

1. Literature Review

1.1. Introduction

Natural gum is a colloidal polysaccharide substance that is gelatinous when moist but harden on drying, that is exuded by plants or extracted from plants by solvents and either soluble in or swelling up with water. Natural gum is prepared to be used in industries such as in pharmacy or cloth finishing or for adhesives and cosmetics, emollients, as stabilizer in confectionery (Al-Assaf et al., 2009).

Polysaccharides are composed of many monosaccharide residues that are joined one to the other by O-glycosides linkages. The great diversity of structural features of poly saccharides, which originates from differences in the monosaccharide composition, linkage types and patterns, chain shapes, and degree of polymerization, dictates their physical properties including solubility, flow behavior, gelling potential, and/or surface and interfacial properties. The structural diversity also dictates the unique functional properties exhibited by each polysaccharide (Islam et al., 1997); (Al-Assaf et al., 2005).

Gums is exudates from *Acacia* (family leguminosae) which in semi-arid land across sub-Saharan Africa. Sudan is the world's largest producer with production reaching 40,000 tons in 1996; Nigeria is the second largest, followed by Chad, Mali and Senegal (Islam et al., 1997). It consists mainly of high molecular mass polysaccharides and their calcium, magnesium and potassium salts, which on hydrolysis yield arabinose, galactose, rhamnose and glucuronic acid.

A. nilotica species is widely distributed in subtropical and tropical Africa from Egypt and Mauritania southward to south Africa and in Asia eastwards to India .Subspecies *tomentosa* and *nilotica* tolerate and thrive under condition of periodic inundation and are most commonly found bordering seasonal watercourses ,irrigation canals, and depressions subjected to annual flooding (EL Amin, 1977;Voget,1995). In Sudan *A. nilotica* var. *tomentosa* prevail in a highly distributions in Sinnar and Blue Nile state, survey in these states predicted that subsp. *tomentosa* representing about 90% among *A. nilotica* and other subspecies in Sinnar state.

1.2. *Acacia* Genus

Acacia, which has often told us, may be widely present in the landscape, but its pollen is seldom found in any abundance. The pollen grains are heavy and probably not capable of long-distance transport, and even where they dominate the vegetation, their pollen is greatly under represented. Compounding the problem, *Acacia* pollen tends to break up into individual units that are difficult to identify (Brummitt, 2011).

1.3. *Acacia* Genus World Distribution

The Leguminosae form the third largest plant family in the world, comprising about 650 genera and 18000 species. The subfamily Mimosoideae, with 3000 species in 50–60 genera, is distributed worldwide and is abundant in tropical, subtropical and warm-temperate areas, Australia, Africa, and Madagascar, throughout the Asia - Pacific region and the Americas. (Polhill, and Raven 1981). Figure(1.1). *Acacia* is the most significant genus of the subfamily Mimosoideae. It is estimated that there are roughly 1380 species of *Acacia* worldwide, about two-third of them native to Australia and rest spread around tropical and subtropical regions of the world (Saini, et. Al, 2008). *Acacia* species although distributed throughout Pakistan, are mostly found in Sindh and Punjab Province. In Pakistan 34 species of *Acacia* are reported, most of them growing wild (Nasir and Ali 1974; Akhtar, 1992)



Figure.1.1: Distribution of *Acacia* trees over the world

1.4. *Acacia* Genus in Africa

African *Acacia* study started at the Oxford Forestry Institute (OFI) in 1987 when the first of four research schemes on the study and assembly of the genetic resources was funded by the Forest Research Programmed (FRP) of the Overseas Development Administration of the United Kingdom government (ODA), now the Department for International Development (DFID). Six species of *Acacia* have been recognized as being both widespread in Africa and as having the capacity to fulfill various combinations of roles in different environments in which there is a critical demand for their ameliorating qualities (Barnes and Fagg, 1995).

1.5. *Acacia* of the Sudan

Acacia species cover about two – third of the area of the Sudan (EL Amin, 1977). They extend from tropical rainforests in the south through deciduous savanna woodlands in central Sudan, to the sub-desert and desert of Northern Sudan, There are so far thirty one species of *Acacia* in Sudan (EL Amin,1977,Voget,1995), species with greatest distribution include *A. senegal* var *senegal* (Hashab), *A. seyal*(Talha), *A. polyacantha* (Kakamut), *A. laeta* (Shubahi),

A. mellifera (Kitir), *A. nilotica* (sunot), which have Three subspecies are found in the Sudan, namely subsp. *tomentosa* that characterized by the tomentose to pubescent pods and grow throughout Sudan, subsp. *nilotica* that characterized by the glabrous pods to pubescent and grow along the White Nile, and subsp. *adstringens* that characterized by the broad pods and grow in western Sudan (Elkhalifa ,K.F.,1996), *A. sieberiana* (kuk), and *A. oerfota* (nubica , laot) (Abdel Nour,1999).

1.5.1. *A. nilotica* (L.)Del

A. nilotica (L.)Del. is a commercially important, naturally occurring tetraploid tree species widely distributed in subtropical and tropical Africa and in Asia eastwards to India (Figure 1.2) 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 requires direct sunlight and has a deep and extensive root system. *A. nilotica* produces showy bright yellow flowers that are pollinated by bees (Tybirk, 1993). Its seeds exhibit dormancy as the tests is very hard. Mature pods are broken by dry winds or remain indehiscent on the ground and are not designed for long distance dispersal (Luna,1996).Regeneration may occur close to the parent tree resulting in high degree of inbreeding. This species is exceedingly variable with nine subspecies having been recognized with more or less distinctive morphological, ecological and geographical features (Dwivei, 1993). *A. nilotica* which originated from India and Pakistan, commonly known as prickly *Acacia* in Australia, is an introduced weed of national significance. It converts predominantly cattle and sheep grazing lands into impenetrable thickets. These thickets currently cover c. 6.5 million hectares and are costing Australian landholders an additional\$4–9 million annually, due to loss in production and increased control and running expenditure (Spies an March, 2004).



Figure.1.2. Natural distribution range of *A. nilotica*.

1.5.1.1. Classification

Kingdom: Plantae

Class: Magnoliopsida

Order: Fabales

Family: Leguminosae

Subfamily: Mimosoideae

Tribe: *Acacieae*

Genus: *Acacia*

Species: *A. nilotica* (L.) Wild. ex Delile.

Subspecies: *A. nilotica* var. *tomentosa* (tomentose), *A. nilotica* var. *nilotica* (glabrous), *A. nilotica* var. *adstringens*, *A. nilotica* var. *subalata*, synonyms: *A. nilotica* (L.) wild. ex Delile, *A. arabica* (Lam.) wild. *A. scorpioides*, *Mimosa Arabica* Lam., *Mimosa nilotica* (L.) *Mimosa scorpioides* (L).

Latin name: *A. nilotica*

English name: Egyptian thorn, red thorn

Indian name: Babul

Arabic name: Sunt (tree), Garad (fruit). (EL Amin, 1977; Voget, 1995).

1.5.1.2. Description of *A. nilotica* var. *tomentosa* tree

The tree has an ovoid crown (Wickens, 1995), It is 2.5–25 m tall (Bolton et al., 1985), bark dark grey, brown or black, rough and fissured. Stipules spinescent, straight, and white. 1-8 cm long pubescent. Leaves, 1-3 pinnae, 2-7 cm long, pinnae 4-9 pairs, 2.5-3 cm long. Leaflets 7-30 pairs. 1.5–6 x 0.5 mm. Inflorescence capitate, yellow, on pubescent peduncles 1.5–3 cm long, involucre on upper part of peduncle, subtending 1-3 flowers, floral bract pubescent, 1.5–0.3 mm, flower bisexual and male, sessile, yellow, pubescent, sepals 1.5 - 0.6 mm, petals 2.5 x 0.8 mm, anthers free, 5.5 – 6 mm long glandular. Fruits have variable pods, straight or slightly falcate 5 -20 x 1.2 cm, ridged, grey, tomentose to pubescent. seeds 10 -12, longitudinal in pods, elliptic to sub circular, 8 mm, long brownish –black, areoles u-shaped or closed o-shaped. Funicles 3 mm long, thin brown. Flowers July–September. Fruits March – May. (EL Amin, 1990). Figures (1:3, and 1:4).



Figure 1.3. *A. nilotica* var *tomentosa* trees in wad eljuzuli forest 15min from singa city by car near Blue Nile river, Sudan (2015)



Figure.1.4: *A.nilotica* var *tomentosa* trees and gum in valley 30 min from Singer city,Sinnar stae, Sudan (2015)

1.5.1.3. General uses of *A. nilotica*

A. nilotica an important source of wood, gums, tannins, fuel and animals fodder. They have significant pharmacological and toxicological effects. In Africa and the Indian subcontinent; *A. nilotica* is extensively used as a browse, timber and firewood species (Gupta 1970, Mahgoub 1979). The bark and seeds are used as a source of tannins (Shetty 1979, New 1980), it is also used for medicinal purposes. Bark of *A. nilotica* has been used for treating hemorrhages, colds, diarrhea tuberculosis and leprosy while the roots have been used as an aphrodisiac and the flowers for treating syphilis lesions (New, 1980). The gum of *A. nilotica* is sometimes used as a substitute for gum Arabic (obtained from *A. senegal*) although the quality is inferior (Gupta 1970). Indian gum is sweeter in taste than that of the other varieties and is used in paints and medicine. *A. nilotica* is suitable for the production of paper and has similar pulping properties to a range of other tropical timbers (Nasroun, 1979).

The *A. nilotica* is traditionally used for tanning and retanning in tropical Africa, and is one of the most important tanning materials in Northern India (Sarkar, 1991). The Sudanese leather industry uses mainly imported vegetable and mineral tanning materials (chrome). Local vegetable tannins such as garad (from the pods of *A. nilotica*) are abundant, but they do not produce the same quality of leather as wattle (bark is used).

Concrete is a highly energy and cost-intensive industry. The negative impacts of CO₂ emissions caused by cement production are well understood by the scientific community today. Therefore, the aim for future development is to align the concrete industry with the principles of sustainable development. This entails producing high performance concrete systems at reasonable cost with minimum carbon footprint. *A. nilotica* gum in addition to cement replacement with less energy and cost intensive mineral admixtures, fly ash (FA) and limestone powder (LSP), to produce low cost cementations systems with reduced carbon footprint. Commonly used branded chemical VEAs are costly (Lachemia, 2004) and their presence may pose compatibility problems with increase in cost of production of SCCs. *Acacia* gum, however presents itself as a low- cost natural admixture .

1.5.1.4. *A. nilotica* subspecies

A. nilotica is classified into nine subspecies (Ross, 1979) as shown in Table (1.1). The fruit (pods), is the main factor to differentiate between sub-species in terms of size, form and constriction between the seeds Table(1.2), distinguished by the shape and pubescent of pods such as *A. nilotica* var. *tomentosa* which have a beaded pods and *tomentose*, *A. nilotica* var. *nilotica* also beaded pods, but glabrous , *A. nilotica* var. *adistringens* have no beaded pods, margins entire or crenate Figure (1.5), and *A. nilotica* var. *subulata* (Brenan) no beaded pods,

margins entire,(ELAmin,1990). *A. nilotica* var. *cupressiformis*, the pods, moniliform, narrowly and regularly constricted between the seeds, *A. nilotica* var. *hemispherica* not moniliform, narrow (11–13mm) wide, margins, slightly crenate to straight, *A. nilotica* var. *indica* moniliform, narrowly and regularly constricted between the seeds, *A. nilotica* var. *kraussiana* (Benth.) not moniliform, oblong, (10–19mm) wide, margins shallowly crenate. *A. nilotica* var. *leiocarpa* (Brenan) not moniliform, oblong narrow (10–13 mm) or slightly crenate (Wickens, 1995). Other variation in the habit ranging from subsp. *tomentosa*, subsp. *nilotica* and *indica*, in addition to pods, was being ovoid crowned, ever green or semi evergreen to the deciduous and spreading subsp. *adstringens*, *subalata* and *kraussiana* while the subsp. *Cupressiformis* and subsp. *hemispherica* differ in having narrow, erect and bushy crown (Wickens, 1995). Subspecies *subalata*, *leiocarpa* and *adstringens* grow in wooded grassland, dry scrub forests and savanna. subspecies *nilotica* and *tomentosa* grow in riverine habitats and seasonally flooded areas. Subspecies *kraussiana* prefers dry grasslands savanna, especially on compacted sandy loam, shallow granite or clay soils along drainages and rivers, on the subcontinent, subspecies *indica* forms low altitude dry forests frequently on alluvium soils, subspecies *hemispherica* is restricted to dry sandy streams beds near Karchi, subspecies *cupressiformis* has similar preferences to subsp. *indica* though is less resilient to weed competition (Fagg, 1992) .

A. nilotica (L.) Wild. Ex Del. ssp. *indica* (Benth.) Brenan, which is reported to be salt tolerant and capable of growing on soils with salt contents up to 3% (FAO 1995), morphologic (Brenan, 1983) and leaf phenolic studies (Hannan-Jones, 1999) that the Australian populations of *A. nilotica* are most likely *A. nilotica* var *indica* (Benth.) Brenan. However, the morphology of the *A. nilotica* species complex is highly variable, with five of these (*indica*, *cupressiformis*, *hemispherica*, *adstringens*, *subalata*) found on the Indo-Pakistan subcontinent (Ali and Qaiser, 1980). Brenan's (1983) key to subspecies may be tenuous for two reasons. Firstly, the characters used can exhibit a wide range of diversity within individuals, populations and subspecies, making subspecies difficult to designate (especially without seed pods). Secondly, hybridization between particular subspecies occurs commonly and produces many morphological types. Ali and Faruqi (1969), and Ali and Qaiser (1980, 1992) have shown hybridization between subspecies *indica* and subspecies *hemispherica* or hybridization between subspecies *indica* and subspecies *cupressiformis*. Subspecies of *A. nilotica* are distributed from southern Africa through the Arabian peninsula to the Indo-Pakistan subcontinent (Ali and Qaiser,1980). The main characteristics currently used for subspecies identification are tree canopy habit, branchlet pilosity (i.e. glabrous, glabrescent, puberulous, pubescent, tomentose), pod shape, pod margin shape and pod pubescence. The diversity

observed in these morphological characters, the undetermined phylogenetic relationships of *A. nilotica* subspecies world- wide and their extensive distribution are hampering the search for suitable biocontrol agents.

Table.1.1. *A. nilotica* subspecies and synonyms (Ross, J.B.1979)

<i>A.nilotcia</i> Subspecies	Synonyms
<i>.tomentosa</i>	1- <i>A.nebneb</i> Adans 2- <i>A.neboueb</i> Bail 3- <i>A.arabica</i> var. <i>tomentosa</i> Benth. 4- <i>A.scorpioides</i> var. <i>pubescens</i> A. Chev 5- <i>Acacia nilotica</i> var. <i>tomentosa</i> (Benth.) A.F. Hill
<i>.nilotica</i>	1- <i>Mimosa nilotica</i> L. 2- <i>Mimosa scorpioides</i> L. 3- <i>Mimosa arabica</i> Lam. 4- <i>A.arabica</i> (Lam.) Willd. 5- <i>A.Vera</i> Willd. 6- <i>A.arabica</i> var. <i>nilotica</i> (L.) Benth 7- <i>A.aegyptiaca</i> Baillon. 8- <i>A.nilotica</i> var. <i>genuia</i> o. Kuntse. 9- <i>A.scorpioides</i> (L.)W.F. Wight 10- <i>A.nilotica</i> var. <i>Typica</i> Fiori 11- <i>A.scorpioides</i> var. <i>.nilotica</i> , (L.)A. chev 12- <i>A.cacia nilotica</i> var. <i>nilotica</i> Cufod.
<i>.adstringens</i>	1- <i>Mimosa adstringens</i> Schumach.et Thonn. 2- <i>A.adansonii</i> Guill. et Per. 3- <i>A.nilotica</i> var. <i>adansonii</i> (Guill et Perr.) Kuntse. 4- <i>A.arabica</i> var. <i>adansoniana</i> Dubard. 5- <i>A.scorpioides</i> var. <i>adstringens</i> (Schumach et Thonn.) A. Chev 6- <i>A.arabica</i> var. <i>adstringens</i> (Scumach. et Thonn.) Bak. 7- <i>A.nilotica</i> var • <i>adstringens</i> (Schumach. et Thonn.) Chiov. 8- <i>A.nilotica</i> var • <i>adansoniana</i> (Dubard) A.F.Hill. 9- <i>A.nilotica</i> subsp. <i>adstringens</i> var. <i>adstrin gens</i> Roberty. 10- <i>A.nilotica</i> subsp. <i>adstringens</i> var. <i>adanso. nii</i> (Guill et Perr.) Roberty. 11- <i>A.adstringens</i> (Schumach. et Thonn) Berhaut 12- <i>A.nilotica</i> subsp. <i>adansonii</i> . (Guill. Et Perr.) Brenan.

Following table 1.1.....

<i>subulata</i>	1- <i>A.subalata</i> Vatke. 2- <i>A.taitensis</i> Vatke.
<i>cupressiformis</i>	1- <i>A.arabica</i> var. <i>cupressiformis</i> J.L. Stewart
<i>hemispherica</i>	Nell
<i>indica</i>	1- <i>A.arabica</i> var. <i>indica</i> Benth. 2- <i>A.nilotica</i> var. <i>indica</i> (Benth.) A.F. Hill.
<i>Kraussiana</i>	1- <i>A.arabica</i> var. <i>Kraussiana</i> Benth. 2- <i>A.benthamii</i> Rochebr. 3- <i>A.nilotica</i> var. <i>kraussina</i> (Benth.) A.F Hill.
<i>leiocarpa</i>	Nell



A

B

C

Figure.1.5. *Acacia nilotica* subsp.*tomentosa* A, subsp.*nilotica* B, and subsp. *adstringens* C pods from Sudan

Table.1.2. *A. nilotica* subspecies, distribution, pods descriptions

Subspecies	Distribution (native, naturalized & cultivated)	Pod Pubescence	Pod Shape & Margins
<i>tomentosa</i> (Benth.) Brenan	northern tropical Africa	Gray- dark grey-white minutely tomentose	moniliform, narrowly and regularly constricted between the seeds
<i>nilotica</i> (Brenan)	northern tropical Africa from Senegal to Egypt, Tanzania, Iraq, southern Arabian Peninsula	glabrous to Pubescence	moniliform, narrowly and regularly constricted between the seeds
<i>adstringens</i> (Schumach. & Thonn.) Roberty	northern tropical Africa east to India	densely tomentose	not moniliform, 13–21 mm wide, margins distinctly and often irregularly crenate
<i>cupressiforms</i> (J. L. Stewart) Ali & Faruqi	Pakistan, India	gray-white tomentellous	moniliform, narrowly and regularly constricted between the seeds
<i>hemispherica</i> Ali & Faruqi	Pakistan	sub glabrous with very short	not moniliform, narrow (11–13 mm wide), margins slightly crenate to straight
<i>indica</i> (Benth.) Brenan	Angola, Tanzania north to southern Arabian Peninsula and east to Myanmar, Vietnam, Australia	densely white tomentellous	moniliform, narrowly and regularly constricted between the seeds
<i>kraussiana</i> (Benth.) Brenan	southern Africa to southern Arabian Peninsula	pubescent becoming glabrescent and, later, shiny black on raised areas over the seeds	not moniliform, oblong, 10–19 mm wide, margins +/- shallowly crenate
<i>keiocarpa</i> (Brenan)	coastal eastern Africa from Ethiopia south to Mozambique	glabrous or almost so, rarely slightly puberulous	not moniliform, oblong, narrow (10–13 mm wide), margins straight or slightly crenate
<i>subalata</i> (Vatke) Brenan	Tanzania north to Sudan and then east to India and Sri Lanka	densely sub tomentose	not moniliform, 15–22 mm wide, margins straight or slightly crenate

1.5.1.5. Phytochemical Constituents of *A. nilotica* Subgenus

Plants have the ability to synthesize a wide variety of chemical compounds that are used to perform important biological functions and to defend against attack from predators such as insects, fungi and herbivorous mammals. At least 12,000 such compounds have been isolated so far; a number estimated to be less than 10 % of the total (Tapsell, 2006, Lai, and Roy, 2004). Bark is the outermost layer of stems and roots of woody plants. A plant with bark includes trees, woody vines and shrubs, the powdered bark of the plant with little salt is used for treating acute diarrhea (Gill L.S, 2009). The bark is also used extensively, bleeding piles and leucoderma (Del, 2009) and also possesses antibacterial activity (Deshpande, Kadam, 2013). It is also used for treatment of various diseases (Singh, et.al,2009) .solvent extraction technique, found the compounds , Carbohydrate, Leucoanthocyanin, Alkaloids, Steroids , Chalcones, Cardiac Glycosides , Saponin, Lignin's, Vitamin C. Flavonoids, Fatty Acids, Phenol ,and Quinones (Sawant ,et.al, 2014). The seeds contain much more protein (19% dry matter) and fiber (29% dry matter). Those phenolic tend to reduce the palatability and feeding value of *A. nilotica* browse and pods (Ngwa, et.al, 2002,Mlambo, et al, 2008).The presence of large amounts of tannins can give rise to artificially high fiber contents (Mlambo, et al, 2008).

1.5.1.6. Ecology of *A. nilotica* trees

There is some evidence that *A. nilotica* is a weed in its native habitat of South Africa (Holm et al1979), but in other areas it is planted for forestry or reclamation of degraded land (Puri and Khybri 1975, Shetty 1979). The ecological implication of using *A. nilotica* as a browse source while maintaining in appropriate stocking rates is land degradation. It grows well in two types of soils i.e. riverian alluvial soil and black cotton soil. This species grow on saline, alkaline soils and those with calcareous pans. *A. nilotica* grows under climatic conditions ranging from sub-tropical to tropical. It withstands extremes of temperature ($> 50\text{ C }^{\circ}$) and conditions of drought however; adequate moisture is needed for full growth and development. It is frost tender when young and trees of all age classes are adversely affected by conditions of severe frost. It is fire tender and both seedlings and saplings are adversely affected by fire. The average annual rainfall varies from 250-1500 mm.

1.5.1.7. Economic Importance of *A. nilotica* trees

Acacias are established as very important economic plants since early times as source of tannins, gums, timber, fuel and fodder. They have significant pharmacological and toxicological effects In Africa and the Indian subcontinent; *A. nilotica* is extensively used as a browse, timber and firewood species (Gupta 1970, Mahgoub 1979, New 1980). The bark and seeds are used as

a source of tannins, (Shetty 1979, New 1980). The species is also used for medicinal purposes. Bark of *A. nilotica* has been used for treating Nemours diseases while the roots have been used as an aphrodisiac and the flowers for treating syphilis lesions (New 1980). The gum of *A. nilotica* is sometimes used as a substitute for Gum Arabic (obtained from *A. senegal* var *senegal*) although the quality is inferior (Gupta 1970). Indian Gum is sweeter in taste than that of the other varieties and is used in paints and medicine. The species is suitable for the production of paper and has similar pulping properties to a range of other tropical timbers (Nasroun 1979). The dark brown wood is strong, durable, nearly twice as hard as teak, very shock resistant and is used for construction, tool handles and carts. It has a high calorific value of 4950 kcal/kg, making excellent fuel wood and quality charcoal. It burns slow with little smoke when dry. It has 25% more shock resisting ability than teak. At the time of tree felling total wood production was estimated 167 Mg ha⁻¹ that included 45m² marketable timbers (Pandey and Sharma, 2005)

1.5.1.8. Effect of *A. nilotica* trees on soil characteristics

It was reported that the tree of *A. nilotica* improves soil fertility under its canopy by reducing proportion of sand with simultaneous increase in clay particles, mainly due to protection of soil from the impact of raindrops. Nutrient cycling through leaf litter and protection of soil from erosion (Nair 1993 Palm 1995, Pandey et al.2000,). *A. nilotica* is reported to be well modulated with Rhizobium species (Dreyfus and Dommergues1981).This nodulation behaviour help in biological nitrogen fixation which help to meet the nitrogen requirement in nutrient-poor soils. In addition, this species form symbiotic associations with naturally occurring soil fungi called vesicular arbuscular mycorrhizae (VAM) (Kaushik and Mandal 2005). This association assists the roots to exploit more soil volume and to gain improved access to available nutrients especially phosphorus under stress and also makes the unavailable forms of nutrients into utilizable forms (Bowen 1973).

1.5.1.9. Allelopathic Effect of *A. nilotica*

El-khawas and Shehata, (2005) reported that the leaf leachates of *A. nilotica* inhibited the germination and growth of *Zea mays* and *Phaseolus vulgaris*. Duhan and Lakshinarayana (1995) found that the growth of *Cyamopsis tetragonoloba* and *Pennisetum* growing at distance of 1-2 and 7.5 m from tree of *A. nilotica* was inhibited. Velu, et al (1999) reported that *Acacia* spp. Have phytotoxic effects on the tree crops of legumes. These results suggested that the inhibitory effect of *A. nilotica* on seed germination and seedling growth is related to the presence of allelochemicals including tannins, flavonoids and phenolic acids. Moreover, the toxicity is caused due to synergistic effect rather than single one (Fag and Stewart, 1994). According to Stratmann and Ryan (1997) and El- Khawas (2004) allelopathic effect of *Acacia* spp. induced

the formation of stress proteins. These proteins are responsible for folding, assembling, translocation and degradation in a broad array of normal cellular processes such as improvement of plant growth, physiological and molecular characteristics (Wang et al. 2004). This allelopathic ability of *A. nilotica* may have the potential as herbicide and can be used in biological control of weeds (Li and Wang, 1998).

1.6. Gummosis

Plant exudation is caused as a result of wound response by plant cells at the site of injury in which it gives out a sticky viscous fluid which oozes out to cover or seal the opening and eventually becoming a glossy, translucent hard mass as in Acacia plants. According to (Dexter et al., 2005), plant exudates are produced by plants so as to seal-off infected sections of the plant and prevent loss of moisture due to physical injury or fungal attack. (Rana et al. 2011) reported that plant gum exudates are produced by several plants as a result of the protection, mechanism against mechanical or microbial injury.

1.6.1. *A. nilotica* var *tomentosa* gum

A. nilotica var. *tomentosa* is one of an important and high density among *A. nilotica* subspecies, in a survey both Sinnar and Blue Nile states, subsp. *tomentosa* grown on the rivers bank, valleys and autumn streams. Differences in shape and size of subsp. *tomentosa* trees depends on the area of growth, Figure (1.6), 90% of *A. nilotica* subspecies in Sinnar state was *tomentosa* subsp, and 10% of *nilotica* subsp. *A. nilotica* var. *tomentosa* grows under favorable soil and irrigation on the rivers bank in Sinnar state. Cultivation of industrial uses. It is harvested on (15 – 20) years rotation, among this period the trees add about (2-3) cm in diameter each year, it's grows rapidly up to (20-25) m high. Under suitable condition, *A. nilotica* var. *tomentosa* produces a small amount of gum, (all gum samples of *A. nilotica* var. *tomentosa* in this study are natural exudates).

1.6.1.1. The gum belt

The gum belt refers to a broad band, situated at a latitude of between 12° and 16° North, stretching across sub-Saharan Africa, from Mauritania in the West, through Senegal and Mali, Burkina Faso, Niger, Northern Nigeria to Sudan, Eritrea, Ethiopia, Kenya, Somalia and Northern Uganda in the East Figure (1.6). Most of these countries appear in the statistics as sources of gum arabic, although they differ greatly in terms of the quantities involved. The gum belt in Sudan as shown in (Figure.1.7).

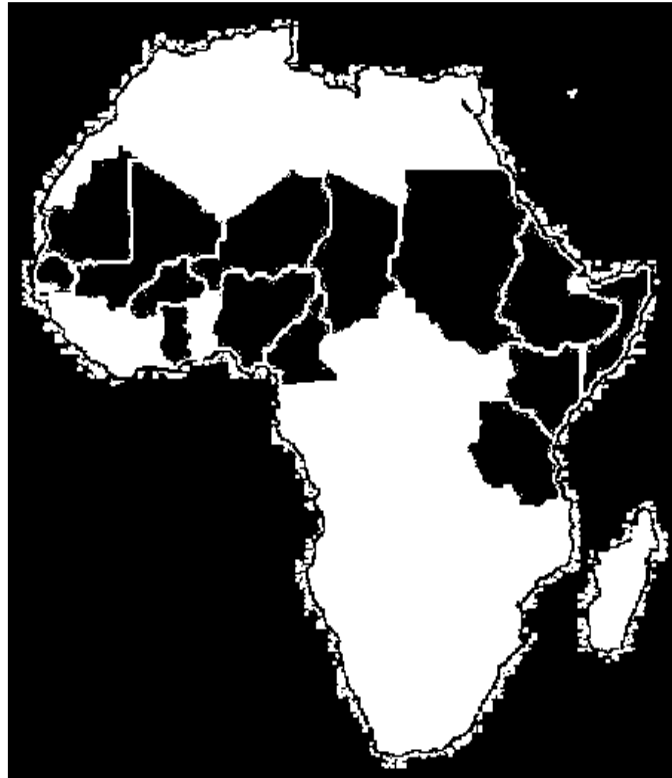


Figure.1.6: Gum Arabic producing countries



Figure 1.7: Gum belt in Sudan

1.6.1.2. Gum collection

Gums are collected following tapping, which involves removing sections of the bark with an axe. Tapping begins when the trees are just starting to shed their leaves, around the end of October or the beginning of November. In order to reach this stage, trees have to grow for a period of 3 to 5 years depending on the method of establishment. Again in the Sudan, there are two tapping seasons, an earlier one before the onset of the colder weather which is between the months of December and March and a later one in the dry spell after March. After tapping, exudation occurs gradually forming a hard but slightly elastic nodule. As more gum exudes the outer skin expands or cracks and the nodule grows to about 15–30 mm in diameter. When the outer casing becomes so hard that the liquid cannot force it to expand any further, the nodule is ready for picking. The time taken to reach this stage is from 3-6 weeks and as soon as the nodules are picked, new ones start to form and within 10-15 days a second picking is possible. Several branches are treated in this manner at one tapping.

In the following years, other branches or the reverse side of the same treated branches are tapped. An average of four pickings is common. The nodules are picked by hand and placed in a basket and sorted according to colour and size (John Macrae 2002). Some typical grades of Sudanese gums available are listed in Table (1.3). The production and trade of gum arabic has been dominated by Sudan followed by Nigeria and Chad.

1.6.1.3. Gums processing

The crude exudate of Gums are processed according to the quality required for marketing. Air drying is the easiest method to be applied, which together with mechanical milling (kibbling), are used in order to produce a granular material that is much more soluble than the raw product. Other processing methods are spray drying and roller drying. These methods involve dissolving exudate in water under controlled heating conditions and constant stirring. Heating must be mild to avoid distortion of the gum which could have a detrimental effect on its functional properties

. After removing the insoluble material by decantation or filtration, the solution is pasteurized and subjected to spray or roller drying. Spray drying involves spraying the solution into a stream of hot air. Water is completely evaporate and the dry powder is obtained, Figure (1.8), resulting in 50 to 100 m particles. During the roller-drying, the solution is passed to the hot rollers and the water is evaporated by the air flow .The thickness of the resulting Gum film is controlled by adjusting the distance between the rollers. The film is separated from the roll by scraping blades giving way to particle scales of several hundred m in size. Gum Arabic samples produced by spray drying and drying rollers have an advantage over raw gum as they are

virtually free of microbial contamination and dissolve much faster, (Williams, 2000, John Macrae 2002).

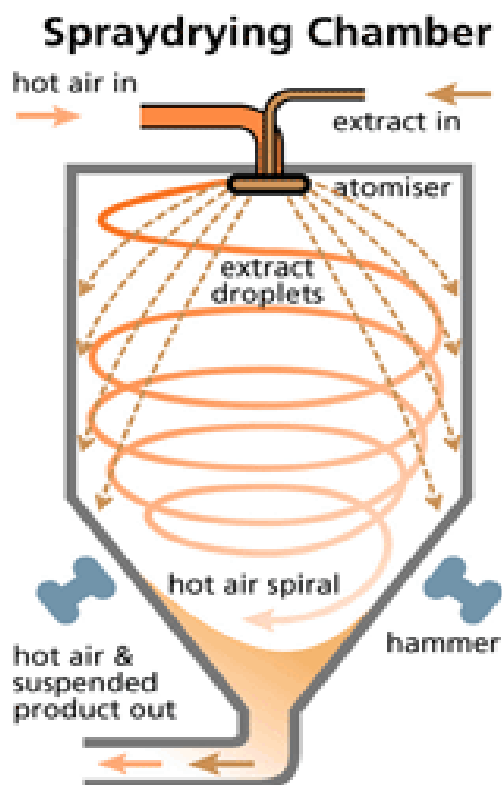


Figure 1.8: Schematic diagram depicting spray drying chamber

Table 1.3: Grades of gum arabic (Williams, 2000, John Macrae 2002)

Grade	Description
Hand-picked selected	The most expensive grade. Cleanest, lightest colour and in the form of large whole nodule, $\text{Ø} > 20$ mm.
Cleaned and sifted	The material that remains after hand-picked selected and siftings are removed. Comprises whole or broken lumps varying in colour from pale to dark amber.
Cleaned	The standard grade varying from light to dark amber. Contains siftings but dust removed. Whole nodules plus fragments, $10 < \text{Ø} < 20$ mm.
Siftings	Fine particles remaining following sorting of the choicer grades. Contains some sand, bark and dirt. Fragments and siftings, $2.5 < \text{Ø} < 10$ mm.
Dust	Very fine particles collected after the cleaning process. Contains sand and dirt. $\text{Ø} < 2.5$ mm.
Red	Dark red particles - Rejects – local use only.

1.6.1.4. Chemical Composition and Chemical Structure

The highly branched polysaccharide structure of gums consists of 1, 3-linked b-D-galactopyranose monomers with side branches linked to the main chain mainly through substitution at O-6 position. Units of a-L-arabinofuranosyl and a-L-rhamnopyranosyl are distributed in the main and side chains while b-D-glucuronopyranosyl and 4-O-Methyl-b-D-glucuronopyranosyl are mostly end units, Figure(1.9) (Anderson and Stoddart, 1966). (Street and Anderson, 1983) proposed that *Acacia* gum structure could be explain in terms of repeated fragments.

The former, *A.senegal*, would be composed mainly by repeated fragments of ramified chains of galactose with arabinose side chains of varying length and glucouronic and 4-O-Me-glucuronic acids end units. In contrast, the structure of *A.seyal* would be a mix of two or three ramified fragments type I with significant single units of galactose linked to one arabinose chain of varying length, type II (Street and Anderson, 1983), Figure (1.10). The structure of *A.senegal* was suggested to be more ramified and more regular than the *A.seyal* structure. Recently, (Nie et al. 2013) proposed structural models for the polysaccharide backbone of *A.senegal*, (Figure.1.11) and *A.seyal* gums. (Figure.1.12), based on the previous work, with substitution of side chains at O-6, O-2, or O-4 positions. Polysaccharide chains are linked to proteins by covalent links in serine- and Hydroxyproline-rich domains (Anderson and McDougall, 1987), Typically, *A.senegal* gum is richer in protein than *A.seyal* (1.8% wt vs. 0.9% wt respectively) (Islam et al., 1997).

Acacia gums are described as heterogeneous, poly disperse, and hetero-poly molecular system having more than one component with different monomer composition, molecular weight, and mode of linking and branching, (Anderson and Stoddart, 1966), (Islam et al., 1997). Using hydrophobic interaction chromatography (HIC) or size exclusion chromatography (SEC), multiple macromolecular fractions were separated from *A. Senegal* gum (Anderson et al., 1984); (Randall et al., 1989, Vandeveld and Fenyó, 1985). The three main fractions obtained by HIC were named the arabinogalactan (AG) fraction, the arabinogalactan-protein (AGP) fraction, and the glycoprotein (GP) fraction. The most abundant fraction, AG, represents approximately 85-90 % of the total gum with a molecular weight around 2.8×10^5 g mol⁻¹ and traces of protein, a peptide of about 40 amino acids (Mahendran, et al, 2008; (Randall et al., 1989). The second main fraction, AGP, represents around 10% of total gum and contains ~12% of protein. The AGP fraction is generally composed of high molecular weight (Mw) macromolecules ($1 \times 10^6 < Mw < 4 \times 10^6$ g mol⁻¹) (Randall et al., 1989); (Renard et al., 2012), The minor GP fraction, around 2% of the total gum, contains the highest content of proteins

around 25-40 %. This fraction is composed of at least three glycoprotein populations with molecular weight ranging from 2.5×10^5 to $2.6 \times 10^6 \text{ g}^{-1} \text{ mol}^{-1}$. *A. Seyal* gum was also fractionated using HIC and the three main molecular fractions obtained were also named AG, AGP, and GP (Siddig et al., 2005).

More recently Gum Arabic was described as a compact, elliptical structure in solution, the significance of which for biotechnological use is indicated, characterize by using complementary hydrodynamic techniques including, Sedimentation velocity in the analytical Ultracentrifuge (AUC-SV), and the system consisted of two columns (TOSOH Biosciences TSK 3000 and 4000) and a guard column (TSK Guard TWH) and 3 Wyatt Technology (Santa Barbara, USA) detectors: multi angle light scattering (MALS - Dawn Helios II), differential pressure imbalance viscometry (ViscoStar) and refractive index concentration measurement (OptiLabrEX), (Richard. Gillis, 2016) Fig (1:13). Partial specific volume was measured as 0.635ml/g, with no dependence on ionic strength. AUC-SV and SEC-MALS-IV found that increasing ionic strength increased the sedimentation coefficient and decreased the intrinsic viscosity, respectively. Compiled results obtained through these hydrodynamic techniques were able to yield an estimate for the ellipsoid structure of gum arabic using Single HydFit, in the form of a prolate ellipsoid with an average axial ratio of 1.9 with some indication of a reduction with increase in ionic strength. This form of hydrodynamic modeling is not just applicable for polysaccharides, but other biopolymers and synthetic polymers (Richard B. Gillis, 2016).

Gel permeation chromatography studies using both refractive index and UV(260 nm) absorption detections have confirmed that both *A.senegal* and *A.seyal* gums consist of three main components (Islam et al., 1997), (Idris et al., 1998), (Al-Assaf et al., 2006): A main fraction (88-90%) of a polysaccharide of β -(1 \rightarrow 3) galactose, highly branched with units of rhamnose, arabinose and glucuronic acid (which is found in nature like salts of magnesium, potassium and calcium). This fraction is called Arabinogalactan (AG) and contains a low protein content (~0.35%) and MW \approx 300 kDa (Sanchez et al., 2006) A secondary fraction constituting ~10% of the total, with a protein content of 11% and a molecular weight of 1400 kDa, corresponding to a complex Arabinogalactan-Protein (AGP) (Goodrum et al., 2000), and a smaller fraction (1% of the total) composed of glycoprotein (GP) consisting of the highest protein content (50 wt.%) with an amino acid composition different from the complex AGP (Williams et al., 1990a).

Although the total content of carbohydrate fractions of the three components is similar, as reported by (Williams et al., 1990a), it was found that protein-rich fractions have a significantly lower glucuronic acid content. Studies conducted on different GA fractions showed that only the AGP and GP components have a secondary structure (Sanchez,et al., 2006). The AGP

fraction was isolated by gel filtration chromatography and subjected to glycosylation with hydrofluoric acid (HF) to separate the protein (Qi et al., 1991). About 400 amino acids were contained by the AGP protein fraction (~33% are hydroxyl proline residues). In addition, it was shown that the AGP fraction is composed of blocks of carbohydrates attached to the polypeptide chain glycoside link through serine and hydro proline residues (Mahendran et al., 2008).

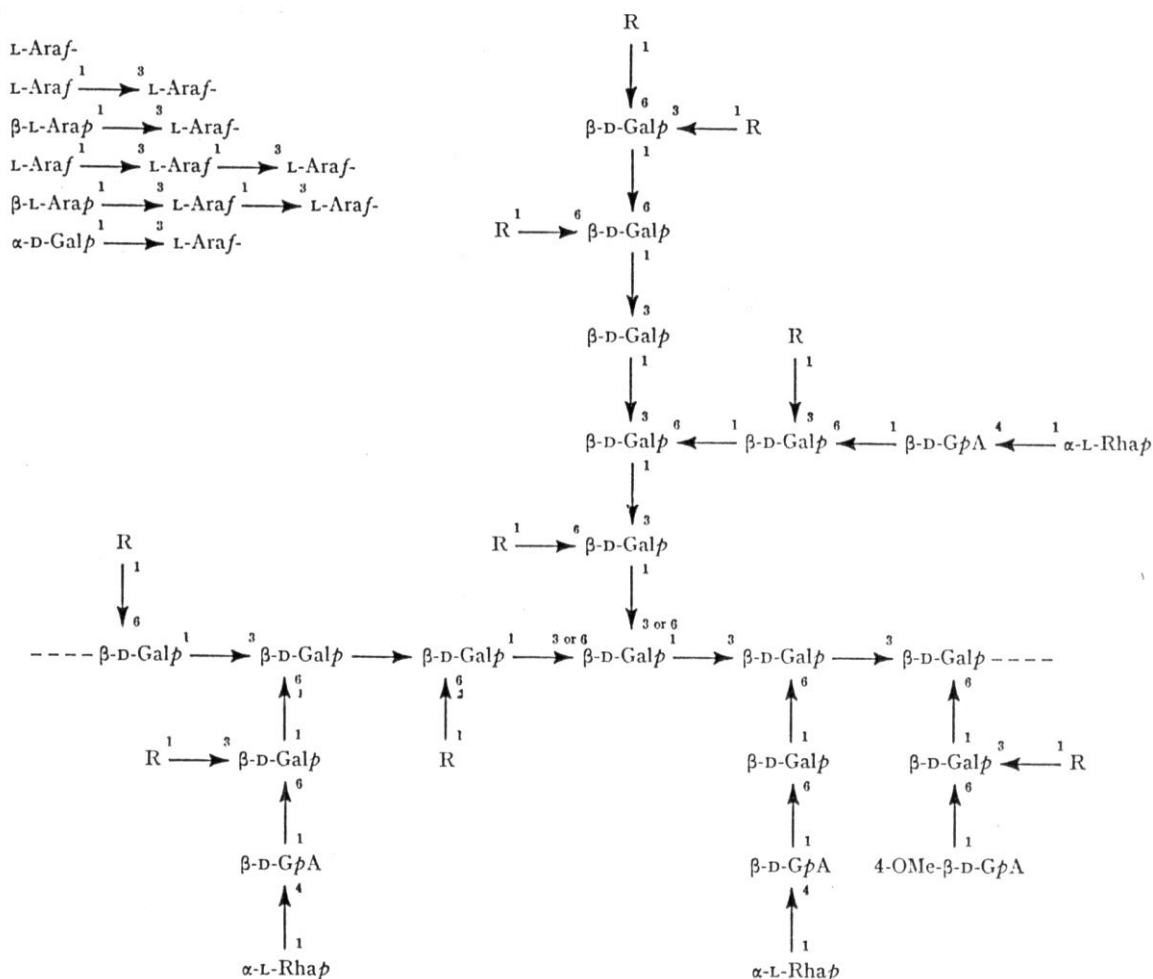


Figure.1.9: Possible structural fragment in *A. senegal* gum (Anderson et al., 1966)

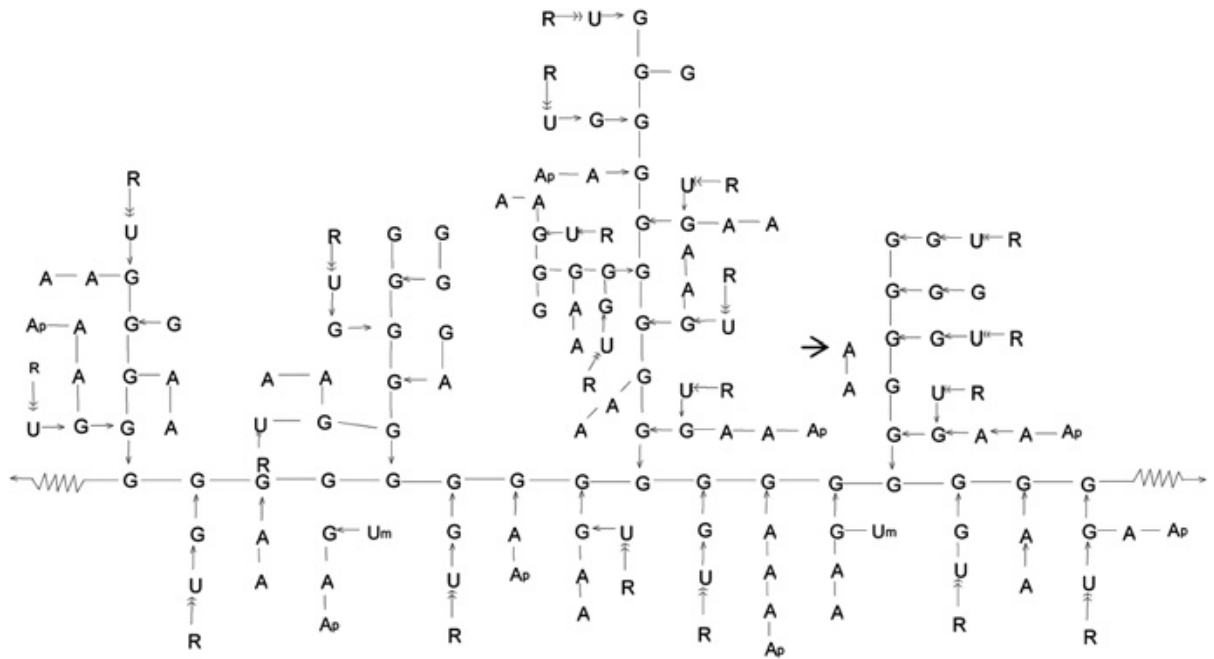


Figure (1:10). Illustration of a possible structural fragment of *A. senegal* gum (Street and Anderson, 1983), R = rhamnose; Um = 4-O-methylglucuronic acid; U = glucuronic acid; Ap e arabinopyranose; A e arabinose; G e galactose.

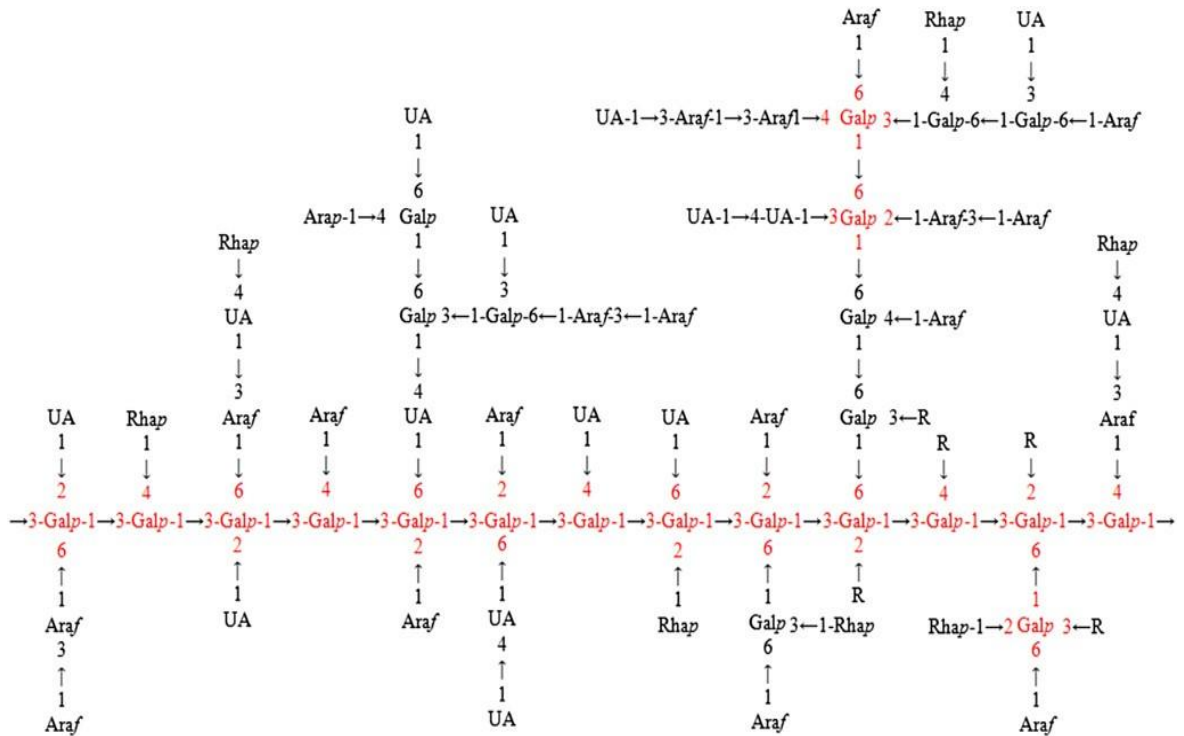
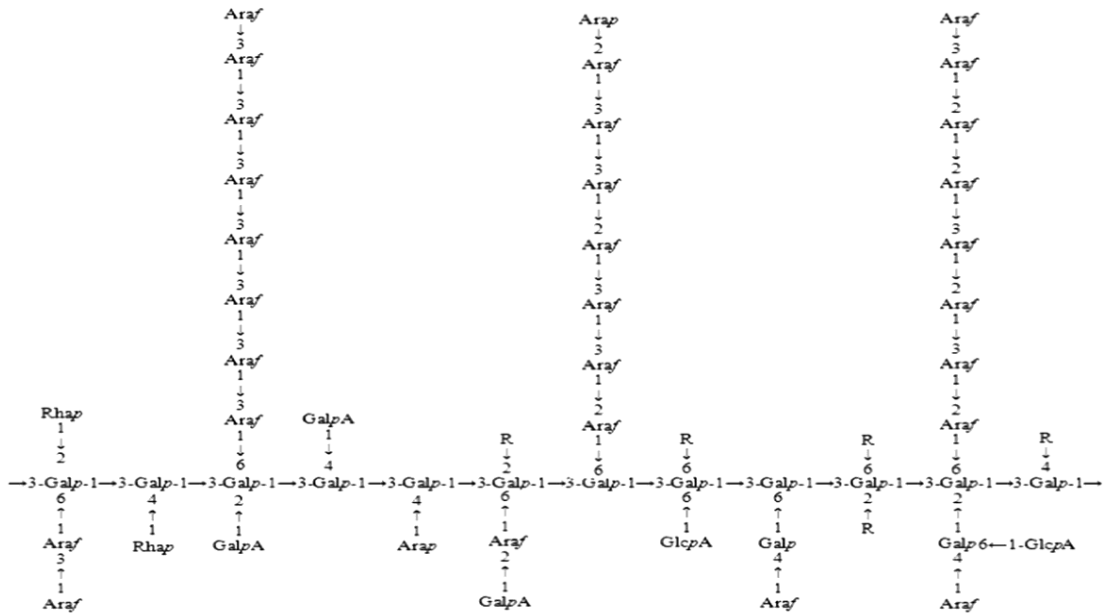


Figure.1.11. Proposed structure of Gum Arabic (*A. senegal*). (Nie et al. (2012)



R is one of these following residues: T-Rhap1→, T-L-Araf1→, T-L-Arap1→, T-GlcpA1→, T-GalpA1→, T-L-Araf1→3-L-Araf1→, T-L-Araf1→2-L-Araf1→. The galactose moieties are in β -D form, with the galacturonic acid, arabinose and rhamnose in α -L form.

Figure.1.12. Proposed structure of the carbohydrate in *A. seyal* (Nie et al. (2012))

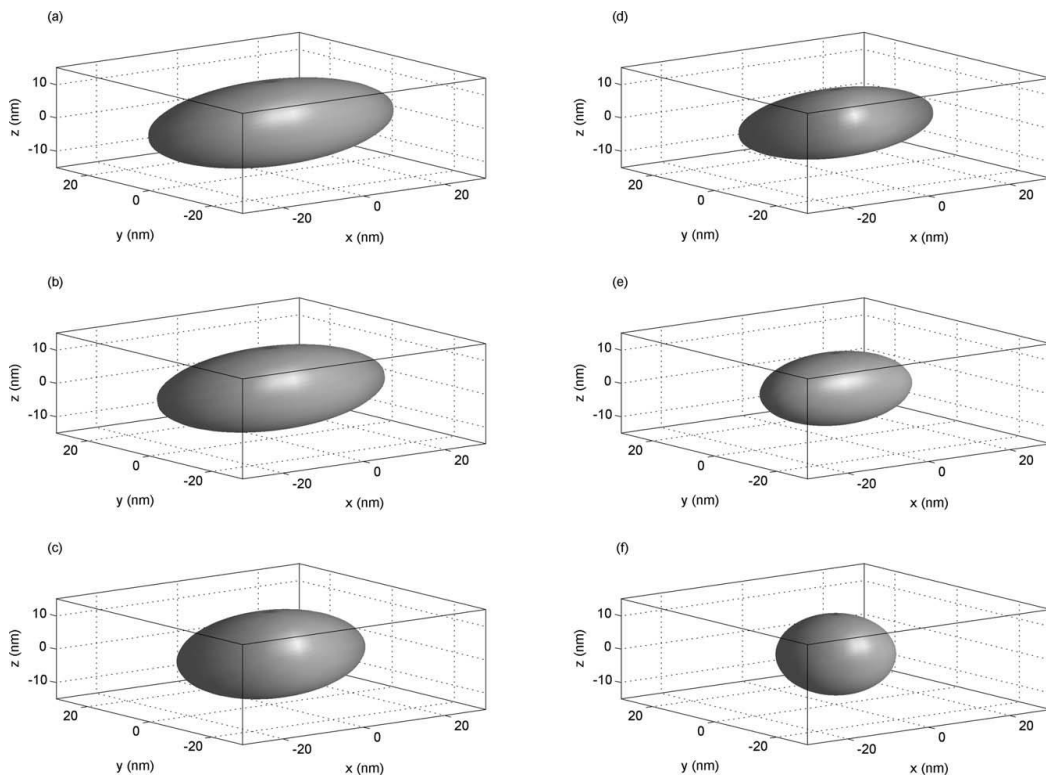


Figure.1.13. Prolate ellipsoid representations for Gum Arabic at three ionic strengths. (a) GAB at I 0.1M, (b) GAB at I 0.3M, (c) GAB at I 0.5M, (d) GAG at I 0.1M, (e) GAG at I 0.3M, (f) GAG at I 0.5M. (Richard B. Gillis, 2016)

This minor protein fraction is thought to be associated with the main AG fraction. It was proposed that in the structure of AGP, the polypeptide chain of 400 amino acids acts as "cable connector" of the blocks of carbohydrates (≤ 40 kDa) which are covalently linked to the protein ("wattle blossom" model) (Fincher *et al.*, 1983; Mahendran *et al.*, 2008).

Connolly *et al.*, (1988) calculated the molecular mass of the blocks to be of the order of 2×10^5 . Randall *et al.* (1988) also fractionated the gum by GPC and obtained five fractions which differed significantly in molecular mass and protein content, thus supporting the findings of Connolly *et al.*, (1988). A high proportion (~60%) of the total protein present was found to be associated with one fraction which constituted ~10% of the total gum. Also the molecular mass decreased on treatment with pronase and hence supported the proposed 'wattle blossom' model. Randall *et al.*, (1989) fractionated the gum using hydrophobic affinity chromatography and isolated four fractions. The carbohydrate compositions of each showed slight variations, but there were significant differences observed in their relative sizes and protein contents. Most of the gum was found to have low protein content and was referred to as an arabinogalactan (AG). The minor fractions constituting ~12% of the total were rich in protein and were referred to as an AGP and glycoprotein, GP. The hydroxyproline and serine were the major amino acids in fractions 1 and 2, the amino acid composition of fraction 3 was significantly different with aspartic acid being the most abundant. The relatively small hydrodynamic radii were taken as evidence for a highly branched structure and this was confirmed by NMR spectroscopy and methylation analysis (Williams *et al.*, 1990).

Further fractionation studies using hydrophobic affinity chromatography on a number of gum samples gave similar findings (Osman *et al.*, 1993, Osman *et al.*, 1995). In addition, GPC and SDS-PAGE studies showed that the fractions obtained were polydisperse (Osman *et al.*, 1993). Silver staining of SDS-PAGE gels indicated that each of the fractions contained several proteinaceous components varying in molecular mass from 30 000 to 200 000. All of the fractions were found to interact to varying extents with anti-AGP monoclonal antibodies through anti-carbohydrate epitopes and were precipitated with Yariv reagent, indicating that they were all AGPs. The effect of proteolytic enzyme on the molecular mass and the GPC profiles were investigated before and after treatment. For all fractions, the high molecular mass, protein-rich component corresponding to AGP peak was degraded to lower molecular mass units. This was taken as further evidence of the 'wattleblossom' structure. The protein-deficient component corresponding to AG peak was not degraded, as might be expected, but it was also noted that the protein-rich component corresponding to GP peak did not degrade either. This is

due to the fact that the protein in this fraction is buried in the core of the molecule and inaccessible to the enzyme.

Osman *et al.*, (1995) also fractionated two samples of the gum by ion exchange chromatography using DEAE-Cellulose. The fractions were very different to those obtained by hydrophobic affinity chromatography and all were polydisperse, illustrating the heterogeneous nature of the gum. Qi *et al.* (1991) separated the gum into two fractions using GPC. One high molecular mass fraction (corresponding to the AGP fraction), which represented ~10% of the total, was found to contain ~10% protein, consistent with the findings of Randall *et al.* (1988). On deglycosylation, it yielded a hydroxyproline-rich polypeptide chain consisting of ~400 amino acid residues with a possible repeating sequence of (HYP₄ Ser₂ Thr Pro Gly Leu His). The fraction interacted with Yariv reagent, but differed from typical AGPs by its much lower alanine and acidic amino acid content. The carbohydrate component was subjected to alkaline hydrolysis and following subsequent analysis, they concluded that the carbohydrate was attached to the polypeptide chain in small units of ~30 sugar residues through galactosehydroxyproline linkages. (Figure 1.16). This was supported by electron microscopy studies which revealed rod-like molecules ~150 nm long. They suggested that the structure resembled a 'twisted hairy rope' in contradiction to the 'wattle blossom' model. However, Osman *et al.*, (1995) have argued against this. The enzyme-linked immunosorbent assays (ELISAs) was used to identify specifically gum from *A.senegal* and differentiate it from other *Acacia* species. An ELISA has been developed using polyclonal antibodies raised against gum arabic in rabbits (Osman, 1993, Osman, *et al.*, 1993). It was found significant structural differences between the *Acacia* species. The antibody was shown to interact more strongly with the protein-rich components of the gum. Since these fractions are known to be responsible for the gum's excellent emulsification properties, it has been suggested that the ELISA could be used as a quality control tool in assessing emulsification capability. Menzies *et al.*, (1996) found that whereas *A.senegal* gum samples interacted with β -glucosyl Yariv reagent, which is typical behaviour for AGPs, *A.seyal* gum samples showed either a very weak interaction or no interaction at all. Significant differences between the two gums were also observed with monoclonal antibodies which recognize the arabinose residues present in AGPs. ¹³C NMR has also been used to differentiate gum from *A.senegal* and *A.seyal* for the unambiguous identification of *A.senegal* gums (Anderson *et al.*, 1990).

1.6.2. Applications

Gums are widely used for industrial purposes such as a stabilizer, a thickener, an emulsifier and an encapsulating in the food industry, and to a lesser extent in textiles, ceramics, lithography, cosmetic, and pharmaceutical industry (Depypere *et al.*, 2003). In the food

industry, gum arabic is primarily used in confectionery, bakery, dairy, beverage, and as a microencapsulating agent. Table (1.4) shows various types of gum arabic applications.

Table.1.4: Gums application with specific uses

Application	Specific use	Reference
Food additives	Enhance the emulsion viscosity and stability. Improves consistency and self – live of puree, spreads, and preserves. Stabilize water-in-oil-in-water emulsion. As emulsifier provides flavor, color, and turbidity to juices and beverages. Helps immobilize α -amylase in industrial bioreactors.	(Marki and Doxastakis, 2006). (Pua et al., 2007) (Su et al., 2008) (Mirhosseini et al., 2009) (Egwim and Oloyede, 2011)
Self-life enhance	Alone or with combination with chitosan, wax, glycerol, it's used as edible coating of fruits and vegetables, such as banana, apple, and mushroom. It delayed change in weight loss, firmness, tetra table acidity, total soluble solids, decay, and color. With essential oils (lemongrass, cinnamon), it exerts synergistic action on <i>Collectotrichum</i> spp, mycelia inhibition.	(Maqbool et al., 2011) El-Anany et al, 2009 Jang et al, 2011 (Maqbool et al., 2011)
Microencapsulator	Stabilize freeze- dried strawberry powder by reducing hygroscopicity. Also it stabilized oleoresin (cardamom, cumin, oregano), ginkgo leaf polyphenols.	Mosquera et al, 2011 Krishanan et al, 2005 (Kanakdande et al., 2007) (Haidong et al., 2012)
Cardio-, reno-, gut-, dental protective	Decreases systolic blood pressure. Increases intestinal and renal excretion of Mg^{2+} and Ca^{2+} enhances creatinine clearance and urinary antidiuretic hormone excretion, while decreasing Na^{+} excretion. Decreases plasma phosphate and urea concentrations. Enhances remineralization of teeth and protects against the harshness of acids	(Glover et al., 2009) (Nasir et al., 2008) Nasir et al., 2012. (Onishi et al., 2008) (Beyer et al., 2010)
Inducer of satiety and anti-obesity	Causes significant reduction in energy intake. Reduces age-dependent fat deposition by β 3-adrenergic stimulation of adipocytes	(Calame et al., 2011) (Ushida et al., 2011)
Antimicrobial agent	Shows inhibition against fungal pathogen <i>Candida albicans</i> and <i>Cryptococcus neoformans</i> , and leishmania causative agent <i>Leishmania donovani</i> . Attenuates the level of parasites in blood <i>Plasmodium falciparum</i>	Nishi et al., 2007a Ballal et al., 2011

Following Table.1.4.....

Anti-inflammatory agent and anticoagulant	<p>Boosts the NF-κ B p65 activity of cathartics.</p> <p>Protects gut against the adverse effects of drug Meloxicam.</p> <p>Ameliorates the oxidative stress and DNA damage.</p> <p>Exerts significant anticoagulation effect.</p>	<p>Wapnir et al., 2008, Abd El-Mawla and Osman, 2011, Ali et al., 2011, Hadi et al., 2010.</p>
Drug delivery agent	<p>Shows promise in tissue engineering and drug delivery Helps in sustained release of drugs (FeSO₄, naproxen, primaquine). Amenable to modification for development of pH-responsive and high cross-linking density hydrogel.</p> <p>Augments colloidal stability and promotes cellular uptake of Nanomedicine.</p>	<p>(Paulino et al., 2011) (Batra et al., 1994) (Lu et al., 2003) (Pinto Reis et al., 2006) Nishi et al. 2007b Zhang et al., 2009 (Avadi et al., 2010)</p>
Sensor and tumor imaging.	<p>Manifests ideal properties (electrically active, water-soluble, and redox) for semiconductor sensor devices</p>	<p>Tiwari, 2007</p>
In nanotechnology	<p>Shows promise for dispersing nanoparticles in aqueous solutions, stabilizing, and enhancing biocompatibility (γ -Al₂O₃);</p> <p>Interesting for diagnostic and therapeutic applications in nanomedicine (AuNPs).</p> <p>Enhances biomolecular attachment of magnetic nanoparticles.</p> <p>Offers fast microbial detection by magnetic nanoparticles.</p> <p>Forms films with desirable polar properties.</p> <p>Reduces surface energy and improves the tensile strength of starch film</p>	<p>Williams et al., 2006. Wu and Chen, 2010. Kattumuri et al., 2007. Zhang et al., 2007 (Roque and Wilson Jr, 2008) Chockalingam et al., 2010. Onyari et al., 2008. Vigneshwaran et al., 2011.</p>

1.6.2.1. Confectionery and baking

Gums are employed in a variety of products including gum, lozenges, chocolates, and sweets. In these products, Gums performs two important functions: to delay or to prevent sugar crystallization, and to emulsify fat to keep it evenly distributed throughout the product. In baking, Gums are extensively used for its low moisture absorption properties. Gums solubility in cold water allows greater formation of clear solutions than in sugar solutions. It has also favorable adhesive properties to be used in glaze and meringues, and it provides softness when used as an emulsion stabilizer. Baking properties of wheat and rye flours can be improved by

adding a small amount of Gums since its capacity for retaining moisture reduces the hardening of bread

1.6.2.2. Dairy products

In the dairy products Gums are used as a stabilizer in frozen products like ice-cream due to its water absorption properties. The role of Gums in these products is to cause a fine texture and growth by inhibiting the formation of ice crystals which is achieved by combining a large amount of water and holding it as water of hydration, being its higher melting point the main attraction of ice-cream.

1.6.2.3. Beverages

Gums are used as an emulsifier in beverages such as citrus juices, beer, and cola drinks. Gum arabic ability to stabilize foams is used in the manufacture of beer and soft drinks. Besides, it can be used for clarifying wines.

1.6.2.4. Microencapsulation

In the food industry, microencapsulation is an important process to improve the chemical stability of sensitive compounds, to provide the controlled release of microencapsulated compounds and to give a free flowing powder with improved handling properties (Rosenberg and Sheu, 1996), the encapsulating material must preserve and protect the encapsulated compounds during manufacture, storage, and handling to release them into the final product during manufacture or consumption. Solubility and low viscosity emulsion properties have facilitated the use of Gum as an encapsulating agent for retention and protection of chemically reactive and volatile commercial food flavoring. (Reineccius, 1988) has reported on the encapsulation of orange oil using Gum as wall material. The cost may not be relevant as long as extra protection or stability is achieved for microencapsulated high-value products, and in food or pharmaceutical fields. Gum is mainly used for fat microencapsulation because it produces stable emulsions in the case of most oils in a wide pH range, and it has the ability to form films. (Barbosa et al., 2005) studied the photo stability of the microencapsulated carotenoid bixin in different edible polysaccharide. They found out that microencapsulated bixin in Gum Arabic was three to four times more stable than the one microencapsulated with maltodextrin, and about ten-fold than in homogeneous solvents.

1.6.2.5. Silver powders (ultrafine)

Ultrafine silver powder has been widely used in microelectronics (Kosmala et al., 2011), optical devices (Velikov, 2003), and chemical catalysis (Lu, et al, 2010) due to its unique electrical, optical, catalytic, and thermal properties. Recently, silver paste for front side metallization of crystalline silicon solar cell has been in commercial use, which employs silver

powder as a major component. The rheology of silver paste and the electrical performance of solar cell are influenced by the parameters of silver particles, such as shape, size distribution and tap density (TD) of the silver particles (Tsai, et al, 2013). Thus, it is necessary to explore the synthesis process of silver powder.

To date, a variety of methods have been developed to prepare silver powder, such as wet-chemical reduction (Lee, et al, 2010), spray pyrolysis (Lu, 2010), and electro-reduction [M. S. Kim, et al 2009]. To obtain silver powder with good dispersibility, most wet- chemical reduction processes are conducted in the presence of dispersants, such as polyvinyl pyrrolidone (PVP), polyvinyl alcohol (PVA), and gelatin (Guo, et al, 2010). However, the majority of studies focus on the preparation of silver powder. Only a few reports have emphasized the dispersive mechanisms of dispersant in the synthesis of silver powder. Zhang and Wang et al. reported the PVP protective mechanisms of ultrafine silver powder synthesized by chemical reduction processes. They found that the O and N atoms of PVP reacted with silver ions and accelerated the reduction of silver ions. The silver particles were protected by a PVP steric layer (H. S. Wang, et al, 2005). Guo et al. proposed the dispersive mechanisms of PVA in the preparation of silver powder: chemical adsorption mechanism and steric effect mechanism. They believed that PVA adsorbed on the surface of silver particles by coordination bond prevented diffusion and aggregation of silver particles. The long chain structure of PVA may help to reduce aggregation due to steric effect. .Ao, et al, (2007). proposed the gelatin dispersive mechanisms in the preparation of spherical silver particles. They found that the coordinative complex of silver ions with gelatin could enhance the reduction of silver ions and the nucleation of metallic silver particles, thus enhancing the availability of the monodisperse spherical silver particles. Recently, a natural polymer, Gum , has been widely used as dispersant in the synthesis of well-dispersed silver particles. Liu and co-workers synthesized spherical and mono-disperse micro-silver powder with average particle size of about 1-2 μm in the presence of Gum (Liu, et al, 2012). The silver nanoparticles could be converted into conductive films at 100 C^o, which displayed good electrical conductivity (Balantrapu, et al, 2009).

Well-dispersed ultrafine silver powder was prepared by reducing silver nitrate with ascorbic acid in the presence of Gum as a dispersive agent (Huang et al., 2014),The UV-Vis spectra and FTIR spectra proved that the dispersive mechanisms of Gum for preparing good dispersive ultrafine silver powders could be divided into three stages. First, the -COOH and -NH₂ groups of Gum Arabic reacted with Ag to form complex compounds. Second, silver nuclei formed on Gum polymer chains, which work as seeds in the growth of primary particles, and Gum polymer chains serve as templates during the formation of silver

pheres. stiff-chain contributes to excellent dispersability of silver particles via steric stabilization (Huang et al., 2014).

1.6.2.6. Cosmetics

Cosmetic industry is using Gum Arabic for a large range of functionalities: stabilizer, viscosity agent, film former, emulsifier, binding agent. Gum Arabic is used in creams, lotions, mascaras and cake cosmetics as a protective colloid.

1.6.2.7. Enhancement of vegetable self-life time

The perishability of fruit and vegetables is a major concern. An edible coating on them to retain freshness, quality, to enhance their shelf-life, and delay further ripening is a prevalent strategy to avert the above issues. Gum arabic accentuates the appearance, retain moisture, and reduce weight loss. The coatings used on fruits and vegetables must meet the food additive regulations of the U.S. Food and Drug Administration. As a substitute of paraffin wax, performance of Gum Arabic was commercially suitable for extending the storage life of bananas up to 33 days.

At 13° C and 80% relative humidity (RH), fruits can be stored significantly longer than the controls. The shelf-life prolongation is supposed to be due to the reduced rate of respiration and ethylene evolution, (Maqbool et al., 2011). The effect of a blend of Gum Arabic, on the shelf-life and quality of apple during cold storage at 0° C and 90–95% RH. The results indicated that the coated apples attain delayed change in weight loss, firmness, titratable acidity, total soluble solids, decay, and color, compared to uncoated one, (El-Anany et al. 2009). The potential of Gum Arabic in coating tomatoes for their shelf-life extension after post harvest storage. It was observed that tomato coated with 10% Gum Arabic shows a significant delay in changes of weight, firmness, treatable acidity, soluble solids concentration, ascorbic acid content, percentage decay, and color development compared to the uncoated one (Ali et al., 2010). Antifungal effect of Gum Arabic combined with essential oils such as lemongrass and cinnamon oils in checking the post harvest of banana and papaya. A synergistic blend of 10% Gum Arabic, 0.05% lemongrass, and 0.4% cinnamon showed inhibition of mycelia growth and spore germination. It was observed that Gum Arabic, along with cinnamon oil, significantly delays the ripening process and maintains the quality more effectively during the entire storage period, (Maqbool et al., 2011). The efficacy of a blend of Gum Arabic and natamycin in improving the quality and shelf-life of shiitake mushroom, for as long as 16 days, (Jiang et al., 2013). Studied the efficacy of Gum Arabic as a color preservative and inhibitor of non-enzymatic browning of dehydrated tomato during storage with sodium metabisulfite. Tomato homogenates were treated with 1, 2.5, 5, 7.5, and 10.0% Gum Arabic and

1.0% sodium metabisulfite, respectively, dehydrated, and color changes were monitored during four months of storage. Water activity decreased and Brix values increased significantly in Gum Arabic treated samples. Lightness value increased significantly with the addition of 5–10% Gum Arabic compared to the dehydrated control. Gum Arabic at a dose of 5–10% (w/w) preserved color of dehydrated tomatoes during the studied storage period, (Idris et al, 2013).

1.6.2.8. Cardiovascular, Renal, and Intestinal Effect

The treatment with Gum Arabic significantly increases both intestinal and renal excretion of Mg^{2+} and Ca^{2+} . The latter was accompanied by decreased urinary excretion of inorganic phosphate and decreased plasma concentrations of 1, 25-dihydroxy vitamin D. GA increased 24 h creatinine clearance and urinary antidiuretic hormone excretion, and decreased daily urine output as well as the urinary excretion of Na^+ . The treatment with Gum Arabic resulted in moderate but significant increases creatinine clearance and altered electrolyte excretion, (Nasir et al, 2012). Cardiovascular and renal effects of dietary Gum Arabic, *A. Senegal* in normal individuals and a group of diabetic nephropaths. The normal diet supplemented with 25 g of day for a period of 8–12 weeks, showed a consistent fall in the mean systolic blood pressure of healthy volunteers. However, there were no effects of GA on renal function and hemodynamics of patients with diabetic nephropathy, (Glover et al., 2009) . The quantity 10% Gum Arabic when consumed with water increases urinary excretion of Ca^{2+} and decreases plasma phosphate and urea concentrations. Gum Arabic decreases blood pressure and proteinuria in diabetic mice and might be of clinical importance in diabetic nephropathy, (Nasir et al, 2012).

1.6.2.9. Antimicrobial Activity

The adjuvant role of oxidized Gum Arabic in amphotericin B therapy against fungal pathogen *Candida albicans*, *Cryptococcus neoformans*, and *Leishmania donovani* (Nishi et al, 2007a). The drug conjugate was stable, nonhaemolytic, and free of any toxicity to internal organs of the treated animal while exerting appreciable anti-fungal and anti-leishmania. Human erythrocytes were in vitro infected with *Plasmodium falciparum*. Mice were in vivo infected with *Plasmodium berghei* ANKA by intraperitoneal injection of parasitized murine erythrocytes. The oral administration of 10% Gum Arabic, ten days prior to the infection, showed attenuated level of parasites in blood. GA degradation product of butyrate is attributed to the reduced vigor of malaria, (Ballal et al., 2011).

1.6.2.10. Antioxidant activity

Several reports suggest that Gum Arabic has antioxidant capacity. However, there are controversial results of it, mainly in vivo studies. For example, Gum Arabic has been reported to exert a protective effect against gentamicin and cisplatin nephrotoxicity (Al-Majed et al.,

2002, 2003), and doxorubicin cardio toxicity (Abd-Allah et al., 2002) used as biological models in rats. However, Ali et al., (2003) reported that treatment of rats with Gum Arabic causes only a slight palliative effect of gentamicin nephrotoxicity. Later, Trommer and Neubert (2005) studied lipid peroxidation antioxidant and reducing effects in vitro of various polysaccharides (including Gum Arabic). They found that Gum Arabic reduction of lipid peroxidation of skin is a dose-dependent. In contrast, Ali (2004) reported that administration of Gum Arabic at concentrations of 2.5%, 5.0% and 10.0% in drinking water for eight consecutive days to rats did not significantly alter the concentrations of free radical scavenger's glutathione and acid ascorbic acid, and superoxide dismutase, or lipid peroxidation. Consequently, the antioxidant activity of Gum Arabic in biological systems is still an unresolved issue, and therefore it requires a more direct knowledge of the antioxidant capacity of Gum Arabic that can be obtained by in vitro experiments against different types of oxidant species. The total antioxidant activity of a compound or substance is associated with several processes that include scavenging free radical species (eg. HO•, ROO•), ability to quench reactive excited states (triplet excited states and/or oxygen singlet molecular $1O_2$), and/or sequester metal ions (Fe^{2+} , Cu^{2+}) to avoid the formation of HO• by Fenton type reactions.

1.6.2.11. Protective Effect against Dental Erosion

Gums are considered to have an ability to enhance remineralization, because of its high concentration of Ca^{2+} . The cariostatic activities of Gums using histopathological methods. After incubation in demineralization solution, human molar teeth were exposed to 10 mg/ml of Gum Arabic, sodium fluoride at 1000 ppm (NaF, a salt with well-established cavity fighting ability), or double distilled water, then subjected to demineralization-remineralization cycles. Contact micro- radiographs of the molars exposed to Gum Arabic were similar to that of those exposed to NaF, showing significant remineralization of caries, (Onishi et al., 2008). Investigation of the protective effect of Gum Arabic against acidic soft drink-caused enamel erosion. The enamel samples were exposed to polymer-modified citric acid solutions for 30, 60, and 120 s, respectively. Atomic force microscopy (AFM)-based nano-indentation was used to analyze the nano-mechanical properties of the treated enamel samples and scanning electron microscopy was used to scan their surface morphologies. Enamel samples treated with Gum Arabic-enriched citric acid showed higher hardness and smoother surface compared to the enamel surfaces of samples treated only with citric acid. It is hypothesized that Gums adsorbed as a protective layer on the eroded enamel surface moderating the harshness of the acid, (Beyer et al., 2010) .

1.6.2.12. Anti-Inflammatory and Anticoagulation Effect

The inflammation modulation capacity of Gums alone or in combination with cathartics (substance that accelerates in defecation). In male juvenile rats, the NF- κ B p65 activity was highest after administration of cathartics followed by Gum Arabic. Mucosal IL-1 β was overexpressed in tissues from cathartic-treated rats and rats given high Gum Arabic solutions, (Wapnir et al, 2008). When given 0.2 mg/kg bw meloxicam followed by 1 g gum in the same doses per day for a period of 21 days, pronounced protective effect of Gums are extract on the histology of rat intestine was observed. Also, a significant increase in the intestinal enzymes; lipase, amylase, ALP, and lactate dehydrogenase (LDH) were recorded, (Abd El-Mawla and Osman, 2011). Studied the role of inflammation and oxidative stress in adenine-induced chronic renal failure and the possible ameliorative effect of Gums. Rats were given adenine combined with Gums for four weeks, at the end of which urine, blood, and kidneys were subjected to tests. Adenine-induced increase in the concentrations of urea and creatinine in plasma, decrease in creatinine clearance, and increase in the inflammatory mediators were normalized by Gums intake. Further, the oxidative stress and DNA damage were ameliorated, (Ali et al, 2013). Calculated a randomized test to investigate the effect of Gum Arabic on the coagulation system of Wister rats are done. After administering Gums along with drinking water for four weeks, blood samples were collected and coagulation parameters were determined. The bleeding time of rats treated with 6g GA/100 ml was significantly prolonged; whereas, the prothrombin time of rats treated with 10g GA/100 ml were significantly longer, (Hadi et al, 2010).

1.6.2.13. Drug Delivery Agent

Drug excipients made of synthetic materials are generally toxic and expensive. So, non-toxic natural excipients to deliver the bioactive formula is sought-after. An injectable, biodegradable drug depot with controlled release of drugs for long-term delivery is required. An increase in the amount of Gums decreased the rate of release due to their inherent gelling property. The gel layer acts as a barrier and retards the rate of diffusion of FeSO₄ through the pellet, (Batra et al., 1994). Gums can be used in preparation of a monolithic osmotic tablet system for slow release of water-insoluble drugs. The model drug naproxen was released to about 81% of its initial content at pH 6.8 after 12 h. The diffusion was independent of environment media and stirring rate, suggesting the use of Gum Arabic in oral drug-controlled delivery, (Lu et al., 2003). A pH-responsive hydrogel from Gum Arabic chemically modified with glycidyl methacrylate. The cross-linking reaction led to the formation of a hydrogel. At high pH, the water transport depended on polymer relaxation. The pH-responsive hydrogel

appeared promising for further tests as drug carriers. Primaquine, a potent malaria drug, forms a cross-linked gel with periodate-oxidized Gum Arabic by rapid mixing of the two constituents. It was observed that higher degree of Gums oxidation leads to higher cross-linking density. In vitro release of primaquine into phosphate buffered saline (PBS) at 37° C demonstrated that the extent of release depended on the cross-linking density and drug payload. Repeated extraction using PBS soon after gel formation showed that not all of the primaquine was conjugated to the polysaccharide and the release seen in vitro was mostly from the unconjugated drug especially from matrices with higher cross-linking density. The gels were found to degrade in PBS and MTT assay against L929 mouse fibroblasts showed only very mild cytotoxicity at 0.025 g/mL. This conjugate with desirable characteristics can be of considerable importance in battling of numerous diseases, (Reis et al. 2006). Synthesized and characterized of magnetic iron oxide nano-particles (MNP) coated with 15.6% Gum Arabic, The Gum Arabic coating enhanced colloidal stability and provided reactive functional groups suitable for coupling of bioactive compounds. Significant cellular uptake of GA-MNP was evaluated in 9L glioma cells which suggested that the composite might be utilized as a MRI-visible drug carrier in achieving intracellular drug delivery, (Zhang et al. 2009). Chitosan and Gum Arabic induced diffusion and relaxation could effectively control the release of nano-particles from polymer chains, (Avadi et al., 2010).

1.6.2.14. Sensor and Tumor Imaging

Fabrication an electrically active, water-soluble radical copolymer of GA with redox property. With a battery of high-end technical characterization, the shelf-life and electrical conductivity of the copolymer was monitored. Results indicate possibilities of their application in the fabrication of semiconductor sensor devices, (Tiwari, 2007). Gum Arabic coating on MNP enhanced the colloidal stability and provided reactive functional groups suitable for coupling of bioactive compounds. MRI confirmed the accumulation of GA-MNP at the 9L glioma tumors site after intravenous administration in rats while electron spin resonance (ESR) spectroscopy reported fold-increase in GA-MNP (Zhang et al, 2009).

1.6.2.15. Nanotechnology

Several studies have been conducted on the potential utility of Gums in nano-constructs and molecular imaging. Gums acts as reducing and oxidizing agent, so vital for molecular functionalization of nanomaterial. Functionalization by this biopolymer has been evidenced to cause toxicity elimination, pathogen detection, stability improvement, and better dispersion of nano-particles

Functionalized magnetite nano-particle surfaces by Gums coating, to enhance stability. Particle characterization was performed using transmission electron microscopy (TEM) and dynamic light scattering (DLS) to analyze the morphology and quantify the size distribution of the nano-particles, respectively Figure 1.14. The results from DLS indicated that the Gum Arabic-treated nano-particles formed smaller agglomerates as compared to the untreated samples over a 30 h time frame.

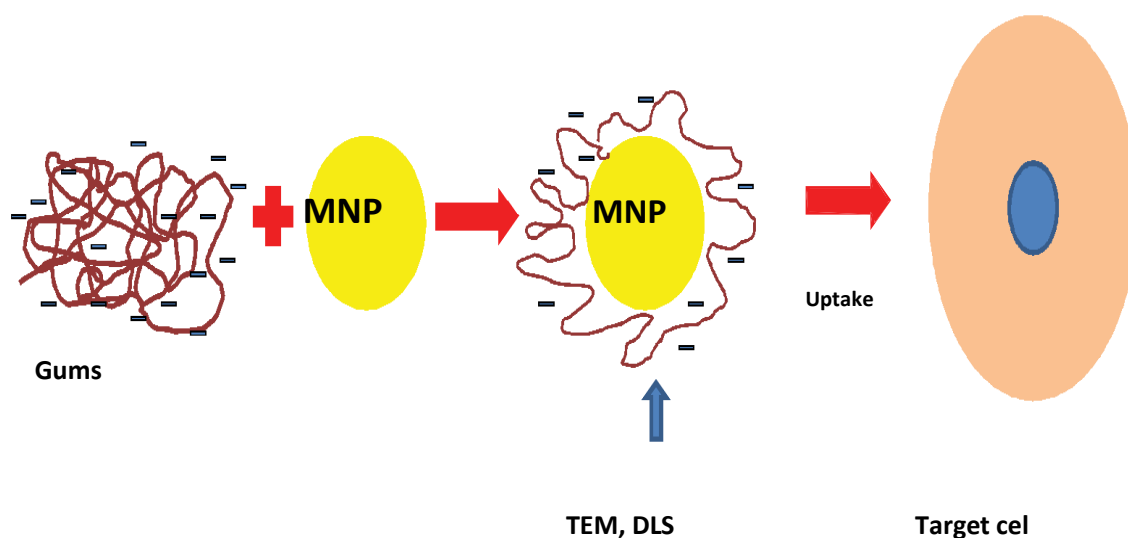


Figure 1.14 . Graphical illustration of the stabilizing effect of negatively charged gum arabic on iron oxide magnetic Nano-particles. Gum arabic provides functionalization and cell selectivity. It provides increased electrostatic repulsion for better dispersal and stabilization of the particles, facilitating uptake by the cells.

Thermo-gravimetric analyses indicated an average weight loss of 23%, showing that Gums have a strong affinity toward the iron oxide surface. Gums show promise for dispersing nanoparticles in aqueous solutions. Gold nanoparticles (AuNPs) are very stable against oxidation, thus significant in the advancement of clinically useful diagnostic and therapeutic nano-medicines. However, the huge potential of AuNP-based nano-medicinal products is blighted by toxicity, rendering it unsuitable for intravenous mode, (Williams et al., 2006). Gum can be used as a non-toxic material in the production of readily administrable biocompatible AuNPs for diagnostic and therapeutic applications in nano-medicine. Gamma- Al_2O_3 nano-particles were synthesized and modified using Gums to avoid agglomeration (clustering) in aqueous solutions. Results showed that the nano-particles dispersed well in aqueous solutions after Gums modification. Also it increased adsorptive desulfurization and bio desulfurization capacity, assumed to be due to improvement in the dispersion and biocompatibility of γ - Al_2O_3 nano-particles post Gums modification, (Kattumuri et al, 2007). The covalent immobilization of Gums at the surface of aldehyde-activated or aminated MNPs

yielded negatively charged surfaces which showed promise for better biomolecular attachment, (Roque et al. 2009). Gums - modified MNPs capable of isolating *S. aureus* bacteria at 8–10 colony forming units (cfu)/ml within 3 min. This alternative fast detection technique can be employed for other microbial detection, (Chockalingam et al. 2010). Synthesis of AuNPs using Gums as reducing as well as stabilizing agent. Gums proved helpful in complete reduce the Au (III) ions and stabilizing the nano-particles, (Wu and Chen, 2010). Studding of various polylactic acid and Gums blends showed that it is possible to prepare films of varying hydrophobic-hydrophilic properties for various applications. Uniform distribution of the nano-cellulose fillers in starch film matrix posed a hurdle in exploiting the full potential of nano-materials. Gums as additive distributed nano-cellulose uniformly by reducing surface energy and improved its tensile strength. Further more, the vapor permeability of the starch film was reduced two-fold, (Onyari et al.2008).

1.6.3. Physicochemical properties of *Acacia* gums

The Physicochemical properties of Gums, established as quality parameters, and also assist to differentiate between different *Acacia* gums. These properties vary with gums of different botanical sources, and even substantial differences in gum from the same species when collected from the plant at different seasons of the year, different places and different ages of the same plant. Several parameters can be used in this study but the most important included moisture, total ash content, pH value, intrinsic viscosity, specific optical rotation, molecular weight distribution, tannin content, nitrogen content, protein, amino acid, uranic acid, . Cationic metal and sugar content..

1.6.3.1. Moisture content

Moisture content gives indication about the hardness of the gum and microbial content. Moisture content can be determined from weight loss after evaporation of water. Reducing the moisture content of the natural Gum can be readily used as a tenable method of reducing the microbial content. Amira, (2011) reported the moisture content of *A.nilotica* var. *nilotica* gum samples collected from difference regions of Sudan, fall in the range 9.85-11.69% with an average value of 10.81%. *A. senegal* var. *senegal* samples reported by Omar B, et al. (2013) fall between 11.76% and 14.80%, and recent studies of some *Acacia* species reported by Rabeea, et al, (2016), namely *A. senegal* var. *senegal*, *A. mellifera*, *A.seyal* var. *seyal*, and *A. tortilis* var. *raddiana*, found the reported a Moisture content of 9.76%, 9.56%, 8.35%, and 8.49% respectively, Table (1.5)

Table 1.5: Analytical data of the gum exudates from *Acacia* trees

Species	Moisture (%)	Ash (%)	Nitrogen (%)	protein (%)	pH	Mw * 10 ⁶	Intrinsic viscosity cm ³ g ⁻¹	Sp. Rot (degree)	Tannin %	Acid equivalent weight	Glucouronic acid%	Authors
<i>A. nilotica</i>	-	2.48	0.02	-	-	2.2	9.5	+ 108 ⁰	-	1890	9	Anderson, (1976)
<i>A. nilotica</i> var <i>.tomentosa</i>	5.80	0.04	0.10	0.62	4.48	-	-	+80.16	0.14	-	-	Karamalla, (1999)
<i>A.nilotica</i>	-	-	-	4.7	-	-	35	+ 21	-	-	21	Al-Assaf et al., 2005
<i>A.seyal</i> var <i>seyal</i>	-	0.21	-	0.96	-	5.3	11.9-17.6	+53	-	1489	11.9	Hassan <i>et al.</i> , (2005)
<i>A.seyal</i>	-		0.15	1.0	-	-	14	+45	-	-	16	Siddig <i>et al.</i> , (2005)
<i>A.senegal</i> var <i>senegal</i>	-	3.27	0.35	2.3	-	-	14.6	-32	-	1161	15.2	Omer (2006)
<i>A.seyal</i> var <i>seyal</i>	-	2.61	0.14	0.93	-	-	11.4	+49.4	-	1107.9	15.9	Omer (2006)
<i>A.senegal</i> var <i>senegal</i>	-	3.32	0.37	2.4	-	-	15.4	-31.5	-	1153.8	16.8	Abdurrahman (2008)
<i>A.seyal</i> var <i>seyal</i>	-	2.43	0.14	0.95	-	-	11.6	+61	-	1185.8	16.4	Abdurrahman (2008)
<i>A.senegal</i> var <i>senegal</i>	-	4.89	0.35	2.3	4.78	-	18.9	-30	-	1620	11.89	Younes (2009)
<i>A.seyal</i> var <i>seyal</i>	-	4.47	0.22	1.4	5.16	-	15.5	+52	-	1180	16.34	Younes (2009)
<i>A. nilotica</i> var <i>nilotica</i>	10.81	1.91	0.02	0.16	5.15	-	10.19	+99.17	0.10	1908.37	10.18	Amira et al (2011)
<i>A.senegal</i> var <i>senegal</i>	13.49	3.27	0.35	2.31	-	-	14.61	-32	-	1161	15.2	Omer et al (2013)
<i>A.senegal</i> var <i>senegal</i>	9.76	3.40	0.33	2.16	4.94	0.24	-	-31.75	-	-	-	Rabeea et al (2016)
<i>A.seyal</i> var <i>seyal</i>	9.56	2.50	0.63	4.16	4.53	2.01	-	+48.25	-	-	-	Rabeea et al (2016)
<i>A. mellifera</i>	8.35	3.13	0.24	1.61	4.84	2.95	-	+56.00	-	-	-	Rabeea et al (2016)
<i>A. tortilis</i> var. <i>raddiana</i>	8.49	2.05	1.55	10.34	4.45	2.06	-	+86.75	-	-	-	Rabeea et al (2016)

1.6.3.2. Ash content

The ash content is to investigate the presence of inorganic elements existing in salt form the critical levels of foreign matter, insoluble matter in acid, calcium, potassium and magnesium (Mocak et al., 1998). The ash residue is used to determine the specific levels of heavy metals in the gums (FAO, 1990). Hassan *et al.*, (2005) reported an average of 0.21% ash content for *A. seyal* gum from different locations of Sudan, Omer (2006) reported that the an average value of the ash content for *A. senegal* 3.27%, and 2.61% for *A. seyal* gum, the mean value of ash content reported by Abdurrahman (2008) for *A. senegal*, and *A. seyal* gum have an average of 3.32% and 2.43% respectively, Younes (2009) reported the mean value of ash content for *A. senegal* gum was 4.89%, and *A. seyal* gum 4.47%, Ameira, (2011) for *A. nilotica* var. *nilotica* gum, found the mean value of ash content was found to be 1.91%, Omar B, et al. (2013) reported Ash percentage of *A. senegal* var. *senegal* fall between 2.63%, and 3.99%, and recent studies reported by Rabeea, et al, (2016) of four species of *Acacia* gum, namely *A. senegal* var. *senegal*, *A. mellifera*, *A. seyal* var. *seyal*, and *A. Tortilis* var. *Raddiana*, found the ash content were equal to 3.40%, 2.50%, 3.13%, and 2.05% respectively Table (1.5).

1.6.3.3. pH

Measurement of acidity or alkalinity of water soluble substances (pH stands for potential of Hydrogen). The pH value had been determined by Younes (2009), he reported a value of 4.78 for *A. senegal* and 5.16 for *A. seyal* gum, Ameera, et al, (2011) reported that pH values for *A. nilotica* var. *nilotica* gum, was found to be 5.15. Recent studies of four species of acacia gum reported by Rabeea M.A, et al, (2016), namely *A. senegal* var. *senegal*, *A. mellifera*, *A. seyal* var. *seyal*, and *A. Tortilis* var. *Raddiana*, found the pH value were equal to 4.94%, 4.536%, 4.84%, and 4.45% respectively. Table (1.5).

1.6.3.4. Specific Optical Rotation

Optical rotation is used to determine the nature of gum arabic sugars as well as to identify the source of production. Many substances possess the inherent property to rotate the plane of incident polarized light; this property is called optical activity. The measurement of optical activity is used for establishing the identity of the substance; it may also be employed to test the purity of the substance. The optical rotation is the angle through which the plane of polarization is rotated when polarized light passes through a layer of a solution. Substances are described as dextrorotatory or levorotatory according to whether the plane of polarization is rotated clockwise or counterclockwise, respectively, as determined by viewing towards the light source. Dextrorotation is designated (+) and levorotation is designated (-)

In principle the rotation produced by a molecule is equal in magnitude but opposite in sign to that produced by its mirror image. An assembly of molecules with freedom of rotation, such as that which occurs in solution, will produce an observable net effect only if the individual molecules are optically asymmetric. The direction and magnitude of rotation are sensitive to the detailed structure in the vicinity of the asymmetric center of the molecule (IPh, 2006).

Hassan (2005) reported $+53^\circ$ mean value of specific optical rotation of *A. seyal* gum, optical rotation of *A. seyal* gum had been determined by Siddig *et al.*, (2005) which equal to $+45^\circ$, Omer (2006) reported that an average values of specific optical rotation equal to -32° , and $+49.4^\circ$ for *A. senegal* and *A. seyal* respectively, Abdelrahman (2008) reported the average value of optical rotation of *A. senegal* gum -31.5° , whereas equal to $+61^\circ$ for *A. seyal* gum, Younes (2009) reported a value of -30° specific rotation for *A. senegal* and $+52^\circ$ for *A. seyal* gum, and Omar B, et al. (2013) reported *A. senegal* var. *senegal* have specific rotation values fall between (-26) , and (-38) . The previous studies of *A. nilotica* var. *nilotica* studied by Ameera, et al, (2011), showed that the highest value of specific optical rotation was $+107.5$ whereas the lowest was $+72.5$.and the average values were found to be $+99.2$. Recent studies of four species of *Acacia* gum reported by Rabea M.A, et al, (2016), namely *A. senegal* var. *senegal*, *A. mellifera*, *A. seyal* var. *seyal*, and *A. tortilis* var. *raddiana*, found the specific optical rotation which equal to -31.75% , $+48.25\%$, $+56.00\%$, and $+86.75\%$ respectively Table (1.5) .

1.6.3.5. Tannin Content

Tannin is polyphenolic compounds of vegetable tissues with different chemical structures depending on their origin. They are usually classified in condensed and hydrolysable tannins (Haslam, 1989). Condensed tannins have flavanol units in their structure, while hydrolysable ones are composed of a molecule of glucose, joined to phenolic acids (Hasler et al., 1992). Besides classical applications of tannins in hide tanning and wine preparation, several new applications are emerging in adhesive industries by replacing hazardous phenol in novolac resins (Peña et al., 2006); (Pizzi et al., 2009) for reducing gelation, pressing time and formaldehyde emissions of resole resins (Bisanda et al., 2003); (Stefani et al., 2008). On the other hand, because of their antioxidant capacity and astringency properties, and to increase colour intensity, tannins have been also employed in wine preparation. Tannins have other physiological properties such as (anti-allergenic, anti-inflammatory, antimicrobial, cardio protective and antithrombotic) (Balasaundram et al., 2006) which make these compounds a very interesting raw material for the development of green polymeric materials which would not involve the use of toxic components prohibited for food packaging and medical applications.

A. nilotica is traditionally used for tanning, retaining in Africa, and in India (Sarkar, 1991). The assessment of analytical methods to estimate the total polyphenol in beverages and foods, such as teas, fruits and fruit-based products, herbs, and medicinal plants. For this purpose, some methods have been developed, tested and validated: individual determination of phenolic compounds using high-performance liquid chromatography (Granato, et al 2011); HPLC coupled with mass spectrometry (Slatnar et al., 2014), gas chromatography (Wang and Zuo, 2011); HPLC tandem mass spectrometry and high resolution mass spectrometry (Alakolanga et al., 2014); biosensors (Portaccio et al., 2006); spectrophotometric assays that employ specific chromophores, such as the Folin-Ciocalteu reagent and specific inorganic salts that react with phenolic compounds in aqueous solutions, such as potassium hexacyanoferrate (III) and Fast Blue BB diazonium salt (Rodríguez Delgado et al., 1995); (Lester et al., 2012); (Ferreira Zielinski et al., 2014). Chromatographic and biosensor analyses are somewhat expensive, time-consuming, require sample preparation, and use of solvents in the mobile phase of HPLC may represent a limitation to some laboratories. Thus, the use of spectrophotometric assays to estimate total phenolic content of plant materials and food extracts is advantageous and takes less time. One important observation should be made here: Chromatographic techniques (coupled to different detectors) are used for the separation and identification of phenolic compound. In the same sense, colorimetric assays are a very useful approach for screening and quantification. Thus the results obtained by colorimetric and chromatographic methods complementary Table (1.6). When considering gums as food additives. It was established that tannins are anti-nutritional (Karamallah, 1999). Amira, (2011) reported a tannin content of (0.08%, 0.1%) of *A. nilotica* var. *nilotica* gum. Table (1.5).

Table.1.6. Tannin content of *A. nilotica* reported by (Karmalla, 1999)

<i>Acacia</i> species	Tannin contents
<i>A. senegal</i> var. <i>senegal</i>	0.00
<i>A. seyal</i> var. <i>seyal</i>	0.11
<i>A. seyal</i> var. <i>fistula</i>	0.09
<i>A. laeta</i>	0.13
<i>A. nilotica</i> subsp. <i>nilotica</i>	0.05
<i>A. nilotica</i> subsp. <i>tomentosa</i>	0.14
<i>A. drepanolobium</i>	0.03
<i>A. gerrardi</i>	0.16
<i>A. polyacantha</i>	0.16
<i>A. tortillis</i> subsp. <i>raddiana</i>	1.63
<i>A. mellifera</i>	0.10
<i>A. echrenbergiana</i>	0.17
<i>A. seiberana</i> var. <i>seiberana</i>	0.08

1.6.3.6. Solubility and Viscosity

Viscosity is a property common to gases and liquids (i.e. fluids). It is a measure of the frictional resistance that a layer of a fluid in motion offers to another. Viscosity is produced by the shearing effect of one layer of the fluid moving past another. In case of liquid, there are strong attractive cohesive forces between the different molecules. When a layer is moving faster than the other, there is slowing down of the faster layer i.e., viscous drag is there due to strong attractive forces.

Viscosity of a polymer solution depends on concentration and size of molecules (i.e., molecular weight) of the dissolved polymer. By measuring the solution viscosity we should be able to get an idea about molecular weight. Solution viscosity is basically a measure of the size or extension in space of polymer molecules.

It is empirically related to molecular weight for linear polymers, the simplicity of the measurement and the usefulness of the viscosity-molecular weight correlation are so great that viscosity measurement constitutes an extremely valuable tool for the molecular characterization of polymer. Dilute solution viscosity is usually measured in capillary viscometer of the Ostwald-Fenske or Ubbelohde type. The latter has the advantage that the measurement is

independent of the amount of solution in the viscometer, measurement at a series of concentrations can easily be made by successive dilution (Billmeyer, 1962).

The intrinsic viscosity has great practical value in molecular weight determinations of high polymers. This concept is based on the Mark-Houwink relation suggesting that the intrinsic viscosity of a dilute polymer solution is proportional to the average molecular weight of the solute raised to a power in the range of 0.5 to 0.9. Values of the proportionality constant and the exponent are well known for many polymer-solvent combinations. Solutions viscosities are useful in understanding the behavior of some polymers. Measurements of solution viscosity are usually made by comparing the efflux time t required for a specified volume of polymer solution to flow through a capillary tube with the corresponding efflux time t_0 for the solvent. From t , t_0 , and the solute concentration, several quantities whose defining equations and names are given below, are derived.

Relative viscosity $\eta_r = \frac{\eta_{sol}}{\eta_{solv}} = \frac{t}{t_0}$ (2.8)

Specific viscosity $\eta_{sp} = \frac{\eta_{sol} - \eta_{solv}}{\eta_{solv}} = \eta_r - 1$ (2.9)

Reduced viscosity $\eta_{red} = \frac{\eta_{sp}}{C}$ (2.10)

Inherent viscosity $\eta_{inh} = \ln \left[\frac{\eta_{red}}{C} \right]$ (2.11)

Intrinsic viscosity $[\eta] = \lim_{C \rightarrow 0} \left[\frac{\eta_{sp}}{C} \right] = \ln \left[\frac{\eta_{red}}{C} \right]_{C \rightarrow 0}$ (2.12)

In these equations, η_{sol} is solution viscosity, η_{solv} is viscosity of the pure solvent, and C is concentration g/dL. Relative viscosity is the ratio of the viscosity of the solution, η_{sol} to the viscosity of the solvent, η_{solv} .

Specific viscosity expresses the incremental viscosity due to the presence of the polymer in the solution. Normalizing η_{sp} to concentration gives $\frac{\eta_{sp}}{C}$ which expresses the capacity of a polymer to cause the solution viscosity to increase, i.e., the incremental viscosity per unit concentration of polymer. As with other polymer solution properties, the solutions used for viscosity measurements will be non-ideal and therefore $\frac{\eta_{sp}}{C}$ will depend on C . The extrapolated value of $\frac{\eta_{sp}}{C}$ at zero concentration is known as the intrinsic viscosity (η).

Intrinsic viscosity (η) will be shown to be a unique function of molecular weight (for a given polymer-solvent pair) and measurements of (η) can be used to measure molecular weight.

The remaining form for the viscosity is the inherent viscosity. Like η_{sp} , $\ln \eta_{red}$ is zero for pure solvent and increases with increasing concentration, thus $\ln \eta_{red}$ also expresses the incremental viscosity due to the presence of the polymer in the solution. Normalizing $\ln \eta_{red}$ to concentration or $\ln \frac{\eta_{red}}{c}$ gives the inherent viscosity in the limit of zero concentration, η_{red} extrapolates the same as $\frac{\eta_{sp}}{c}$ and becomes equal to the intrinsic viscosity.

The intrinsic viscosity (η) is a measure of the hydrodynamic volume occupied by a macromolecule, which is closely related to the size and conformation of the macromolecular chains in a particular solvent (Higiro *et al.*, 2007). Experimental results with polymer solutions has revealed that the slope of the $\frac{\eta_{sp}}{c}$ vs. C curve, k , depends on molecular weight of the polymer. Huggins found that a plot of k versus $(\eta)^2$ was linear and passed through the origin.

Gums has high water solubility and a relatively low viscosity compared to other gums. same gums don't dissolve in water in concentrations above 5% due to their high viscosity. However, Gum Arabic dissolves in water up to 50% w/v, forming acidic solution (pH ~4.5). The highly branched structure of the gum arabic molecules leads to compact relatively small hydrodynamic volume and, consequently gum arabic will only become a viscous solution at high concentrations. Solutions of less than 10% gum arabic have a low viscosity corresponding to Newtonian behavior (Williams *et al.*, 1990b). However, steric interactions of hydrated molecules increase viscosity in those solutions 30% of gum arabic resulting in an increasingly pseudo plastic behavior. Its high stability in acidic solutions is exploited to emulsify citrus oils. The viscosity of gum arabic solutions can be modified by the addition of acids or bases as these ones change the electrostatic charge on the macromolecule. In very acidic solutions, a more compact conformation of the polymer is induced which leads to decreased viscosity; while of high pH (less compact molecule) results in maximum viscosity around pH 5.0-5.5. In very basic solutions, the ionic strength increment reduces the electrostatic repulsion between gum arabic molecules producing a more compact conformation of the biopolymer and thus reduces the viscosity of the solution (Anderson and Weiping, 1990); (Williams *et al.*, 1990b). Hassan *et al.*, (2005) reported that the intrinsic viscosity of *A. seyal* in the ranges between 11.9–17.6 cm^3g^{-1} , Al-Assaf *et al.*, (2005) reported an intrinsic viscosity of sixty seven samples of *A. senegal* in the range 9.7-26.5 cm^3g^{-1} , the intrinsic viscosity of *A. seyal* gum had been determined by Siddig *et al.*, (2005), it was found to be 14 cm^3g^{-1} , Omer (2006) found that an average values of intrinsic viscosity equal to 14.6 cm^3g^{-1} , and 11.4 cm^3g^{-1} for *A. senegal* and *A. seyal* respectively, Abdelrahman (2008) reported the average value of intrinsic viscosity of *A. senegal* gum 15.4 cm^3g^{-1} whereas equal to 11.6 cm^3g^{-1} for *A. seyal* gum, Younes (2009) reported a value of 18.9

cm^3g^{-1} intrinsic viscosity for *A. senegal* and $15.5 \text{ cm}^3\text{g}^{-1}$ for *A. seyal* gum, the intrinsic viscosity of *A. senegal* var *senegal* gum fall between, 13.32 ml/g and 15.83 ml/g which reported by Omar B, et al. (2013), and Amira, et al, (2011) reported the intrinsic viscosity of *A. nilotica* var. *nilotica* was ranged between 10.19 - $10.65 \text{ cm}^3\text{g}^{-1}$, Table (1.5).

1.6.3.7. Fractionation of Acacia gums

Gums had been fractionated using different techniques. Vandavelde and Fenyo (1985) using gel permeation chromatography (GPC) showed that the gum of *A. senegal* consists of two distinct fractions: the major fraction which constituted ~70% of the gum, containing very little proteinaceous material, and a minor fraction which was protein-rich and which they suggested as an arabinogalactan- protein complex.

Osman *et al.*, (1993) fractionated *A. senegal* using hydrophobic interaction chromatography (HIC) on Phenyl-Sepharose CL-4B. They obtained four fractions of similar carbohydrate composition, whilst differing in protein content, amino acid composition, and molecular mass distribution. The fractions were subjected to enzymatic (pronase) and alkaline hydrolysis, and the molecular mass distribution of the products was monitored by gel permeation chromatography. The fractions showed various degrees of resistance to hydrolysis, thus illustrating differences in their macromolecular structure. The improved molecular mass separation achieved using the Sepharose 6 GPC column indicates that these fractions are considerably polydisperse with respect to molecular mass. The differences in chemical composition and size, clearly illustrate the heteropolymolecular nature of the gum. They found the high molecular mass component was degraded giving rise to products of molecular mass $2-3 \times 10^5$, and, therefore, their finding was supportive to the wattle blossom model.

Osman *et al.*, (1994) fractionated two samples of *A. senegal* using ion exchange chromatography (IEC) on diethylaminoethyl cellulose (DEAE-cellulose). They used this technique to demonstrate the heterogeneity of the gum and its fractions. The gum fractions had been extensively characterized using an array of physicochemical and immunochemical techniques. They found all fractions were polydisperse depicting the high level of heterogeneity of gum. Fraction 1 showed no affinity to DEAE-cellulose and was eluted by phosphate buffer only. Fractions 2, 3, 4 and 5 were eluted by stepwise increase of ionic strength of the phosphate buffer using NaCl, from 0.04 to 0.29 mol/dm^3 in increment of 0.04 mol/dm^3 .

Hassan *et al.*, (2005) fractionated *A. seyal* using GPC technique and *A. senegal* was used as control. He reported that two fractions were obtained for *A. seyal* and *A. senegal*. High molecular weight fraction with an average molecular mass of 5.3×10^6 and 2.2×10^6 were obtained for *A. seyal* and *A. senegal* respectively, and a low molecular weight fraction with an

average molecular mass of 1.0×10^6 and 3×10^5 were obtained for *A. seyal* and *A. senegal* respectively. He concluded that the protein distribution in *A. seyal* is different from that in *A. senegal*, whereas it is exclusively associated with the high molecular weight component (AGP) in *A. senegal*. For *A. seyal* the protein is distributed between the molecular weight fractions and the lower $\sim 1 \times 10^5$ molecular weight component.

Flindt *et al.*, (2005) studied enzyme degradation for both *Vulgares* and *Gummiferae* series considering the generality of enzyme action in relation to structure of *Acacia* gums. They studied *A. senegal* and *A. seyal* and other gums which were the prototype members of these series, and show molecular weight characteristics which are typical of the series as a whole (Al-Assaf *et al.*, 2005). They demonstrated the greater variability of the *Gummeferae* series, reflected also in the *A. seyal*. They subjected the samples to the enzyme degradation to establish the generality of the behaviour, in view of the very large variation which seems inherent in *A. seyal* samples collected from various geographical regions. The changes in average molecular weight and in the high molecular weight component (peak 1), after enzymatic treatment for 24 and 72 h. They found that there is a clear distinction between *A. senegal* and *A. seyal*, and that these are typical of the series they represent. They found that the enzymic hydrolysis is completed after 24 h.

These enzyme experiments confirmed the conclusion that the high molecular weight component near peak 1 for *A. seyal* is made up of two components, one of which can be enzymatically degraded, and the other which is resistant, Pickles *et al.*, (2007) fractionated four samples of *A. senegal*, one control (Mw 6.2×10^5 g/mol) and three enhanced samples (*Acacia (sen) SUPER GUM™*) with different molecular weights ranging from $1.2 \times 10^6 - 2.5 \times 10^6$ g/mol using hydrophobic interaction chromatography (HIC) on a DIAION HP-20 column, into two fractions, hydrophilic (fraction 1, yield $\sim 80\%$) and hydrophobic (fraction 2, yield $\sim 2\%$). The elution profile and weight average molecular weight of fraction 1 were similar to the starting materials but contained slightly more arabinogalactan protein (AGP).

1.6.3.8. Molecular association

The tendency of polysaccharides to associate in aqueous solution is well known. These molecular associations affect their function in a particular application due to their influence on molecular weight, shape and size, which determines how molecules interact with other molecules and water. There are several factors such as hydrogen bonding, hydrophobic association, an association mediated by ions, electrostatic interactions, which depend on the concentration and the presence of protein components that affect the ability to form super molecular complexes. (Al-Assaf *et al.*, 2007) , reported that molecular associations in gum

arabic can lead to an increase in molecular weight in the solid state by maturation under controlled heat and humidity. The process does not involve change in the basic structural components and, while maturation takes place, the level of association increases giving way to AGP with higher molecular weight and protein content. This process mimics the biological process which produces more AGP throughout the tree growth, and gets maturation to continue during the storage of gum arabic after harvest. Subsequently, (Al-Assaf et al., 2009), analyzed the role of protein components in gum arabic to promote molecular association when the gum is subjected to different processing treatments as, spray drying and irradiation. Results demonstrate the ability of protein components to promote hydrophobic associations that influence the size and proportion of the high molecular weight component AGP. When gum arabic undergoes maturation there is an increase in the hydrophobic nature of the gum and therefore an increase of its emulsifying properties. Spray drying involves not the aggregation through hydrophobic associations but also changes in the surface properties of peptide residues increasing gum arabic hydrophobicity compared with the association promoted by the treatment of maturity in the solid state. Ionizing radiation in both aqueous solutions and solid state induces cross-linking between polysaccharide blocks by the formation of –C-C- bonds. It was also reported that using mild UV-radiation, it is possible to induce gum arabic crosslinking (Kuan et al., 2009). The process reduced the solution viscosity and improved emulsification properties. Gum arabic modification can be used in food products requiring better reduced viscosity and enhanced emulsifying properties such as dressings, spreads, and beverages, as well as in other nonfood products such as lithographic formulations, textiles, and paper manufacture.

1.6.3.9. Nitrogen and Protein Content

The Kjeldahl method was used to determine the total nitrogen in gum samples according to AOAC (1990). The method consists of three basic steps such as digestion of the sample in sulfuric acid with a catalyst, which results in conversion of nitrogen to ammonia, distillation of the ammonia into a trapping solution, and quantification of the ammonia by titration with a standard solution. The reactions involved in these steps can be shown as follows:

- Sample + H₂SO₄ (conc.) catalyst +Heat → (NH₄)₂SO₄
- (NH₄)₂SO₄ + 2 Na OH → 2NH₃ + Na₂SO₄ + 2H₂O
- NH₃ + H₃BO₃ → NH₄⁺ + H₂BO₃
- H₂BO₃⁻ + HCl → H₃BO₃ + Cl⁻

Nitrogen and protein content of *A. senegal* var *senegal* calculated using nitrogen conversion factor 6.6 (Anderson et al., 1986),. Hassan *et al.*, (2005) reported protein content of *A. seyal* of a

mean value of 0.96%. The nitrogen content of *A. seyal* gum had been determined by Siddig *et al.*, (2005), it was found to be 0.15% and hence protein content found to be 1.0%. Omer (2006) determined the nitrogen content for samples of *A. senegal* and *A. seyal* from different locations, the values were 0.35% and 0.14% for *A. senegal* and *A. seyal* respectively, whereas protein content had a value of 2.3% and 0.93 respectively. Abdelrahman (2008) reported the average value of nitrogen content of *A. senegal* gum 0.37% whereas equal to 0.14% for *A. seyal* gum, and he found that protein content of *A. senegal* gum 2.4% and equal to 0.95% for *A. seyal* gum. Recent study by Younes (2009) determined nitrogen content for *A. senegal* 0.35% and protein content 2.3%, for *A. seyal* the author reported nitrogen content 0.22% and protein content 1.4% . Omar, et al. (2013) reported an average nitrogen and protein content of *A. senegal var senegal* samples are 0.35 % and 2.31 % respectively, the mean percentages of nitrogen and protein content of *A. nilotica var nilotica* ranged between 0.02% and 0.16%, the total protein content was calculated using nitrogen conversion factor (NCF) of 6.51 from amino acid analysis, (Amira, 2011). Table (1.5).

1.6.3.10. Acid equivalent weight and uronic acid

The acidity represented the acid equivalent weight of gum, from which the uronic acid content, can be determined (Anderson and Bell, 1977), (Vandeveldel and Fenyo, 1985), (Jurasek et al., 1993). Hassan *et al.*, (2005) studied seventy four authenticated different samples of *A. seyal* from different location using acid–base titrimetric method, he reported a mean value of equivalent weight 1489 and the uronic acid 11.9%. Siddig *et al.*, (2005) reported uronic acid for *A. seyal* 16%. Omer (2006) reported an average acid equivalent weight of 1161, and 15.2% glucouronic acid for *A. senegal*, whereas acid equivalent weight was to be 1107.9 in average and in average glucouronic acid of 15.9% for *A. seyal*. Abdelrahman (2008) reported the value of 16.8% uronic acid of *A. senegal* gum and 1153.8 acid equivalent weight value, and a uronic acid of 16.4% *A. seyal* and 1185.8 acid equivalent weight, acid equivalent weight and uronic acid had been determined by Younes (2009), he reported the mean value of acid equivalent weight 1620 and uronic acid 11.89% for *A. senegal* gum, also he reported a value of 1180 acid equivalent weight and 16.34% uronic acid for *A. seyal*. The acid equivalent weight and corresponding calculated uronic acid content of *A. nilotica var. nilotica* gum shows 1908.37 for acid equivalent weight, and with the corresponding uronic acid having the mean value of 10.18% (Amira, 2011). The acid equivalent weight of *A. senegal var senegal* samples fall between 1081 and 1306 with the corresponding glucouronic acid within the range of 13.5% and 16.3% with an average values of 1161 and 15.2, respectively (Omar, et al. 2013), Table (1.5).

1.6.3.11. Cationic composition:

Gums are salts of elements such as. Calcium; Magnesium, Potassium, Sodium, Iron, and Copper are the most abundant elements in all gum samples. The mean values in the table show that the major elements in *A.senegal* var. *senegal* samples are, in the increasing order, K, Ca, Fe, Mg, Na, and Cu, (Omar, et al. 2013).. Cationic composition of *A. nilotica* var. *nilotica* gum samples was determined using atomic absorption spectrophotometric technique and the major elements were in the order: K > Ca > Mg > Na > Pb > Fe > Cu > Zn. Potassium, Calcium and Magnesium recorded high values, indicating that the gum is a salt of potassium, calcium and magnesium. (Amira, 2011).

1.6.3.12. Fractionation and molecular weight determination

1.6.3.12.1. Light scattering

Light Scattering occurs when polarizable particles in a sample are placed in the bath of an oscillating electric field of a beam of light. Varying the field induces oscillating dipoles in the particles and these radiate lights in all directions. This important and universal phenomenon is the basis for explaining why the sky is blue, why fog and emulsions are opaque and other observations. It has been utilized in many areas of science to determine particle size, molecular weight, shape, diffusion coefficients etc. In the 19th century Lord Rayleigh offered the first explanation for the sky's blue color. From Rayleigh's initial theory representing a simplification of Maxwell's electromagnetic theory for the case of very small particles compared to the wavelength of the incident light, the theory was extended to describe the scattering of light by larger macromolecules in solution. This is called the Rayleigh-Gans-Debye (RGD) theory of light scattering to recognize the roles of the various scientists involved in its development.

1.6.3.12.2. Rayleigh scattering Small size parameters approximation

The size of a scattering particle is parameterized by the ratio x of its characteristic dimension r and wavelength λ :

$$x = \frac{2\pi r}{\lambda} \dots\dots\dots (1.1)$$

Rayleigh scattering can be defined as scattering in the small size parameter regime where $x \ll 1$. Scattering from larger spherical particles is explained by the Mie theory for an arbitrary size parameter x . For small x the Mie theory reduces to the Rayleigh approximation. The amount of Rayleigh scattering that occurs for a beam of light is dependent upon the size of the particles and the wavelength of the light. Specifically, the intensity of the scattered light varies as the sixth power of the particle size and varies inversely with the fourth power of the wavelength.

The intensity I of light scattered by a single small particle from a beam of unpolarized light of wavelength λ and intensity I_0 is given by:

$$I = I_0 \frac{1 + \cos^2 \theta}{2R^2} \left(\frac{2\pi}{\lambda} \right)^4 \left(\frac{n^2 - 1}{n^2 + 2} \right)^2 \left(\frac{d}{2} \right)^6 \dots\dots\dots (1.2)$$

Where R is the distance to the particle, θ is the scattering angle, n is the refractive index of the particle, and d is the diameter of the particle. The scattering cross-section is given by:

$$\sigma_s = \frac{2\pi^5}{3} \frac{d^6}{\lambda^4} \left(\frac{n^2 - 1}{n^2 + 2} \right)^2 \dots\dots\dots (1.3)$$

The Rayleigh scattering coefficient for a group of scattering particles is the number of particles per unit volume N times the cross-section. As with all wave effects, for incoherent scattering the scattered powers add arithmetically, while for coherent scattering, such as if the particles are very near each other, the fields add arithmetically and the sum must be squared to obtain the total scattered power.

Rayleigh scattering also occurs from individual molecules. Here the scattering is due to the molecular polarizability α , which describes how much the electrical charges on the molecule will move in an electric field. In this case, the Rayleigh scattering intensity for a single particle is given by:

$$I = I_0 \frac{8\pi^4 \alpha^2}{\lambda^4 R^2} (1 + \cos^2 \theta). \dots\dots\dots (1.4)$$

The amount of Rayleigh scattering from a single particle can also be expressed as a cross section σ . For example, the major constituent of the atmosphere, nitrogen, has a Rayleigh cross section of $5.1 \times 10^{-31} \text{m}^2$ at a wavelength of 532 nm (green light) (Sneep, 2005). This means that at atmospheric pressure, about 10^{-5} fraction of light will be scattered for every meter of travel. The strong wavelength dependence of the scattering ($\sim \lambda^{-4}$) means that shorter blue wavelengths are scattered stronger than longer (red) wavelengths. This results in the observation of indirect blue light coming from all regions of the sky. Rayleigh scattering is a good approximation to the manner in which light scattering occurs within various media for which scattering particles have a small size parameter. In a typical Rayleigh scattering experiment, a well collimated, single frequency polarized light beam (e.g. from a laser) is used to illuminate a solution containing a suspension of the macromolecules of interest. The electric field of the polarized light beam is generally produced perpendicular to the plane in which the intensity and angular dependence of the subsequently scattered light is to be measured. The intensity carries information about the molar mass, while the angular dependence carries information about the size of the macromolecule. Light scattering is a technique for characterizing macromolecules and a wide range of particles in solution. In contrast to most methods for characterization, it does not

require calibration. In this sense it is an absolute technique. There are two different types of light scattering measurements for absolute molecular characterization:

Classical Light Scattering/ Static Light Scattering: Here, the intensity of the scattered light is measured as a function of angle. For the case of macromolecules, this is often called Rayleigh scattering and can yield the molar mass, root mean square (rms) radius, and second virial coefficient (A_2). For certain classes of particles, classical light scattering can yield the size, shape, and structure.

Quasi- elastic Light Scattering (QELS) or Dynamic Light Scattering (DLS): In a QELS measurements, time-dependent fluctuations in the scattered light signal are measured using a fast photon counter. QELS measurements can determine the hydrodynamic radius of macromolecules or particles.

Light scattering is a technique that can be applied in either batch or chromatography mode. In either instance the sample may be recovered at the end of the measurement. Since light scattering provides the weight-averaged molar mass for all molecules in solution, it is generally more useful to utilize chromatography, though each technique has its advantages.

Although absolute molecular weights can be determined using mass spectrometry, membrane osmometry, and sedimentation equilibrium (analytical centrifugation), only light scattering covers so broad a range of macromolecules including their oligomeric states. Most importantly, light scattering permits measurement of solution properties of macromolecules. While a sedimentation equilibrium run may require 72 hours, a size exclusion chromatography/light scattering study may be completed in well under an hour and batch mode analysis in a few minutes. These comparatively short run times coupled with the absolute determination of molar mass, size, and make light scattering the method of choice for accurate and fast macromolecular characterization.

1.6.3.12.3. Intensity of Scattered Light and Molar Mass

When laser light impinges on a macromolecule, the oscillating electric field of light induces an oscillating dipole within it. This oscillating dipole will re-radiate light, much like the antenna for a radio station sends out radio waves. The intensity of radiated light depends on the magnitude of the induced dipole. The more polarizable the macromolecule, the larger the induced dipole, and hence, the greater the intensity of the scattered light. Therefore, in order to characterize the scattering from a solution of such macromolecules, it is necessary to know their polarizability. This may be determined from a measurement of the change, dn , of the solution's refractive index n with the molecular concentration change, dc , by measuring dn/dc . When there

are many macromolecules in solution, each macromolecule scatters light of induced dipole mechanism.

Consider a system of scattering centers, each with the same scattering properties and mass. If two scattering centers are connected into one larger particle, then there is a definite phase relation between the light scattered from each scattering center because the particle is moving together as whole. Therefore, the scattered light adds coherently.

If the two scattering centers are separated, the Brownian motion of each center is different. Therefore, the phase relationship changes with time between the scattered light from each center, and the scattered light averages over time to add incoherently.

1.6.3.12.4. Angular Dependence of Scattered Light and Size

Macromolecules much smaller than the wavelength of the incident light can be treated as though they were essentially point scatters. For such very small molecules, the scattered light in the plane perpendicular to the polarization of the incident light is independent of scattering angle. It is the same at every scattering angle.

For larger macromolecules, however, there are variations in the phase of the scattered light from different parts in the macromolecule. This can lead to either destructive or constructive interference of the scattered light. The net result is that the intensity of scattered light away from the direction of the laser beam is changed and, for small molecules compared to the wavelength of the incident light, is reduced. Each macromolecule is assumed to be made up of very small elements, each of which scatters light independently.

However, during the time of passage of the incident light wave front over the macromolecule, each element scatters in phase with the scattering of adjacent elements. Thus the scattered waves will add destructively or constructively producing constructive or destructive interference in certain directions. If the angular dependence of the scattered light is measured, it is possible to determine the size of the molecule. Here, the size measurement is known as the root mean square (RMS) radius, or "radius of gyration". The latter term is a misnomer since it describes a kinematic measure of a molecule rotating about a particular axis in space. The RMS radius, on the other hand is a measure of its size weighted by the mass distribution about its center of mass, as shown in Figure (1.15). Once the molecule's conformation is determined, (e.g., random coil, sphere, or rod), the RMS radius can be related to its geometrical dimensions. For a sample containing a broad distribution of molecular masses, following separation by chromatographic means, the measured RMS radius may be plotted against the correspondingly measured molar mass to determine the sample's conformation.

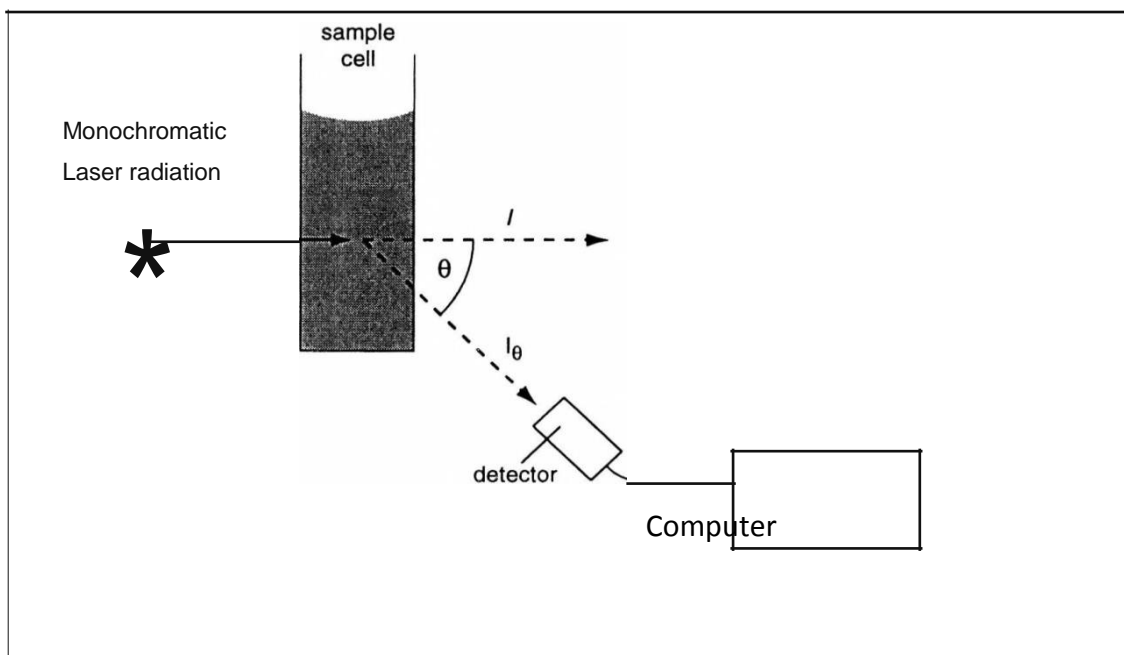


Figure 1.15. Schematic diagram depicting light scattering from molecules

1.6.3.12.5. Equations and Data Analysis

The theoretical foundation lay out by (Zimm, 1948) and (Ibid, 1948) makes it possible to condense the results of the Rayleigh-Debye-Gans theory of light scattering into a simple equation. As described by (Wyatt, 1993) Zimm's development leads to the expression:

$$\frac{K^*c}{R(\theta,c)} = \frac{1}{M_w P(\theta)} + 2A_2 c \dots\dots\dots (1.5)$$

Where:

- $R(\theta,c)$ is the excess Rayleigh ratio of the solution as a function of scattering angle θ and concentration c . It is directly proportional to the intensity of the scattered light in excess of the light scattered by the pure solvent.
- c is the solute concentration.
- M_w is the weight-averaged solute molar mass.
- A_2 is the second virial coefficient in the virial expansion of the osmotic pressure.
- K^* is the constant $4\pi^2(dn/dc)^2 n_0^2 / N_a \lambda_0^4$.
- N_a is Avogadro's number. This number always appears when concentration is measured in g/ml and molar mass in g/mol.

- $P(\theta)$ describes the angular dependence of the scattered light, and can be related to the rms radius.

The expansion of $P(\theta)$ to first order gives:

$$p(\theta) = 1 - \frac{16\pi^2 n_0^2}{3\lambda_0^2} \langle r_g^2 \rangle \sin^2 \frac{\theta}{2} \dots\dots\dots (1.6)$$

Where n_0 is the index of refraction of the solvent, λ_0 is the vacuum wavelength of the laser, and r_g is the rms radius. Here, the relation between the size and angular dependence of the scattered light is clear. For larger sizes (r_g greater than approximately 50 nm) it is necessary to include higher moments in the expansion of $P(\theta)$.

At low angles, its variation depends only on the mean square radius $\langle r_g^2 \rangle$, and is independent of molecular conformation or branching. A plot of $K \cdot c/R(\theta)$ vs. $\sin^2(\theta/2)$ in the limit of very low concentrations, e.g. chromatography experiments, yields a curve whose intercept gives Mw and whose slope at low angles gives $\langle r_g^2 \rangle$ as shown in Figure (1.16).

The basic light scattering equation holds true at all angles, not just one. With modern computers we can now collect all of the angular data and apply a Global Fit, since the relationship between mass, size, and the quantities measured is valid at all angles.

The so-called “extrapolation,” to which some light scattering vendors may refer, consists actually of collecting a complete set of independent data points and using this full view of the scattering pattern to find the most accurate value of the molar mass, size and conformation. The value of M_i is then determined from the intercept, of the plot. Thus information about the weight average molecular weight (M_w), number average molecular weight (M_n), molecular weight distribution, polydispersity index (M_w/M_n) and radius of gyration can be obtained, using Equations. (1.7 – 1.9) Astra Software (Wyatt Technology, SB, USA).

Weight average molecular weight

$$M_w = \frac{\sum(c_i M_i)}{\sum c_i} \dots\dots\dots (1.7)$$

The number average molecular weight

$$M_n = \frac{\sum c_i}{\sum \frac{c_i}{M_i}} \dots\dots\dots (1.8)$$

Z-average mean square radius

$$(r^2)_z = \frac{\sum(c_i M_i (r^2)_i)}{\sum(c_i M_i)} \dots\dots\dots (1.9)$$

The quantities c_i , M_i and $(r^2)_i$ in the above equation are, respectively, the concentration, molecular weight and mean square radius of the i^{th} slice.

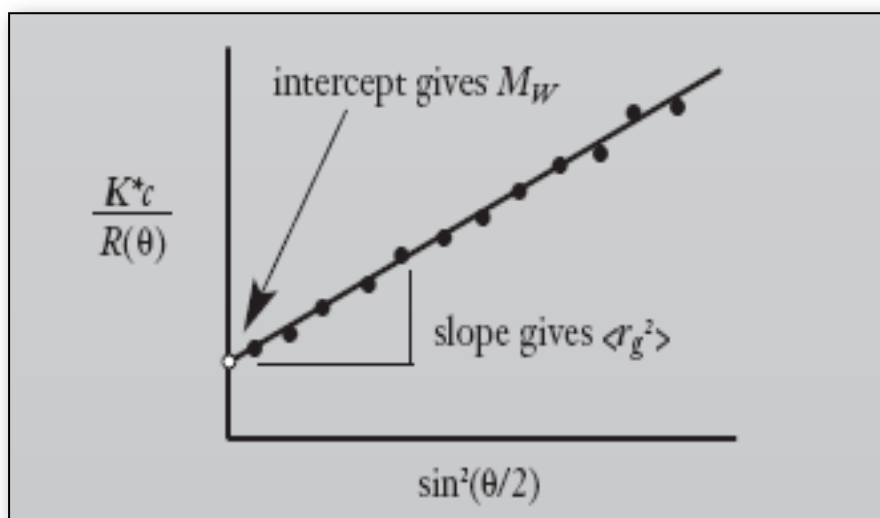


Figure 1.16: A plot of $K^*c/R(\theta)$ vs. $\sin^2(\theta/2)$

1.6.3.12.6. Principles of GPC / SEC

Gel Permeation Chromatography (GPC) or Size Exclusion Chromatography (SEC) is a special application of the High Performance Liquid Chromatography (HPLC) but in an ideal case without interaction due to absorption or partition. A polymer solution (typical concentration 0.1% by weight) passes through a column of a porous gel/material at pressures of 30-100 bars and a flow rate of typically 1ml/min. In contrast to HPLC the separation is based on a size exclusion mechanism and not on absorption. The pores of volume V_x contain the same solvent than the interstitial volume V_o (dead volume of the packing). Molecules which are larger than the size of the pores can only pass through the interstitial volume and cannot penetrate into the pores of the packing material and therefore leave the column first at the same volume V_o called the upper exclusion limit (total exclusion) above of which the sizes of the larger particles cannot be resolved. Molecules which are smaller than the pore size enter all pores and leave them without a separation. They all elute with the same maximum elution volume (total permeation volume) $V_{tot}=V_o+V_x$, which exceeds the interstitial volume by the total pore volume V_x . This is the lower limit of the range of separation, which is called the separation threshold (total permeation).

The physical property which determines the elution volume is the hydrodynamic volume of the polymer coil. If the elution volume of two different polymers is the same they exhibit identical hydrodynamic volumes although their topology or chemical structure might be different.

Conversely it is possible that polymers of the same molar mass (but different chemical structure) have a different hydrodynamic volume and therefore elute with a different elution volume. The driving force for the penetration of the polymer coils into the pores is the gradient of concentration between the pore volume V_x and the interstitial volume V_o . There is a concentration gradient into the pores if it is only filled with solvent. If the coil has entered the pore the concentration gradient will be in direction of the interstitial volume and the coil diffuses out of the pore. It is usual and practical to indicate the steric exclusion limit and the separation threshold by molar mass values which enable the user immediately to determine the problems for which the various gel types are suitable. The solvent and the polymer should be stated in addition due to the fact that the dimensions of the polymer and the gel as well depend on the solvent.

For samples having molecular sizes above the upper exclusion limit, the distribution constant, K , is zero. As the molecular sizes decreases, K increases, reaching its maximum value $K=1$ at the separation threshold. While in the absorption mechanism also higher values of K may occur (corresponding to an enrichment of the substance in the stationary phase) in the steric exclusion mechanism the highest possible concentration in the stationary phase is equal to that in the solution. Particles whose sizes lie between the steric exclusion limit and the separation threshold are more or less strongly retained. Their elution volume V_e range between the dead volume V_o and the maximum retention volume

$$V_{tot}: V_e = V_o + K \cdot V_x \quad \text{with } 0 \leq K \leq 1$$

The distribution constant K is therefore a measure of the volume fraction of the pore volume for a given size. A GPC column set is used to separate the macromolecules according to size, in the usual big first order of elution. After leaving the column, the molecules flow past a light scattering detector (using one or more angles) and then to a concentration detector. The usual choice for the concentration detector is a differential refractive index instrument. As it is easily damaged by back pressure, the DRI is placed last. If the time lag between the two detectors is well known, the scattering intensity at a time t can be compared well to the concentration of scatterers in the cell. In addition, the UV detector at 214 nm, which shows the amount of protein in fractionated material. The intensities may be converted to the Rayleigh factors in the usual way, as for a conventional Zimm plot. If the intensities are measured at sufficiently low angles, or if multi-angle detectors are used so that low-angle intensities may be obtained by

extrapolation, then absolute molecular weights can be obtained. If the column separates the polymers well, then not only all the moments of the distribution, but also the distribution itself, can be recreated. All this in the same time, about 20-60 minutes, as a simple GPC run. Additionally, GPC/LS can see certain components that GPC misses. This is because the differential refractive index signal in normal GPC is proportional to concentration, c , while the light scattering signal is proportional to cM , where M is the molecular weight. This is very handy in identifying the existence of high mass components present at low concentrations, it is also useful in identifying aggregates. In order to determine accurately the molecular weight using light scattering a reliable refractive index increment, dn/dc , is essential.

1.6.3.12.7. Specific Refractive Index Increment dn/dc

The quantity dn/dc , also called the “specific refractive index increment” describes how much the refractive index of a polymer solution changes with respect to the concentration of the solute.

Measurement of dn/dc is essential for the absolute characterization of the molar mass, since it is a term used in the molar mass calculation. Polymers with larger values of dn/dc scatter more light at the same mass than those having smaller values. Therefore, knowing dn/dc permits the deduction of molar masses from the light scattering data. Because dn/dc changes with wavelength, it is vital to measure it at the same wavelength as the light scattering apparatus. dn/dc must be measured as the polymer concentration approaches zero.

dn/dc depends on polymer composition, solvent, wavelength, and molecular weight. To measure dn/dc , a series of dilutions of the sample are made. These dilutions are then injected into the instrument and data collection is automatically performed with the *DNDC* software. The software then calculates the dn/dc based upon the signal strength from the refractive index (dn) and the concentrations of the dilutions (dc). The instrument interferometric refractometer is an extremely sensitive and stable detector. It measures the optical phase difference between two light beams passing through a sample and a reference cell.

1.6.3.13. Rheological Properties of *Acacia nilotica* var *tomentosa* gum

Rheology means to study of the deformation and flow of matter. This definition was accepted when the American Society of Rheology was founded in 1929, on the properties and behaviour of such widely differing materials as asphalt, lubricants, paints, plastics and rubber, which gives some idea of the scope of the subject and also the numerous scientific disciplines which are likely to be involved. Nowadays, the scope is even wider. Significant advances have been made in biorheology, in polymer rheology and in suspension rheology. There has also been a significant appreciation of the importance of rheology in the chemical processing industries.

Opportunities no doubt exist for more extensive applications of rheology in the biotechnological industries.

1.6.3.13.1. Definition of flow behavior

1.6.3.13.1.1. Newtonian

The viscosity is independent of the shear rate, e.g: water, certain oils and dilute resin solutions. This is the simplest type of fluid flow where the materials viscosity is constant and independent of the shear rate. The rate of deformation is directly proportional to the applied force. This is shown in the two different plot types in Figure (1.17). Newtonian liquids are so called because they follow the law of viscosity as defined by Sir Isaac Newton:

1.6.3.13.1.2. Structural viscosity Broad

Term for all non-Newtonian flow phenomena

1.6.3.13.1.3. Pseudoplastic

The viscosity shows Newtonian flow properties at low shear rates but the viscosity decreases above a critical shear rate Figure (1.17).. A large number of liquids show a large decrease in viscosity when the shear rate is increased and this type of flow is defined as pseudoplastic or shear thinning behavior. Emulsions, suspensions and dispersions are typically pseudoplastic as are many paint, ink and adhesive systems. At higher shear rates the flow behaviour becomes more linear (Newtonian).

1.6.3.13.1.4. Plastic

The viscosity decreases with increasing shear rate Figure (1.17).

1.6.3.13.1.5. Dilatant

The viscosity increases with increasing shear rate (shear thickening), these phenomena called dilatant. Dilatant fluids show the opposite type of behaviour to pseudoplastic systems. It is seen in highly concentrated suspensions or slurries Figure (1.17)...

1.6.3.13.1.6. Thixotropic

The viscosity decreases at constant temperature and constant shear rate over time and returns to its original state in a finite time when the shear is removed. This is typical of the behaviour observed in gelled paints applied to a vertical surface, where the viscosity reduces under the shear of the brush or roller and then recovers to prevent sagging. This is represented in the plot shown in Figure (1.17)

1.6.3.13.1.7. False thixotropy

The viscosity decreases at constant temperature and constant shear rate over time and does not return to its original state in a finite time when the shear is removed.

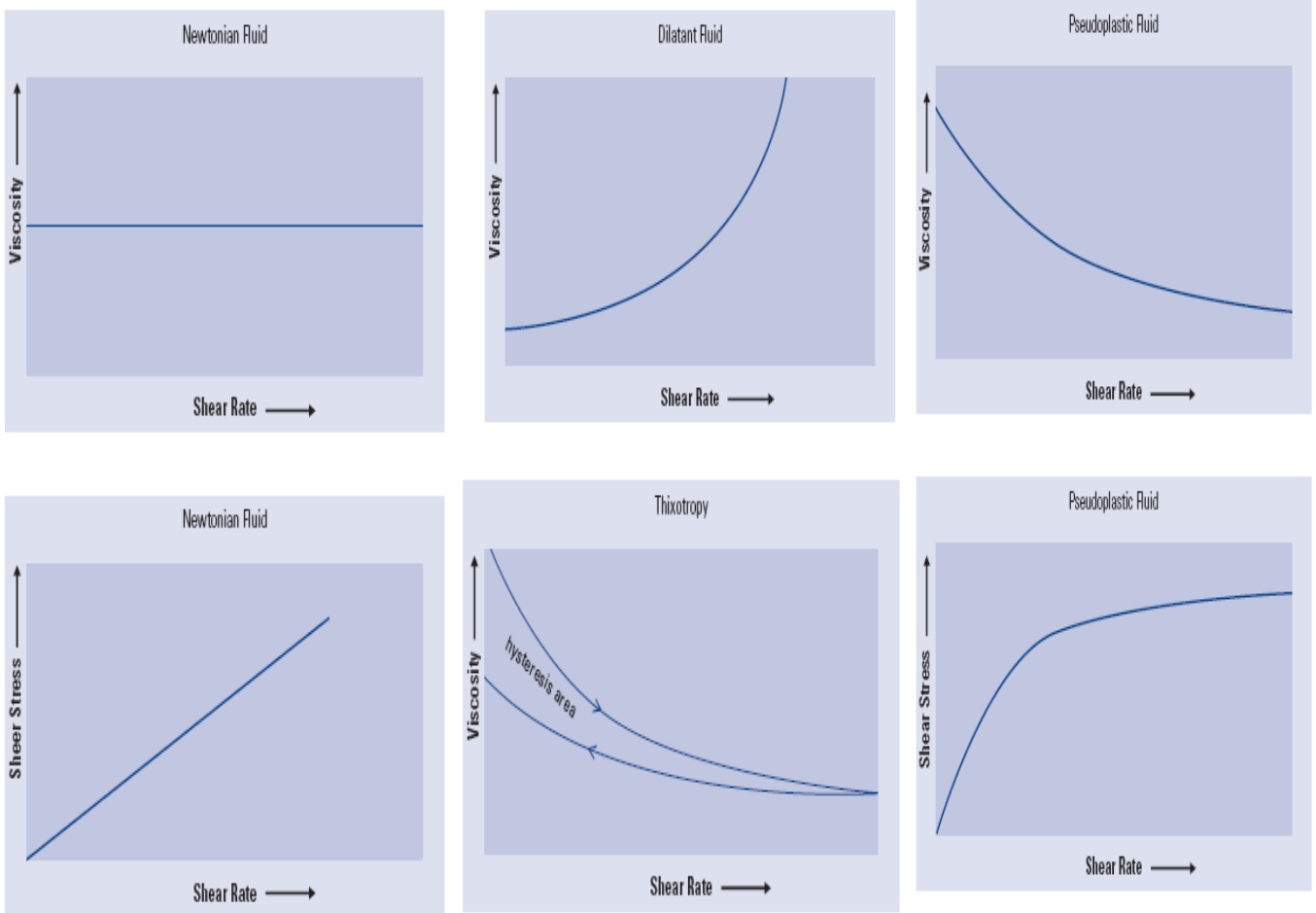


Figure. 1.17. Different viscosity curves

1.6.3.13.2. Types of Viscometers for measuring shear viscosity

1.6.3.13.2.1. One-Dimensional Parallel Plates Model

The Obvious example of this type was, spreading butter on a slice of bread. We have three starting materials: the slice of bread, the butter and the knife. The bread and knife can be thought of as two flat plates and the butter as a viscous fluid between them. We have two (D. Laba, 1993) plane parallel plates (Figure. 1.18). Located between them in our example is butter of thickness h . The top plate with an area A [m²] is moved with a velocity v [m/s] by the force F [N = kgm/s²]. Between the two plates a shift in the minute laminar fluid layers takes place. The flow arising is laminar and not turbulent.

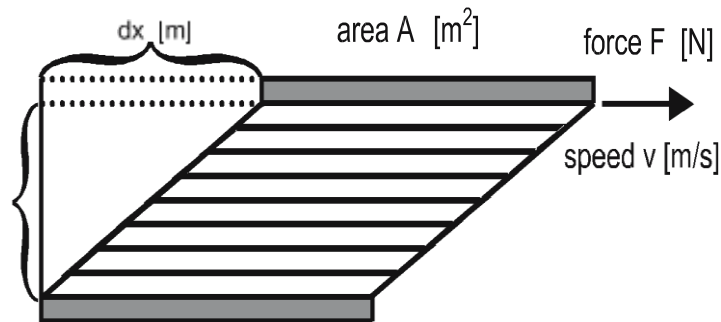


Fig. 1.18. Shear flow in the parallel plates model of one-dimensional stress

The ratio of the force F to the area A is called the shear stress:

$$\tau = F/A \text{ [N/m}^2 = \text{Pa].} \quad (1.21)$$

The ratio of the velocity v to the thickness h is the shear rate:

$$\dot{\gamma} = v/h \text{ [1/s].} \quad (1.22)$$

The deformation arising is:

$$\gamma = x/h \text{ [dimensionless].} \quad (1.23)$$

This experiment indicates that shear stress increase is proportional to the shear rate. The proportionality factor was called viscosity by Sir Isaac Newton:

$$\tau = \eta \cdot \dot{\gamma} \text{ [Pa} \cdot \text{s]}. \quad (1.24)$$

This law applies only to a very small category of substances called Newtonian fluids.

1.6.3.13.2.2. Parallel Plate Measuring System

The Parallel Plate (pp) measuring system Figure (1.19) has a constant, defined radius R and a variable plate gap h . In DIN 53018 part 1 a plate gap ranging from 0.3 to 3 mm is recommended. The radius R should be several times larger than the gap h . The angular speed in the gap $\omega(h)$ is constant in levels parallel to the plates and increases with the height:

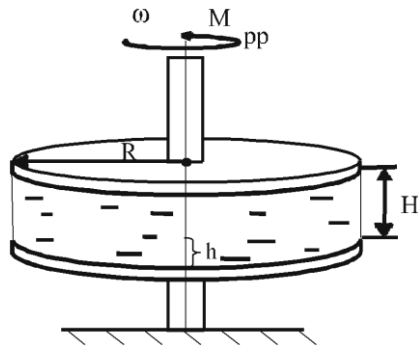


Figure. 1.19. Parallel plate model

The angular velocity ($\omega = 2\pi \cdot n/60$) is expressed in rad/s and the rate of rotation in min^{-1} . By varying the gap between the plates it is possible to regulate the shear rate. Increasing the gap h (the denominator becomes larger) decreases the shear rate if the angular velocity or rate of rotation remains constant. Care must be taken to ensure that the gap does not become too small because then frictional effects would falsify the measuring results. As a rule of thumb, the gap should be at least five times larger than the largest particles contained in the sample. Consequently, the model is most suitable for semi-solid materials and has the added advantage of being easy to clean (T. Mezger, 2000).

1.6.3.13.2.3. Cone-Plate Measuring System

The Parallel Plate has the disadvantage of variable shear rates. The replacement of the top plate of the Parallel Plate model with a cone with its tip resting as the bottom plate the result is the cone-plate model (Figure.1.20), which known as the CP measuring system (J.M.G, 1991). This rheometer type is well known as ASTM D4287 for paint and colors and ASTM D3205 for asphalt.

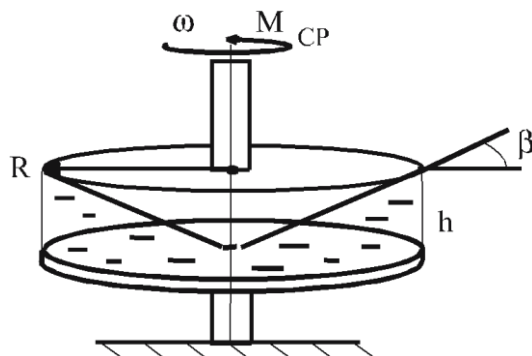


Figure .1.20. Cone-Plate Model

1.6.3.13.2.4. Coaxial Cylinder Systems

Liquids are stored in a jar or cup or stirred with a beater or mixing rod. If we apply this image to a rod rotating in a cup, the result is the coaxial measuring system (Hiemenz, 1984), also known as the concentric cylinder system Figure (1.21). There are basically two types of cylinder systems. One is the Couette system Figure (1.21a) in which the outer cup is moved and the resulting force measured. The other is the Searle system Figure (1.21b) in which the outer cup remains fixed and only the inner cylinder rotates and also measures the resulting force

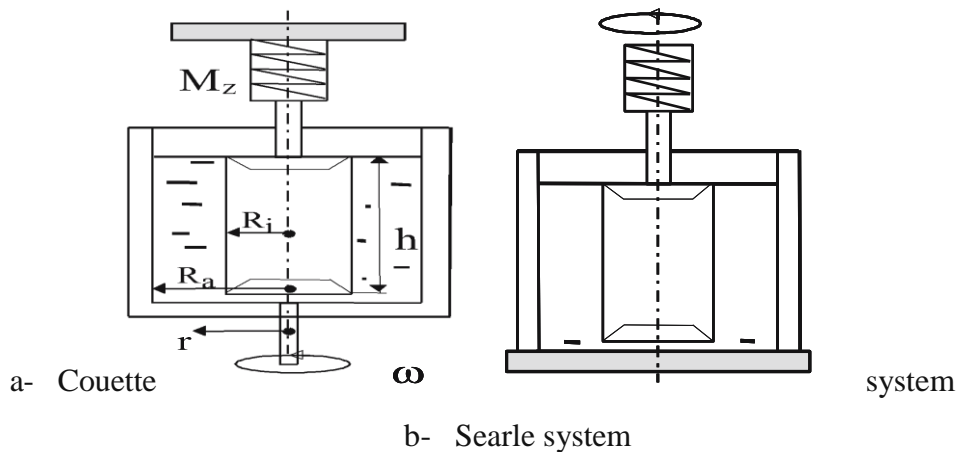


Fig. 1.21. Cylinder systems

1.6.3.13.2.5. Double Gap Measuring System

This special coaxial cylinder measuring system (Lechner, 1993) has a very large shearing area has been standardized for very low viscosities. The actual sample holder is an axially symmetrical gap into which another cylinder is fitted Figure (1.22).

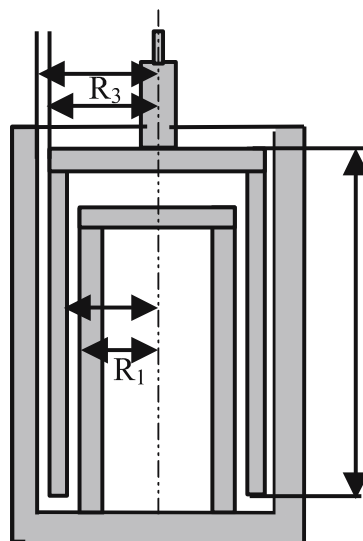


Figure. 1. 22. Double gap system

1.6.3.13.3. Mathematical descriptions of flow curves (non-Newtonian)

To describe the shear stress, and shear rate relationship of non-Newtonian fluids. The following are some examples of just some of the simpler forms of equations which fit different parts of a flow curve.

1.6.3.13.3.1. The Power-law liquid

The power law is good for describing a materials flow under a small range of shear rates. Most materials will deviate from this simple relationship over a sufficiently wide shear rate range.

$$\tau = K \gamma^n \dots \dots \dots (1.25)$$

Where

τ is the shear stress, K is consistency index, γ is the shear rate and n is the flow behavior index which indicates the tendency of the fluid to shear thinning. It is often referred to as the power law index of the material. If n is less than one, the material is shear thinning, if n is more than one then material is shear thickening, when the value of n is equal to 1.0, the power law reduces to the Newtonian model. This model is valid for the linear, i.e., center section, of the curve Figure (1.23). In the power law model, the viscosity term from the Newtonian model is replaced by a constant, K , serves as a viscosity index of the system. The consistency index has the unusual set of units, Force-secⁿ/Area. In addition, the shear rate term is raised to the n^{th} power, thus the term power law.

This equation can also be expressed in terms of apparent viscosity, (η_a).

$$\eta_a = K \gamma^{n-1} \dots \dots \dots (1.26)$$

When the log of the shear stress is plotted against the log of the shear rate, a straight line with a slope equal to n and an intercept equal to $\log K$ results. A plot of the log of the viscosity versus log of the shear rate also results in a straight line. Although this is one of the most popular models used, no known fluid exhibits power law behavior over the entire range of shear rate conditions. The power law model cannot be used to predict viscosities at shear rates in the upper and lower Newtonian regions.

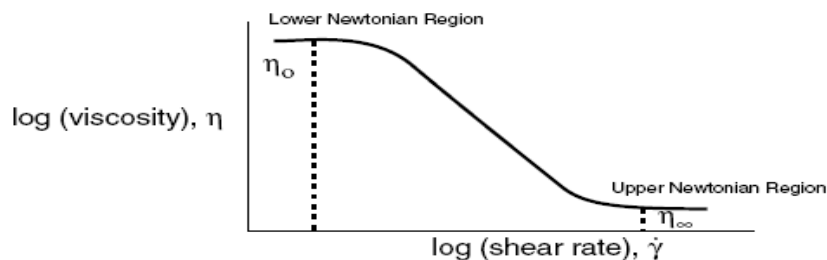


Figure 1.23: Idealized Power law model fluid.

1.6.3.13.3.2. Bingham Plastic model

Some materials exhibit an 'infinite' viscosity until a sufficiently high stress is applied to initiate flow. Above this stress the material then shows simple Newtonian flow. The Bingham model covers these materials. Fluids that exhibit Bingham Plastic behavior are characterized by limiting shear stress (yield stress point (τ_0)) and a plastic viscosity η_p that is independent of the shear rate, Figure (1.24).

$$\tau = \tau_0 + \eta_p \dot{\gamma} \dots \dots \dots (1.27)$$

This model is interesting but not very useful in describing the behavior of polymer based fluids. Many concentrated suspensions and colloidal systems show Bingham behaviour (Macosko, 1994).

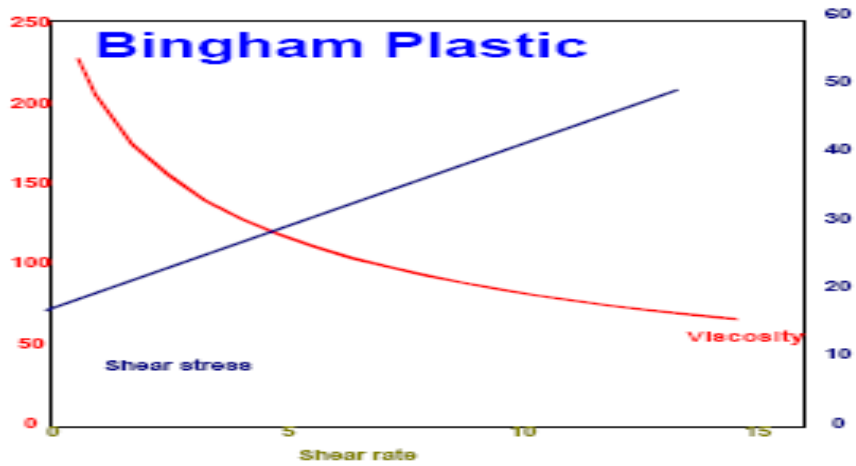


Figure 1.24: Idealized Bingham plastic model fluid.

1.6.3.13.3.3. Herschel-Bulkley model

This model incorporates the elements of the two previous models. Fluids that exhibit a yield point and viscosity that is stress or strain rate dependent cannot be adequately described by the Bingham Plastic model. The Herschel- Bulkley model, Figure (1.25), corrects this deficiency by replacing the plastic viscosity term in the Bingham model with a power law expression, Equation (1.28).

$$\tau = \tau_0 + K \dot{\gamma}^n \dots \dots \dots (1.28)$$

The model is reduced to the power law if there is no yield point and to the Bingham model if n is equal to one. The primary limitation of this and all other models that cannot be easily linearized is curve fitting to evaluate model parameters. Computers and good non-linear curve fitting techniques have overcome this limitation.

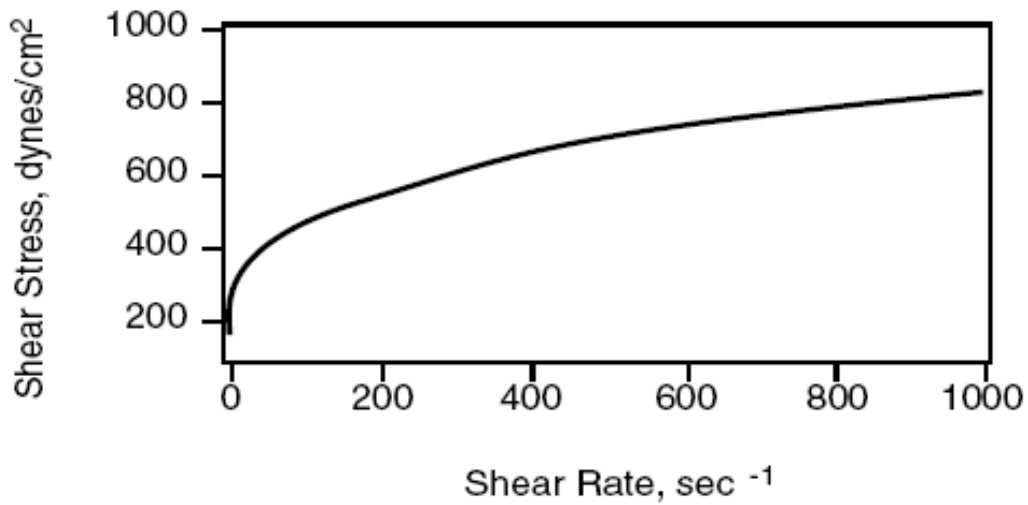


Figure 1.25: Idealized Herschel-Bulkley model fluid.

1.6.3.13.3.4. Sisko model

The Sisko model, Equation (1.26) is another three parameter model, which is useful in describing flow in the power law and upper Newtonian regions.

$$\eta = \eta_{\infty} + K \gamma^{n-1} \dots \dots \dots (1.29)$$

The Sisko model, Figure (1.28) is best suited to describe the flow behavior of fluids in the high shear rate regions (100 -10000 sec⁻¹). This model may be useful in evaluating fluid behavior at high flow rates to determine viscosity impact on pressure drops (Macosko, 1994).

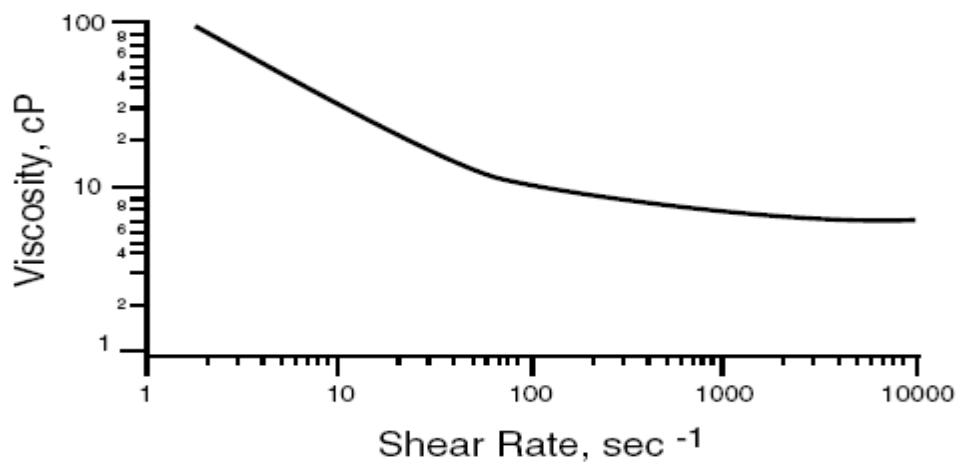


Figure 1.26: Idealized Sisko model fluid.

1.6.3.13.3.5. Ellis model

This model describes materials with power law behavior at high shear rates but Newtonian behavior at low shear rates, Figure (1.27)

$$\gamma = K_1\tau + K_2\tau^n \dots \dots \dots (1.30)$$

Where K_1 and K_2 are simple constants and n is material index.

This model is often used to describe polymeric systems as it generally gives a better representation than the power law model.

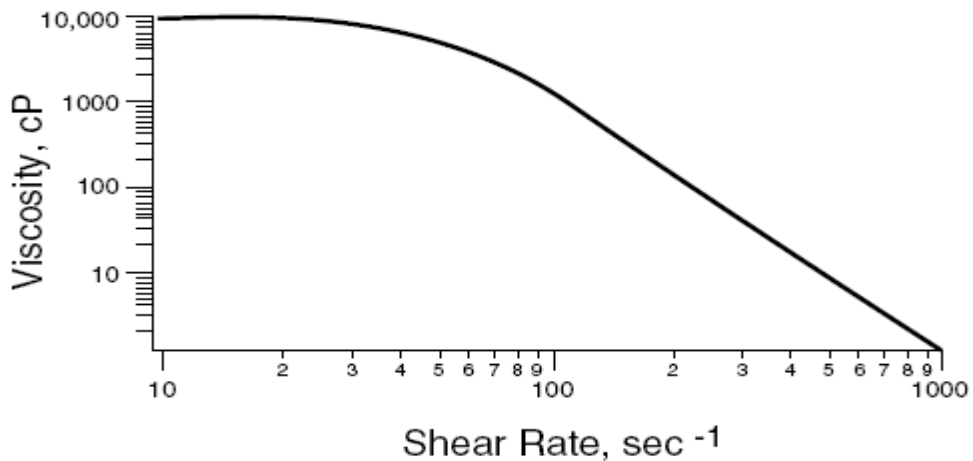


Figure 1.27: Idealized Ellis model fluid.

1.6.3.13.3.6. Carreau model

This model, Equation (1.28) is an example of a four parameter model that should describe the flow behavior over the entire range of shear rates.

$$\frac{\eta - \eta_\infty}{\eta_0 - \eta_\infty} = [1 + (\lambda\dot{\gamma})^2]^{(n-1)/2} \dots \dots \dots (1.31)$$

The parameter, λ , is a time constant, calculated from the point on the viscosity versus shear rate curve where the flow changes from the lower Newtonian region to the Power Law region. The other parameters have been previously defined. This model has received a lot of attention in rheological literature, however, it has not been extensively used in describing oil field fluids due to difficulties in obtaining data to define upper and lower Newtonian regions. Figure (1.30) is an idealized fluid with a lower and upper Newtonian region. (Macosko, 1994).

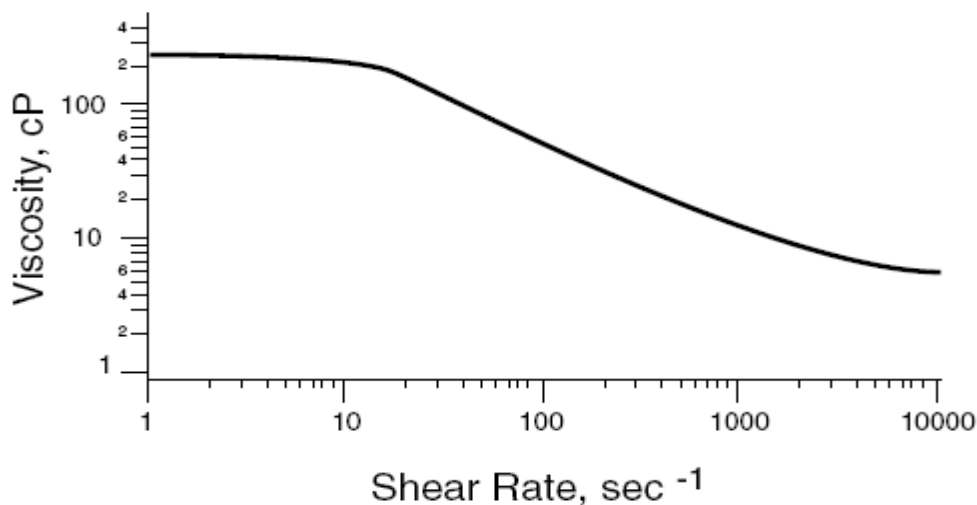


Figure 1.28: Idealized Carreau model fluid.

1.6.3.14. Linear viscoelastic measurement

Oscillatory deformation testing is used to investigate the viscoelasticity of a sample and probes its structure before it begins to flow. Most inks, paints and coatings are not completely solid or completely liquid but instead exhibit viscoelastic properties. Under certain conditions essential for application they flow, and in other circumstances they do not, helping product control.

In oscillation experiments the rheometer is used to determine whether the material has greater viscous tendencies (more likely to flow) or is predominantly elastic with more structural stability and also which behaviour will dominate under specific conditions. Viscoelasticity is a time-dependent property in which a material under stress produces both viscous and elastic responses (Goodwin *et al.*, 2008).

A viscoelastic materials exhibit viscous flow under constant stress, but a portion of mechanical energy is conserved and recovered after stress is released. Often associated with polymer solutions, melts and suspensions. Viscoelastic properties are usually measured as responses to an instantaneously applied or removed constant stress or strain or a dynamic stress or strain. Oscillatory testing involves the application of shear stress (or shear strain) as a sinusoidal wave. Measuring the induced strain (or stress) enables calculation of modulus, a measure of sample stiffness. Because the stress is applied in waveform, it is possible to observe whether the resultant strain is in phase with the applied force, or whether there is a lag, quantified by the parameter phase angle.

A purely elastic material (solid-like behavior) produces a phase angle of zero, indicating that the 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''), terms mathematically derived from the modulus of the material and the phase angle, the loss factor, $\tan\delta$ (G''/G').

G' value 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'' value is a measure of the deformation energy used by the sample during the shear and lost to the sample afterwards, representing the viscous behavior of a sample (Mezger, 2002).

If $G' > G''$ the sample exhibits solid-like behavior (elastic properties or recoverable 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 the material – the oscillation time scale or frequency and the amplitude of the applied stress (or strain).

1.6.3.15. Rheological properties of gums

Ameira, A. E. Satti (2011), reported that the flow curves at increasing shear rates showed that the apparent viscosity (η_0 , Pa.s) decreased as the shear rate increased. After a sharp reduction, the viscosity change was smoothed at high shear rates ($\sim 100 \text{ s}^{-1}$). 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 0.1 s^{-1} . At intermediate shear rates (above roughly 10 s^{-1}) a trend to a high-shear Newtonian plateau was observed, for *A. nilotica* var *nilotica*.

Mothé *et al.*, (1999), reported that gum arabic solutions show Newtonian flow behaviour in the shear rate range from 50 s^{-1} to 100 s^{-1} , even at gum arabic concentration as low as 4%. In the shear rate range from 1 s^{-1} to 50 s^{-1} , shear thinning behaviour has been 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). 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). Solution above 30% shows higher solution viscosity and exhibits pseudoplasticity (Williams *et al.*, 1990).

The rheological complexity of gum arabic is also evident from the increase of viscosity/elasticity with time, which has been attributed to the interfacial activity of gum arabic, gradually developing an elastic interfacial film between sample and measuring geometry (Sanchez *et al.*, 2002). The sample solutions investigated by Sanchez *et al.* were centrifuged at 24,500 rpm for 30 min to remove air bubbles and insoluble material. Air bubbles significantly influence the rheological properties of solutions (Tanaka *et al.*, 2006).

The effects of molecular association on rheological behavior of gum Arabic solution were investigated by transient shear stress (Li *et al.*, 2011). Thixotropic behavior was observed in gum Arabic solution for the first time. The effect of shear history was observed, which arose from the difference of the amount of molecular associations in gum Arabic solution. The molecular associations were resumable with given sufficient rest time. Stress jump experiments were able to distinguish the effects of molecular association on the hydrodynamic (viscous) and structural (elastic) contributions to the total stress. At low shear rates, the stress is dominated by the elastic contribution and the apparent stress is elastic-like, reflecting the existence of a larger number of molecular associations in the solution. When the shear rate was higher than 10 s^{-1} , only the viscous contribution is dominant with complete breakdown of molecular association. At this condition gum arabic solution shows a purely viscous and Newtonian behavior. The elastic and viscous contributions were also investigated by transient flow during the time evolution. The two contributions increased with rest time, but the elastic contribution increased faster than the viscous contribution, indicating a fast rate of buildup of molecular associations of gum arabic. Thus the presence of molecular associations in gum arabic solutions induced the deviation from a Newtonian behavior, so showing thixotropy for gum arabic solution at low shear rates. The elastic contribution to stress was strongly influenced by the existence of molecular association (Li *et al.*, 2011).

The interfacial rheology of diluted solutions of gum arabic at liquid air interface was first studied by Warburton (1966) and subsequently received further attention due to the relationship of this property to emulsification performance (Dickinson *et al.*, 1988, Fauconnier *et al.*, 2000). Warburton (1966) concluded that the gum arabic molecule is spheroidal or flat cylinder-like in shape, rather than a long chain. Sharrif and Warburton (1974), using an oscillatory surface rheometer, reported that interfacial elasticity of *A. senegal* increases with increasing concentration and ageing time. Dickinson *et al.*, (1989), using Couette-type surface rheometer, investigated the time dependent surface viscosity of gum arabic, at the oil–water interface, and

the effect of extensive dilutions of the aqueous phase. The surface viscosity was found to be initially insensitive to dilution but evidence for a small but significant reduction was only observed over the time scale of 100 h. Their results indicated that only a small fraction, with high nitrogen content, adsorbs at the oil–water interface in agreement with the studies by Randall *et al.*, (1988) and that this results in a strong thick film.

Moules *et al.*, (1990) using an oscillating ringsurface rheometer investigated the interfacial rheology of aqueous solutions of differing concentrations of *A. senegal* gum over a period of 5 min. They found that the interfacial elasticity increased as a function of both concentration and time and predicted that the growth of film would continue over many hours and may indeed never stop completely. Burgess *et al.*, (1997) observed a strong elastic film for gum arabic solutions using a Mark II surface rheometer and noted a reduction in the surface elasticity and an increase in the surface tension when it was mixed with bovine serum albumin (BSA). This was attributed to a possible interaction between glucuronic acid groups in gum arabic and BSA which resulted in the formation of an insoluble complex. Fauconnier *et al.* (2000) investigated the interfacial properties of films made from *A. senegal* and *A. seyal* and their fractions obtained by hydrophobic interaction chromatography. Using a Langmuir trough they showed that *A. senegal* exhibits better interfacial properties (more elastic) than *A. seyal*. Interfacial rheological studies on protein based systems have been shown to be a good indicator of adsorption and interaction. It has also been shown the addition of polysaccharides can modify the interfacial rheology and interfacial tension depending on how they interact with the protein. Addition of dextran to BSA was shown to reduce the interfacial rheology and increase the interfacial tension while dextran sulphate resulted in the formation of a soluble complex and as a consequence increased interfacial rheology and reduced interfacial tension.

Dickinson *et al.*, (1989) suggested a strong correlation between the amount of proteinaceous components within gum arabic and the surface rheology. Elmanan *et al.*, (2008) have concluded that both *A. senegal* and *A. seyal* have surface active properties. The higher interfacial elasticity and viscosity generated by *A. senegal* compared to *A. seyal* would appear to be associated with the difference in nature and distribution of protein between the two gums. The total amount of protein is less for *A. seyal* than for *A. senegal* and the effective high molecular weight protein, part of which is arabinogalactan protein (AGP) is not so accessible in *A. seyal*. This difference could account for their surface behaviour and for the greater effect shown by *A. senegal*. For emulsification at the oil–water interface, both gums can reduce to differing extents the oil–water interfacial tension, thereby facilitating the disruption of emulsion droplets surface-active molecule that adsorbs to the surface of the oil to form a protective membrane that prevents them

from aggregating. *A. seyal* due to its lesser ability to promote this process cannot support the emulsion stability over longer periods.

1.6.4. Emulsification properties

Emulsions are a class of disperse systems consisting of two immiscible liquids (Binks, (1998). The liquid droplets (the disperse phase) are dispersed in a liquid medium (the continuous phase), Figure (1.29). Several classes may be distinguished: oil-in-water (O/W), water-in-oil (W/O), and oil-in-oil (O/O). The latter class may be exemplified by an emulsion consisting of polar oil (e.g., propylene glycol) dispersed in nonpolar oil (paraffinic oil) and vice versa. To disperse two immiscible liquids, one needs a third component, namely, the emulsifier. The choice of the emulsifier is crucial in the formation of the emulsion and its long-term stability (Tadros, T. (2005). Emulsions may be classified according to the nature of the emulsifier or the structure of the system. This is illustrated in (Table 1.7)

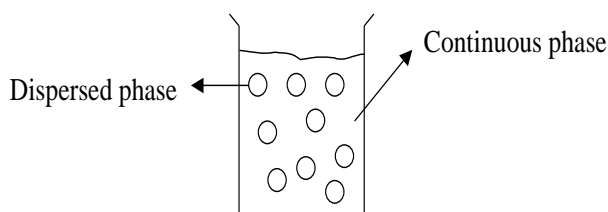


Figure .1.29. Emulsion system

Table.1.7. Classification of emulsion types.

Nature of emulsifier	Structure of the system
Simple molecules and ions	Nature of internal and external phase: O/W, W/O
Surfactant mixtures	Micellar emulsions (microemulsions)
Ionic surfactants	Macroemulsions
Nonionic polymers	Bilayer droplets
Polyelectrolytes	Double and multiple emulsions
Mixed polymers and surfactants	Mixed emulsions

1.6.4.1. Nature of the Emulsifier

The simplest type is ions such as OH^- that can be specifically adsorbed on the emulsion droplet thus producing a charge. An electrical double layer can be produced, which induced electrostatic repulsion. This has been demonstrated with very dilute O/W

emulsions by removing any acidity. Clearly that process is not practical. The most effective emulsifiers are nonionic surfactants that can be used to emulsify O/W or W/O. In addition, they can stabilize the emulsion against flocculation and coalescence. Ionic surfactants such as sodium dodecyl sulfate (SDS) can also be used as emulsifiers (for O/W), but the system is sensitive to the presence of electrolytes. Surfactant mixtures, for example, ionic and nonionic, or mixtures of nonionic surfactants can be more effective in emulsification and stabilization of the emulsion. Nonionic polymers, sometimes referred to as polymeric surfactants, for example, Pluronics, are more effective in stabilization of emulsion, but they may suffer the difficulty of emulsification (to produce small droplets) unless high energy is applied. Polyelectrolytes such as poly (methacrylic acid) can also be applied as emulsifiers. Mixtures of polymers and surfactants are ideal in achieving ease of emulsification and stabilization of the emulsion. Lamellar liquid crystalline phases that can be produced using surfactant mixtures are very effective in emulsion stabilization. Solid particles that can accumulate at the O/W interface can also be used for emulsion stabilization. These are referred to as Pickering emulsions, whereby particles are partially wetted by oil and aqueous phase.

1.6.4.2. Emulsifiers Mechanism

Mechanism of of emulsifiers depends the formation of a film at the interface of two phases. There are three types of films formed by emulsifying agents (Paul, 2005).

1.6.4.2.1. Monomolecular films

Emulsifying agents with stabilizing action form monolayer at the oil-water interface. This monolayer prevents coalescence (Paul, 2005).

1.6.4.2.2. Multimolecular films

Multimolecular films around the droplets of dispersed phase are formed by hydrophilic colloids. They act as coats around the droplets making them highly resistant to coalescence. They have the ability of swelling to increase the viscosity of the system (so that droplets are less likely to merge (Pual, 2005).

1.6.4.2.3. Solid particle films

Small solid particles like bentonite ($\text{Al}_2\text{O}_3 \cdot 4\text{SiO}_2 \cdot \text{H}_2\text{O}$), veegum (magnesium, aluminum and silicate), hectorite, magnesium hydroxide, aluminum hydroxide and magnesium trisilicate, that are wetted to some degree by both oil, and water act as emulsifying agents. This results from their being concentrated at the interface, where they produce a particulate film around the dispersed droplets to avoid coalescence (Paul, 2005)

1.6.4.3. Structure of the System

1.6.4.3.1. O/W and W/O macroemulsions:

These usually have a size range of 0.1–5 μm with an average of 1 – 2 μm .

1.6.4.3.2. Nanoemulsions:

these usually have a size range of 20 – 100 nm. Similar to macroemulsions, they are only kinetically stable.

1.6.4.3.3. Micellar emulsions or microemulsions:

These usually have the size range of 5 – 50 nm. They are thermodynamically stable.

1.6.4.3.4. Double and multiple emulsions:

These are emulsions-of-emulsions, W/O/W, and O/W/O systems.

1.6.4.3.5. Mixed emulsions:

These are systems consisting of two different disperse droplets that do not mix in a continuous medium..

Several breakdown processes may occur on storage depending on particle size distribution and density difference between the droplets and the medium. Magnitude of the attractive versus repulsive forces determines flocculation. Solubility of the disperse droplets and the particle size distribution determine Ostwald ripening. Stability of the liquid film between the droplets determines coalescence. The other process is phase inversion.

1.6.4.4. Theories of Emulsification

Theories of emulsification explain the action of emulsifying agents in stabilizing emulsions. It is the surface or more accurately the interface between the two immiscible liquids that plays the foremost role. Emulsifying agents affect the interface in such a way that they enhanced the fraction of stable emulsions (John, 1976). There are several theories proposed to explain the action of emulsifying agents in stabilizing emulsions. Among these theories, some may be applied to specific emulsifying agents under certain conditions like pH of the system and proportion of the two phases. The most well-known theories include surface tension theory, the oriented wedge theory and the interfacial film theory (Paul, 2005).

1.6.4.4.1. Surface tension Theory

Molecules in a liquid are attracted equally by the surrounding molecules; however, at the surface, there is an inward attraction of molecules due to the imbalance of attractive forces. Due to this attraction, a stress or tension is produced known as surface tension (John, 1976). When two immiscible liquids come in contact, the force causing each liquid to resist breakage is known as

interfacial tension. In accordance to surface tension theory of emulsification, the emulsifying agents cause a reduction in the interfacial tension of the two immiscible liquids, reducing the repelling force between the liquids and withdrawing the attraction of liquids for their own molecules. In this way, the surfactants convert large globules into small ones and avoid small globules from coalescing into large ones (Paul, 2005).

1.6.4.4.2. The oriented Wedge theory of emulsions

According to this theory the oil-like or non-polar ends of the emulsifying agents turn towards the oil and the polar ends towards the polar liquid. The oriented Wedge theory of emulsions indicates that if the non-polar end of the emulsifying agent is smaller, the emulsion will be oil-in-water (o/w) and if the polar end is smaller, the emulsion will be water-in-oil (W/O) (Harkins and Norvil, 1925).

1.6.4.4.3. The interfacial film theory

The interfacial film theory suggests that the emulsifying agents make an interface between the two immiscible phases of the emulsion, surrounding the droplets of the internal phase as a thin film. This film prevents the coalescence of the dispersed phase (Paul, 2005)

1.6.4.5. Emulsions Breakdown

The various breakdown processes are illustrated in (Figure.1.19). The physical phenomena involved in each breakdown process are not simple, and it requires analysis of the various surface forces involved. In addition, the above-mentioned processes may take place simultaneously rather than consecutively and this complicates the analysis. Model emulsions, with monodisperse droplets, cannot be easily produced, and hence, any theoretical treatment must take into account the effect of droplet size distribution. Theories that take into account the polydispersity of the system are complex, and in many cases, only numerical solutions are possible. In addition, measurements of surfactant and polymer adsorption in an emulsion are not easy and one has to extract such information from measurement at a planer interface. In the following sections, a summary of each of the above-mentioned breakdown processes and details of each process and methods of its prevention are given.

1.6.4.5.1. Creaming and Sedimentation

This process results from external forces usually gravitational or centrifugal. When such forces exceed the thermal motion of the droplets (Brownian motion) Figure 1.18, a concentration gradient builds up in the system with the larger droplets moving faster to the top (if their density is lower than that of the medium) or to the bottom (if their density is larger than that of the medium) of the container. In the limiting cases, the droplets may

form a close-packed (random or ordered) array at the top or bottom of the system with the remainder of the volume occupied by the continuous liquid phase.

1.6.4.5.2. Flocculation

This process refers to aggregation of the droplets (without any change in primary droplet size) into larger units Figure 1.18. It is the result of the van der Waals attraction that is universal with all disperse systems. Flocculation occurs when there is not sufficient repulsion to keep the droplets apart to distances where the van der Waals attraction is weak. Flocculation may be “strong” or “weak,” depending on the magnitude of attract energy.

1.6.4.5.3. Ostwald Ripening (Disproportionation)

This results from the finite solubility of the liquid phases. Figure 1.30 Liquids that are referred to as being immiscible often have mutual solubilities that are not negligible. With emulsions, which are usually polydispersity, the smaller droplets will have larger solubility when compared with the larger ones (due to curvature effects). With time, the smaller droplets disappear and their molecules diffuse to the bulk and become deposited on the larger droplets. With time, the droplet size distribution shifts to larger values

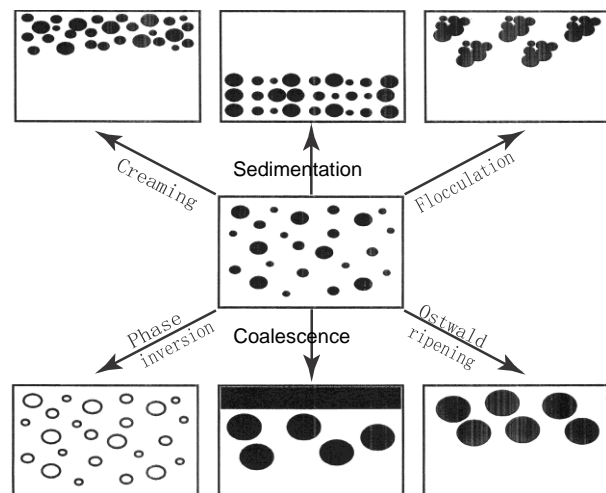


Figure.1.30. Schematic representation of the various breakdown processes in emulsions

1.6.4.5.4. Coalescence

This refers to the process of thinning and disruption of the liquid film between the droplets with the result of fusion of two or more droplets into larger ones Figure 1.18. The limiting case for coalescence is the complete separation of the emulsion into two distinct liquid phases. The driving force for coalescence is the surface or film fluctuations which results in close approach of the droplets whereby the van der Waals forces is strong thus preventing their separation.

1.6.4.5.5. Phase Inversion

This refers to the process whereby there will be an exchange between the disperse phase and the medium. For example, an O/W emulsion may with time or change of conditions invert to a W/O emulsion Figure 1.18. In many cases, phase inversion passes through a transition state whereby multiple emulsions are produced.

1.6.4.6. Emulsification process

Milk is a natural emulsion, which consists of fatty globules surrounded by a layer of casein, suspended in water. The theory of emulsification is based on the study of milk. (Christopher and Dawn, 2008).

1.6.4.6.1. General method

In this method, O/W emulsion is prepared by dividing the oily phase completely into minute globules surrounding each globule with an envelope of emulsifying agent and finally suspends the globules in the aqueous phase. Conversely, the W/O emulsion is prepared by dividing aqueous phase completely into minute globules surrounding each globule with an envelope of emulsifying agent and finally suspending the globules in the oily phase (Christopher and Dawn, 2008).

1.6.4.6.2. Phase inversion method

In this method, the aqueous phase is first added to the oil phase so as to form a W/O emulsion. At the inversion point, the addition of more water results in the inversion of emulsion which gives rise to an O/W emulsion (Herbert et al., 1988).

1.6.4.6.3. Continental and dry gum method

Emulsions are usually made by continental or dry gum method. The emulsion is prepared by mixing the emulsifying agent (usually *Acacia*) with the oil which is then mixed with the aqueous phase. Continental and dry gum methods differ in the proportion of constituents (Christopher and Dawn, 2008).

1.6.4.6.4. Wet gum method

The proportion of the constituents is same as those used in the dry gum method; the only difference is the method of preparation. Here, the mucilage of the emulsifying agent (usually *Acacia*) is formed. The oil is then added to the mucilage drop by drop with continuous trituration (Christopher and Dawn, 2008).

1.6.4.6.5. Membrane emulsification method

It was based on a novel concept of generating droplets “drop by drop” to produce emulsion. Here direct pressure is applied to the dispersed phase which seeps through a porous membrane into the continuous phase and in this way the droplets formed are then detached from the membrane surface due to the relative shear motion between the continuous phase and membrane surface (Nita et al., 2009).

1.6.4.7. Droplet Characteristics

The physicochemical properties of emulsions are strongly influenced by the characteristics of the droplets they contain, such as their concentration, size, charge, interfacial properties and interactions (Hasenhuettl, 2008, McClements, 2005).

1.6.4.7.1. Droplet Concentration

The concentration of droplets in an emulsion influences its texture, stability, appearance, and nutritional quality (McClements, 2005). Droplet concentration is usually characterized in terms of the dispersed phase volume fraction (ϕ), which is equal to the volume of emulsion droplets (V_D) divided by the total volume of emulsion (V_E): $\phi = V_D/V_E$. Practically, it is often more convenient to express the droplet concentration of an emulsion in terms of the dispersed phase mass fraction (ϕ_m), which is equal to the mass of emulsion droplets (m_D) divided by the total mass of emulsion (m_E): $\phi_m = m_D/m_E$.

The relationship between ϕ_m and ϕ is given by the following Equations:

$$\phi_m = \phi(\phi + (1 - \phi)\rho_1/\rho_2)^{-1} \dots\dots\dots (1.10)$$

$$\phi = \phi_m(\phi_m + (1 - \phi_m)\rho_2/\rho_1)^{-1} \dots\dots\dots (1.11)$$

where, ρ_1 and ρ_2 are the densities of the continuous and dispersed phases, respectively. When the densities of the two phases are equal, the mass fraction is equivalent to the volume fraction. The droplet concentration may also be represented as either a dispersed phase volume percentage ($\phi\% = 100 \times \phi$) or disperse phase mass percentage ($\phi_m\% = 100 \times \phi_m$).

1.6.4.7.2. Droplet Size

The size of the droplets in an emulsion has a strong impact on its stability, optical properties, and its rheology (Dagleish, 2001). It is therefore particularly important to be able to reliably measure and accurately specify the size of the droplets present within an emulsion.

When all droplets in an emulsion have the same size, the emulsion is referred to as monodisperse, and a single number, either the droplet radius or droplet diameter, can be used to characterize the droplet size. In practice, food emulsions contain a range of different droplet sizes, and are therefore referred to as being polydisperse.

A polydisperse emulsion is characterized by its particle size distribution, which defines the concentration of droplets in different size classes. The huge number of droplets in most food emulsions means that the particle size distribution can be considered to be continuous.

When constructing or interpreting a particle size distribution (PSD), the particle concentration is usually presented as either the volume percent (Volume %) or number percent (Number %) of droplets, whereas the particle size is usually presented as either the mid-point particle radius or the mid-point particle diameter.

It is important to realize that a number of different mean particles sizes can be derived from a full particle size distribution and each mean size can have a different magnitude and physical meaning. In general, the mean (x_{ab}) and relative standard deviation (c_b) of a distribution can be defined by the following equations (Walstra, 2003):

$$x_{ab} = \left(\frac{\sum_{i=1}^N n_i x_i^a}{\sum_{i=1}^N n_i x_i^b} \right)^{1/(a-b)} \dots\dots\dots(1.12)$$

$$c_b = \left(\frac{(\sum_{i=1}^N n_i x_i^b)(\sum_{i=1}^N n_i x_i^{b+2})}{(\sum_{i=1}^N n_i x_i^{b+1})^2} - 1 \right)^{1/2} \dots\dots\dots(1.13)$$

where, a and b are integers (usually between 0 and 4), n_i is the number of droplets with size x_i , and N is the total number of size categories present.

The three most commonly used mean particle size values are:

The number weighted mean diameter ($d_{10} = \sum n_i d_i / \sum n_i$)..... (1.14)

The surface weighted mean diameter ($d_{32} = \sum n_i d_i^3 / \sum n_i d_i^2$).(1.15)

The volume weighted mean diameter($d_{43} = \sum n_i d_i^4 / \sum n_i d_i^3$).(1.16)

Generally, the volume weighted mean diameter is more sensitive to the presence of large particles than the number weighted mean diameter. Appreciable differences between the values

of d_{10} , d_{32} and d_{43} generally indicate that the particle size distribution is broad or multimodal. One must therefore be very careful when interpreting or reporting particle size data to identify which mean particle size value is being used.

1.6.4.7.3. Droplet Charge

The droplets in most emulsions have an electrical charge because of adsorption of molecules to their surface that are ionized or ionizable, such as proteins, polysaccharides, ionic surfactants, phospholipids and some small ions. The electrical characteristics of a droplet surface depend on the type and concentration of ionized charge species present at the surface, as well as the ionic composition and physical properties of the surrounding liquid. The charge on an emulsion droplet is important because it determines the nature of its interactions with other charged species or its behavior in the presence of an electrical field. The droplets in many emulsions are prevented from aggregating using ionic emulsifiers that adsorb to their surface and prevent them from coming close together because of electrostatic repulsion (Dickinson, 1992, Dalgleish, 2001, McClements, 2005).

The electrical characteristics of a droplet are usually characterized in terms of their surface electrical potential (ψ), surface charge density (σ) and zeta potential (ζ). The surface charge density is the amount of electrical charge per unit surface area. The surface electrical potential is the amount of energy required to increase the surface charge density from zero to σ , by bringing charges from an infinite distance to the surface through the surrounding medium. The zeta potential (ζ) is the electrical potential at the shear plane, which is defined as the distance away from the droplet surface below which the counterions remain strongly attached to the droplet when it moves in an electrical field. Practically, the droplet charges are characterized in terms of ζ (Hunter, 1986).

1.6.4.7.4. Interfacial Properties

The droplet interface consists of a narrow region (~1 to 50 nm thick) that surrounds each emulsion droplet, and contains a mixture of oil, water, and emulsifier molecules. The interfacial region only makes a significant fraction of the total volume of an emulsion when the droplet size is less than 1 μm . The properties of the interfacial region are determined by the type, concentration, complexation, competitive adsorption and layer by layer formation. The electrical charge on the droplet interface influences its interaction with other charged molecules, as well as its stability to aggregation. The thickness and rheology of the interfacial region influences the stability of emulsions to gravitational separation, coalescence and flocculation, and determines the rate at which molecules leave or enter the droplets (Dickinson, 2003, McClements, 2005).

1.6.4.7.5. Colloidal Interactions

Colloidal interactions govern whether emulsion droplets aggregate or remain as separate entities, and determine the characteristics of any aggregates formed, such as their size, shape, porosity and deformability (Friberg *et al.*, 2004, McClements, 2005). The interactions between two emulsion droplets can be described in terms of an interaction potential. The interaction potential is the energy required to bring two emulsion droplets from an infinite distance apart to a surface to surface separation. Generally, droplets tend to aggregate when attractive interactions dominate, but remain as individual entities when repulsive interactions dominate (McClements, 2005).

1.6.4.8. Testing emulsifier effectiveness

The type of emulsifier used to stabilize an emulsion is one of the most important factors determining its overall performance and long term stability. The suitability of an emulsifier for a particular food application is determined by a number of factors, including the minimum amount required to stabilize an emulsion, its ability to produce small droplets during homogenization, and its ability to prevent droplets from aggregating (McClements, 2005). These factors depend on the nature of the emulsifier itself, but they also depend on the characteristics of the food in which it is present, such as pH, ionic strength, ion type, oil type, ingredient interactions, and thermo mechanical history.

The two relatively simple empirical procedures used to test different aspects of emulsifier efficiency are: emulsifying capacity (EC) and emulsion stability index (ESI).

1.6.4.8.1. Emulsifying Capacity

It is often important for a food manufacturer to establish the minimum amount of a given emulsifier that can be used to create a stable emulsion. The emulsifying capacity (EC) of a water soluble emulsifier is defined as the maximum amount of oil that can be dispersed in an aqueous solution containing a specific amount of the emulsifier without the emulsion breaking down or inverting into a water in oil emulsion (Dickinson, 1992). Experimentally, the EC is usually determined by placing an aqueous emulsifier solution into a vessel and continuously agitating using a high speed mixer as small volumes of oil are titrated into the vessel. The end point of the titration occurs when the emulsion breaks down or inverts, which can be determined by optical, rheological or electrical conductivity measurements. The greater the volume of oil that can be incorporated into the emulsion before it breaks down, the higher the emulsifying capacity of the emulsifier. A stable emulsion is prepared by homogenizing known amounts of oil, water and emulsifier. The total droplet surface area covered by the adsorbed emulsifier is given by:

$$S = 6\phi V_e/d_{32} \dots\dots\dots (1.17)$$

where ϕ is the disperse phase volume fraction, V_e is the emulsion volume and d_{32} is the volume surface mean droplet diameter.

1.6.4.8.2. Emulsion Stability Index

Another measure of an emulsifier’s effectiveness for a particular application is its ability to produce emulsions that remain stable to droplet aggregation. This is usually achieved by measuring the change in particle size of an emulsion after storage for a specified length of time or after exposure to some environmental stress such as heating, freezing and stirring. The smaller the increase in particle size, the better is the emulsifier at stabilizing the system. One parameter that used to compare the effectiveness of different emulsifiers at stabilizing emulsion droplets against aggregation is called the emulsion stability index (Dickenson, 1992). Originally, the emulsion stability index (*ESI*) was determined from measurements of the turbidity of a dilute emulsion carried out using an UV visible spectrophotometer at a particular wavelength:

$$ESI = \frac{\tau_0 t}{\tau_t - \tau_0} \dots\dots\dots (1.18)$$

where τ_0 is the initial turbidity of the emulsion and τ_t is the turbidity measured at time t . Indeed, the emulsion turbidity may either increase or decrease with increasing particle size, depending on the initial particle size. Consequently there are much more accurate and reliable methods available for determining emulsion stability such as particle size analyzers. A more suitable expression for the ESI, based on particle size measurements, is given below:

$$ESI = \frac{d_0 t}{d_t - d_0} \dots\dots\dots (1.19)$$

where d_0 is the initial mean droplet diameter of the emulsion and d_t is the mean droplet diameter measured at time t . The major advantage of this method is that the mean droplet diameter can be determined using analytical instruments specifically designed for particle size analysis such as light scattering, electrical pulse counting or ultrasonic spectroscopy rather than on turbidity measurements. In this definition, ESI would be equivalent to the reciprocal of the slope of a plot of mean droplet diameter versus time normalized with respect to the initial mean droplet diameter assuming that the droplet diameter changed linearly with time. Numerically, the ESI is equal to the time required for the mean particle diameter to double in size. There are a number of potential practical problems associated with any method used to define an emulsion stability index for comparing the effectiveness of different emulsifiers:

The mean particle size does not usually increase linearly with time, so that the value of ESI may depend on the time that the measurements were carried out. It is therefore important to use a standardized incubation time when comparing emulsifier effectiveness, e.g., 24 hours or 1 week. The particle size distribution may change from mono-modal (single peaked) to multi-modal (multi peaked) with time. In addition, ESI will depend strongly on the type of mean particle size used to represent the full particle size distribution in a multi modal system, such as d_{10} , d_{32} or d_{43} .

The particle growth rate depends on initial droplet size, droplet concentration and continuous phase rheology. These parameters may vary from system to system and therefore it is usually important to utilize standardized conditions when comparing the effectiveness of different emulsifiers at stabilizing emulsions against droplet aggregation.

Emulsifier effectiveness at stabilizing droplets against aggregation is demonstrated by reporting the measured mean particle diameters or full particle size distributions, rather than as a calculated emulsion stability index. Nevertheless, ESI is useful when one is comparing a series of emulsifiers under standardized conditions, or when one is examining the influence of specific changes in solution or environmental conditions on the functionality of a particular emulsifier (McClements, 2007).

1.6.4.9. Particle Size Analyzers

A variety of analytical instruments are commercially available that can be used to measure the particle size distribution of emulsions. Many of these instruments are fully automated, and provide rapid and precise measurements of the full particle size distribution of an emulsion. Particle sizing instruments considerably differ according to the physical principles upon which they operate, such as light scattering, particles velocity in a field, scattering or absorption of ultrasonic waves, counting of particles, measurement of restricted molecular diffusion. Consequently, each particle sizing technology is suitable for analyzing emulsions with different droplet sizes and concentrations. Analytical techniques that can be used to measure the particle size distribution of emulsions are, Static Light Scattering, Dynamic Light Scattering, Electrical Pulse Counting, Sedimentation Measurements, Ultrasonic Spectrometry, and NMR Techniques

1.6.4.9.1. Static Light Scattering

Particle sizing instruments that utilize static light scattering, also called laser diffraction are based on the principle that the scattering pattern (intensity of scattered light versus scattering angle) produced when a laser beam is directed through a dilute emulsion depends on particle size distribution. Instruments come with software that contains a mathematical model, usually the “Mie theory”, that can predict the scattering pattern of an emulsion from the characteristics

of the particles that it contains such as refractive index ratio, absorption coefficient, and diameter. The software finds particle size distribution that gives the best fit between the measured scattering pattern and the theoretically predicted one, and then reports the data as a table or plot of particle concentration such as number or volume versus particle size such as diameter or radius. Commercial static light scattering instruments are capable of determining particle diameters within the range of about 100 nm to 1000 μm . These instruments normally require that the droplet concentration be relatively low, $< 0.1 \text{ wt}\%$ so as to be able to pass a light beam through and to avoid multiple scattering effects. Consequently, many food emulsions need to be diluted considerably prior to analysis (McClements, 2007).

Emulsions with various compositions and properties are commonly used in industry, agriculture, and medicine, they also have household uses. Many foods, such as milk and egg yolks, are multi component emulsions, as are unrefined petroleum and the milky juices of plants. Among the products that take the form of emulsions are cooling lubricants and various pesticides, cosmetics, drugs, and binders for latex paints. Asphalt emulsions are used in construction.

1.6.4.10. Emulsion parameters

- The Volume Median Diameter (VMD) = $D_{0.5}$.
- Polydispersity (span)% = $(D(v, 90) - D(v, 10)) / D(v, 50)$(1.20)

Where $D(v, 90)$, $D(v, 10)$ and $D(v, 50)$ are the equivalent volume diameters at 90, 10 and 50 % cumulative volume, respectively.

1.6.4.10.1. Definition of parameters

- $D_{0.5}$: This is the value of the particles size which divides the population into exactly into two equal halves, i.e. there is 50% of the distribution above this value and 50% below.
- $D_{0.9}$: This is the value of the particles size which describes the population at and below 90% of the distribution. Figure (1.31) shows the schematic illustration of emulsion parameters

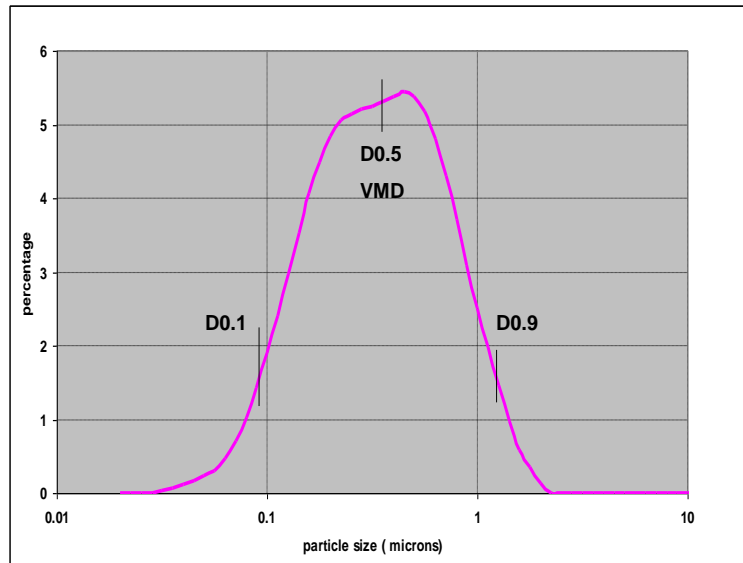


Figure 1.31 : Schematic illustration of emulsion parameters

1.7. Objectives of work

The objectives of this project are:

- To investigate the physicochemical properties of *A. nilotica* var. *tomentosa* gum and its fractions.
- To compare and contrast the physicochemical properties of *A. nilotica* var. *tomentosa* gum with *A. nilotica* var. *nilotica* gum
- To investigate the relationship between tannins and colour Gardner
- To determine the calorific value of *A. nilotica* var. *tomentosa* gum.
- To determine the dynamic rheological properties of crude gum .
- To study the emulsification properties of *A. nilotica* var. *tomentosa* gum fractions and their blending with Gum Arabic.

2. Materials and methods

2.1. Materials

2.1.1. Samples

Ten samples of *A. nilotica* var. *tomentosa* gum obtained from each, Sinnar (S) and Blue Nile (BN) states, Sudan. They represent an important range of the natural distribution of this Subspecies in the country. Soba Forestry Research Centre Herbarium, Sinnar and Blue Nile state forestry corps confirmed the species identity.. The samples were classified into groups:

2.1.1.1. Purification of crude gum

The gum samples which used in this study were dried under shade and cleaned to remove any impurities such as bark, leave fragments and the cleanest nodules were selected and made into fine powder using mortar and pestle then kept in sealed polyethylene bags. The composite samples were prepared by mixing equal amount from each sample, taken from each location (on dry weight basis).

2.1.1.2. The composite samples of Sinnar state

- The first composite sample is prepared by mixing the equal weight of that samples collected from Wad-alguzoli forest near Singa city.
- The Second composite sample is prepared by mixing the equal weight of that samples collected from Al-majaj forest near Singa city One
- The Third composite sample is prepared by mixing the equal weight of that samples collected from Sairo forest near wad Elnyal city.
- The Fourth composite sample is prepared by mixing the equal weight of that samples collected from Singa city.
- The Fifth composite sample is prepared by mixing the equal weight of all samples collected from Sinnar state.

2.1.1.3. The composite samples of Blue Nile state

- The first composite sample is prepared by mixing the equal weight of that samples collected from North of Addamazin.
- The Second composite sample is prepared by mixing the equal weight of that samples collected from Middle of Addamazin.
- The Third composite sample is prepared by mixing the equal weight of that samples collected from South of Addamazin.
- The Fourth composite sample is prepared by mixing the equal weight of all samples collected from Blue Nile state.

- The total number of samples is twenty nine.
- Composite samples were prepared by mixing equal weights from each sample, considering the moisture content. Details of the gum samples are given in Table (2.1) for season 2015.

Table.2.1. Sample code, location, date of collection, soil type and rain fall of *A.nilotica* var, *tomentosa* gum, season 2015

Code	Location		Date of collection	Type of soil	Rain fall
	State	Specific area			
S1	Sinner	Wad-alguzoli forest	Jan-15	Clay	< 400mm
S2	Sinner	Wad-alguzoli forest	Jan-15	Clay	< 400mm
S3	Sinner	Wad-alguzoli forest	Jan-15	Clay	< 400mm
S4	Sinner	Al-majaj forest	Jan-15	Clay	< 400mm
S5	Sinner	Al-majaj forest	Jan-15	Clay	< 400mm
S6	Sinner	Al-majaj forest	Jan-15	Clay	< 400mm
S7	Sinner	Sairo forest	Jan-15	Clay	< 400mm
S8	Sinner	Sairo forest	Jan-15	Clay	< 400mm
S9	Sinner	Singa city	Jan-15	Clay	< 400mm
S10	Sinner	Singa city	Jan-15	Clay	< 400mm
CoS1	Is prepared by mixing equal amounts of (S1 to S3)				
CoS2	Is prepared by mixing equal amounts of (S4 to S6)				
CoS3	Is prepared by mixing equal amounts of (S7 to S8)				
CoS4	Is prepared by mixing equal amounts of (S9 to S10)				
CoS5	Is prepared by mixing equal amounts of (S1 to S10)				
BN1	Blue Nile	North of Addamazin	Feb -15	Clay	< 400mm
BN2	Blue Nile	North of Addamazin	Feb -15	Clay	< 400mm
BN3	Blue Nile	North of Addamazin	Feb -15	Clay	< 400mm
BN4	Blue Nile	Middle of Addamazin	Feb -15	Clay	< 400mm
BN5	Blue Nile	Middle of Addamazin	Feb -15	Clay	< 400mm
BN6	Blue Nile	Middle of Addamazin	Feb -15	Clay	< 400mm
BN7	Blue Nile	Middle of Addamazin	Feb -15	Clay	< 400mm
BN8	Blue Nile	South of Addamazin	Feb -15	Clay	< 400mm
BN9	Blue Nile	South of Addamazin	Feb -15	Clay	< 400mm
BN10	Blue Nile	South of Addamazin	Feb -15	Clay	< 400mm
CoBN1	is prepared by mixing equal amounts of (BN-1 to BN-3)				
CoBN2	is prepared by mixing equal amounts of (BN-4 to BN-7)				
CoBN3	is prepared by mixing equal amounts of (BN-8 to BN-10)				
CoBN4	is prepared by mixing equal amounts of (BN-1 to BN-10)				

2.2. Methods

2.2.1. Determination of Moisture Content

Moisture content of the gum samples was determined according to AOAC, (1980) method. 1g of gum sample was accurately weighted in a clean, dry pre weighted shallow weighing dish. The weighted dish and its contents were dried in an oven at 105°C for five hours, then cooled in a desiccator and reweighed. The loss on drying was calculated as follows(Osman et al., 1993)

$$\text{Moisture content (\%)} = \frac{W_1 - W_2}{W_1} \times 100 \dots\dots\dots(2.1)$$

W_1 = Original weight of sample (g).

W_2 = Weight of sample after drying (g).

2.2.2. Determination of ash content

Accurately 1g of the dried sample was weighted on dry porcelain crucible and ignited at 550°C in a muffle furnace (Carbolite, BAMFORD, SHEFFIELD, ENGLAND,S30 2AU) until free from carbon, cooled in a desiccator and weighed. Then the total ash % was calculated as follows: (FAO, 1991).

$$\text{Ash (\%)} = \frac{W_3 - W_1}{W_2 - W_1} \times 100 \dots\dots\dots (2.2)$$

Where

W_1 = Weight of the empty crucible (g).

W_2 = Weight of the crucible + the sample (g).

W_3 = Weight of the crucible + ash (g).

2.2.3. PH measurement

PH meter was calibrated by using three different buffer solutions one adjusted at pH 4, 7 and other at pH 11(3505 jenway). Then after calibration it was used to determine the pH of crude gum samples, of 1g/100 ml aqueous solution (w/v) calculated on dry weight basis.

2.2.4. Determination of specific optical rotation

The optical rotation was determined for 1% solution on dry weight basis, the sample was dissolved in distilled water, mixing on a roller mixer until the sample fully dissolved (approximately 4 hours), after filtration of the gum solution through whatman cellulose nitrate membrane filter paper (0.8µm), optical rotation was measured at room temperature (25°C) using polarimeter (POLAX-2L,Atago Co ,Japan) with a D-line of Na (589.3nm) fitted with a cell of

path length of 20.0 cm. The specific optical rotation was calculated according to the relationship (Osman et al., 1993)

$$\text{Specific Optical Rotation } [\alpha]_D^T = \frac{\alpha \times 100}{L \times C} \dots\dots\dots(2.3)$$

Where:

α = Observed angle of rotation.

L = the length of sample holder in decimeters (dm).

C = concentration in gm/100ml

T = Temperature.

2.2.5. Nitrogen and protein Content

0.2g of each sample (in Triplicate) was weighed and transferred to Kjeldahl digestion flasks and Kjeldahl tablet (copper sulphate - potassium sulphate catalyst) was added to each. 10 cm³ concentrated, nitrogen free, sulphuric acid was added. The tube was then mounted in the digestion heating system which was previously set to 240°C and capped with an aerated manifold. The solution was then heated at the above temperature until a clear pale yellowish-green color was observed which indicates the completion of the digestion. The tubes were then allowed to attain room temperature. Their contents were quantitatively transferred to Kjeldahl distillation apparatus followed by addition of distilled water and 30% (w/v) sodium hydroxide. Steam distillation was then started and the released ammonia was absorbed in 25 cm³ of 2% boric acid. Back titration of the generated borate was then carried out versus, 0.02M, hydrochloric acid using methyl red as an indicator. Blank titration was carried in the same way.

$$\%N = \frac{14.01 \times M \times (\text{volume of titrant} - \text{volume of blank}) \times 100}{\text{weight of sample (grams)}} \dots\dots\dots(2.4)$$

Where:

M is the molarity of hydrochloric acid.

Protein content was calculated using nitrogen conversion factor resulting from amino acid analysis as follows:

$$\% \text{ protein} = \% N \times 6.51 \dots\dots\dots(2.5)$$

2.2.6. Cationic composition

Cationic composition of *A.nilotica* var *tomentosa* gum was determined by Electronic scanning microscope – XRF spectroscopy Figure (2.1) and the percentage of ions composition as a percentage of gum samples.



Figure.2.1. Electronic scanner microscope – Energy dispersive X- Ray fluorescence spectrometer EDX – 7000/8000

2.2.7. Determination of Total Polyphenol (Tannin %)

The tannin content determined according to modification of Prussian blue assay originally devised by Price and Butler and subsequently, modified (Graham, 1992). Tannin content represents “total phenols” or more accurately the “Gallic acid equivalents” as Gallic acid – 99% in purity was purchased from sigma Aldrich – and used as analytical standard for determining the hydrolysable tannins. 500 µg/g Gallic acid was prepared in distilled water. and serial diluted to 400, 300, 200, 100, and 50 µg/g as standards. 0.10ml of each sample was dispensed in a 30ml universal. 3ml of distilled water was added vortex mixed for 30sec. 1.00ml of 0.016M (0.526g/100ml, w/v) Potassium hexacyano ferrate(III) [$K_3[Fe(CN)_6]$], was added followed by 1.00ml of 0.02(0.324g $FeCl_3$ /100ml d.w+ 0.83ml HCl) Ferric Chloride ($FeCl_3$), and immediately mixed by vortex mixer 30sec. Exactly 15 min after adding the reagent to the sample 5 ml of stabilizer(10.00ml of 85% phosphoric acid, (H_3PO_3), 1.00ml of 1% gum Arabic, and 30 ml of distilled water) was added and vortex mixed 30sec, then exactly after 15 min The absorbance was read at 700 nm in triplicate for standard solutions (Figure.2.3), using (Perkin Elmer Lambda XLS+, UV/Vis spectrophotometer) Figure (2.2). The gum samples were also prepared by adding all reagents. The absorbance was read at 700 nm in triplicate for all using Perkin Elmer Lambda 40 UV/Vis spectroscopy. The error in measuring the tannins content was below 10% for all samples and the average was taken.

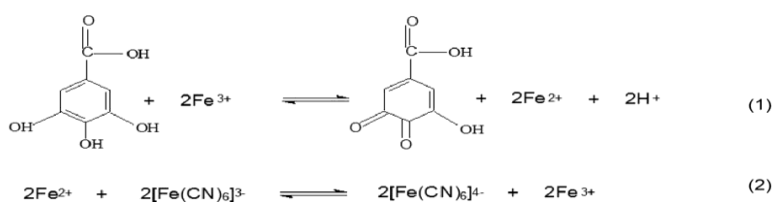




Figure.2.2.. UV/Visible spectrophotometer and the shaker



Figure.2.3. The blank, and standard solutions of standard Gallic acid

2.2.8. Determination of total glucouronic acid

Acid equivalent weight was determined according to the method reported in encyclopedia of chemical technology (1966) with some modification. Cation exchange column packed with Amberlite-120 resin (acid form) was thoroughly washed with 2M Hydrochloric acid. Leave to stand for 10 min then continuous washing with about 150 cm³, followed by distilled water until free of sulphate. Check the presence of sulphate by testing with Barium chloride solution (Saturated solution). 50 cm³ of 3% (w/v) of gum sample were introduced on the top of the column and allowed to elute under gravity action. Adjust the elution rate by one drop per 2 second. Collect the eluent and wash with about 150 distil water; the elution rate does not have to be adjusted. The eluent and washing were collected and titrated against standard 0.1M solution sodium hydroxide using phenolphthalein indicator, (Osman et al., 1993)

$$\text{Acid equivalent weight} = \frac{\text{weight of sample} \times 100}{\text{volume of titrant} \times \text{molarity of alkali}} \dots\dots\dots(2.6)$$

$$\text{Uranic acid \%} = \frac{\text{molar mass of uronic acid unhydride} \times 100}{\text{acid equivalent weight}} \dots\dots\dots(2.7)$$

2.2.9. Determination of intrinsic viscosity

The gum solutions were prepared by dissolving 3 gram, of each sample, in 100 ml, 0.2 M, sodium chloride. The solutions were then filtered through Whatmann No. 40 filter paper. 15 ml of the filtrate were then transferred into an Ostwald viscometer contained in water path set at 25 C^o and left for half an hour. The efflux time was then measured for the original solution and six of its dilutions (2.5%, 2%, 1.5%, 1%, 0.5%, and 0.25%). The average of three measurements was taken for each concentration. The efflux time of the solvent, 1 M, sodium chloride was then measured and the intrinsic viscosity, for each sample, was calculated. The intrinsic viscosity of the cations free gum solutions was also calculated as given above.

2.2.10. Determination of Colour Gardner.

A calibrated Lovibond Spectrophotometer PFX-i series Figure (2.4), colorimeter was used to determine colour Gardner of the *A.nilotica* var *tomentosa* gum samples. Measurements were carried out using 10 mm path length cell on 1wt% gum solutions prepared in distilled water and filtered through 100 mm mesh filter. The Gardner colour scale is from 1 to 18 with 1 containing the least amount of colour and 18 with the maximum amount of colour. The Colour Gardiner was measured after 3 Hours, 24 Hours, and after 48 Hours.



Figure.2.4.Lovibond Spectrophotometer PFX-i series

2.2.11. Determination of Calorific value

The calorimeter IKA® C1 Figure (2.5), was to determine the calorific value of solid and liquid materials according to national and international standards (e.g. DIN 51900, BS 1016 T5, ISO1928, and ASTM 5468, 5865, 4809). The system was calibrated by Benzoic acid tabs 1g (2 Tabs) Figure (2.4), of cal.val. 26461J/g, RSD 0.03%, and LOT SZBD2180V, at 19 C°, gas pressure of 30 bars, and the pump flow of 2700 rpm. 0.5g of *A. nilotica* var *tomentosa* gum samples were placed into a plastic bag C12A, big bag Figure (2.4) with cross cal. Val. 46383. The samples were combusted in an oxygen atmosphere. The calorific value of the sample was calculated, and the net cal.val, was calculated by adding moisture content calorific value.

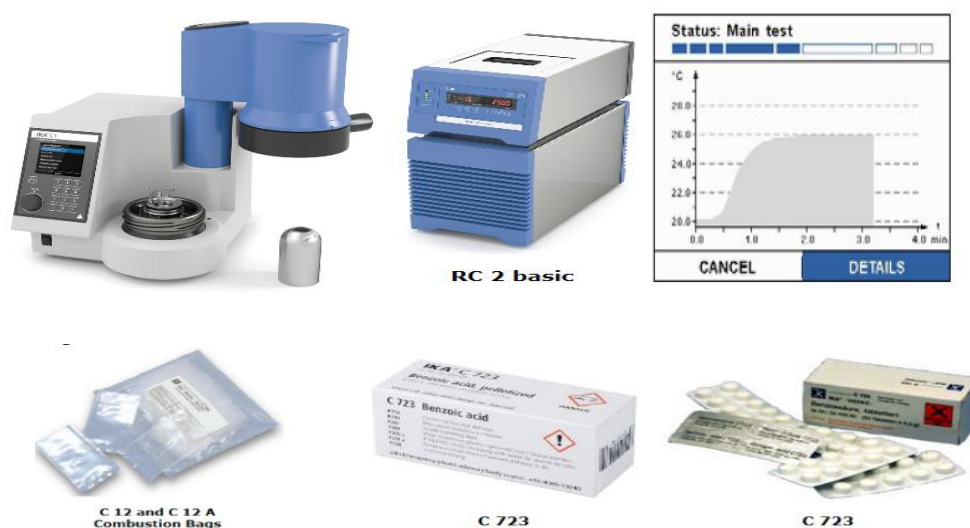


Figure.2.5. Calorimeter IKA C1System, plastic bags, and standard Benzoic acid

2.2.11. Fractionation and molecular weight determination

2.2.11.1. Instrumentation

Gel permeation chromatography coupled to a multi-angle laser light scattering detector (GPC-MALLS) (Figure.2.6) system was used to determine the molecular weight and molecular weight distribution. Loading sample injector equipped with 100 ml sample loop. The system utilizes Waters (Division of Millipore, USA) Solvent Delivery System Model 6000A connected to a column containing Superose 6 (Amersham Biosciences) (10 x 300mm), manual Rheodyne Model 7125 syringe. The column eluent was monitored by three detectors, refractive index (RI) Wyatt Optilab DSP interferometric refractometer operated at 633 nm (Wyatt Technology Corporation, USA), multi-angle laser light scattering photometer DAWN EOS using He-Ne laser at 690 nm (Wyatt Technology Corporation, USA), and an Agilent 1100 series G1314A UV detector (214 nm, Agilent Technologies) (Al-Assaf *et al*, 2005). RI provides an accurate concentration profile, MALLS enables absolute molecular mass and radius of gyration (R_g), and the UV detects the proteinaceous components of the gum. (Katayamaa *et al*, 2006). The data was processed by the Astra for Windows software (version 4.90.07, Wyatt Technology Corporation).

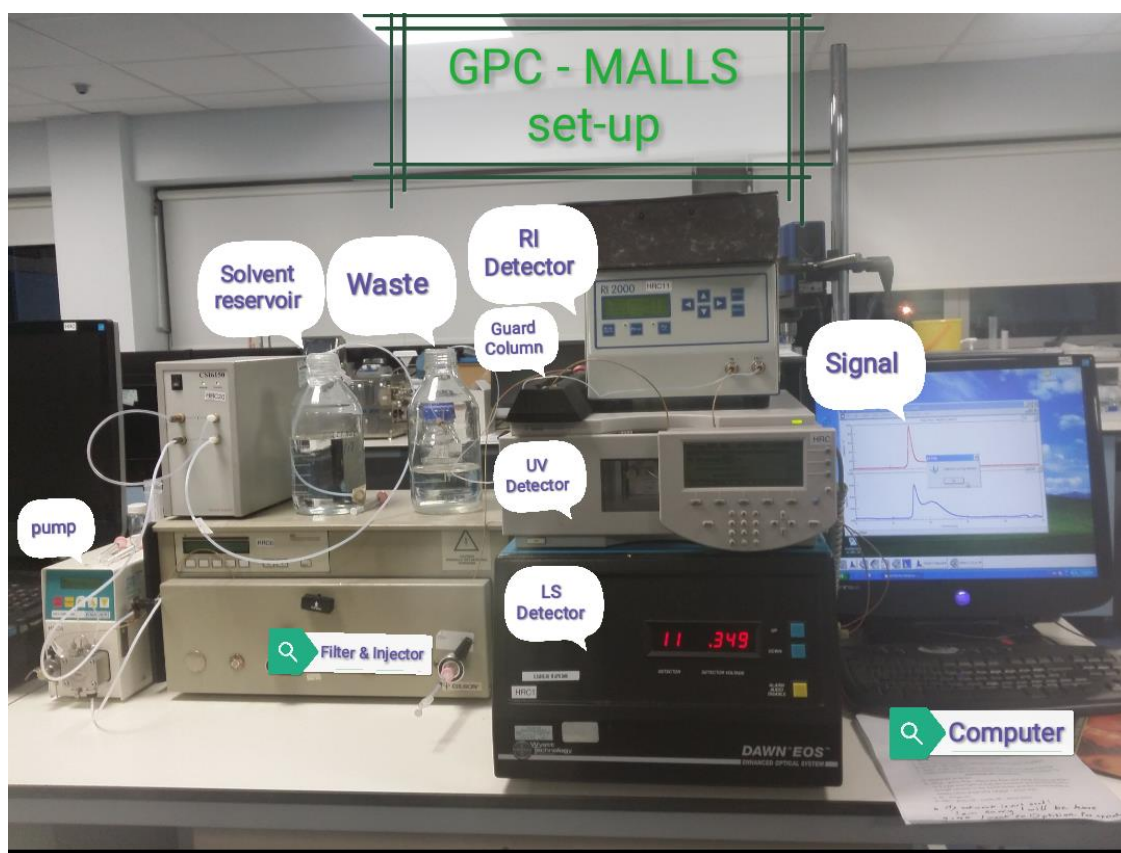


Figure 2.6: GPC-MALLS set-up

2.2.11.2. Sample preparation

0.02 g in 10ml of 0.2M NaCl (based on dry weight) was prepared, and hydrated by roller (SRT9. Stuart Scientific, UK) mixed overnight. The solution was then centrifuged for 10 minutes at speed of 3000 rpm using Megafuge 1.0R (Heraeus SEPATECH, Germany) centrifuge, then filtered using 0.45- μm nylon filter (Whatman, 13 mm) prior to injection into the GPC-MALLS system.

2.2.11.3. Gel permeation chromatography

To investigate the performance of *A.nilotica* var. *tomentosa* gum as stabilizer of oil in water emulsions. This would be analyzed by measuring the droplet size distribution of the emulsion as fresh sample and after storage for 3 and 7 days at 60°C, also comparing the droplet size distribution of the emulsion in different gum concentration 5%, 10%, 15%, 20% as fresh sample and after storage for 3 and 7 days at 60°C.

2.2.12. Determination of Rheological Properties

2.2.12.1. Solutions preparation

50% w/w (based on dry weight) gum solutions were prepared in water containing 0.005 % w/v NaN_3 as a preservative. The solutions agitated on a tube roller mixer (SRT9. Stuart Scientific, UK) (Figure (2.7.A)) overnight to ensure that the sample is fully dissolved. The solution was centrifuged for 10 minutes at 3000 rpm using (Megafuge 1.0R, Heraeus SEPATECH, Germany) centrifuge.

one dilution 25%(w/v) was prepared from stock solution recentrifuged and stored at 4°C prior to investigation of their rheological behaviour.

2.2.12.2. Rheological measurements

Rheological measurements were carried out using KINEXUS Pro⁺ (Malvern Instruments) Figure (2.7) fitted with cone and plate geometry with a cone diameter of 40 mm and an angle of 2°. Steady shear viscosity curves were measured for gum solutions 25%, and 50 % w/v both upon shear rate ramp-up (from 0.01 to 10000 s^{-1}) and subsequent shear rate ramp-down (from 10000 back to 0.01 s^{-1}). Dynamic rheological measurements, to determine the elastic modulus (G'), viscous modulus (G'') and dynamic viscosity, were performed in 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 done by computer software (Rheology Advantage Data Analysis Program). In all experiments, samples were covered with a solvent trap to prevent evaporation.



Figure.2.7. KINEXUS Pro⁺ (Malvern Instruments)

2.2.13. Emulsification properties

2.2.13.1. Materials

- *Acacia nilotica* var. *nilotica* gum 5%, 10%, 15%, 20%.
- Citric acid 0.12% (prepared as a 10% solution in water).
- Sodium benzoate 0.13% (prepared as a 10% solution in water).
- Octanoic/Decanoic acid triglyceride oil, (ODO) 10%.

2.2.13.2. Emulsion preparation

Distilled water was added to about 8 g of the gum sample (based on dry weight) in glass bottle to become about 40 g in total with a concentration of 20 % (w/w) gum solution. The sample was agitated on a tube roller mixer Figure (2.8A) overnight until the sample completely dissolved and hydrated. Exact calculated grams for each samples (in the range from about 19.97 to about 20 g) of the prepared gum solution was filtered using 100 μ m mesh then mixed with 0.52 ml of 10 % (W/V) sodium benzoate solution as a preservative, and 0.48 ml of 10 % (W/V) citric acid solution to adjust the pH to 4, 15.71ml , and 15.73ml of distilled water was added, then, 4.2 g of ODO oil (10%) was added to the gum solution to give a total of 40 g and final concentration of 10%.The mixed solution was homogenized for 3 minutes using a POLY TRON (PT 2100, KINEMA TICA AC) homogenizer at 22000 rpm Figure (2.8, B).. Impeller (PTDA21 9 mm tip diameter) was used as dispersing tool. To achieve small particle size < 1

micron, the pre-emulsified mixture was homogenized using a high-pressure NanoVater (NV30-FA, MITSUBI SHI GOT1000.) Figure (2.9). In order to achieve effective disaggregation of the gum it was passed twice at 75 MPa.

The final emulsion kept in closed glass universals, and measured emulsion as prepared (amb), then placed at 60°C in the Vacuum Oven (GALLENKAMP. OVA031.XX1.5). Droplet size has been evaluated after 3 and 7 days.



A

B

Figure.2.8. Roller mixture (A) and Poly tron (PT 2100, KINEMA TICA AC) homogenizer (B)

2.2.13.3. Droplet size analysis

The droplet size distribution of the emulsions was measured, using Mastersizer 3000, a laser diffraction particle size analyzer (Malvern Instruments) Figure (2.10). Distilled water was used as dispersant and a value of 1.45 was used for the refractive index for oil phase (ODO). Emulsification stability of samples kept at 60 C was evaluated by particle size change after accelerated stability test for 3 and 7 days. The particle size of the emulsions was described by the volume median diameter (VMD).



Figure.2.9. High-pressure NanoVater (NV30-FA, MITSUBISHI GOT1000.)



Figure.2.10. Mastersizer 3000, a laser diffraction particle size analyzer (Malvern Instruments)

3.Results and discussion

Twenty nine samples of *A. nilotica* var *tomentosa* gum from Sinnar, and Blue Nile states were subjected to physicochemical analysis. The characterization of gums is very important when we need to use the gum in the industrial applications. The study of chemical and physical properties of gum is used to Confirm the purity and to report the specification of the samples under study. Tables (3.1, and 3.2) show analytical data of *A. nilotica* var *tomentosa* gum samples seasons 2015.

3.1. Moisture content

Table (3.1) shows the moisture content of *A. nilotica* var *tomentosa* gum samples from Sinnar, and from the Blue Nile states, ranged between 10.6% – 14.14% with an average value of 10.6% and 10.52 - 14.71 with an average value of 11.95% respectively, which almost show higher value to those obtained by, Karamallah (1999) for *A.nilotica*, and slightly different to those obtained by Amira. A, et al (2011) for *A. nilotica* var *nilotica*. The results show different to those obtained by Omar B, et al. (2013), for *A.senegal* var. *senegal*, but show higher value to those results of *A. seyal* var. *seyal* obtained by Rabeea M.A, et al, (2016), also

3.2. Ash content

Table (3.1) shows the value of ash content of *A.nilotica* var *tomentosa* gum samples from Sinnar, and from the Blue Nile states. The results ranged between 1.65% - 2.59% with an average value of 2.17%, and 1.53 - 2.32 with an average value of 1.94%, which almost show higher value to those, obtained by, Karamallah (1999), and show slightly different to those obtained by Amira. A, et al (2011) for *A.nilotica* var *nilotica*, and to those obtained by Omar B, et al. (2013), in the study of *A.senegal* var. *senegal*. also shows lower value to those results of *A. seyal* var. *seyal* obtained by Rabeea M.A, et al, (2016),

3.3. pH value

Tables (3.1) show the pH values for of *A. nilotica* var *tomentosa* gum samples from Sinnar, and from the Blue Nile states, The mean values were found to be 5.25, and 5.13 respectively, which almost shows high value to those obtained by, Karamallah (1999), and almost similar to those obtained by Amira. A, et al (2011) for *A. nilotica* var *nilotica*, also shows high value to those results obtained by Rabeea M.A, et al, (2016) n the study of *A. seyal* var. *seyal*.

Table3.1. Physicochemical properties of all samples *A. nilotica* var *tomentosa* gum.

Samples code	All samples of Sinnar state					Samples code	All samples of Blue Nile state				
	Moisture %	Ash%	pH	S.O.R+	Cal.val Kcal/g		Moisture %	Ash%	pH	S.O.R+	Cal.val Kcal/g
S1	10.6	1.92	5.45	+90	4.099	BN1	10.52	1.53	5.28	+95	4.001
S2	11.62	1.65	5.51	+100	4.097	BN2	11.25	2.05	5.04	+90	4.031
S3	12.06	2.47	5.17	+100	4.039	BN3	11.91	1.9	5.01	+100	4.034
S4	13.14	1.86	4.94	+95	4.044	BN4	12.41	1.71	5.31	+95	4.031
S5	13.26	2.56	5.1	+90	4.072	BN5	14.36	2.12	5.18	+95	4.034
S6	13.29	2.42	5.49	+95	4.029	BN6	14.71	1.68	5.03	+85	4.028
S7	12.57	2.12	5.26	+100	4.041	BN7	12.66	1.93	5.14	+90	3.996
S8	11.89	2.59	5.21	+95	4.068	BN8	11.31	1.8	5.07	+90	4.043
S9	11.13	2.29	5.18	+100	4.079	BN9	10.78	1.85	5.1	+90	-
S10	12.65	2.02	5.25	+100	4.065	BN10	10.6	1.76	5.19	+100	-
Co.S1	14.14	2.03	5.38	+100	3.997	Co.BN1	12.42	2.16	5.1	+85	4.042
Co.S2	14.5	2.22	5.27	+100	3.955	Co.BN2	11.54	2.27	5.12	+90	4.142
Co.S3	13.76	2.24	5.1	+100	4.035	Co.BN3	11.94	2.32	5.08	+95	4.013
Co.S4	12.94	2.1	5.24	+105	4.000	Co.BN4	10.88	2.05	5.15	+85	3.930
Co.S5	11.45	2.05	5.24	+95	4.012	-	-	-	-	-	-
Average	12.6	2.17	5.25	+97.67	4.04	Average	11.95	1.94	5.13	+91.8	4.03

Table3.2. Physicochemical properties of composite samples *A. nilotica* var *tomentosa* gum .

Samples code	Composite samples of Sinnar state					Samples code	Composite samples of Blue Nile state				
	Acid E.W	Uronic acid	N%	Protein	Intrinsic Viscosity		Acid E.W	Uronic acid	N%	Protein	Intrinsic Viscosity
Co.S1	2137.33	9.08	0.10	0.61	9.65	Co.BN1	2279.72	8.51	0.06	0.35	12.07
Co.S2	2230.77	8.70	0.07	0.44	10.07	Co.BN2	2229.73	8.70	0.04	0.26	12.5
Co.S3	2243.06	8.65	0.08	0.53	11.06	Co.BN3	2107.69	9.20	0.04	0.26	9.84
Co.S4	2226.21	8.71	0.08	0.53	9.87	Co.BN4	2133.77	9.09	0.04	0.26	11.40
Co.S5	2076.92	9.34	0.07	0.44	10.35	-	-	-	-	-	-
Average	2182.86	8.90	0.08	0.51	10.16	Average	2187.73	8.88	0.05	0.28	11.47

3.4. Specific optical rotation

The specific optical rotation is regarded as one of the analytical parameters by means of which an *Acacia* species gums can be distinguished from other *Acacia* species gums. *Acacia nilotica* has a positive specific optical rotation and it belongs to *Gummeferae* series which contains *A. seyal*, *A. siberiana*, *A. tortilis*, *A. Oerfota* ...etc. whereas *A. senegal* has negative specific optical rotation and belong to *Vulgares* series that contains *A. Leata*, *A. polyacantha*, *A. mellifera*....etc.

Table (3.1) shows the highest value of specific optical rotation of specific optical rotation of *A. nilotica* var *tomentosa* gum collected from Sinnar and Blue Nile state fell between +90 – +105 with average value of +97.67, and +85 – +100 with average value of +91.79, which almost similar to those results obtained by, Karamallah (1999), but slightly different to those obtained by Amira. A, et al (2011) in the study of *A. nilotica* var. *nilotica* , Also higher to those results obtained by Rabeea M.A, et al, (2016) n the study of *A. seyal* var. *seyal*, and so different to those obtained by Omar B, et al. (2013), in the study of *A. senegal* var. *senegal*.

3.5. Viscosity

A. nilotica belongs to *Gummeferae* series, it is characterized by its low viscosity (Anderson *et al.*, 1963, 1966). The intrinsic viscosity of *A. nilotica* var. *tomentosa* gum samples from Sinnar, and from the Blue Nile states as shown in Table (3.2) Figure.3.1, and 3.2, which have an average value 10.16ml/g, and 11.47ml/g respectively, these results were almost less than that obtained by an FAO study for Nigerian gum which was reported as 35 cm³g⁻¹ (Al-Assaf *et al.*, 2005), and high to those obtained by Amira. A, et al (2011), for *A. nilotica* var *nilotica*, and lower to those obtained by Omar B, et al. (2013), for *A. senegal* var. *senegal*. The low specific optical rotation value and extremely high intrinsic viscosity value cited in the FAO study may lead to a conclusion that the studied gum material did not belong to *A. nilotica* var. *nilotica* specially when considering the many variants of this species. Both *A. senegal* and *A. seyal* have higher value of intrinsic viscosity compared with *A. nilotica*. (Hassan *et al.*, 2005, Siddig *et al.*, 2005, Omer, 2006, Abdelrahman, 2008, Elmanan *et al.*, 2008 and Younes, 2009).

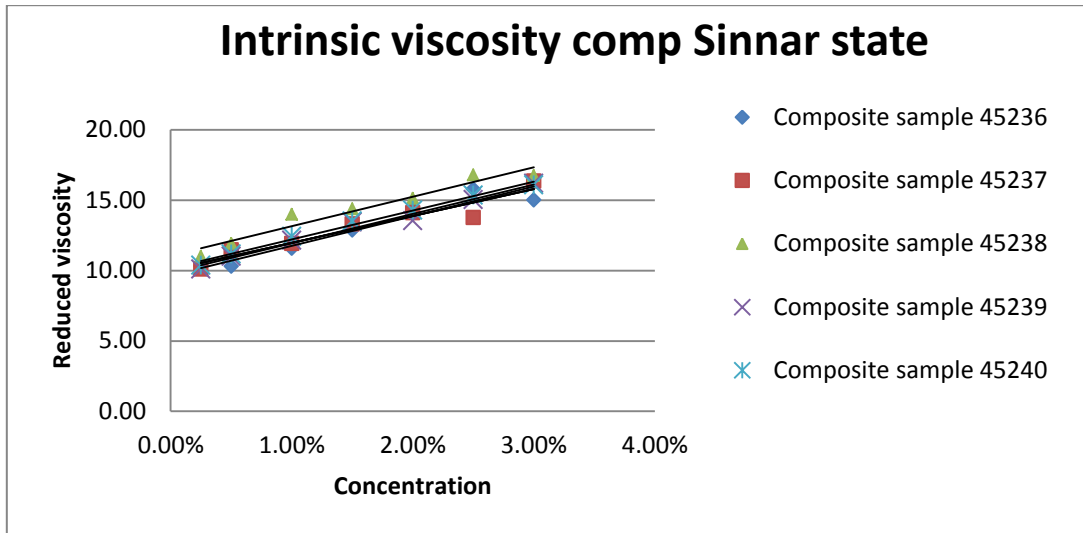


Figure.3.1. Intrinsic viscosity of *A. nilotica* var *tomentosa* of the composite sample from *Sinnar* state

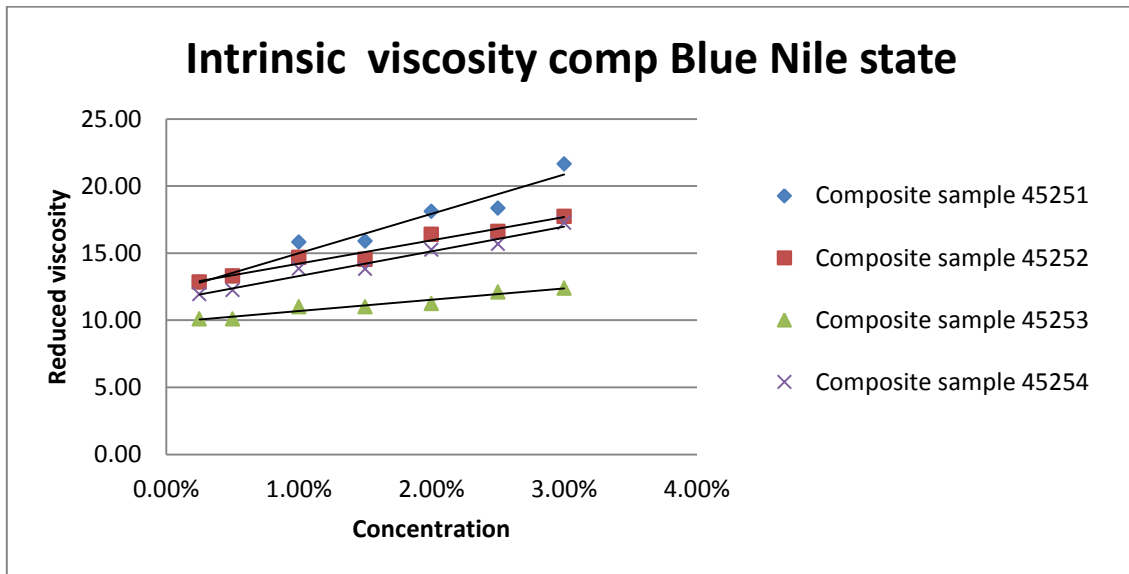


Figure.3.2. Intrinsic viscosity of *A. nilotica* var *tomentosa* of the composite sample from *Blue Nile* state

3.6. Nitrogen and protein content

Table (3.2) show The mean percentages of nitrogen and protein content using Kjeldahl method of *A. nilotica* var *tomentosa* gum samples from Sinnar, and from the Blue Nile states are shown in Table (3.2), the average values were 0.08%, 0.05% and 0.51, 0.28 respectively, which almost show high value to those obtained by Amira. A, et al (2011) for *A. nilotica* var *nilotica*, also show same value to those obtained by, Karamallah (1999) for *A. nilotica*, The protein content obtained from this study is far less than that indicated by a FAO study for Nigerian gum. (Al-Assaf *et al.*, 2005).

The total protein content was calculated using nitrogen conversion factor (NCF) of 6.51 resulting from amino acid analysis (Amira. A, et al, 2011). From literature, the nitrogen conversion factor (NCF) of *A. senegal* was found to be 6.6 (Anderson, 1986 cited in Osman *et al.*, 1993).

A. senegal and *A. seyal* have higher nitrogen and protein content compared with *A. nilotica* var. *tomentosa* (Anderson, 1977, Osman, 1993, Karamallh *et al.*, 1999, Hassan *et al.*, 2005, Siddig *et al.*, 2005, Omer, 2006, Abdelrahman, 2008, Elmanan *et al.*, 2008 and Younes, 2009).

3.7. Acid equivalent weight and uronic acid

The acid equivalent weight and corresponding calculated uronic acid content of *A. nilotica* var *tomentosa* gum samples from Sinnar, and from the Blue Nile states. Table.3.2 shows acid equivalent weight of *A. nilotica* var *tomentosa* gum average value of 2182.86, and 2187.73, which almost show slightly high to those obtained by Amira. A, et al (2011), for *A. nilotica* var *nilotica* gum. and higher value to those obtained to those obtained by Omar B, et al. (2013), for *A. senegal* var. *senegal*, while uronic acid average value of 8.90, and 8.88, which almost far less than that obtained from a FAO study (21%) for Nigerian gum (Al-Assaf *et al.*, 2005), and slightly low value to those obtained by Amira. A, et al (2011), for *A. nilotica* var *nilotica*. Also shows different value to those obtained by Omar B, et al. (2013), for *A. senegal* var. *senegal*. These results are different from the results obtained for *A. senegal* by Osman *et al.*, (1993) and Siddig *et al.* (2005), they reported a range of 1153 to 1500 for acid equivalent weight and a range of 12.93 % to 16.33 % for uronic acid content.

3.8. Colour Gardner

Table (3.3) shows the Colour Gardner after 3 hours, 24 hours, and 48 hours of *A. nilotica* var *tomentosa* gum samples from Sinnar, and Blue Nile states respectively.

The Colour Gardner increased with the period of time, these results indicate the oxidation of polyphenols.

3.9. Cationic composition

Cationic composition of *A. nilotica* var. *tomentosa* gum samples was determined using Electronic scanning microscope – XRF spectroscopy as shown in Table (3.). The major elements were in the order: Ca > K > Fe > Sr.

Calcium, and Potassium recorded high values, indicating that the gum is a salt of potassium, and calcium.

3.10. Tannin content

Table (3.3) shows the tannin content of *A. nilotica* var *tomentosa* gum samples from Sinnar, and from the Blue Nile states respectively. The mean values were found to be 368.48 ppm, and 342.77ppm respectively. They are slightly less than those obtained by Karamallah (1999) for *A.nilotica*, and lower value to those obtained by Amira. A, et al (2011), for *A. nilotica* var *nilotica* gum. *A. senegal*, thus distinguishing itself distantly from other *Acacia* gums. This finding was of significant importance when considering gums as food additives. Tannin content of *A. seyal* gum was found to be 0.11% (Karamallah, 1999). Tannins are antioxidant found in grapes and wine in particular. Figure (3.3) shows the polyphenols (tannins) was directly proportional to the Colour Gardner which effected by oxidation.

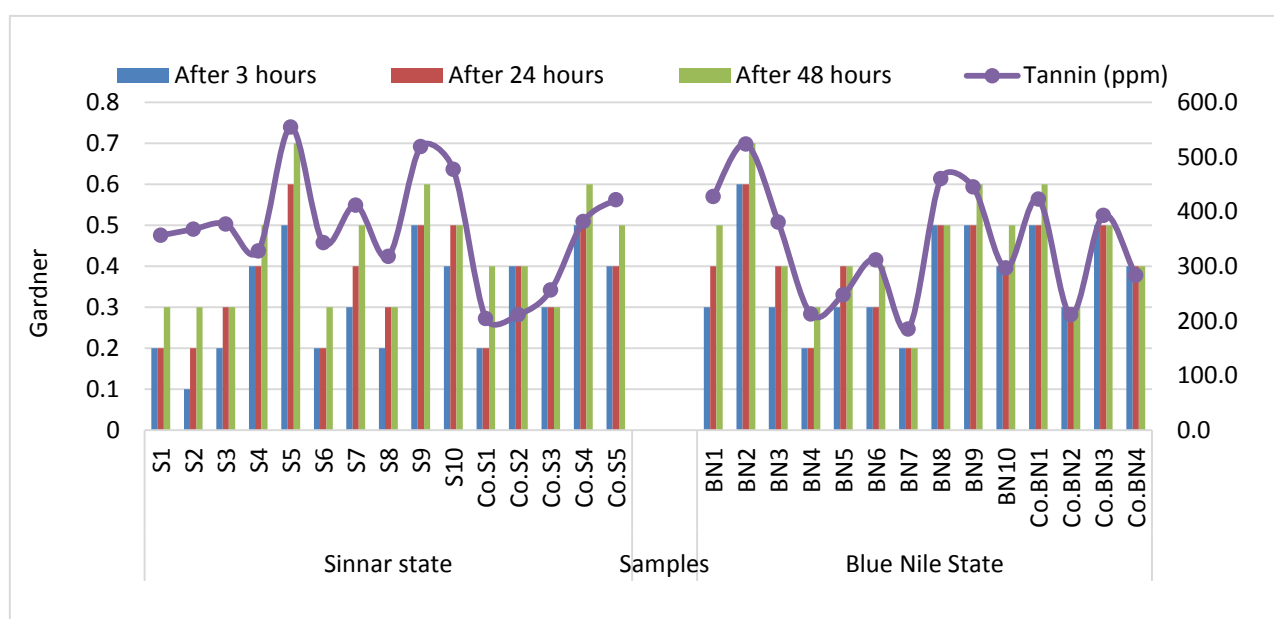


Figure.3.3. the relationship between tannin and Colour Gardner of *A. nilotica* var *tomentosa*, origin Sudan

Table.3.3 Colour Gardner, and tannin content of *A. nilotica* var *tomentosa* from Sinnar, and Blue Nile state

Samples code	Colour Gardner			Tannin (ppm)	Samples code	Colour Gardner			Tannin (ppm)
	After 3h	After 24h	After 48h			After 3h	After 24h	After 48h	
S1	0.2	0.2	0.3	356.3	BN1	0.3	0.4	0.5	427.2
S2	0.1	0.2	0.3	367.6	BN2	0.6	0.6	0.7	523.7
S3	0.2	0.3	0.3	377.2	BN3	0.3	0.4	0.4	380.4
S4	0.4	0.4	0.5	327.9	BN4	0.2	0.2	0.3	212.5
S5	0.5	0.6	0.7	554.4	BN5	0.3	0.4	0.4	247.7
S6	0.2	0.2	0.3	343.2	BN6	0.3	0.3	0.4	311.3
S7	0.3	0.4	0.5	411.5	BN7	0.2	0.2	0.2	184.6
S8	0.2	0.3	0.3	317.8	BN8	0.5	0.5	0.5	460.1
S9	0.5	0.5	0.6	519.1	BN9	0.5	0.5	0.6	444.9
S10	0.4	0.5	0.5	477.5	BN10	0.4	0.4	0.5	296.6
Co.S1	0.2	0.2	0.4	204.4	Co.BN1	0.5	0.5	0.6	422.7
Co.S2	0.4	0.4	0.4	211.1	Co.BN2	0.3	0.3	0.3	211.0
Co.S3	0.3	0.3	0.3	256.0	Co.BN3	0.5	0.5	0.5	393.0
Co.S4	0.5	0.5	0.6	381.9	Co.BN4	0.4	0.4	0.4	283.1
Co.S5	0.4	0.4	0.5	421.5					
Average	-	-	-	368.48	Average	-	-	-	342.77

3.11. Calorific value

Tables (3.1) show the Calorific values for of *A. nilotica* var *tomentosa* gum samples from Sinnar, and from the Blue Nile states. The mean value of calorific value of was found to be 4.04 Kcal/g, and 4.03 Kcal/g respectively, which suitable to use as food additive. These values were identical to the Calorific values of other acacia species such as, *A. nilotica* var *nilotica*, *A. nilotica* var *adstringen*, *A. senegal*, *A. seyal*, *A. Polyacantha*, *A. tortillis milifera*, *A. tortillis spirocarpa*, and *A. orfota* as shown in as shown in Figure (3.4).

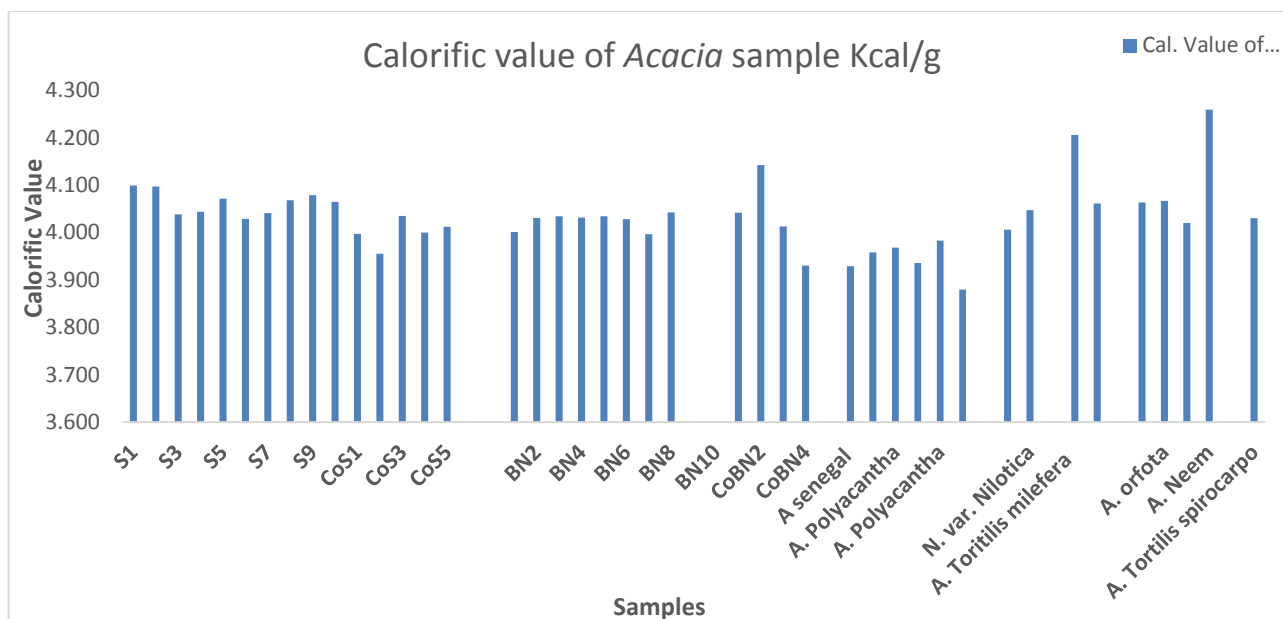


Figure.3.4. Calorific value of *A. nilotica* var *tomentosa*, and other *Acacias*

3.12. Molecular weight and molecular weight distribution

Figures (3.5, 3.6, 3.7, and 3.8) shows the elution profiles of *A. nilotica* var. *tomentosa*, *A. nilotica* var. *nilotica*, *A. senegal* and *A. seyal* gum respectively using multi-angle laser light scattering (MALLS) are given in. The Figures show elution profiles as indicated by detectors measuring refractive index, light scattering at 90° and UV at 214nm. The light scattering response reflects the mass and concentration and shows two distinctive peaks. The first peak has a high response since it corresponds to the high molecular weight material arabinoglactan protein complex (AGP) content. The second peak has a lower response.

The refractive index (RI), concentration detector response shows also two peaks, the first peak has a high, narrow response corresponding to the minor peak which appeared at the elution volumes of ~ 7.8 ml. The second peak is broader with lower response corresponding to the major peak which appeared at an elution volume of ~10 ml. In *A. senegal* gum the RI response is opposite to that in light scattering as shown in Figure (3.7).

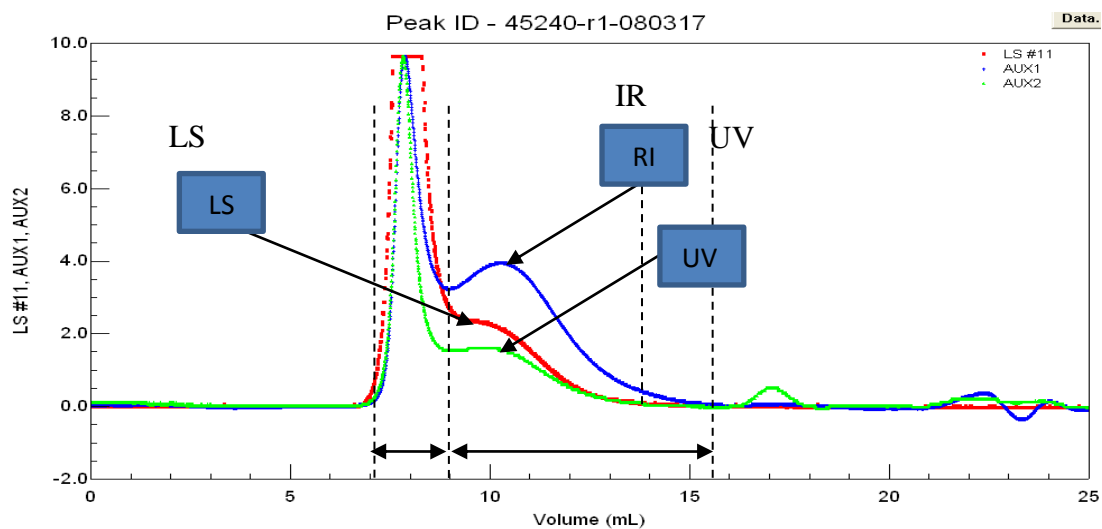


Figure.3.5. GPC chromatogram of composite sample of *A. nilotica var tomentosa* gum from Sinnar state

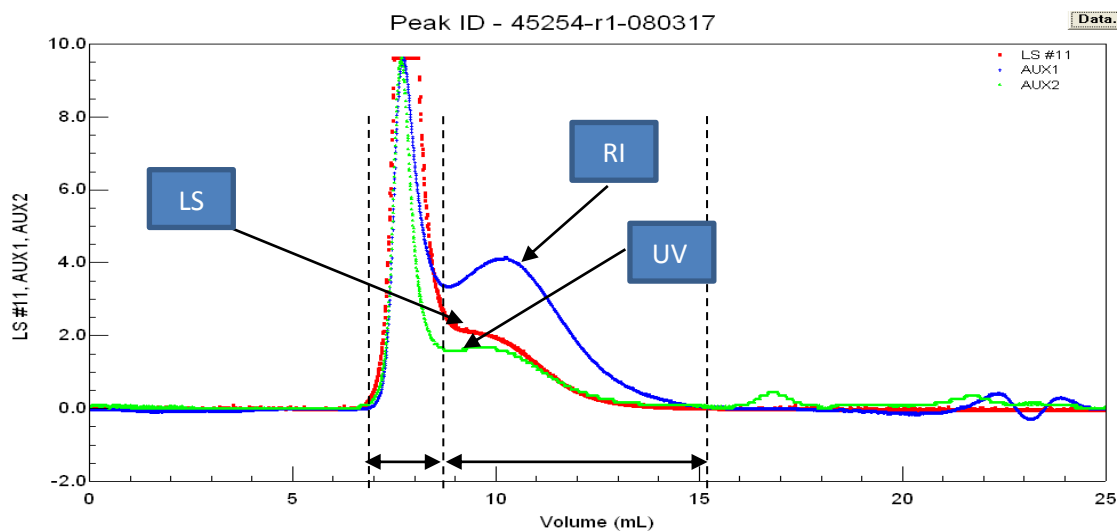


Figure.3.6. GPC chromatogram of composite sample of *A. nilotica var tomentosa* gum from Blue Nile state

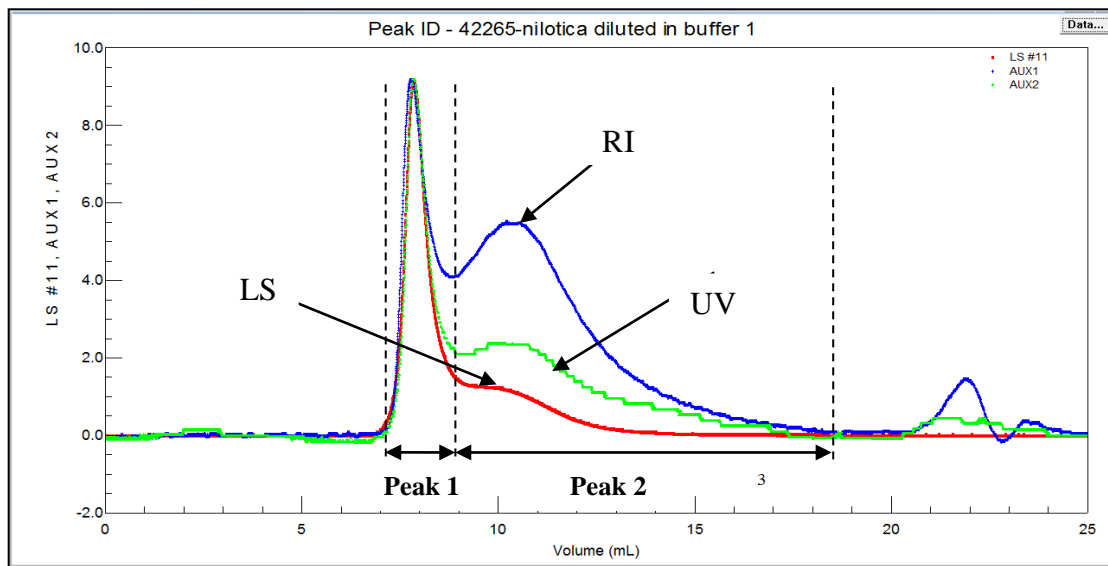


Figure.3.7. GPC chromatogram of *A. nilotica* var *nilotica* gum, (Amira, 2011)

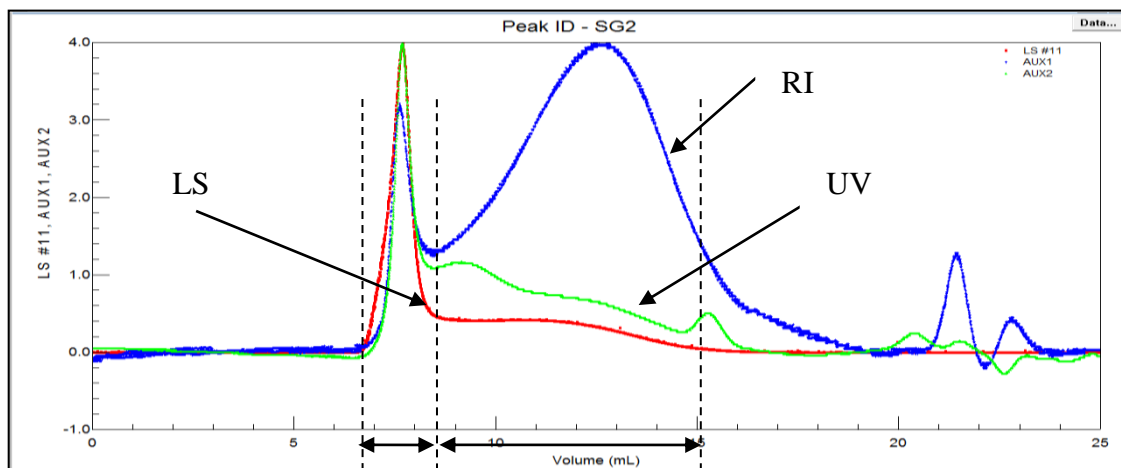


Figure .3.8. GPC chromatogram of *A. senegal* gum

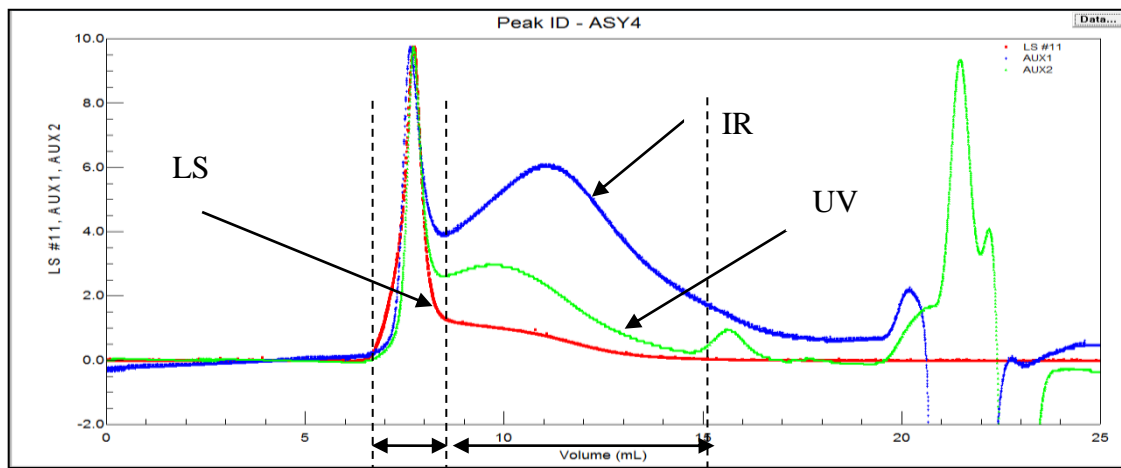


Figure .3.9. GPC chromatogram of *A. seyal* gum

The UV response shows two peaks. The first peak (peak 1) is for the (AGP) which has the protein core and the attached carbohydrate. The second peak (peak 2) appears after the (AGP) and corresponds to the arabinogalactan (AG), and glycoprotein (GP), this also one of the similarities between *A. nilotica* var. *tomentosa*, and *A. nilotica* var. *nilotica*. Also one of the differences with *A. seyal* and *A. senegal* gum.

A. senegal has a GP peak eluting before the total volume, but the GP peak was not detected on the light scattering detector since it has low molecular weight. Also it cannot be seen on the refractive index (concentration detector) (Al-Assaf *et al.*, 2007), indicating a trace amount of protein.

Figures (3.5 to 3.9) shows *A. nilotica* var *tomentosa*, *A. seyal* and *A. senegal* peaks were located at ~15 ml volume, whereas *A. nilotica* var *nilotica* had a peak at ~17 ml volume.

It is acknowledged that in *A. senegal*, the high molecular weight component, designated previously as an arabinogalactan protein, is more significant and is present in greater proportion than for *A. seyal*. It is the fraction which contains most protein (Siddig *et al.*, 2005). The protein is distributed differently in *A. seyal*. The protein is less in concentration, and not mainly located in the high molecular weight component (AGP) as for *A. senegal*. The indications are that its core structure is dense than *A. senegal*, and contains the majority of the protein. This significant difference in protein location could explain the general opinion in the beverage industry that *A. seyal* is not as effective as an emulsifier, particularly, for long-term stability when compared with *A. senegal*.

A. nilotica var. *tomentosa*, *A. nilotica* var. *nilotica* which reported by Amiera, A, et al, (2011) and *A. senegal* most of the protein content is located in peak 1, whereas in *A. seyal* more of the protein is associated with peak 2. (Flindt *et al.*, 2005, Hassan *et al.*, 2005).

The molecular weight was measured for the whole gum and as two peaks, the first peak which corresponds to (AGP) and the second peak which corresponds to the (AG) and (GP) as identified by the refractive index detector.

Table (3.4) illustrate the results of the molecular weights parameters of all *A. nilotica* var. *tomentosa* samples.

The (AGP) molecular weight value ranged from 5.03×10^6 to 8.9×10^6 g/mol avoiding the unusual value. The amount of AGP in these samples ranged from 24.5% to 54.7%,

and radius of gyration between 25.9 to 55.9 nm. The molecular weight of the (AG+GP) component changed from 15.1×10^6 to 18.6×10^6 g/mol, whereas its amount ranged from 45.3% to 75.5%.

The weight average molecular weight (M_w) for the whole gum ranged from 5.03×10^6 to 8.9×10^6 g/mol with an average value of 7.0×10^6 , which is different from that reported by Amiera, A, et al (2011), for *A. nilotica* var. *nilotica*. They cited a value of 2.5×10^6 to 5.34×10^6 g/mol, with an average value of 3.58×10^6 g/mol, also different from that reported by Anderson *et al.*, (1969) for *A. nilotica* var. *nilotica* gum. They cited a value of 2.27×10^6 g/mol. The value obtained from this result is higher than the value reported by Al-Assaf *et al.*, (2005) which was 6.74×10^5 .

The weight average molecular weight of *A. nilotica* var. *tomentosa* gum obtained from this study is high compared to other gums such as *A. seyal* and *A. senegal*. The reported values of weight average molecular weights (M_w) for *A. seyal* were 8.5×10^5 (Anderson *et al.*, 1969) and 1.94×10^6 g/mol (Hassan *et al.*, 2005). Anderson *et al.*, (1969) reported that *A. senegal* has 5.8×10^5 and 6.0×10^5 (M_w) whereas Randall *et al.*, (1989) reported a value of 9.0×10^5 g/mol.

The radius of gyration lied between 25.9 to 55.3 nm with an average value of 44.3 nm which is different from that reported by Amiera, A, et al (2011), for *A. nilotica* var. *nilotica*, and higher value than the value reported by Al-Assaf *et al.*, (2005). They cited a value of 26 nm. Also it is high compared to the values reported for *A. seyal* and *A. senegal*, that have an average value of 25.7 nm and 33.9 nm respectively (Hassan *et al.*, 2005).

Hence the molecular size of *A. seyal* is smaller compared to that of *A. senegal*, reflecting a compact structure (Hassan *et al.*, 2005). The high molecular weight and compact structures suggest high degree of branching of *A. seyal*. This explains the lower viscosity and high water solubility of this gum.

Despite *A. nilotica* var. *tomentosa* has quite same molecular weight compare with *A. nilotica* var. *nilotica* gum, and a higher molecular weight fallowed with higher molecular size compared with *A. seyal* and *A. senegal*, the average intrinsic viscosity is same with *A. nilotica* var. *nilotica* gum, and lower than *A. seyal* and *A. senegal* gums, indicating that the molecule has an overall spheroidal shape that appears to be characteristic of such proteoglycans.

Table.3.4. GPC-MALLS Molecular weight parameter of *A.nilotica* var. *tomentosa* gum samples from Sinnar and Blue Nile states

Sample code	Whole gum			AGP			AG+GP	
	Mw x 10 ⁵	% mass	Rg /nm	Mw x 10 ⁶	% mass	Rg	Mw x 10 ⁶	% mass
<i>S1</i>	36.3	104.5	34.0	6.5	40.8	38.6	16.5	59.2
<i>S2</i>	30.4	110.7	31.2	6.0	31.5	32.4	16.9	68.5
<i>S3</i>	40.4	110.3	35.8	7.1	44.4	39.6	15.6	55.6
<i>S4</i>	66.7	91.5	85.7	12.6	44.2	92.0	17.4	55.8
<i>S5</i>	46.5	105.1	49.5	8.6	42.2	55.3	17.2	57.8
<i>S6</i>	26.3	109.3	31.4	5.8	24.5	40.4	15.8	75.5
<i>S7</i>	27.6	109.2	26.5	5.8	28.6	30.9	15.4	71.4
<i>S8</i>	39.0	109.8	33.9	7.1	41.4	38.0	16.1	58.6
<i>S9</i>	38.3	109.0	35.1	7.2	38.1	40.0	16.9	61.9
<i>S10</i>	30.7	106.6	35.1	6.8	27.9	42.8	16.1	72.1
<i>CoS1</i>	47.0	102.1	54.3	8.9	41.6	55.3	17.1	58.4
<i>CoS2</i>	62.4	89.2	94.5	13.0	39.3	100.8	18.3	60.7
<i>CoS3</i>	37.3	102.5	48.5	7.0	37.6	50.2	17.7	62.4
<i>CoS4</i>	34.6	107.4	56.1	7.3	31.8	54.0	16.3	68.2
<i>CoS5</i>	32.2	110.0	46.8	5.3	40.4	47.1	17.9	59.6
<i>BN1</i>	26.2	107.5	22.7	5.4	28.1	27.0	15.3	71.9
<i>BN2</i>	52.9	99.8	74.5	11.5	37.2	82.0	15.7	62.8
<i>BN3</i>	35.1	104.6	30.6	6.9	36.7	34.6	15.1	63.3
<i>BN4</i>	31.1	107.0	44.2	5.6	36.4	28.6	16.8	63.6
<i>BN5</i>	45.2	102.0	31.7	6.7	54.7	34.2	18.6	45.3
<i>BN6</i>	31.7	102.8	27.5	6.3	34.5	31.4	15.0	65.5
<i>BN7</i>	26.4	107.3	21.8	5.3	29.5	25.9	15.4	70.5
<i>BN8</i>	38.5	104.4	27.3	6.1	47.2	30.4	18.0	52.8
<i>BN9</i>	28.4	108.5	26.2	5.7	30.7	29.7	15.6	69.3
<i>BN10</i>	32.7	105.6	26.6	5.7	39.4	30.1	16.5	60.6
<i>CoBN1</i>	31.9	99.5	37.8	6.3	33.7	44.0	15.7	66.3
<i>CoBN2</i>	30.3	107.2	37.9	5.3	39.3	44.5	15.5	60.7
<i>CoBN3</i>	30.9	105.1	23.3	5.4	38.3	26.3	16.3	61.7
<i>CoBN4</i>	31.9	98.7	52.3	5.3	39.7	38.0	17.8	60.3
Average	36.8	104.5	43.5	7.0	37.3	44.3	16.6	62.7

The (AGP) molecular weight value ranged from 5.3×10^6 to 8.9×10^6 g/mol with an average value of 7.0×10^6 which is quite same than the value reported by Amiera, A, et al (2011). They cited a value of 7.71×10^6 g/mol, and higher than the value reported by Al-Assaf *et al.*, (2005). They cited a value of 1.17×10^6 g/mol. Also it is higher compared to the values reported for *A. seyal* (5.3×10^6 and 5.57×10^6) (Hassan *et al.*, 2005 and Abdelrahman 2008), and *A. senegal* which ranged between $1-4 \times 10^6$ g/mol (Randall *et al.*, 1989, Vandavelde and Fenyo, 1985 and Al-Assaf *et al.*, 2005).

The molecular weight of the (AG) component changes from 1.53×10^6 to 2.02×10^6 g/mol with an average value of 1.77×10^6 g/mol. The reported value of (AG) molecular weight cited by Al-Assaf *et al.*, (2005) was 3.86×10^5 . Whereas it was in the average of 1.0×10^6 g/mol for *A. seyal* (Flindt *et al.*, 2005, Hassan *et al.*, 2005), and in the range of $1.5-3.0 \times 10^5$ for *A. senegal* (Al-Assaf *et al.*, 2005) which were less compared to *A. nilotica*.

The results show insignificant effect of location and seasons in molecular weight values of *A. nilotica* var. *nilotica* gum.

3.12. Emulsification properties of *A. nilotica* var *tomentosa* gum

The particle size distribution emulsion as prepared and after the acceleration test was measured using a particle size distribution analyzer (Mastersizer 3000).

Tables (3.5) show the span%, specific surface area (m^2/g) and mean diameters of cumulative droplet distributions ($d_{0.1}$, $d_{0.5}$ and $d_{0.9}$) measurement of *Acacia nilotica* var. *tomentosa* emulsions at different conditions (fresh emulsion and after storage for 3 and 7 days at 60°C respectively). The emulsion at different conditions showed a low degree of polydispersity (span %), indicating a good uniformity of the droplet size, the span ranged from 1.224-1.404%, and 2.579-3.117% for Sinnar, and Blue Nile state respectively. However, the specific surface area of most samples decreased when the emulsion was stored for 7 days at 60°C .

The particle size of the emulsions was described as volume median diameter (VMD) for Sinnar, and Blue Nile state respectively. The mean particle diameters emulsions was found to be 0.612 and $0.523 \mu\text{m}$ for fresh emulsion and 0.63 and $0.666 \mu\text{m}$ for emulsion stored for 7 days at 60°C .

Table 3.5: Span%, specific surface area (m²/g) and mean diameters of cumulative droplet distributions (µm) of freshly and stored emulsions for (3 and 7 days at 60 °C) of *A. nilotica* var. *tomentosa* gum season 2015.

Time	Code	Conc	Span%	d(0.1)	d(0.5)	d(0.9)
1. As prepared	SCo5	5%	2.784	0.0276	0.54	1.530
		10%	1.224	0.32	0.612	1.07
		15%	1.298	0.231	0.479	0.853
		20%	1.167	0.223	0.436	0.731
	BNCo4	5%	4.413	0.0294	0.862	3.83
		10%	2.579	0.0277	0.523	1.38
		15%	1.941	0.0414	0.669	1.34
		20%	1.168	0.374	0.687	1.18
2. After 3 days At 60C°	SCo5	5%	4.706	0.466	0.735	1.157
		10%	1.169	0.338	0.627	1.07
		15%	1.372	0.241	0.496	0.921
		20%	1.338	0.206	0.43	0.782
	BNCo4	5%	5.289	0.112	1.53	8.2
		10%	3.213	0.0278	0.609	1.98
		15%	2.057	0.0539	0.724	1.54
		20%	1.298	0.373	0.707	1.29
3. After 7 days At 60C°	SCo5	5%	5.404	0.355	0.707	1.206
		10%	1.404	0.321	0.63	1.2
		15%	1.34	0.246	0.501	0.917
		20%	1.324	0.207	0.43	0.779
	BNCo4	5%	2.724	0.176	3.55	9.84
		10%	3.117	0.0313	0.666	2.11
		15%	2.215	0.0326	0.636	1.44
		20%	1.271	0.38	0.711	1.28

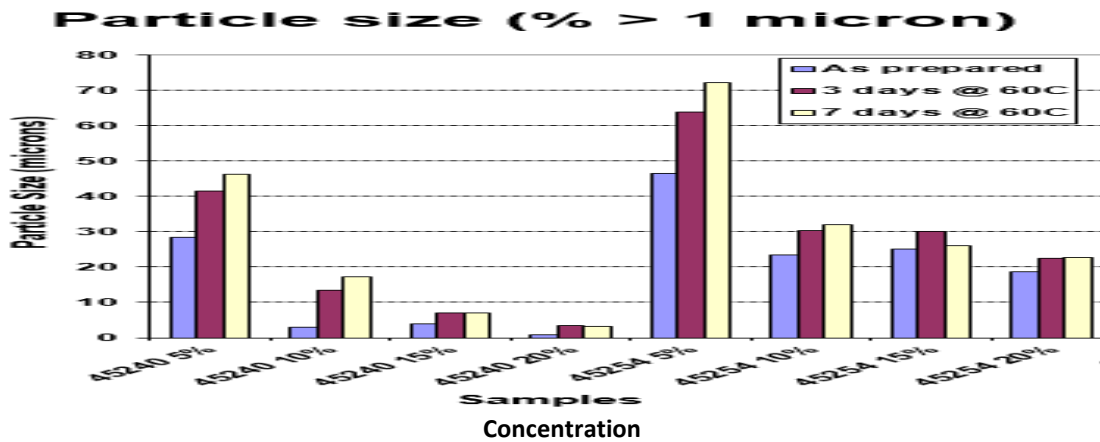


Figure.3.10. Effect of different concentration (5%, 10%, 15%, and 20%) of emulsions stability of *A.nilotica var tomentosa* gum from Sinnar and Blue Nile states,.

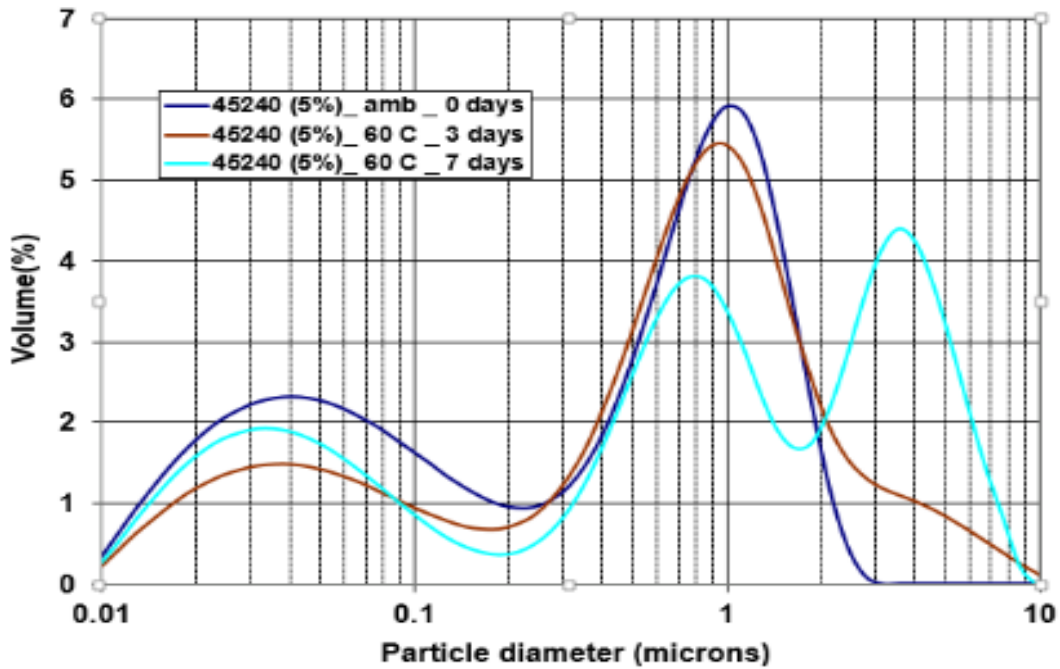


Figure.3.11. Particles size distribution of *A.nilotica var tomentosa* gum (5%) from Sinnar state under different storage time at 60Co

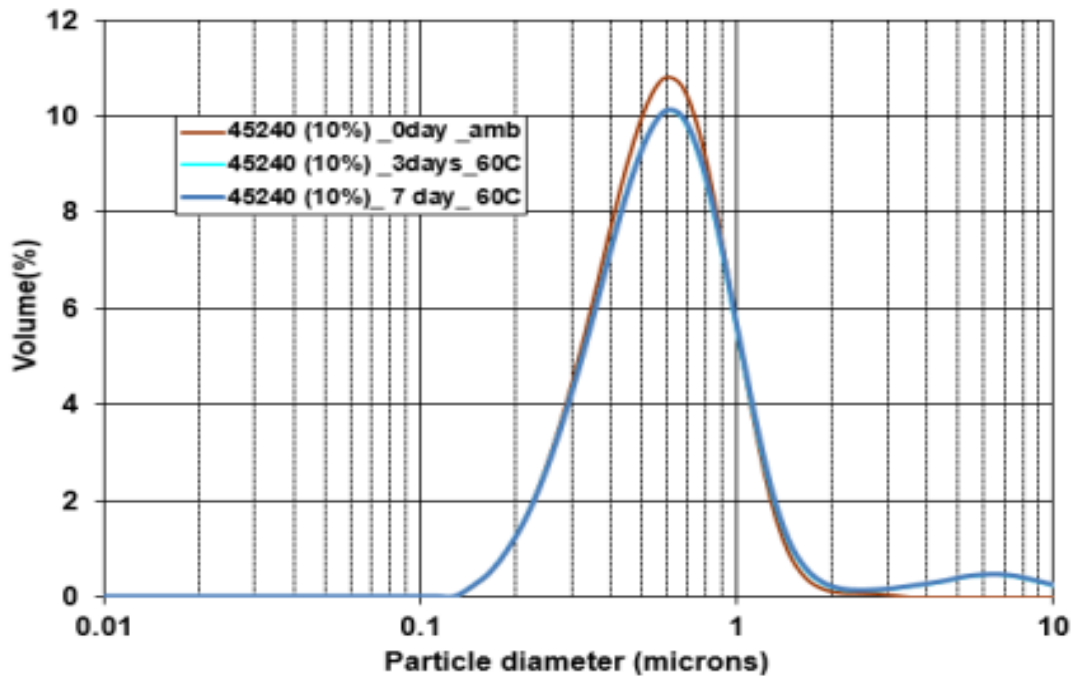


Figure.3.12. Particles size distribution of *A.nilotica* var *tomentosa* gum (10%) from Sinnar state under different storage time at 60Co

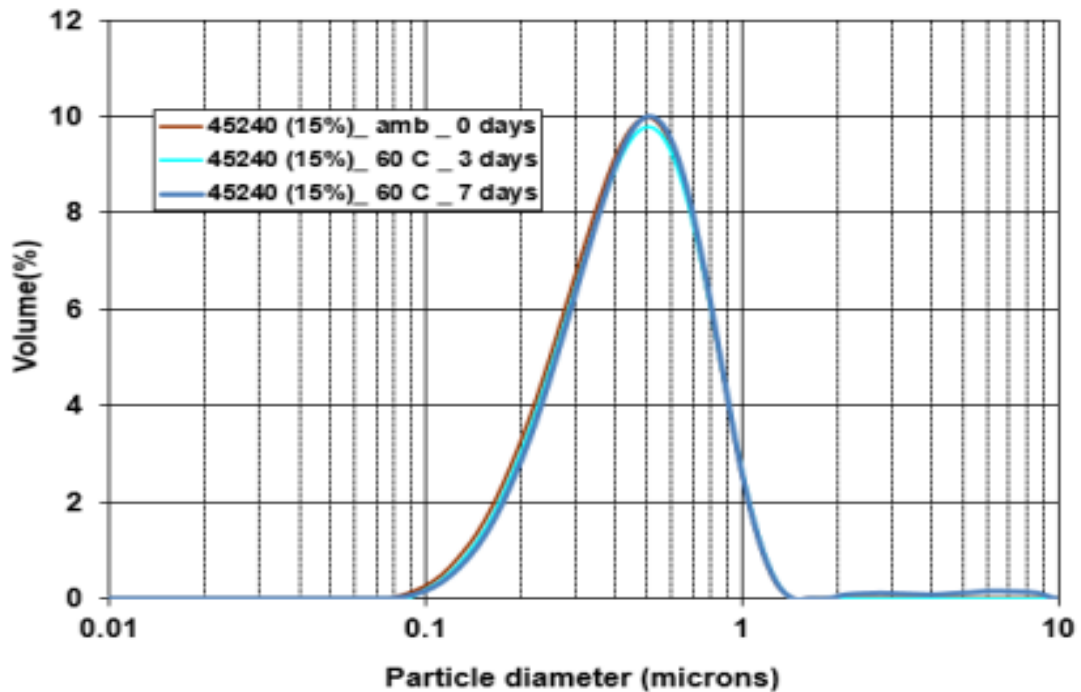


Figure.3.13. Particles size distribution of *A.nilotica* var *tomentosa* gum (15%) from Sinnar state under different storage time at 60Co

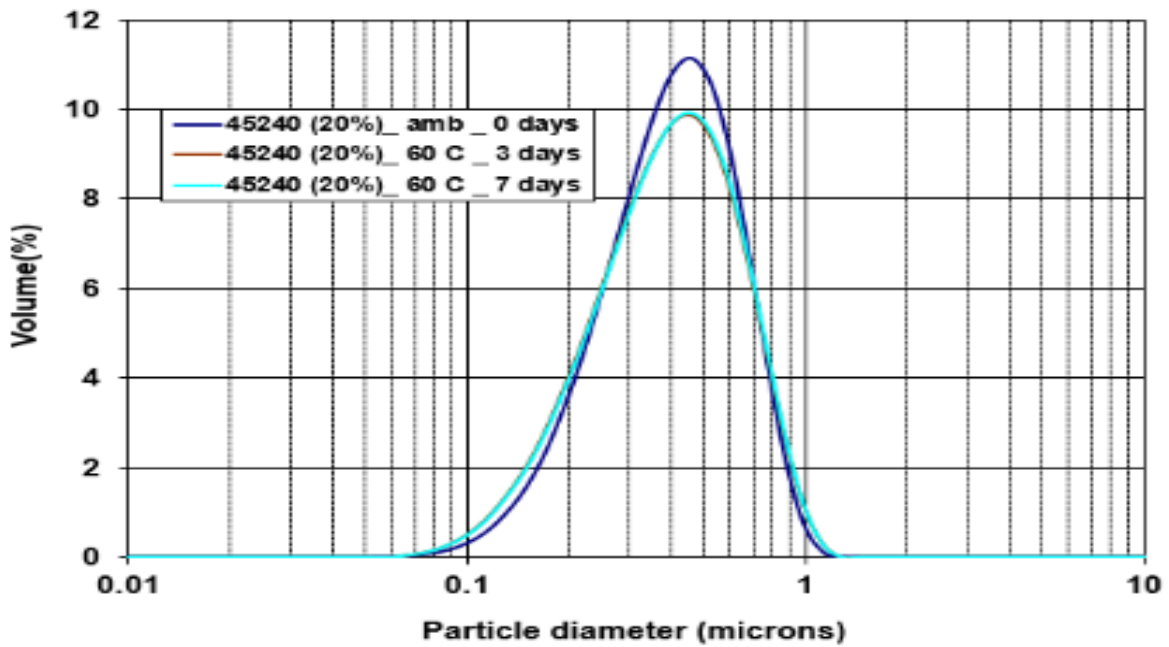


Figure.3.14. Particles size distribution of *A. nilotica* var *tomentosa* gum (20%) from Sinnar state under different storage time at 60Co

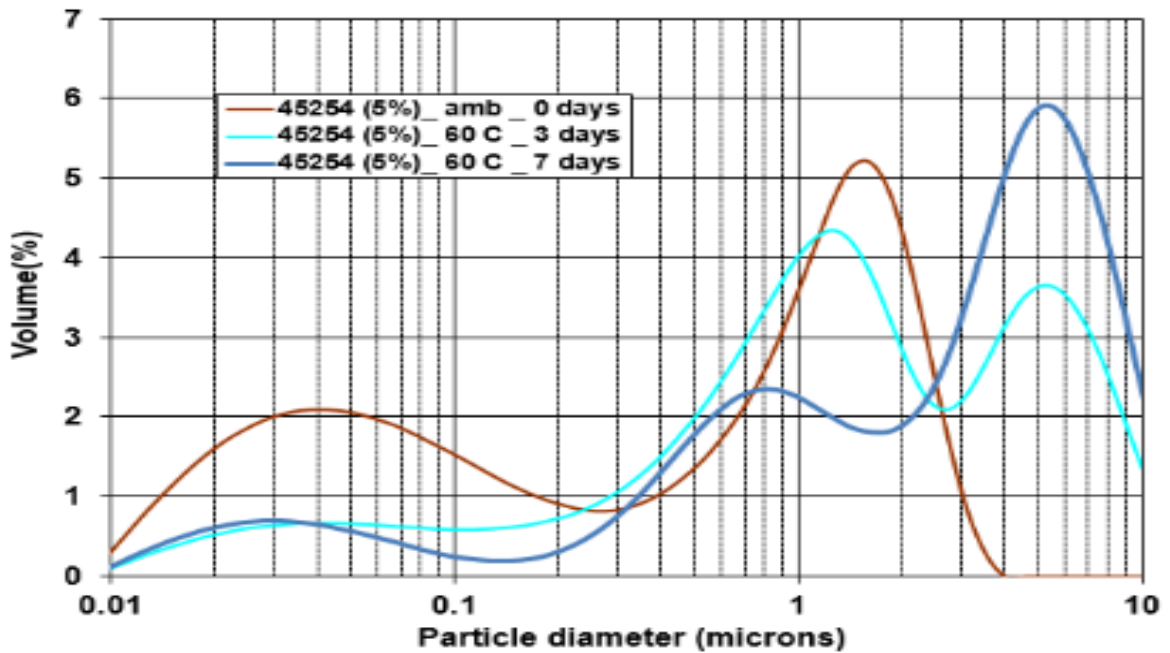


Figure.3.15. Particles size distribution of *A. nilotica* var *tomentosa* gum (5%) from Blue Nile state under different storage time at 60Co

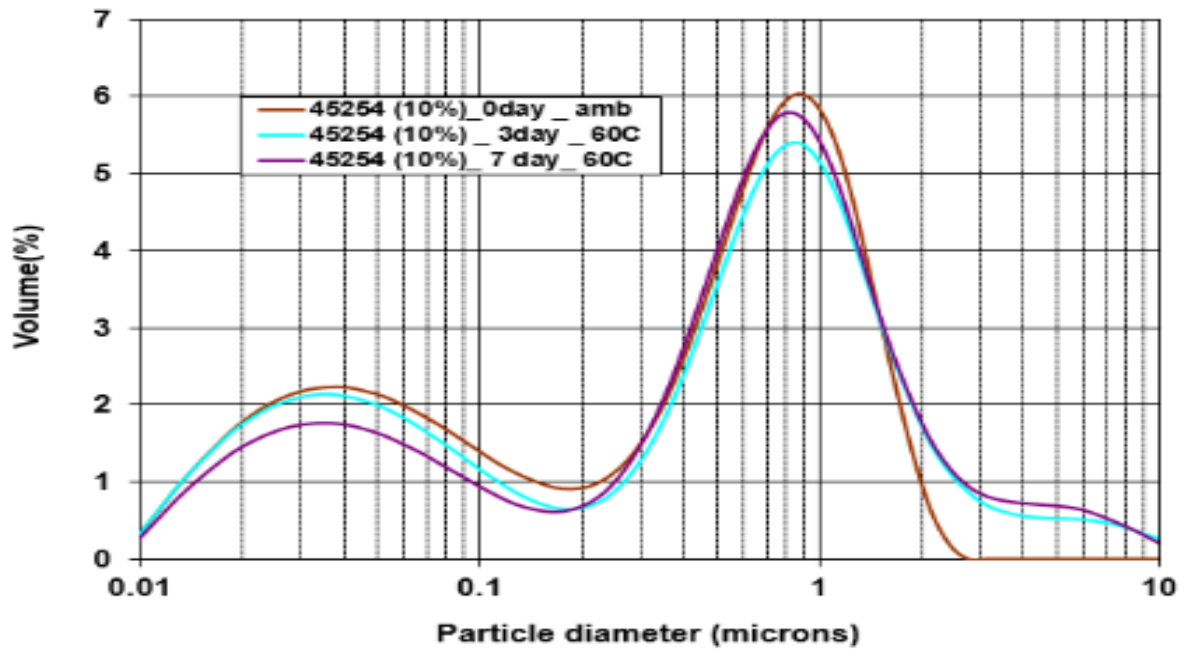


Figure.3.16. Particles size distribution of *A. nilotica* var *tomentosa* gum (10%) from Blue Nile state under different storage time at 60C

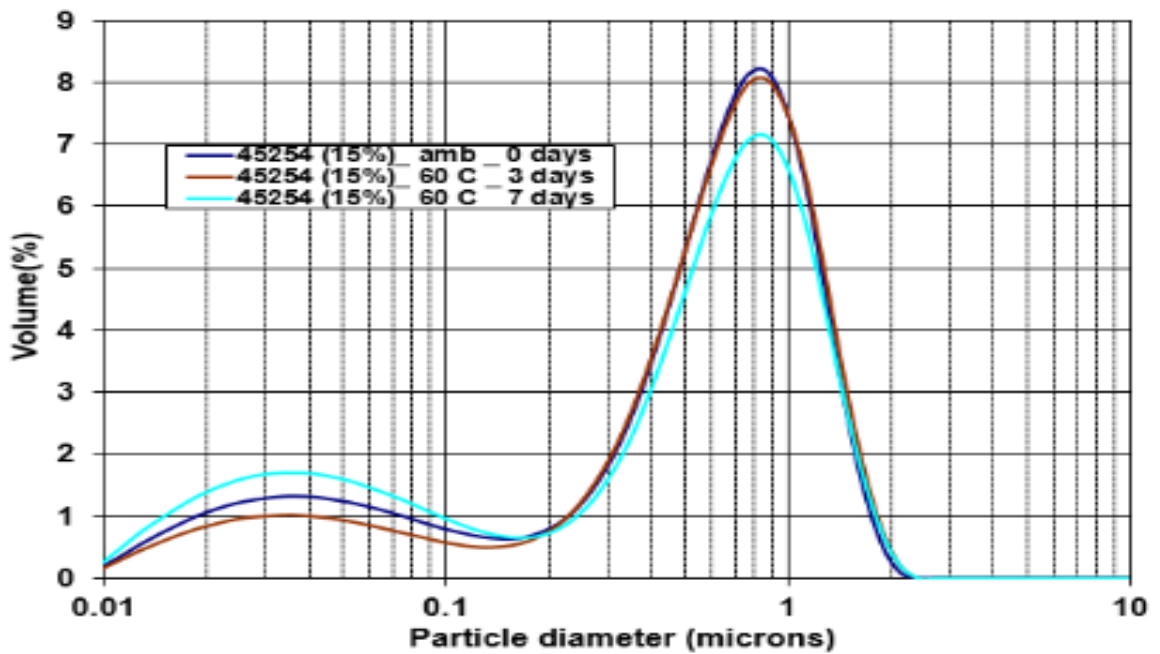


Figure.3.17. Particles size distribution of *A. nilotica* var *tomentosa* gum (15%) from Blue Nile state under different storage time at 60C

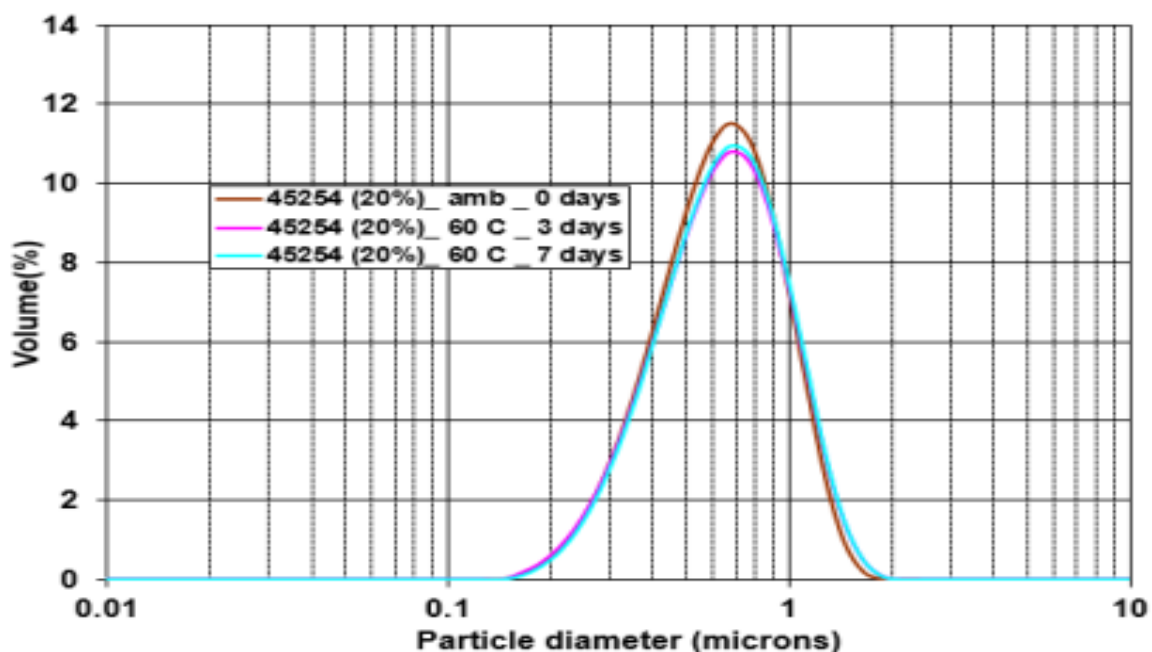


Figure.3.18. Particles size distribution of *A. nilotica* var *tomentosa* gum (20%) from Blue Nile state under different storage time at 60C°

Emulsification stability was evaluated by the change in the particle size of emulsion after acceleration test. Emulsion stability index (ESI) was calculated according to PHRC grading system using the equation:

$$ESI = d_{0.5 \text{ as prepared}} + (d_{0.5 \text{ 3 days@60C}} - d_{0.5 \text{ as prepared}}) + (d_{0.5 \text{ 7 days@60C}} - d_{0.5 \text{ as prepared}})$$

where $d_{0.5}$ is volume median diameter.

Emulsion stability index was taken as a parameter to designate the grade of the gum sample. Therefore, the gum samples which showed a change of 0.7 μm or less were classified as grade 1 (good emulsifier). A change between 0.7–0.85 μm was classified as grade 2. The less stable emulsions which showed a change $>0.85 \mu\text{m}$ were allocated grade 3 (poor emulsifier).

The droplet size and size distribution of different concentration (5%, 10%, 15%, 20%) for *A. nilotica* var. *tomentosa* from Sinnar, and Blue Nile state respectively, before and after the accelerated breakdown procedure were shown in Figures (3.11 to 3.18) and Table (3.5).

Figures (3.12, and 3.16) compared with (3.19 to 3.20) show that gum from *A. nilotica* var. *tomentosa* has a functional ability to act as emulsifier and stabilizes oil-in-water emulsion similar to *A. nilotica* var. *nilotica* gum *A. senegal*.

Although the droplet size of *A. nilotica* var. *tomentosa* emulsion was larger than that of *A. senegal*, the gum of *A. nilotica* stabilize dispersed particles of oil droplets in aqueous system and it is able to form highly stable emulsions in the same manner as gum arabic. Results clearly showed that no change was found in most emulsions during the incubation for 7 days at 60°C. In terms of particle size distribution profile for 10% emulsion, *A. nilotica* var. *tomentosa* gum produced Gaussian profiles which were very stable on storage. The suitable oil droplet size of *A. nilotica* var. *tomentosa* gum compared to *A. nilotica* var. *nilotica* gum, may be a result of sufficient pressure applied during homogenization, and larger oil droplet size of *A. nilotica* var. *tomentosa* gum compared to *A. senegal* may be a result of insufficient pressure applied during homogenization.

The applied high pressure plays an important role on the final oil droplet size. (Aoki *et al*, 2007). In their study, Castellani *et al*, (2010) concluded that the parameter which exerted the greatest influence on the final oil droplet size is the high pressure applied during homogenization. For a fixed emulsifying system (oil concentration and emulsifier) there is a maximum interfacial area which can be covered by the emulsifier, and to generate this area the corresponding amount of energy must be supplied (McClements, 1999). Perrier-Cornet *et al* (2005) found that using multiple passes of whey protein concentrates in the high pressure jet (three cycles) leads to a smaller droplet size compared to a single treatment.

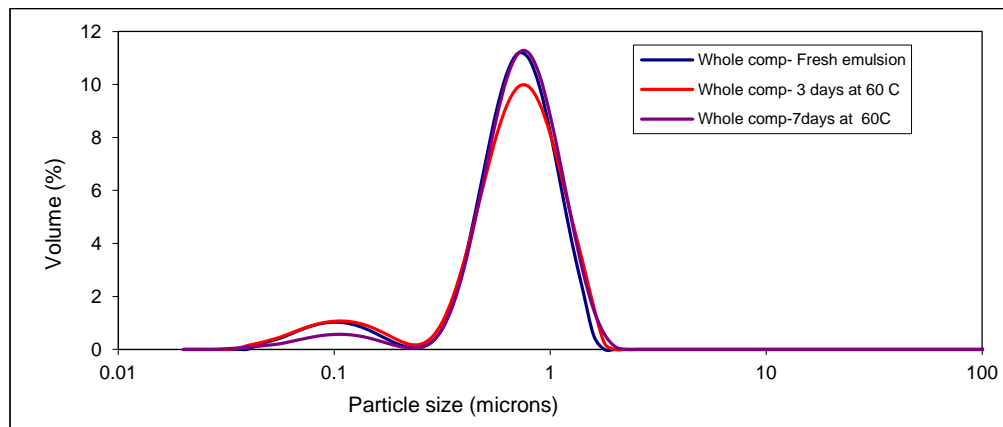


Figure.3.19: Particle size distributions of *Acacia nilotica* var. *nilotica* emulsion samples (Amira, 2011)

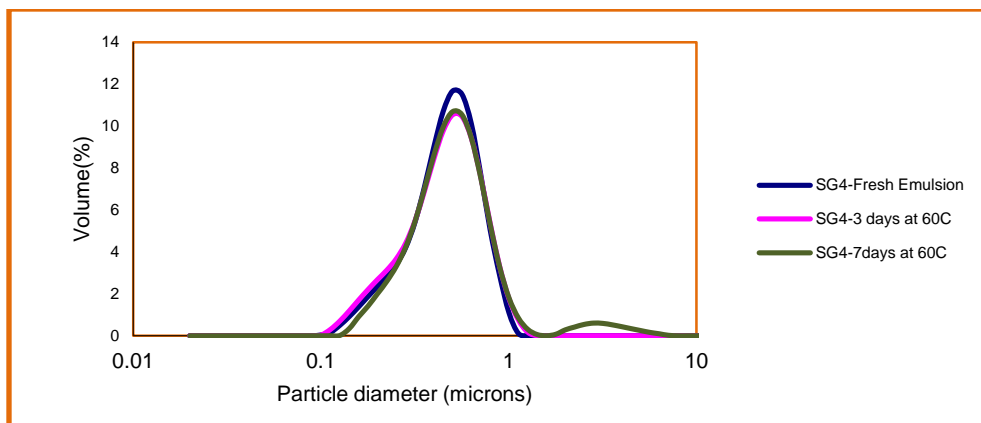


Figure.3.20: Particle size distributions of *A. senegal* (SG) emulsion at different conditions (Younes 2010)

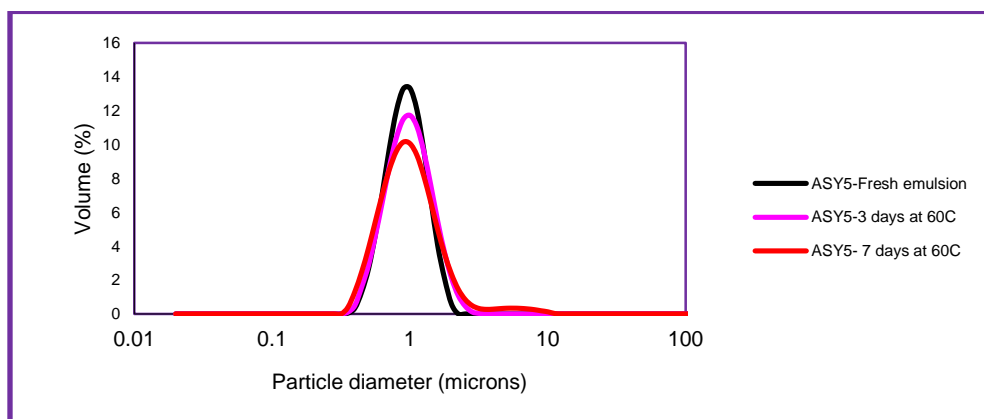


Figure.3.21: Particle size distributions of *A. seyal* (ASY5) emulsion at different conditions (Younes 2010)

A. nilotica var. *tomentosa* gum has higher molecular weight in general and a higher molecular weight of AGP and smaller amount of nitrogen content as *A. nilotica* var. *nilotica* gum (Amira, 2011), compared with *A. senegal*. The long term stability on emulsion offered by the gum of *A. nilotica* var. *tomentosa* may be due to emulsion concentration which is directly proportional to the emulsion stability as shown in Fingers (3.11 to 3.18). Also may be due to the AGP fraction increase in the first peak, it established that there is a direct relationship between the proportion of the AGP component and emulsification stability.

Table 3.6: Emulsion stability index (ESI, μm) and grade of *Acacia nilotica* var. *tomentosa* gum

Sample code	Emulsion concentration	Initial VMD (μm)	ATST VMD (μm) after 3 days @60°C)	ATST VMD (μm) after 7 days @60°C)	ESI (μm)	Grade
SCo5	5%	0.54	0.735	0.707	1.156	3
	10%	0.612	0.627	0.63	0.645	1
	15%	0.479	0.496	0.501	0.518	1
	20%	0.436	0.43	0.43	0.426	1
BNCo4	5%	0.862	1.53	3.55	4.218	3
	10%	0.523	0.609	0.666	0.752	2
	15%	0.669	0.724	0.636	0.691	1
	20%	0.687	0.707	0.711	0.731	2

*ATST: Accelerated temperature stress test for 3 and 7 days at 60 °C.

* VMD: Volume Median Diameter

Another reason for the stability of emulsion of *A. nilotica* var. *tomentosa* gum is due to uronic acids which have also been suggested to contribute to emulsion-stabilizing properties of polysaccharides, as has been reported for some galactomannans (Garti, 1994) and xanthan gum (Ikegami *et al.*, 1992). It has been suggested that there is some correlation between protein content of gum arabic and interfacial tension at equilibrium (Dickinson *et al.*, 1988).

There does not appear to be a direct correlation between nitrogen content and emulsifying effectiveness. Rather it appears that it is the proportion of the three main components which controls the emulsification behaviour (Dickinson *et al.*, 1988 and Dickinson *et al.*, 1991). The general view is that it is the AGP fraction which determines the emulsifying and interfacial properties of the gum (Fauconnier *et al.*, 2000, Randall *et al.*, 1988).

Since the protein content of *A. nilotica* var. *tomentosa* gum is very small (~0.28 – 0.51%) compared to *A. senegal* gum (~2.4%), the most suitable explanation of the high stability of emulsion offered by the gum of *A. nilotica* var. *nilotica* is a "Thin Oblate Ellipsoid" model of arabinogalactan fraction (Sanchez *et al.*, 2008).

The results show, emulsions of *A. nilotica* var. *tomentosa* gum have different grades of different Concentration.

3.13. Rheological properties

3.13.1. Viscosity shear rate

The effect of shear rate on viscosity, at 25°C, for *A. nilotica* var. *tomentosa* gum solutions of different concentrations (25%, and 50%) is shown in Figures (3.23, 3.24, and 3.25).

Figure (3.23) illustrates the viscosity-shear rate profile at 25% concentration. The flow curves increasing shear rates showed that the apparent viscosity (η_0 , Pa.s) decreased as the shear rate increased. After a sharp reduction ($\sim 1 \text{ s}^{-1}$), the viscosity change was smoothed at high shear rates ($\sim 100 \text{ s}^{-1}$). 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 0.1 s^{-1} . At intermediate shear rates (above roughly $\sim 10 \text{ s}^{-1}$) a trend to a high-shear Newtonian plateau was observed. This flow behaviour is quite similar from a qualitative point of view to that exhibited by several aqueous dispersions of different gum exudates.

In 25% solution, a shear-thinning behaviour was observed at very low shear rate that may be regarded as arising from modifications in the macromolecular organization of the solution as the shear rate changes. With increasing shear rate, the disruption predominates over formation of new entanglements, molecules align in the direction of flow and the viscosity decreases (Dakia *et al.*, 2008). Similar shear-thinning flow behaviour has been reported for *A. nilotica* var *nilotica* gum (Amira, 2011) Figure (3.22), and gum arabic (Williams *et al.*, 1990, Mothé *et al.*, 1999, Sanchez *et al.*, 2002). 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 the gum solutions. The freedom of movement of individual chains is progressively restricted and consequently increases the time needed to form new entanglements to replace those destroyed by the external deformation. Therefore, the shear rates values for which the behaviour becomes shear-thinning decrease as the concentration increases. At concentrations of 50% solutions, gum exhibit Newtonian flow. Therefore, the rheological behaviour of gum solutions approach Newtonian character as the gum concentration increases, Figure (3.24). Newtonian behaviour were expected as a result of the relatively compact conformation of branched gum (Tanaka *et al.*, 2006). The apparent viscosity values increase when gum concentration rises,

The effect of concentration on viscosity has also been observed for gum exudates from *A. senegal* (Mothé *et al.*, 1999) and *A. tortuosa* (Munoz *et al.*, 2007). In gum arabic, the fact that solutions of high concentration (50%) and low viscosity can be obtained has led to its extensive use in confectionery products.

Acacia nilotica gum solutions exhibit a high viscosity at low shear, shear thinning properties at higher shear rates and eventually a high-shear rate Newtonian region similar to that found for gum arabic. The breakdown of microstructures can be enhanced with increasing the applied shear rate while the relevant rebuildup occurs with the decrease of shear rate. The rheograms were best fitted with the Sisko model ($\eta = \eta_{\infty} + K \dot{\gamma}^{n-1}$). Figure (3.25), shows the viscosity of solutions at the same concentration was quite similar at higher shear rates.

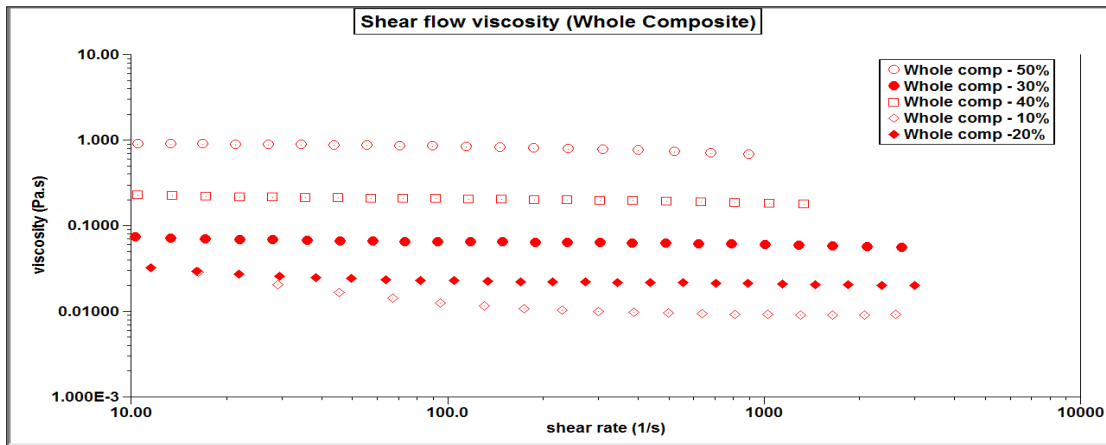


Figure 3.22: Viscosity-Shear rate profile of *Acacia nilotica* var. *nilotica* gum solutions at 10, 20, 30, 40 and 50 % concentration (Whole comp),(Amira, 2011)

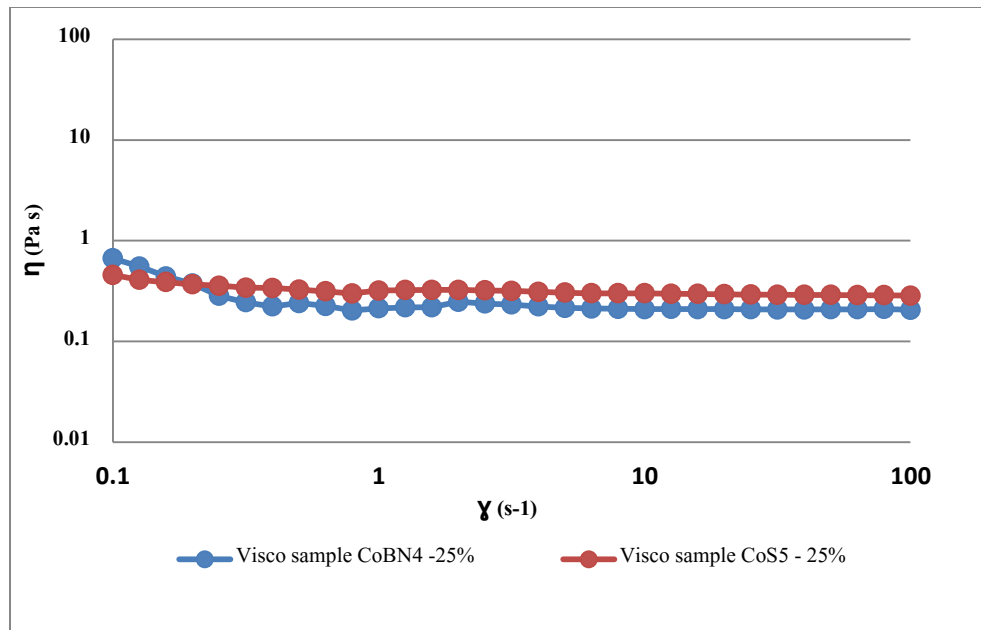


Figure 3.23: Viscosity-Shear rate profile of *A. nilotica* var. *tomentosa* gum solutions at 25% concentration for composite samples (whole) from Sinnar (*CoS5*), and Blue Nile state (*CoBN4*).

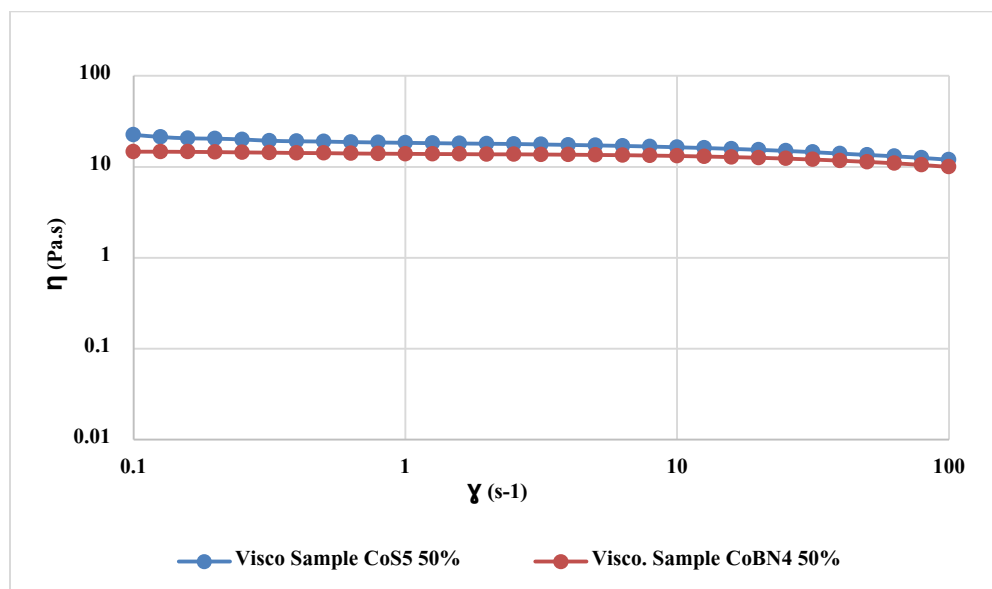


Figure 3.24: Viscosity-Shear rate profile of *Acacia nilotica* var. *tomentosa* gum solutions at 50% concentration for composite samples (whole) from Sinnar (*CoS5*), and Blue Nile state (*CoBN4*).

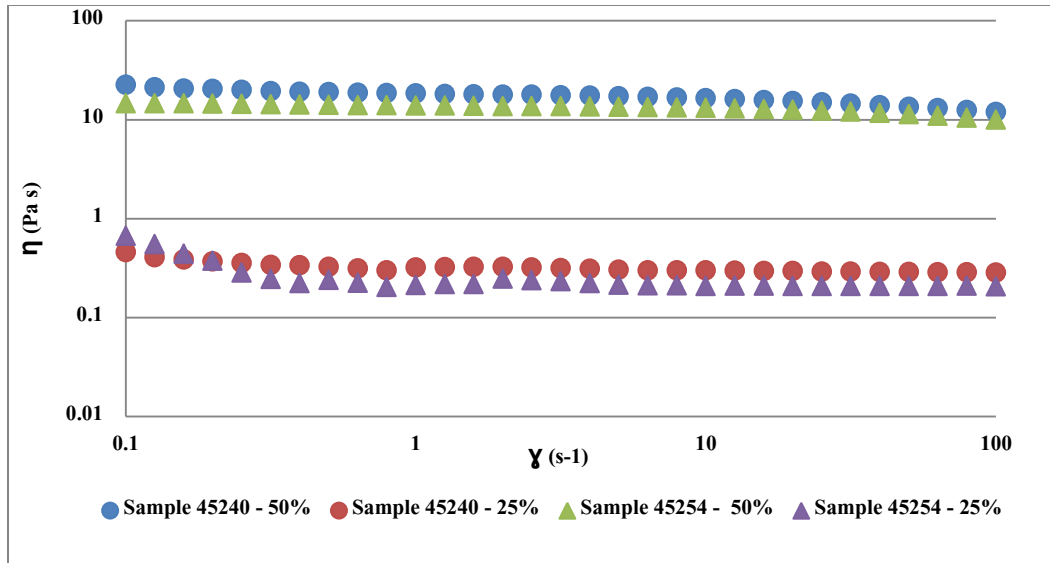


Figure 3.25: Comparison of viscosity-Shear rate profile of *Acacia nilotica* var. *tomentosa* gum solutions between 25%, and 50% concentration for composite samples (whole) from Sinnar (CoS5), and Blue Nile state (CoBN4).

The gum solution structure was almost completely disrupted, exhibiting less dependency of the viscosity to the shear applied. The degree of shear-thinning nature can be indicated by the flow behavior index (n), which decreases when shear-thinning increases. The flow behavior index <1 , reflect the shear-thinning nature of the gum solution. The smaller flow behavior index for samples indicate that the shear thinning behavior was more pronounced in these samples. The flow behavior index for the samples of high concentration (50%) is almost equal to one which is Newtonian behaviour.

In terms of the consistency coefficient (k), the solutions of high concentration (50%) showed the highest consistency. The consistency coefficient (k) is an indicator of the solution viscous nature. Aqueous dispersions of gum arabic from *A. senegal* are known to show low viscosities up to a gum concentration of 30% wt (Williams *et al.*, 1990), although slight shear thinning (non-Newtonian) response can already be observed for the 10% wt solution at 25°C (Al-Assaf *et al.*, 2008).

3.13.2. Dynamic Rheological Behaviour

A. nilotica var. *tomentosa* gum solutions exhibit viscoelastic properties at different concentrations which determined by using oscillatory testing. Mechanical spectra of solutions revealed a typical liquid-like behaviour (Figures 3.27 to 3.29). The loss modulus (G'') was higher than the storage

modulus (G'), the energy used to deform the material is dissipated viscously and the sample exhibits liquid-like behaviour. The evolution of G' and G'' as a function of angular frequency followed a power law behaviour with exponents less than 2 for G' and less than 1 for G'' which classically found for viscoelastic liquids, revealing that the *A. nilotica* var. *nilotica* gum solutions were structured liquids. The moduli showed less frequency dependence at lower frequency range and relatively higher frequency dependence at higher frequency range..

The effect of temperature in the dynamic rheological behaviour of both *A. senegal* and *A. seyal* was studied by Hassan (2000). *A. seyal* gum at temperatures less than or equal to 60°C reflects a viscous behaviour, where G'' is greater than G' , i.e. energy was dissipated, irrecoverably, as frictional heat. At temperature equal to 70°C the behaviour became elastic at the low frequency region. Also *A. senegal* at temperatures less than or equal to 60°C shows viscous behaviour, but at 70°C *A. senegal* had a completely different behaviour. The gain modulus G' is greater than G'' . At high temperature the molecular motion increases hence enhancing the probability of molecular interaction. High temperatures facilitate hydrophobic interactions a matter that might contribute positively to stabilization of molecular aggregation or networks that might have been formed due to entanglements.

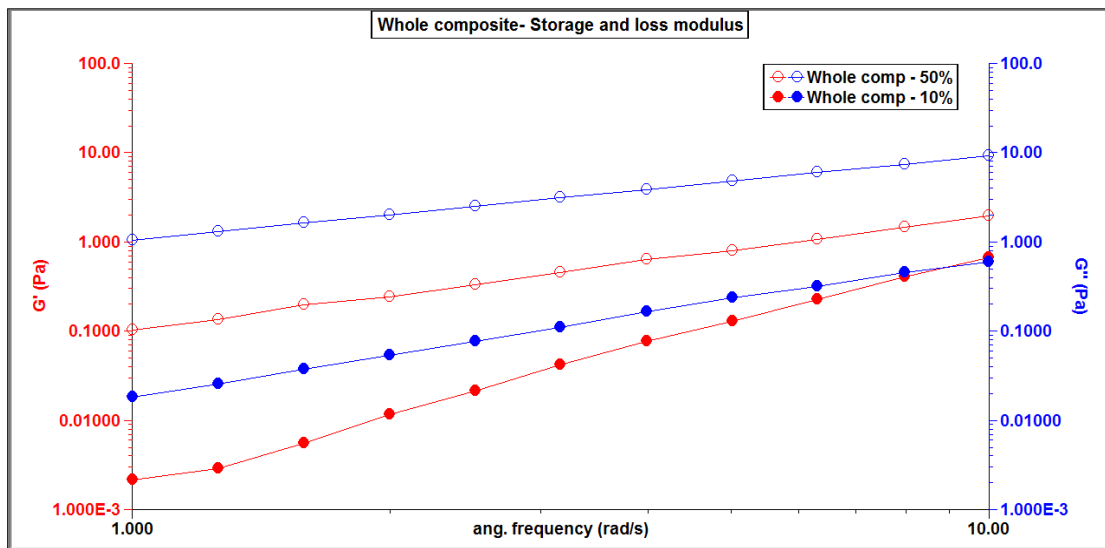


Figure 3.26: The dynamic rheological behaviour of *Acacia nilotica* var. *nilotica* gum solutions at 10 and 50% concentration (whole composite) Amira, (2011)

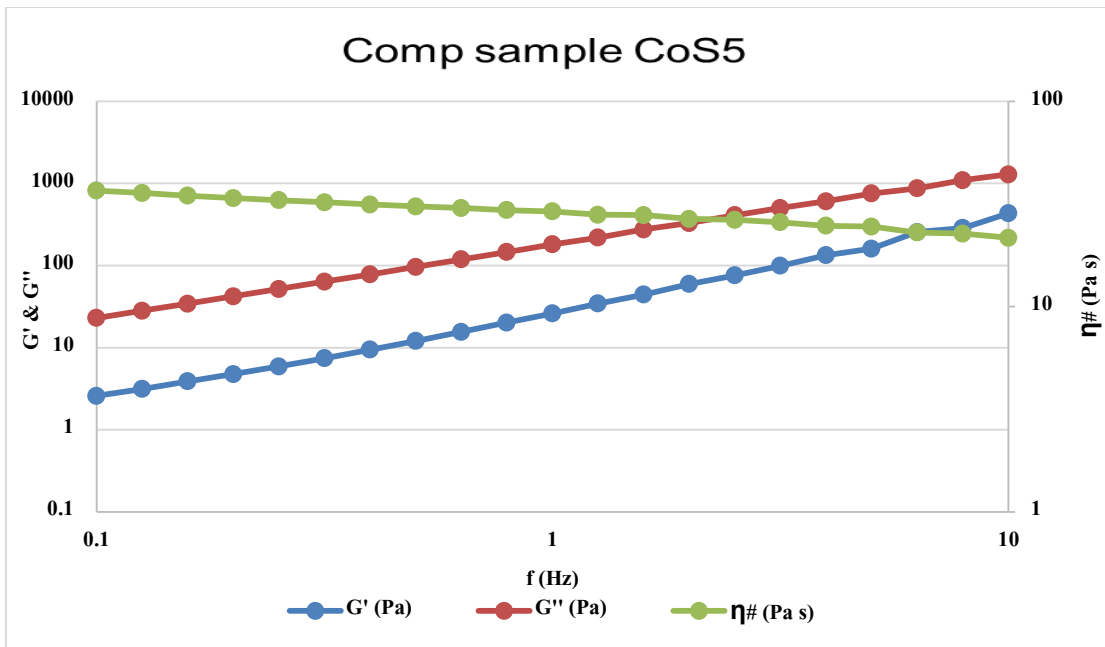


Figure 3.27: The dynamic rheological behaviour of *A. nilotica* var. *tomentosa* gum solutions at 50% concentration from Sinnar State *CoS5* (whole composite)

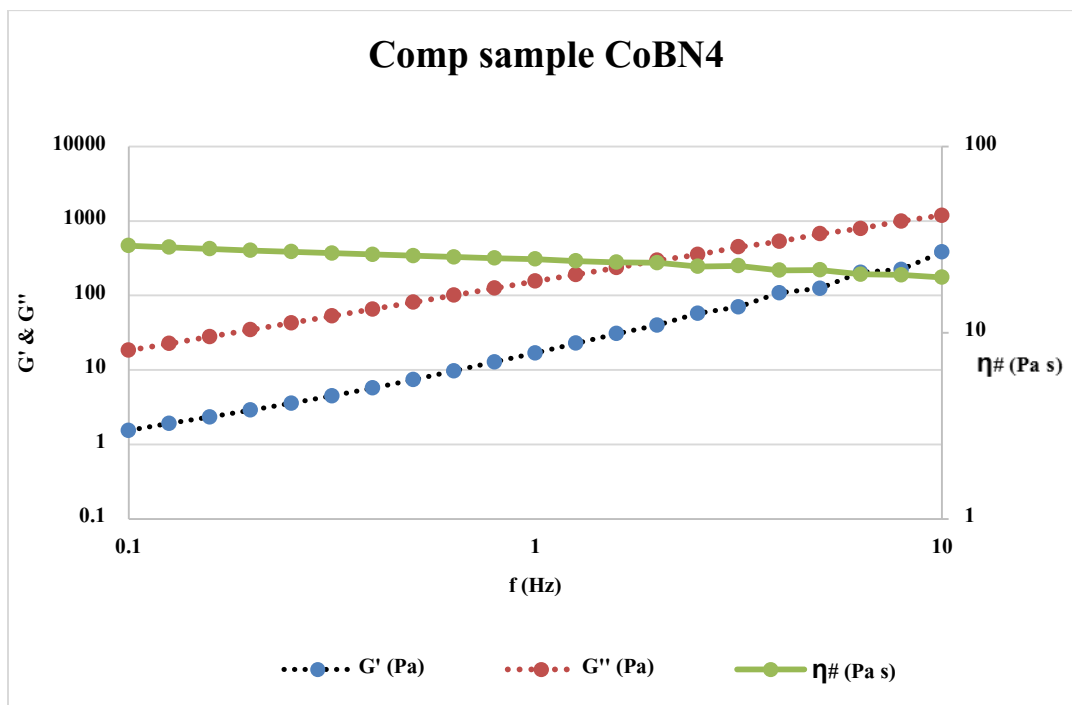


Figure 3.28: The dynamic rheological behaviour of *A. nilotica* var. *tomentosa* gum solutions at 50% concentration from Blue Nile State *CoBN4* (whole composite)

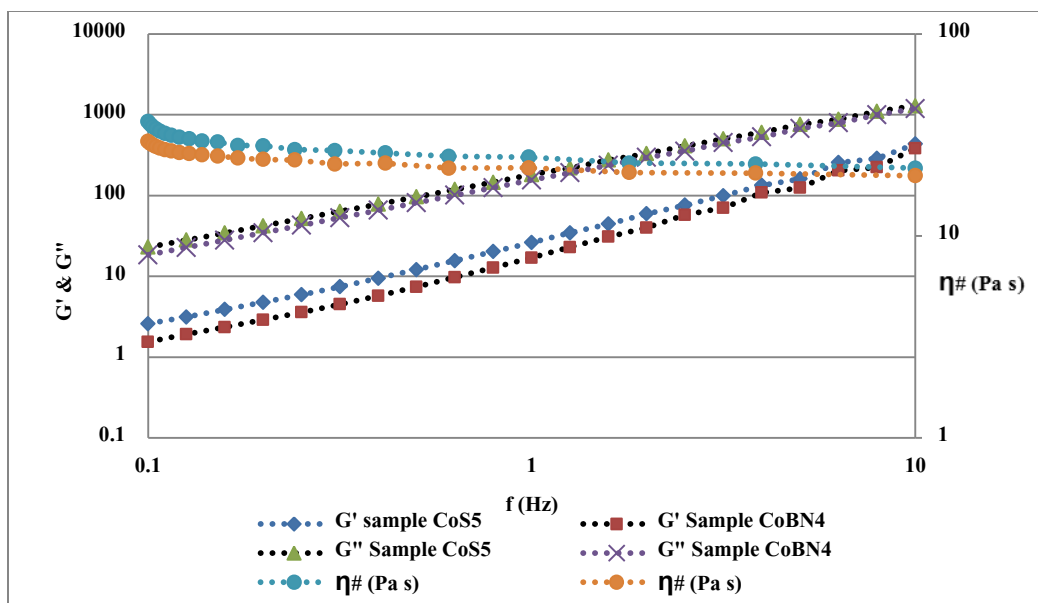


Figure 3.29: Comparison between dynamic rheological behaviour of *A. nilotica* var. *tomentosa* gum solutions at 50% concentration from Sinar State *CoS5* Blue Nile State *CoBN4* (whole composite)

3.14. Conclusion

Investigation of physicochemical properties of *A. nilotica* var *tomentosa* gum shows, slightly different in compared with *A. nilotica* var *nilotica* gum and high difference for *A. senegal*, and *A. syal*, but It's contained identical calorific value in compared with them. The calorific value was suitable for human to use gum as food additives. *A. nilotica* var *tomentosa* gum exhibit identical Shear flow viscosity, and Dynamic rheological behaviour compared with *A. nilotica* var *nilotica* gum (Amira, 2011). They show Newtonian flow behaviour at high concentration, and exhibits liquid-like behaviour.

A. nilotica var *tomentosa* gum, exhibit high molecular weight distribution (5.3×10^6) compared with *A. senegal* var *senegal*, and *A. seyal* var *seyal*, and different to that of *A. nilotica* var *nilotica* gum. *A. nilotica* var *tomentosa* gum classified as a good emulsifier, and the different concentrations exhibited different emulsion stability with different droplet size. The more concentration the smaller droplet size and more stable emulsion.

3.15. References

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