DYNAMIC MECHANICAL ANALYSIS and THERMAL PROPERTIES OF BITUMEN-ACACIA SAP COMPOSITES

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ABSTRACT

Bitumen binder mechanical and thermal properties have been unsatisfactory. Different synthetic binder modifies that have been used to improve its performance have led to environmental problems such as incineration and landfill. Acacia sap, a natural and environment-friendly polymer, has been used successfully as a modifier. Composites of bitumen-acacia sap with different composition of sap percentage ranging from 0% to 62.5% cell sap were prepared by injection drawing process. The composites were analyzed by dynamic mechanical analysis (DMA) for mechanical properties and Thermogravimetric Analysis for thermal properties. Storage modulus and Loss modulus of bitumen binder increased with acacia sap loading. Glass transition temperatures were found to shift to higher values as acacia sap loading increased. Activation energies were determined from the thermogravimetric data of the bitumen-acacia composites using the Broido model. Pure bitumen binder had the highest thermal stability. Modification of bitumen binder with 25% acacia sap loading gave optimum mechanical properties. Further studies should dwell more on understanding morphological properties of bituminous binding elements and using different kinds of natural polymers and different grades of bitumen obtained from different crudes.

Key words: Acacia, Bitumen, Modulus, Thermogravimetric

1.0 INTRODUCTION

Bitumen is a low molecular weight hydrocarbon obtained by fractional distillation of crude oil and catalytic cracking of hydrocarbons **[11].** Because of its good adhesive, impermeability and viscoelastic properties , It has wide range of applications such as used as a binder of aggregate in road construction, 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 **[4]**. However, its performance when subjected to high traffic levels and rigorous climatic changes has been unsatisfactory. 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 **[6]**. Different types of binder modifiers used to improve performance have led to environmental problems such as incineration and landfill. Most commonly used synthetic 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. Use of acacia sap (natural polymer) as a modifier has improved bitumen performance and has a much better disposal solution compared synthetic polymers which cause environmental problems during disposal. Viscoelastic properties of the modifiers are important in predicting road characteristics over wide range of temperatures and traffic loadings **[9, 14]**. Materials that are stable at extremely low and high temperatures are likely to be better performances. Since the binders are subjected to very low and high temperatures and to high traffic loadings during their applications, knowledge of mechanical properties and thermal degradation behavior of the modified binders is essential for understanding their performance. This study was carried out with the objective of investigating the mechanical and thermal properties of bitumen binders modified using different proportions of acacia sap.

MATERIALS AND METHODS

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^{o}C. The acacia sap was obtained from Acacia trees.

Bitumen 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^{o}C and maintained at that temperature for 5 minutes to melt the bitumen. Dry acacia sap was added and the mixture mechanically stirred continuously with a screw for 5 minutes to obtain 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 2.1. 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 as illustrated in Figure 2.2. The mixture was allowed to cool at room temperature. 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 acacia sap weight percentage was added to bitumen and the mixing was maintained at 160^{o}C. After mixing, the resulting dispersion was poured into the Petri dish and then stored at room temperature to retain the morphology. 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±0.5mm x 10±0.5mm x 2±0.5mm.

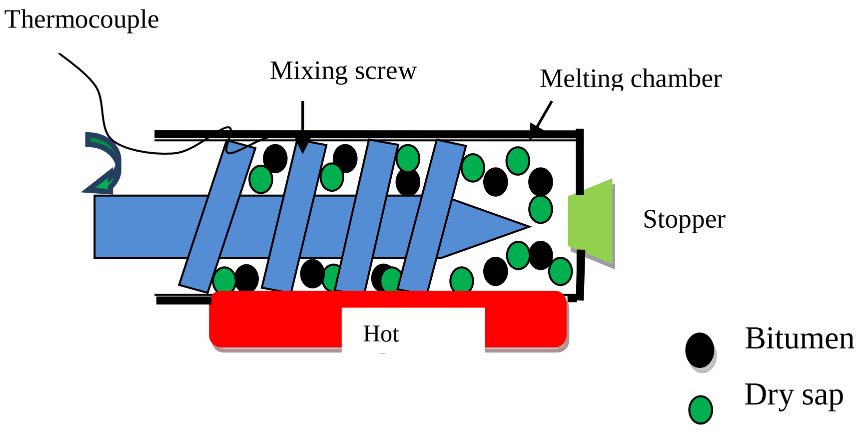

Figure 2.1: Heating process

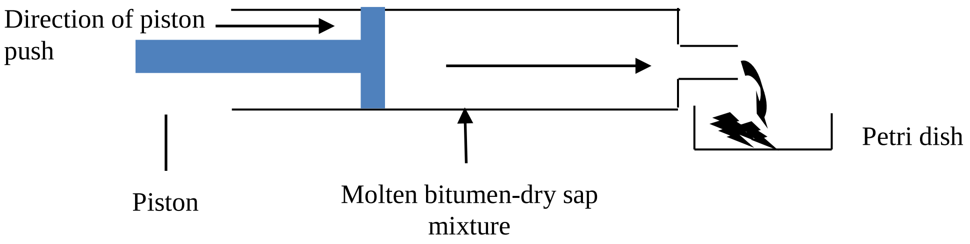

Figure 2.2: Injection drawing process

2.5 Thermogravimetric Analysis of the composites

The thermogravimetric analysis (TGA) was carried out using the Lindberg/blue TF55035C mini Tube furnace in oxidative atmosphere. Heating was done from room temperature (25^{o}C) at a rate of 5^{o}C/min in the range of 80-550^{o}C with aluminium containers as reference materials. 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.

2.3 Dynamic Mechanical Analysis

Dynamic mechanical analysis was carried out using DMA 2980 TA instrument in the shear sandwich mode on samples about 10 ±0.5 mm x 10±0.5 mm x 2±0.2 mm that were 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. Measured data on dynamic mechanical analyzer TA 2980 and TGA was analyzed using microcal card origin 8 software.

3.0 RESULTS AND DISCUSSION

3.1 Thermal analysis

3.1.1 Thermogravimetric analysis

TGA studies have been carried out to determine thermal stability and degradation temperatures of the composites. Figure 3.1 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 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 derivative thermogravimetric 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.

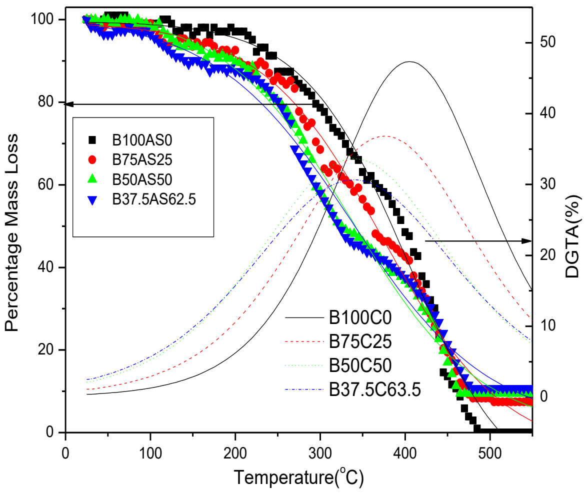

Figure 3.1: TGA and DTGA thermograms for pure bitumen and bitumen-acacia sap composites containing 0, 25, 50 and 62.5wt% acacia sap loading at heating rate of 5°C/min.

Table 3.1 Decomposition temperature of the bitumen-acacia sap composites

SAMPLE	Decomposition Temperature(°C)
B100AS0	432.30 ± 2.55
B75AS25	429.41± 1.78
B50AS50	400.19± 2.34
B37.5AS62.5	379.73± 1.47

It is also evident from Figure 3.1 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 was 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.

3.1.2 Decomposition temperature of the composites

The peak decomposition temperature of the bitumen-acacia sap composites were obtained from the maximum peak temperature of the DTG curves shown in Figure 3.1. Bitumen has a high molecular mass (10000 to 100000) than acacia sap (10000 to 15000) **[8]** polymer, this resulted in decomposition of bitumen at higher temperature than the bitumen-acacia sap composites. The peak decomposition temperatures decreased with increase in acacia sap loading in the composites as shown in Table 3.1. 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 other researchers **[9]**. The decomposition temperature of bitumen according to literature ranges from 440 to 650 °C [20] while that of cellulose-dry acacia sap from 250 to 350 °C **[8]**.

3.1.3 Determination of Activation Energies

Figure 3.2 shows the kinetic curves of thermal degradation of bitumen-acacia sap composites. The solid lines have been fitted using the Broido model **[1]**.

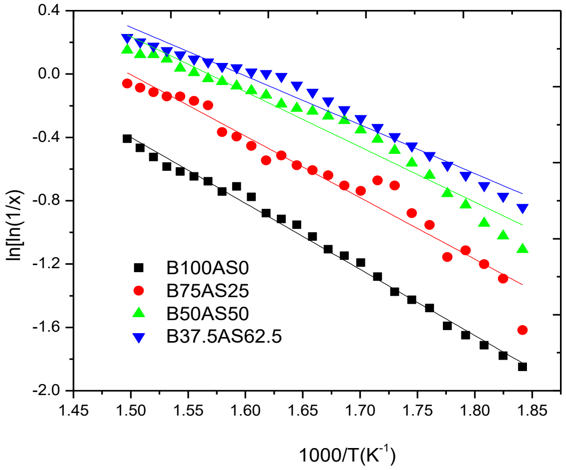

Table 3.2: Activation energies of bitumen-acacia sap composites

Bitumen-acacia sap composites	Activation energy (kJ/Mol)
B100AS0	34.65 ± 0.56
B75AS25	32.30 ± 1.44
B50AS50	28.96 ± 1.24
B37.5AS62.5	25.61 ± 0.88

Figure 3.2: Natural logarithm of fraction of residual mass versus reciprocal temperature of the composites.

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 3.2 that the composites 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 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. 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 **[2]** using the Friedman's technique.

3.2. Rheological properties of bitumen-acacia sap composites

3.2.1. Storage Modulus

The storage modulus E', is a measure of the rigidity (stiffness) and resistance to deformation of the sample. The storage modulus of the pure bitumen decreased with increase in temperature due to softening. It also shifted to the right with increase of frequency as shown in Figure 3.3 (a). 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.

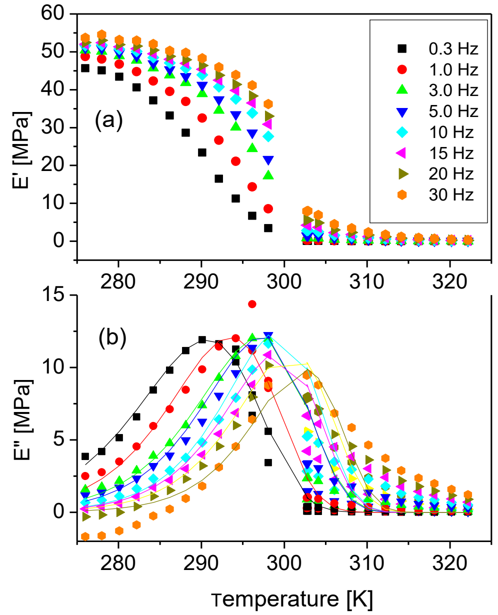

Figure 3.3: Variation of a) Storage modulus E'; b) Loss modulus E" of pure bitumen with temperature at different frequencies

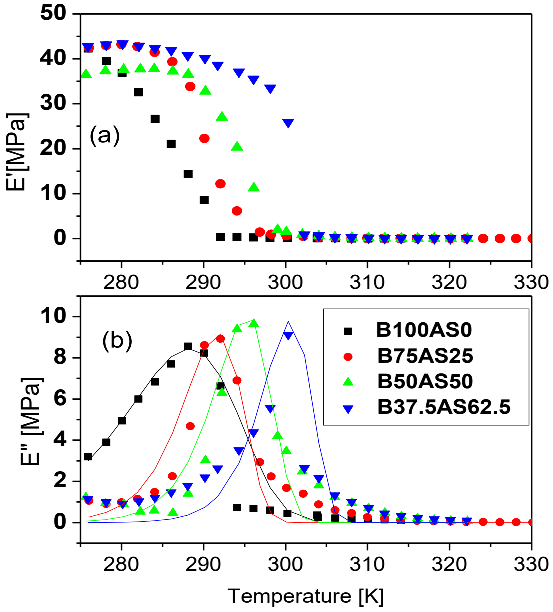

Figure 3.4: a) Storage modulus E' b) Loss modulus E'' for bitumen-acacia sap blends at 1 Hz

The storage moduli of the bitumen-acacia composites are greater than that of bitumen as shown in Figure 3.4 (a), 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. The composites softened at higher temperatures than bitumen. This results from crystallization. A phenomenon 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 also reached a plateau at higher temperatures than bitumen; this is due to existence of molecular entanglements which makes the chains temperature resistant. These plateaus terminated at 320 K when the samples began to flow due to softening. These patterns of behaviour 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 other researchers **[5]**.

3.2.2 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 3.3 (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 **[13]**.

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

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 refers to different processes which contribute to mechanical response.

From figure 3.3b, 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 is 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. In addition, from Figure 3.4b; 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 **[6]**.

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 conformations 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 other researchers **[3, 17, 19**]. 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.

3.2.3 Time-temperature dependence of relaxation time

Table 3.3 VFT fitting parameters

Sample	VFT-Parameters A	B	T_o (K)
B100C0	11.51 ± 2.16	242.08 ±98.86	271.46 ±4.30 a
B75C25	7.85 ± 0.49	74.15 ± 0.60	281.85 ±0.63
B50C50	8.74 ± 0.63	103.79 ±16.87	283.16 ±0.93
B37.5C6 2.5	10.28 ± 6.75	71.90 ± 6.99	295.39 ±1.93

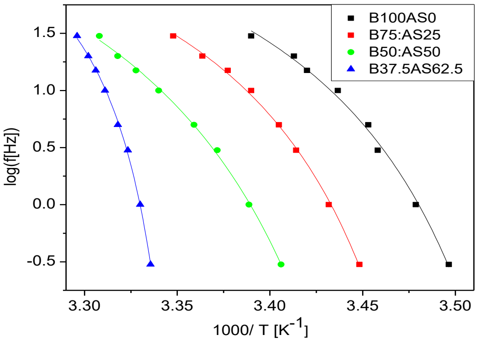

Figure 3.5: Time-temperature dependence of the relaxation process in bitumen- acacia sap composites

Figure 3.5 show that the 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 **[15]**

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

The fit parameters obtained are as shown in Table 3.3. The glass transition temperature (T_g) obtained from the VFT for pure bitumen was ≈ 50 + T_o = 321.5K or 48.5° C while the T_g obtained from the maximum loss modulus peak in Figure 3.3 at 1Hz = 288K or 15° C while the one reported in literature is 11.4°C **[18]**. The discrepancies in the glass transitions are associated with method used. The glass transition temperatures for the composites can also be obtained by adding 50°C to T_o. From Figure 3.5, 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 **[3, 9]**.

3.3 CONCLUSIONS

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 were made: The thermal stability of the bitumen-acacia sap binders decreased with increase in acacia sap loading, this is evidenced by decreased activation energy values. Addition of acacia sap to bitumen binder led to increased values of the storage and loss moduli. The glass transition temperature was increased; this is evident by the shift of the glassy region to higher temperatures. Modification of bitumen binder with 25% acacia sap loading gave optimum mechanical properties.

3.4 RECOMMENDATIONS AND FURTHER WORK

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.

3.5 ACKNOWLEDGEMENT

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