_0 \) is the free volume at \( T_o \) and \( \alpha_T \) is the thermal expansion coefficient of free volume fraction. The shift factor can be defined as shown by equation 3.36:

\[ a_T = \frac{t}{t_o} = \frac{\eta}{\eta_o} \]  
(3.36)

where \( \eta_o \) and \( t_o \) are material viscosity and relaxation time at reference temperature \( (T_o) \), respectively, likewise for \( t \) and \( \eta \). From equation 3.36, equation 3.37 can be derived as:

\[ \ln a_T = \ln \frac{\eta}{\eta_o} = \ln \eta - \ln \eta_o = [\ln \eta = \ln A + B \left( \frac{1}{f} - 1 \right)] - \ln \eta = \ln A + B \left( \frac{1}{f_o} - 1 \right) \]

\[ ] = B \left( \frac{1}{f} - \frac{1}{f_o} \right) \]  
(3.37)

Equation 3.37 can be written as expressed in equation 3.38:

\[ \log a_T = \frac{B}{2.303} \left( \frac{1}{f} - \frac{1}{f_o} \right) \]  
(3.38)

This is because \( 2.303 \ln a_T = \ln a_T \). Substituting equation 3.35 into equation 3.37, equation 3.39 is obtained as:

\[ \log a_T = \frac{-B}{2.303 f_o} \left( \frac{T - T_o}{f_o + \frac{T - T_o}{\alpha_T}} \right) \]  
(3.39)

Since \( \frac{-B}{2.303 f_o} = C_1 \) and \( \frac{f_o}{\alpha_T} = C_2 \), William Landel Ferry (WLF) equation can be derived from equation 3.39, as shown in equation 3.40:
\[ \log a_T = \frac{-C_1(T - T_o)}{C_2 + T - T_o} \]  

(3.40)

where \( a_T \) is the time shift factor, \( T_o \) is the reference temperature and \( T \) is the temperature at which is shifted. The constants \( C_1 \) and \( C_2 \) are material dependent.

### 3.5.2 Master curves

In order to predict long-term behavior from short term measurements, it is generally assumed that the polymer does not change its structure with time, so the time-temperature-superposition (TTS) principle holds. The creep curves obtained at different temperatures are superposed by horizontal shifts along a logarithmic time scale (\( \ln a_T \)) to obtain a master curve. The accurate measurement of long term creep behavior has always been difficult. A commonly used test procedure is application of time-temperature superposition method, measurement of creep at a number of different elevated temperatures for a relatively short period of time and shifting of the results to a reference temperature to obtain a master curve for a longer period of time [Gibson et al., 1990]. This is done by moving translating small curves obtained from creep relaxation at different temperatures along the logarithm of time axis until they are all superimposed to form a large composite curve. This curve of the compliance versus time and temperature provides a useful description of polymer behavior and allows one to estimate among other things either relaxation or retardation spectrum [Cowie, 1973]. A long term temperature performance of polymeric materials can be predicted by a short term experiment since the higher temperature data sets can be shifted to longer times until they completely overlap the curve of the reference temperature. The plot obtained represents the master curve that covers a wide range of time.
3.6 Thermal Degradation
Thermal degradation of polymers is ‘molecular deterioration as a result of overheating’. At high temperatures the components of the long chain backbone of the polymer can begin to separate (molecular scission) and react with one another to change the properties of the polymer. It is part of a larger group of degradation mechanisms for polymers that can occur from a variety of causes such as: Heat (thermal degradation and thermal oxidative degradation when in the presence of oxygen), Light (photodegradation), Oxygen (oxidative degradation), and Weathering (generally UV degradation).

In general, the ability of a polymer to resist these degradation causes is called the stability of the polymer. Thermal degradation generally involves changes to the molecular weight (and molecular weight distribution) of the polymer and typical property changes include: Reduced ductility and embrittlement, Chalking, Color changes, cracking and general reduction in most other desirable physical properties.

3.6.1 The Mechanism of Thermal Degradation
Most types of degradation follow a similar basic pattern. The conventional model for thermal degradation is that of an autoxidation process which involves the major steps of initiation, propagation, branching and termination. Initiation: The initiation of thermal degradation involves the loss of a hydrogen atom from the polymer chain as a result of energy input from heat or light. This creates a highly reactive and unstable polymer ‘free radical’ and a hydrogen atom with an unpaired electron. Propagation: The propagation of thermal degradation can involve a variety of reactions and one of these is where the free radical reacts with an oxygen molecule to form a peroxy radical which can then remove a hydrogen atom from another polymer chain to form a hydroperoxide. The hydroperoxide
can then split into two new free radicals, which continue to propagate the reaction to other polymer molecules. The process can therefore accelerate depending on how easy it is to remove the hydrogen from the polymer chain. Termination: The termination of thermal degradation is achieved by ‘mopping up’ the free radicals to create inert products. This can occur naturally by combining free radicals or it can be assisted by using stabilizers in the polymer. In some polymers it is also possible to get ‘branching’ of the polymer chains, this is where two polymer chains become linked together and results in cross-linking and embrittlement of the polymer.

3.6.2 Decomposition of cellulose

Cellulose decomposes in temperatures range of 250 to 352 °C. It involves at least four processes in addition to simple desorption of physically bound water. The first is the cross-linking of cellulose chain, with the evolution of water (dehydration). The second concurrent reaction is the unzipping of the cellulose chain; Levoglucosan is formed from the monomer unit. The third reaction is the decomposition of the dehydrated products (dehydrocellulose) to yield char and volatile products; finally, the levoglucosan can further decompose to yield smaller products, including tars and eventually carbon monoxide. Some levoglucosan also depolymerize. Below 250 °C, the dehydration reaction and the unzipping reaction proceed at comparable rates and the basic skeletal structure of the cellulose is retained. At higher temperatures, unzipping is faster, and the original structure of the cellulose begins to disappear. The cross-linked dehydrated cellulose and the repolymerised levoglucosan begin to yield polynuclear aromatic structures.
3.6.3 Activation energy

The activation energies for the decomposition of the polymer blends are important in assessing the reaction mechanisms. When a polymer sample degrades, its mass decreases.

For the very general reaction is expressed in equation 3.41 below:

\[ S(s) = P_1(s) + P_2(s) \]  \hspace{1cm} (3.41)

The disappearance rate of the species \((S)\) can be calculated as shown by equation 3.42:

\[ \frac{dx}{dt} = kf(x) \]  \hspace{1cm} (3.42)

with \(S(s)\) the reactant, \(P_1(s)\) and \(P_2(s)\) the remainder and gaseous product, \(k\) – the rate constant which obeys the Arrhenius equation for the early stage of the reaction, \(x\) – the conversion factor of the decomposed compound at time \(t\), is expressed by equation 3.43:

\[ x = \frac{m - m_f}{m_o - m_f} \]  \hspace{1cm} (3.43)

With \(m\)= mass remaining at time \(t\), \(m_o\)= initial mass and \(m_f\)= final mass. The overall kinetic equation in terms of the conversion factor, \(y\) is given by equation 3.44:
\[ \frac{dx}{dt} = A(x)^n \exp\left(\frac{-E_a}{RT}\right) \]  

(3.44)

\( E_a \) is the activation energy, \( A \) is a pre exponential factor, \( R \) is universal gas constant, \( T \) is the temperature in kelvin and \( n \) is the order of reaction. If the temperature of the sample is changed by a constant heating rate \( \beta = \frac{dT}{dt} \) the variation in the conversion factor can be analyzed as a function of temperature, this temperature depends on the time of heating. Thus, the reaction rate is defined as by equation 3.45:

\[ \frac{dx}{dt} = \frac{A}{\beta} (x)^n \exp\left(\frac{-E_a}{RT}\right) \]  

(3.45)

Using a different assumption for performing the integration of equation 3.45, [Broido, 1969] derived a non-integral equation. 3.46 is valid only for the first order reaction as shown below.

\[ \ln(\ln \frac{1}{x}) = -\frac{E_a}{RT} + \ln \frac{RZT}{E_a\beta} \]

(3.46)

\( Z \) is the frequency factor and \( T_m \) is the temperature of the maximum reaction rate.

![Figure 3.14: Rate coefficient against reciprocal Temperature](image)
3.7 Diffusion

Diffusion in polymers occurs by transport of a penetrant via random molecular motion [Crank and Park, 1968]. Diffusion of liquid in a polymer blends can be visualized as a series of jumps in which Brownian motion of chain segments of the polymer produces transient voids in the vicinity of the liquid penetrant, enabling it to move within the polymer. Diffusion is a time-dependent process. The quantity of an element transported within another is a function of time. Diffusion flux ($J$) defined as the mass ($m$) diffusing through and perpendicular to a unit cross-sectional area of solid per unit time. It is expressed in differential form as shown by equation 3.47:

$$J = \frac{1}{A} \frac{dm}{dt}$$  (3.47)

where $A$ is the area of cross section and $t$ is the elapsed diffusion time. If the diffusion flux and the concentration gradient vary with time, with a net accumulation or depletion of diffusion species, the Fickian diffusion can be described using the one dimensional form of Fick’s second law of diffusion as shown by equation 3.48:

$$\frac{\partial C}{\partial t} = -D \frac{\partial^2 C}{\partial X^2}$$  (3.48)

Which gives the change in concentration, $C$, as a function of diffusion coefficient, $D$, and time, $t$, at any plane ($X$) in a material. The basis for most diffusion measurements in polymers/penetrants systems is measurement of total mass uptake by polymer as a function of time the second law can be source for the phase of uptake (short times) to obtain equation 3.49 as:

$$\frac{M_t}{M_\infty} = 4\left(\frac{Dt}{\pi t^2}\right)^{\frac{1}{2}}$$  (3.49)
where \( M_t \) is the relative mass uptake at a time, \( t \), \( M_\infty \) is the mass uptake at equilibrium, \( l \) is the film thickness and \( D \) is diffusion coefficient. The value of \( D \) can be deduced from an observation of the initial gradient of a graph of \( \frac{M_t}{M_\infty} \) as a function of \( \left( \frac{t}{l^2} \right)^{\frac{1}{2}} \). Fickian diffusion behavior in a material can be confirmed if the following characteristics are observed [Crank and Park, 1968]:

(a) Both uptake and desorption plots of \( \frac{M_t}{M_\infty} \) versus \( t^{\frac{1}{2}} \) are initially linear.

(b) This linear region extends to at least \( \frac{M_t}{M_\infty} = 0.6 \) for uptake.

(c) Above the linear region, the curves are concave against the abscissa.

(d) Uptake curves obtained by plotting \( \frac{M_t}{M_\infty} \) versus \( \frac{t^{\frac{1}{2}}}{l} \) should coincide regardless of film thickness.

(e) Plots of uptake and desorption will only coincide when \( D \) does not vary with concentration of the penetrant.

Many techniques are available for measuring penetrant uptake, including laser interferometry, microdielectrometry, Raman spectroscopy, nuclear magnetic resonance imaging and the use of radiolabelled penetrants among others. The most common technique, due to its simplicity and versatility, is gravimetric sorption. Gravimetric sorption involves exposing the specimen to a penetrant and monitoring the change in specimen mass with time. Mass uptake is referenced to the original mass and it is calculated using equation 3.50:
\[ M_u = \frac{M_t - M_o}{M_o} \]  

(3.50)

where \( M_o \) is the mass uptake, \( M_o \) is the original dry mass, and \( M_t \) is the mass of the wet specimen at time \( t \).

### 3.8 Biodegradability

#### 3.8.1 Overview of biodegradation of polymers

Biodegradable polymers can be entirely converted by microbial activity in a biologically active environment to biomass and biological by-products. The biodegradability of the blends is characterized by use of natural soil as the environment for the biodegradability test. Weight loss of the degraded sheets in soil is calculated using equation 3.51:

\[ W_{\text{loss}} = \left[ \frac{W_b - W_a}{W_b} \right] \times 100\% \]  

(3.51)

where \( W_{\text{loss}} \) is the weight loss, \( W_b \) and \( W_a \) are the weights of the dried sheets before and after being buried in soil, respectively. A general overview of biodegradation of polymers over a period of time is schematically represented in Figure 3.15 [Arutchelvi et al., 2007].

![Figure 3.15: Overview of degradation of polymers](image)
Polymeric materials released into the environment can undergo physical, chemical and biological degradation or combination of all these due to the presence of moisture, air, temperature, light [photo-degradation], high energy radiation [ultra violet, gamma-radiation] or micro-organisms [bacteria or fungi].

3.8.2 Mechanism of biodegradation

Biodegradation of polymers involves the following steps; [Arutchelvi et al., 2007];

(a) Attachment of micro-organisms to the surface of the polymer.

(b) Growth of micro-organisms utilizing the polymer as the carbon source.

(c) Primary degradation of the polymer.

(d) Ultimate degradation.

Micro-organisms can attach to the surface, if the polymer surface is hydrophilic. Since PP has only CH$_2$ groups, the surface is hydrophobic. Initial physical or chemical degradation leads to the insertion of hydrophilic groups on the polymer surface making it more hydrophilic. Once the organisms get attached to the surface, it starts growing by using the polymer as the carbon source.
CHAPTER FOUR

MATERIALS AND METHODS

4.1 Materials

The materials used in this study were polypropylene and cellulose. Neat polypropylene pellets with a density of 905 kg/m$^3$ and a melting point of 160 °C was used in this study as the base polymer matrix. These pellets were obtained from Pan Plastic, Babadogo chemical company Kenya. The cellulose was extracted from cell sap of acacia tree in Taita-Taveta County, Kenya. The chemical structure of PP and cellulose are shown in Figure 4.1(a) and 4.1 (b) respectively.

\[
\text{Figure 4.1: (a) Chemical structure of polypropylene}
\]

\[
\text{Figure 4.1: (b) Chemical structure of cellulose}
\]

4.1.1 Melting chamber

Acacia cell sap pellets that were extracted from acacia tree were dried at 90 ± 2 °C for 12 hours then ground into fine powder then sieved. Cellulose powder was mixed with molten polypropylene in the weight ratio of 0:10, 0.5:9.5, 1:9, 1.5:8.5 and 2:8 respectively. A total of 50 grams of the blend were used. Polypropylene and cellulose mixed blends were put in a cylindrical melting chamber of diameter 30 mm and a length of 300 mm placed on a hot plate. With the injection hole closed by a stopper screw, the
mixing screw was rotated through an angle of 360° every 4 minutes for 20 minutes to ensure that all the polypropylene melts evenly. Cellulose powder were added at 18\textsuperscript{th} minute and mixed for 2 minutes to obtain homogeneous mixture. The temperature in the melting chamber was selected at 189 °C. This temperature was selected in order to reduce the thermal degradation of cellulose blends extrusion and to achieve good cellulose dispersion in the matrix. Still hot, and the stopper screw removed the melt was quickly injected through the injection hole of diameter 5.0 mm into the circular disc molder of diameter 150 mm with a plate separation of 2 mm using a piston as shown in Figure 4.3.

![Figure 4.2: Heating and mixing process](image)

![Figure 4.3: Injection molding process](image)
4.1.2 The test samples

The mold takes the shape of the circular disc molder when cooled for about 3 minutes. The mold was taken and a rectangular film sample of approximately $20 \pm 0.5 \times 4 \pm 0.5 \times 2 \pm 0.5 \text{ mm}$ was cut.

![Diagram of sample](image)

**Figure 4.4: Nomenclature and dimensions of the sample**

4.2 Measurements

The main measurements in this research was Dynamic mechanical analysis measurements, however, creep, thermal degradation, diffusion and biodegradability measurements were also done to provide information relating dimensional stability on loading, thermal stability, diffusion and biodegradability analysis.

4.2.1 Dynamic Mechanical Analysis Measurement

Dynamic mechanical behavior of the samples was studied using dynamic mechanical analyzer (DMA 2980 TA instrument) using single cantilever mode. The samples dimensions were about $20 \pm 0.5 \times 4 \pm 0.5 \times 2 \pm 0.5 \text{ mm}$. The equipment was programmed
to scan across a frequency range of 1 to 30 Hz. The temperature used was in the range of -30 to 120 °C and in steps of 2 °C after every frequency sweep.

4.2.2 Creep Measurements

The short-time creep and recovery experiment test were performed using single cantilever mode at different temperatures ranging from 30 to 60 °C in a dynamic mechanical analyzer (DMA 2980) at a constant span of 12 minutes. In these temperatures, isothermal creep tests were run on the specimens with a stepwise increment of 10 °C. Test samples of dimensions 20±0.5 x 4±0.5 x 2±0.5 mm were used for creep tests.

4.2.3 Thermal Degradation Measurements

Thermal stability of pure PP and its blends samples were studied using 10 g weight samples. The thermogravimetric analysis (TGA) was carried out for PP and the blends using the Lindberg/blue-TF55035C Tube furnace in oxidative environment. Heating were done in the range of 25 to 550 °C at a heating rate of 5 °C/min. The initial and final degradation temperature and corresponding percentage weight loss for the samples were noted.

4.2.4 Diffusion measurements

The molded specimens of 0.14 g of each composition were dried for 12 h at 50 ± 2 °C, cooled in desiccators and immediately weighed using an analytical balance until consecutive weighing gave same mass. The samples were then put in water at room temperature. After 1 day, 7 days, 30 days, 60 days, 90 days and 120 days the test
specimens were removed from the test liquid one at a time, gently blotted with a cotton material to remove the excess of water on the surface, and weighed immediately. The difference between the saturated weight and the dried weight was calculated as the water absorption. From Fick’s second law diffusion coefficient, D was calculated.

4.2.5 Biodegradability measurements

Soil was sifted to remove large clumps and plant debris. Ph, temperature and water moisture of the soil were recorded. Samples of each composition (0.14 g) were dried for 12 h at 50 ± 2 °C, cooled in desiccators and immediately weighed until consecutive weighing gave same mass. Samples were removed after 1 day, 7 days, 30 days, 60 days, 90 days, 120 days and 150 days washed in water and dried at 50 ± 2 °C for 12 hours. Samples were then allowed to cool in desiccators at least 12 hours and weighted until a constant mass was obtained on subsequent weighing. The weight of each sample was measured before and after degradation.
CHAPTER FIVE

RESULTS AND DISCUSSION

5.1 Storage modulus (E’) and Loss modulus, (E’’) of pure polypropylene

5.1.1 Effect of frequency

The effects of temperature and frequency on the storage and loss modulus of the samples are shown in Figure 5.1(a) and Figure 5.1(b) from 240 to 393 K at 1, 10 and 30 Hz.

![Graph showing variation of storage modulus (E') and loss modulus (E'') with temperature at different frequencies of pure PP.]

Figure 5.1: Variation of (a) storage modulus E’; (b) loss modulus E’’ of pure PP with temperature at different frequencies of pure PP

It is observed in Figure 5.1(a) that as the frequency is increased, the storage modulus increased. This indicates that, as the frequency increases it becomes more difficult for the
polymer chains to respond to the applied forces and tends to remain in a frozen state. A frozen system stores more energy than a free system. It is also observed in Figure 5.1(a) that the storage modulus decreases with increasing temperature. The reduction in storage modulus with increasing temperature is related to the increase in viscosity and polymer chain mobility of the matrix at higher temperatures.

In Figure 5.1(b) the solid lines have been fitted using equation 3.12 (the loss superposition model function). Two transitions are observed, the first peak (β transition) is a local process associated with inter-lamellar shearing. This is seen at a temperature range of 255 to 275 K. Its intensity decreases with increase in frequency showing poor damping characteristics.

The second peak which is observed at the range of 320 to 355 K is the α-transition related to the main chain motions within the crystals. Its intensity also decreases and shifts to higher temperatures with increase in frequency. These shifts to higher temperatures at higher frequencies is due to the main chain motion which does not allowed enough time to respond to the applied sinusoidal stress and becomes very difficult for the chains to follow the movement of the oscillation showing true relaxation.

5.1.2 Effect of cellulose
A plot showing the variation of storage and loss modulus with respect to temperature is shown in Figure 5.2 and Figure 5.3. It is observed in Figure 5.2(a) that the storage modulus decreases as cellulose intake increases especially at lower temperatures but as the temperature increases, the storage modulus increases with cellulose intake particularly in comparison of 80 PP/20 CL with pure PP as shown in Figure 5.3(a). At
lower temperatures the intensity of storage modulus for pure PP sample is higher than its cellulose blends, this can be attributed to poor interfacial adhesion and incompatibility between the polar cellulose group and the non-polar PP matrix. At higher temperatures, the samples are soft and flexible therefore, when more cellulose are blended with PP, the attractive effects of OH groups in cellulose restricts the chain mobility of the PP matrix leading to increase in storage modulus. This shows that cellulose has increased the stiffness of the blends.

Loss modulus spectra of PP and its cellulose blends loading are shown in Figure 5.2(b) and Figure 5.3(b). From the equation 3.12; that is the loss superposition model function, two major transitions were obtained, the β-transition and α-relaxation. The β-transition is related to the inter-lamellar shearing.

![Figure 5.2(a) Storage modulus; (b) Loss modulus against temperature (240-390 K) of PP and its cellulose blends](image-url)
The intensities of β-transition peaks of 95 PP/5 CL and 90 PP/10 CL is higher than that of pure PP indicating good damping properties. A slight shift to higher temperatures in β-transition is seen especially in comparison between 100 PP/0 CL and 80 PP/20 CL. These indicate that the process in which this transition occurred was delayed by the presence of cellulose so that more energy was required for β-transition to occur.

From Figure 5.3(b), it can be observed that the intensity of α-relaxation peaks of 85 PP/15 CL and 80 PP/20 CL are higher than that of pure PP. This shows that with increase in cellulose intake, the molecular environment participating in the relaxation process increases leading to good damping characteristics. Alpha relaxation (α-relaxation) process is associated with the main chain motion.
5.2 Time-temperature dependence of relaxation time

Figure 5.4 shows that the α-relaxation obeys VFT laws and the process exhibited showed that the motion is main chain motion. Relaxation frequency shows overlaps with cellulose intake. This confirms that cellulose loading has no effect on free volume for relaxation, hence overlapping Vogel temperature \( (T_o) \).

The corresponding VFT fitting parameters are given in Table 5.1. The solid line and VFT parameters have been obtained using Vogel-Fulcher-Tamman model [Vogel, 1921] equation 3.16.
The glass transition temperature ($T_g$) of PP and its blends can be obtained by adding 50 °C to Vogel temperature ($T_o$) [Vogel, 1921].

### 5.3 Creep

#### 5.3.1 Percentage Strain and Recovery

Figure 5.5 shows the strain percentage as a function of time for pure PP and its cellulose blends. From Figure 5.5, the creep stages can be clearly seen, these are instantaneous, primary and secondary deformation. Percentage creep strain increased with increase in temperature for pure PP and its blends, this is due to the fact that temperature decreases the activation barrier for bond dissociation thus allowing molecular chains to untangle, slip and reorient more easily. It is also clearly seen that pure PP sample have lower percentage strain than the blended samples. This can be attributed to the incompatibility between polar cellulose and non-polar PP hence disturbing the PP structure causing more slippage. But as the cellulose concentration increases, attraction of the OH effects

---

Table 5.1 VFT fitting parameters for activation plots of PP/CL blends

<table>
<thead>
<tr>
<th>PP/CL (%) blends</th>
<th>VFT – parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>A</td>
</tr>
<tr>
<td>100:0</td>
<td>4.30 ± 1.53</td>
</tr>
<tr>
<td>95:5</td>
<td>3.80 ± 1.24</td>
</tr>
<tr>
<td>90:10</td>
<td>3.84 ± 1.27</td>
</tr>
<tr>
<td>85:15</td>
<td>3.83 ± 1.27</td>
</tr>
<tr>
<td>80:20</td>
<td>2.24 ± 0.28</td>
</tr>
</tbody>
</table>
increases hence, the structures of the PP matrix are reinforced reducing the deformation of the structure. This can be confirmed by the fact that the deformations of the blends are higher than pure PP but decreases as cellulose intake increases.

From Figure 5.5, the creep stages can be clearly seen, these are instantaneous, primary and secondary deformation. Percentage creep strain increased with increase in temperature for pure PP and its blends, this is due to the fact that temperature decreases the activation barrier for bond dissociation thus allowing molecular chains to untangle, slip and reorient more easily. It is also clearly seen that pure PP sample have lower percentage strain than the blended samples. This can be attributed to the incompatibility between polar cellulose and non-polar PP hence disturbing the PP structure causing more slippage. But as the cellulose concentration increases, attraction of the OH effects increases hence, the structures of the PP matrix are reinforced reducing the deformation
of the structure. This can be confirmed by the fact that the deformations of the blends are higher than pure PP but decreases as cellulose intake increases.

Introduction of cellulose to the PP matrix also disturbs the structure hence affecting the recovery process. The structure recovers poorly but upon increasing cellulose intake, the recovery process increases. This is because the attractive effect of OH groups helps in recovery process.

5.3.2 Creep compliance

The superposition technique exploits the sensibility of the molecular relaxation process to temperature. Under simplifying assumptions, a quantitative equivalence between time and temperature can be achieved. Thus, a long time experiment can be replaced by a shorter one at higher temperatures. To predict long-term data, the creep compliance data at various temperatures were shifted according to the time – temperature superposition principle. The reference temperature selected was 30°C and all the individual creep curves corresponding to different temperature levels were shifted along the logarithmic time axis to superpose to a master curve as shown in Figure 5.6(b). It can be observed from Figure 5.6(a) that all the samples showed an increase in the compliance with increase in temperature this is due to higher macromolecular mobility and softening of the matrix leading to high deformation during creep. From the time temperature superposition technique, the long-time experiment was predicted to be approximately $10^4$ seconds.
Figure 5.7 shows master of master curve of pure PP and its cellulose blends at different period of time. It can be clearly seen that the creep compliance of pure PP is less than its blends over a short time but as the time increases it complies more. It can be predicted that once cellulose are introduce to the PP matrix, it first interrupts the structure of the PP matrix but as the cellulose content increases in the blends, the attractive effect of OH groups increases. Therefore, when the sample entered into a viscoelastic state over a long time, the attractive OH groups offers good reinforcement and stiffness hence reducing deformation. It can also be seen that as the cellulose concentration increases, the creep compliance decreases. This indicates that, the introduction of cellulose enhance creep resistance of the PP material giving it a good creep performance.
The experimental shift factors were tested with WLF model (equation 3.40). Figure 5.8 shows that WLF equation describes the temperature dependence of shift factors for PP and its blends. This shows that the deformation depends on free volume.

5.3.3 Temperature dependence shift factors

Figure 5.7: Master of master curve constructed from the short term creep data compliance of PP and its cellulose blends at different temperatures

Figure 5.8: Temperature dependence of the shift factor ($\alpha_T$) for PP/CL blends
It can be observed from Figure 5.8 that with increase in cellulose content the temperature dependence shift factors decreased. This indicates that, the deformation of the samples depends on free volume. The temperature dependence shift factors obeyed the WLF law.

The WLF fit parameters are shown in table 5.2.

<table>
<thead>
<tr>
<th>PP/CL (%) blends</th>
<th>C₁</th>
<th>C₂</th>
<th>T₀</th>
</tr>
</thead>
<tbody>
<tr>
<td>100:0</td>
<td>11.3±0.25</td>
<td>186.0±1.32</td>
<td>29.9±0.18</td>
</tr>
<tr>
<td>95:5</td>
<td>5.7±0.17</td>
<td>74.8±1.55</td>
<td>29.9±0.26</td>
</tr>
<tr>
<td>90:10</td>
<td>3.9±0.24</td>
<td>36.7±1.86</td>
<td>30.0±0.15</td>
</tr>
<tr>
<td>85:15</td>
<td>5.4±0.19</td>
<td>52.2±0.98</td>
<td>30.0±0.54</td>
</tr>
<tr>
<td>80:20</td>
<td>7.6±0.22</td>
<td>64.0±1.13</td>
<td>29.9±0.37</td>
</tr>
</tbody>
</table>

The values of C₁ and C₂ depend on the morphology or structure of a given material. From table 5.2, the values of C₁ and C₂ have an inconsistent trend with cellulose loading indicating that cellulose has no effect on free volume with respect to temperature. According to Champion et al. [2001], an increase in C₁ and C₂ of a particular material implies that the material is more crystalline or cross-linked as a result of increase in free volume and expansion with respect to temperature.
5.4 Thermogravimetry Analysis (TGA)

5.4.1 Thermogravimetric analysis of PP/CL blends

TGA studies have been carried out to determine thermal stability and degradation temperatures of polypropylene and its cellulose blends. The thermal degradation behavior of pure PP with various percentage of cellulose loading has been studied employing TGA and DTG thermograms, as shown in Figure 5.9(a) and 5.9(b).

![Figure 5.9(a) TGA and 5.9 (b) DTG thermo grams for pure PP and its blends](image)

From Figure 5.9(a), it is observed that as the cellulose loading increases, the thermal stability of the blends decreases while the ash content increases. This in turn retards thermal degradation and reduce the production of toxic gases as reported by Dimitrova et al., 2008.
It can also be seen from Fig 5.9(a) that the weight loss of pure PP matrix and its blends showed two stage degradation processes in the range of 40 to 160°C and 280 to 520 °C. These results are confirmed by the presence of two peaks in the derivative weight loss curve as seen in Figure 5.9(b). The first stage which occurs at lower temperatures was probably due to the random chain scission or branching and breakage of glucosidic linkage in cellulose that is the unzipping of the cellulose chain (transglycosidation) to form Laevoglucosan [Girija et al., 2005; Lomankin et al., 2011].

The second peak which occurs at higher temperatures is attributed to decrease in degradation of the carbon chains of the PP matrix (PP backbone) as the cellulose increases. Cellulose decomposes at a temperature of 250 °C to 350 °C [Lomankin et al., 2011]. Table 5.3 shows a variation of peak decomposition temperature of PP and its cellulose blends from DTG curves.

<table>
<thead>
<tr>
<th>PP/CL (%) blends</th>
<th>Peak decomposition T (°C) ± 2 °C</th>
<th>Chain scission and branching T (°C) ± 2 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>100:0</td>
<td>478</td>
<td>96</td>
</tr>
<tr>
<td>95:5</td>
<td>458</td>
<td>130</td>
</tr>
<tr>
<td>90:10</td>
<td>442</td>
<td>132</td>
</tr>
<tr>
<td>85:15</td>
<td>436</td>
<td>180</td>
</tr>
<tr>
<td>80:20</td>
<td>425</td>
<td>209</td>
</tr>
</tbody>
</table>

It can be seen from Table 5.3 that as the cellulose concentration increases the decomposition temperature decreases.
5.4.2 Activation energy

The activation energy was directly obtained from the slope of the linearly regressed line of \( \ln(\ln(1/x)) \) versus 1000/T as shown in Figure 5.10. The curves are linear suggesting a good agreement with the Broido equation. The solid lines have been fitted using the model equation (3.46)

![Figure 5.10: Natural logarithm of reciprocal residual mass versus reciprocal temperature of PP and its blend](image)

The results obtained are summarized in Table 5.4. The results showed two activation energies for each sample. The activation energies \((E_{a1})\), are due to the additives to polypropylene, dehydration and decomposition of cellulose. The activation energies \((E_{a2})\), are due to the thermal decomposition of polypropylene and its blends since the energy required for the process to occur decrease with cellulose loading. This indicates that the thermal stability of PP and its cellulose blends decreases as the amount of cellulose increases.
Table 5.4 Activation energies for pure PP and PP/CL blends

<table>
<thead>
<tr>
<th>PP/CL (%) blends</th>
<th>$E_{a1}$ due to branching and chain-scission.</th>
<th>$E_{a2}$ due to thermal decomposition</th>
</tr>
</thead>
<tbody>
<tr>
<td>100:0</td>
<td>30.2 ± 0.23</td>
<td>72 ± 0.78</td>
</tr>
<tr>
<td>95:5</td>
<td>26.2 ± 0.42</td>
<td>59.1 ± 0.86</td>
</tr>
<tr>
<td>90:10</td>
<td>20.9 ± 0.59</td>
<td>59.9 ± 0.71</td>
</tr>
<tr>
<td>85:15</td>
<td>22.6 ± 0.17</td>
<td>40.1 ± 0.69</td>
</tr>
<tr>
<td>80:20</td>
<td>19.2 ± 0.30</td>
<td>40.6 ± 0.55</td>
</tr>
</tbody>
</table>

The activation energy ($E_{a2}$) due to thermal decomposition of pure polypropylene (72 kJ/mol) is in agreement with the activation energy for pure PP of 61.8 and 66.7 kJ/mol reported by Al-Mulla et al. [2003] and Dimitrova et al. [2008] respectively using the Friedman's technique. The difference in our calculated value is probably due to difference in method used.

5.5 Diffusion

5.5.1 Diffusion Results

Figures 5.11 present the average water uptake for PP and its cellulose blends immersed in water for four months at room temperature. For the first 750 hours, water uptake increased and starts to decrease slowly up to around 1500 h beyond this time; a plateau was formed for all the blends. After exposure to the water bath, samples with 20 %, 15 %, 10 %, 5 % and 0 % cellulose absorbed just over 6 %, 4.7 %, 2.7 %, 1.6 % and 0.21 % respectively of water when equilibrium was reached.
Equilibrium in the water bath was reached at approximately 1300 hours for 20 % cellulose, 1700 hours for 15 % cellulose, and 2200 hours for 10 % cellulose and 2500 hours for 5 % cellulose. Moisture uptakes of the blends increased with increased cellulose contents and immersion time. Thus, in agreement with that reported by Khalid et al. [2009] that moisture uptake increased with immersion time and increasing filler concentrations. During injection molding process, a full skin of hydrophobic PP forms at the surface of the blends providing a barrier against water absorption but water can still be absorbed through surfaces where the cellulose is exposed as a result of breakage or cutting. The control PP absorbed only 0.21 % water as a result of exposure indicating that water is absorbed by the cellulose component in the blends. Because the PP absorbed minimal amount of water, it can be assumed that all the water absorbed by the blends is absorbed by hydrophilic cellulose and not hydrophobic PP.
The decrease in the rate of water intake with time of immersion could be due to concentration gradient across the two materials. Initial water molecules added to cellulose fibers are strongly bonded as in a hydrate [Danjaji et al., 2002]. Bhattacharya and Mani [1998] also argued that when water penetrated into the polymer blends and bonded with the OH groups, the cellulose granules swelled and reduced the gap between their molecules and space to the matrix molecules. As the cellulose content rose, the particles crowded and the gap became smaller and narrower. Thus diffusion of water became difficult and the rate of water intake reduced.

To determine the diffusion coefficient (D), plots of $\frac{M_t}{M_{\infty}}$ against $t^{1/2}$ for pure PP and its blends in water was plotted as shown in Figure 5.12.

Figure 5.12: Fickian diffusion plots of $\frac{M_t}{M_{\infty}}$ versus $t^{1/2}$ for PP/CL blends
From Figure 5.12, the absorption curves are linear in the initial stages and above the linear portion the curves form a plateau. The linear initial curves indicate that diffusion followed a Fickian process. This was used to calculate the diffusion coefficient (D). The diffusion coefficient for PP/CL blends are given in the Table 5.5.

Table 5.5: Diffusion coefficient of PP/CL blends

<table>
<thead>
<tr>
<th>PP/CL (%) blends</th>
<th>D (cm²/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>100:0</td>
<td>4.89 E-10</td>
</tr>
<tr>
<td>95:5</td>
<td>1.04 E-08</td>
</tr>
<tr>
<td>90:10</td>
<td>1.54 E-08</td>
</tr>
<tr>
<td>85:15</td>
<td>2.77 E-08</td>
</tr>
<tr>
<td>80:20</td>
<td>4.21 E-08</td>
</tr>
</tbody>
</table>

The diffusion coefficient for pure PP sample is $4.89 \times 10^{-10}$ cm²/s. This value is close to $7.5 \times 10^{-9}$ reported by Ramazan and Basel [2006] for pure polypropylene. The difference is probably due to the differences in the temperature used, film thickness and the method used to determine D. Diffusivity increases with cellulose intake due to polar hydroxyl groups in the matrix since hydrogen bonding with water molecules increased water uptake. Hence, blending cellulose with polypropylene can improve the permeability of polypropylene material.
5.6 Biodegradability

5.6.1 Biodegradability Results

Figure 5.13 shows the change in the weight as a function of time for the PP/CL blends buried in the soil. Reduction in weight loss was observed after a specific period of time.

The degradation process could be divided into two stages. In the first stage from 10-90 days, the rate of biodegradation increases rapidly and this can be attributed to the availability of highly polar hydroxyl groups in cellulose increasing hydrophilicity hence making the blend more compatible with microorganisms. The second stage from 90 days onwards forms a plateau. This is attributed to the degradation of PP matrix. Table 5.6 gives the number of years the samples could completely degrade.
Table 5.6: Lifespan of PP and its blends

<table>
<thead>
<tr>
<th>PP/CL (%) blends</th>
<th>Time in years</th>
</tr>
</thead>
<tbody>
<tr>
<td>100:0</td>
<td>20,000± 100</td>
</tr>
<tr>
<td>95:5</td>
<td>164± 10</td>
</tr>
<tr>
<td>90:10</td>
<td>9± 2</td>
</tr>
<tr>
<td>85:15</td>
<td>7.2± 2</td>
</tr>
<tr>
<td>80:20</td>
<td>5± 1</td>
</tr>
</tbody>
</table>

The biodegradation period was calculated using regression lines. Pure PP was resistant to biodegradation due to the presence of additives, antioxidants and other stabilizers which make it toxic to microorganisms hence slow down biodegradation. It is also due to the hydrophobic backbones consisting of long carbon chains that give high resistivity against hydrolysis [Khabbaz et al., 2001]. Cellulose are more susceptible to microorganisms thus, when PP/CL blends are deposited in the environment, various microorganisms consume the cellulose, which leave the PP blend in form which is full of voids. This form enables the easier disintegration of the material into small pieces. It also increases the total surface area accessible to oxygen. As a result, the oxidation of PP becomes easier.
CHAPTER SIX

CONCLUSION AND RECOMMENDATION

6.1 Introduction

In this research, a number of experiments have been conducted and analysed. These includes DMA, creep test, diffusion and degradability behaviour of PP/CL blends. This chapter summarizes the important outcomes, findings and analysis of this research and suggests future research works.

6.1.1 Conclusion

The dynamic mechanical properties [the storage modulus (E’) and loss modulus (E’’)] were investigated based on the DMA spectra as a function of frequency and temperature. These dynamic properties were influenced by the presence of frequency, temperature and cellulose in the PP matrix. As the frequency increased, the storage modulus increased. At lower temperatures the intensity of storage modulus for pure PP sample is higher than its cellulose blends showing that the blends have poor damping characteristics. At higher temperatures, the samples are soft and flexible therefore, when more cellulose are blended with PP, the attractive effects of OH groups in cellulose restricts the chain mobility of the matrix leading to increase in storage modulus. This shows that cellulose has increased the stiffness of the blends. From the loss superposition model function, two major transitions were obtained, the β-transition and α-relaxation. The β-transition is related to the inter-lamellar shearing while Alpha relaxation (α-relaxation) process is associated with the main chain motion. Percentage creep strain increased with increase in temperature for pure PP and its blends. Pure PP sample have lower percentage strain than the blended samples. This can be attributed to the incompatibility between polar cellulose
and non-polar PP but as the cellulose concentration increases, attraction of the OH effects increases hence, the structures of the PP matrix are reinforced reducing the deformation of the structure. Introduction of cellulose to the PP matrix also disturbs the structure hence affecting the recovery process. The structure recovers poorly but upon increasing cellulose intake, the recovery process improves. This is because the attractive effect of OH groups helps in recovery process.

The values of activation energies decreased with increase in cellulose loading indicating that the thermal stability of PP/CL blends are lower than pure PP. This shows that the toxic by-products decrease with increase in cellulose intake leading to less environmental pollution.

From the Fickian diffusion plots of $\frac{M_t}{M_{\infty}}$ versus $t^{1/2}$ for PP/CL blends, the diffusion of water followed Fickian process. The rate of uptake was greater with increase in cellulose content. Diffusion coefficient calculated from the mass uptake revealed that the equilibrium uptake was directly proportional to the diffusion coefficient. Based on this study, it can be observed that cellulose has strongly affected the diffusion of PP/CL blends.

The higher the content of cellulose in polypropylene matrix showed more facile biodegradation in the PP blends than pure PP promising non-environmental pollutants. Cell surface hydrophobicity showed an important role in biofilm formation, which is prerequisite for biodegradation.
6.1.2 Recommendations
Different techniques such as Differential Scanning Calorimetry (DSC), Dielectric Spectroscopy and scanning electron microscopy (SEM) may be used in order to reveal more light on rheological structure of the blends and hence the ability to give a more accurate explanations of the molecular dynamics of these PP/CL blends. Differential scanning calorimetry and Dielectric spectroscopy could shed more light on glass transition temperatures and dipole relaxation processes respectively. Scanning electron microscopy could shed more light on morphology. To improve compatibility and interfacial adhesion, polypropylene and cellulose should be blended with compatibilizers such as maleic anhydride grafted polypropylene (MA-PP)

Due to the nature of viscoelasticity of PP to temperature and stress, the combined effect of stress and temperature is a critical concern for the application of PP/CL blends. Therefore, instead of simple constant loading stress, cyclic loading may be used since this happens in practical situations. In the study of DMA, creep and TGA only the effect of increasing temperatures was considered, hence, the effect of fluctuating or decreasing temperatures could be considered in the future research.

Other techniques such as laser interferometry, microdielectrometry, Raman spectroscopy, nuclear magnetic resonance imaging or radiolabelled penetrants can be used to determine water uptake in the future research. In the study biodegradability, use of natural soil that is outdoor environment was experimented. Thus for future research, the use of direct application of microbes such as bacteria and fungi in indoor environment can be tested.
From the research study it is clearly seen that blending PP with cellulose improves its dynamic mechanical and diffusion properties. Also it would help in reducing accumulation of these plastics in the environment and also reduce emission of toxic gases in the atmosphere since cellulose reduces thermal stability of the polypropylene. Hence, PP/CL blends can be used in different sectors such as automotive parts, furniture, computer components, packaging etc.


APPENDIXES

APPENDIX I: Dynamic Mechanical Analyzer 2980 TA
APPENDIX II: Components of the DMA

The DMA 2980 dynamic mechanical analyzer (TA instrument) is based on a patent-pending design that optimizes the combination of these critical components. Specifically, the analyzer incorporates a noncontact **direct drive motor** to deliver reproducible forces (stresses) over a wide dynamic range of 0.001-18N; an **air bearing shaft support and guidance system** to provide frictionless continuous travel over 25mm from evaluating polymers at large oscillating amplitude (±0.5–10,000μm); and **optical encoder displacement sensor** to provide high resolution of oscillation amplitude, which results in excellent modulus precision and tan δ sensitivity (0.0001); and a **bifilar-wound furnace** complemented by a gas cooling accessory to allow a broad temperature range (-150 to 600 °C) to be covered. The DMA 2980 also features a variety of damping configuration to accommodate rigid bars, fibers, thin films and viscous liquids in bending, compression, shear, and tension modes of deformation.
APPENDIX III: Single/Dual cantilever clamp

Single/Dual Cantilever Clamp Installed (Shown with Sample Mounted)

TA INSTRUMENTS DMA 2980
APPENDIX IV: Lindberg/blue mini-mite tube furnace