Comparative rheological study of A. nilotica subspecies of Sudanese origin

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Abstract
Solutions at relatively high concentration (25% - 50%) of Composite samples of subspecies, A. nilotica var. tomentosa, A. nilotica var. nilotica from Sinnar, Blue Nile, and A. nilotica subsp. adistringen from Kordofan state, were subjected to Shear flow viscosity, and Oscillating flaw behaviour. At (50%) concentration, the results show Newtonian flow behaviour in the shear rate range 0.1 s\(^{-1}\) to 100 s\(^{-1}\), for subsp. tomentosa, and adistringen, while subsp. nilotica show Newtonian flow behaviour in the shear rate range 10.0 s\(^{-1}\) to 100 s\(^{-1}\), at (25%) concentration the results show subsp. tomentosa, and subsp. adistringen exhibit shear thinning behaviour in the shear rate range 0.1 s\(^{-1}\) to 1 s\(^{-1}\), while subsp. nilotica at 10%, 20%, 30%, 40% concentration exhibit shear thinning behaviour in the shear rate range 0.1 s\(^{-1}\) to 10 s\(^{-1}\). The loss modulus (G\(_{\prime\prime}\)) of the above A.nilotica subspecies was higher than the storage modulus (G\(_{\prime}\)). Energy of deformation is dissipated viscously and the samples exhibits liquid-like behaviour.

Keywords: Comparative rheological study, A.nilotica subspecies, Sudanese origin

1. Introduction
A. nilotica (L.), Del. is a ‘commercially’ important, a naturally occurring tetraploid species widely distributed in subtropical and tropical Africa and in Asia eastwards to India. It is essentially, a tree of semiarid and arid regions. A. nilotica is mostly restricted below 450 m elevation and grows on a variety of soils. It has a deep and extensive root system. It produces showy bright yellow flowers that are pollinated by bees (Tybirk, 1993) \(^9\). Its seeds exhibit dormancy. Mature pods are broken by dry winds or remain indehiscent on the ground and are not designed for long distance dispersal (Luna, 1996) \(^5\). Regeneration occur close to the parent tree resulting in high degree of inbreeding. These species are exceedingly variable with nine subspecies having been recognized with more or less distinct morphological, ecological and geographical features (Dwivedi, 1993) \(^3\). A.nilotica which originated from India and Pakistan, commonly known as prickly Acacia in Australia, is an introduced weed of national significance. It cans predominantly cattle and sheep grazing lands into impenetrable thickets.

A.nilotica plantations of the Sudan Blue Nile flood basins form a significant resource with an area exceeding, 5. 7 million hectares. The contribution of A.nilotica species to the total sawn timber production in Sudan is estimated at 40%-50%. Its contribution to the production of timber is considered as second to Eucalyptus. The latter continues to be the major source of timber in the Sudan. A.nilotica (Sunt) also adds substantial volume to the production of fuel wood estimated at 10%-15% of the country's total full energy production. There were three main subspecies of A.nilotica in Sudan. A. nilotica var. tomentosa is one of an important and high density trees among A.nilotica subspecies in Sinnar state, in a survey of Sinnar, Blue Nile states and Kordofan, 90% of A. nilotica var tomentosa found in Sinnar state, A. nilotica var nilotica is widely distributed in the Blue Nile state. A.nilotica var adistringen prevail in Kordofan state. The main factor of distinguishing between A.nilotica subspecies is the fruit pods Figure (1.1).
Viscoelasticity is a time-dependent property in which a material under stress produces both a viscous and an elastic response (Goodwin et al., 2008) [4]. A purely elastic material (solid-like behavior) produces a phase angle of zero, indicating that induced strain is exactly in phase with the applied stress. A purely viscous sample (liquid behavior) has a phase angle of 90°, the stress and strain being a quarter of a cycle out of phase. Viscoelastic materials can produce phase angles between 0-90°, hence solid-like or liquid-like, characteristics depending on applied deformation conditions. Phase angle is referred to indirectly using the parameters storage modulus (G′) and loss modulus (G″), the terms were mathematically derived from the modulus of the material and the phase angle, the loss factor, \(\tan\delta = (G″/G′)\). G′ is a measure of the deformation energy stored in the sample during the shear process, representing the elastic behavior of a sample. In contrary, G″ is a measure of the deformation energy used up during shearing and lost afterwards, representing the viscous behavior of a sample (Mezger, 2002) [6]. If G′ > G″ the sample exhibits solid-like behavior (elastic properties dominate). However, if G′ < G″, the energy used to deform the material is dissipated viscously and the sample exhibits liquid-like behavior (viscous properties dominate). In practice, two key variables can be altered during oscillatory testing to investigate the characteristics of material the oscillation timescale or frequency and the amplitude of the applied stress (or strain). It has been reported that gum arabic solutions show Newtonian flow behaviour in the shear rate range from 50 s\(^{-1}\) to 100 s\(^{-1}\), even at concentration as low as 4% (Mothé et al., 1999) [9]. In the shear rate range from 1 s\(^{-1}\) to 50 s\(^{-1}\). However shear thinning behaviour was observed. In the gum arabic concentration range between 10 and 25%, gum arabic solutions show a significant shear thinning behaviour, as compared with that of solutions with concentration in the range 30-50% (Mothé et al., 1999) [9]. Time dependent thickening flow behaviour has been observed for 3 wt% gum arabic solutions at shear rate below 1 s\(^{-1}\). Gum arabic solutions have shown shear thinning behaviour at concentrations between 3 and 32 wt% (Sanchez et al., 2002) [10]. Gum solution above 30% shows higher solution viscosity and exhibit pseudoplasticity (Williams et al., 1990) [11].

2. Material and Method

2.1 Material

Two composite samples of \textit{A. nilotica var. tomentosa}, and two composite samples of \textit{A. nilotica var nilotica} gum were collected from Sinnar and Blue Nile states, while other one composite sample of \textit{A.nilotica var adistiringen} was collected from Kordofan state (Figure 2.1), the samples represent a wide range of the natural distribution of these subspecies in the country. Originally of samples was authenticated by Soba Forestry Research Centre Herbarium, and Sinnar, Blue Nile, and Kordofan states forestry corporation.

### 2.1.1 Purification of crude gum.

The gum samples were relatively pure; however, impurities such as wood pieces and sand particles were carefully removed by hand. Each sample was reduced to a fine powder using a mortar and pestle, and kept in labeled self-sealed polyethylene bags.

![A. nilotica Subspecies gum samples, subsp. tomentosa (A), subsp. nilotica (B), subsp. adistiringen (C)](image-url)
2.2 Method
2.2.1 Solutions preparation
50% w/w (based on dry weight) gum solutions were prepared in water containing 0.005% w/v Na3PO4 as a preservative. The solutions were agitated on a tube roller mixer (SRT9, Stuart Scientific, UK) overnight to ensure complete dissolved. Solutions were then centrifuged for 10 minutes at speed of 3000 rpm using (Megafuge 1.0R, Heraeus SEPATECH, Germany) centrifuge. Dilutions were prepared from stock solutions recentrifuged and stored at 4°C.

2.2.2 Rheological measurements
Rheological measurements were carried out using KINEXUS Pro+* (Malvern Instruments) fitted with cone (40 mm, 2°) and plate geometry. Steady shear viscosity curves were measured for gum solutions at (50%, and 25%) concentration upon shear rate of 0.10 to 10000 s⁻¹, and subsequent shear rate ramp-down (from 10000 back to 0.01 s⁻¹) of A.nilotica var tomentosa and adstringen, while shear viscosity curves of A.nilotica var nilotica were measured for gum solutions at (50%, and 30%) concentration upon shear rate of 10.0 to 10000 s⁻¹, and subsequent shear rate ramp-down (from 10000 back to 10.0 s⁻¹). Dynamic rheological measurements, to determine the elastic modulus (G'), viscous modulus (G''), and dynamic viscosity, were performed within the frequency range of 0.1–10 Hz. The linear viscoelastic region was assessed, at 1 Hz. The temperature of the samples were controlled within 0.1°C using a Peltier element. The rheometer control and data processing was programmed uses computer software (Rheology Advantage Data Analysis Program).

3. Results and Discussion
3.1 Shear flow viscosity
The effect of shear rate on viscosity, at 25°C, of A. nilotica subspecies, gum solutions at different concentrations are shown in Figures (3.1 – 3.3). The results show Newtonian flow behaviour in the shear rate range from 0.1 s⁻¹ to 100 s⁻¹, for subsp. tomentosa, and adstringen, but subsp. nilotica show Newtonian flow behaviour in the shear rate range from 10.0 s⁻¹ to 100 s⁻¹ at (50%) concentration. At low concentration in the shear rate range from 0.1 s⁻¹ to 10 s⁻¹ the shear thinning behaviour has been observed for all above subspecies. The flow curves at increasing shear rates showed that the apparent viscosity (ηp, Pa.s) decreased as the shear rate increased. After a sharp reduction, the viscosity change was smoothened at high shear rates ~ 100 s⁻¹ this can be related to the reduction in the size of colloidal aggregates as the shear rate increases. No evidence of a trend to a Newtonian low-shear plateau (the so-called zero-shear viscosity) was observed even at shear rates as low as 0.1s⁻¹. At intermediate shear rates (above 10 s⁻¹) for subsp. nilotica, and (above 1 s⁻¹) for subsp. tomentosa, and subsp adstringen a trend to a high-shear Newtonian plateau was observed.

As shown in Figure (3.1 – 3.3) increasing shear rate the disruption predominates over formation of new entanglements. This could be attributed to the fact that molecules align in the direction of flow and the viscosity decreases (Dakia et al., 2008). Similar shear-thinning flow behaviour has been reported for gum arabic (Williams et al., 1990, Mothé et al., 1999, Sanchez et al., 2002)[11, 9, 10]. The apparent viscosity values increase when gum concentration rose. The Newtonian plateau limit shifts to a lower shear region (~1s⁻¹) for subsp. tomentosa, and subsp adstringen, and (~10 s⁻¹) for subsp. nilotica compared to the lower concentration solutions similar to that for polysaccharides (Castelain et al., 1987)[12]. The flow behaviour of gum solutions is related to the colloidal nature, the average particle size and the size distribution. The presence of a large number of high molecular weight molecules increases the resistance to flow which, in turn, increases the apparent viscosity of gum solutions (Tanaka et al., 2006)[13].

![Fig 3.1: Comparison of viscosity-Shear rate profile of A. nilotica var. tomentosa gum solutions between 25%, and 50% concentration of composite samples (whole) from Sinnar (CoS5), and Blue Nile state (CoBN4).](image-url)
3.2 Dynamic rheological behaviour

Viscoelastic properties of *A.nilotica* subspecies, *tomentosa*, *adstringen* and *nilotica*, gum solutions at 50% concentrations were determined using oscillatory testing. Mechanical spectra of solutions revealed a typical liquid-like behaviour Figures (3.4 - 3.7). The loss modulus (G″) of all samples of *A.nilotica* subspecies was higher than the storage modulus (G′), the energy used to deform the material is dissipated viscously and the samples exhibits liquid-like behaviour. The moduli showed less frequency dependence at lower frequency range and relatively higher frequency dependence at higher frequency range. There was a cross over point in the curves of Figure (3.7) at 10% concentration of subsp. *nilotica*, where the values of G′ equaled that of G″ (G′= G″) after which the value of gain modulus exceeds that of the loss modulus. This indicates an elastic response due to formation of some weak gel-like structure.
**Fig 3.4:** The dynamic rheological behaviour ($G'$, and $G''$) of A. nilotica var. tomentosa gum solutions at 50% concentration from Sinnar State CoS5 (whole composite), Seifeldawla, et al (not publish)

**Fig 3.5:** The dynamic rheological behaviour ($G'$, and $G''$) of A. nilotica var. tomentosa gum solutions at 50% concentration from Blue Nile State CoBN4 (whole composite) Seifeldawla, et al (not publish)

**Fig 3.6:** The dynamic rheological behaviour ($G'$, and $G''$) of A. nilotica var. adstringen gum solutions at 50% concentration from Kordofan State (whole composite), Abeer, et al (not publish)
4. Conclusion
All A. nilotica subspecies, tomentosa, adstringen and nilotica, gum exhibit identical Shear flow viscosity, and Dynamic rheological behaviour. They show Newtonian flow behaviour at high concentration, and exhibits liquid-like behaviour.

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6. References
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