MECHANICAL PROPERTIES AND THERMAL DEGRADATION OF BITUMEN-ACACIA SAP COMPOSITES

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I56/CE/11500/2007

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

November 2012
**DECLARATION**

I declare that the work presented in this thesis is my original work and has not been presented for the award of any degree or any other award in any University

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We confirm that the work reported in this thesis was carried out by the candidate under our supervision.

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<th>Dr. A. S. Merenga</th>
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DEDICATION

To my beloved father, mother and my daughter Neema
ACKNOWLEDGMENTS

I am deeply grateful to Dr. A. S. Merenga for his continuous support throughout the entire work. I have gained a lot from his knowledge in polymers and more so his kindness, interest, open-minded approaches to ideas and constant guidance that has brought this research to successful completion.

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<tr>
<td>$a_T$</td>
<td>Horizontal shift factor</td>
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<tr>
<td>$E_a$</td>
<td>Activation energy</td>
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<td>$\eta$</td>
<td>Dynamic viscosity</td>
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<td>$\varepsilon$</td>
<td>Strain</td>
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<td>$\eta^*$</td>
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<td>$\tau_o$</td>
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<td>Complex compliance</td>
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<td>$k$</td>
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<td>$M$</td>
<td>Relaxation modulus</td>
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<td>$n$</td>
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<td>Universal gas constant</td>
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<td>Glass transition temperature</td>
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<td>$T$</td>
<td>Absolute temperature</td>
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<td>$T_o$</td>
<td>Vogel temperature</td>
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<td>Symbol</td>
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<tr>
<td>$T_m$</td>
<td>Melting temperature</td>
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<td>$V$</td>
<td>Total volume</td>
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<td>$V^*$</td>
<td>Minimum volume</td>
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<td>$V_o$</td>
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<td>$\delta$</td>
<td>Phase lag</td>
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<td>Dashpot stress</td>
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<td>$\tau$</td>
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<tr>
<td>$\omega$</td>
<td>Angular frequency</td>
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<td>$x$</td>
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# ABBREVIATIONS AND ACRONYMS

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<tbody>
<tr>
<td>B</td>
<td>Bitumen</td>
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<tr>
<td>AS</td>
<td>Acacia sap</td>
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<tr>
<td>CRMB</td>
<td>Crumb rubber modified bitumen</td>
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<tr>
<td>DMA</td>
<td>Dynamic Mechanical Analysis</td>
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<tr>
<td>DMTA</td>
<td>Dynamic mechanical thermal analyzer</td>
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<tr>
<td>DSC</td>
<td>Differential scanning calorimetry</td>
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<tr>
<td>dT/dx</td>
<td>Heating rate</td>
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<tr>
<td>EBA</td>
<td>Ethylene butyl acrylate</td>
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<td>EVA</td>
<td>Ethylene-vinyl-acetate</td>
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<tr>
<td>MS</td>
<td>Mass spectrometry</td>
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<tr>
<td>FTIR</td>
<td>Fourier transforms infra-red</td>
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<tr>
<td>IR</td>
<td>Infrared spectrometry</td>
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<tr>
<td>PMA</td>
<td>Polymer modified additives</td>
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<tr>
<td>PMB</td>
<td>Polymer modified bitumen</td>
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<tr>
<td>RPE</td>
<td>Recycled polyethylene</td>
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<tr>
<td>SBR</td>
<td>Styrene butadiene rubber</td>
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<tr>
<td>SBS</td>
<td>Styrene butadiene styrene</td>
</tr>
<tr>
<td>SEBS</td>
<td>Styrene-ethylene-butylene-styrene</td>
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<tr>
<td>SLS</td>
<td>Standard linear solid</td>
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<tr>
<td>TA</td>
<td>Thermal analysis</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>
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<tr>
<td>VFT</td>
<td>Vogel-Fulcher-Tamman</td>
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<td>WLF</td>
<td>William-Landel-Ferry</td>
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ABSTRACT

The rapid increase in traffic intensity, axle loading, rigorous climatic changes and commercial road transport continues to impose severe demands of load and environment on the highway system. Bitumen mostly used as a binder for road construction, waterproofing agent, coating, and insulation among others has poor mechanical and thermal properties. Different synthetic binder modifies that are being used to improved performance lead to environmental pollution during disposal. Therefore, there is need to use natural modifies which are environmental friendly and improve performance. Acacia sap which is stiff has been used successfully for bitumen modification. Composites of bitumen-acacia sap with different composition of sap percentage ranging from 0% to 62.5% were prepared by injection drawing process. The composites were analyzed by dynamic mechanical analysis (DMA 2980 TA) for relaxation processes and creep analysis, and thermogravimetric analysis (TGA) for thermal properties. The dynamic mechanical analysis measurements were carried out in the frequency scan of 0.3, 1, 3, 5, 10, 15, 20 and 30 Hz and temperature range from 3 to 50 °C. The dynamic mechanical analysis measurement indicated significant increase of the storage modulus and Loss modulus of modified bitumen; depending on the sap content in the bitumen matrix. One relaxation process was observed which was assigned to main chain motion followed Vogel-Fulcher-Tamman (VFT) law. There was also a shift towards a higher value of glass transition temperature of the modified bitumen as acacia sap loading increased. This implies increased resistance to deformation of the binder. Creep analysis showed that the creep decreased with increase of acacia sap loading in the composites and also increased with increase of time and temperature. Temperature dependence of storage master curves follows William-Landel-Ferry (WLF) law. The time-temperature superposition principle master curves indicated prediction of the long-term property of composites and extend up to more than 10^6 s in time scale. The composites with 25% sap and more showed a tendency of faster decrease in storage modulus, which indicates that a low content of sap can enhance creep resistance of materials to a large extent. Thermal degradation measurements were carried out in an oxidative atmosphere using Lindberg/blue-TF55035C tube furnace at heating range of 25-550°C at a rate of 5 °C/min. TGA measurements for all composites showed a single step weight loss. The activation energy of thermal degradation of the blends decreased with acacia sap intake. This implied decreased thermal stability.
CHAPTER ONE

INTRODUCTION

1.1 Background to the Study

Bitumen is a natural polymer of low molecular weight mainly used as a binder in road construction. It is a byproduct obtained by fractional distillation of crude oil and catalytic cracking of hydrocarbons (Saleh, 2004). Bitumen is a black, sticky thermoplastic hydrocarbon made of four main components namely; saturates, aromatics, resins and asphaltenes. Bitumen has good adhesive, high impermeability and viscoelastic properties i.e. at low temperatures it is rigid and brittle, at room temperature it is flexible, and at higher temperatures it flows. It has wide range of applications such as construction of roads with an aggregate, paving of airfield, waterproofing agent, coating, insulation, to more specialized purposes such as when blended with proportion of polymers used in built up membranes for the roofing industry (Fawcett et al., 2003). However, bitumen’s viscoelastic behavior is poorly related to its microstructure since a precise molecular structure and repeat unit is not established.

With increased traffic levels, axle loadings and the rigorous climatic changes, high performance roads are required. Road performances depend mainly on the rheological properties (storage modulus, loss modulus and loss factor) of the bitumen because in asphalt mixtures bitumen is the only deformable component and continuous phase (Frederika et al., 2010). Viscoelastic properties are of great importance in predicting road characteristics over wide range of temperatures and loadings. The deformation properties of bitumen are determined mostly by its chemical composition and the
structure of its molecules; but even when the ratio of asphaltenes to maltenes (aromatics, saturates and resins) is optimal, there is a narrow temperature range in which pure bitumen exhibits suitable rheological behavior necessary for good road performance. Moreover, research have been carried out in order to extend the workability of bitumen to prevent road defects like thermal cracking and rutting at lower and higher temperatures respectively. This includes modification of bitumen with polymers. Bitumens modified with polymers have improved strength and resistance to aging (Frederika et al., 2010). However, only a few polymer products are suitable for the bitumen modification such as polyethylene and rubber among others. This is because of poor compatibility of the modifier and bitumen since bitumen and the polymers have different properties and molecular parameters. This results to production of polymer networks with poor rheological properties and different morphological properties that does not favour improvement of the bitumen. Polymers have narrow temperature range, which limits their applications. Materials that are stable at low and high temperatures are likely to be better performances.

The physical properties of the polymers can be improved by increasing chain interactions between the polymers or by chain stiffening. Chain interaction can be enhanced by use of crystalline materials, since crystalline materials are more stable than amorphous materials. This crystallinity is enhanced by symmetric regular structures and highly polar groups. Polar side groups enhance the intermolecular forces due to presence of OH and CN groups. Acacia sap is semi-crystalline because of its regular structure. The softening temperature of the bitumen can be increased by chain-stiffening. This is achieved by use of aromatics or heterocyclic structures in the polymer chain such as -CO-, -NH-, -CH₂-, O-CO- and –O-CO-O-.
1.2 Statement of the Research Problem

Bitumen mechanical and thermal properties have not been satisfactory during its application. Different synthetic binder modifies that are being used to improve its performance have led to environmental pollution during disposal. Therefore, there is need to use natural binder modifies which improves performance and are environmental friendly instead of incineration and land fill. This research has focused on the various proportions in which bitumen was mixed with natural polymer (acacia sap) to improve its performance, disposal, rheological and morphological properties. A combination of dynamic mechanical analysis, creep analysis and thermal degradation measurements on bitumen-acacia sap composites are expected to give more insight into interchain interactions due to the highly polar hydroxyl groups in acacia sap.

1.3 Objectives of the research study

1.3.1 Main objective

This research work is aimed at investigating the mechanical and thermal properties of bitumen-acacia sap composites.

1.3.2 Specific objectives

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

i) Thermal degradation and stability in bitumen.

ii) Relaxation processes in bitumen.

iii) Phase inversion in bitumen.

iv) Creep behavior of bitumen.
1.4 Rationale

Bitumen, obtained from distillation plants and catalytic cracking of hydrocarbons has wide application such as road paving, waterproofing agent, roofing, insulation and coating among others. Bitumen by itself often cannot meet the performance requirements for its application. For example, increased use of roads by heavy traffic as well as high temperatures has resulted in flow of bitumen in our roads, and cracking at low temperatures. This is as a result of poor thermal and mechanical properties of bitumen. A number of approaches have been developed to modify bitumen to improve its properties in order to meet its performance requirements. These approaches includes; blending it with other polymers, addition of additives such as glass fibers, rubber among others. Acacia sap is stiff. Bitumen flows very fast under applied load. Therefore, mixing bitumen with acacia sap improves its mechanical properties such as reduced flow by making it stiff and improves deformation and thermal properties such as stability and degradation. Dynamic mechanical analysis, creep and thermal degradation measurements provides information related to the mechanical properties, dimensional analysis, stability and degradation of the blends.
CHAPTER TWO

LITERATURE REVIEW

2.1 Introduction

This chapter discusses briefly some bitumen modifications that have been made with different modifiers and their effects on thermal stability, miscibility, deformation rheology and morphology of the bitumen.

2.2 Bitumen Blends

Most commonly used polymers for bitumen modification are styrene-butadiene styrene (SBS), styrene-butadiene rubber (SBR), ethylene-vinyl-acetate (EVA), styrene-ethylene-butylene-styrene (SEBS), ethylene butyl acrylate (EBA) and polyethylene among others. When SBS is blended with bitumen, it absorbs the oil from the bitumen and swells up; continuous polymer phase is formed throughout the polymer modified bitumen (PMB) and significantly increases the elasticity of the bitumen (Sengoz and Isikyakar, 2008). Sassan and Nader (2009) carried out a research in Iran to investigate the effect of SBR on thermal susceptibility, elastic behavior, and fatigue cracking resistance and ageing stability of bitumen, the research showed that addition of 10-18% rubber improves service temperatures of bitumen. According to Becker et al. (2001), SBR latex polymers increase the ductility of bitumen pavement, which allows the pavements to be more flexible and crack resistance at low temperatures. The addition of additives (SBS, linker, polyoctenamer, wax and polyphosphoric acid) to CRMBs increases the values of both storage and loss moduli, and decreases the values of the loss tangent, in relation to the additive-free binder, this results to increase in the viscoelasticity of the bitumen (Gonzalez et al. 2010). Isaacsson and Xiaohu (2001) carried out a research to investigate the effect of
SEBS and EBA on the rheological and morphological properties of bitumen. They found that SEBS improves bitumen rheology over a wide temperature range, decreased complex modulus and increased phase angle while EBA increased complex modulus and decreased the phase angle. Serfass and Samanos (1996) carried out studies to investigate the effect of the addition of fibers to asphalt concrete. They found that addition of fibers to asphalt improved the fixation of the asphalt binder in the mix, improved skid resistance over unmodified mixtures and reduced temperature susceptibility.

Fawcett et al., (1999) carried out a study to investigate the effects of Polyolefins on the stiffness of bitumen. The study revealed that bitumen became stiff on addition of Polyolefins and the stiffness decreased with increase of temperature. Joel (1995) carried out a number of studies on the effect of hemicelluloses in bitumen. The studies revealed that hemicellulose lowered the loss modulus and raised the storage modulus. Cristina et al. (2008) carried out a research to determine the effect of recycled polyethylene (RPE) on thermal and mechanical properties of bitumen. The study showed that addition of RPE modifies its rheological properties such as increases storage and loss moduli, viscosity, decreases thermal susceptibility and glass transition temperature. Garcia et al. (2004) carried out a research to study the effect of modification of bitumen with EVA recycled polymer. The research revealed that EVA enhances bitumen service properties, increases viscosity, with the consequent improvement of temperature and changes in the flow behavior due to changes of the microstructure in the PMA morphology.
Meltem et al. (2009) carried out a research to determine the effect of epoxy resin on the rheological properties of bitumen. The research showed that addition of 2% epoxy increased viscosity, softening point, glass transition temperature and stability but decreased heat sensitivity, surface energy, penetration and stripping. Therefore, modified bitumen can be recommended for use in hot climates, humid regions, in roads with heavy traffic levels, at road curves and at bus stations to prevent rutting, bleeding, cracking, stripping and aging. Waste epoxy powder could be substituted for epoxy resin for further economy and environmental advantage.

2.3 General Polymer blend studies

Some polymers can be made to degrade photo-chemically by incorporation of carboxyl groups that absorb ultraviolet (UV) radiation to form excited states that are energetic enough to undergo bond cleavage (Gindl, 2006). A combination of light-sensitive and hydrolysable functional groups are more effective in degrading high molecular weight polymers in natural environments (Rosenau, 2005). Cellulose ethers prepared by pretreating cellulose with base then reacting with halogens compounds are degradable (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 form a group of biodegradable cellulose (Barbut and Mittal, 1996). Chen and Wen (2010) carried out a research on the effect of EVA graft copolymer on bitumen thermal stability; the study showed that thermal stability slightly increased with addition of EVA.

Francisco et al. (2010) carried out a research to determine the effect of ground tire rubber and novel recycled polyethylene on thermo-mechanical properties of bitumen. The study showed that ground tire rubber improves the thermo-rheological behavior
of bitumen at low in-service temperatures while the recycled polyethylene improves the high in-service temperatures.

Decoene (1990) studied the effects of cellulose fibers on bleeding, void content reduction, abrasion, and drainage in porous asphalt. Cellulose fibers in the mixture allowed asphalt contents to be increased while drastically decreasing bleeding of the binder. No changes were observed in either void content or abrasion with the addition of cellulose fibers. Stuart and Malmquist (1994) evaluated two loose cellulose fibers, a pelletized cellulose fiber, and two polymers. The mixtures were evaluated for binder drain-down and resistance to rutting, low temperature cracking, aging and moisture damage. Drain-down tests showed that all mixtures with fiber drained significantly less than those with polymers or the control. Fiber modified mixtures were the only ones to meet test specifications for drain down. The control samples were found to have excellent resistance to rutting and no significant difference was observed between the control and mixtures with modified binder. Low temperature and moisture damage results were inconclusive. Polymer modified mixtures were found to have better resistance to aging.

Cellulose fibers were used in the study of stone matrix asphalt by Selim et al. (1994). Testing included binder drain-down, moisture susceptibility (reported as tensile strength ratio), and static creep modulus and recovery efficiency. Fibers were added to mixtures containing standard and polymer modified binders. Binder drain-down results show dramatic improvement in all mixtures containing the cellulose fibers. Mixtures with plain asphalt binder and fibers exhibited the highest indirect tensile strength and tensile strength ratio after conditioning compared to polymer modified
mixtures containing fibers that showed the lowest tensile strength and resistance to moisture induced damage of all the mixtures tested. Although variable, statistical analysis proved that creep modulus and recovery efficiency were better in mixtures containing fibers and plain binder rather than with fibers and polymer modifier.

Khalid et al. (2009) carried studies on the effect of cellulose on thermal and dynamic behavior of polypropylene polymer; they found that thermal stability and decomposition temperature decreased, storage modulus increased and loss modulus decreased with increase of addition of cellulose. Mechanical behavior of a polymer depends upon the temperature in relation to the glass transition temperature ($T_g$) of the polymer and the time scale of deformation (Sperling, 1992). Fawcett and Lort (2003) carried out a study of blends of bitumen with polyethylene; the study showed that bitumen lowered the melting point and the glass transition of the polyethylene. Mohammed et al. (2003) carried a research to investigate the effect of addition of glass fiber to bitumen. They found that it increases the flow value and resistant to structural distress that occur in road pavement as a result of traffic loading thus improving the fatigue life by increasing the resistance to cracking and permanent deformation.

Jakab et al. (2000) analyzed the effect of cellulose derivatives on polypropylene, polystyrene and polyethylene thermal degradation. He found that the presence of cellulose materials produced a slight increase on the degradation temperature associated with a change in the degradation of polypropylene. The yield of monomer and trimmer from thermal decomposition of polystyrene was reduced in the presence of cellulose derivatives, indicating that the radical chain reactions are hindered by the
presence of lignocellulosic char. On the other hand, the effect of polypropylene on thermal decomposition of cellulose was negligible. The polymer matrix can influence the thermal degradation of cellulosic materials. Shaopeng and Ling (2008) carried out a study to investigate the effects of photo-oxidation of bitumen by exposing pressed thin films of bitumen; the results showed that the level of UV irradiation intensity had a significant influence on the level of photo-oxidation of the bitumen. Naskar et al. (2010) carried out a study to investigate the effect of waste plastics on bitumen; they found that waste plastics increased thermal stability of bitumen. Vasiljevic et al. (2010) carried out a study to investigate influence of LDPE on mechanical properties of bitumen; they found that LDPE increased the storage and loss moduli of bitumen. Gupta et al. (2003) carried out a research to investigate the effect of mineral fillers on mechanical properties of bitumen; the results showed that mineral fillers increased the softening point and miscibility of bitumen.

Despite the researches that have been done on bitumen and cellulose, there is limited information on the influence of acacia sap on the mechanical, creep and thermal degradation of bitumen-acacia sap composites. This research gives an insight into the dynamic mechanical properties, creep behavior and thermal degradation of bitumen-acacia sap composites.
CHAPTER THREE

THEORETICAL ASPECTS OF THE MEASUREMENT TECHNIQUES

3.1 Introduction

Molecular dynamics of polymers can be studied by dynamic mechanical analysis (DMA), dynamic mechanical thermal analyzer (DMTA), dielectric spectroscopy, X-ray scattering, FTIR spectroscopy techniques, thermogravimetric analysis (TGA) among others. The methods of interest in this study are dynamic mechanical analysis, creep and thermogravimetric analysis. The dynamic mechanical analysis is well established for polymer characterization and analysis. The storage modulus and loss modulus curves are used to interpret the dynamics of polymers when the polymer chain changes. Environmental changes affect chain movement, which has a macroscopic effect on the material in terms of its mechanical strength, ductility, flow, viscosity and other physical characteristics. Curves of storage and loss modulus reveal a lot of information about the mechanical state of the material and even a possibility of predicting the mechanical behavior of the material over a long period of time. Thermogravimetric analysis is used to reveal thermal properties of the blends. In order to understand the mechanical, thermal properties and measurements involved in polymers, a brief theory is presented below.

3.2 Dynamic Mechanical Analysis Technique

Dynamic mechanical analysis, DMA, is a very popular and powerful technique that measures the transitions in materials because it is sensitive to side chain or main chain motions and local models in polymers. It characterizes the mechanical responses of materials by monitoring property changes with respect to temperature and/or frequency of oscillation. The technique separates the dynamic response of materials
into two distinct parts: an elastic part \( (E') \) and a viscous damping component \( (E'') \).

Specifically in DMA a variable sinusoidal strain \( (\varepsilon) \) or stress \( (\sigma) \) is applied to a sample and the resultant sinusoidal stress or strain is measured (Ward and Hadley, 1993). If the material being evaluated is purely elastic, the phase difference between the stress and strain is zero (i.e. stress and strain are in phase). The stress \( \sigma \) and the deformation (strain) \( \varepsilon \) are related through the Young modulus \( E \) as follows:

\[
\sigma = E \varepsilon
\]  

(3.1)

The modulus is often known as the rigidity and is a quantity that is a representative of the materials resistance to deformation. Its reciprocal is the compliance, \( J \).

If a material is purely viscous, the phase difference is 90°. However, most real-world materials including polymers are viscoelastic, both behave as elastic (Hookean) solid and viscous (Newtonian) liquid, such materials exhibit a phase difference between the extremes. This phase difference, together with the amplitudes of the stress and strain waves, is used to determine a variety of fundamental material parameters, including storage and loss modulus, loss factor (\( \tan \delta \)), complex and dynamic viscosity, storage and loss compliance, transition temperatures, creep, and stress relaxation as well as related performance attributes such as rate of degree of cure, sound absorption impact resistance, and morphology (William and Perkins, 1999).

Dynamic mechanical analysis measures the viscoelastic properties using either transient or dynamic oscillatory tests. Transient tests include creep and stress relaxation. In a creep relaxation, a stress is applied on a sample and held constant while the deformation is measured versus time. After a short time, the stress is removed and the recovery is measured as a function of time. In a stress relaxation, a
deformation is applied to the sample and held constant, and the degradation of the stress required in maintaining the deformation is measured as a function of time. The sample is then released to an unstressed state, and its recovery is measured as a function of time. The dynamic oscillatory test is the most common, where a sinusoidal stress (or strain) is applied to a material and the resultant sinusoidal strain (or stress) is measured. Most DMA measurements are made using a single frequency and constant deformation (strain) amplitude while varying temperature (Sepe, 1992).

3.2.1 Dynamic mechanical measurement (complex modulus)

An alternative experimental procedure to creep and stress relaxation is to subject the specimen to an alternating strain and simultaneously measure the stress. For linear viscoelastic behavior, when the equilibrium is reached, the stress and strain varies sinusoidally, but the strain lags behind the stress. If stress \( \sigma(t) \) is applied, then altered with time \( t \) and angular frequency \( \omega \) the governing equation is

\[
\sigma(t) = \sigma_0 \sin \omega t
\]  

(3.2)

where \( \sigma_0 \) is the amplitude. An ideal elastic body deformation instantly follows an applied stress, and consequently,

\[
\varepsilon(t) = \varepsilon_0 \sin \omega t
\]  

(3.3)

Neither polymers nor bitumen are ideal elastic bodies; they are viscoelastic materials. In such cases the deformation (strain) lags behind the applied stress as shown in Figure 3.1.
With ideal viscoelastic bodies, the resulting phase angle \( \delta \) in the corresponding vector diagram can be assumed to be constant, such that the deformation follows eq (3.3) while the stress is given by

\[
\sigma(t) = \sigma_0 \sin(\omega t + \delta)
\]  

(3.4)

The stress vector can be considered to be the sum of two components. One component, \( \sigma' = \sigma_0 \cos \delta \), is in phase with the deformation, the other component, on the other hand, \( \sigma'' = \sigma_0 \sin \delta \), is out of phase with deformation. A modulus can be assigned to each of the components. The real modulus, or storage modulus, \( E' \), measures the rigidity and resistance to deformation of the sample. It is related to the complex modulus of rigidity \( E^* \) by

\[
E' = \sigma' / \varepsilon_0 = (\sigma_0 / \varepsilon_0) \cos \delta = E^* \cos \delta
\]  

(3.5)

The imaginary, or loss modulus, \( E'' \), on the other hand, reflects the loss of useful mechanical energy through dissipation as heat. Similarly, \( E'' \) is given by

\[
E'' = \sigma'' / \varepsilon_0 = E^* \sin \delta
\]  

(3.6)
The loss factor spectra can be quantitatively described by a superposition of model function, (Vauderschueren and Gasiot, 1979).

\[ E'(T) = \sum_{i=1}^{2} A_i \exp \left\{ - \frac{E_i}{kT} - \frac{T^2}{T_m^2} \exp \left[ \frac{E_i}{k} \left( \frac{1}{T_m} - \frac{1}{T} \right) \right] \right\} \tag{3.7} \]

In this model function A is a constant, k is Boltzmann constant, T is 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.

Introducing the complex variables, one may rewrite eq (3.3) and eq (3.4) as follows to give us eq 3.8 and eq 3.9 respectively;

\[ \varepsilon^* = \varepsilon_0 \exp(i\omega t), \tag{3.8} \]

\[ \sigma^* = \sigma_0 \exp(i(\omega t + \delta)). \tag{3.9} \]

The complex modulus E* may be then expressed as;

\[ E^*(\omega) = E'(\omega) + iE''(\omega), \tag{3.10} \]

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

Instead of following the deformation (strain) produced by a given stress, the sample can be strained and the resulting stress can be measured. The complex compliance J* = 1/E* is obtained in this case, and the storage and loss compliance are correspondingly given by

\[ E' = J' / [(J')^2 + (J'')^2], \tag{3.11} \]

\[ E'' = J'' / [(J')^2 + (J'')^2]. \tag{3.12} \]

The complex dynamic shear modulus at frequency \( \omega \), \( E^*(\omega) \) expressed in Pa, is given by the ratio between the magnitude of the dynamic shear stress, \( \tau(\omega) \), and the magnitude of the applied dynamic shear strain, \( \varepsilon(\omega) \).
The loss factor, storage modulus and loss modulus vary with frequency of loading as shown in Figure 3.2.

![Diagram](image)

Figure 3.2: The complex modulus, \( E^* = E' + iE'' \), as a function of frequency (Ward and Hadley, 1993).

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 difficulty for the chains to respond to the applied forces and tend 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, hence we encounter quasistatic conditions and observe 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 and the system reacts to the average strain only, which is zero. Crossover from one regime to the other occurs at $\omega \tau \cong 1$ (Ward and Hadley, 1993; Strobl, 1997).

The phase angle, expressed as its sine or tangent, is an important parameter for describing the viscoelastic properties of a paving material. The complex, storage and loss moduli, and the phase angle are illustrated by the trigonometry of a right triangle, as shown in Figure 3.3.

![Figure 3.3: Relation among dynamic E', E'' and phase angle, $\delta$.](image)

It follows that the loss tangent can be calculated simply as the tangent of the phase angle, or alternatively, as the ratio of the loss to storage moduli:

$$\tan \delta = \frac{E''}{E'} = \frac{1}{\omega \tau}, \quad (3.14)$$

and that

$$E^* = \left[ (E')^2 + (E'')^2 \right]^{1/2}, \quad (3.15)$$

where $E^*$, is the ratio of the peak stress to the peak strain, reflects the total stiffness. The in-phase component of $E^*$, i.e. the shear storage modulus, $E'$, represents the part of the input energy which is stored (the elastic portion). The out-of-phase component of $E^*$, i.e. the shear loss modulus $E''$, represents viscous component of it. The complex dynamic shear viscosity $\eta^*$ can be obtained from $E^*$ divided by the frequency, while the dynamic viscosity is $\eta = E'' / \omega$. 
3.2.2 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 $T_g$, 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 the temperature dependency of the relaxation time $\tau$ is often described by the Arrhenius equation (Sperling, 1992; Fried, 1995).

$$\tau = \tau_o \exp \left[ \frac{E_a}{kT} \right]$$  \hspace{1cm} (3.16)

where $\tau_o$ is the pre-exponential factor, $E_a$ is the activation energy, $k$ is Boltzmann constant and $T$ is the absolute temperature.

In contrast to local motions, relaxation times $\tau$ 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).

$$\tau = \tau_o \exp \left( \frac{BV_o}{V-V_o} \right)$$  \hspace{1cm} (3.17)
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 (Ward and Hadley, 1993), given in eq. 3.18

$$
\log \frac{\tau(T)}{\tau(T_g)} = -\frac{C_1(T - T_g)}{C_2 + T - T_g},
$$

(3.18)

where $\tau(T)/\tau(T_g)$ is the shift factor relative to the reference temperature, $T_g$. $C_1$ & $C_2$ = empirically determined constants and $T_g$ is a glass transition temperature. For temperatures less than the reference temperature the shift factor shifts the curves to the right while for higher temperatures to the left.

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 $C_1 = 17.44$ and $C_2 = 55.6$. As the sample becomes more crystalline (e.g. polyethylene or the asphalt paraffins) 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 $T_g$:

$$
\tau = \tau_o \exp \left[ \frac{K}{T - T_o} \right],
$$

(3.19)
where $\tau_0$ is the characteristic time at which free volume would be zero, $K = \left( \frac{BV_o}{\alpha} \right)$ is a constant and $T_o$ is ideal (Vogel) temperature which is 50°C below $T_g$, temperature at which free volume would be zero.

\[
\frac{1000}{T} (K^{-1})
\]

Figure 3.4: Comparison of the Arrhenius and VFT/WLF relationship (Sperling, 1992; McCrum, 1997)

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. When measurements taken at different temperatures the loss modulus is shifted to higher frequencies as shown in Figure 3.5.

Figure 3.5: Loss modulus against frequency at different temperatures.
3.3 Creep, Recovery behaviour and Creep Models

Creep is a time- and temperature-dependent phenomenon, occurring under load control. It occurs at both high and low temperatures. For polymers, creep regime occurs above the glass transition temperature. It is a combination of behaviors of viscous liquids and elastic solids (Harikishan et al., 2007). Creep in polymers occurs by chains untangling and slipping relative to one another; since a polymer consists of long chain-like molecules in a tangled and coiled arrangement. Polymeric materials exhibit viscoelastic behavior. The concept of viscoelasticity comes from the fact that most materials do not exhibit purely elastic (ideal solids) or purely viscous (ideal liquid) behavior but a combination of both viscous and elastic in varying amounts, meaning that a polymeric system does not follow a Hookean (elastic), or viscous (Newtonian flow) behavior. Various models have been proposed to explain viscoelastic behavior. The spring element as shown in Figure 3.6, shows instantaneous elasticity due to loading and recovery due to unloading. This model fits well to purely elastic materials. Spring, which represent the elastic component of a viscoelastic material, obey Hooke's Law:

\[
\varepsilon = \frac{\sigma}{E},
\]

Figure 3.6: Linear spring-Elastic component(Ward and Hadley, 1993).

For the spring model, eq. 3.1 can be expressed as

\[
\sigma_s = E\varepsilon,
\] (3.20)
where $\sigma$ is the applied stress, $E$ is the creep modulus of the material, and $\varepsilon$ is the strain. The spring represents the energetic or elastic component of the model's response. The spring element cannot be used for describing viscoelastic models like bitumen. The time dependency of viscoelastic materials are generally modelled with linear viscous dashpot. The dashpot continously deform at a constant rate when constant stress is applied.

Dashpot, which is shown in Figure 3.7, represents the viscous component of a viscoelastic material. In these elements, the applied stress varies with the time rate of change of the strain:

\[
\frac{d\varepsilon}{dt} \quad \varepsilon \quad \eta
\]

Figure 3.7: Linear dashpot-Viscous component (Ward and Hadley, 1993).

The constitutive equation of this element is

\[
\sigma_d = \eta \frac{d\varepsilon}{dt}
\]

(3.21)

where $\eta$ is viscosity of the dashpot component. Several mathematical models are developed to describe the nature of viscoelastic materials using a spring and dashpot. These include Kelvin-Voigt, Maxwell, Burgers and standard linear solid models, among others (Williams, 1980; Sperling, 1992; Fried, 1995).
3.3.1 Kelvin Model

The Kelvin–Voigt model, also called the Voigt model, can be represented by a purely viscous damper and purely elastic spring connected in parallel as shown in Figure 3.8 (a) and resulting deformation and recovery is shown in Figure 3.8(b).

Since the two components of the model are arranged in parallel, the strains in each component are identical:

$$\varepsilon_T = \varepsilon_1 = \varepsilon_2$$

(3.22)

Similarly, the total stress will be the sum of the stress in each component:

$$\sigma_T = \sigma_1 + \sigma_2$$

(3.23)

From these equations we get that in a Kelvin–Voigt material, stress, $\sigma$, strain, $\varepsilon$, and their rates of change with respect to time $t$ are governed by equations of the form:

$$\sigma(t) = E\varepsilon(t) + \eta \frac{d\varepsilon(t)}{dt}$$

(3.24)

where $E$ is the Young’s modulus of elasticity, $\eta$ is the viscosity and $\frac{d\varepsilon(t)}{dt}$ is the dashpot strain (Ward and Hadley, 1993). The equation can be applied either to the shear stress or normal stress of a material. If we suddenly apply some constant stress,
\( \sigma_0 \), to Kelvin–Voigt material, then the deformations would approach the deformation for the pure elastic material \( \left( \frac{\sigma_0}{E} \right) \) with the difference decaying exponentially to give

\[
\varepsilon(t) = \frac{\sigma_0}{E} \left( 1 - e^{-\frac{t}{\tau}} \right),
\]

(3.25)

where \( t \) is time and \( \tau \) is the relaxation time, \( \tau = \frac{\eta}{E_1} \).

Although the Kelvin–Voigt model is effective for predicting creep, it is not good at describing the relaxation behavior after the stress load is removed.

### 3.3.2 Maxwell Model

The Maxwell model can be represented by a purely viscous damper and a purely elastic spring connected in series, as shown in Figure 3.9(a). Figure 3.9(b) shows the resulting deformation and recovery.

![Figure 3.9: (a) Maxwell model, (b) Creep and Recovery behavior(Ward and Hadley, 1993).](image)

The total stress, \( \sigma_T \) and the total strain, \( \varepsilon_T \) can be defined as follows:

\[
\sigma_T = \sigma_1 = \sigma_2,
\]

\[
\varepsilon_T = \varepsilon_1 + \varepsilon_2.
\]

(3.26)
In this model, stress, $\sigma$, strain, $\epsilon$, and their rates of change with respect to time $t$ are governed by equations of the form:

$$\frac{d\epsilon}{dt} = \frac{\sigma}{\eta} + \frac{1}{E} \frac{d\sigma}{dt},$$

(3.27)

where $E$ is the elastic modulus and $\eta$ is the material coefficient of viscosity. If a Maxwell material is suddenly subjected to a stress $\sigma_0$, then the elastic element would suddenly deform and the viscous element would deform with a constant rate given by eq. 3.28.

$$\epsilon(t) = \frac{\sigma_0}{E} + \frac{\sigma_0}{\eta} t,$$

(3.28)

The Maxwell Model is not ideal for predicting the creep behavior of a material since it describes the strain relationship with time as linear.

### 3.3.3 Burgers Model

Burgers model combines Maxwell model in series with a certain number of Kelvin-voigt models as shown in Figure 3.10(a). It is one of the most used models to give the relationship between the morphology of the blends and their creep behavior (Findley et al., 2007). Its resulting deformation and recovery is shown in Figure 3.10(b). For linear viscoelastic solid, the total strain is the sum of three essentially separate parts: the immediate elastic deformation, the delayed elastic deformation and the Newtonian flow, which is identical with the deformation of a viscous liquid obeying Newton’s law of viscosity.
If a constant stress is applied to the extremities of the mechanical model. Because of the equilibrium, the same stress is shared by each element while the strains and strain rates are additive giving eq. 3.29.

$$\epsilon(t) = \sigma \left[ \frac{1}{E_o} + \frac{1}{\eta_o} + \sum_{i=1}^{n} \frac{1}{E_i} \left( 1 - e^{-\frac{t}{\tau_i}} \right) \right]$$  \hspace{1cm} (3.29)

As can be seen, parameters are necessary for completely describing the generalized burgers model, namely $E_o, \eta_o, E_i$ and $\tau_i = \frac{\eta_i}{E_i}$ (i = 1,2,3,…), which are, respectively, the instantaneous elastic modulus, the viscosity of the Maxwell element, delayed elastic modulus and the relaxation time of the generic i-th voigt element. The strain per unit of applied stress provides the so called creep compliance, from eq. (3.29), we
recognize that the generalized burgers model provides an exponential decay of the creep compliance. This is not surprising because in this model spring and dashpot yield forces that are proportional to derivatives of zero-th order (spring) and first order (dashpot).

3.3.4 Standard Linear Solid Model

The standard linear solid model combines a spring and a Kelvin element in series as shown in Figure 3.11.

![Standard Linear Solid model](image)

Figure 3.11: Standard Linear Solid model (Ward and Hadley, 1993).

By considering equilibrium of stress and compatibility of strains, the governing equation for this model is eq.3.30.

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

(3.30)

For a constant stress \(\sigma_0\), the corresponding strain is obtained by solving equation (3.30). Since stress is a constant,

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

and eq. 3.30 becomes,

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

(3.31)

and this can be rewritten as,

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

(3.32)

Integrating eq. 3.32, yields strain as
\[ e^\frac{E_d}{\eta} = (E_1 + E_2) - \frac{e}{E_1} e^{\frac{E_d}{\eta}} + C \]  

(3.33)

At \( t = 0 \), \( \varepsilon = \frac{\sigma_0}{E_1} + \frac{\sigma_0}{E_2} \) substituting these values in eq. 3.33 and solving for \( C \), we obtain an expression of strain as,

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

(3.34)

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, \( E_1 \) and \( E_2 \) are elastic moduli. At \( t = 0 \), \( \varepsilon = \frac{\sigma_0}{E_1} \) and \( \tau = \frac{\eta}{E_2} \), where \( \eta \) is viscosity, \( \tau \) is retardation (relaxation) time, which is defined as the time take for the stress to fall to a value \( \frac{1}{e} = \frac{1}{2.7} \) of the original stress. In other words it is the measure of how quickly a material recovers. This is illustrated in Figure 3.12, where the function of \( \sigma, \varepsilon \) and plotted with respect to time.

![Figure 3.12: Creep response of Standard linear solid model (Ward and Hadley, 1993).](image-url)
The time dependences of the relaxed moduli in the creep ($C_p$) and subsequent recovery ($R$) processes at different loading levels are given by eq. 3.35 below,

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

where, $E_0$, 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, and $E'_o$, is the initial modulus in the subsequent strain recovery process at 10s after 3600s 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 Creep Stages

A typical creep curve, exhibits three stages namely; primary, secondary and tertiary. However, there exists one more component of creep observed just prior to the primary stage and is called the instantaneous deformation. A typical creep curve is represented in Figure 3.13.
Figure 3.1: Typical creep curve (Ward and Hadley, 1993).

**Instantaneous deformation:** under the application of an initial and relatively small load, a material behaves as elastic. There occurs a sudden deformation as soon as the initial load is applied. The strains are fully recoverable, which can be explained by the behavior of a Hookean spring. In other words, no permanent strain is generated during a loading and unloading cycle.

**Primary stage:** if the load is continuously applied, the material continues to deform with a decreasing rate. In other words, the permanent strain rate slows down with time. The deformation characteristic can be simply explained by the Kelvin model. The behavior is that after unloading the material, a part of deformation is recoverable. The physical damage process during the primary stage is called strain hardening. This damage occurs due to the movement of dislocations in the asphalt concrete under repeated traffic loading. This results in increase in the plastic strain. On the contrary, the dislocation intersections decrease the movement in the body which causes a permanent strain rate reduction.
Secondary stage: Secondary creep also known as steady-state creep and it is the part that when the micro-cracks are initialized. Microcracking is a damage process during the secondary stage. At this point where microcracking initiates the decrease in the permanent strain ends. During this stage, slope deformation is nearly linear, at this stage, the strain rate eventually reaches minimum and becomes nearly a constant. The stress dependency of this rate is related to the creep mechanism. The deformation characteristic in this stage can be represented by the dashpot of a Maxwell element in the model. The deformation that accumulates at this stage is unrecoverable.

Tertiary stage: the permanent deformation rate starts to increase, and rapidly accumulates in this stage. The damage process is called microcracking which leads to permanent deformation. Macrocracks are formed with the combinations of microcracks under continuous loading. With the initiation of the macrocracking, the deformation rate is accelerated. This stage represents the plastic failure of the material.

Tyre pressure and wheel load are the major factors affecting the creep behavior of bitumen, under repeated traffic load; an increase in tire pressure decreases the contact area between the tire and pavement surface, therefore increases stress in hot mix asphalt. Permanent strain increases due to the increase in the stress and the failure duration under high stress becomes shorter than low stress levels. Other factors that affect creep are temperature, moisture, load frequency and mixture properties. Temperature affects the stiffness of bitumen, the stiffness decreases with increase in the temperature. The frequency of load, short pulse periods cause higher cumulative permanent strain in the repeated load creep tests, that is, higher loading rates increases
the permanent strain. Figure 3.14 (a) shows that creep increases with temperature, at low temperature the material is stiff hence high creep percentage. The measure of stiffness is shown in Figure 3.14 (b) which shows clearly the stiffness increases with decrease in temperature.

![Figure 3.14: a) Creep at constant load as a function of temperature vs time and b) Modulus vs. time.](image)

### 3.5 Standard linear model solution for creep and relaxation

The simplest combination is shown in Figure 3.11 and consists of a Voigt model with a spring in series. If we let the modulus of the additional spring be $E_1$ and of the spring in the Voigt model be $E_2$ as shown then the differential equation is

$$
\frac{d\varepsilon}{dt} + \frac{E_2\varepsilon}{\mu} = \frac{E_1 + E_2}{\mu} \frac{1}{E_1} \sigma + \frac{1}{E_1} \frac{d\sigma}{dt},
$$

(3.36)

From which it can be seen that both creep and relaxation result in satisfactory relationships. The creep compliance function is

$$
J(t) = \frac{1}{E_1} + \frac{1}{E_2} \left[ 1 - \exp \left( -\frac{t}{\tau_2} \right) \right],
$$

(3.37)

where $\tau_2 = \mu/E_2$ and the relaxation modulus:
where \( \tau_1 = \mu/(E_1 + E_2) \)

Thus adequate qualitative representations of both relaxation and creep behavior are obtained is a single model and the time parameters for the two responses, \( \tau_1 \) and \( \tau_2 \), are different. The forms of the functions are of interest and they are shown schematically in Figure 3.15. Both \( M(t) \) and \( 1/J(t) \) tend to \( E_1 \) as \( t \to 0 \) and \( E_1E_2/(E_1 + E_2) \) as \( t \to \infty \) which is apparent from an inspection of the model. The curves are sigmoidal in the form and their shape depend on \( \tau_1 \) and \( \tau_2 \). The bulk of the change takes place over the time range where \( t \approx \tau_1 \) or \( \tau_2 \) and thus, as \( \tau_1 < \tau_2 \) in this case, the \( M(t) \) curve will always be the lower of the two. This shape of curve gives rise to the concept of the short time modulus \( E_1 \) and a long time modulus \( E_1E_2/(E_1 + E_2) \) which is sometimes used. If any attempt is to be made to fit these curves to real data then it is apparent that the fixed shape allows little flexibility. It is therefore usual to consider models with very many elements to reproduce some shape and in general a large number of Maxwell models in parallel are used to predict relaxation behavior giving a function of the form:
Figure 3.15: Modulus functions for the standard linear solid.

\[ M(t) = \sum_{i=1}^{n} E_i \exp \left( -\frac{t}{\tau_i} \right) \]

\[ M(t) = \int_{0}^{\infty} \sum_{i=1}^{n} E(\tau) \exp \left( -\frac{t}{\tau_i} \right) d\tau \]  \hspace{1cm} (3.39)

This is the relaxation spectrum concept in which changes in M(t) may be linked with relaxation times within the spectrum. The long time modulus for this system tends to zero. Similarly, a set of voigt models in series gives an equation of the form:

\[ J(t) = \int_{0}^{\infty} \frac{1}{E(\tau)} \left[ 1 - \exp \left( -\frac{t}{\tau} \right) \right] d\tau \]  \hspace{1cm} (3.40)

which gives a spectrum of times for creep behavior. This approach has been commonly used in attempts to relate molecular structure to macroscopic properties, and in particular to relate the various relaxation times to identifiable molecular motions within the structure.
Returning to the standard linear solid, we find that by using \( J(t) \) and \( M(t) \) the expression for constant stress rate and constant strain rate may be derived. For a constant stress rate this may be written in the form of a modulus:

\[
E_{\text{stress}} = \frac{E_1 E_2}{E_1 + E_2} \left[ \frac{1}{1 - \frac{\tau_1}{t} \left[ 1 - \exp \left( -\frac{t}{\tau_2} \right) \right]} \right]
\]  

(3.41)

and for constant strain rate:

\[
E_{\text{strain}} = \frac{E_1 E_2}{E_1 + E_2} \left[ 1 + \frac{E_1}{E_2} \left( 1 - \exp \left( -\frac{t}{\tau_1} \right) \right) \right]
\]  

(3.42)

Eq. 3.37 and eq. 3.38 may be written to give comparable forms:

\[
E_{\text{creep}} = \frac{E_1 E_2}{E_1 + E_2} \left[ \frac{1}{1 - \frac{E_1}{E_1 + E_2} \exp \left( -\frac{t}{\tau_2} \right)} \right]
\]

and

\[
E_{\text{relax}} = \frac{E_1 E_2}{E_1 + E_2} \left[ 1 + \frac{E_1}{E_2} \exp \left( -\frac{t}{\tau_1} \right) \right]
\]  

(3.43)

The four expressions give the slopes of the isochronous curves for the four systems of loading for any given value of \( t \). All tend to the long time modulus for \( t \rightarrow \infty \) but for other values of \( t \) they are in fixed order namely: \( E_{\text{relax}} < E_{\text{creep}} < E_{\text{strain}} < E_{\text{stress}} \)

### 3.6 Sinusoidal Loading

Sinusoidal loading is of considerable practical interest and it is convenient to consider it in relation to the standard linear solid. If we consider first a cyclic stress input:

\[
\sigma = \sigma_0 \sin \omega t
\]  

(3.44)

Where \( \omega \) = the angular frequency this function can be used together with \( J(t) \) from eq. 3.37 to give the convolution integral:
\[ \varepsilon(t) = \int_0^t \left[ \frac{1}{E_1} + \frac{1}{E_2} \{1 - \exp \left( -\frac{t - \tau}{\tau_2} \right) \} \sigma_0 \omega \cos \omega \tau d\tau \right] , \]

which may be evaluated to give:

\[ \varepsilon(t) = \sigma_0 \left( \frac{1}{E_1} + \frac{1}{E_2} + \frac{1}{1 + \omega^2 \tau_2^2} \right) \sin \omega t - \frac{\sigma_0}{E_2} \frac{\omega \tau_2}{1 + \omega^2 \tau_2^2} \cos \omega t + \frac{\sigma_0}{E_2} \frac{\omega \tau_2}{1 + \omega^2 \tau_2^2} \exp \left( -\frac{t}{\tau_2} \right) \]

It can be seen that the first term may be regarded as in-phase with the sinusoidal input and the second term as out-of-phase. The third term is a transitory effect which tends to zero for long times and is usually ignored. The results are conventionally written in terms of in-phase and out-of-phase moduli designated \( E' \) and \( E'' \) respectively which in this case are:

\[
\frac{1}{E} = \frac{1}{E_1} + \frac{1}{E_2} \cdot \frac{1}{1 + \omega^2 \tau_2^2} \tag{3.46}
\]

and

\[
\frac{1}{E''} = \frac{1}{E_2} \cdot \frac{\omega \tau_2}{1 + \omega^2 \tau_2^2} \tag{3.46}
\]

For high frequencies (\( \omega \tau_2 >> 1 \)), \( E' \rightarrow E_1 \) and \( E'' \rightarrow \infty \) while for low frequencies (\( \omega \tau_2 << 1 \)), \( E' \rightarrow E_1 E_2/(E_1 + E_2) \) and \( E'' \rightarrow \infty \). Again an inspection of the model confirms these results. A further parameter of practical importance is the loss factor written as:

\[
\tan \delta = \frac{\text{Out-of-phase component}}{\text{In-phase component}}
\]

which in this case becomes:

\[
\tan \delta = \frac{E_1 \omega \tau_2}{(E_1 + E_2) + E_2 \omega^2 \tau_2^2} \tag{3.47}
\]

Two special cases of interest are the Maxwell model with \( E_2 = 0 \) and hence:

\[ E' = E_1, E'' = \omega \mu \]

and the voigt model with \( E_1 = \infty \) giving:
\[ E' = E_2(1 + \omega^2 \tau_1^2), \quad E'' = E_2 \frac{1 + \omega^2 \tau_2^2}{\omega \tau_2} \]

If the input is of the form:
\[ \varepsilon = \varepsilon_o \sin \omega t, \quad (3.48) \]

which may be regarded as strain cycling compared with stress cycling used previously, then \( M(t) \), eq. 3.38, must be used in convolution integral and the results become:
\[ \sigma(t) = \varepsilon_o \frac{E_1 E_2}{E_1 + E_2} \left( 1 + \frac{E_1}{E_2} \frac{\omega^2 \tau_1^2}{1 + \omega^2 \tau_1^2} \right) \sin \omega t + \varepsilon_o \frac{E_1^2}{E_1 + E_2} \frac{\omega \tau_1}{1 + \omega^2 \tau_1^2} \cos \omega t \]
\[ - \varepsilon_o \frac{\omega \tau_1}{1 + \omega^2 \tau_1^2} \frac{E_1^2}{E_1 + E_2} \exp \left( -\frac{t}{\tau_1} \right) \]

As before, for long times the third term tends to zero and we have:
\[ E' = \frac{E_1 E_2}{E_1 + E_2} \left( 1 + \frac{\omega^2 \tau_1^2}{1 + \omega^2 \tau_1^2} \right) \]
\[ E'' = \frac{E_1^2}{E_1 + E_2} \frac{\omega \tau_1}{1 + \omega^2 \tau_1^2} \]

(3.49)

As would be expected from the difference in creep and relaxation moduli, the moduli from stress cycling and from strain cycling are different. For example, if both expression for \( E' \) are written in terms of \( \tau_1 \), we have, from eq. 3.48.

\[ E'_{strain} = \frac{E_1 E_2}{E_1 + E_2} \left[ 1 + \frac{\omega^2 \tau_1^2}{1 + \omega^2 \tau_1^2} \frac{E_1}{E_2} \right], \quad (3.50) \]

and from eq. 3.39

\[ E'_{stress} = \frac{E_1 E_2}{E_1 + E_2} \left[ 1 + \frac{\omega^2 \tau_1^2}{E_1 + E_2 + \omega^2 \tau_1^2} \frac{E_1}{E_2} \right], \quad (3.51) \]
The only difference is in the term $E_2/(E_1 + E_2)$ and clearly $E_\text{Strain} < E_\text{Stress}$ as expected. The two expressions are shown plotted in Figure 3.16 as a fraction of $\log 1/\omega \tau_i$ and for low frequencies, $\omega \tau_i << 1$, both tend to a value of $E_1 E_2/(E_1 + E_2)$ which corresponds to the long time response as shown in Figure 3.7 for other histories. Similarly at high frequencies, i.e. short times, both tend to a value of $E_1$.

The loss factor is given by:

$$\tan \delta_2 = \frac{E_1 \omega \tau_1}{E + (E_1 + E_2) \omega^2 \tau_1^2} = \frac{E_2 \omega \tau_2}{E_2 + (E_1 + E_2) \omega^2 \tau_1^2} = \tan \delta_1$$

Thus the loss factor expression is the same for both types of loading and is shown in Figure 3.8 (b). At both high and low frequencies it tends to zero and there is a maximum of:

$$\tan \delta = \frac{1}{2} \frac{E_1}{E_2} \sqrt{\frac{E_2}{E_1 + E_2}}$$  \hspace{1cm} (3.52)

$$\omega \tau_i = \sqrt{\frac{E_2}{E_1 + E_2}}$$  \hspace{1cm} (3.53)

The special cases for strain cycling are: for the Maxwell model ($E_2 = 0$)

and for the Voigt model ($E = \infty$)

$$E' = E_2, E'' = \omega \mu$$

The result for the Maxwell model is used to define relaxation spectra from $E'$ and $E''$ as functions of $\omega$ in a similar manner to creep and relaxation data so that:

$$E' = \int_0^\infty E(\tau) \frac{\omega^2 \tau^2}{1 + \omega^2 \tau_i^2} d\tau \quad \text{and} \quad E'' = \int_0^\infty E(\tau) \frac{\omega \tau}{1 + \omega^2 \tau_i^2} d\tau$$  \hspace{1cm} (3.54)
3.7 Thermal Degradation

Thermal degradation of polymers is ‘molecular deterioration as a result of heating’. 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).

The ability of a polymer to resist these degradation causes is called the ‘stability’ of the polymer and in this research we have concentrated on the process of thermal
degradation with particular emphasis on thermal degradation in service as opposed to thermal degradation during processing. All polymers experience some type of degradation during service and these results in a steady decline in their properties. In fact, degradation is inevitable and the resulting chain reaction accelerates resulting in a loss in properties. The chemical reactions involved in thermal degradation lead to physical and optical property changes relative to the initially specified properties. 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. The dominant mechanism of degradation and the degree of resistance to degradation depends on the application and the polymer concerned.

3.8 Thermogravimetry of Polymers

Thermogravimetry (TG) is the study of the relationship between a sample’s mass and its temperature. It can be used to study any physical (such as evaporation) or chemical process (such as thermal degradation) that causes a material to lose volatile gases. Polymers have different thermal stabilities and thus the qualitative “fingerprint” afforded by TG in terms of temperature range, extent and kinetics of decomposition provides a rapid means to distinguish one polymer from another using only milligram quantities of material (Duncan and Douglas, 2000). Experiments are most commonly carried out under conditions where the temperature is increased in a linear fashion with time or the sample is held isothermally at an elevated temperature, although more sophisticated temperature profiles are occasionally used for compositional and kinetic analysis. Processes which do not result in a change in sample mass are not detected by TG. Therefore simultaneous measurements by differential scanning
calorimetry (DSC) are useful. Volatile decomposition products may be detected and identified (e.g. by infrared (IR) spectrometry or mass spectrometry (MS)) in order to elucidate the mechanism of mass changes. TG is used for quantitative compositional analysis of polymers, lifetime prediction and kinetic studies, making the technique valuable in all stages of polymer development, fabrication and component testing.

3.8.1 Thermal Stability Assessment and Compositional Analysis

The assessment of thermal stability is one of the most important applications of TG to the study of polymers. Thermogravimetric curves provide information about the decomposition mechanisms for various materials. In addition, the decomposition profiles may be characteristic for each type of polymer and in some cases can be used for identification purposes (Aboulkas and Harfi, 2008). The onset of mass loss often defines the upper limit of thermal stability for the material, though it must be appreciated that extensive degradation of the polymer structure by, for example, cross-linking, may have already taken place before the point at which detectable changes in mass occur. The routes by which polymers degrade can be categorized according to six main mechanisms (Duncan et al., 2000):

i. main-chain scission

ii. Side group scission

iii. Elimination

iv. Depolymerization

v. Cyclization

vi. Cross-linking

Main-chain scission: this involves breaking of bonds in the main polymer chain, resulting to decrease in molecular weight and volatile formation. It may occur at the chain end or at random locations in the chain. End chain scission in which individual
monomer units are successively removed at the chain end, results in production of monomer and the process is often known as unzipping. Random chain scission in which chain scission occur at apparently random locations in the polymer chain, results in generation of both monomers and oligomers (polymer units with 10 or fewer monomer units) as well as a variety of other chemical species. Cross-linking occurs after some chain stripping (in which atoms or groups not part of the polymer chain or backbone are cleaved) and involves creation of bonds between two adjacent polymer chains. This process is very important in the formation of chars, since it generates a structure with a higher molecular weight that is less easily volatized. Side group scission involves elimination and cyclization reactions. In elimination reaction, the bonds connecting side groups of the polymer chain to the chain itself are broken, with the side groups often reacting with other eliminated side groups. In cyclization reactions, two adjacent side groups react to form a bond between them, resulting in production of a cyclic structure. This process is important in char formation. Cyclization and cross-linking rarely result in any change of sample mass unless they occur in conjunction with i–iv and are not detected by TG. Routes i–iv usually results in the evolution of volatile products with an accompanying mass change. In an inert atmosphere, some polymers give an almost quantitative yield of their parent monomers. In air, complete oxidation of the sample to oxides of its constituent elements commonly occurs. Nitrogen containing polymers usually generate some ammonia or hydrogen cyanide. Halogen-containing polymers yield the respective hydrogen halides.

3.8.2 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 repolymerise. 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.

![Diagram](image)

Figure 3.17: Formation of Levoglucosan through unzipping of the cellulose chain (Lomankin et al., 2011).

### 3.8.3 Thermal decomposition scheme of bitumen

Weight loss of bitumen occurs in one or a combination of three ways: first one, might have been as a result of a random chain scission and subsequent pyrolysis of the bitumen or due to loss of volatiles and low molecular weight fragments such as saturates and aromatics. The second way of weight loss may be attributed to
decomposition of light hydrocarbons (Resins and Aromatics) and lastly, due to decomposition of high molecular weight fragments and heavy hydrocarbons (asphaltenes) (Lucena et al., 2004) as shown in Figure 3.18.

![Figure 3.18: Representation structures for the four bitumen fractions: saturates, aromatics, resins and asphaltenes (Lucena et al., 2004).]

3.8.3 Activation energy

When a polymer sample degrades, its mass decreases. For the very general reaction

\[ S(s) = P_1(s) + P_2(s) \]  \hspace{1cm} (3.55)

The disappearance rate of the species (S) can be calculated as follows:

\[ \frac{dx}{dt} = kf(x) \]  \hspace{1cm} (3.56)

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 \( t \), i.e.

\[ x = \frac{m - m_f}{m_o - m_f} \]  \hspace{1cm} (3.57)

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 eq. 3.58.

\[ \frac{dx}{dt} = A(x)^n \exp\left(\frac{-E_o}{RT}\right) \]  \hspace{1cm} (3.58)
The activation energy, $E_a$ is a pre-exponential factor, $R$ is the 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:

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

(3.59)

Using a different assumption for performing the integration of eq. 3.59, Broido (1969) derived a non-integral equation (3.59) valid only for the first order reaction.

$$\ln(\ln \frac{1}{x}) = -\frac{E_a}{RT} + \ln \left(\frac{RZT_m^2}{E_a\beta}\right)$$

(3.60)

where $x$ is the residual mass, $Z$ is the frequency factor, and $E_a$ is the activation energy. The parameters, $R$, $T$, $T_m$ and $\beta$ represent the universal gas constant, absolute temperature, temperature at maximum reaction, and heating rate respectively. The Figure 3.19 below shows the plot of natural logarithm of the residual mass against reciprocal temperature which shows linear dependency, suggesting good agreement with the Broido eq. 3.60. The activation energy $E_a$ is calculated directly from the slope.

Figure 3.19: Natural logarithm of residual mass against reciprocal temperature.
CHAPTER FOUR

MATERIALS AND METHODS

4.1 Introduction

In this chapter the materials, apparatus used, and the experimental procedure adopted are described. Sample preparation is also described and a brief account of sample reproducibility test is presented.

4.2 Materials

The materials used in the study were bitumen and acacia sap. Bitumen, 80/100 penetration grade was obtained from Kenya oil Refineries companies in Mombasa, Kenya, with an asphaltene content of 25 wt.% and softening point of 52 °C. The acacia sap was obtained from Acacia trees in Taita-Taveta District. The bitumen and acacia sap (cellulose) molecular structures are shown in Figure 4.1.

![Molecular structure of Cellulose and Bitumen](image)

Figure 4.1: Molecular structure of, (a) Cellulose (Lomakin et al., 2011) and (b) Bitumen (Carbognani et al. 2010).
Some of the typical properties of bitumen and cellulose are shown in the Table 4.1.

Table 4.1: Summary of the typical properties of cellulose and bitumen.

<table>
<thead>
<tr>
<th>PROPERTY</th>
<th>BITUMEN</th>
<th>CELLULOSE (ACACIA SAP)</th>
<th>REFERENCES</th>
</tr>
</thead>
<tbody>
<tr>
<td>Appearance</td>
<td>Black</td>
<td>white powder</td>
<td>(Fawcett, 2003), (Gindl, 2006)</td>
</tr>
<tr>
<td>Softening point (°C)</td>
<td>41 - 52</td>
<td>Decompose (from 250-350°C)</td>
<td>(Fawcett, 2003), (Reddy, 2005)</td>
</tr>
<tr>
<td>Molecular structure</td>
<td>C(<em>n)H(</em>{2n+2})</td>
<td>(C(<em>6)H(</em>{10})O(_5))(_n)</td>
<td>(Girija, 2005), (Reddy, 2005)</td>
</tr>
<tr>
<td>Molecular mass (g/mol)</td>
<td>10000-100000</td>
<td>10000-15000</td>
<td>(Girija, 2005), (Frederika, 2010)</td>
</tr>
<tr>
<td>Density (g/cm(^3)), 25°C</td>
<td>1.05</td>
<td>1.5</td>
<td>(Ramanujam, 2000)</td>
</tr>
<tr>
<td>Viscosity (Pa.s)</td>
<td>54 - 69</td>
<td>-</td>
<td>(Abdelaziz, 2005)</td>
</tr>
</tbody>
</table>

4.3 Injection Machine

The injection machine consisted of a cylindrical melting chamber made of brass. It had a length of 40mm and an internal diameter of 10mm. It was open at one side but the other side was closed leaving a 2mm diameter hole from where injection of the polymer melt was done. A stopper screw to fit into the hole was used during the heating process and removed just before the mixture melt was injected into the Petri dish. A screw with a pitch width of about 1.5cm was used for the mixing. The screw fitted well to the sides of the chamber so that it provided thorough mixing. A sensitive thermocouple was fitted to the chamber to measure the temperature. The machine also consisted of a piston that fitted in the open end of the melting chamber. This was used to push the mixture through the small hole into the Petri dish. Figure 4.2 shows the heating and injection process while Figure 4.3 shows the injection process.
4.4 Sample Preparation

4.4.1 Preparing blends ratios

A bitumen mass of 4g was used as the reference mass to determine the concentration in the composites. The formula

\[
\text{Sap concentration} = \frac{x}{4g} \times 100\%
\]  

(4.1)

was used to give the percentage concentration, where \( x \) is the mass of dry acacia sap in grams.

A table of the bitumen-acacia sap composites percentage concentration of the samples prepared is shown in Table 4.2.
Table 4.2: cellulose/bitumen blends percentage concentration of the samples

<table>
<thead>
<tr>
<th>CONCENTRATIONS</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>(Percent, %)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Acacia sap</td>
<td>0</td>
<td>100</td>
</tr>
<tr>
<td>Bitumen</td>
<td>25</td>
<td>75</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>50</td>
</tr>
<tr>
<td></td>
<td>62.5</td>
<td>37.5</td>
</tr>
</tbody>
</table>

A top pan electronic balance with an accuracy of ± 0.0001 g was used to obtain exact values of masses that were used in preparing the composites. The term ‘concentration’ was used to refer to the concentration of dry sap in the composites.

4.4.2 Mixing and injection process

Dry Acacia sap was crushed into fine powder using crucible and sieved with sieve gauge one. A total of 4 g mass of the bitumen-acacia sap composite was used. Bitumen (solid) was put in a melting chamber with the opening closed by a stopper screw. The melting chamber was placed on a hot plate at 160 °C and maintained at that temperature for 5 minutes to ensure that all the bitumen melted. Still molten, dry sap was added and the mixture mechanically stirred continuously with a screw for 5 minutes to ensure a homogeneous composite. The mixing process was achieved by using the mixing screw that almost fitted to the inside walls of the chamber as shown Figure 4.2. During mixing the screw was rotated in a direction such as to push the melt forward towards the injection hole. Due to the fact that the hole was closed
during mixing, the mixture squeezed itself back between the inside walls of the chamber and the mixing screw. The rotation of the mixing screw forced the mixture forward again and in the process it was thoroughly mixed. During injection, the mixing screw and the stopper screw were carefully removed. A piston was used to quickly inject the mixture into the Petri dish which was at room temperature, as illustrated in Figure 4.3.

The mixture was then allowed to cool at room temperature. When cooled, the mixture was in form of a paste. This procedure was repeated in preparing all the composites. However, bitumen-acacia sap composites samples which were highly viscous in such a way that they could not be injected were prepared by mechanical stirring. The corresponding polymer cellulose weight percentage was added to bitumen and the mixing was maintained at 160 °C. After mixing, the resulting dispersion was poured into the Petri dish and then stored at room temperature to retain the morphology.

4.4.3 Sample Dimensions

The paste was scooped and stuck in the jaws of the shear sandwich clamp. It was then compressed by application of force on the screw producing circular sheets. The sheets were then cut into rectangular shapes of dimensions $10 \pm 0.5\text{mm} \times 10 \pm 0.5\text{mm} \times 2 \pm 0.5\text{mm}$ using sharp cutter. The dimensions of the samples were chosen in accordance with the DMA shear mode.
4.5 Measurements

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

4.5.1 Dynamic Mechanical Analysis Measurement Procedure

Dynamic mechanical analysis was done using DMA 2980 TA instrument (Appendix II) in the shear sandwich mode on film samples about 10 ± 0.5 mm x 10±0.5 mm x 2±0.2 mm that was cut off from the composites of bitumen-acacia sap. The instrument was calibrated according to the manufacturer specifications, as outlined in the user manual. The instrument parameters were set at 0.44, data sampling interval of 2.0 sec/point, static force of 0.5 N and oscillation amplitude of 20 μm. The storage modulus (E”), loss modulus (E””) and loss tangent (tan δ) were recorded in DMA multi-Frequency tensile shear sandwich mode system in order to get required data. A suitable configuration for the geometry of the samples was used. The equipment was programmed to scan across a frequency range of 0.3, 1, 3, 5, 10, 15, 20, and 30 Hz. The temperature used was in the range of 276 to 323 K and in steps of 2 K after every frequency sweep. It took about 120 minutes to run a measurement.

4.5.2 Creep measurements Procedure

The creep (strain) behavior, recovery and creep compliance as a function of time and temperature was measured by Dynamic mechanical analyzer DMA 2980, using Shear sandwich clamp (see Appendix VI) in the creep mode system. The DMA equipment was set in a temperature range of 20-37 °C and the samples were allowed to creep for 20 min, displace 12 min, equilibrate 12 min and was then released to unstressed state.
and allowed to recover for 20 min. All the creep tests were carried out by applying a constant shear stress level at the selected temperature of 20, 25, 30 and 35 °C. Stress of 0.0875 MPa, static force of 0.5 and 18 N was applied and the corresponding strain recorded at an interval of 10 min for 3 hours.

4.5.3 Thermal Degradation Measurements Procedure

The thermogravimetric analysis (TGA) was carried out for bitumen and the composites(140mg) using the Lindberg/blue TF55035C mini Tube furnace (Appendix I) in oxidative atmosphere. Heating was done from room temperature (25°C) at a rate of 5°C/min in the range of 80-550°C with aluminum containers as reference materials since from room temperature to 80°C no weight loss occurred. Weight loss of the composites was calculated. The natural logarithm of fraction decomposed was plotted against reciprocal temperature to determine the activation energy of the bitumen composites. Differential weight loss was also plotted against temperature to determine the peak decomposition temperature of the composites.

4.6 Data Analysis

Measured data on dynamic mechanical analyzer TA 2980 and TGA was analyzed using microcal card origin 8 software.
CHAPTER FIVE

RESULTS AND DISCUSSION

5.1 Introduction

In this chapter, the experimental results of thermogravimetric analysis, DMA and creep measurements are presented. The discussion focused on three main areas; effect of acacia sap on the thermal properties, mechanical properties and creep behavior of bitumen.

5.2 Effects of acacia sap on thermal properties of bitumen

5.2.1 Thermogravimetric analysis of bitumen composites

TGA studies have been carried out to determine thermal characteristics of materials such as thermal stability and degradation temperatures. Figure 5.1 shows the TGA thermograms of pure bitumen and bitumen-acacia sap composites obtained at heating rate of 5°C/min. The curves follow sigmoidal fit shown by solid lines. The curve of pure bitumen show single stage of remnant mass with well-defined initial and final degradation temperatures, this has been attributed to random chain scission and pyrolysis of the sample occurring concurrent (Naskar et al., 2010) or evaporation of moisture associated with release of gases prior to decomposition. This result may be confirmed by the presence of single peak in the DTG curve at temperature of 432 °C, the point at which mass loss is most apparent. Above 480°C, the quantity of bitumen residue was very small due to breakdown of the bitumen residue into gaseous products at a higher temperature.
It is also evident from Figure 5.1 that percentage remnant mass for all composites correspond to single-stage degradation, which might have been the result of chain scission and branching occurring concurrently. This result is also confirmed by the presence of single peak in the DTG curve as shown by solid lines. The total remnant mass of the composites decreased with increase in acacia sap content at same temperature because the thermal degradation temperature of the sap is lower than that of bitumen. Thermal degradation retarded above 480 °C due to increased ash content. From the TGA thermograms it is also seen that below 100 °C there was no mass
change and above 100 °C volatilization of low molecular weight species took place along with pyrolysis resulting to mass change. There is also shifting of the onset temperature of thermal degradation of the composites to lower values with increase of sap content due to low thermal stability of the acacia sap(cellulose).

5.2.2 Decomposition temperature of the composites

The peak decomposition temperature of the bitumen-acacia sap composites was obtained from the maximum peak temperature of the DTG curves shown in Figure 5.1. Bitumen has a high molecular mass (10000 to 100000) than cellulose- acacia sap (10000 to 15000) (Lomankin et al., 2011) polymer, this results in decomposition of bitumen at higher temperature than the bitumen-acacia sap composites. The peak decomposition temperature decreased with increase in acacia sap loading in the composites as shown in Table 5.1. This is due to low molecular weight and semicrystalline nature of the cellulose-acacia sap which makes them less temperature resistant. This is in agreement with results reported by Naskar et al. (2010). The decomposition temperature of bitumen according to literature ranges from 440 to 650 °C (Zainal et al., 2007) while that of cellulose-dry acacia sap from 250 to 350 °C (Lomankin et al., 2011).

<table>
<thead>
<tr>
<th>SAMPLE</th>
<th>Decomposition Temperature(°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>B100AS0</td>
<td>432.30 ± 2.55</td>
</tr>
<tr>
<td>B75AS25</td>
<td>429.41 ± 1.78</td>
</tr>
<tr>
<td>B50AS50</td>
<td>400.19 ± 2.34</td>
</tr>
<tr>
<td>B37.5AS62.5</td>
<td>379.73 ± 1.47</td>
</tr>
</tbody>
</table>
5.2.3 Determination of Activation Energies

Figure 5.2 shows the kinetic curves of thermal degradation of bitumen-acacia sap composites. The solid lines have been fitted using the Broido model as described by eq. 3.60.

![Plot showing kinetic curves of thermal degradation for different bitumen-acacia sap composites.](image)

Figure 5.2: Natural logarithm of fraction of residual mass versus reciprocal temperature of the polymer composite.
Table 5.2: Activation energies of bitumen-acacia sap composites

<table>
<thead>
<tr>
<th>Bitumen-acacia sap composites</th>
<th>Activation energy (kJ/Mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>B100AS0</td>
<td>34.65 ± 0.56</td>
</tr>
<tr>
<td>B75AS25</td>
<td>32.30 ± 1.44</td>
</tr>
<tr>
<td>B50AS50</td>
<td>28.96 ± 1.24</td>
</tr>
<tr>
<td>B37.5AS62.5</td>
<td>25.61 ± 0.88</td>
</tr>
</tbody>
</table>

The activation energy ($E_a$) values were directly obtained from the slope of the linearly regressed line of ln(ln 1/x) versus 1000/T at a constant heating rate of 5°C/min. There was a significant change in the activation energy values between the composites and the pure component. It can be inferred from values presented in Table 5.2 that the composite containing higher acacia sap concentration exhibit lower activation energy than composites with low acacia sap concentration. This shows that the thermal stability of bitumen- acacia sap composites decreased with increase in acacia sap content. The thermal stability of the bitumen-acacia sap composites was substantially reduced by the incorporation of semi crystalline cellulose-acacia sap to the amorphous bitumen matrix. At lower acacia sap content, composites appear to be in a continuous phase and swollen by the miscible components of the bitumen and forms an interconnected three- dimensional structure but at higher polymer content polymeric network collapses due to poor compatibility and coalescence of polymer molecules resulting in phase separation (Perez-lepe et al., 2006). The value of activation energy obtained for the pure bitumen was close to the value reported in literature for the bitumen of 30 kJ/mol (Carbognani et al., 2010) using the Friedman's technique.
5.3 Effects of Acacia sap on Relaxation Processes of Bitumen

5.3.1 Storage Modulus, $E'$ and Loss Modulus, $E''$ of Pure Bitumen

5.3.1.1 Storage Modulus

The storage modulus $E'$, is a measure of the rigidity (stiffness) and resistance to deformation of the sample. Figure 5.3 (a) shows variation of storage modulus with temperature while Figure 5.3(b) shows variation of loss modulus with temperature all at different frequencies.

Figure 5.3: Variation of a) Storage modulus $E'$; b) Loss modulus $E''$ of pure bitumen with temperature at different frequencies.
The storage modulus of the bitumen decreased with increase in temperature due to softening. It also shifted to the right with increase of frequency. At high frequency (shorter period) the sample behaves like an elastic solid while at low frequency (longer period) it’s rubbery. The storage modulus dropped suddenly at 300 K due to softening i.e. phase inversion.

**5.3.1.2 Loss Modulus, $E''$**

Loss modulus reflects the amount of mechanical energy dissipated by a material. It’s a relaxation process assigned to main chain fluctuations i.e. dynamic glass transitions. Figure 5.3 (b) show plots of the loss modulus against temperature for different frequencies of pure bitumen. The solid lines have been fitted using loss superposition model function

$$E''(T) = \sum_{i=1}^{2} A_i \exp \left\{ -\frac{E_a}{kT} - \frac{T^2}{T_{m_i}} \exp \left[ \frac{-E_a}{k \left( \frac{T_{m_i}}{T} - 1 \right)} \right] \right\}$$

(5.1)

In this model function, $A$ is a constant, $k$ Boltzmann constant, $T$ absolute temperature, $T_{m}$ temperature at maximum loss modulus, $E_a$ is the activation energy and $i$ refers to different processes which contribute to the mechanical response.

From Figure 5.3(b), it is clearly seen that the relaxation process is narrow indicating narrow distribution of relaxation times. The maximum dissipation is observed at 3Hz. The loss modulus peaks shifts to the right (higher temperatures) as the frequency is increased. This shift can be attributed to the fact that at low frequency, almost all the chains are able to follow movement of the oscillations. At higher frequency, however, it becomes very difficult for all the chains to follow the movement of the oscillations. A few, probably the ones with a shorter chain length, would be able to oscillate thus
giving a shift of the loss modulus to higher temperatures. There is also sudden drop of the loss modulus at 300 K indicating structural changes. This is due to softening of the bitumen as temperature rises.

5.3.2 Storage Modulus, E’ and Loss Modulus, E’’ of Bitumen-acacia sap Composites

![Graphs showing storage modulus E’ and loss modulus E’’ for bitumen-acacia sap composites](image)

Figure 5.4: a) Storage modulus E’ (stiffness); b) Loss modulus E’’ (dissipation) with composition for bitumen-acacia sap composites at 1Hz.
Figure 5.4 (a) shows variations of storage modulus with composition for bitumen-acacia sap composites while Figure 5.4 (b) shows variations of loss modulus with composition for bitumen-acacia sap composites with bitumen at 1Hz.

The storage moduli of the bitumen-acacia composites are greater than that of bitumen, and increases with increase in acacia sap loading, this is because acacia sap stiffens the bitumen matrix. The composites also show a plateau at 305 K due to limited free volume which prevents molecular motion (Gupta et al., 2003). The composites softened at higher temperatures than bitumen. This results from crystallization. According to Frederika et al. (2010) this phenomenon is attributed to physical hardening as a result of reorientation of some aromatic structures present in bitumen and crystallization of waxes possible to happen at lower temperatures. The storage modulus of the composites reached a plateau at higher temperatures than bitumen; this is due to existence of molecular entanglements which makes the chains temperature resistant. The storage modulus curves of the 25 and 50% acacia sap content reached a plateau at approximately 315 K, and composite with 62.5% acacia sap content at about 318 K. These plateaus terminated at 320 K when the samples began to flow due to softening. These patterns of behavior are consistent with the network structure which disperses when the polymer melts, and as has been described for several polymer-solvent systems, this is in agreement with work by Fawcett et al. (1999).

5.3.3 Loss Modulus, $E''$ for Bitumen-acacia sap Composites

Loss modulus reflects the amount of mechanical energy dissipated by a material. It’s a relaxation process assigned to main chain fluctuations i.e. dynamic glass transitions. Figure 5.4 (b) show plots of the loss modulus, $E''$ against temperature for bitumen –
acacia sap composites. The solid lines have been fitted using loss superposition model function eq. 5.1. The values of A and $T_m$ obtained are given in Table 5.3.

Table 5.3 Frequency factor, A and $T_m$ values of bitumen- acacia sap composites

<table>
<thead>
<tr>
<th>Sample</th>
<th>A(Hz)</th>
<th>$T_m$(K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>B100AS0</td>
<td>2.7E17</td>
<td>296.86±2.34</td>
</tr>
<tr>
<td>B75AS25</td>
<td>2.26E34</td>
<td>297.60±3.55</td>
</tr>
<tr>
<td>B50AS50</td>
<td>2.4E34</td>
<td>300.12±1.56</td>
</tr>
<tr>
<td>B37.5AS62.5</td>
<td>2.4E36</td>
<td>301.44±2.43</td>
</tr>
</tbody>
</table>

The values of $T_m$ increased with increase in acacia sap content indicating increased stiffness of the bitumen matrix.

The loss modulus intensity for the composites increased with increase in percentage of acacia sap content indicating stiffening. Cellulose-acacia sap being a semicrystalline material, when mixed with bitumen (amorphous material) the crystallites impose chain constrains, which restricts the number of chains participating in the relaxation process, thus increasing the loss modulus, this is in agreement with literature (Frederika et al, 2010). Therefore an increase in temperature in bitumen makes the relaxation process become faster due to softening of the polymer and increases intensity due to chain constraints imposed by crystallization. The introduction of acacia sap changes the molecular environment and the molecular response to strains due to polar hydroxyl groups. The loss modulus peaks also shifts to higher temperatures with increasing acacia sap concentration. This shift is due to acacia sap introducing rigid phases resulting from molecular interactions. This
produces a more rigid interface in the bitumen matrix. This restricts the number of chains participating. Cellulose-acacia sap being semicrystalline introduces some ordering of the chains thus making the response to be collective. This is because the chains cannot take up all the conformational possibilities that are theoretically possible. With the presence of crystalline phases, the molecular dynamics become more cooperative in nature thus giving a shift of the loss modulus. This observation is in agreement with reports from William and Perkins, (1999); Young and Baird, (2000) and Carnerio and Maia, (2000). The curves also show that with increase in acacia sap content in the composites, phase inversion is delayed due to hydroxyl groups as more energy is needed to soften the stiff polymer matrix.

5.3.4 Time-temperature dependence of relaxation time

![Graph showing time-temperature dependence](image)

Figure 5.5: Time-temperature dependence of the relaxation process in bitumen-acacia sap composites
Figure 5.5 show time-temperature dependence of mean relaxation time for the pure bitumen and bitumen-acacia sap composites follows VFT law confirming that these are dynamic glass transition processes. The solid line has been fitted using the VFT model equation

$$
\tau = A \exp \left[ \frac{B}{T - T_o} \right]
$$

(5.2)

where $A$ is pre-exponential factor, $B$ is constant explain in section 3.2.2, $T$ is absolute temperature and $T_o$ is ideal (Vogel, 1921) temperature which is $50^\circ C$ below $T_g$.

The fit parameters obtained are as shown in Table 5.4. The glass transition temperature ($T_g$) obtained from the VFT for pure bitumen was $\approx 50 + T_o = 321.5K$ or $48.5^\circ C$ while the $T_g$ obtained from the maximum loss modulus peak in Figure 5.4 at $1Hz = 288K$ or $15^\circ C$ while the one reported in literature is $11.4^\circ C$ (Xiaohu and Isacsson, 2001). The discrepancies in the glass transitions are associated with method used.

<table>
<thead>
<tr>
<th>Sample</th>
<th>VFT-Parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$A$</td>
</tr>
<tr>
<td>B100C0</td>
<td>$11.51 \pm 2.16$</td>
</tr>
<tr>
<td>B75C25</td>
<td>$7.85 \pm 0.49$</td>
</tr>
<tr>
<td>B50C50</td>
<td>$8.74 \pm 0.63$</td>
</tr>
<tr>
<td>B37.5C62.5</td>
<td>$10.28 \pm 6.75$</td>
</tr>
</tbody>
</table>

The time-temperature dependence of the mean relaxation frequency ($\tau$) for the composites is shown in Figure 5.5. The glass transition temperatures for the composites can be obtained by adding $50^\circ C$ to $T_o$. 

The solid line has been fitted using the VFT model equation 

$$
\tau = A \exp \left[ \frac{B}{T - T_o} \right]
$$

(5.2)
From Figure 5.5, it can also be seen that the relaxation processes exhibited are glass transition processes, due to shifts; confirming that the molecular motions are cooperative. It can also be inferred from the results that as acacia sap loading increases the relaxation frequency is reduced. This is attributed to the induced chain stiffness by the sap and is in agreement with literature (Naskar et al., 2010 and Carneiro and Maia (2000).

5.4 Effect of acacia sap on creep and creep recovery behaviour of bitumen

5.4.1 Creep and recovery

The viscoelastic creep and recovery data were obtained under constant stress. On the base of creep data the isothermal curves of the creep strain percentage versus time for each composite was obtained as shown in Figure 5.6

![Creep master curve at 20, 25, 30 & 35°C at constant stress as a function of temperature for bitumen-acacia sap composites; B100AS0, B75AS25, B50AS50 & B37.5AS62.5. Inset: magnified creep curves at 20, 30 & 35°C.](image)
The creep data for bitumen at 20°C are great, while at 25, 30 and 35°C creep values are very small due to viscous flow as shown in Figure 5.6. This is in agreement with results reported in literature for bitumen primary viscoelastic functions (Xiaohu and Isacsson, 2001). The creep values of the bitumen-acacia sap composites at 20°C are small in comparison with pure bitumen as shown in Figure 5.6. As the content of acacia sap increases in the composites the creep at 20 °C also decreases due to stiffening. This shows good creep response. It is also evident from the curves that creep values of the composites at 25 °C are greater than at 20 °C and increases with increase of acacia sap loading in the composite that is phase inversion occurs due to weakening of bitumen-acacia sap interface thus allowing deformation. This may also be attributed to chains untangling and slipping relative to one another which increase with temperature and time. This trend is also shown by the master curve in Figure 5.6.

From the Figure 5.6, it is also evident that at 30 and 35 °C creep values for all composites are very small and almost overlapping. This is due to the fact that at higher temperature polymers become too viscous and flow like liquids. This shows that creep increases with increase with temperature until it reaches a threshold value where it no longer creeps. The creep behavior of a material indicates its susceptibility to deformation under stress.

Recovery is the ability of a material to return to its original state once the stress or stretching force acting on it has been removed. From the recovery data, the recovery percentage versus time was plotted as shown in Figure 5.7.
Figure 5.7: Recovery master curves vs time for bitumen-acacia sap composites at 20, 25, 30 and 35 °C.

The recovery data for bitumen at 20°C is small, while at 25, 30 and 35 °C the creep recovery is very high due to flow shown in Figure 5.7. The recovery values at 20 and 25 °C for bitumen-acacia sap composites are negligible due to molecular reorientation and slippage of chains. The composites recovered fully at 30 and 35 °C due to less chain entanglement. The recovery increases with acacia sap loading in the composites. Acacia sap stiffens the bitumen matrix thus decreasing chain entanglement this results to increase in recovery.

The hydroxyl groups in the bitumen-acacia sap composites together with bitumen-acacia sap composites chains untangling and slipping relative to one another results in a continuous polymer network formation in the bitumen and imparts elastic behavior to the composites. This elastic behavior is reflected through the higher creep and recovery values of composites at all examined temperature in comparison with
bitumen. This suggests that the network formation strongly depends on the bitumen-acacia sap ratio and their interactions.

### 5.4.2 Creep modulus, E

It’s the ratio of stress to strain. The creep modulus is dependent on time and temperature. It decreases with increase of time and temperature. From the creep data the isothermal curves of the creep modulus, E, versus time was plotted as shown in Figures 5.8 (a) to Figure 5.8 (d).

![Figure 5.8](image)

Figure 5.8: Creep modulus versus time for bitumen-acacia sap for a) B100AS0, b) B75AS25, c) B50AS50 & d) B37.5AS62.5 respectivefully.

From these Figures, it can be seen that the creep modulus for all composites decreased with increase in temperature and time due to softening and long periods of heating.
From the master curves in Figures 5.9 (a) to (d), it can be seen that the creep modulus, \( E \), for all composites increased with increase in acacia sap loading at the same temperature. This is because acacia sap stiffens the bitumen matrix. It can also be inferred from the Figures that the creep moduli obtained for all composites at 20 °C are greater than at 25, 30 and 35 °C. This shows that creep modulus decreases with increase in time and temperature. At low temperature (short times) polymers are stiff thus strain less, as temperature increases (longer times) polymers become soft and strains more.

By selecting as the reference the curve for 20°C, and then shifting all other isothermal curves of the creep modulus vs. time obtained at 25, 30 and 35°C with respect to time
horizontally, the master curves of creep modulus vs. time at references temperature for all composites are regenerated as shown in Figure 5.10.

Figure 5.10: Master curves of creep modulus vs. time for all bitumen-acacia sap composites.

Figure 5.11: Temperature dependence of the shift factor $a_T$ for bitumen-acacia sap composites containing 0, 25, 50 and 62.5wt% acacia sap loading.
The shift factor is a measure of how a material’s frequency response changes with the variation of temperatures. From the curves it was deduced that at short time intervals the composites exhibited a relatively high creep modulus while at longer times viscous flow occurred and the composites exhibited a relatively low modulus. The results displayed in Figures 5.9 (a) to (d), may be explained as follows. Creep modulus is very high for bitumen-acacia sap composites at short times because the acacia sap resists the slippage, re-orientation and motion of the polymer chain in the bitumen. As time increases the creep modulus decreases this is due to the fact that stress decreases the activation barrier for bond dissociation, thus allowing the molecular chains to move more easily. Hence under a constant stress polymers undergo molecular relaxation or rearrangements which become more pronounced with time and are faster at higher temperatures. From the shift master curves in Figure 5.10 it can be inferred that creep modulus for pure bitumen is lower than that of composites and is highest for blend with highest acacia sap content. This shows that creep modulus increases with increase in acacia sap loading which indicates the reinforcing effectiveness of acacia sap.

The experimental data for shift factors, \( a_T \), were tested with Arrhenius eq. 5.3 and WLF eq. 5.4 models.

\[
\tau = \tau_o \exp \left[ \frac{E_o}{kT} \right] \tag{5.3}
\]

\[
\log a_T = -\frac{C_1(T - T_o)}{C_2 + T - T_o} \tag{5.4}
\]

\( C_1 & C_2 \) are empirically determined constants, \( T \) is the selected temperature, in °C or K, and \( T_o \) is the reference temperature, in °C or K. \( \tau \) is relaxation time, \( \tau_o \) is the pre-
exponential factor, $E_a$ is the activation energy and $k$ is the Boltzmann constant. The experimental data showed good agreement with the William Landel Ferry as shown in Figure 5.11. The shift factor master curves in Figure 5.11 shows that the shift factor increases with increase in acacia sap being greatest in composites with 62.5% acacia sap loading. The values of $C_1$ and $C_2$ determined from WLF equation are recorded in Table 5.5.

Table 5.5: Values of $C_1$ and $C_2$ from WLF model eq. 5.4

<table>
<thead>
<tr>
<th>Sample</th>
<th>$C_1$</th>
<th>$C_2$</th>
<th>$T_o$ (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>B100AS0</td>
<td>3.50±0.14</td>
<td>5.00±0.60</td>
<td>20.00±0.60</td>
</tr>
<tr>
<td>B75AS25</td>
<td>4.03±0.34</td>
<td>5.95±1.32</td>
<td>19.99±0.11</td>
</tr>
<tr>
<td>B50AS50</td>
<td>4.69±0.59</td>
<td>6.60±1.95</td>
<td>20.00±0.19</td>
</tr>
<tr>
<td>B37.5AS62.5</td>
<td>5.51±0.76</td>
<td>7.24±2.44</td>
<td>20.01±0.22</td>
</tr>
</tbody>
</table>

The values of $C_1$ and $C_2$ depend on the particular morphology or structure associated with a given sample. From Table 5.5, it is seen that the values of $C_1$ and $C_2$ increased with increase in acacia sap loading indicating changes in the free volume with respect to temperature. According to Champion et al. (2001), as the sample becomes more crystalline (e.g. polyethylene or the asphalt paraffins) 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. The shift factor indicates that prediction of the long-time extends upto more than $10^6$ s in time scale.
CHAPTER SIX

CONCLUSIONS AND RECOMMENDATIONS

6.1 Conclusions

The purpose of this research was to study the dynamic mechanical and thermal properties of bitumen-acacia sap composites. Specifically, the research was geared towards improvement of bitumen rheological properties to minimise thermal cracking at low temperatures, rutting at high temperatures and improve its thermal properties such as stability and degradation.

An investigation on the mechanical and thermal properties of the injected drawn composites of bitumen and acacia sap has been presented. From the analysis of the results, the following conclusions can be made: The thermal stability of the bitumen blends decreased with increase in acacia sap loading, this is evidenced by decreased activation energy values and peak decomposition temperatures.

One glass transition that shifts to higher temperature with acacia sap intake due to induced stiffness is observed. In the low and high in-service temperatures, addition of acacia sap led to increased values of the storage and loss moduli. In addition, the glass transition temperature was increased; this is evident by the shift of the glassy region to higher temperatures. Phase inversion in bitumen was observed, evident at 25 °C.
The creep modulus of the composites was found to decrease with increase of temperature and time. This shows the reinforcing effects of acacia sap. As a result, bitumen modification with acacia sap had enhanced improvement of its rheological properties. That is, increased resistance to permanent deformation or rutting at high temperatures, better flexibility at low temperatures and also enhanced thermal and fatigue cracking resistance. In addition, they have also narrowed the relaxation spectrum and stiffened the bitumen.

### 6.2 Recommendations and Further work

A number of issues have come up in this research that need more investigation using supplementary measurements methods like the x-ray diffractometry, scanning electron microscopy, among others. These techniques will reveal more on the rheological structure of the composites and hence the ability to give a more accurate explanations of the molecular dynamics of these materials. Due to frequency limitation of mechanical measurements, it is important to make broadband frequency measurements preferably using dielectric spectroscopy with broadband measurements to reveal dipole relaxation processes, differential scanning calorimetry to confirm glass transition temperatures. Models can be developed and employed that govern molecular dynamics in relation to acacia sap concentration.

Surface treatment of roads with bitumen is important for transport as this improves the resistance to deformations of the roads as a result of heavy traffic levels and load effect. Highway road pavement should be made with bitumen modified with acacia sap to prevent flow at high temperatures since acacia sap is stiff. Further studies should dwell more onto understanding morphological properties before applying the
modifier in bituminous binding elements. The conclusion of this study covers utilization of acacia tree sap and 80/100 bitumen penetration grade. More research should be carried out by using different kinds of natural polymers and different grades of bitumen obtained from different crudes. Thus, acacia sap can be used in bitumen modification in order to improve road pavement applications.
REFERENCES


Sepe, P. M. (1992). Dynamic and mechanical analysis; *Journal of advanced materials and processes;* **32**:34.


APPENDIX I: Lindberg/Blue mini-mite Tube Furnace
APPENDIX II: Dynamic Mechanical Analyzer 2980 TA

DMA 2980 TA machine

Monitor
Processor
Mouse
Keyboard
APPENDIX III: Thermogravimetric analysis

APPENDIX IV: Samples
APPENDIX V: 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 VI: Shear Sandwich clamp
APPENDIX VII: DMA module connection