

**PHYSICOCHEMICAL AND RHEOLOGICAL MODELING OF  
SYNERGISTIC INTERACTION OF SOME PLANT GUM EXUDATES.**

**By**

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**AUGUST, 2014**

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**By**

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**DEPARTMENT OF CHEMISTRY,  
FACULTY OF SCIENCE,  
AHMADU BELLO UNIVERSITY, ZARIA  
NIGERIA**

**AUGUST, 2014**

## DECLARATION

I declare that the work in this Thesis entitled “Physicochemical and Rheological Modeling of Synergistic Interaction of some plant gum Exudates” has been carried out by me in the Department of Chemistry. The information derived from the literature has been duly acknowledged in the text and a list of references provided. No part of this thesis was previously presented for another degree or diploma at this or any other Institution.

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Date

## CERTIFICATION

This thesis entitled **PHYSICOCHEMICAL AND RHEOLOGICAL MODELING OF SYNERGISTIC INTERACTION OF SOME PLANT GUM EXUDATES** by **DAVID EBUKA ARTHUR** meets the regulation governing the award of the degree of M.Sc Physical Chemistry of the Ahmadu Bello University, and is approved for its contribution to knowledge and literary presentation.

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## DEDICATION

This work is dedicated to my mom, you are an embodiment of love.

## ACKNOWLEDGMENT

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## ABSTRACT

The visco-elastic properties of *Khayasenegalensis* (KS gum), *Anacardium occidentale* (AO gum) and *Acacia senegal* (AS gum) blends in dilute solution were investigated. The gums were evaluated for intrinsic viscosity and the elastic component. Molecular conformation of the complex of AS-KS was assessed by the power law and the results showed that the b values for AS 40%—KS 60% and AS 20%—KS 80% given as 1.98 and 1.67 which were significantly larger than that of the pure gums and all other blend used within the course of this research. A 20% AS—80% KS blend exhibited the strongest attraction between Khaya gum and gum Arabic molecules since the blend had the highest value of intrinsic viscosity (69.1 dL/g), while 80% AS—20% AO blend had the least attraction as evidenced by the polymer miscibility coefficient (0.0009), the elastic component and a positive Huggins coefficient found to be less than one, indicating there is no aggregation in the blend. The power-law model was successfully applied to predict the molecular conformation of AS, AO and KS alone in dilute solutions and they exhibited random coil conformation except for AO gum. Their hydrodynamic interaction value indicates that the blends become more soluble in water when more concentration of gum arabic is added to the blends (AS:AO, AS:KS). The power-law coefficient decreased with an increased addition of the KS fraction in the blends, suggesting a more flexible AS-KS, AS-AO complex dependent on KS and AO respectively. FTIR and GCMS analyses were carried out for proper characterization of the components of the gum blends, other analysis included rheological study on the gum with corresponding effects from increased temperature and effects of added salts. Physicochemical properties of the gum blends as well as the pure gums were determined, these included salinity, pH, turbidity, total dissolve solid, conductivity, density, colour and solubility.

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## CHAPTER 1

### INTRODUCTION

#### 1.1 Background of the study

Gums are considered to be pathological products formed following injury to the plant or owing to unfavorable conditions, such as drought, by a breakdown of cell) (Jani *et al.*,2009). They are complex carbohydrate derivatives of a polysaccharide nature and are either soluble in water as in the case of gum arabic or form mucilages by the absorption of large amounts of water (gum tragacanth). Their principal use is in foodstuffs owing to their ability to impart desired qualities to foods by influencing their viscosity, body and texture; most frequently in confectionery food, flavouring and soft drinks. They also have pharmaceutical and industrial applications as demulcents, adhesives in pill manufacture, lithography, paints, inks, corrosion inhibitors and as emulsifying agents. The use of natural gums taken from the exudates and extracts of plants have been given a strong attention due to the many and lucrative possibilities for industrialization and to the excellent international market, example being gum arabic which in current production potential is around 30,000 to 40,000 tonnes per annum, of which bulk (80%) originates in Sudan; Nigeria being the second largest producer (Da silva *et al.*, 1992). Virtually all gum arabic in the Sahelian zone is exported, either immediately or after a period of storage or stockpiling. Sudan dominates the world exports, accounting for 70% to 80%, the balance being accounted for by the Sahelian countries of West Africa (Nigeria, Mali, Niger, Burkina Faso, Chad, Tanzania and Kenya). One billion pounds are consumed in the United States each year where the growth in demand exceeds 8% per year (JECFA/FAO, 1988). Another example is the cashew gum, which by natural exudation or by means of incisions, produces a gum or resin of a yellowish color, soluble in water, and which presents a great potential for industrialization, appears on the trunk

and branches of the cashew tree. It is similar to gum arabic and may be used as a substitute for liquid glue in book binding, in the pharmaceutical cosmetic industry as an agglutinant for capsules and pills, and in the food industry as a stabilizer of juices, beer and ice cream, as well as for clarification of juices, and can also be utilized in the making of cashew wine (JECEFA/FAO, 1986).

Besides proving to be strong wood glue when mixed with water, it presents a fungicidal and insecticidal action, and because of this is much used in book binding. Research already exists on its utilization in the making of inks and varnishes (JECFA/FAO, 1988).

Cashew gum extraction represents one more source of revenue for the producer, in addition to the cashew nut and the peduncle, as well as an alternative for the utilization of unproductive cashew trees, in phase of decline or senescence (Jani *et al.*, 2007).

From a wider point of view, cashew gum not only can end the importation of gum arabic, which costs Brazil US\$ 1,900,000/year, but can also become an export item (Jani *et al.*, 2007).

The Embrapa Tropical Agro industry, which develops the technology, invites potential industrial partners for the processing and industrialization phases of the product and, later, for marketing. This is a unique opportunity to gain a potentially significant market for importation substitution and for participating in the external market.

These gums found wider application because of their physical, rheological and chemical properties (such properties include solubility, water sorption, swelling capacity, pH, effect of temperature, and viscosity among others) (De Paul *et al.*, 2001)

There is increasing demands for gums globally because of its vast application, which causes the increase in prices of the existing gums in the local and international market. For the

price to be stable and less expensive there is need to look for alternative or discoveries of more suitable natural gums which will be of the same quality or even surpass the existing ones.

Studies on the physicochemical and rheological properties of some gum exudates have been carried out. Gum exudates from *Khaya senegalensis* plants grown in northern Nigeria were investigated for its physicochemical properties such as pH, water sorption, swelling capacity and viscosities at different temperatures using standard methods as reported in literature. It was found that Khaya gum appeared to be colourless to reddish brown translucent tears. 5 % w/v mucilage has pH of 4.2 at 28 °C. The gum is slightly soluble in water and practically insoluble in organic solvents. Water sorption studies revealed that it absorbs water readily and is easily dehydrated in the presence of desiccants. A 5 % w/v mucilage concentration gave a viscosity value which was unaffected at temperature ranges (28 – 40°C). The results indicated that the swelling ability of *Khaya senegalensis* gum may provide potentials for its use as a disintegrant in tablet formulation, as a hydro gel in modified release dosage forms and the rheological flow properties may also provide potentials for its use as suspending and emulsifying agents owing to its pseudo plastic and thixotropic flow patterns.

Mhinzi (2002) analysed gum samples from three selected *Albizia* species from Tanzania and determined their commercial potential by comparing their properties with those of *Albizia zygia* and *Acacia* gums. The properties of the gum exudates from *Albizia amara*, *Albizia pertesiana* and *Albizia harveyi* were found to be similar to those of *A. zygia* gum except that their aqueous solutions possess slightly lower viscosity and higher levels of tannin. The *Albizia* gums were much less soluble in water than acacia gums; However their methoxyl contents and acid equivalent weights (AEW) were similar to those of some *Acacia* gums.

Rheological properties of Xanthan and locust beans gums have been studied by Higiroy *et al.* (2006) and the gums were found to obey Huggins and power law models and from the rheological modeling of the gums, the conformation of the gums were established. Xanthan gum interacts with galactomannans to form mixed gels with high viscosity at low-total-polysaccharide concentrations (Tako *et al.*, 1984), and this interaction is more pronounced with locust bean gum (LBG) than with any other polysaccharide or galactomannan (Dea *et al.*, 1977). The interaction between xanthan and LBG is largely exploited in food applications in which thickening or gelling is desired. Considerable work has been published to elucidate the mechanisms behind xanthan and LBG interaction (Cairns *et al.*, 1986; Cairns *et al.*, 1987; Tako *et al.*, 1984; Wanget *al.*, 2002; Williams *et al.*, 1991). Physical and physicochemical techniques have been used to study xanthan–galactomannans interaction, and results demonstrated the existence of an “order (helix)–disorder (coil)” transition for xanthan; this transition responds to changes in ionic strength and temperature, and may play a major role in such interactions (Morris, 1995a). High temperatures favor the “disordered” transition, whereas high ionic strength favors the “ordered” transition (Morris, 1995a).

Lopes *et al.*, (1992) studied the interaction of xanthan and guar gum at low temperature in water and  $2 \times 10^{-2}$  M NaCl by using viscosity methods. The authors noticed a small synergistic effect between the two gums in  $2 \times 10^{-2}$  M NaCl; the effect became more pronounced in water. They concluded that xanthan adopted a disordered conformation in water, whereas the conformation was in an ordered form in  $2 \times 10^{-2}$  M NaCl. These findings were supported by Dalbe (1992); he used small deformation oscillation methods to study xanthan–glucomannan mixture and reported that addition of  $8.56 \times 10^{-2}$  M NaCl or  $6.71 \times 10^{-2}$  M KCl to gum mixtures led to a dramatic reduction in gel strength, which was not altered by further addition of electrolytes. Similar results

were reported by Wang et al. (2002). The authors used rheological methods to study the conformational role of xanthan in interaction with LBG, and reported a decrease in viscosity and texture strength for xanthan–LBG solutions and gels, respectively, associated with the addition of  $4 \times 10^{-2}$  M NaCl. In the absence of electrolytes, the xanthan molecules may self associate to reduce the interfacial energy.

Early work suggested that a specific interaction occurred between the ordered xanthan molecule and the galactomannan chain (Dea and Morrison, 1975; Dea *et al.*, 1977; Morris *et al.*, 1977; McCleary 1979). This interaction depended on the mannose/galactose ratio, as well as on the fine structure of the galactomannan. Tako *et al.*, (1984), Tako and Nakamura (1985) and Tako (1991) reported that the intermolecular interaction between xanthan and galactomannans occurred between the side chains of xanthan and the backbone of galactomannans, as in a lock-and-key model. Cairns *et al.*, (1986, 1987), by means of X-ray fiber diffraction, suggested that gelation occurred only if xanthan was first denatured by heating above the order-disorder transition temperature and the interaction occurred between the xanthan backbone in an extended 2- fold cellulose-like conformation and LBG in a similar 2-fold conformation. Recent evidence strongly suggested that destabilization of the xanthan helix facilitated xanthan and galactomannan binding (Cheetham and Mashimba, 1988; Zhan *et al.*, 1993; Foster and Morris 1994; Goycoolea *et al.*, 1994).

It has been shown that gelation could occur when xanthan and LBG were mixed at temperatures below the xanthan helix-coil transition (Williams *et al.*, 1991; Mannion *et al.*, 1992; Foster and Morris, 1994; Goycoolea *et al.*, 1994); the melting temperatures of the mixed gels were independent of ionic strength (Zhan *et al.*, 1993) and xanthan conformation (Goycoolea *et al.*, 1994); the modulus of the mixed gels increased with increasing disorder of the xanthan helix

(Zhan *et al.*, 1993). Hence, it has been suggested that galactomannan acts like a denaturant to disturb the helix-coil equilibrium of xanthan and to displace the ordered conformation of xanthan to the conformation required for efficient binding to it within the heterotypic junctions (Zhan *et al.*, 1993; Goycoolea *et al.*, 1994; Morris *et al.*, 1994; Morris, 1996; Morris, 1996).

To date, much work has been accomplished on the gelling properties of gums and their inherent visco-elastic properties, as evidenced by many published papers; but the evaluation of gums interaction in solution has been studied to a lesser extent (Casas *et al.*, 1999; Cuvelier and Launay, 1986), and most of the research was performed by using the Ubbelohde or rotational viscometer.

### **1.1 Aim of the study**

The aim of the present study is to investigate and model the functional properties of the blends prepared from *Anacardium occidentale*, *Khaya senegalenses* and *Acacia senegal* gum exudates using recommended methods of analyses.

### **1.2 Objectives of the study**

The objectives of the study were as follows:

- i. to collect, identify and purify gums from *Anacardium occidentale* L, *Khaya senegalensis*, *Acacia Senegal*;
- ii. to investigate physicochemical (colour, pH, absorbance, solubility in various solvents, turbidity, total dissolved solid content, conductivity and salinity) and rheological properties of the gum exudates as well as their blends using using recommended methods and appropriate instruments;

- iii. to investigate the structure and surface morphology of the natural polymers (gum exudates) blends in aqueous media;
- iv. to adequately model Rheological properties of the gum blends using Huggins, Kraemer, Arrhenius, Tanglertpaibul and Rao models;
- v. to determine the active functional groups in each of the gums using FTIR spectrophotometer;
- vi. to carry out rheological studies on the gums using different types of viscometer and a rheometer. From rheological data, effect of viscosity on temperature, concentration, pH, ionic strength of various electrolyte ( $K^+$ ,  $Al^{3+}$ ,  $Br^-$  and  $Cl^-$ ) and conformations of the gums (coil-coil overlap) shall be modeled using appropriate equations; and
- vii. to determine and model kinetic and thermodynamic parameters of flow for the gums and these shall include activation energy of flow, activation entropy and enthalpy of flow and activation free energy of flow.

### **1.3 Justification for the study**

This research entails the effect of ionic environment on the interaction of plant gums in dilute solution as well as other conditions: temperature, salt and acid etc. there by improving on the search for alternative gums with better quality through polymer blending and hence reduce the increasing demands for gums globally as well as their prices in the local and international market.

## 1.4 Gums selected for study

### 1.4.1 *Anacardium occidentale* L

The cashew is a tree in the family Anacardiaceae. Its English name cashew is derived from the Portuguese name for the fruit of the cashew tree, caju, which in turn derives from the indigenous Tupi name, acajú. Originally native to Northeast Brazil, it is also called kaju in Yoruba, Fisa in Hausa and Kantonoyo in Igbo.

Cashew tree (*Anacardium occidentale* L.) resin is synthesized in the epithelial cellslining pockets or canals and then secreted into these internalcavities. Synthesis generally occurs in all organs of the plant,with different quantitative composition; appearing to be geneticallycontrolled and little influenced by environmentalconditions. The gum is similar to gum arabic and may beused as to a substitute for liquid glue for paper, in the pharmaceutical/cosmetic industry and as an agglutinant for capsulesand pills (Bovin 1998; De Paula *et al.*, 1998 and Amadeo *et al.*,2003). Fifteen species of trees or perennialbushes compose the genus *Anacardium*, native of tropicalparts of South America and Central and of western India (Carver 1997 and León de Pinto 1994).

The exudate gum is a mixture of acid polysaccharides containing various metal ions as neutralized cations. The nature and content of these constituents depend on the composition of the soil upon which the trees grew. The major cations of *A.occidentale* L. are  $K^+$ ,  $Na^+$ ,  $Ca^{+2}$  and  $Mg^{+2}$ . The crude *A.occidentale* gum, containing these cations tends to be naturally transformed into Na salt, after purification or dialysis against NaCl (0.15 M) (De Paula *et al.*, 1998, Charlwood *et al.*, 1998, Carver 1997 and León de Pinto 1994).

#### **1.4.2 *Khaya senegalensis* gum**

*Khaya senegalensis*, commonly called African mahogany in English, ‘Homra’ in Arabic, ‘Dalehi’ in Fulani, ‘Madaci’ in Hausa, ‘ono’ in Igbo and ‘ogonowo’ in Yoruba, belongs to the Family, *Meliaceae*.

*Khaya senegalensis* is a tall plant of 15-30 meters in height and about 1 meter in diameter. It is recognized by its ever green crown. The crown has dark shiny pinnate leaves and characteristics round dark grey capsules. The bark is dark grey with small reddish tinged scales.

The plant is widely distributed in the riverine forest and is scattered within the highest rainfall savannah woodlands. In the first year of growth, the seedlings develop a strong deep tap root which makes it most drought resistant of all khaya species. The plant can be planted in swampy regions as it is very resistance to flooding. It remains dominant specie in most of its range except when removed by logging.

*Khaya* gum occurs in long, thin glass-like translucent fragments. The gum is colourless to light brown. It is known to contain highly branched polysaccharides consisting of D-galactose, L-rhamnose, D-galacturonic acid and 4-O-methyl-D-glucuronic acid (Aspinall and Bhattacharjee, 1970).

*Khaya* gum has been evaluated as a directly compressible matrix system for controlled release. The findings suggested that the gum could be useful in the formulation of sustained release tablets for up to 5 h and may provide a time independent release for longer periods when appropriately combined with hydroxypropyl methycellulose (Oluwatoyin, 2006). It has also been

evaluated for use as binder in paracetamol tablets and the findings suggested that, the gum can be developed into a commercial binding agent for particular tablets (Oluwatoyin, 2002).

### **1.4.3 *Acacia senegal* Gum**

Gum Arabic is obtained from tree called *Acacia senegal* which is leguminous tree, belonging to the family mimosaceae and genus which has triple spines at the base of the node while the bark is fissured, flaky and whitish grey in colour. The leaves are pinnate and alternate with 3-6 pairs of pinnae. Flowers are cream-coloured, fragrant and arranged in spikes, while the fruits or pods are flattened with straight edges. Although there are other members of gum-producing acacia species (like *A. seyal* and *A. albida*) the best gum is collected entirely from *Acacia senegal* known as *Acacia verec*.

Gum arabic as found in nature exists as neutral or slightly acidic calcium, magnesium or potassium salts of complex polysaccharide (Glicksman and Sand, 1973; Mantel, 1954)

Uncharged gum arabic acid molecules have an equivalent radius of  $555 \text{ \AA}$  and an effective volume of  $7.2 \times 10^{-6} \text{ cm}^3/\text{mole}$ .

The glycosidic bonds vary in stability, autohydrolysis of Arabic acid in water (pH 2) yields 34.4% L-arabinose, 14.2% L-rhamnose, and 3-O-D-galactopyranosyl-L-arabinose, and partially degraded gum Arabic. Further hydrolysis with mineral acid produced 42.1% D-galactose, 15.5% D-glucuronic acid, and 6-O-(β-D-glucopyranosyluronic acid)-D-galactose. Gum Arabic from different species contains the same sugar in varying proportion (Glicksman and Sand, 1973; Mantell, 1954; NTIS, 1972).

The main structural feature of gum Arabic is a backbone chain of (1-3)-linked D-galactopyranose units, some of which are substituted at the C6 position with various side chains. Three

aspects of the molecular structure are the various acid groups associated with rhamnose located on the periphery of the molecule, the branched framework of D-galactopyranose residues, and the positions of the molecule that give rise to acidic oligosaccharide fragments. The galactan framework contains numerous chains with (1-3)- linked units bearing (1-6)-linked side chain location of the (1-6)-linkages is uncertain, but some of the L-rhamnopyranose residues in gum arabic are joined (1-4) to glucopyranosyl-uronic acid residues (Glicksman and Sand 1973; Mantell, 1954).

Vendevelde and Fenyo (1985) noted that gum Arabic contains a low molecular mass protein rich fraction arabinogalactan protein complex and a low-molecular mass protein deficient fraction on arabinogalactan. Fincher *et al.*, (1983) suggested that the gum from *Acacia senegal* is an arabinogalactan-protein. The amino acids hydroxyproline and serine are the major constituents of the proteinaceous component of the gum.

## CHAPTER 2

### 1. LITERATURE REVIEW

#### 2.1.1 POLYMER BLENDING

The polymer industry traces its beginning to the early modifications of shellac, natural rubber (NR an amorphous *cis*-1,4-polyisoprene), gutta-percha (GP a semi-crystalline *trans*-1,4-polyisoprene), and cellulose. In 1846, Parkes patented the first polymer blend: NR with GP partially co-dissolved in carbon disulphide. Blending these two isomers resulted in partially crosslinked (co-vulcanized) materials whose rigidity was controllable by composition. The blends had many applications ranging from picture frames, table ware, ear trumpets, to sheathing the first submarine cables.

Polymer blends constitute about 36 wt% of the total polymer consumption, and their pertinence continues to increase. About 65% of polymer alloys and blends are produced by polymer manufacturers, 25% by compounding companies and the remaining 10% by the transformers.

#### 2.1.2 Benefits of Blending

The following material-related benefits can be cited:

- i. Providing materials with full set of desired properties at the lowest price.

- ii. Extending the engineering resins' performance.
- iii. Improving specific properties, viz. impact strength or solvent resistance.
- iv. Offering the means for industrial and/or municipal plastics waste recycling.

Blending also benefits the manufacturer by offering:

- i. Improved process-ability, product uniformity, and scrap reduction.
- ii. Quick formulation changes.
- iii. Plant flexibility and high productivity.
- iv. Reduction of the number of grades that need to be manufactured and stored.
- v. Inherent recyclability, etc.

### **2.1.3 Compatibilization in polymer blend**

The miscibility of polymer blends depends on the balance of small enthalpic and non-configurational entropic effects. Sensitivity of this balance to small variation of the macromolecular structure is illustrated in the series of papers on miscibility of model polyolefins (Rabeony *et al.*, 1998). Another example is provided by the photoisomerization initiated, reversible phase separation of poly (vinyl methyl ether)PVME blends with stilbene substituted polystyrene (Ohta *et al.*, 1998).

While miscibility is limited to a specific set of conditions, the immiscibility dominates and most polymers form immiscible blends that require compatibilization. Alloys' performance depends on the ingredients, their concentration, and morphology. The alloying process must result in stable and reproducible properties of the polymer blend. Thus, the morphology must either be stable, unchanged during the forming steps, or the changes must be well predicted. The alloying

makes use of an appropriate dispersing method (through mechanical mixing, solution or latex blending) and compatibilization.

The latter process must accomplish three tasks:

- i. Reduce the interfacial tension, thus finer dispersion,
- ii. Stabilize the morphology against thermal or shear effects during the processing steps.
- iii. Provide interphasial adhesion in the solid state.

The compatibilization strategies comprise:

- i. addition of a small quantity of co-solvent and a third component, miscible with both phases,
- ii. addition of a copolymer whose one part is miscible with one phase and another with another phase,
- iii. mechano-chemical blending, etc.

#### **2.1.4 Rheology of polymer blends**

Rheology by definition is the science of deformation and flow of matter. Rheological measurements provide useful behavioral and predictive information for various products in addition to knowledge of the effects of processing, formulation changes, and ageing phenomena (Ebewele, 2000).

Rheology is a branch of physics that deals with the deformation and flow of matter under stress. It is particularly concerned with the properties of matter that determine its behaviour when a mechanical force is exerted on it. Rheology is distinguished from fluid dynamics because it is concerned with the three traditional states of matters rather than only liquid and gases. Rheological properties have important implications in many and diverse applications. Often, an

additive is used to impart the desired flow behaviour. Among these, organoclay products, formed by the reaction of organic cations with smectite clays, are the most widely used additives for solvent based coatings. The often used cation, usually a quaternary ammonium salt, influences the performance of the resultant organoclay. Criteria to consider in the choice of a cation are molecular size, compatibility with the fluid in which the organoclay is to be used, stability and reactivity.

For miscible blends, the free volume theory predicts a positive deviation from the log additivity rule. However, depending on the system and method of preparation, these blends can show either a positive deviation, negative deviation, or additivity (Utracki, 1989a). Upon mixing, the presence of specific interactions may change the free volume and degree of entanglement, which in turn affect the flow behavior (Couchman, 1996). For immiscible blends the flow is similarly affected, but in addition there are at least three contributing phases: those of polymeric components and the interphase in between. Flow of suspensions provides good model for blends with high viscosity ratio,  $\lambda > 4$ , while for blends with  $\lambda = 1$ , the emulsion model is preferred. The block copolymer is a good model for wellcompatibilized polymer alloys.

The fundamental assumption of the classical rheological theories is that the liquid structure is either stable (Newtonian behavior) or its changes are well defined (non-Newtonian behavior).

Owing to variability of the blend structure with flow, the rheological responses are sensitive to the way they are measured. Since the structure depends on strain, the responses measured at high and low values of strain are different. For this reason, the selected test procedure should reflect the final use of the data. When simulation of flow through a die is attempted, the large strain capillary flow is useful.

For most blends, the morphology changes with the imposed strain. Thus, it is expected that the

dynamic low strain data will not follow the pattern observed for the steady state flow. One may formulate it more strongly: in polymer blends the material morphology and the flow behavior depend on the deformation field, thus under different flow conditions, different materials are being tested. Even if low strain dynamic data could be generalized using the t-T principle, those determined in the steady state will not follow the pattern.

Applications of rheology are important in many areas of industries involving metal, plastic, and many other materials. The results from rheological investigations provide the mathematical description of the viscoelasticity behaviour of matter. An understanding of the rheology of a material is important in the processing of composites, whether the task is designing an injection molded part or determining the cure cycle for a prepregs. For many years, rheology has been used as semi quantitative tools in polymer science and engineering. The relationship between the structure and rheology of a polymer is of practical interest for two reasons: firstly, rheological properties are very sensitive to certain aspect of structure and they are simpler to use than analytical methods, such as nuclear magnetic resonance. Secondly, it is the rheological properties that govern the flow behavior of polymers when they are processed in the molten state. Considering the structures of polymers by means of the size and shape of molecules and the distribution of these characteristics among the molecules, structure formation and controlled assembly are the focus of joint simulations and various experiments.

Neves *et al.*, (2004) investigated the main rheological features of vaginal hydrophilic polymer gels and elucidated the relationship between these characteristics, gels composition and their general influence in therapeutic/usage purpose. In their studies, two vaginal gels were studied by the cone and plate rheometry, at body temperature. Several parameters (apparent viscosity, complex viscosity, storage modulus, loss modulus, critical oscillatory stress,  $\tan \delta$ , thixotropy

and yield stress) were measured and/or calculated. They found that the rheological behaviour of vaginal gels strongly depended on the type of gelling agent used; which potentially influences their spreading and retention properties when administered in the vaginal canal. Small variations in gels composition can result in substantial changes in their features, namely: viscosity, yield stress and thixotropy. Rheological properties of tested gels appeared to have correlated strongly with their therapeutic or usage purpose. Material processability can also be determined through rheological studies.

Rheology deals with those properties of materials that determine their response to mechanical force. For solids, rheological studies involve elasticity and plasticity. For fluids, on the other hand, this involves viscosity measurements. Viscosity is a measure of the internal friction of a fluid.

Based on the variation of viscosity with shear rate or shear rate with shear stress, gums can be classified as Newtonian or non-Newtonian. Newtonian fluids are those fluids that obey Newton's law of flow (Brookfield, 2007). The law states that for laminar flow, the shear stress needed to maintain the motion of a plane of fluid at a constant velocity is proportional to the strain rate. At a given temperature, the viscosity of a Newtonian fluid is independent of the strain rate, fluids that do not obey Newton's law of viscosity are known as non-Newtonian fluids. For non-Newtonian fluids, when the strain rate is varied, the shear stress does not vary in the same proportion, i.e. the viscosity is not independent of the shear rate (Ebewele, 2000). Several reports on the various types of non-Newtonian behavior have revealed that some are dilatant, pseudoplastic or Bingham. According to Sharma *et al.*, (2007), pseudoplastic fluids display a decrease in viscosity with increasing shear rate (Sharma *et al.*, 2007). A dilatant fluid is characterized by an increase in viscosity with increasing shear rate.

Dilatant behaviour can be observed in fluids containing high levels of deflocculated solids such as clay slurries, candy compounds, corn starch in water, sand/water mixtures. For fluids that exhibit plastic behavior, a certain amount of stress is required to induce flow. The minimum stress necessary to induce flow is frequently referred to as the yield value. Ram (2006) has identified this type of behaviour in Tomato catsup.

In addition, some fluids will show a change of viscosity with time at a constant shear rate and in the absence of a chemical reaction. Two categories of this behavior are encountered: thixotropy and rheopexy. A thixotropic fluid undergoes a decrease in viscosity, whereas a rheopectic fluid displays an increase in viscosity with time under constant strain rate. Greases, heavy printing inks, paint exhibit thioxotropic behaviour while Rheopectic behaviour is rarely encountered.

### **2.1.5 Distinction between Rheology and viscometry**

A simple linear relationship between shear stress and shear strain rate is observed in a wide variety of fluids. The constant slope of the line labeled Newtonian is the (shear) viscosity of the fluid. Fluids demonstrating such a relationship are known as *Newtonian fluids*. Many common fluids like air, gasses in general, water, or simple oils demonstrate Newtonian behavior meaning constant viscosity with respect to strain rate over a very wide range (many orders of magnitude) of strain rates.

The measurement of the shear viscosity of Newtonian fluids is referred to as *viscometry*.

Fluids with more complicated molecular structures (e.g. polymers) or fluids with other phases suspended in them (e.g. mixtures, slurries, colloids etc.) often demonstrate more complicated shear stress to strain rate behaviors. Fluids exhibiting such behaviors are broadly characterized as “Non-Newtonian” fluids. Non-Newtonian fluids can be further classified according to how they

react to changes in shear deformation rates, to the duration of application of the applied loading, and to whether or not they exhibit a threshold elastic (solid like) shear resistance prior to deforming like a fluid.

Fluids that show increasing *apparent viscosity* (the *apparent viscosity* is the local slope of the stress vs. strain rate curve) as the applied strain rate increases are called “shear thickening” or *dilatant* fluids. The classic example of a shear thickening fluid is a mixture of corn starch in water. If one attempts to shear this fluid quickly (e.g. hit it with a hammer) the viscosity will rise to such a level that the fluid seems almost solid, the hammer blow will bounce off the surface. Yet at lower shear rates the mixture will act like a “normal” fluid (e.g a hammer set on its surface would sink right into the fluid).

Fluids which show the opposite behavior (decrease in apparent shear viscosity with increasing strain rate) are called “shear thinning” or pseudo-plastic fluids. A common example of a shear thinning fluid would be “no drip” paint, which behaves as a fairly thick (viscous) fluid while adhering to a paintbrush (a low shear rate circumstance), but which spreads easily (i.e. exhibits lower viscosity) when the paintbrush is dragged along a surface thereby increasing the shear strain rate applied to the fluid. Some fluids will “thin” (produce a lower shear stress resisting the motion) or “thicken” (produce a higher shear stress resisting the motion) as the *duration* for which a constant strain rate is applied increases. Fluids exhibiting the former behavior are referred to as “thixotropic” the latter as “rheopectic.” Such fluids are also sometimes referred to as “time-thinning” (thixotropic) or “time thickening” (rheopectic) fluids. Examples of thixotropic fluids include yogurt and some classes of paint. Rheopectic behavior is rare. Examples include gypsum paste and printers ink (coleparmer.com). Newtonian fluids exhibit constant strain rate with regard to loading duration for a constant applied shear stress.

Newtonian fluids will exhibit constant strain rate to shear stress behavior down to very low (theoretically zero) applied shear stresses. However some fluids, called “Bingham plastic” fluids will initially show “solid like” behavior until a threshold shear stress (called the “yield stress”) is applied; after which they will show “fluid like” behavior (continuously deforming while the shear stress is applied). A common example of this type of fluid is toothpaste, which will not flow at all until a threshold shear value is exceeded. Broadly, this kind of behavior is described as visco-elasticity. Bingham plastic materials can show dilatant, Newtonian, or pseudo-plastic behavior after their yield point. It is also worth noting that these terms are often not consistently applied.

#### **2.1.6 Developing Commercial Blends**

There are several methods of blending, viz., mechanical (dominant), solution, latex, fine powder, as well as several techniques adopted from the interlock polymer network (IPN) technology. Not always the finest dispersion is desirable the size and shape of the dispersed phase must be optimized considering the final performance of the blend.

Polymer blends’ performance depends on the properties of ingredients’, their content, and morphology. Since the cost is virtually fixed by the material and the compounding method, the economy depends on blend’s morphology, tailored for a specific application.

Blends have been developed for the economic reasons, through improvement of either a specific property (e.g., impact strength) or engendering a full set of required properties, extending engineering resin performance, improving processability, recycling, etc.

However, with growing frequency the blend economy is based on the replacement calculations, comprising the total cost, that of material, compounding, forming, assembling, customer satisfaction, esthetics, service life-spans, then the ease of disposal or recycling.

For the resin manufacturers, blending provides means to improve and broaden the resin performance and therefore it enhances the demands and sale. By contrast, the resin users start with a set of performance parameters that the material must possess. In both cases the basic preposition is the same to have a blend with desired characteristics, one must use a component that already shows this characteristic, or simply, one cannot create something out of nothing.

While extension of the engineering resin performance constitutes the largest part of the high performance blends' production, the most difficult and interesting task is the development of blends with a full set of desired properties.

To achieve this goal a systematic approach has been developed (Utracki, 1994). The procedure starts with the selection of blend components, each possessing at least one of the desired properties. For example, to improve impact strength an elastomer should be used, to induce flame retardancy a nonflammable polymer, to improve modulus a stiffer resin should be incorporated, etc.

Since polymer blends' performance depends on morphology, the goal is to ascertain the desired structure by selecting an appropriate resin grade (rheology), as well as the methods of compatibilization, compounding, and processing.

## **2.2 Gums**

The term gum is generally applied to a wide variety of colloidal substances that are similar in appearance and have peculiar characteristics. Ghani (1988) describe gums as a group of non-

crystalline polysaccharides which usually contain sugars such as mannose and galactose and their uronic acid derivatives. In practical terms, gums are defined as molecular structures, tending to high molecular mass, usually with colloidal properties, that, in an appropriate solvent produce gels or suspensions of high viscosity or solutions of low matter content that can absorb water at ten times their weight. (Umoren *et al.*, 2006d). Plant gums are obtained as an exudation from fruit, trunk or branches of the trees spontaneously or after mechanical injury of the plant by incision of the bark, or after the removal of the branch, or after invasion by bacteria or fungi. The exudates become hard nodules or ribbons on dehydration to form a protective sheath against microorganism. They form clear glassy masses, which are usually colored from dark brown to pale yellow. These gums are classes of high molecular weight polymeric compounds composed mainly of C, H, O and N are capable of possessing colloidal properties in an appropriate solvent, or swelling agent at low dry weight. They occur naturally as salts (especially of calcium and magnesium) and in some cases proportion of the hydroxyl group are esterified most frequently as acetates. In practical term gums are either hydrophobic or hydrophilic. Hydrophobic gums are insoluble in water and include resins, rubber, etc where as hydrophilic gums are soluble in water and can be subdivided into natural, semi-synthetic and synthetic gums (Sarah, 1998).

Gums serve as a food reserve or to check excessive transpiration, tannin protects against frost, animals and fungi while resins acts as protection against plant injury. These substances occur in larger quantities in some plants as compared to others.

### **2.2.1 Origin of gums**

There is no agreement as to the origin of gums exudates. Some thought that they are a product of normal plant metabolism and some suggest that they are arising from pathological conditions.

(Smith and Montgomery, 1959). Others think it is likely to be as a result of nonparasitic disease and bacteria activity (Ghani, 1988). *Acacia senegal* and *Acacia penninervis* exudates were found to have bacterial activity. The isolate from these species of acacia was called *Bacterium acaciae*. This bacterium produced shines when grown on artificial media. The shine was found to contain a gum of *Arabin galactin* type (Sanni, 1992).

Collett and Michael(1993) reported that because acacia is source naturally, it may be contaminated by microorganisms and therefore may require sterilization before use. It also contains peroxidase enzymes which may affect susceptible products but which are destroyed by heating at 100°C.

### **2.2.2 Classification of gums**

Gums whether they are occurring naturally or synthetically are divided into two groups. Group I contains acid gums of which the acid components are L- glucuronic acid, D-glucuronic acid, D-galacturonic acid, sulphate group, phosphate groups while Group II comprises the neutral gums of which the neutral components are hexoses, 6-deoxyhexoses, pentoses, sugar alcohols and ethers of all these classes (Davidson, 1980).

In the classification of plant gums, substances such as resins which are not true gums are often included (Davidson, 1980). True gums exuded by plants are soluble in water or if not soluble, absorb large amount of water to form gluey solutions. Resins on the other hand, are completely insoluble in water but soluble in ethanol, while true gums are precipitated in the presence of ethanol.

The chemical nature of true gums is complex. Generally, they contain carbon, hydrogen, oxygen, calcium, magnesium and potassium in the form of metallic salts which occur in various organic

compounds. Ha and Thomas (1988) were able to distinguish the components of various gums. The reported that significant quantities of xylose and fructose were the only sugars found in tragacanth gum while ghatti gum has low quantities of these sugars. Cherry gum has low levels of xylose and rhamnose, and a large amount of arabinose. On the other hand, Karaya, guar and locust bean gums contain no arabinose while a large quantity of mannose occurs in the locust bean and guar gums. Trangacanth, ghatti and arabic gums all contain arabinose and rhamnose. The gums can be distinguished from one another by the levels of sugars they contain. Higher levels of these sugars are seen in tragacanth followed by ghatti while gum arabic has the least content as compared to the other two gums. Karaya and trangacanth were found to contain galacturonic acid while gums arabic, cherry and ghatti contain glucuronic acid. Khaya gum has been reported to contain both D- glucuronic and D-galacturonic acids. Analysis of the gum showed that approximately 50% was in the free acid form and the remainder was largely the calcium salt (Aslam *et al.*, 2006).

### **2.2.3 Sources of gums**

Natural gums are produced from different sources, viz

- i. They can be exudative (produced from plant by incision or injury) e.g. gum arabic, karaya gum, and trangacanth. They are said to be extractive when extracted from seaweed e.g. alginates, agar, e.t.c.
- ii. They are called seed gums when obtained from seeds e.g locust bean seed, guar gum, e.t.c.

- iii. Gums obtained from citrus fruits are called pectin while those produced from animal skin and bones are called gelatin. Gums can also be produced by fermentation e.g. xanthan and lichen gums.

#### **2.2.4 Types of plant gums**

These are polyanionic polysaccharides obtained from trees of genera *Sterculia*, *Albizia*, *Acacia*, *Meliaceae*, *Astragalus* and *Anogeissus*.

##### **2.2.4.1 Gum Karaya**

Gum *Karaya* is defined as the dried exudate obtained from *Sterculia Uren Roxd.* And other related species of *Sterculia*, and variously known as *Sterculia* gum, Indian gum, kadayo gum, katilo gum, kullo gum, kutero and mucara gum. (JECFA/FAO, 1988).

Gum *Karaya* consists mainly of high molecular weight acetylated polysaccharides which on hydrolysis yields galactose, rhamnose and arabinose to gather with a small amount of glucuronic acid (Anderson *et al.*, 1982). Gum *Karaya* contains approximately 0.17% W/W nitrogen content presumably in amino acid form (Anderson *et al.*, 1982). Gum *Karaya* possesses high viscosity at extremely low gum concentration and commercial gum has specific rotation of +58° (Anderson *etal.*, 1982) and it has a low solubility in water so it tends to swell rather than dissolve in water and a coarse particle of gum *Karaya* can absorb water and swell to 60-100 times its original volume (Meer,1980), a property useful in bulking agents.

##### **2.2.4.2 Gum Albizia**

*Albizia* gum derived from trees of the genus *Albizia* is formed as round elongated warts of variable size and colour ranging from yellow to dark brown (Mital and Adotey, 1973).

Chemical analysis reveals the presence of L-arabinose D- galactose D-glucuronic acid, Dmannose and 4-O-methyl glucuronic acid and L-rhamnose with slight acetylation and methylation. Metal ion analysis suggests that gum exudates derived from the genus *Albizia* are complex salts of calcium, potassium, magnesium and sodium, in decreasing proportions. Other metals like zinc, copper, iron, lead and aluminium are present in trace amount (Anderson and Morrison, 1990). *Albizia* gum is soluble in water forming a colourless mucilage with a bland taste (Mital and Adotey, 1973).

#### **2.2.4.3 Gum Arabic**

Gum arabic is the dried gummy exudation of *Acacia Senegal* or closely related species of Acacia family leguminosae (JECFA/FAO,1990). Gum arabic occurs as a mixture of calcium magnesium and potassium salts of arabic acid and is composed of six carbohydrate moieties namely galactose, arabinopyranose, arabinofuranose, rhamnose, glucuronic acid and 4-O methyl glucuronic (Anderson and Karamalla, 1966). The gum is highly soluble in water and solutions of up to 60% w/v gum concentration can be prepared (Glicksman, 1983). Gum arabic solutions are slightly acidic with maximum viscosity obtained at the neutral pH. It is principally used in the food and pharmaceutical industries as stabilizer, thickener, suspending and binding agent in the manufacture of confections, dairy products, beverages, cotton -seed oil emulsion and tablets (Glicksman,1983).

#### **2.2.4.4 Gum Tragacanth**

Gum *Tragacanth* is the dried exudation obtained from stems and branches of *Astragalus gummifer labillardiere* and other Asiatic species of *Astragalus* (Family leguminosae (JECFA/FAO,1986). Gum is a complex mixture of acid polysaccharides containing galacturonic acid,galactose, fucose, arabinose, xylose and small amounts of rhamnose and glucose. It swells inwater to give thick gel like dispersions which show typical pseudo plastic behaviour (Gordon, 1992). Gum *tragacanth* has been used extensively in food products (Gordon, 1992).

#### **2.2.4.5 Gum Ghatti**

Gum Ghattiis a dried gummy, translucent exudate obtained from *Anogeissus latifolia* (Family Combretaceae), a large tree found in India and Sri Lanka. The exudations are natural butthe yield can be increased by making artificial incisions. Gum ghattiooccurs naturally as a calcium and magnesium salt of a complex polysaccharides acid -complex. Acid hydrolysis hasshown the gum to consist of L-arabinose, D-galactose, D-mannose, D-xylose and D-glucuronicacid in the ratio 10:6:2:1:2 (Jefferies *et al.*, 1977). On dispersion in water, gum ghatti forms viscous solutions, intermediate between those of gum arabicand gum karaya. The dispersions have emulsifying and adhesive properties equivalent or superior to those described for gum arabic(Jefferies *et al.*, 1977). Gum ghattiis used as food additive besides being used in medicines, textiles and adhesives (Topalian and Elsesser, 1966).

#### **2.2.5 Properties and application of plant gum**

The most fundamental property of a gum which makes it unique amongst polysaccharide generally is its solubility and viscosity. (Meer, 1980).The majority of gums dissolve in water at different concentration (e. g gum Arabic can form solutions of up to 60% forming viscous

solutions). These properties of gums are exploited in many applications. The major application of gum is in food industry where emulsifying and stabilizing properties are utilized. The gum is also used in the pharmaceutical and medical fields, in addition to other industries (cosmetic, adhesive paints and inks). According to Glicksman and Schachat (1959) the major use (55%) of gum (gum *Arabic*) in the USA is in the food industry, primarily in confectionery. In Western Europe food uses of gum arabic accounted for 76% of the market (Gordon, 1992). Its main functions in confectionery are the prevention of sugar crystallization and as an emulsifier in fat-based sweets, e.g. toffees. The gum acts as an emulsifier by keeping the fat evenly distributed throughout the toffee there by preventing the fat from 'leaching out' and forming an oxidisable film on the surface.

The gum is also used to incorporate flavours in confectionery such as pastilles and gum drops and in the preparation of lozenges. Gum arabic has also been used to stabilize frozen dairy products such as ice cream and sherbets due to its high water- absorbing properties. In this context the gum imparts a smooth texture to the frozen product by inhibiting the formation of ice crystals.

In baking industry, gum arabic is used in glazes and topping, and in the encapsulation of spray-dried flavours into foods. In another application when used as flavour fixative, the gum forms a thin and impenetrable film around the flavor particle protecting it from oxidation, evaporation and absorption of moisture. In the soft drinks industry, gum is used as a flavor emulsifier in oil-in water emulsions and as a foam-stabilizing agent (Glicksman, 1969).

Gum (gum arabic) is used as a suspending and emulsifying agent in the pharmaceutical industry. In the area of cosmetics gum arabic imparts spreading, viscosity and protective characteristics to lotions and protective cream by stabilizing the emulsion. Other application of plant gums are in

the manufacture of adhesives, for postage, stamps and in the formulation of paints and inks and in lithography and textile industry as a sizing and finishing agent (Meer, 1980). Gums have also been used as corrosion inhibitors recently.

## **2.3 Viscosity**

The viscosity of a liquid is its resistance to shearing, to stirring or to flow through a capillary tube. Anderson and Dea (1967) stated that viscosity is one of the most important analytical and commercial parameters in polymers because it is affected by the size and shape of macromolecules. Early investigators sought to establish relationships between the viscosity of polymer solutions and the molecular weight of the polymer. In addition to providing a measure of polymer molecular weight, measurements of dilute solution viscosities are now recognized as being useful in the study of polymer branching, polymer dimensions and its temperature dependence, chain flexibility, and association of polymers in solution.

In rheology, various forms of viscosity have been identified. This includes relative viscosity, specific viscosity, reduced viscosity, inherent viscosity and intrinsic viscosity. It is also presented as kinematic or dynamic viscosity.

### **2.3.0 Analytical methods for polymers**

#### **2.3.1 Measurement of viscosity:**

Viscometers are designed to make use of the theoretical relationship between shear stress and strain rate to measure viscosity. They do this using simple flow (1-D, steady, fully developed) in which both the shear stress and strain rate can be measured. There are three primary types of viscometers: flow, drag and resonant. The flow type viscometers measure the rate of flow of the fluid in a tube or through an orifice. The shear stress can be calculated from theory (capillary tube viscometer) or estimated based on theory (orifice cup viscometers). Use of these types of viscometers yields values for kinematic viscosity.

Design parameters for flow type viscometers include minimizing entrance and exit effects, maintaining a constant pressure head (which drives the flow), minimizing surface tension effects and mitigating effects of temperature variation. Drag type viscometers measure either the force on an object as it moves at a specified rate in the fluid (rotational viscometers) or measure the time it takes for an object to move a specified distance through the fluid (falling object and bubble tube viscometers). Use of these types of viscometers yields values for absolute viscosity (except the bubble tube). Design parameters for drag type viscometers include minimizing the effects of turbulence and flow separation through the specification of a flow condition (generally low Reynolds number), controlling for transients, minimizing surface tension effects and mitigating effects of temperature variation. The third type of viscometer is the resonant (vibration) viscometer. These are most commonly used as process viscometers. These are designed so that changes in the viscous damping bring about significant changes in the resonance behavior of the instrument. Use of these types of viscometers yields values for kinematic viscosity Viswanath *et al.*, (2007).

Viscosity of different fluids can be measured using viscometer of which are of different types but note the essential components of a capillary viscometer are

- i. A liquid reservoir,
- ii. A capillary of known dimensions,
- iii. A provision for measuring and controlling the applied pressure,
- iv. A means of measuring the flow rate, and
- v. A thermostat to maintain the required temperature.

### **I. Ostwald Viscometer**

The Ostwald Viscometer is one of the simplest capillary tube viscometer. As shown in the Schematic below, this is a U-shaped viscometer that is used in the measurement of Newtonian fluids. It has two bulb marks (upper and lower). Liquids flow is aided by gravitational force from the upper mark to the lower mark in a vertical capillary tube. The time of flow of the liquid under test is compared with time required for a liquid of known viscosity.

To use the viscometer one partially fills it and then draws the fluid to the upper mark above the right side bulb (typically using a syringe system). The fluid is released to flow through the capillary tube and the time for the upper bulb to empty (fluid level at upper marks to lower marks) is measured. Some of the problems

associated with the use of the Ostwald viscometer include the need to keep the viscometer vertical, the requirement for a specific volume of fluid and the effect of temperature on the viscosity measurement. A number of Modified Ostwaldtype viscometers exist. These include the Cannon-Fenske routine viscometer, Pinkevitch viscometer, Zeitfuchs, (Viswanath *et al.*, 2007). Each is designed to address some of the sources of error found in the Ostwald type. For example the Cannon-Fenske Routine viscometer is designed to minimize the effect of tilt angle by placing the upper and lower bulbs along the same vertical axis.

## **II. Cup and Bob Viscometer**

It is the rotational viscometer that measures the viscosity of non-Newtonian fluids. In this viscometer, the material is sheared in the space between the outer wall of a bob and inner wall of a cup in which the bob fits. The viscous material as a result of this shearing action causes the bob to turn. The resultant torque is proportional to the viscosity of the material.

## **III. Cone and Plate Viscometer**

In this type of viscometer, the sample is placed in the center of the plate which is then raised into position under the cone. The cone is driven by a variable speed motor and the sample is sheared in the narrow gap between the stationary plate and the rotating cone. The rate of shear in revolution per minute (rpm) can be varied by a dial and shear produced on the cone is read on a dial indicator. A graph of shear rate versus shear stress can be plotted (Cater, 2005). It is used for measuring viscous liquids and semi-solid materials.

## **IV. Digital Viscometer**

This type of viscometer measures Newtonian and non-Newtonian fluids. The instrument gives an absolute viscosity value. It measures the torque required to rotate an immersed spindle in a fluid. The spindle is driven by a motor through a calibrated spring; deflection on the spring is indicated by a display. There are several speeds that can be used interchangeably to measure viscosity values. In this type of viscometer, the viscous drag is proportional to the speed of rotation, size and shape of spindle. Thus, the resistance to flow increases as rotational speed increases.

## **2.4 Physicochemical properties of gum exudates**

### **i. Purification**

The acidic polysaccharides in crude gums usually exist in the form of neutral or slightly acidic salts, with calcium, magnesium, iron, sodium and potassium, usually present as cations. Purification is frequently carried out by dissolving the gum in water and filtering then followed by one of the following methods (Cater, 2005):

- (i) Electrodialysis
- (ii) Precipitation
- (iii) Ion exchange chromatography
- (iv) Electrophoresis

The different purification methods don't appear to alter significantly the physical properties of the gum. However, Balabanova and Khristora (1982) reported that purification of gum material by different methods exhibited certain difference in fraction pattern at the same treatment.

## **2.5 Physical Properties of Gums**

The solubility, colour, taste, odour and viscosity are important parameters in determining the uses and commercial values of gums.

Regarding to the solubility the true gums are divisible into three classes (Howes, 1949):

- (i). Soluble gums that dissolve in water forming transparent solution, e.g. *Acacia Senegal* gum.
- (ii) Insoluble gums which also absorb water but on addition of sufficient water break down into very thick transparent solutions, e.g. tragacanthgum.
- (iii) Half- soluble gums that partially dissolve but on addition of more water pass into solution; e.g. ghatti gum.

The colour of the gums varies from almost colourless through various shades of yellow, orange to dark brown, some of the best gum arabic "*Acacia senega!*" are almost colourless. On the other hand, dark or even black gums sometimes occur, e.g. Mesquite gum (Howes, 1949). The colour of *Anogeissus leiocarpus* gum may be yellow or light brown(Samia, 2009).

Gums as collected in natural states are represented by a variety of shape and form. Usually the fragments are irregularly globular or tear shaped. The grading of gum is based on shape, size and colour of gum nodules.

Moisture content of the gum determines the hardness of the gum and hence the variability of densities and the amount of air entrapped during nodule formation.

The role of nitrogen and nitrogenous component in the structure, physico–chemical properties and functionality of gum arabic was recently subjected to intensive investigation (Anderson, 1986). On the other hand, Erick Dickinson (1991) studied the emulsifying behavior of gum arabic and concluded that there was a strong correlation between the proportion of protein in the gum and its emulsifying stability.

## **2.6 Spectrophotometry and Spectroscopy**

### **2.6.1 Absorption Spectrophotometry**

Is the measurement of the selective absorption by atoms, molecules, or ions of electromagnetic radiations having a definite and narrow wavelength range of approximating monochromatic light. Absorption spectrophotometry encompasses the following wave-length regions: Ultra-violet (185 to 380 nm), visible (380 to 780 nm), near infra-red (780 to 3,000 nm) and infrared (2,500 to 40,000nm).

### **i. Ultraviolet (UV)**

Ultra-violet is not used primarily to show the presence of individual functional groups, but rather to show the relationship between functional groups chiefly conjugation either between carbon-carbon or carbon-oxygen double bond, between double bonds, and in aromatic ring and even in the presence of aromatic ring itself. It can in addition reveal the number and location of substituent attached to the carbons of the conjugated systems (Morrison and Boyd, 1978).

### **ii. Atomic Absorption Spectroscopy**

Atomic absorption spectroscopy is the measurement of the radiation absorbed by the unexcited atoms of the chemical substance that has been aspirated into a flame or in the absence of a flame directly into the path of radiation. Nuclear magnetic resonance (NMR) has lately been used with great success in the differentiation among the fine structures of very similar polysaccharide molecules e.g. *Acacia Senegal* gum and *Acacia seyal* gum, resembling different "finger prints" (Defaye and Wong, 1986).

### **2.7.1 Determination of intrinsic viscosity**

The intrinsic viscosity  $[\eta]$  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 (Lai and Chiang, 2002). The intrinsic viscosity  $[\eta]$  is determined experimentally from measurements of the viscosity of very-low-concentration (C) solutions. Denoting solution and solvent viscosity as, respectively,  $\eta_{\text{solution}}$  and  $\eta_{\text{solvent}}$ ,  $[\eta]$  is defined by the following relationships:

$$\text{Relative viscosity: } \eta_{rel} = \frac{\eta_{\text{solution}}}{\eta_{\text{solvent}}} \text{----- (2.1)}$$

$$\text{Specific viscosity: } \eta_{sp} = \eta_{rel} - 1 \text{----- (2.2)}$$

$$\text{Intrinsic viscosity: } [\eta] = \lim_{C \rightarrow 0} \frac{\eta_{sp}}{C} \text{----- (2.3)}$$

The intrinsic viscosity can be obtained by measuring specific viscosities at different concentrations at the same shear-rate, and extrapolating the course of specific viscosity to infinite dilution (Heitmann and Mersmann, 1995). The intrinsic viscosity  $[\eta]$  is, therefore, obtained by extrapolating data to zero concentration by using a linear regression, which will be called the graphic double-extrapolation procedure (GDEP) in this study. McMillan (1974) showed that  $\frac{\eta_{sp}}{C}$  also called reduced viscosity, could be written in the form of a Huggins equation (Huggins, 1942)

$$\frac{\eta_{sp}}{C} = [\eta] + K^l [\eta]^2 C \text{----- 2.4}$$

where  $k^l$  is the Huggins constant. The determination of the intrinsic viscosity is, therefore, the extrapolation of reduced viscosity to the value at zero solute concentration. The extrapolations are usually done in very dilute regimes ( $C \ll C^*$ ) with relative viscosity values between 1.2 and 2.0, the corresponding specific viscosities being between 0.2 and 1.0 (Da Silva and Rao, 1992).  $C^*$  is defined as the overlap concentration, the transition from the dilute to the semi-dilute region which mark the onset of polymer entanglement (Launay *et al.*, 1997). In the present work, gum solutions were therefore diluted to be within the described range. In addition, McMillan (1974) reported that the intrinsic viscosity could be obtained from the Kraemer equation (Kraemer, 1938) by extrapolation to zero concentration (C)

$$\frac{\ln \eta_{rel}}{C} = [\eta] + k^{ll} [\eta]^2 C \text{----- 2.5}$$

where  $k^l$  is the Kraemer constant. For very dilute solutions, however, Eq. (2.5) can be shortened by retaining only the first-order term, and  $[\eta]$  can be determined from the slope of a plot of  $C$  against  $\ln \eta_{rel}$  (Sornsrivichai, 1986).

McMillan (1974) showed that methods of determination of the intrinsic viscosity that were based on slopes of plots had higher correlation coefficients and lower standard errors, compared with those based on intercepts of plots.

On the basis of such findings, Tanglertpaibul and Rao (1987) used the following equations to obtain the intrinsic viscosity of tomato serum:

$$\eta_{rel} = 1 + [\eta]C \text{ ----- (2.6)}$$

The intrinsic viscosity  $[\eta]$  is the slope obtained by plotting

$$\eta_{rel} \text{ vs. } C$$

$$\eta_{rel} = e^{[\eta]C} \text{ ----- (2.7)}$$

The intrinsic viscosity  $[\eta]$  is the slope obtained by plotting

$$\ln \eta_{rel} \text{ vs. } C$$

$$\eta_{rel} = \frac{1}{1 - [\eta]C} \text{ ----- (2.8)}$$

The intrinsic viscosity is the slope obtained by plotting

$$1 - \frac{1}{\eta_{rel}} \text{ vs. } C.$$

The intrinsic viscosity  $[\eta]$  was estimated based on the slope of  $\eta_{sp}$  vs.  $C$  for polyelectrolytes, as suggested by Chou and Kokini (1987); this is similar to the method discussed in Eq. (2.6). Chou and Kokini (1987) reported that when there is essentially no molecular interaction, as in dilute solutions, the second term of the Huggins equation (Eq. (2.4)) is negligible, and a plot of  $\eta_{sp}$  against concentration is linear. In this study, the intrinsic viscosity in the dilute domain was

estimated on the basis of Eqs. (2.3), (2.6), (2.7), and (2.8), and the four methods were statistically compared for a better fit.

The intrinsic viscosity of the gum samples was determined in distilled water. The gum solutions were prepared by dispersing 50 mg of each of the gum sample (dry basis) separately in 100 cm<sup>3</sup> of the distilled water at room temperature and mixing with magnetic stirring overnight. 2 cm<sup>3</sup> of solution was transferred into an Ostwald viscometer which was immersed in a precision water bath to maintain the temperature at 25.0±0.1 °C after equilibrated for 10 min. The flow time was determined between the two etched marks. Serial dilution was performed in situ and three readings were taken for each dilution and averaged. The relative viscosity ( $\eta_{rel}$ ) was calculated using the equation

$$\eta_{rel} = \frac{t - t_0}{t_0}$$

Where  $t$  is the flow time of gum solution in seconds,  $t_0$  is the flow time of solvent (water) in seconds.

### 2.7.2 Determination of the molecular conformation and polymer interaction

The power-law equation

$$\eta_{sp} = aC^b \text{ ----- 2.9}$$

was used to estimate the exponent  $b$  from the slope of a double logarithmic plot of  $\eta_{sp}$  against concentration, and provides an indication of the conformation of polysaccharides (Lai *et al.*, 2000). To determine the gums interaction, the verified theory (Chee, 1990; Sun *et al.*, 1992), based on the classical Huggins equation expressing the specific viscosity ( $\eta_{sp}$ ) of a polymer as a function of polymer concentration  $C$ , was used

$$\frac{\eta_{sp}}{c} = [\eta] + bC \text{-----} 2.10$$

and

$$b = K[\eta]^2 \text{-----} 2.11$$

Where  $[\eta]$  is the intrinsic viscosity, and  $b$  and  $K$  are Huggins parameters. Chou and Kokini (1987) reported that for dilute solutions, the term  $bC$  from Eq. (2.11) is negligible, and the plot of the specific viscosity against the concentration gives a straight line. The term  $b$  was approximated from the small intercept value of the plot of specific viscosity against the concentration (Higiro *et al.*, 2006).

According to this theory, the following equation applies to a ternary polymer–polymer–solvent dilute solution, in which there is no aggregation between molecules

$$\alpha = b_m - (\sqrt{b_1}W_1 + \sqrt{b_2}W_2)^2 \text{.....} 2.12$$

Where  $b_m$ ,  $b_1$ , and  $b_2$  are the Huggins coefficients for blend, polymer 1, and polymer 2, respectively.  $W_i$  is the weight fraction of polymer  $i$  in the polymer blend ( $i = 1$  or  $2$ ). The equation may be used to provide qualitative information on polymer–polymer interaction: two polymers are attractive in solution when  $\alpha \geq 0$ , whereas they are repulsive when  $\alpha < 0$  (Wanget *al.*, 2001). Three types of interaction contribute to the value of  $b_m$  for a ternary polymer–polymer–solvent interaction (Cragg and Bigelow, 1955)

1. Long-range hydrodynamic interaction of pairs of single molecules:

$$\begin{aligned} b_{m1} &= b_1W_1^2 + b_2W_2^2 + 2\sqrt{b_1b_2}W_1W_2 \\ &= (\sqrt{b_1}W_1 + \sqrt{b_2}W_2)^2 \text{.....} 2.13 \end{aligned}$$

Where  $b_i$  is the Huggins parameter  $b$  for component  $i$  ( $i = 1$  or  $2$ ).  $W_i$  is the weight fraction of polymer  $i$  in the blend.

2. The formation of double molecules. This assumes actual contact:

$$b_{m2} = k^I([\eta]_1 - [\eta]_2) \dots\dots\dots 2.14$$

Where  $[\eta]_1$  and  $[\eta]_2$  are intrinsic viscosities of double- and single-molecule species, respectively, and  $K^I$  is a constant. In the absence of aggregation between molecules and at sufficiently low concentrations ( $C \ll C^*$ ), this term is neglected.

3. Intermolecular attraction or repulsion:

$$b_{m3} = \alpha \dots\dots\dots 2.15$$

Where  $\alpha \geq 0$  means attraction, whereas  $\alpha < 0$  means repulsion.

Therefore,

$$b_m = b_{m1} + b_{m2} + b_{m3} \approx b_{m1} + b_{m3} \dots\dots\dots 2.16$$

$$b_m = (\sqrt{b_1}W_1 + \sqrt{b_2}W_2)^2 + \alpha \dots\dots\dots 2.17$$

By measuring  $b_m$  from the Huggins equation for polymer–polymer–solvent solution,  $\alpha$  was calculated and the interaction was characterized.

## CHAPTER THREE

### MATERIALS AND METHODS

#### 3.0 Materials

Crude *Khaya senegalensis* (chewstick tree) gum, was obtained as dried exudates from their parent trees grown at Kanya Babba village in Bubura Local Government Area of Jigawa State around mid-November. The plant material had earlier been identified and authenticated and assigned a voucher number 872 in the herbarium of the Department of Biological Sciences of Ahmadu Bello University, Zaria.

The crude *Anacardium occidentale* Lgum were obtained as dried exudates from their parent tree grown at Ahmadu Bello University Zaria, close to the postgraduate school. The crude *Acacia Senegal* gum was obtained from Falgore forest in Doguwa LGA of Kano State. The gums along with its plant were identified at the herbarium, Department of Biological Sciences ABU, zaria.

### 3.0.1 Tapping of gums

The gums were also collected from the plant species by tapping (Smith and Montgomery, 1959) around mid-December during the day time. A small axe was used to break the outer bark. Tapping was carried out by driving an axe underneath the bark which was pulled back until the bark broke horizontally to give two broken ends. The cut was made about 4.0 cm wide. The bark was then carefully peeled along the length of the wounded trunk. Gum droplets formed were 3.0 – 5.5 cm in diameter.

### 3.0.2 Purification of the gum

The procedure adapted for the purification of the gum was that of Femi-Oyewo *et al.*, (2004), but with some modifications. The gums were dried in an oven (BS Size 3, Gallenkamp) at 40°C

for 2 h and the size reduced using a blender (Model. MJ-176 NR, Matsushita Electric Industrial Co., Ltd. Osaka, Japan). It was hydrated in double strength chloroform water for five days with intermittent stirring to ensure complete dissolution of the. Thereafter, the gum was precipitated from the slurry using absolute ethanol, filtered and defatted to dry flakes. The precipitate was dried in the oven at 40 for 48 h. The dried flakes were pulverized using a blender and stored in an air tight container.

### **Preparation of Polymeric Blends**

Ternary solutions for the present system were prepared by mixing the calculated quantity of polymer solutions in different weight ratios up to the concentration of 1.0% (w/v). Dilutions to yield four lower concentrations were made by adding appropriate aliquots of solvent.

To study the interaction between the gums, the following treatments were considered: *Anacardium occidentale* L (AO) 100%, *Khaya senegalensis* (KS) 100%, *Acacia senegal* (AS) 100%, KS 80%- AO 20%, KS 60%- AO 40%, KS 50%-AO 50%, KS 40%-AO 60%, KS 20%-AO 80%, KS 80%-AS 20%, KS 60%-AS 40%, KS 50%-AS 50%, KS 40%-AS 60%, KS 20%-AS 80%, AO 80%-AS 20%, AO 60%-AS 40%, AO 50%-AS 50%, AO 40%-AS 60%, AO 20%-AS 80%.

## **3.1 Physicochemical analysis**

### **3.1.1 Determination of solubility in various solvents**

The solubility of the gums were determined in distilled water and in ethanol. The gum samples (1.0 g each) were added to 50 cm<sup>3</sup> of each of the above mentioned solvents and left overnight. 25ml of the clear supernatants were taken in small preweighted evaporating dishes and heated to dryness over a digital thermostatic water bath. The weights of the residue with reference to the volume of the solutions were determined using a digital top loading balance (Model.XP-3000) and expressed as the percentage solubility of the gums in the solvents (Cater, 2005).

### 3.1.2Determination of pH and Conductivity

The pH and conductivity were determined according to the method of ASTM D3838-80 with slight modification as follows; 1.0g of each gum blend was weighed and transferred into 250 cm<sup>3</sup> beaker and 100 cm<sup>3</sup> of distilled water was added and stirred for 1 h. Samples were allowed to stabilize and then pH measured using an electronic pH/Conductivity meter, Jenway 430 model. The same samples were further used for electrical conductivity (EC) of the blends and the results read off in  $\mu\text{s}$  (Toles *et al.*, 1998). Triplicates measurements were made.

### 3.1.3Effects of Temperature, Concentration and Salts on Viscosities of Gums

The Ostwald viscometer was used as described by Higiroy *et al.*, 2006. 1 % w/v concentrations of each of the gums were prepared and their viscosities at temperature range 30-70°C were determined. Also 1 %w/v concentrations of each of the gums were used to study their specific and reduced viscosity in different concentrations (0.2 to 1.0) M of KCl, AlCl<sub>3</sub> and KBr. Viscosity values of the blends as well as that for the pure gums at different concentrations of the salts were measured

### 3.2 Density

Density measurements were carried out at 35<sup>0</sup>C using 25cm<sup>3</sup> density bottle. For each gum sample, densities of concentration for the samples in aqueous solution were determined. Clean, dry density bottle was weighed (M<sub>0</sub>) on a digital top loading balance. The bottle was then filled with distilled water and weighed again (M<sub>1</sub>). Another weighing (M<sub>2</sub>) was done with the gum solution replacing distilled water in the density bottle. Relative density of gum solution was evaluated as

$$(M_2 - M_0) / (M_1 - M_0) \dots \dots \dots 3.1$$

### 3.3 Metals Composition

Concentration of copper, calcium, iron, lead, cadmium and zinc were determined using a UNICAMM 969 atomic absorption spectrophotometer, while potassium and sodium were determined with the use of a flame photometer. Calibration curves for each element were prepared and the concentration of the element was extrapolated from their respective plots.

### 3.4 FTIR analysis

FTIR analyses of the gums were carried out using Scimadzu FTIR-8400S Fourier transform infrared spectrophotometer. The sample was prepared using KBr and the analysis was done by scanning the sample through the wave number range of 400 to 4000cm<sup>-1</sup>.

### 3.5 GC-MS analysis

GC-MS analysis was carried out on a GC clarus 500 Perkin Elmer system comprising a AOC-20i auto-sampler and gas chromatograph interfaced to a mass spectrometer (GC-MS) instrument employing the following conditions: column Elite-1 fused silica capillary column (30 x 0.25 mm

ID x 1 $\mu$ M df, composed of 100% Dimethyl poly diloxane), operating in electron impact mode at 70eV; helium (99.999%) was used as carrier gas at a constant flow of 1 ml/min and an injection volume of 0.5 $\mu$ l was employed (split ratio of 10:1) at injector temperature 250°C and ion-source temperature at 280°C. The oven temperature was programmed from 110 °C (isothermal for 2 min), with an increase of 10°C/min to 200°C, then 5°C/min to 280°C, ending with a 9min isothermal at 280°C. Mass spectra were taken at 70 eV; a scan interval of 0.5 s and fragments from 40 to 450 Da. Total GC running time was 36 min.

Interpretation on mass spectrum GC-MS was conducted using the database of National Institute Standards and Technology (NIST) United States of America, having more than 62,000 patterns. The spectrum of the unknown component was compared with the spectrum of the known components stored in the NIST library. The name, molecular weight and structure of the components of the test materials was ascertained. Concentrations of the identified compounds were determined through area and height normalization.

### 3.6 Rheological properties

The viscosity of each gum solution and of the blends were measured as a function of shear viscosity by using an Ostwald viscometer.

Rheological measurements were carried out at 20°C by using a temperature- controlled circulating water bath (Haake DC5, Gebr. Haake GmbH, Karlsruhe, Germany).

Microsoft Excel 2000 (Microsoft Corporation, Seattle, WA) was used to plot viscosities against concentrations, as well as to obtain linear regression lines with the corresponding equations and correlation coefficients ( $R^2$ ), to assess the best model.

### 3.7. Statistical Analyses

A two-way factorial design was used to generate the best-fitting intrinsic viscosity model. For each gum blend as well as for the effects of these three salts (KCl, KBr and AlCl<sub>3</sub>) at the concentration of 10g/dm<sup>3</sup> or 1g/dl and were compared with the intrinsic viscosity, the elastic component, the molecular conformation coefficient *b*, the miscibility coefficient  $\alpha$ , and the Huggins coefficient *K*, in a factorial design. In each instance, the analysis of variance and means comparison were conducted by the general linear models procedure (Proc GLM), with Statistical Package for social science (version 16.0). Comparisons among treatments were analyzed by using Duncan and Tukey significant test, with a significance level at  $P < 0.05$ .

## **CHAPTER FOUR**

## 4.0 RESULTS AND DISCUSSION

### 4.1 Physico-chemical parameters

From Table 4.1 the colour of the pure gums i.e. AS, AO and KS gum were found to be navajowhite 1, brownish-yellow and darkorange 4 respectively when they were subjected for proper colour identification using Benjamin moore colour gallery. When the blends of AS and AO gum were checked against that of AS as a standard gum using the same colour identification method, the blends having the composition 80% AS and 20% AO was the lightest in shade and the closer in colour when compared to AS gum, its colour peachpuff 1 was lighter than AS:AO (60:40) which was bisque and this trend falls with increase in composition of AO gum till 20:80 which had a colour of wheat.

In Table 4.3, the colour of the AS:KS gum was quite darker than the blends of AS:AO since given the fact that the lightest in colour of them all was the blend bearing a higher composition of AS gum that is 80% to 20% Ks gum, whose colour was wheat like and found to be similar to that of the AS:AO blend which had the darkest shade. This trend also was found to get darker with increase addition of the KS gum till the last blend which was burly or rather had a burly wood colour when using the colour identification. The colour of the AS:KS blend, with the lightest blend (80:20) having the colour of burlywood 2 and the darkest blend (20:80) having the colour associated with Tan 3.



Fig. 4.1: A photographs of dried and processed of purified plant gum exudates used

The solubility of the pure gums as well as their blends were subjected to solubility studies using ethanol and water at 28°C and the percentage solubility of the gums in the solvents were determined according to method of carter (carter, 2005).

AS gum was the most soluble in water, while AO gum was the least and KS gum is most soluble in ethanol. The percentage of AS:AO blend decreases with increase in composition of AO gum, while for AS:KS blend the percentage solubility decreased as the composition of KS gum is added and finally AO:KS blend which also decreased as the composition of KS is added. When cross referencing all blends for the three gums i.e. AS, AO and KS, the blend AS:KS (80:20) had the highest percentage solubility in water at 10.5, while AS:AO (20:80) the least at 7.1. When the solvent was changed and an organic solvent namely ethanol was used only the blends AS:KS (20:80) and AO:KS (20:80) were soluble at 0.2 and 0.1 respectively, indicating that though these gums are primarily hydrophilic in nature.

The pH of pure KS gum was the least with value of 4.18, indicating that the gum is most acidic when compared to the other two gums AS and AO which were 5.01 and 5.51 respectively. This property of the KS gum affected the blends of AS:KS and AO:KS by increasing the acidity of AO and AS as the percentage composition of KS gum was increased in them respectively. This simply proves that the KS gum has more acidic component or uronic acids present in its pure form, which was further confirmed when the GCMS result of the gum was carried out.

KS gums had the most turbidity value in the pure gums at 376 (FAU) and AS having the least value at 25 (FAU). This indicates that the KS gum had more suspended solids or material that are large enough to settle rapidly to the bottom of the container. This is probably due to the fact that polymeric materials that constitute KS gum are more heavier in molecular weight than that of AS

and AO gums. While the turbidity value of AO:KS blend was found to have the highest value at 411 FAU and AS:AO blend at 54 FAU. This may be as a result of the miscibility effect taking place in the blend solution as well as large molecular weight polymers or high density polymer included therein.

The salinity of the gums in  $\mu\text{s}/\text{cm}$  measured was found to be highest in KS gum at  $0.2\mu\text{s}/\text{cm}$  and 0.1 in AO and AS gum respectively. All the blends have  $0.1\mu\text{s}/\text{cm}$  of value as their salinity except for AS:KS (20:80) and AO:KS (20:80), which is as a result of the high composition of KS gum in the blends, since KS gum has a value of  $0.2\mu\text{s}/\text{cm}$  and could be associated with the presence of salt content such as sodium chloride, potassium chloride, calcium sulphates and bicarbonates, this was confirmed in the AAS result of the gum blends.

The conductivity of KS gum was found to be  $341.10\mu\text{s}/\text{cm}$  which was found to be significantly higher than those of AO and AS gum. The conductivity value of AS and AO gum increased as KS gum were added to the gums, AS:KS (20:80) respectively being the highest for the blend. Hence the ability of the blends to conduct an electric current increases as the composition of KS gum is increased. This property could also be owned to the fact that the KS gum contains more dissolved salt than the other two gums.

This is a measure of the combined content of all inorganic and organic substances contained in the gum solution, in a suspended form. KS gum has the highest TDS value ( $174.8\text{ mg}/\text{L}$ ). The TDS value of the AS:KS and AO:KS blend were significantly higher than that of AS:AO blend. This could be seen from the fact that the clarity of the blend solution improved with decrease in composition of KS gum since the presence of suspended particles be it inorganic or organic were more in  $\text{KS} > \text{AO:KS} > \text{AS} > \text{KS}$  gums. This trend describes the clarity of the blends.

The high  $\lambda_{\text{max}}$  noticed in the gums maybe as a result of high degree of conjugated carbon-carbon double bonds which absorb light in the uv or visible regions of the electromagnetic spectrum.  $\lambda_{\text{max}}$  of KS gum is 300 nm, while that of AS gum is 200 nm. This was found to affect other blends where the composition of KS was higher, the uv increased with increase in composition of KS gum which may contain large percentage of conjugated organic compounds.

Table 4.1: Physicochemical properties determined for pure gums; AO gum “*Anacardium occidentale*”, AS gum “*Acacia senegal*”, KS gum “*Khaya senegalenses*”

Physico-chemical parameter	AO gum	AS gum	KS gum
Colour	Brownish-yellow	Navajowhite 1	Darkorange 4
Solubility (at 27 <sup>0</sup> C) (water) (Ethanol)	6.7 <sup>b</sup> ± 0.1 0.0	9.8 <sup>b</sup> ± 0.1 0.0	8.1 <sup>b</sup> ± 0.2 0.2
pH (at 27 <sup>0</sup> C)	5.51 <sup>b</sup> ± 0.05	5.01 <sup>b</sup> ± 0.03	4.18 <sup>b</sup> ± 0.06
UV Maximum absorption (nm)	210	200	300
Turbidity (FAU)	89	25	376
Conductivity (µs/cm)	133.40 <sup>b</sup> ± 0.01	185.00 <sup>ab</sup> ± 0.03	341.10 <sup>a</sup> ± 0.01
Salinity(µS/cm)	0.1	0.1	0.2
Total Dissolved Solid (TDS) mg/l	67.60 <sup>b</sup> ± 0.12	87.90 <sup>b</sup> ± 0.10	174.80 <sup>a</sup> ± 0.15

Results are expressed as mean ± SD for three replications.

The means were found to be significantly different (p < 0.05), equal variances assumed using Tukey and Duncan.

a = there is a significant difference, b= there no significant difference

Table 4.2: Physicochemical property determined for *Acacia senegal* and *Anacadium occidentale* (AS:AO) gum blends

Physicochemical parameters	AS:AO 80:20	AS:AO 60:40	AS:AO 50:50	AS:AO 40:60	AS:AO 20:80
Colour	Peachpuff 1	Bisque	Bisque 2	Navajowhite 2	Wheat
Solubility (water) (Ethanol)	9.2 ± 0.1 0.0	8.7 ± 0.2 0.0	8.2 ± 0.2 0.0	7.6 ± 0.1 0.0	7.1 ± 0.3 0.0
pH (@ 27 <sup>0</sup> C)	4.53 ± 0.01	4.88 ± 0.04	4.94 ± 0.02	4.81 ± 0.1	4.82 ± 0.05
UV Maximum absorption (nm)	205	215	210	210	210
Turbidity (FAU)	54	120	122	128	136
Conductivity (µs/cm)	185.30 <sup>a</sup> ± 0.11	147.00 <sup>b</sup> ± 0.09	133.80 <sup>b</sup> ± 0.07	139.50 <sup>b</sup> ± 0.14	138.80 <sup>b</sup> ± 0.03
Salinity(µS/cm)	0.1	0.1	0.1	0.1	0.1
Total Dissolved Solid (TDS) mg/l	94.10 ± 0.07	74.50 ± 0.04	67.31 ± 0.03	70.80 ± 0.07	69.81 ± 0.04

Results are expressed as mean ± SD for three replications.

The means were found to be significantly different (p < 0.05), equal variances assumed using Tukey and Duncan.

a = there is a significant difference, b = there no significant difference

Table 4.3: Physicochemical property determined for *Acacia senegal* and *Khaya sengalenses* (AS:KS) gum blends

Physicochemical parameters	AS:KS 80:20	AS:KS 60:40	AS:KS 50:50	AS:KS 40:60	AS:KS 20:80
Colour	Wheat	Wheat 2	Navajowhite 2	Tan	Burlywood
Solubility (water) (Ethanol)	10.5 ± 0.1 0.0	9.7 ± 0.2 0.0	9.3 ± 0.1 0.0	8.9 ± 0.4 0.0	8.5 ± 0.3 0.2
pH (@ 27 <sup>0</sup> C)	4.81 ± 0.06	4.78 ± 0.08	4.70 ± 0.12	4.65 ± 0.11	4.36 ± 0.04
UV Maximum absorption (nm)	225	235	240	245	285
Turbidity (FAU)	103	263	285	319	392
Conductivity (µs/cm)	245.00 ± 0.06	215.00 <sup>a</sup> ± 0.01	236.00 ± 0.02	244.00 ± 0.00	299.00 <sup>b</sup> ± 0.00
Salinity(µS/cm)	0.1	0.1	0.1	0.1	0.2
Total Dissolved Solid (TDS) mg/l	125.1 ± 0.1	110.5 <sup>a</sup> ± 0.2	120.6 ± 0.0	124.6 ± 0.5	153.6 <sup>b</sup> ± 0.1

Results are expressed as mean ± SD for three replications.

The means were found to be significantly different (p < 0.05), equal variances assumed using Tukey and Duncan.

a = there is a significant difference, b = there no significant difference

Table 4.4: Physicochemical property determined for *Anacardium occidentale* and *Khaya sengalense* (AO:KS) gum blends

Physicochemical parameters	AO:KS 80:20	AO:KS 60:40	AO:KS 50:50	AO:KS 40:60	AO:KS 20:80
Colour	Burlywood 2	Burlywood	Tan	Tan 2	Tan 3
Solubility (water) (Ethanol)	8.7 ± 0.1 0.0	8.5 ± 0.2 0.0	8.1 ± 0.1 0.0	7.8 ± 0.2 0.0	7.5 ± 0.1 0.1
pH (@ 27 <sup>0</sup> C)	4.62 ± 0.06	4.57 ± 0.03	4.51 ± 0.02	4.34 ± 0.03	4.25 ± 0.02
UV Maximum absorption (nm)	235	250	245	250	285
Turbidity (FAU)	352	338	336	334	411
Conductivity (µs/cm)	181.90 <sup>a</sup> ± 0.11	190.50 <sup>a</sup> ± 0.16	239.00 ± 0.02	280.00 ± 0.03	316.00 <sup>b</sup> ± 0.04
Salinity(µS/cm)	0.1	0.1	0.1	0.1	0.2
Total Dissolved Solid (TDS) mg/l	92.00 <sup>a</sup> ± 0.02	97.00 <sup>a</sup> ± 0.01	120.90 ± 0.10	142.20 ± 0.08	161.52 <sup>b</sup> ± 0.14

Results are expressed as mean ± SD for three replications.

The means were found to be significantly different (p < 0.05), equal variances assumed using Tukey and Duncan.

a = there is a significant difference, b = there no significant difference

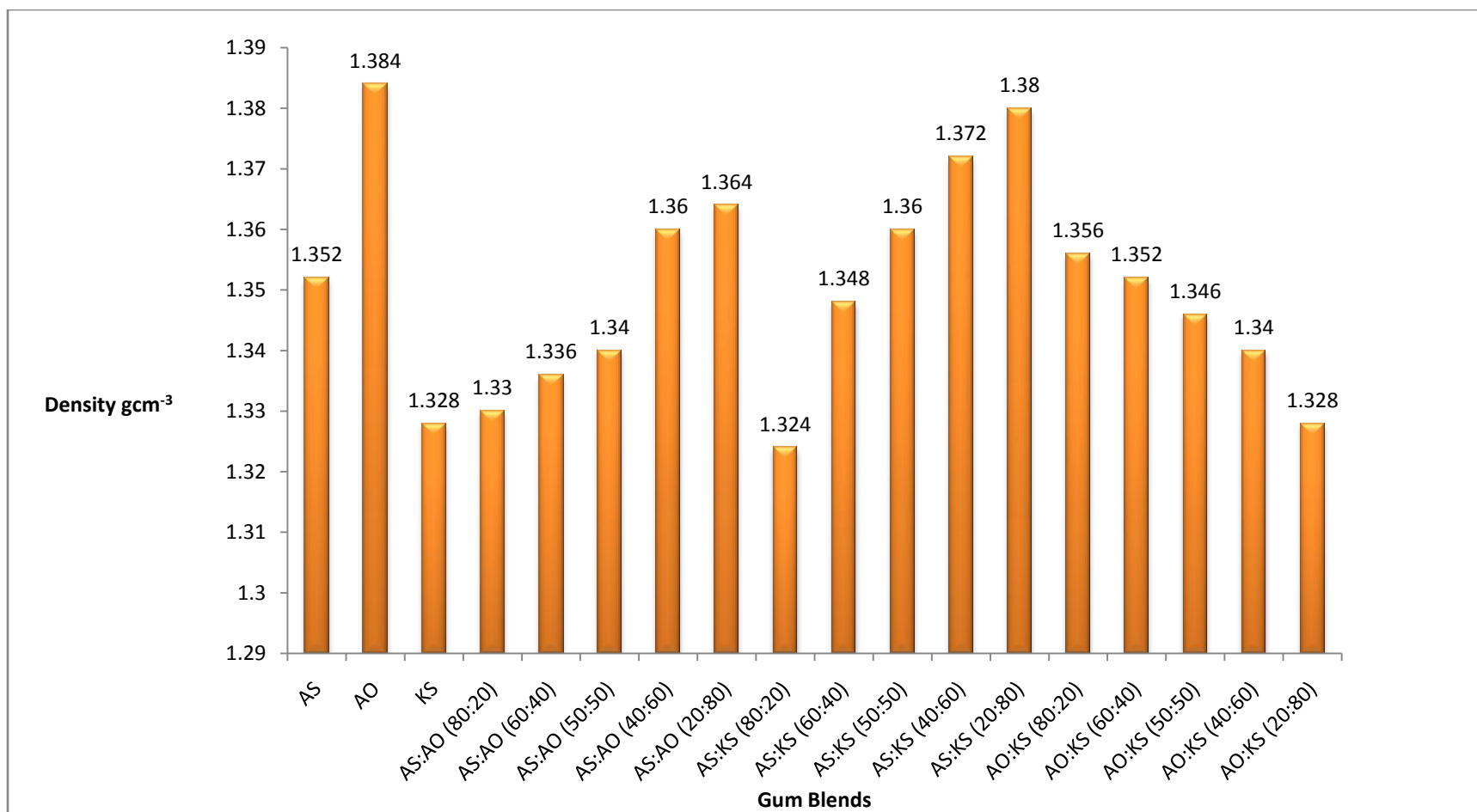


Fig. 4.2: The density of the pure gums and their respective blend

#### 4.2 Effect of concentration on relative viscosity of blends

In general, for all blends of AS and AO, an increase in relative viscosity was observed as the concentration was increased (Fig. 4.3), but a slight decrease was found in the 50:50 blend at concentration between 0.8 and 1.0 g/dl. AS:KS blends follow similar trend, but a more pronounced or sharp increase in relative viscosity was evident for concentration 0.6 g/dl for the 60:40 blend. The relative viscosity of the blends for AS:AO increased slightly as the concentrations of the gums increased but an evident sharp increase was noticed at 0.6 g/dl for the 80:20 blend and at 0.8 g/dl for the 60:40 and 50:50 gum blend.

The effect of concentration of the pure gums led to a decrease in their specific viscosity, with *Acacia senegal* having the highest value of specific viscosity value and *Anacardium occidentale* being the least.

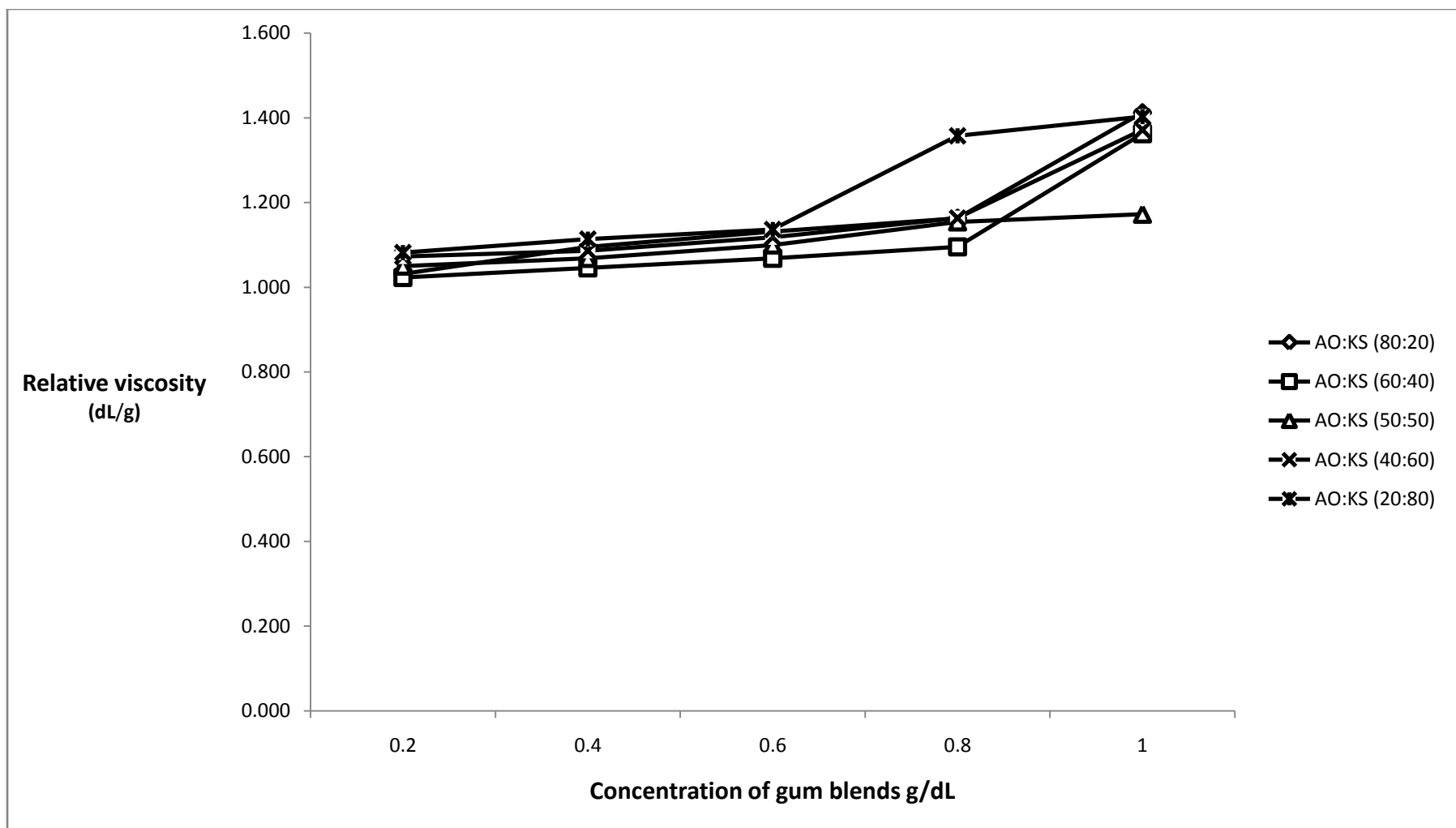


Fig 4.3: variation of relative viscosity of the blend AO:KS with concentration of the blends at room temperature

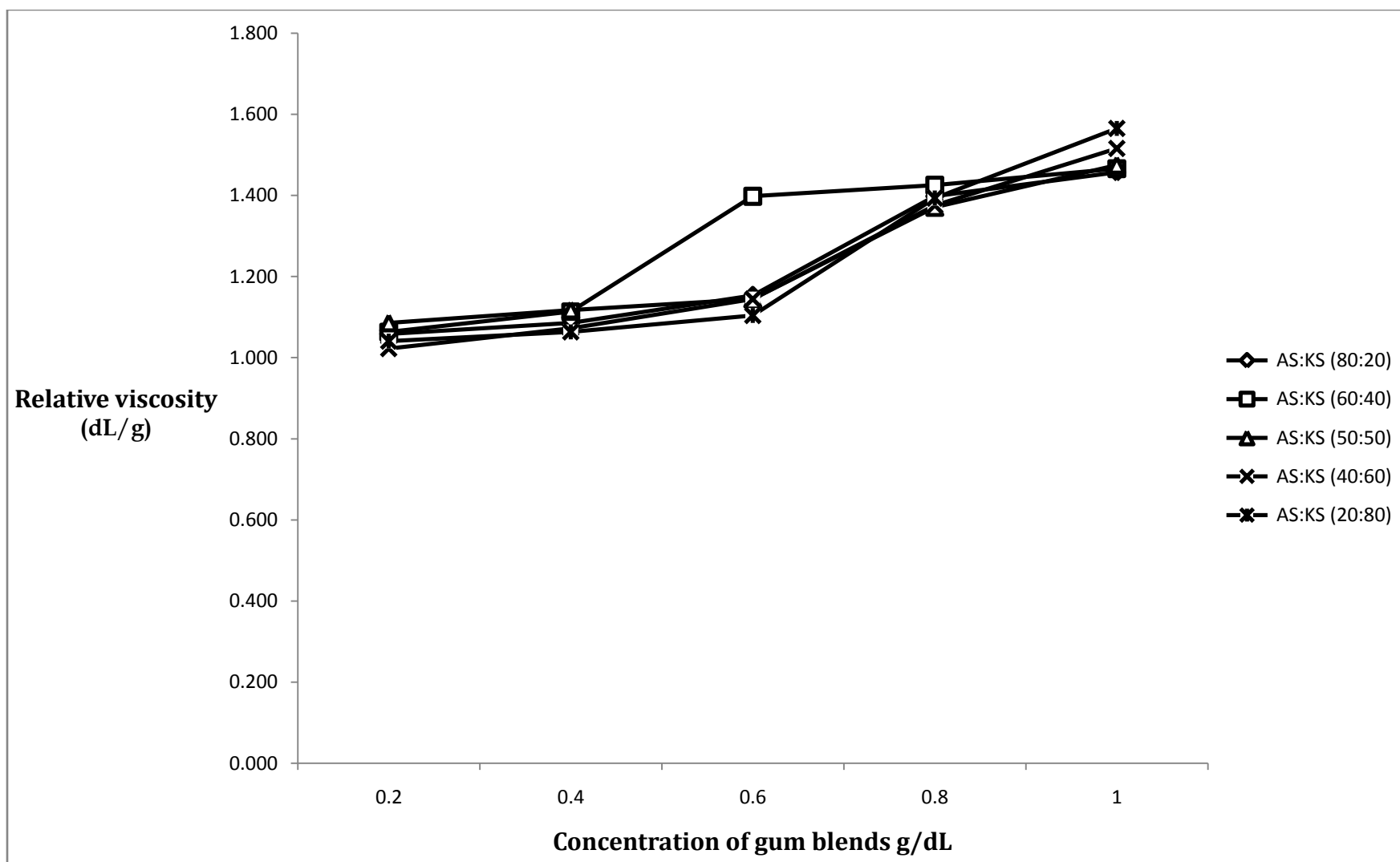


Fig 4.4: variation of relative viscosity of the blend As:Ks with concentration of the blends at room temperature

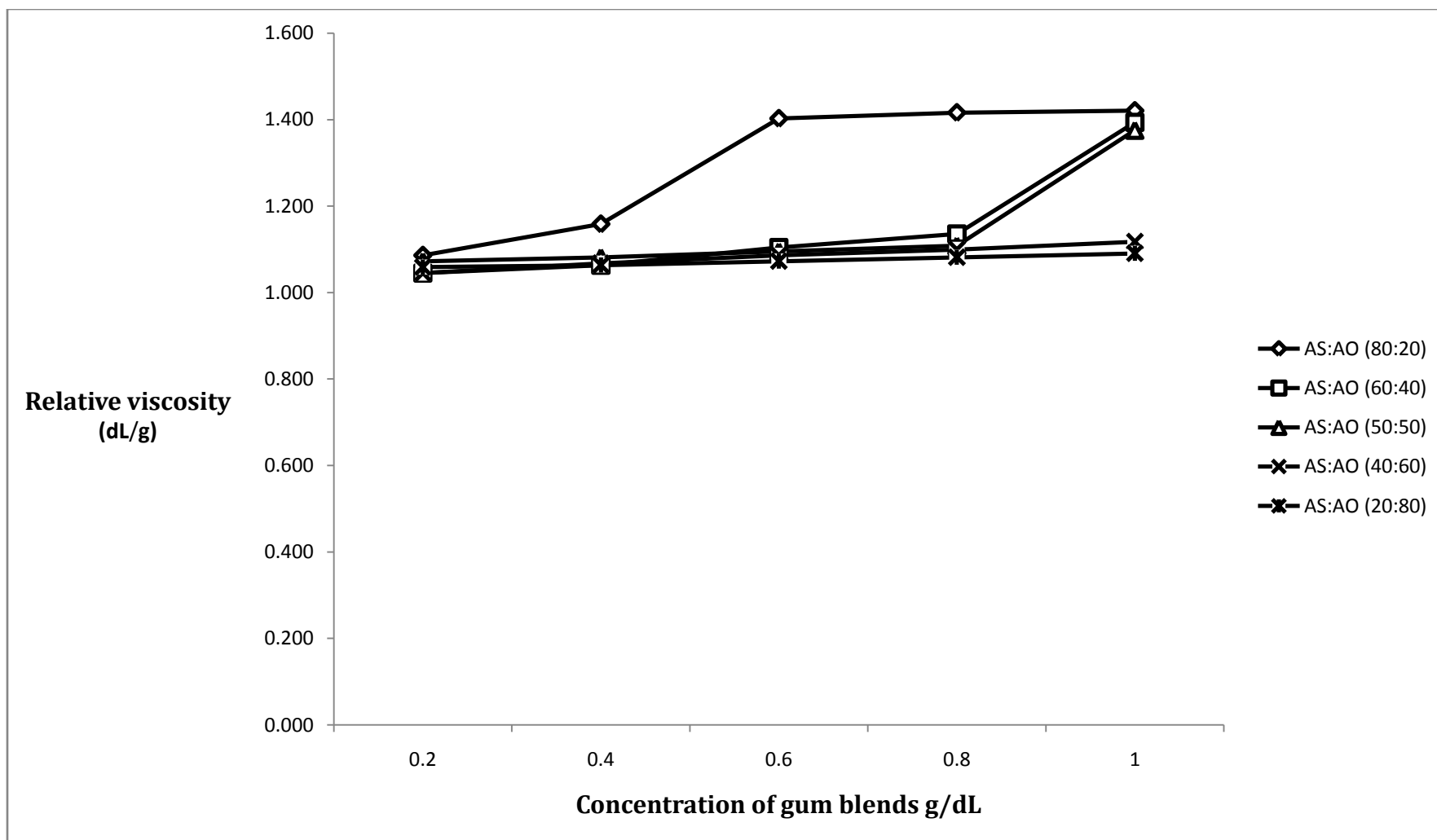


Fig. 4.5: variation of relative viscosity of the blend As:Ao with concentration of the blends at room temperature

### 4.3 Effect of temperature on the specific viscosity of the blends

Thermodynamic and transport properties of gum mixture or blends, help in understanding the nature of molecular interaction taking place in solutions, this further helps in improving on the quality grade of gums used in both food and pharmaceutical industries.

Fig. 4.6, 4.7, 4.8 and 4.9 show plots for the variation of specific viscosity of the pure gums, the blends AS:AO, AO:KS and AS:KS gums with temperature respectively. It was observed from the Figures that viscosity decreased as the temperature of the gums solution was increased. In order to calculate the activation energy of flow for the studied gums, the Arrhenius-Frenkel-Eyring equation (equation 4.17) was used (Eissa, 2013; Menon, 2003).

$$\eta = A \exp\left(\frac{E_F}{RT}\right) \text{-----} (4.1)$$

where A is the pre-exponential factor,  $E_F$  is the activation energy of flow, R is the universal gas constant and T is the absolute temperature in Kelvin.

All blends considered had considerable decrease in specific viscosity as the temperature decreased. In the AS:AO blends there is superimposition between the blend 50:50 and 60:40, where its viscosity slightly increased a bit higher than the latter, this case might be as a result of some synergistic interaction resulting in a helical coil overlap between the AS:AO gum as found in xanthan-LBG blend(Higiro *et al.*, 2006).

In the AS:KS blend the 60:40 and 50:50 blend dropped lower than the rest and the latter having the least viscosity at 70°C but they all slightly increased further as we approach 90°C. While in the AO:KS blends the 50:50 and 80:20 blend had a negative specific viscosity at 70°C indicating that these blends loose a considerable amount of their gumming properties at that temperature.

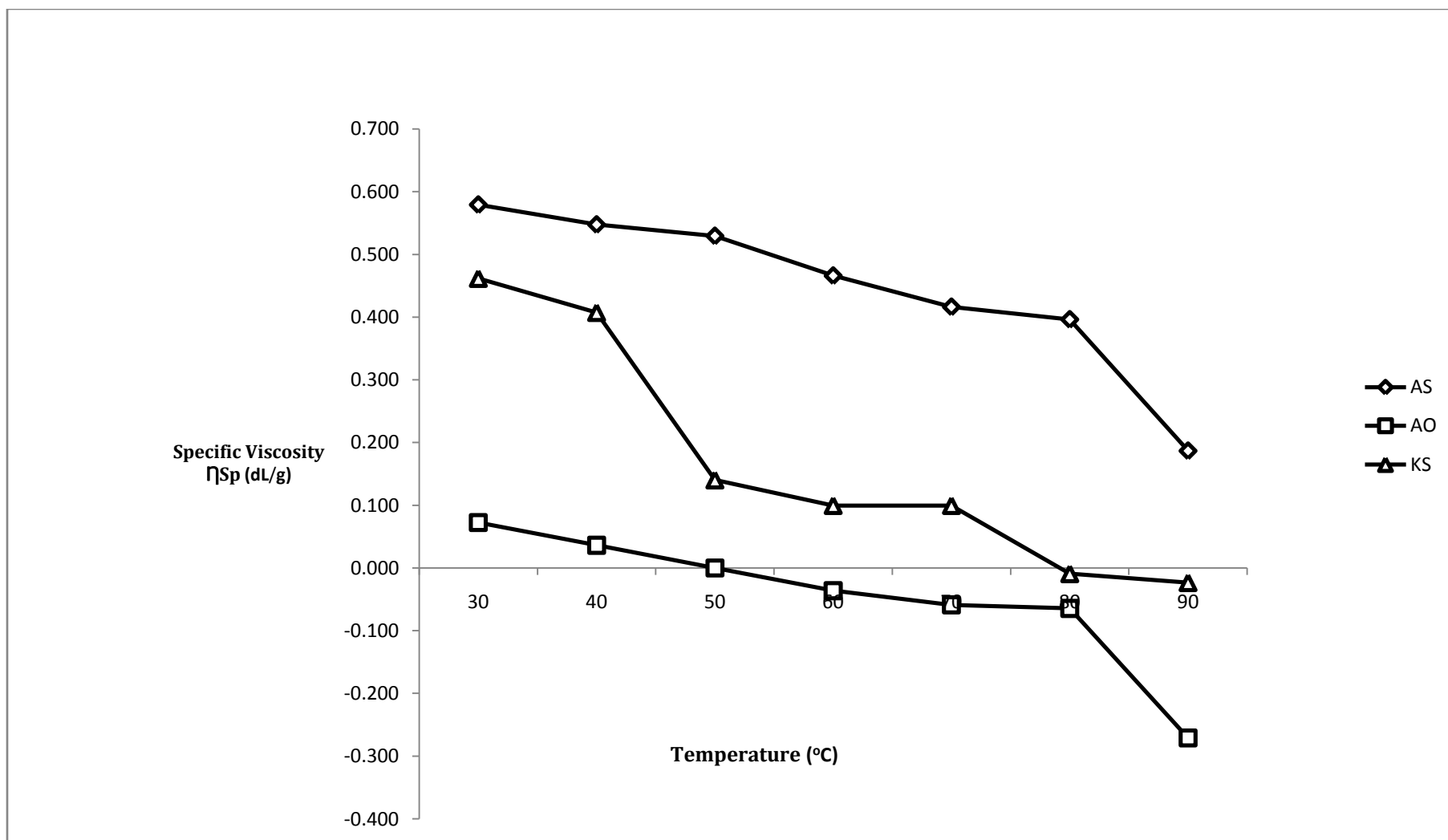
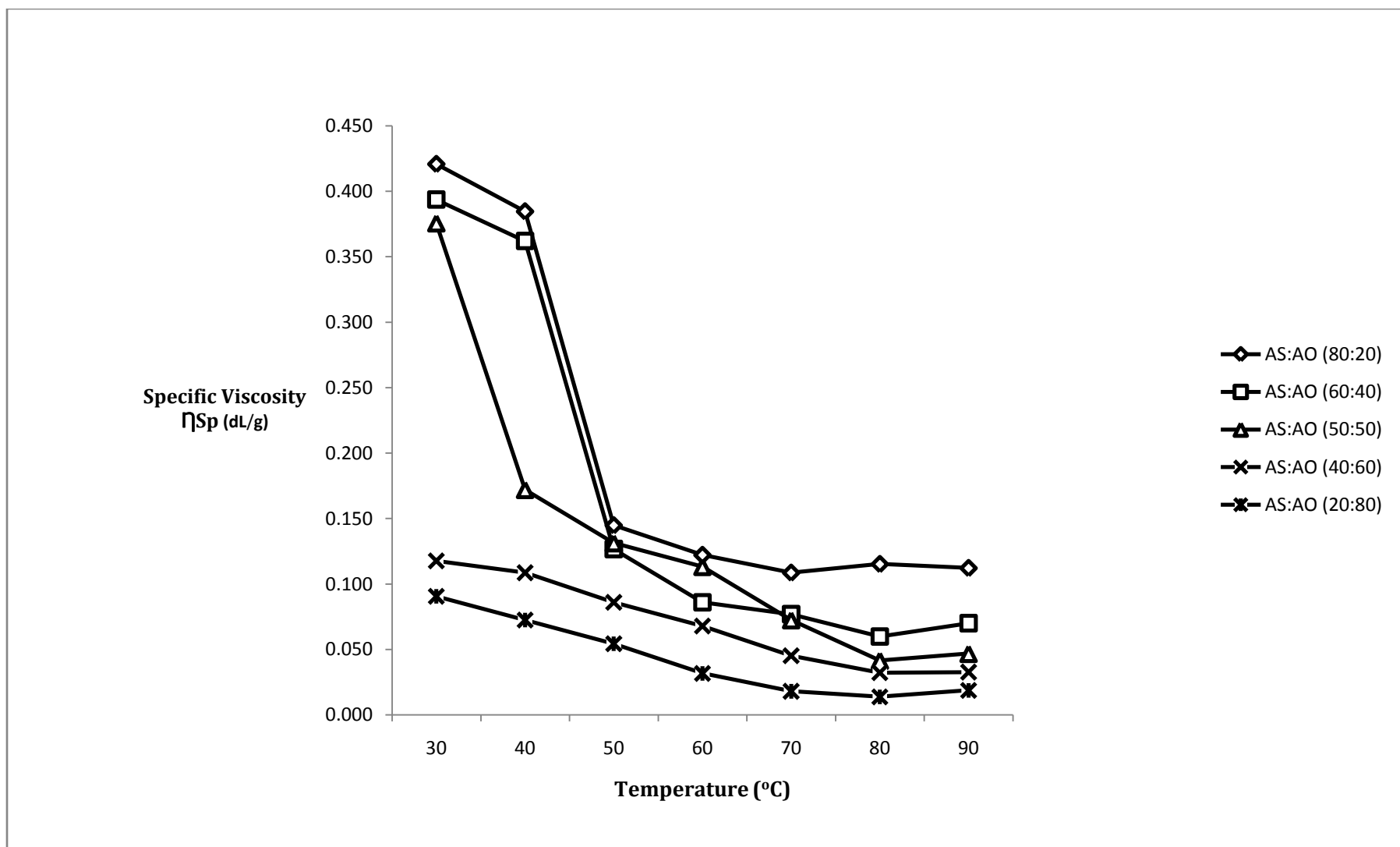
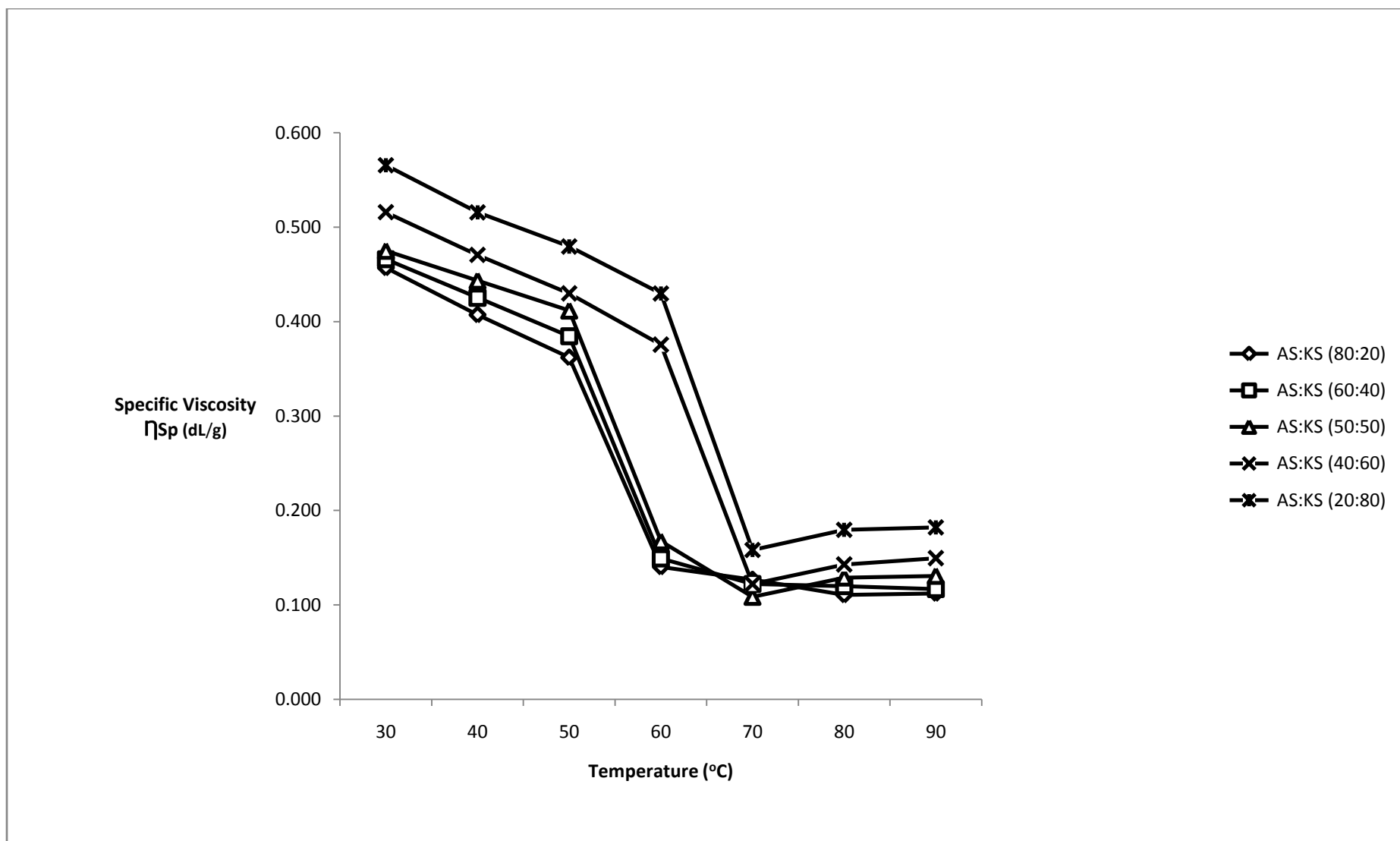


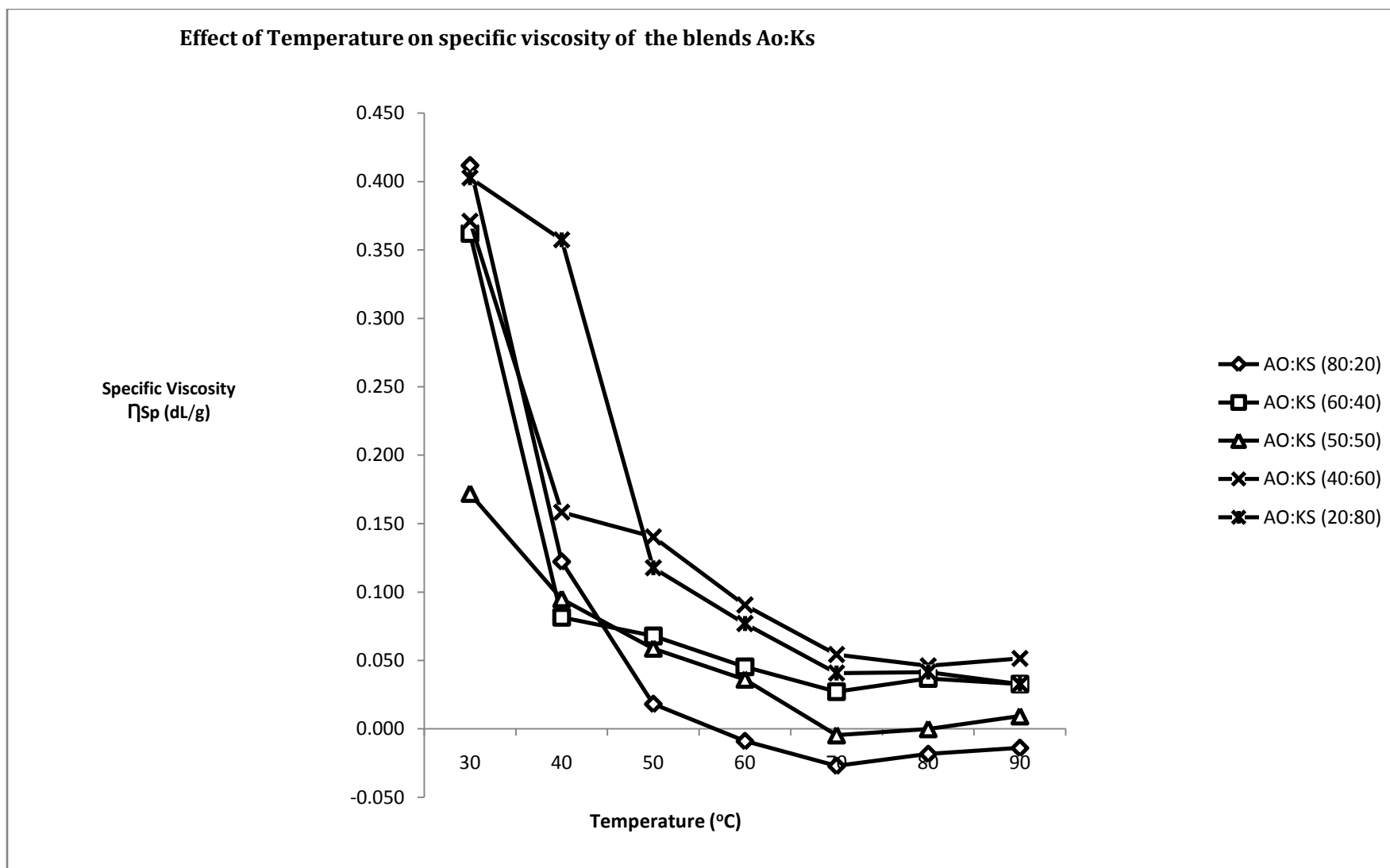
Fig.4.6: variation of specific viscosity of the pure gums with concentration at room temperature



**Fig 4.7: variation of specific viscosity of the blend As:Ao with concentration of the blends at room temperature**



**Fig 4.8: variation of specific viscosity of the blend As:Ks with concentration of the blends at room temperature**



**Fig. 4.9: variation of specific viscosity of the blend Ao:Ks with temperature**

#### 4.4 Effect of Added Salt on Specific Viscosity of the Gums

In order to successfully study the trend in the specific viscosity as a result of addition of inorganic salt, a uniform concentration of the gums were maintained at (1.0 g/dl) while that of the salts chosen were varied from (0.20-1.00 g/dl).

For *Acacia senegal* and all AS-KS, AS-AO blends, a decrease in specific viscosity was observed as the concentration of KBr increased (Figs. 4.15 and 4.17). Increase in intrinsic viscosity was observed when KCl and  $AlCl_3$  were added. A more pronounced increase was observed for gum blend AS:AO (20:80) the concentration of KCl added was 0.6 g/dl. The data for the blends did fit with the linear regression model with a few exception. But the AO-KS blends did not follow similar trend. The viscosity decreased when KCl and KBr were added with an exception of 80:20 and 60:40, which increased as the concentration of the salts added increased. The blends of AO:KS increased in specific viscosity when  $AlCl_3$  was added (Fig. 4.21), whereby a pronounced increase was noticed for 40:60 and 50:50 blends when the concentration added increased between 0.4 – 0.6 g/dl, while a continuous smooth decrease was noticed for 80:20 and 60:40 blends. Due to impracticability in the obtaining a good regression model for the AO:KS blends when these salts are added it would be difficult to generate an intrinsic viscosity at these conditions. In a study of the rheological properties of sodium pectate at various counter-ion concentrations, Pals and Hermans (1952) reported that the specific viscosity/concentration for sodium pectate increased with a small uniform slope with increasing polymer concentration only in excess of added salts, as is true of non-ionic polysaccharides. As ionic strength decreased, the viscosity increased, and a more complex dependence upon concentration was observed, with the appearance of a maximum, becoming more pronounced and shifting to the left. Without salt addition, the specific viscosity/concentration of sodium

pectate increased steadily with dilution, and very rapidly at high dilution. Our results showed an increase of specific viscosity/concentration for 95% of all the blends when  $\text{AlCl}_3$  was added and decreased for the other salts used except AO:KS (80:20 and 60:40) and some salt concentrations. As shown in appendix 6, 7 and 8, the hydrodynamic behavior of *Acacia senegal*, *Khaya senegalenses*, *Anacardium occidentale*, AS:AO, AS:KS and AO:KS blends was strongly affected by ion types and ion concentrations. Within each gum blend, trivalent ions from  $\text{AlCl}_3$  showed a more pronounced effect on the specific viscosity, compared with monovalent ions from KCl and KBr. The increase in ionic strength of the three salts from 0.2 to 1 caused a significant increase in specific viscosity for all gum blends. The specific viscosity increased by more than 30% of the value obtained with the pure gums and their blends when only  $1\text{g}/100\text{cm}^3$  salt was added to the gum blends.

Similar results were reported elsewhere (Lai and Chiang, 2002; Launay *et al.*, 1997; Wang *et al.*, 2002). Such behavior can be attributed to the native gum arabic. In aqueous solution with no added ions, the acacia gum molecule is extended due to electrostatic repulsion of the negatively charged uronic acids (eg rhamnose-glucuronic acid) present there in. When salt is added, charge screening causes the side chains to collapse down to the backbone, hence giving the acacia, khaya gum molecule a rod-like shape and reducing the hydrodynamic volume (Rocheffort and Middleman, 1987). The more pronounced effect of the trivalent ions (aluminium) on the specific viscosity, compared with that of monovalent ions (potassium).

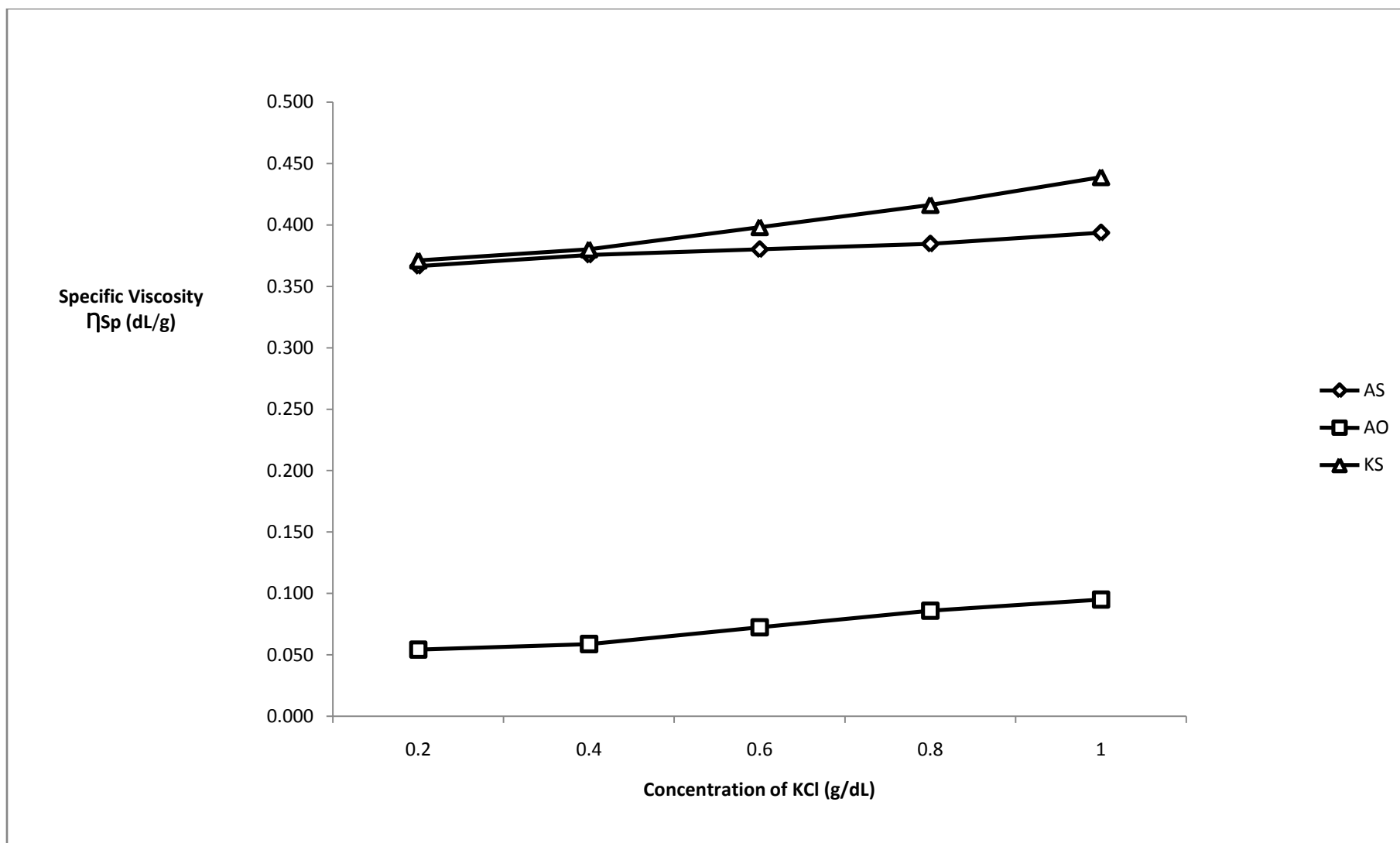


Fig. 4.10: variation of specific viscosity of the pure gums with concentration of KCl

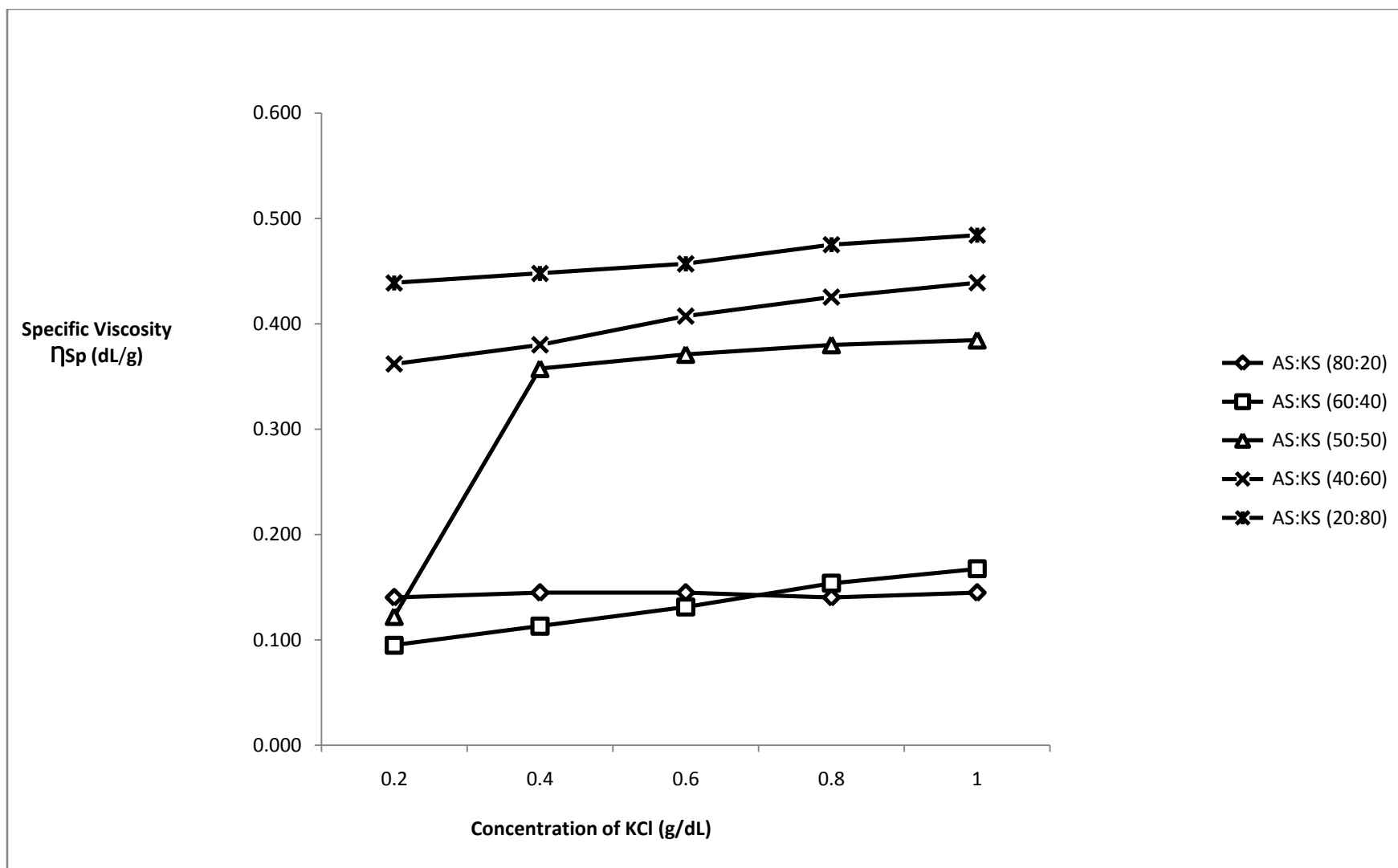


Fig. 4.11: variation of specific viscosity of AS:KS gum blends with concentration of KCl

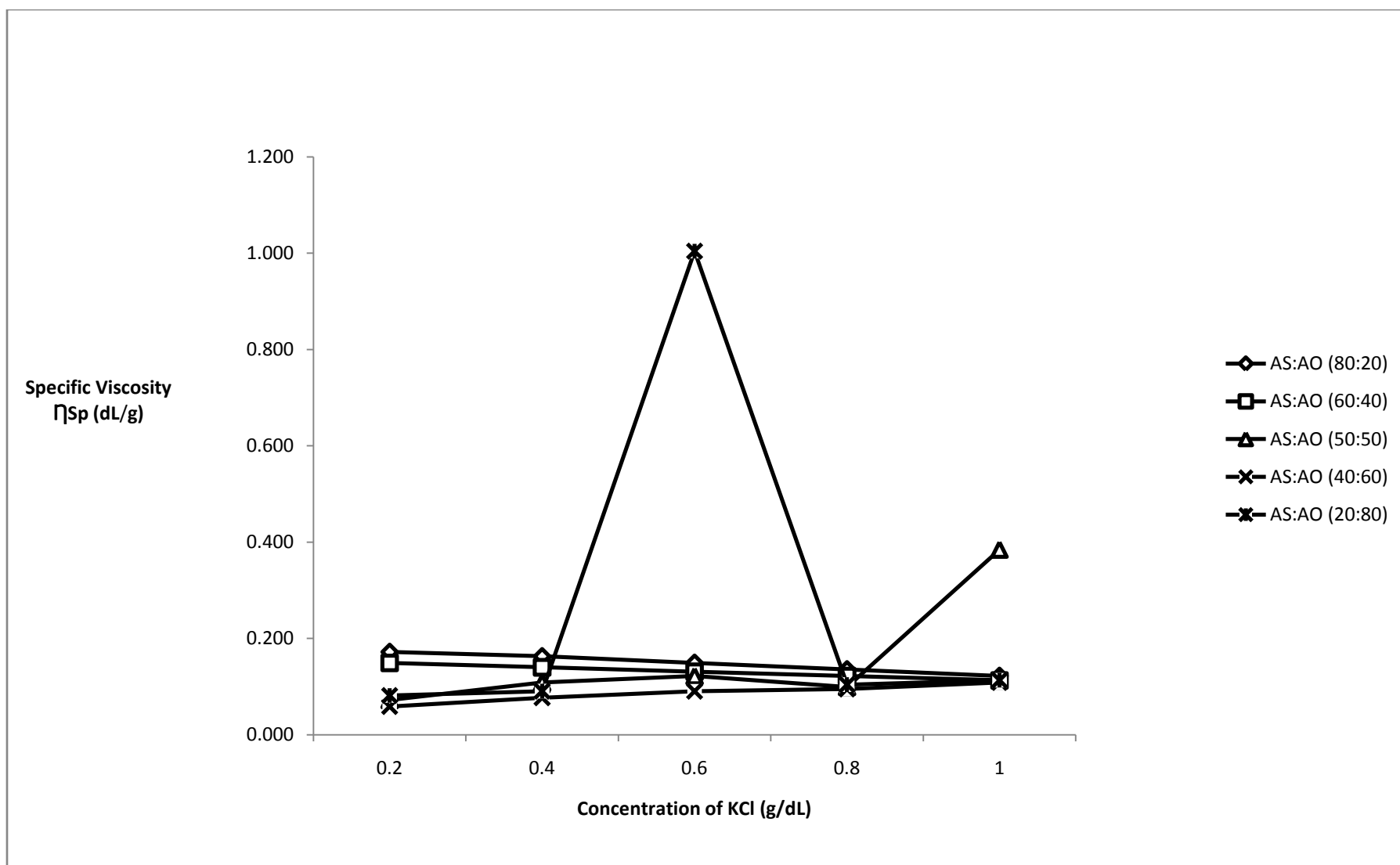


Fig. 4.12: variation of specific viscosity of As:Ao gum blends with concentration of KCl

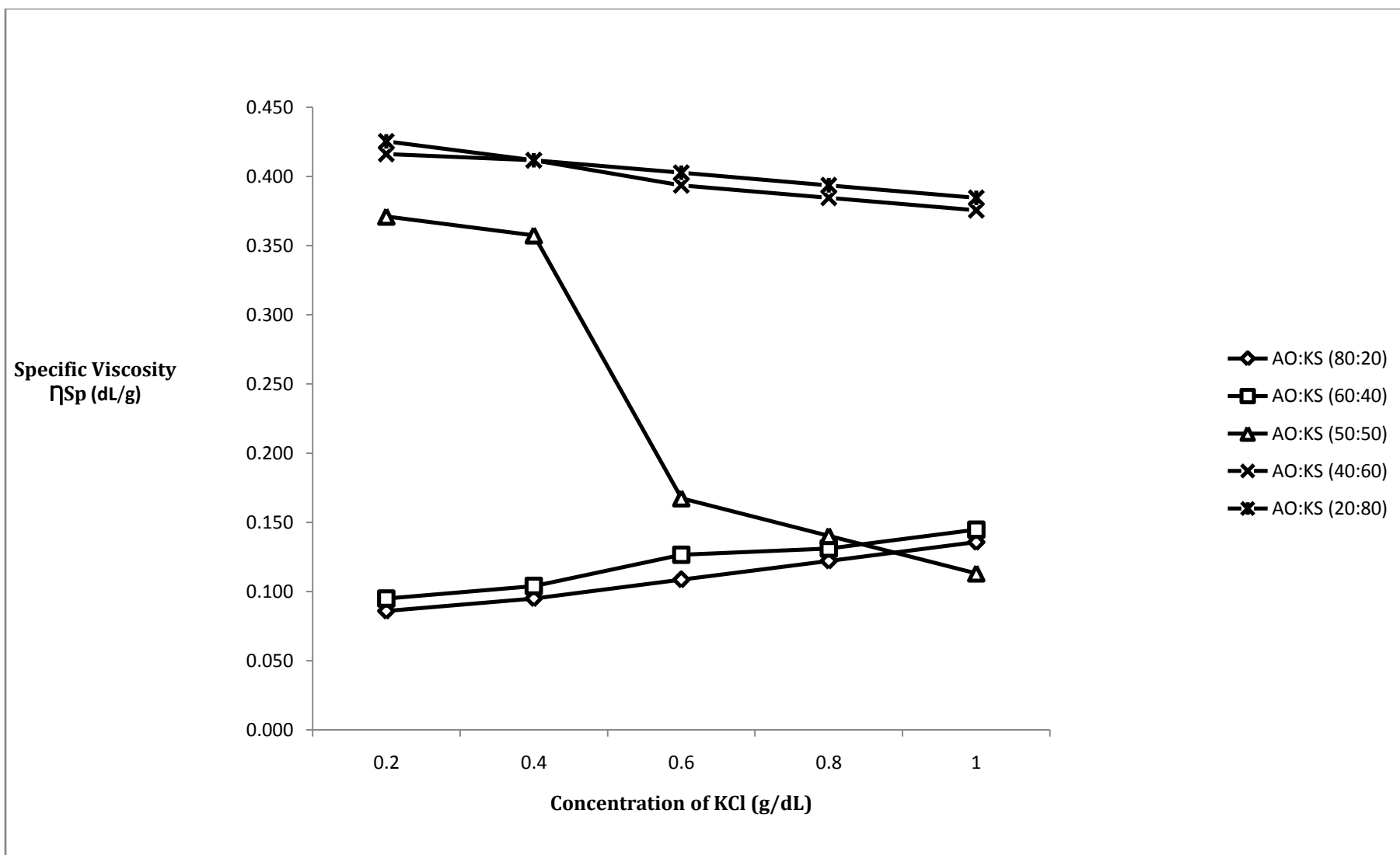


Fig 4.13: variation of specific viscosity of Ao:Ks gum blends with concentration of KCl

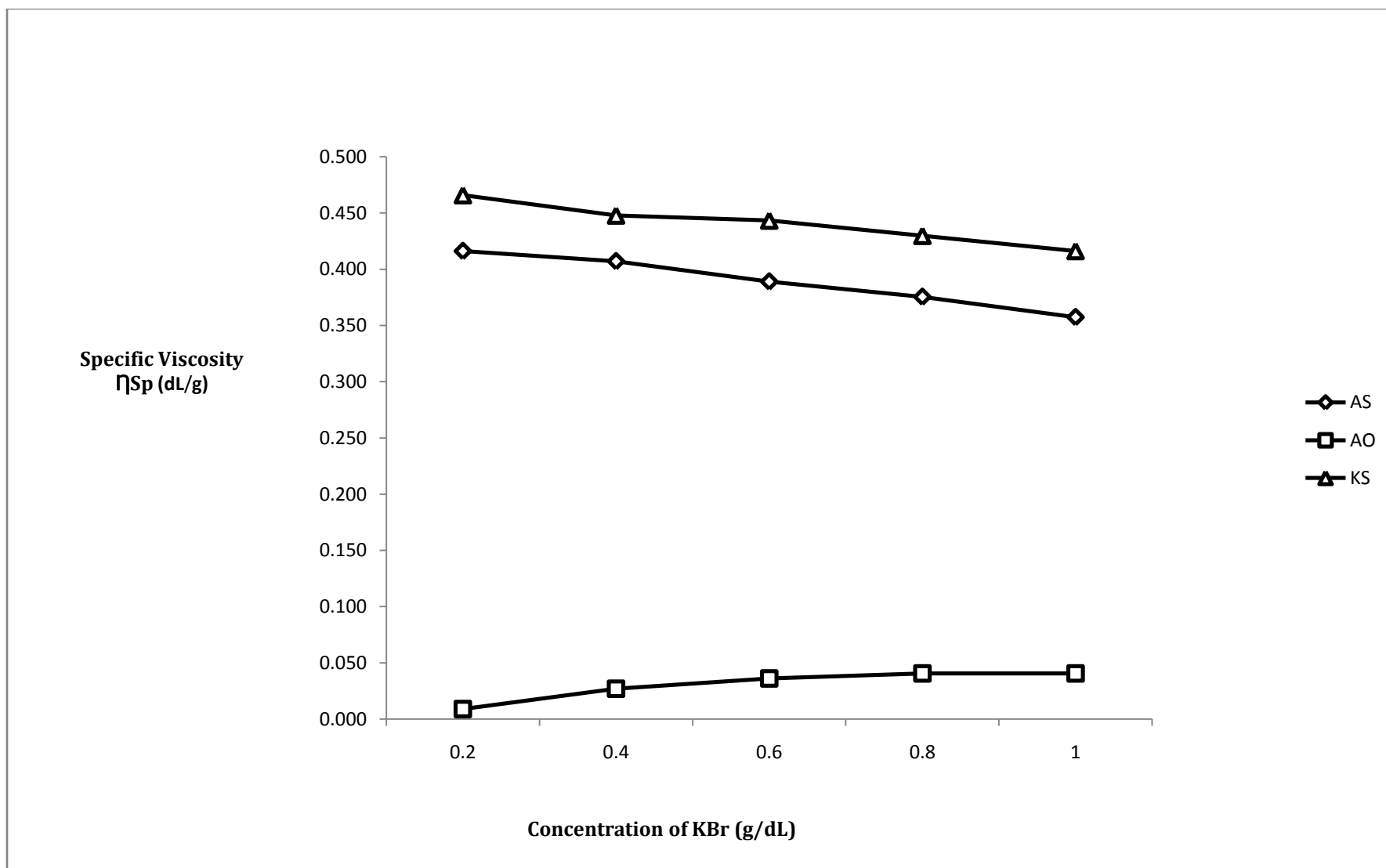


Fig 4.14: variation of specific viscosity of the gums with concentration of KBr

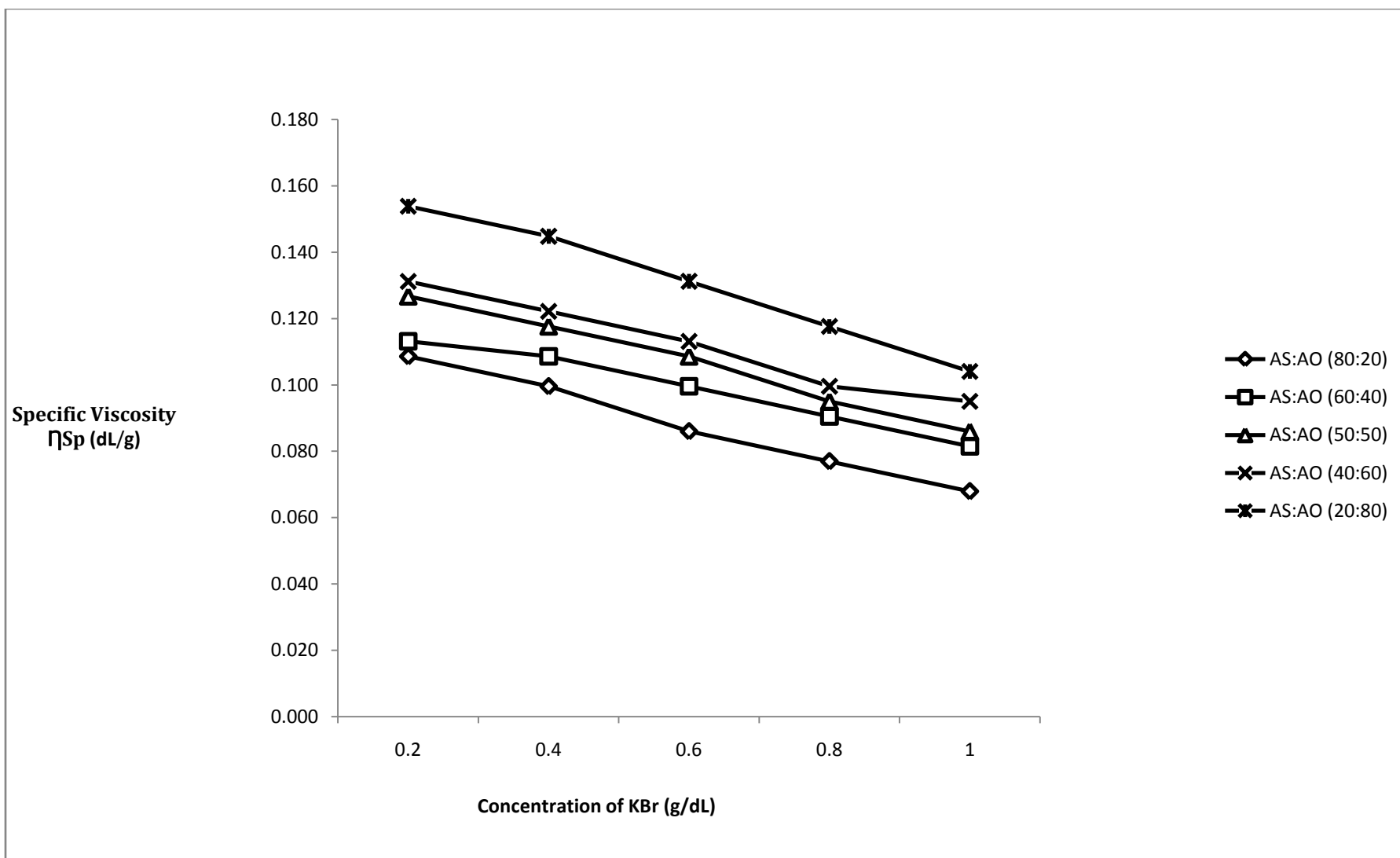


Fig 4.15: variation of specific viscosity of the blend AS:AO with concentration of KBr

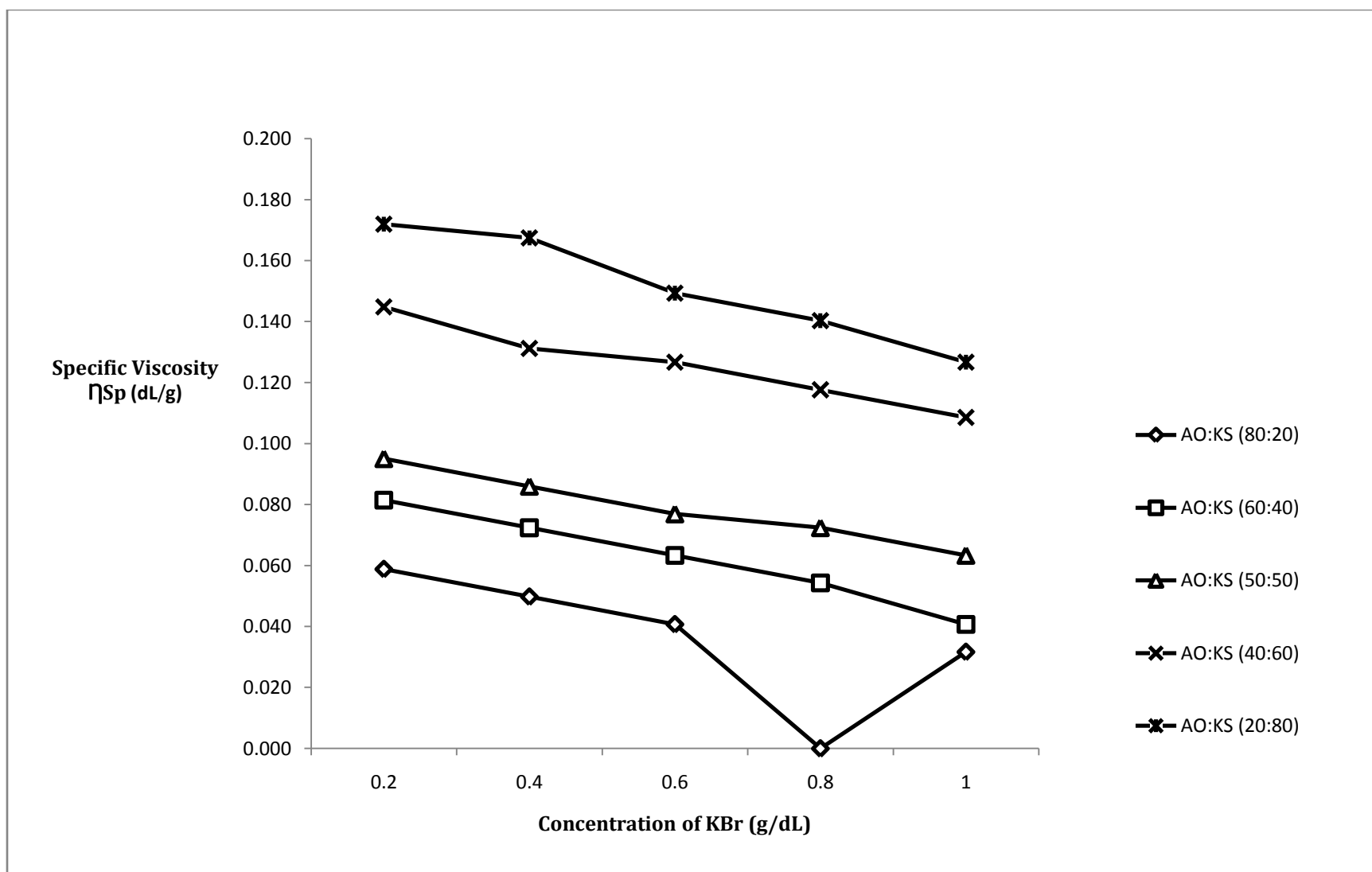


Fig 4.16: variation of specific viscosity of the blend AO:KS with concentration of KBr

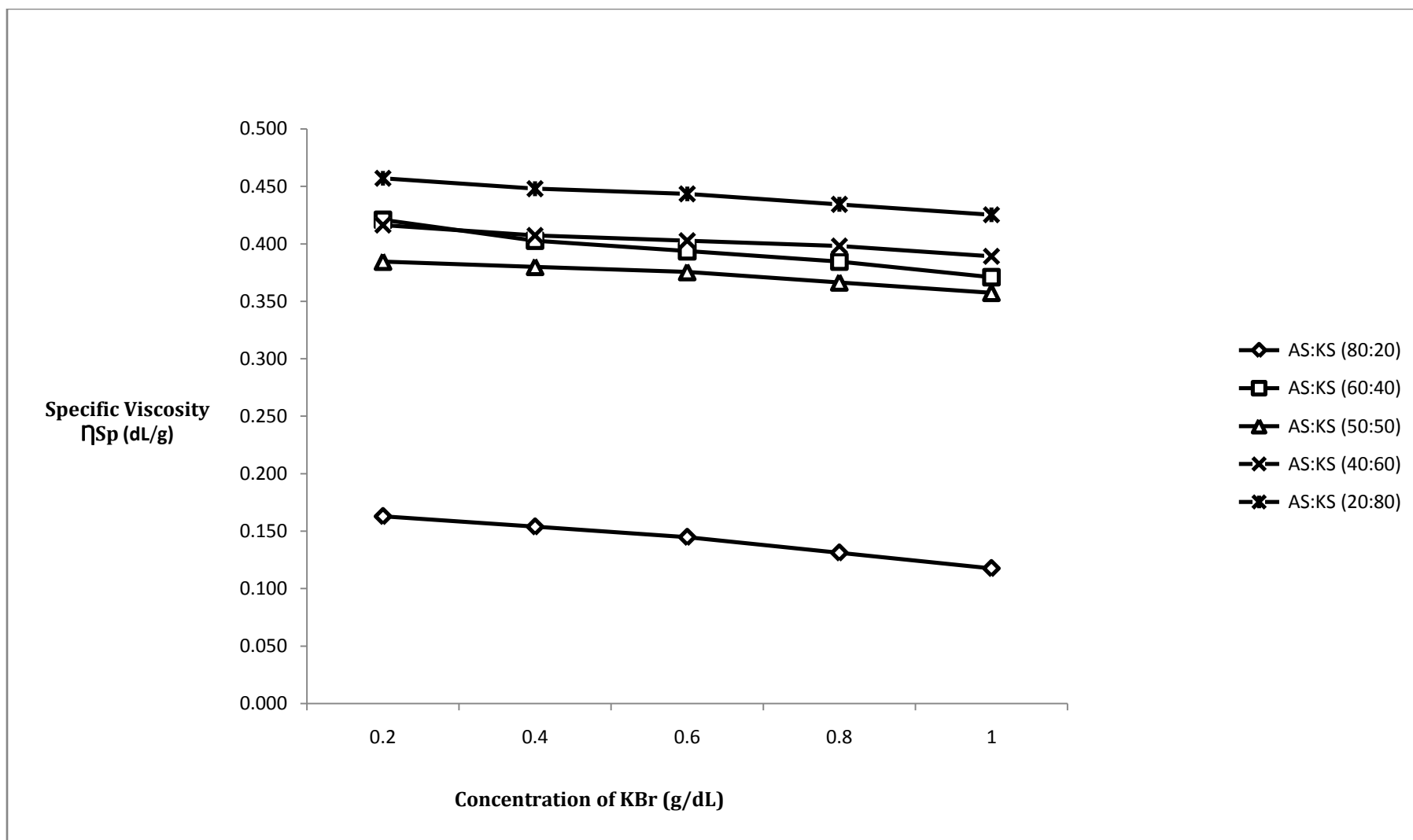


Fig 4.17: variation of specific viscosity of the blend AS:KS with concentration of KBr

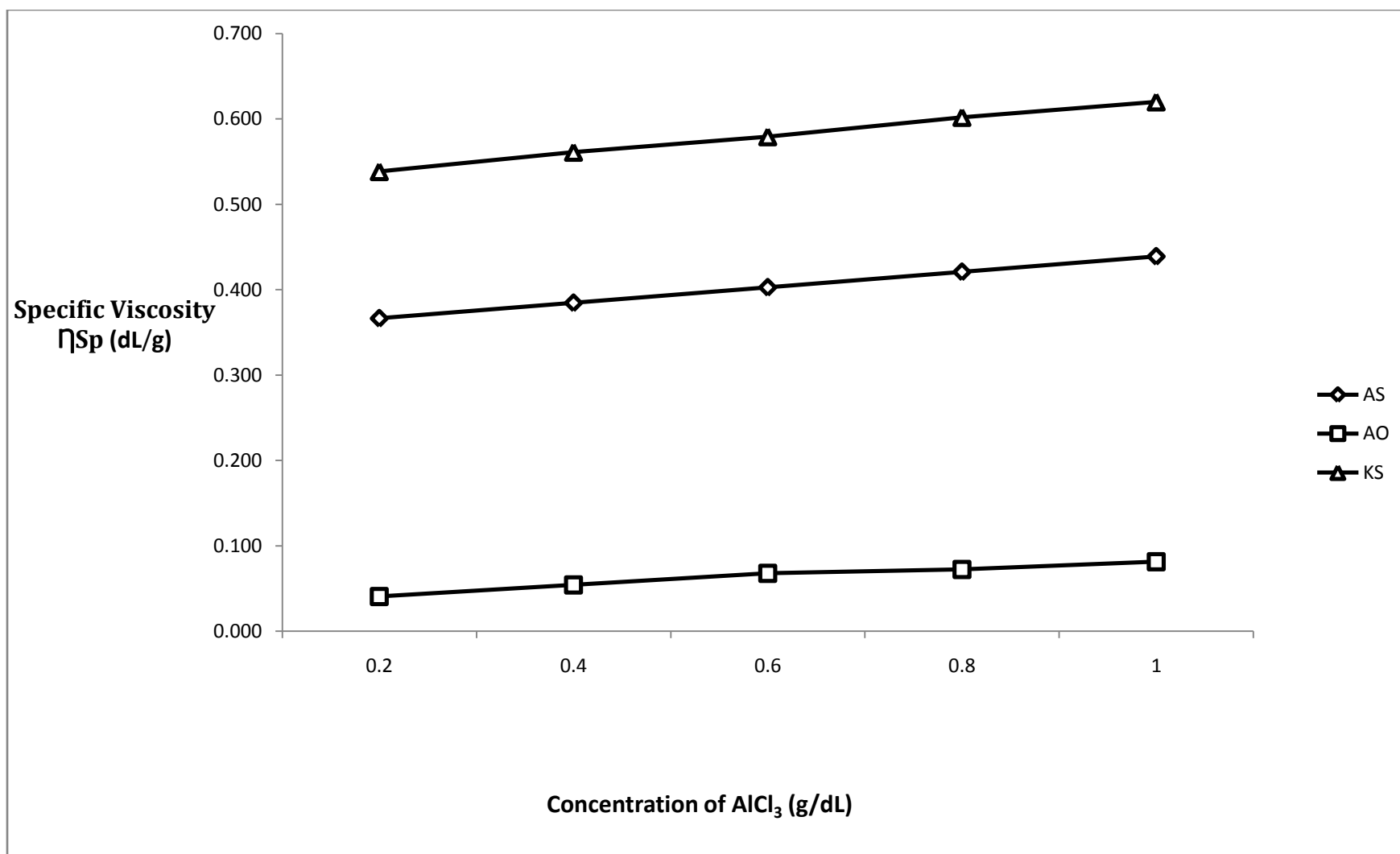


Fig 4.18: variation of specific viscosity of the pure gums with increasing concentration of  $AlCl_3$

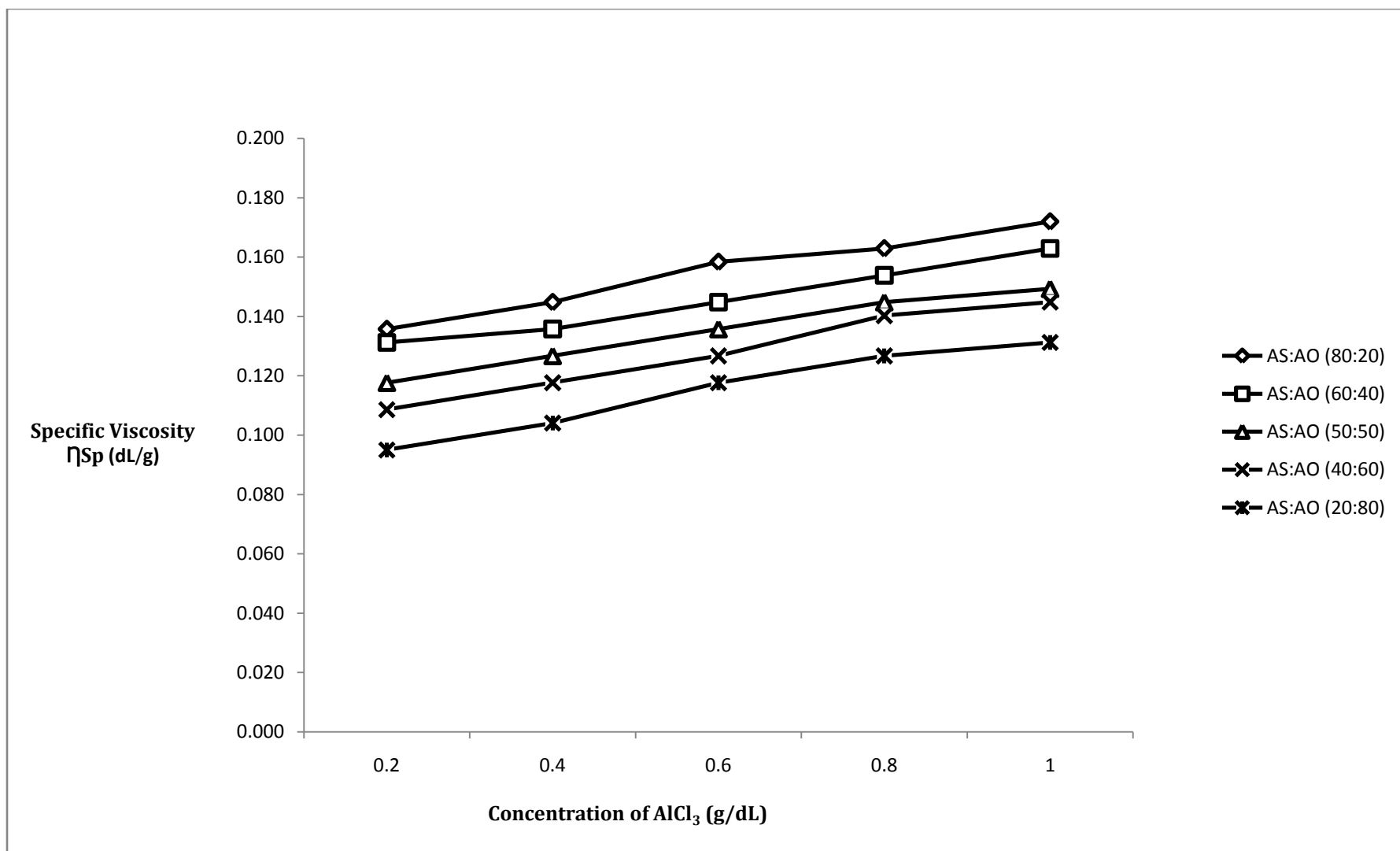


Fig 4.19: variation of specific viscosity of the blend AS:AO with increasing concentration of  $AlCl_3$

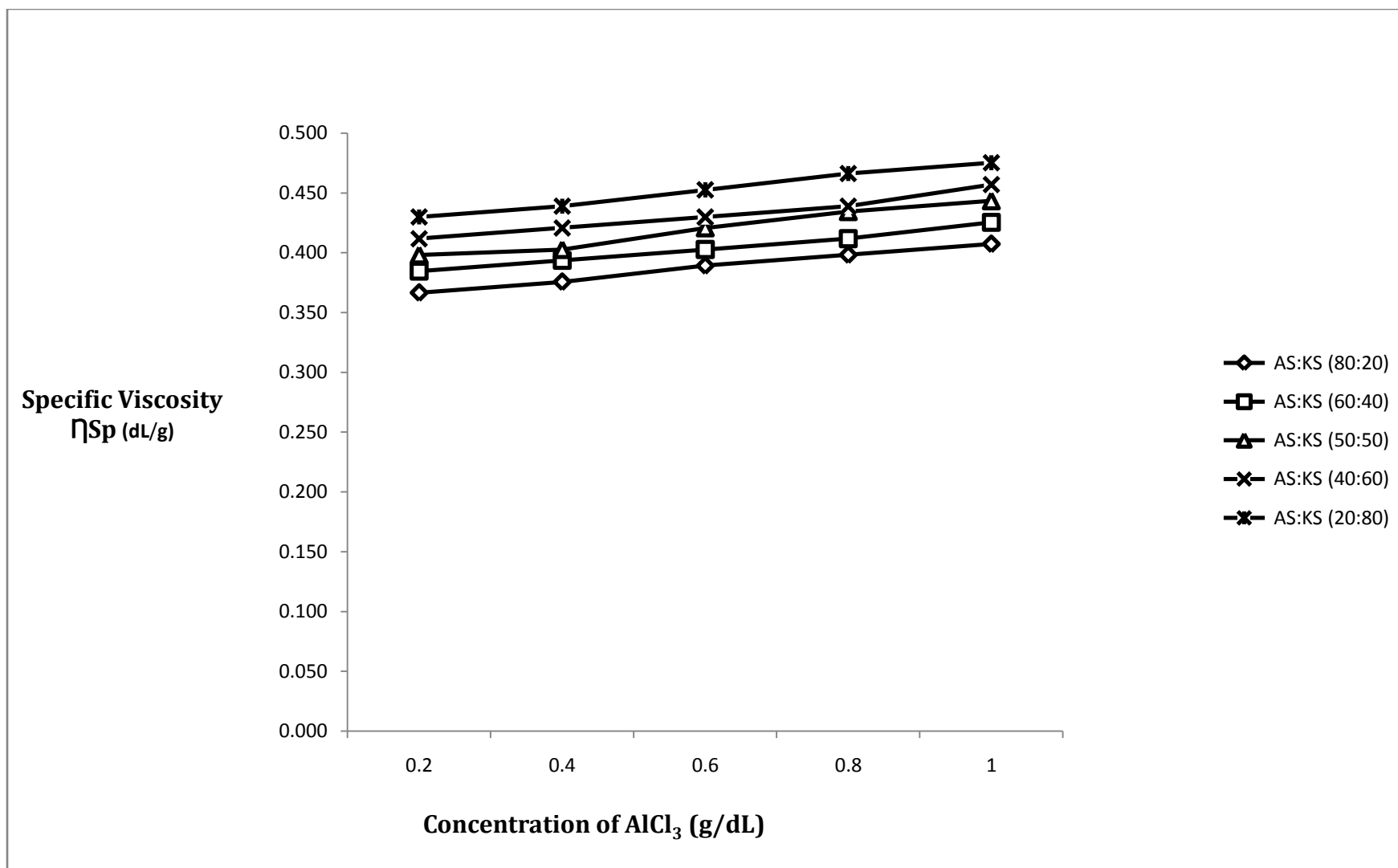


Fig 4.20: variation of specific viscosity of the blend AS:KSs with increasing concentration of  $AlCl_3$

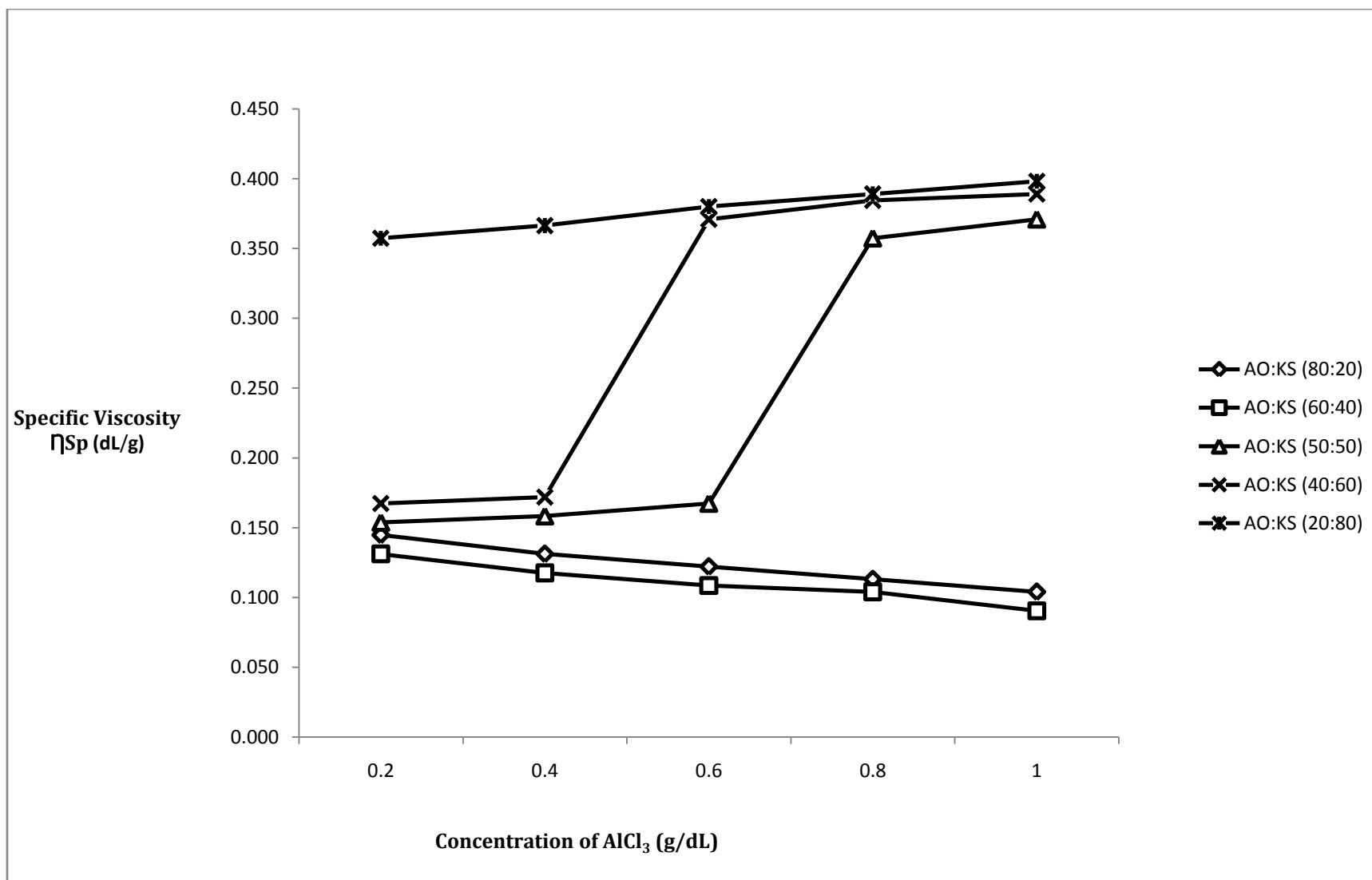


Fig 4.21: variation of specific viscosity of the blend AO:KS with increasing concentration of AlCl<sub>3</sub>

#### 4.5 Intrinsic Viscosity

The intrinsic viscosity determined for all the pure gums and their blends had an increase in relative viscosity which was observed as the concentration increased (Table 4.5), but a more pronounced increase in relative viscosity was evident for concentrations more than 0.4 g/dL. The GDEP therefore failed to generate the intrinsic viscosity for the pure gums and their blends since the data generated did not fit with the linear regression model. The Huggins and Kraemer plots did not provide a better fit and, therefore, Tanglerpaibul and Rao plot was used (Higiro *et al.*, 2006). It was found to have the best fit (Chou and Kokini, 1987; Tanglerpaibul and Rao, 1987). This was done to determine the intrinsic viscosity by plotting  $\eta_{rel}$  vs.  $C$ . Straight-line relationships with large linear regression coefficients were obtained for all the gums. McMillan (1974) reported that methods of determination of intrinsic viscosity based on slopes of plots had larger correlation coefficients and smaller standard errors than those based on intercepts of plots. The values of the intrinsic viscosities resulting from these models differed, but showed similar trends (Appendix 1-5, Table 4.5). Intrinsic viscosity values calculated by using Tanglerpaibul and Rao plot was chosen as the best model for intrinsic viscosity determination because it showed a better linear fit, with higher correlation ( $R^2$ ) for all blends, and the results were similar with other findings (Tanglerpaibul and Rao, 1987). The aggregation effects may have been suppressed for *Acacia senegal* (Gum Arabic) as a result of the blending with *Anacardium occidentale* (cashew gum) in the AS-AO polymer blend hence leading to a considerable decrease in the intrinsic viscosity of the blend as *Anacardium occidentale* gum is added in excess. Launay *et al.*, (1997) reported that xanthan at 0.025 g/dl or less corresponded to the Newtonian viscosity. The dilute Newtonian domain was evidenced by the plot of  $\log(\eta_{sp})$  against  $\log C[\eta]$ , known as the “master curve” (Launay *et al.*, 1997; Morris *et al.*, 1981), as well as by the independence of

gum viscosities from shear rate. The slope of the master curve for about 70% of all the blends were found to be more than 1.3 which is close to the findings from Morris et al. (1981) who determined the slope to be around 1.4 for several food gums in dilute solution.

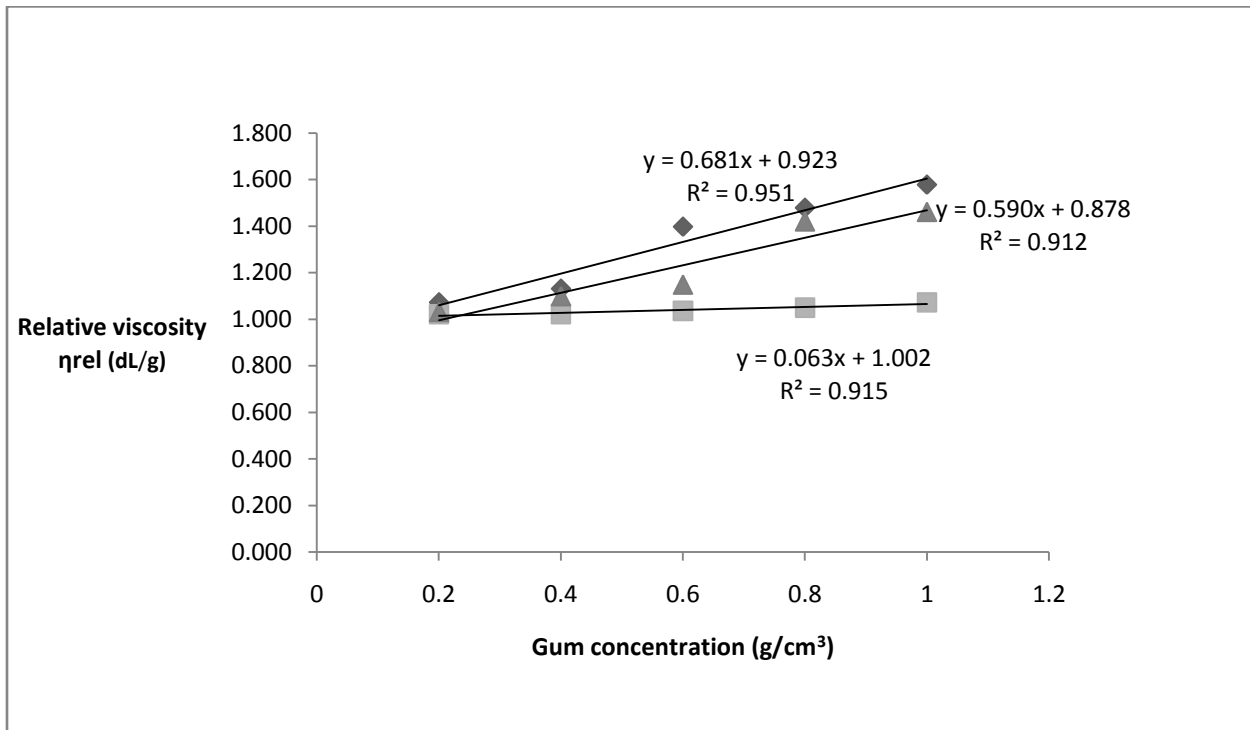


Fig.4.22. A plot of relative viscosity of the gums *Anarcadium occidentale* (Ao), *Acacia senegal* (As) and *Khaya senegalenses* (Ks) against different gum concentrations,

Table 4.5: The intrinsic viscosity calculated from the slope of Tanglertpaibul and Rao (1987) plot are given below

Results are expressed as mean  $\pm$  SD for three replications. The means were found to be significantly different ( $p < 0.05$ )

Gum Blends	Intrinsic Viscosity (dl/g)	R <sup>2</sup>	Gum Blend	Intrinsic Viscosity (dl/g)	R <sup>2</sup>
AS	68.08 $\pm$ 0.03	0.951	AS:KS (60:40)	55.81 $\pm$ 0.02	0.869
AO	6.31 $\pm$ 0.01	0.915	AS:KS (50:50)	51.51 $\pm$ 0.02	0.885
KS	59.02 $\pm$ 0.02	0.912	AS:KS (40:60)	64.46 $\pm$ 0.05	0.934
AS:AO (80:20)	46.31 $\pm$ 0.01	0.823	AS:KS (20:80)	69.07 $\pm$ 0.06	0.870
AS:AO (60:40)	38.40 $\pm$ 0.16	0.738	AO:KS (80:20)	41.41 $\pm$ 0.01	0.809
AS:AO (50:50)	31.78 $\pm$ 0.16	0.608	AO:KS (60:40)	36.37 $\pm$ 0.14	0.689
AS:AO (40:60)	8.81 $\pm$ 0.02	0.992	AO:KS (50:50)	16.52 $\pm$ 0.02	0.968
AS:AO (20:80)	4.10 $\pm$ 0.10	0.987	AO:KS (40:60)	33.71 $\pm$ 0.01	0.764
AS:KS (80:20)	55.44 $\pm$ 0.05	0.905	AO:KS (20:80)	44.31 $\pm$ 0.01	0.874

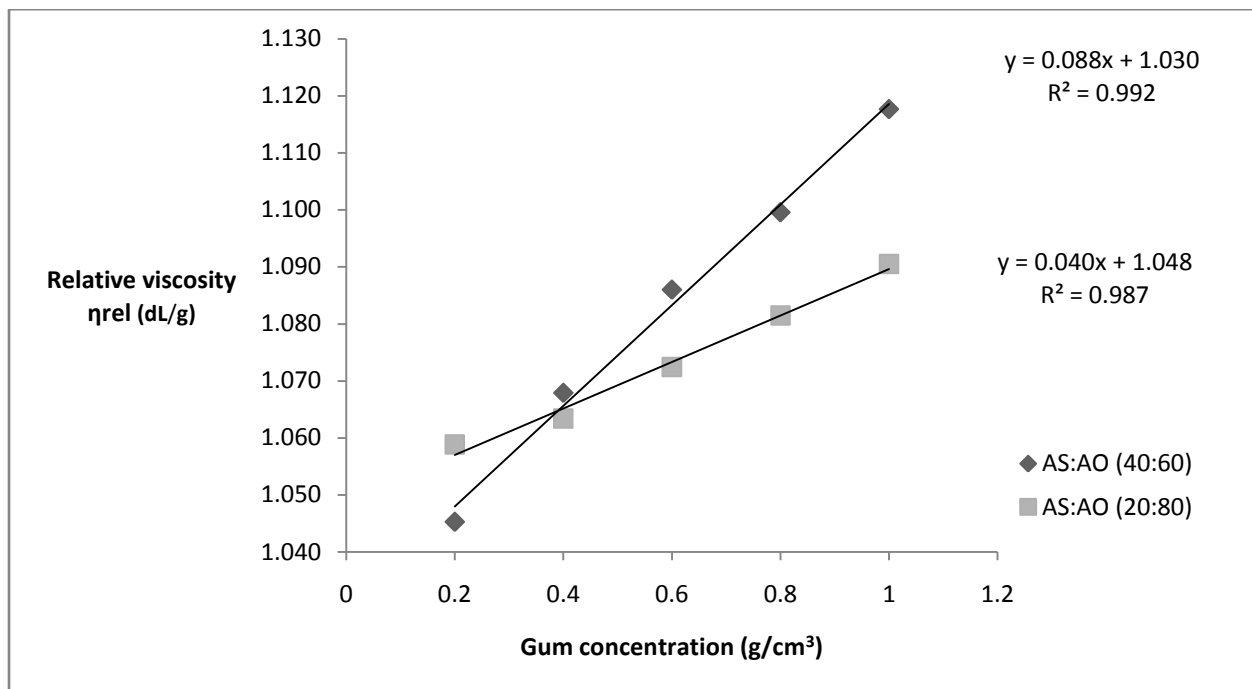
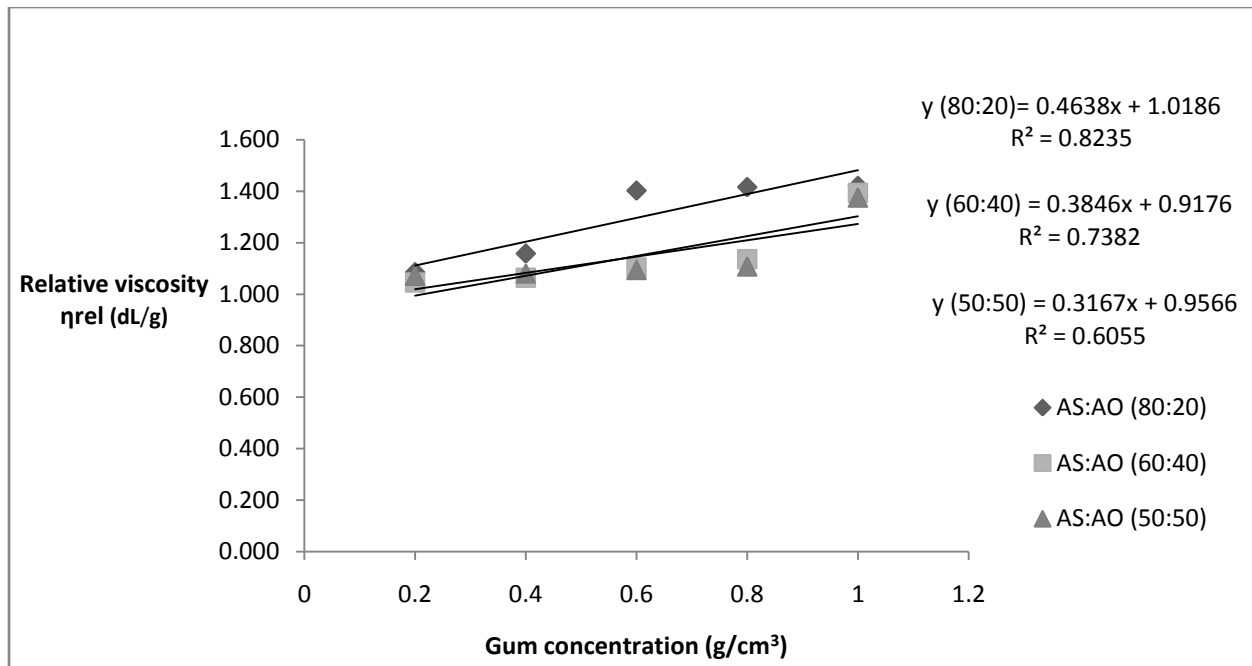


Fig.4.23. Tanglertpaibul and Rao plot for the single gums and for the blends of AS:AO with concentration

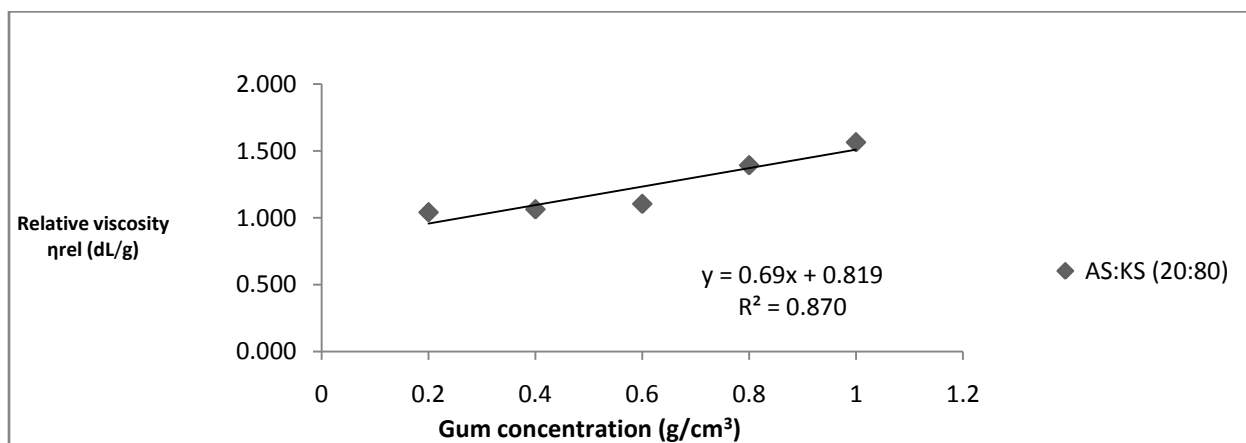
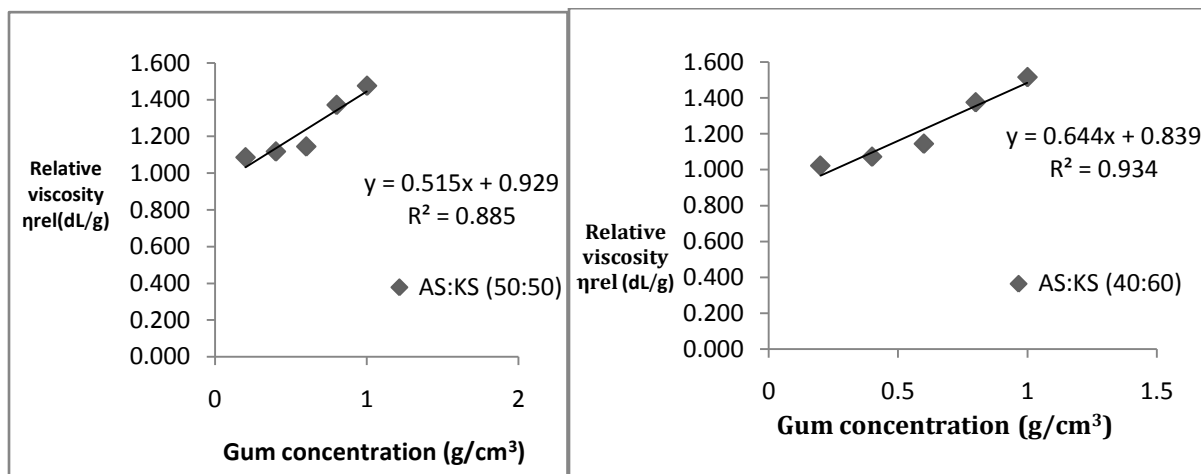
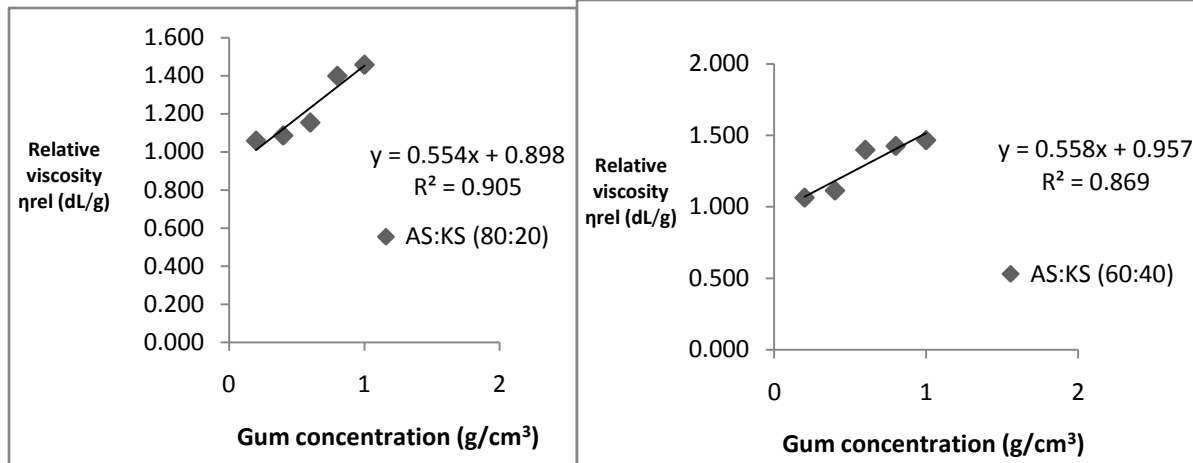


Fig.4.24. Tanglertpaibul and Rao plot for the blends of AS:KS with concentration

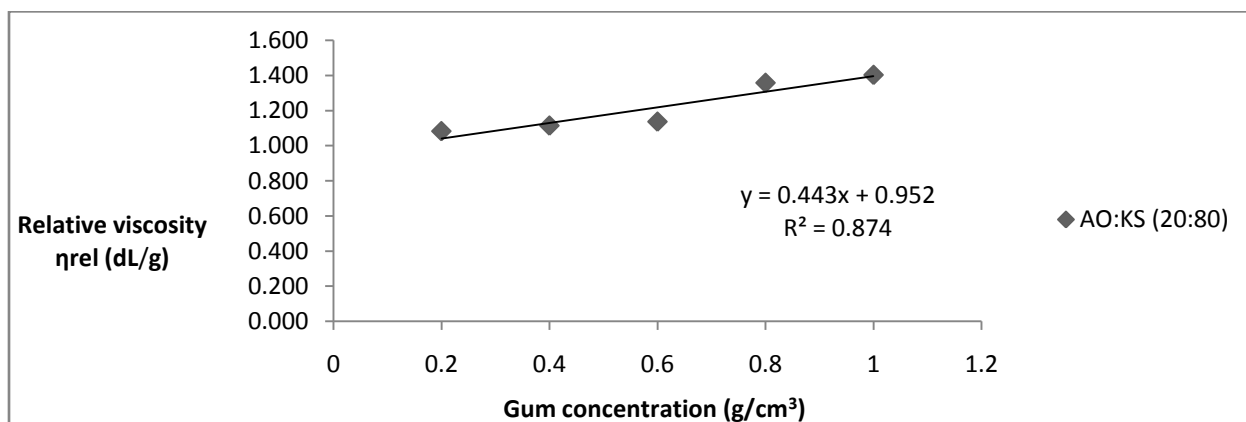
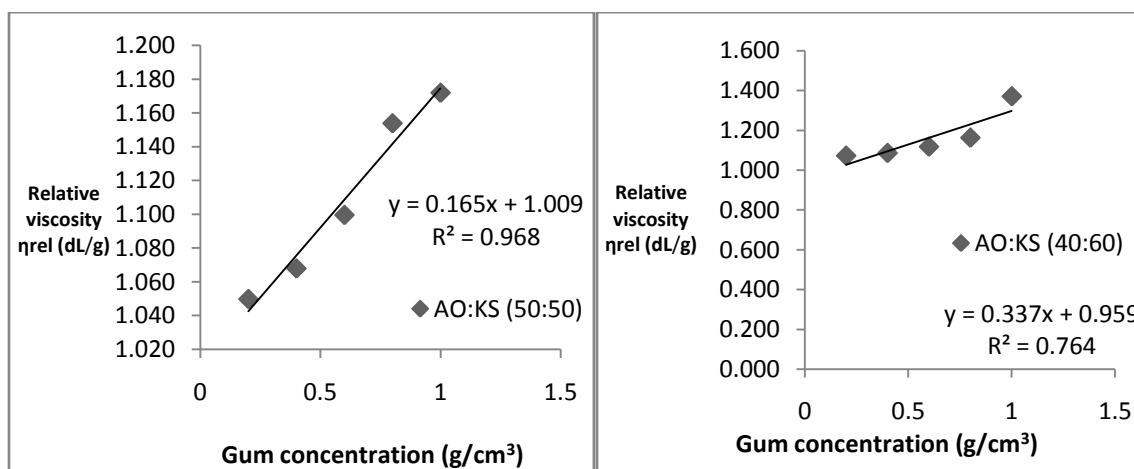
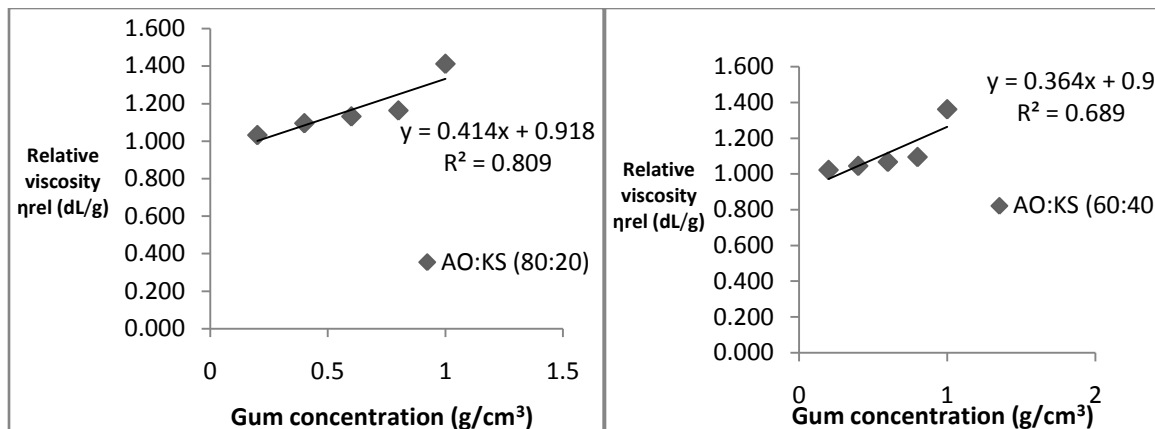


Fig.4.25. Tanglertpaibul and Rao plot for the blends of AO:KS with concentration

The intrinsic viscosity for the blend AS:KS (20:80) was highest intrinsic viscosity value at 69.1 dL/g. The value was seen to be higher than the intrinsic viscosity of gum arabic which served as a standard for food gums. This shows that at that precise blend combination a synergism is archived which could have been as a result of some interaction between the polymeric materials found within both gums. These results suggest an intermolecular synergism between AS and KS gums, which was greater at 20% AS and 40% KS blend. The minimum intrinsic viscosity value was found at 4.01 dl/g for 20% AS and 80% AO blend, which suggests that the intrinsic viscosity of (AS) gum Arabic was greatly reduced from 68.08 dl/g. with this it is difficult to say if the intermolecular interaction between the gums is responsible for this trend or whether the synergism is accompanied by a change in molecular weight of both species remains unclear, and is subject to further investigations.

#### 4.6 Effect of temperature on thermodynamic parameter of viscous flow

Temperature has an important influence on the flow behavior of plant gum hydrocolloids. Since different temperatures are usually encountered during processing of hydrocolloids, their rheological properties are studied as a function of temperature. The Arrhenius equation to a great extent explains the relationship between the temperature and viscosity. The viscosity is dependent on the intermolecular distances. As the temperature is increased, the intermolecular distances increase and therefore the viscosity will decrease for these main reasons. The viscosity is a function of temperature and the dissolved solid concentration, from the logarithm of both sides of equation 4.1, equation 4.2 was obtained,

$$\ln \eta = \ln A + \frac{E_F}{RT} \quad 4.2$$

Equation 4.2 revealed that a plot of  $\ln \eta$  versus  $1/T$  should be linear with slope and intercept equal to  $E_F$  and  $\ln A$  respectively. Activation parameters deduced from the plots are presented in Table 4.6. The results obtained shows excellent correlation. The calculated values of  $E_F$  were 4.98, 6.28 and 10.05 kJ/mol for AS, AO and KS pure gums respectively.

It has been found that low activation energy of flow indicates few inter- and intra-interactions between polysaccharide chains in the concentration range investigated and that the higher the value of  $E_F$ , the less sensitive is the polymer to temperature change (Shaikh *et al.*, 2011; Nair *et al.*, 2002)..

According to Acevedo and Katz (1990), thermodynamic parameters of viscous flow can be calculated using the Frenkel-Eyring equation in the form,

$$\ln \eta = \left( \ln A - \frac{\Delta S_V}{R} \right) + \frac{\Delta H_V}{RT} \quad 4.3$$

where A is the pre-exponential factor, R is the universal gas constant, T is the absolute temperature,  $\Delta S_V$  and  $\Delta H_V$  are the entropy and enthalpy changes of viscous flow. From equation

4.3, a plot of  $\ln \eta$  versus  $1/T$  is expected to be linear with slope and intercept equal to  $\frac{\Delta H_V}{R}$  and  $\left(\ln A - \frac{\Delta S_V}{R}\right)$  respectively. Values of Frenkel-Eyring flow parameters deduced from the plots are presented in Table 4.6. Calculated values of  $\Delta H_V$  were found to be positive. This indicates the attainment of the transition state for viscous flow is accompanied by bond breaking.

Thermodynamic parameters: The enthalpy change and activation energy of melt flow were accounted for using the Arrhenius-frenkel and frenkel-eyring model respectively (Ravindranatha, 2002)

Table 4.6: Values for  $\Delta H$  and  $E_f$  for the gums and their blends

Gum Blends	$\Delta H$ (KJ/mol)	$E_f$ (KJ/mol)	Gum Blends	$\Delta H$ (KJ/mol)	$E_f$ (KJ/mol)
AS	11.482	4.9868	AS:KS (60:40)	17.604	7.6454
AO	14.477	6.2872	AS:KS (50:50)	17.776	7.7200
KS	23.16	10.0581	AS:KS (40:60)	17.359	7.5390
AS:AO (80:20)	15.534	6.7464	AS:KS (20:80)	17.406	7.5595
AS:AO (60:40)	16.99	7.3788	AO:KS (80:20)	19.398	8.4244
AS:AO (50:50)	14.302	6.2109	AO:KS (60:40)	13.657	5.9316
AS:AO (40:60)	4.752	2.0639	AO:KS (50:50)	8.816	3.8293
AS:AO (20:80)	4.256	1.8485	AO:KS (40:60)	14.156	6.1480
AS:KS (80:20)	17.295	7.5111	AO:KS (20:80)	19.04	8.2691

#### 4.7 Molecular conformation and polymer interaction

The power-law model (Eq. 2.10) was used to estimate the exponent  $b$  from the slope of a double logarithmic plot of  $\eta_{sp}$  against concentration (Table 4.7). Results showed that the  $b$  values for AS 40%—KS 60% and AS 20%—KS 80% given as 1.98 and 1.67 were significantly larger than that of the pure gums and all other blend used within the course of this research. The slope of the power-law equation was used to determine the molecular conformational structure of polymers. In this study, the slope of AS and KS were greater than unity, while AO gum is lesser than unity with a value of 0.73. According to Lapasin and Pricl 1995, dilute regimes which have slope values greater than unity were reported to be associated with random coil conformation or entanglement (Morris *et al.*, 1981). Dilute regimes with slope values less than 1 are associated with rod-like conformation. Lai and Chiang (2002) found slopes in the dilute regime ranging from 0.78 to 0.8 while investigating on hsian-tsao leaf gum. They concluded that the molecular conformation of hsian-tsao gum was more rod-like than random coil.

In this study, the slope value for the gum blends of AS and KS were greater than unity, same for all of AO and KS blends with an exception of the 50:50 and 40:60 blends, whose values were less than unity. The result for the AS:AO gum blends were less than unity except for the 80:20 and 60:40 blends.

The data in this study shows that all the AS:KS blends exhibits random like conformation, while two exceptions in the AO:KS blends and the blends of AS:AO with % concentration AO gum greater than 60 have rod-like conformation. The decrease in slope values with the addition of AO to the AS:AO gum blends may suggest a possible conformational change of AS—AO complex molecules from random coil to rod-like.

Table 4.7: Values for the conformation parameter in the gums

Gum Blends	$b_{law}$	Gum Conformation	Gum Blends	$b_{law}$	Gum Conformation
AS	1.392	random coil	AS:KS (60:40)	1.376	random coil
AO	0.730	rod-like	AS:KS (50:50)	1.072	random coil
KS	1.715	random coil	AS:KS (40:60)	1.979	random coil
AS:AO (80:20)	1.094	random coil	AS:KS (20:80)	1.673	random coil
AS:AO (60:40)	1.182	random coil	AO:KS (80:20)	1.414	random coil
AS:AO (50:50)	0.776	rod-like	AO:KS (60:40)	1.482	random coil
AS:AO (40:60)	0.584	rod-like	AO:KS (50:50)	0.809	rod-like
AS:AO (20:80)	0.266	rod-like	AO:KS (40:60)	0.889	rod-like
AS:KS (80:20)	1.356	random coil	AO:KS (20:80)	1.028	random coil

The power-law equation is used to estimate the exponent  $b$  from the slope of double logarithmic plot of against concentration and provides an indication of the conformation of polysaccharides (Lai *et al.*, 2000), If  $b > 1$ , suggest random coil conformation (lapasin and pricl, 1995) and  $b < 1$  is for rod-like conformation (lai and chiang, 2002)

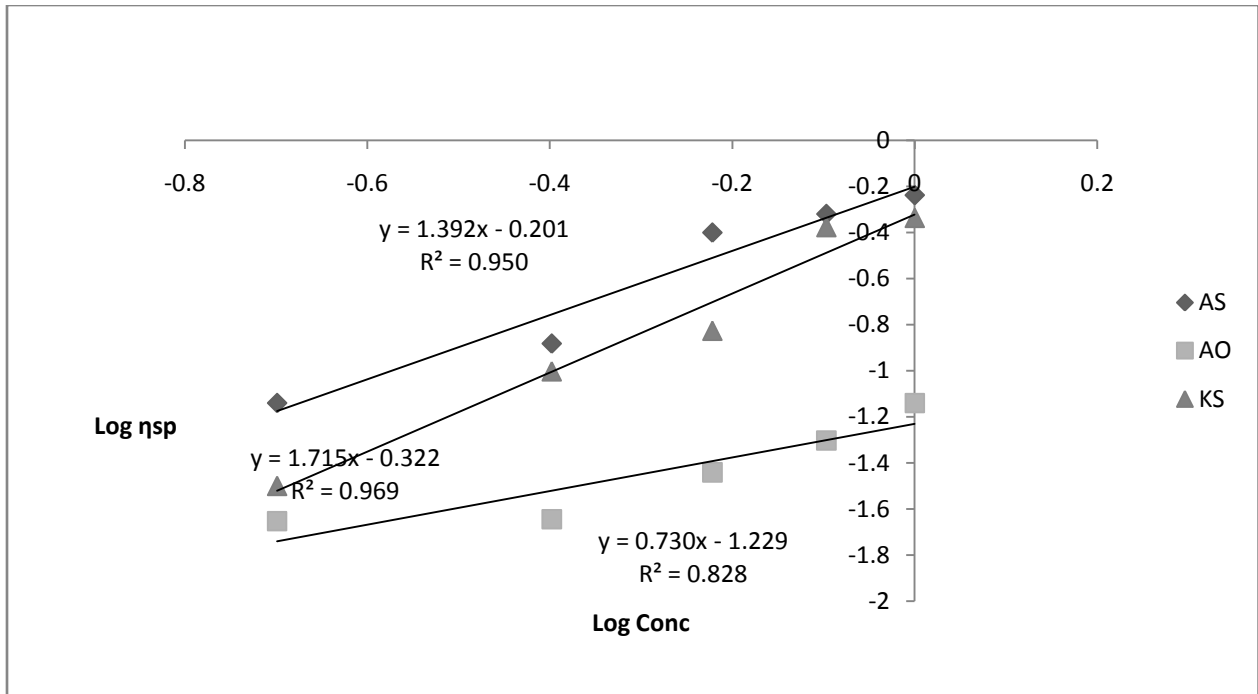


Fig.4.26. Power law plot for the pure gums with log concentration

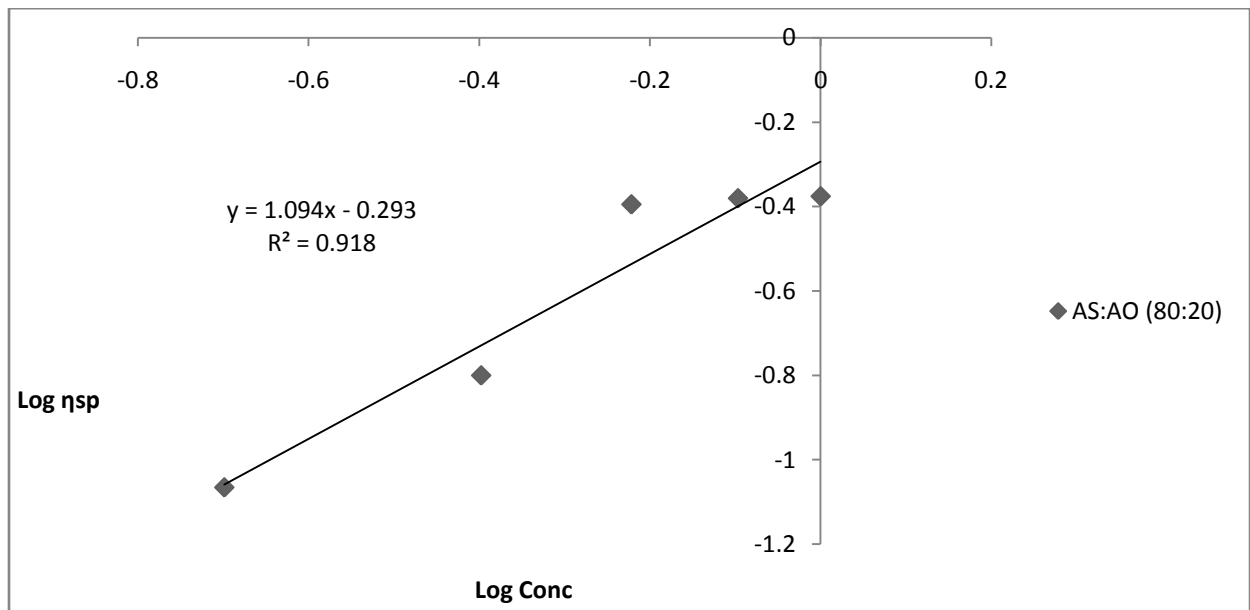


Fig.4.27. Power law plot for the blend AS:AO (80:20) with log concentration

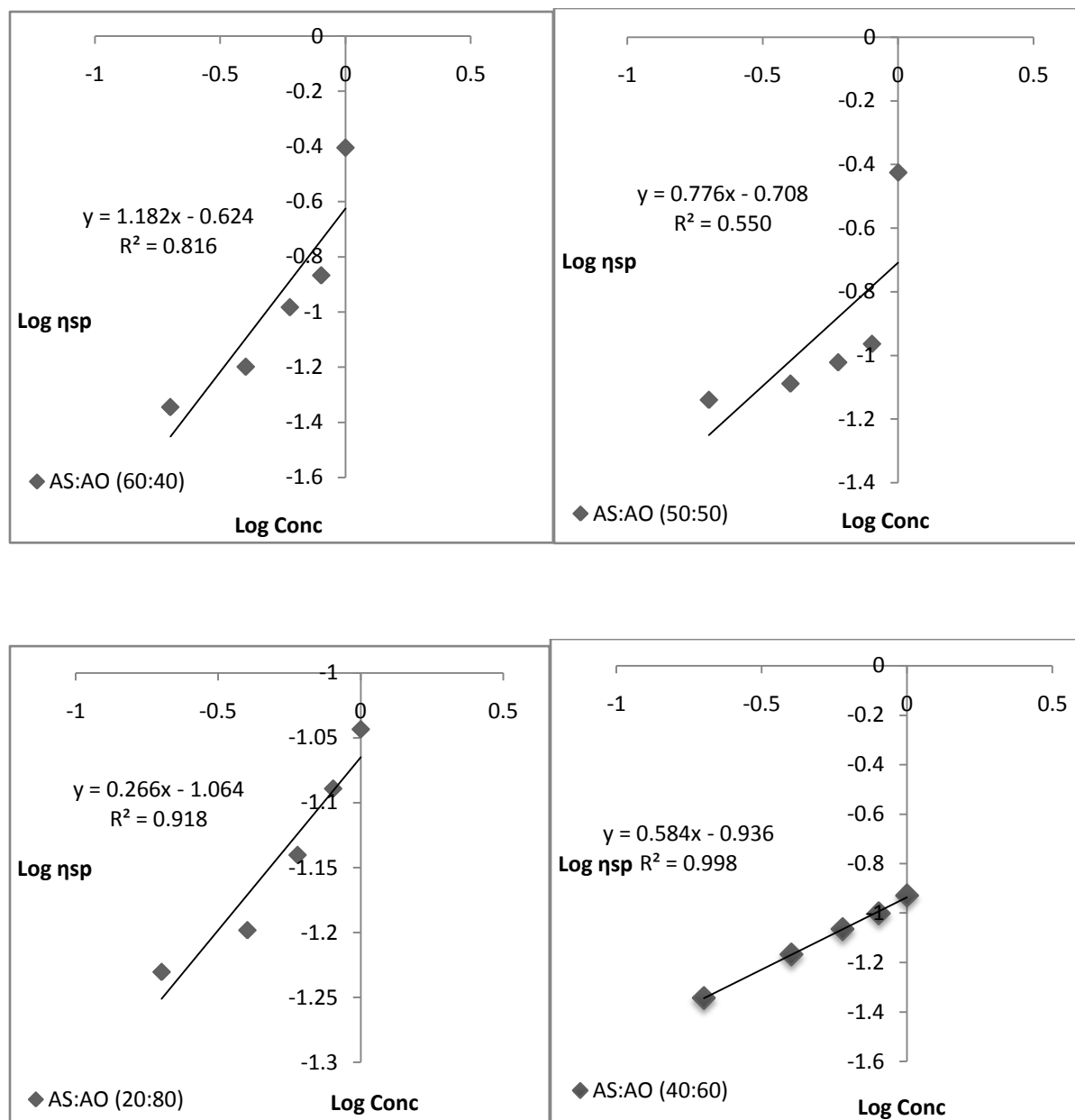


Fig.4.28. Power law plot for AS:AO blends with log concentration

From the classical Huggins equation expressing the specific viscosity of a polymer as a function of polymer concentration  $C$ , was used

$$\frac{\eta_{sp}}{C} = [\eta] + bC$$

Based on the Huggins equation a plot of specific viscosity against concentration, the intercept approximated at very low concentration give s the value of  $b$ , from which the Huggins parameter  $K$  can be calculated (higiro *et al.*, 2006) Hence  $b = K[\eta]^2$

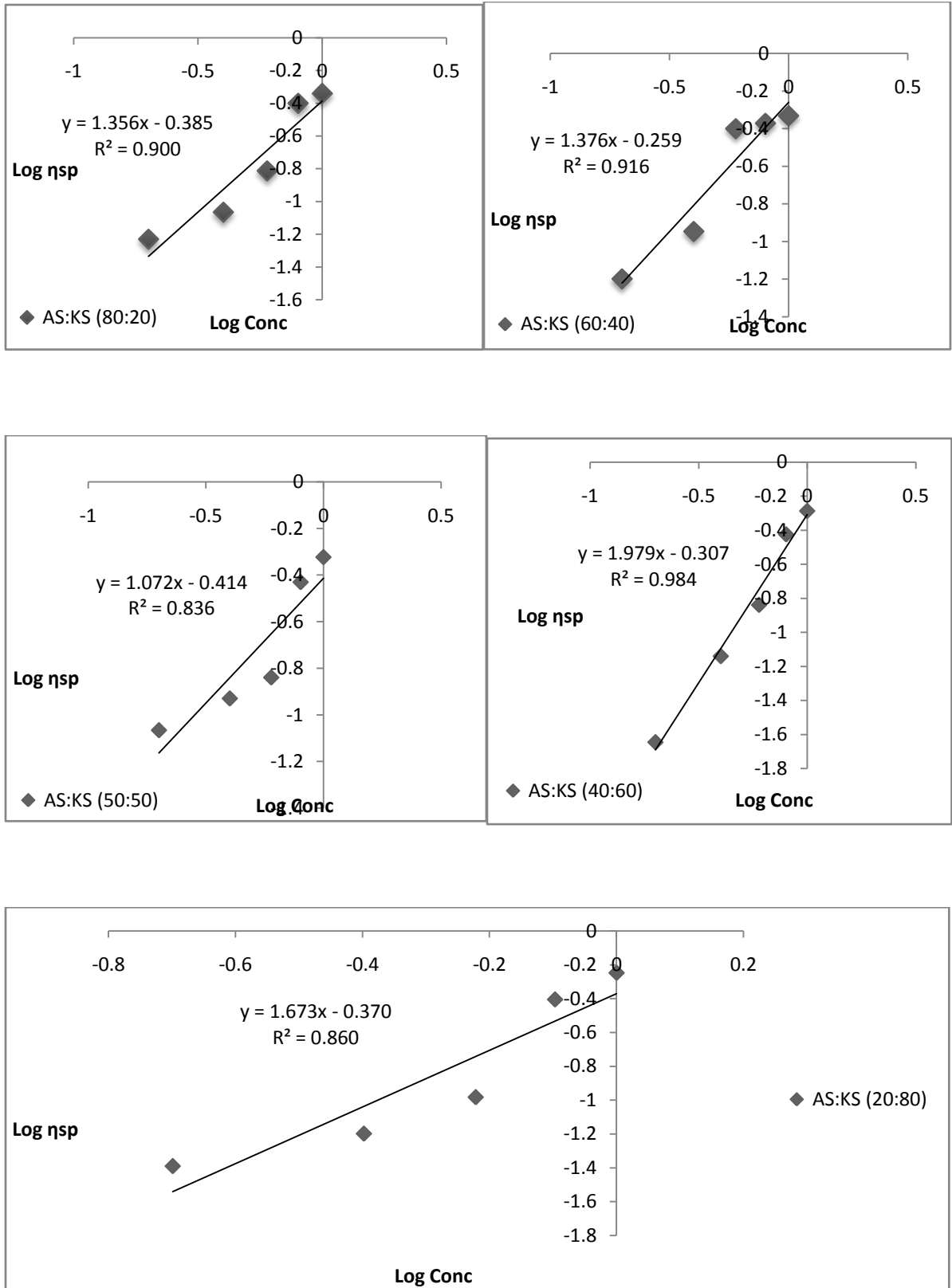


Fig.4.29. Power law plot of AS:KS blends with log concentration

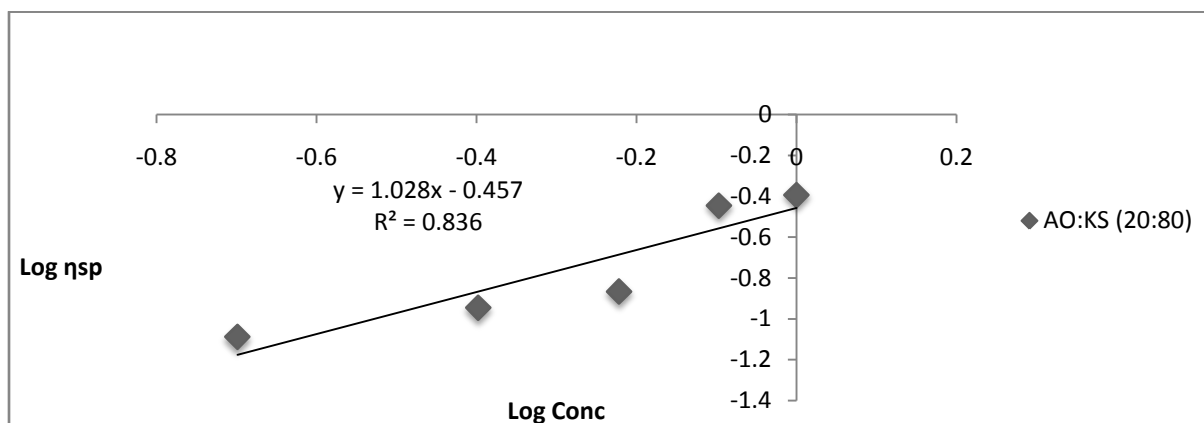
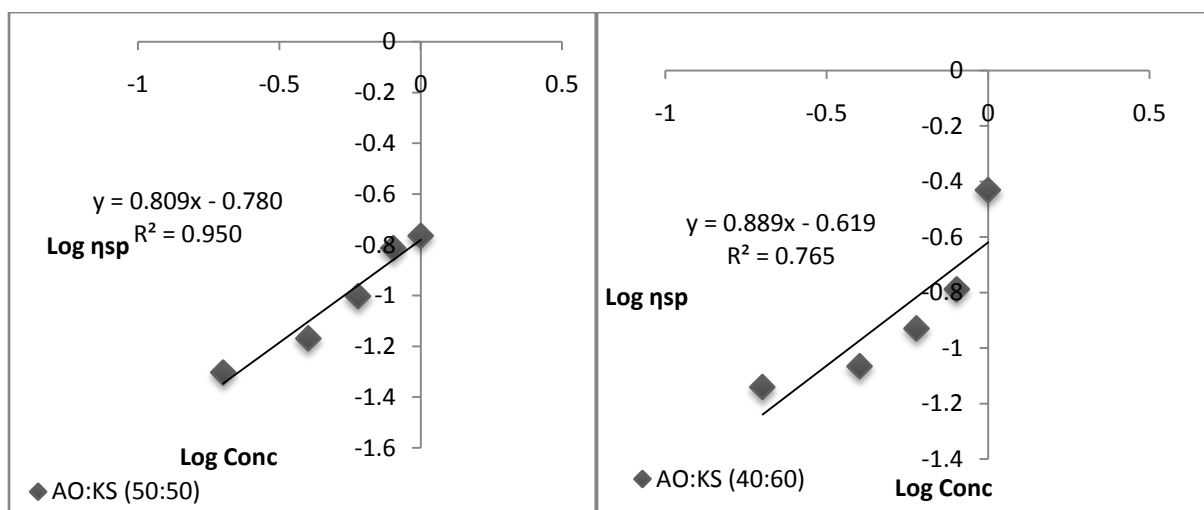
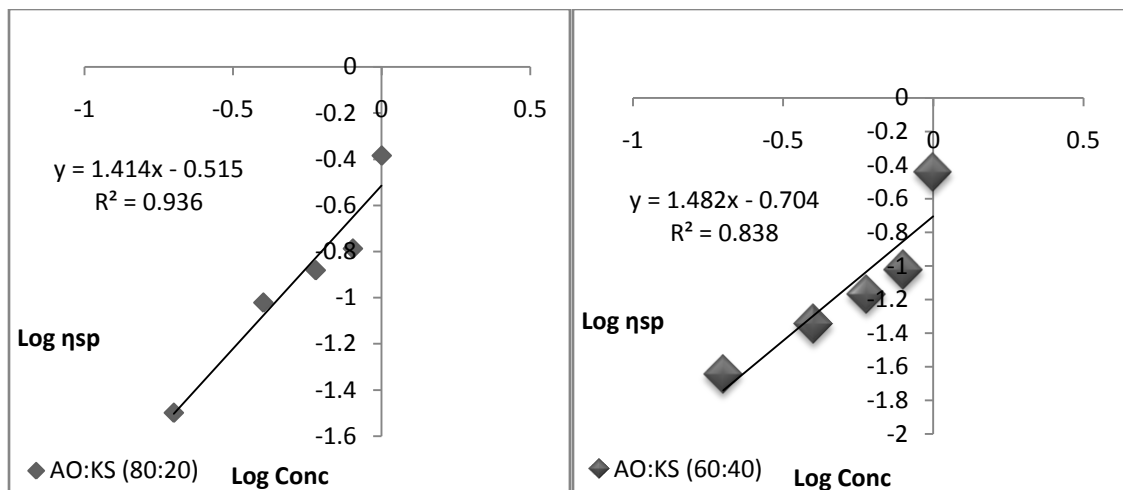


Fig.4.30. Power law plot of AO:KS blends with log concentration

Table 4.8: Value of K, which is the Huggins parameter (interaction parameter), used to check for the possibility of aggregation of polymer molecules in polymer solution

Gum Blends	Huggins Parameter (K)	Interaction Type	Gum Blends	Huggins Parameter (K)	Interaction Type
AS	0.0016	no aggregation	AS:KS (60:40)	0.0014	no aggregation
AO	0.3066	no aggregation	AS:KS (50:50)	0.0027	no aggregation
KS	0.0001	no aggregation	AS:KS (40:60)	0.0039	no aggregation
AS:AO (80:20)	0.0009	no aggregation	AS:KS (20:80)	0.0038	no aggregation
AS:AO (60:40)	0.0056	no aggregation	AO:KS (80:20)	0.0048	no aggregation
AS:AO (50:50)	0.0043	no aggregation	AO:KS (60:40)	0.0075	no aggregation
AS:AO (40:60)	0.0391	no aggregation	AO:KS (50:50)	0.0035	no aggregation
AS:AO (20:80)	0.3056	no aggregation	AO:KS (40:60)	0.0035	no aggregation
AS:KS (80:20)	0.0033	no aggregation	AO:KS (20:80)	0.0024	no aggregation

- when K value > 1 indicates aggregates, whereas K values < 1 indicates no aggregation (Millard et al., 1997).
- The results in this study (Table 8) showed that the K values were all less than unity, suggesting no aggregation of the gums in the solution

Huggins parameters  $b$ ,  $K$ , and  $\alpha$  were used to determine the presence or absence of interaction between polymers. The Huggins parameters were estimated for the pure gums and for the blends. Results (Table 4.7) showed positive and increasing  $b$  values in the AS:KS blends with the addition of Khaya gum (KS). This may suggest that the addition of KS gum assists with the miscibility of AS.

Chee (1990) studied different polymers in different solvents and reported that the miscibility of polymers can be determined with the Huggins parameter  $b$ ; positive values indicated miscibility, whereas negative values corresponded to polymer immiscibility. Morawetz (1965) suggested that polymer systems in which polymers interact with each other might show very large values of  $b$ , compared with the average  $b$  value of the two polymers. The increase was not observed in the present study. Sun *et al.*, (1992) reported that parameter  $b$  should not be regarded as the only criterion for determining the presence of intermolecular interaction between polymers. The authors pointed out that because  $b$  is a measure of the interaction between attractive molecules, this term may erroneously be estimated when repulsive molecules interact due to shear forces.

The  $K$  value indicates the ability for the polymers to aggregate. A  $K$  value greater than unity indicates aggregates, whereas  $K$  values less than unity indicate no aggregation (Millard *et al.*, 1997). The results in this study (Table 4.8) showed that the  $K$  values are all less than unity, suggesting no aggregation of the gums in the solution.

In contrast, Sun *et al.* (1992) reported that  $\alpha$  values (Appendix 14) greater than zero indicate a strong attraction between polymers. The values for all the AS:KS gum blends in this study were all greater than zero suggesting that a strong attraction between gum Arabic and Khaya gum was present. The attraction can be said to be absent in all AS:AO gum blends since all the blends from AS gum and AO gum have their  $\alpha$  to be less than zero or have negative value. While for

AO:KS blend the negative  $\alpha$  value for the 50:50 blend is significantly lower than the other blends for AS:AO, whereby the rest are positive. This shows that no attraction exist within the blend at that composition and hence would be difficult to achieve any desired synergism.

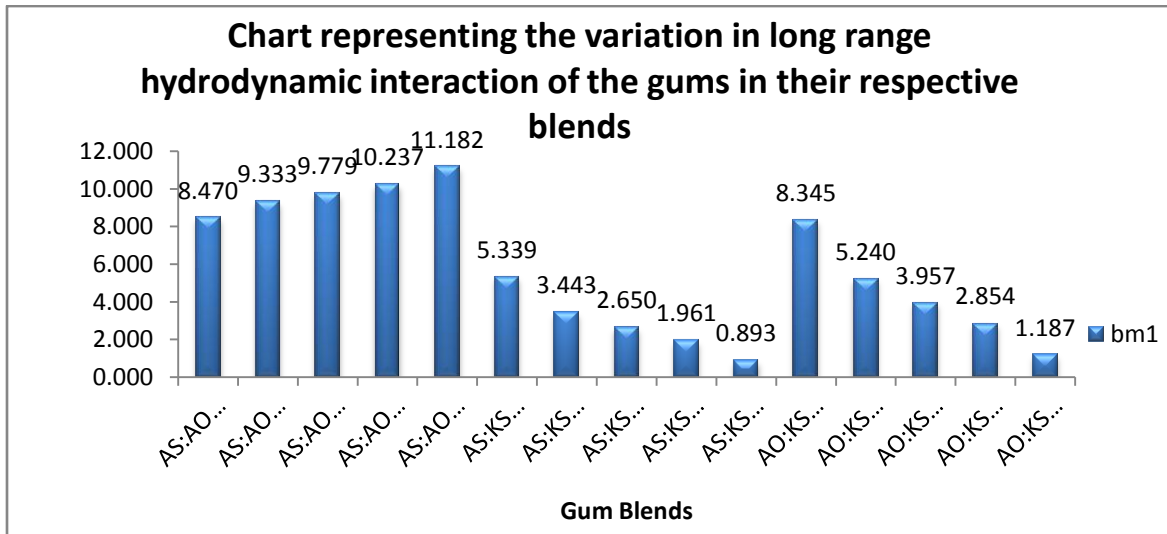


Fig. 4.31: Variation of long range hydrodynamic interaction with the gum blends

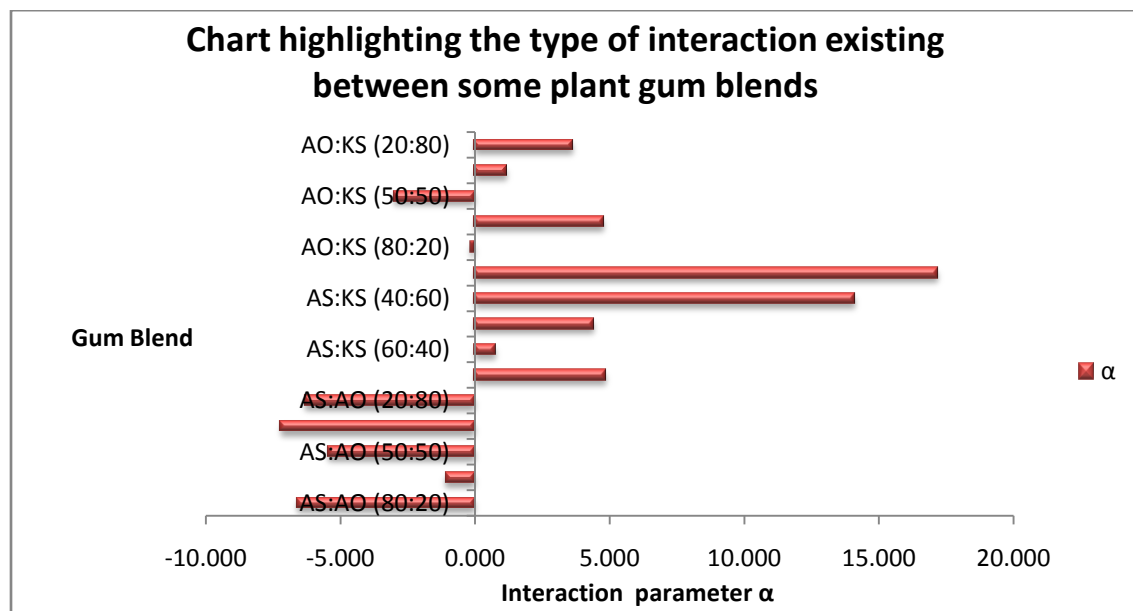


Fig. 4.32: A chart of gum blends with interaction parameter  $\alpha$ , Values of  $\alpha$  in this study were obtained as reported elsewhere (Sun *et al.*, 1992 and Wang *et al.*, 2001). Where  $\alpha \geq 0$  means attraction, whereas  $\alpha < 0$  means repulsion.

#### 4.8 SYNERGISTIC STUDY

Synergy is the interaction of multiple elements in a system to produce an effect different from or greater than the sum of their individual effects. In rheology the combination of a gelling polymer with non-gelling one gives rise to strong synergistic effects as a consequence of interaction among different chains polymers and formation of mixed junction zones. Synergism helps in understanding the miscibility property of some elements present in a system and in achieving new desired properties.

The synergism parameter (S) for the joint effect of each intrinsic viscosity with respect to that for the pure gums were calculated using the equation

$$S = \frac{1-\eta_A-\eta_B+\eta_A\eta_B}{1-\eta_{AB}} \text{-----} (4.4)$$

where  $\eta_A$  and  $\eta_B$  are intrinsic viscosity of gum A and B respectively and  $\eta_{AB}$  is the intrinsic viscosity of the gum blend, hence a modified Ebenso synergism equation (Ebenso, 2003)

The synergism parameter (s) for all the blend were found to be negative and those with values relatively closer to unity (+1) indicates the blend with increased synergy in their rheological properties. Table 4.9 shows that -7.099, -7.608 and -7.850 for AO:KS (20:80), AS:KS (80:20) and AS:AO (80:20) were closer to unity, while AS:AO (80:20) had the least synergistic parameter at -118.543.

Table 4.9 Synergism parameter of the pure gums and their blends

Gum Blends	Synergism Parameter (S)	Gum Blends	Synergism Parameter (S)	Gum Blends	Synergism Parameter (S)
AS:AO (80:20)	-7.85055	AS:KS (60:40)	-71.5404	AS:KS (80:20)	-7.60891
AS:AO (60:40)	-9.50882	AS:KS (50:50)	-71.0182	AO:KS (60:40)	-8.68362
AS:AO (50:50)	-11.6219	AS:KS (40:60)	-77.0653	AO:KS (50:50)	-19.8323
AS:AO (40:60)	-45.5936	AS:KS (20:80)	-61.3849	AO:KS (40:60)	-9.40061
AS:AO (20:80)	-118.543	AO:KS (80:20)	-57.2324	AO:KS (20:80)	-7.09931

#### **4.9 AAS Study and Correlation Coefficient of the Intrinsic Viscosity of the Gums With Some of their Physiochemical Properties**

The metal concentrations determined in the gum samples were found to be below permissible limits for WHO and FDA standards. The concentration of calcium (Ca) was found to be significantly higher in AS:KS (981.71mg/kg) and AO:KS (520.60mg/kg) when compared with that of AS (132.05mg/kg) and the blend AS:AO (68.85), while for iron (Fe) the mean concentration found in AS:KS (970.81) and AO:KS (890.03) were a little lower than that in AS (1431.02) gum but significantly higher than that in AS:AO (498.81mg/kg) blend. With this we assume that due to the significant presence of these metals in the previously named blends, they would be a very good additive for manufacturing paints and varnishes.

In table 4.10 Copper (Cu) was found to be below detection limit. all the gums as well as their blends have higher concentration of magnesium (Mg) and potassium (K) than any other metals detected, hence they serve as important source of electrolytes in the body systems.

Correlation coefficient of the intrinsic viscosity of the gums with some of their physiochemical properties shows that the intrinsic viscosity is positively influenced by increasing the pH of the gums solution. A high positive correlation that is significant at 0.05 p level was found to be 0.831, 0.733 and 0.738 for salinity when correlated with UV, conductivity and TDS values as shown in table 4.7, indicating a high presence of inorganic salts in the gums, hence the large correlation value of TDS or dissolved solutes affects the viscosity of the gums and in turn increases the turbidity and UV values of gums solution (Table 4.2-4.4).

Table 4.10: Mean concentration of some cations in their (50:50)% blends

Cation	Concentration (mg/kg)			
	AS gum	AS:AO (50:50)	AS:KS (50:50)	AO:KS (50:50)
Ca	132.05 ± 0.43	68.85 ± 0.17	981.71 <sub>b</sub> ± 0.12	520.60 <sub>a</sub> ± 0.02
Fe	1431.02 ± 0.04	498.81 ± 0.06	970.81 <sub>b</sub> ± 0.09	890.03 <sub>a</sub> ± 0.06
Cu	BDL	BDL	BDL	BDL
Mg	834.21 ± 0.17	1012.65 ± 0.26	1540.06 ± 0.32	991.51 ± 0.02
Pb	19.52 ± 0.37	17.51 ± 0.21	30.46 ± 0.04	28.27 ± 0.05
Zn	45.04 ± 0.12	19.31 ± 0.15	180.37 ± 0.13	87.90 ± 0.02
Na	1030.04 ± 0.32	366.55 ± 0.23	851.72 ± 0.22	736.97 ± 0.11
K	874.12 ± 0.06	1929.05 ± 0.03	2071.09 ± 0.41	1669.01 ± 0.23

Results are expressed as mean ± SD for three replications.

The means were found to be significantly different ( $p < 0.05$ ), equal variances assumed using Tukey and Duncan.

a = there is a significant difference, b = there no significant difference

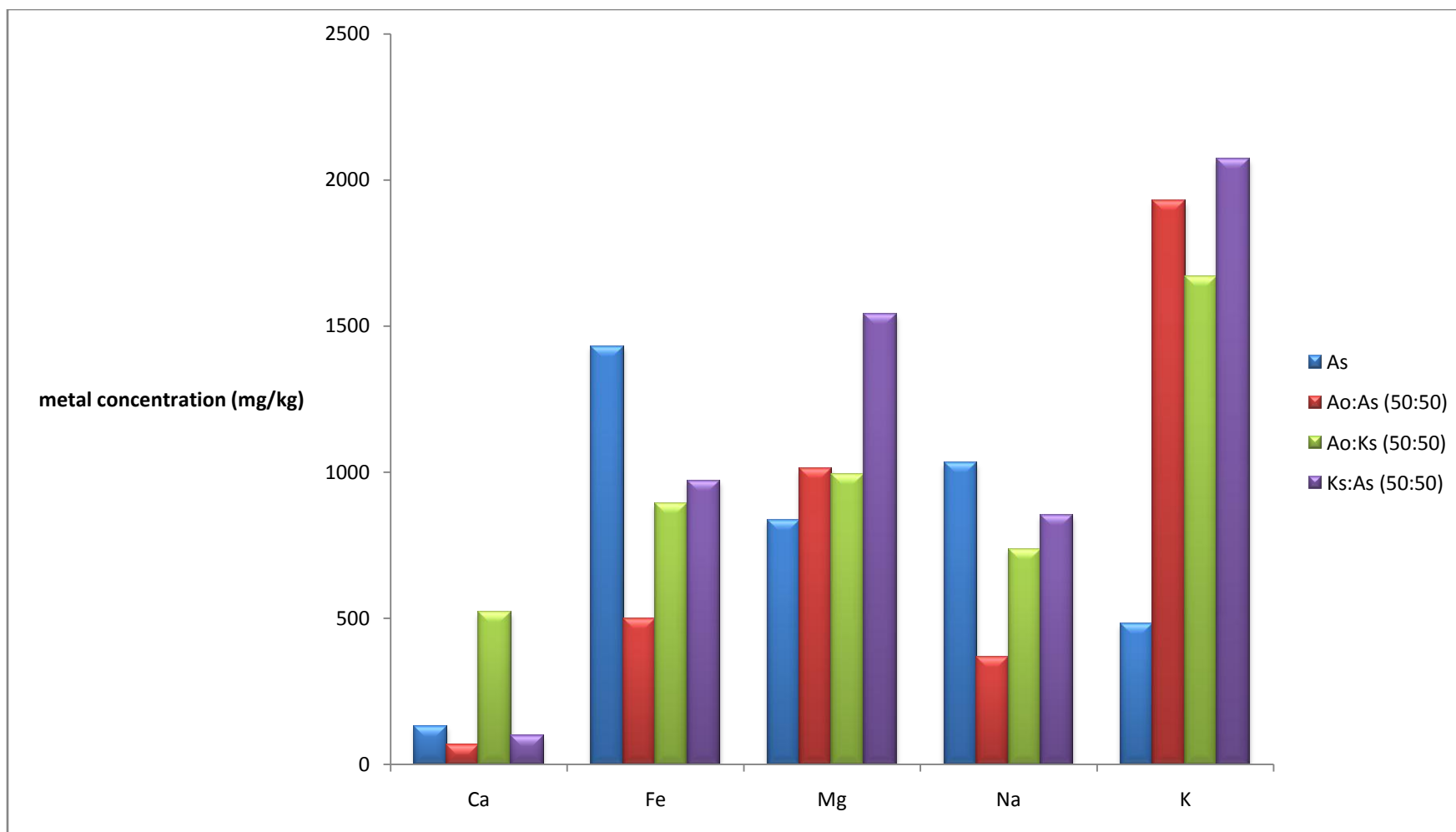


Fig. 4.33: The concentration of Ca, Fe, Mg, Na and K in the pure gum of *Acacia senegal* and its blend

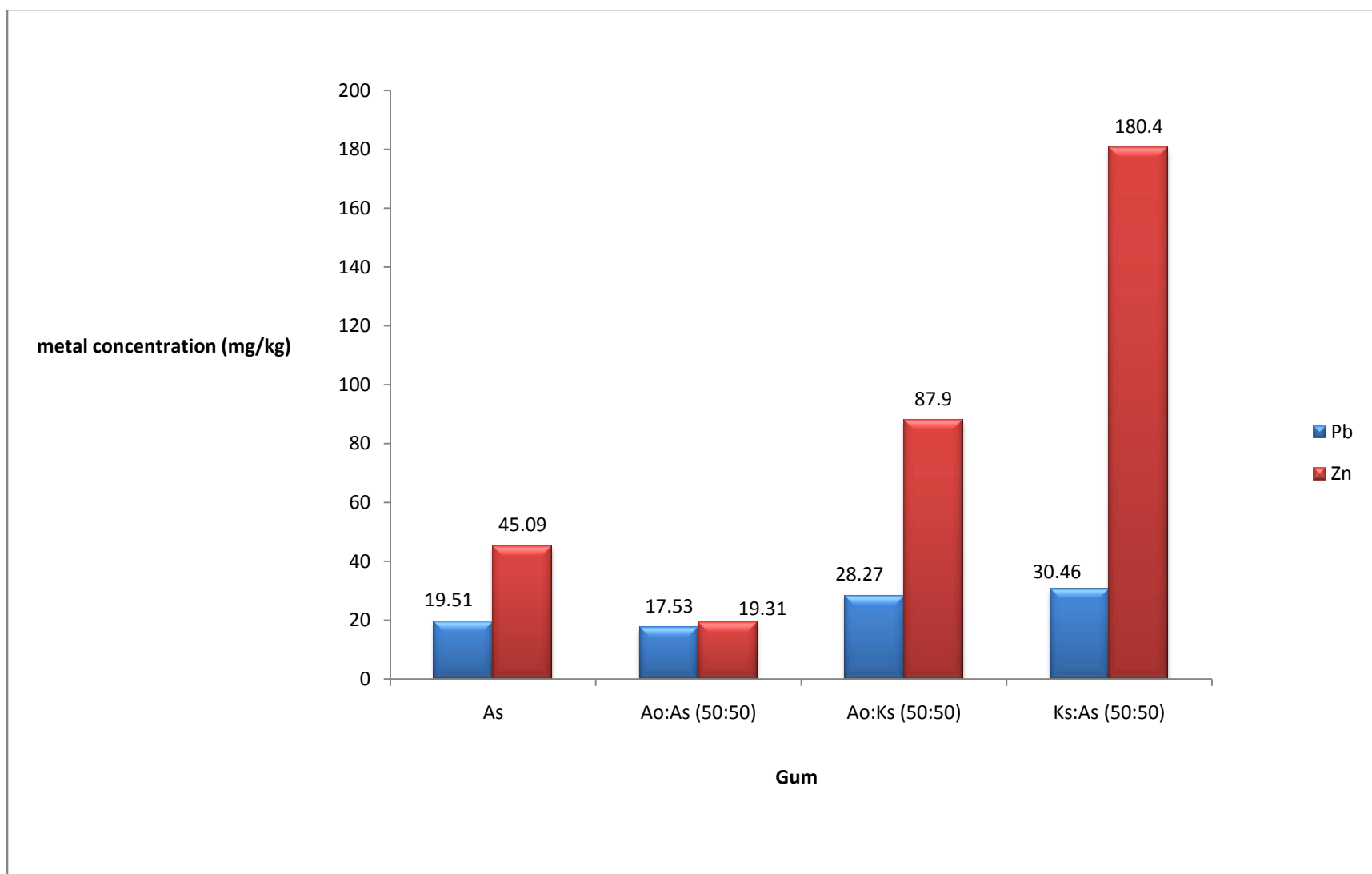


Fig. 4.34: The concentration of Pb and Zn in the pure gum of *Acacia senegal* and some blend

Table 4.11: Correlation coefficients of the intrinsic viscosity of the gums and their blends with some properties

	Viscosity	pH	Salinity	Conductivity	UV	Turbidity	TDS
Viscosity 1							
pH	-0.114 <sup>a</sup>	1					
Salinity	0.370 <sup>a</sup>	-0.615	1				
Conductivity	0.434	-0.795	0.733	1			
UV	0.459	-0.791	0.831	0.894	1		
Turbidity	0.334 <sup>a</sup>	-0.753	0.563	0.732	0.891	1	
TDS	0.457	-0.799	0.738	0.999	0.903	0.743	1

Correlation is significant at the 0.05 level (2-tailed)

While the superscript a means the correlation is insignificant at the 0.05 level (2-tailed)

#### 4.10 FTIR study

The use of infrared spectroscopy for the characterization of polymer blends is extensive (olabisi *et al.*, 1979; coleman and panter, 1984; utracki, 1989; coleman *et al.*, 1991). The IR spectra below shows the graphical, representation of the frequencies of radiation absorbed and the percentage transmittance. It is divided into finger print region ( $500\text{-}200\text{cm}^{-1}$ ). Very strong bands which occur at  $2854\text{-}3008\text{cm}^{-1}$  in the gums can be mostly attributed to absorption of CH stretch and  $\text{CH}_2$ - asymmetric stretch in aliphatic groups closer to those bands. C-O stretch vibration due to carboxylic acid, alcohol, ester and ethers was noticed at  $1054.13\text{ cm}^{-1}$ .

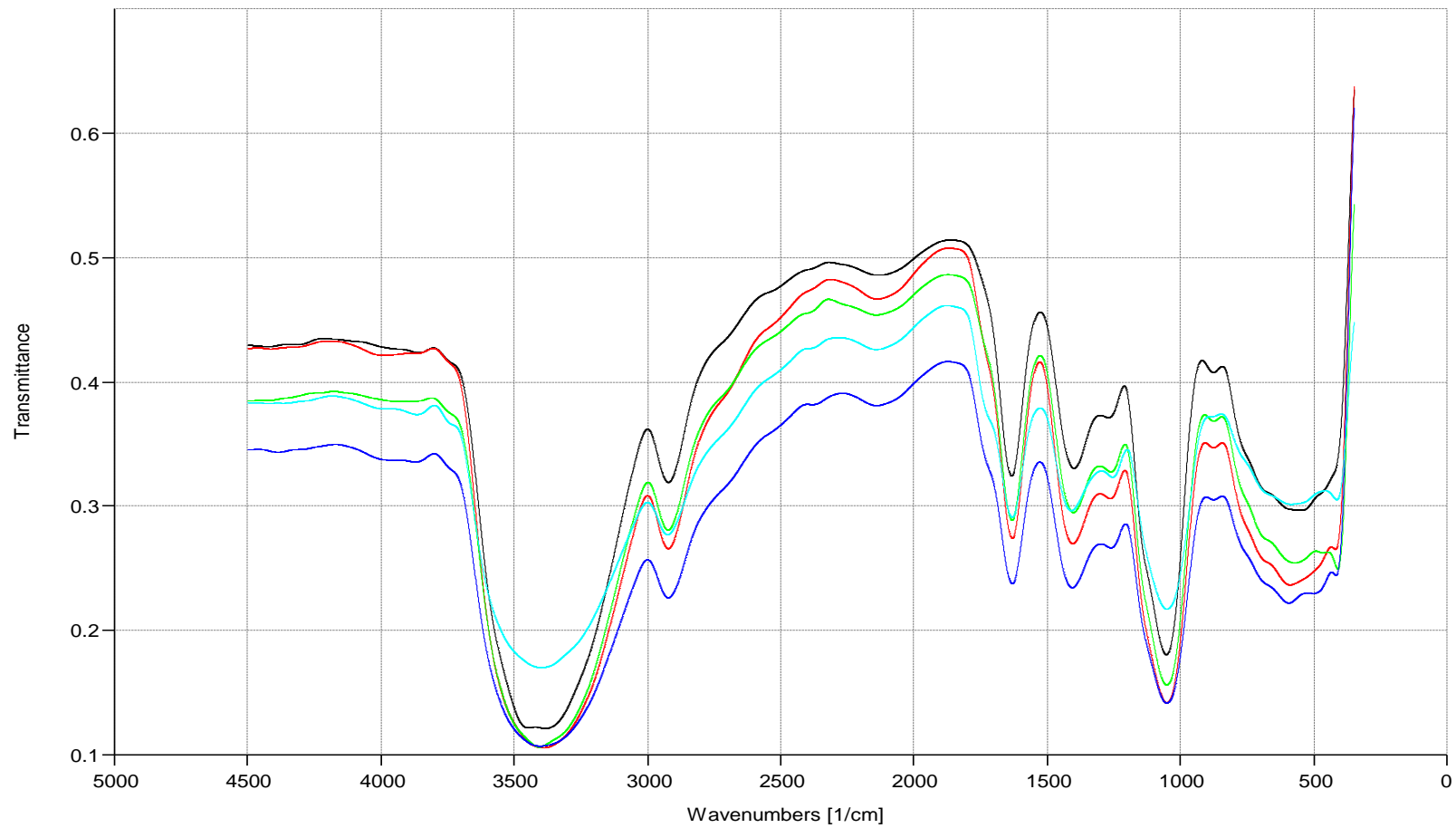
Fig 4.35 shows the IR spectrum of AO:AS blends, the frequencies and peaks of IR absorption of this blend are presented from table 4.14-4.18, from the result it is evident that the blend with 80% composition of AO and 20% AS gum weak peak signals for C-H aliphatic stretch at  $2927.08\text{ cm}^{-1}$  and C-O stretch at  $1053.17\text{ cm}^{-1}$ , the IR transmittance or peak signals becomes more intense as the percentage composition of AS gum in the blend was increased leading to a well successive shift of this peaks, the O-H stretch was shifted to 3405.44, 3409.32 and  $3446.91\text{ cm}^{-1}$  for the blends 60:40, 50:50 and 20:80 (Cunha *et al.*, 2007), but the C-O stretch remained the same in all the blends with an exception of 20:80 for AO:AS which could be seen as a result of O-H dimer presence evident in the peak  $3385\text{cm}^{-1}$ , indicating the presence of more than one type of OH functional group in the blend e.g. carboxylic acid, alcohol etc. some of the functional groups follows this trend for AO:AS blend type indicating that each blend constituted different concentration of the same hydrocolloids present in their mixtures.

Fig 4.36 and 4.37 respectively shows the IR spectra of different blend composition for AS:KS and AO:KS. Peaks and frequencies of IR absorption for each blend type were adequately

presented in table 4.19-4.29. from the results obtained it is evident that positive shift of absorption band of O-H stretch from  $3397.72\text{ cm}^{-1}$  to  $3400.62\text{ cm}^{-1}$ , for the 80:20 and 20:80 composition, could be attributed to the increase composition of the AS gum, although the shift in absorption band for C-H aliphatic stretch is opposite to that of O-H stretching, there is a superposition of the absorption band for 40:60 with that of 50:50, i.e.  $2936.72$  and  $2933.83\text{ cm}^{-1}$  respectively. It was noticed that the percentage transmittance of IR in the blends became more intense for C-H aliphatic stretch and C-O stretch.

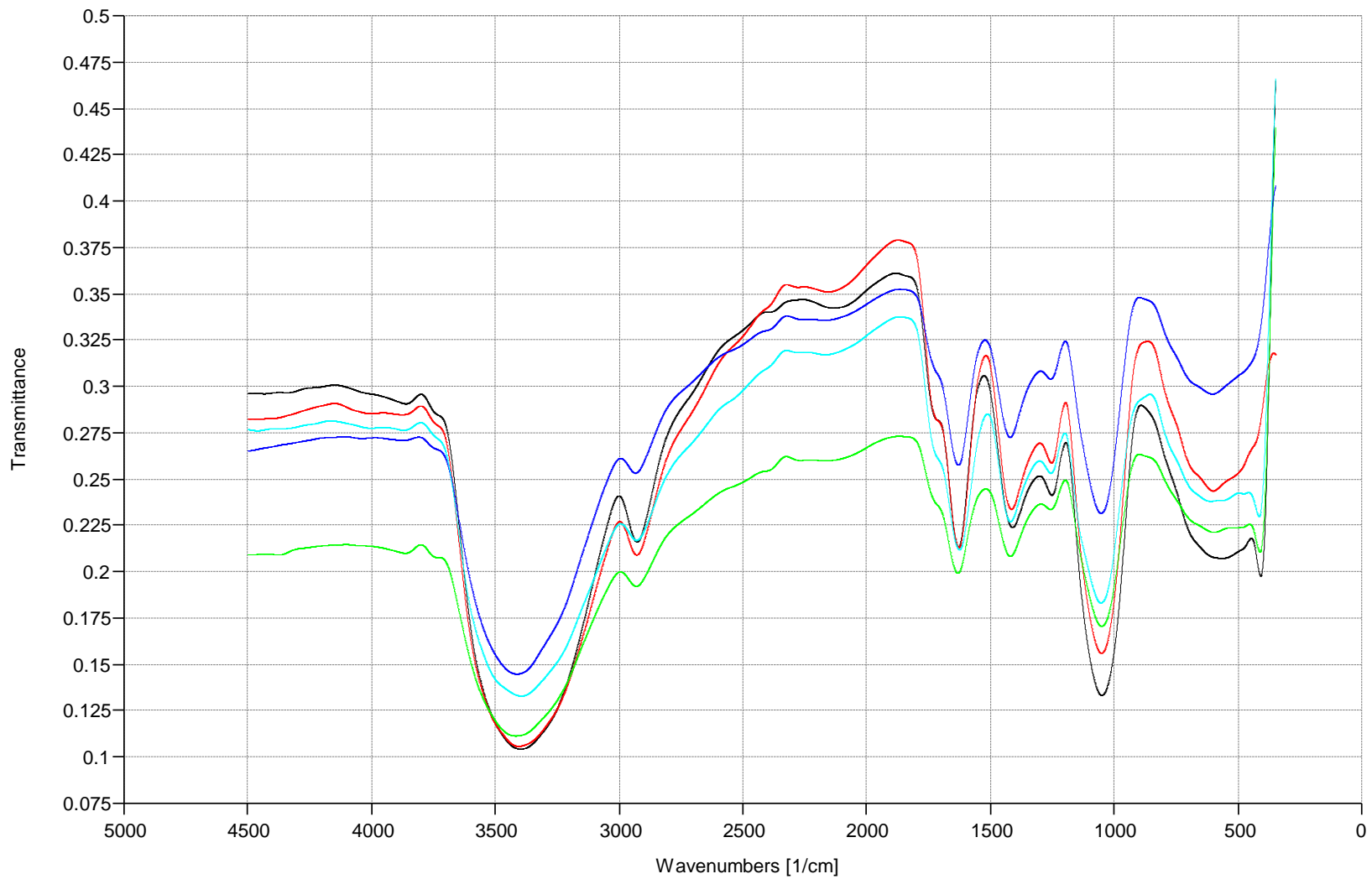
In AO:KS same phenomena was noticed but in this case there was a superposition of the blend AO:KS (20:80) with 40:60 and 50:50 blend composition giving a broad but weak peak signal for O-H stretch (Vinod and Sashidhar, 2010).

The FTIR spectra of AO:KS, AS:KS and AS:AO blends composition respectively showed that the blends did not indicate the existence of any chemical interaction between the components, although thorough analysis of the IR spectra for these blends showed a decrease in the transmittance of the carbonyl group, as well as other vibrational modes in the blend when the composition of khaya gum in the blend was increased in the case of AO:KS.



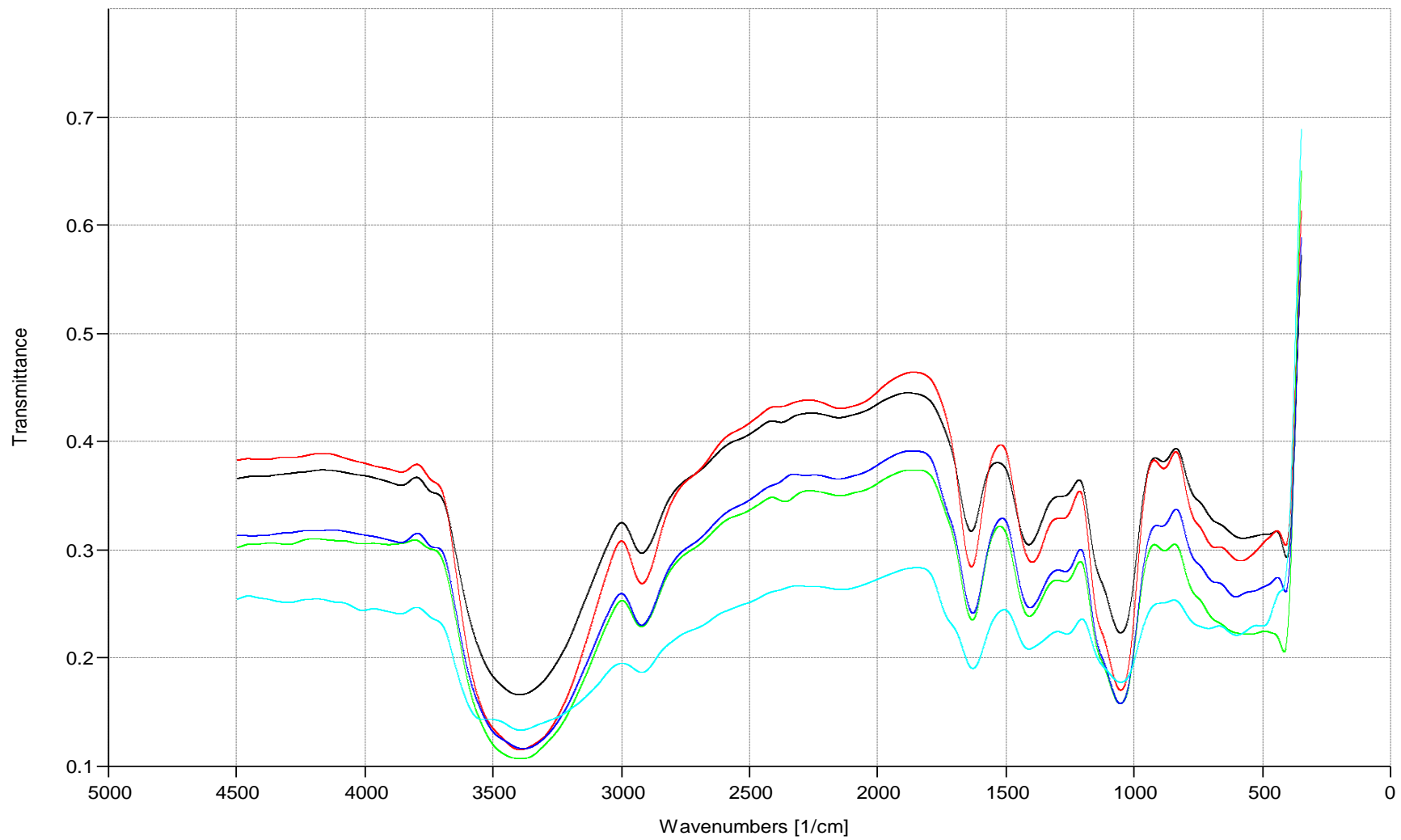
— = (AO:AS) 80:20, — = (AO:AS) 60:40, — = (AO:AS) 50:50, — = (AO:AS) 40:60, — = (AO:AS) 20:80

Fig. 4.35: FTIR spectrum of the gum blends of *Acacia senegal* and *Anacardium occidentale* gum



= (AS:KS) 80:20,      = (AS:KS) 60:40,      = (AS:KS) 50:50,      = (AS:KS) 40:60,      = (AS:KS) 20:80

Fig. 4.36: FTIR spectrum of the gum blends of *Acacia senegal* and *Khaya sengalenses* gum



— (AO:KS) 60:40,    
 — (AO:KS) 80:20,    
 — (AO:KS) 50:50,    
 — (AO:KS) 40:60,    
 — (AO:KS) 20:80

Fig. 4.37: FTIR spectrum of the gum blends of *Khaya senegalenses* and *Anacardium occidentale* gum

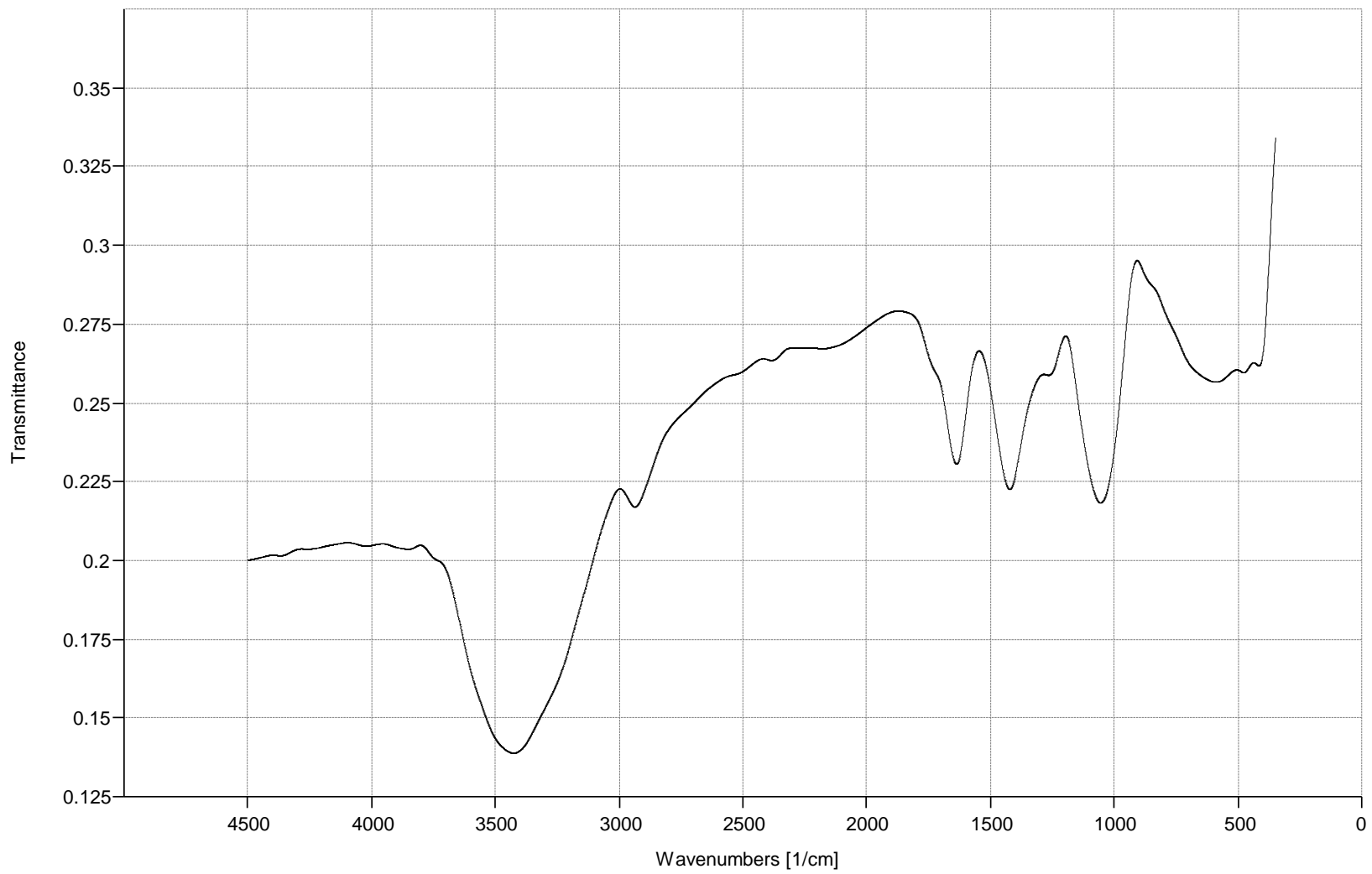


Fig. 4.38: FTIR spectrum of (AS) *Acacia senegal* gum

Table 4.12: Frequencies and peaks of IR absorption by Acacia Senegal gum

Peak	Intensity	Area	Assignments/Functional Groups
479.33	25.957	39.411	C-C bending
1057.03	21.829	175.568	C-O stretch
1268.24	25.885	50.321	C-H wag
1424.48	22.259	159.443	C-H in plane bending (CH <sub>3</sub> )
1639.55	23.062	191.251	C=C stretch
2386.99	26.353	67.829	C=O Asymmetric stretching CO <sub>2</sub>
2938.65	21.703	353.217	C-H Asymmetric stretch
3428.58	13.886	617.181	O-H stretch
3855.83	20.356	103.11	Asymmetric O-H stretching

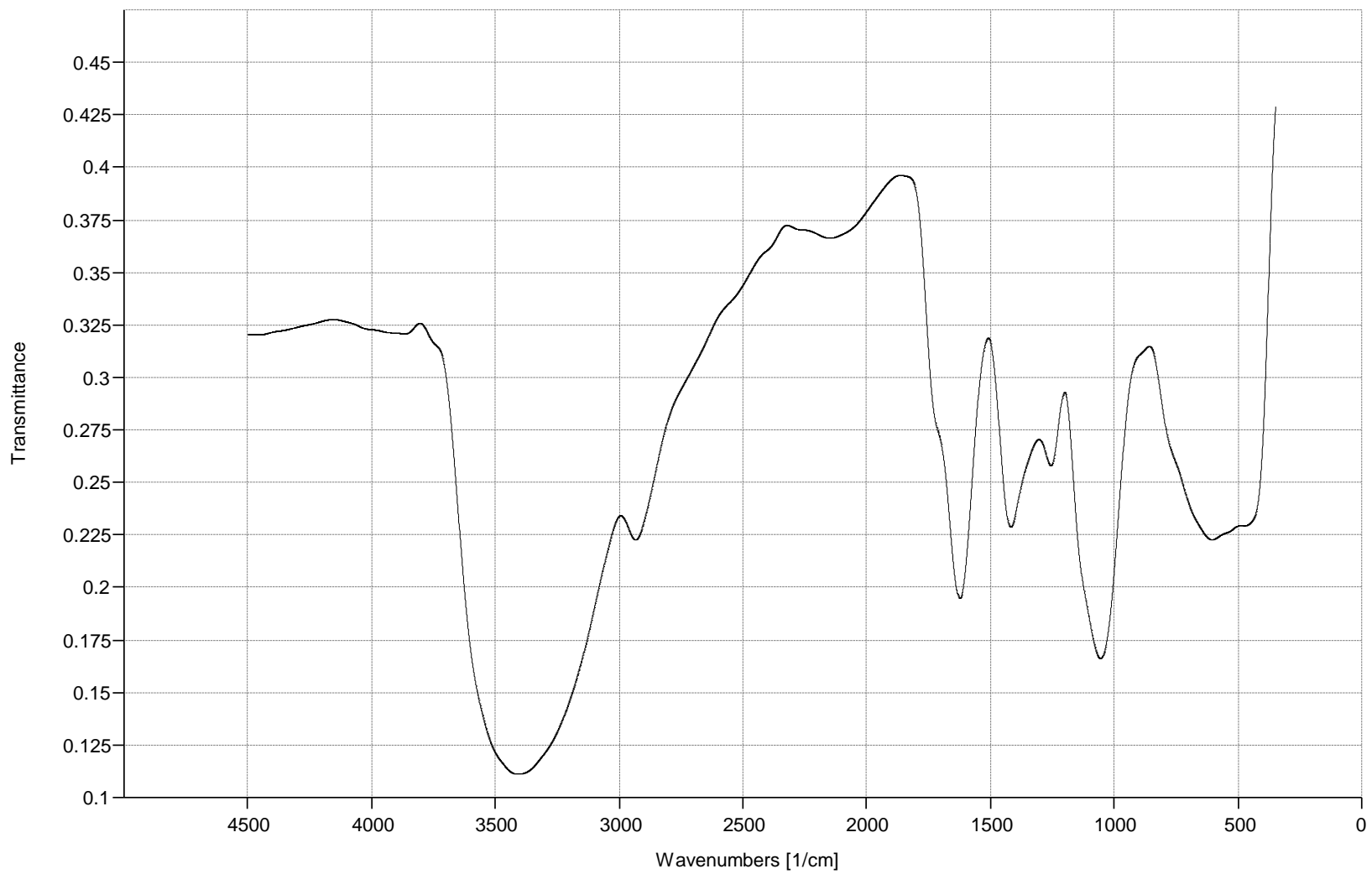


Fig. 4.40: FTIR spectrum of (KS) *Khaya senegalenses* gum

Table 4.13: Frequencies and peaks of IR absorption by *Khaya senegalenses* gum

Peak	Intensity	Area	Assignments/Functional Groups
424.35	25.3259	56.9595	C-C bending
565.16	24.0085	218.8798	CO <sub>2</sub> bending
887.28	34.296	38.6617	=CH out of plane
1054.13	13.8006	194.7923	C-O stretch
1285.6	30.6913	42.1279	C-H wag
1401.33	26.3787	115.3916	C-H in plane bending (CH <sub>3</sub> )
1635.69	38.2701	132.3826	C=C stretch
2920.32	26.1735	281.9871	C-H aliphatic stretch
3391.94	10.4898	587.0486	O-H stretch
3870.3	40.4904	57.6798	Asymmetric O-H stretching

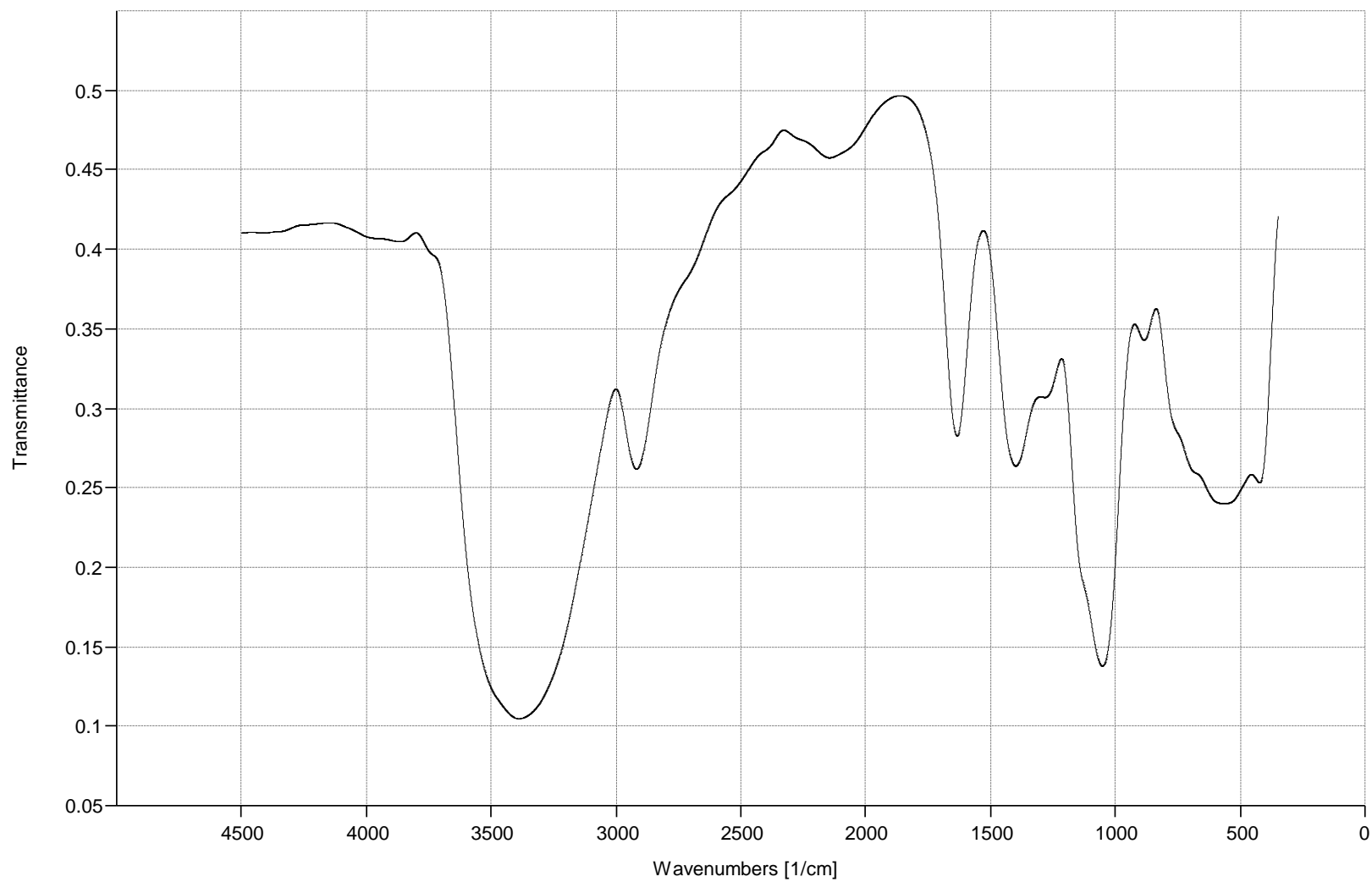


Fig. 4.41: FTIR spectrum of (AO) *Anacardium occidentale* gum

Table 4.13: Frequencies and peaks of IR absorption by Anacardium Occidentale gum

Peak	Intensity	Area	Assignments/Functional Groups
476.43	22.9417	80.0301	C-C bending
1057.63	16.6279	215.7409	C-O stretch
1257.63	25.8119	58.7557	C-H wag
1419.66	22.8866	118.7681	C-H in plane bending (CH <sub>3</sub> )
1625.08	19.4997	192.3215	C=C stretch
2935.76	22.2734	347.5468	C-H stretch
3412.19	11.1294	625.7414	O-H stretch
3872.23	32.0778	170.1499	Asymmetric O-H stretching

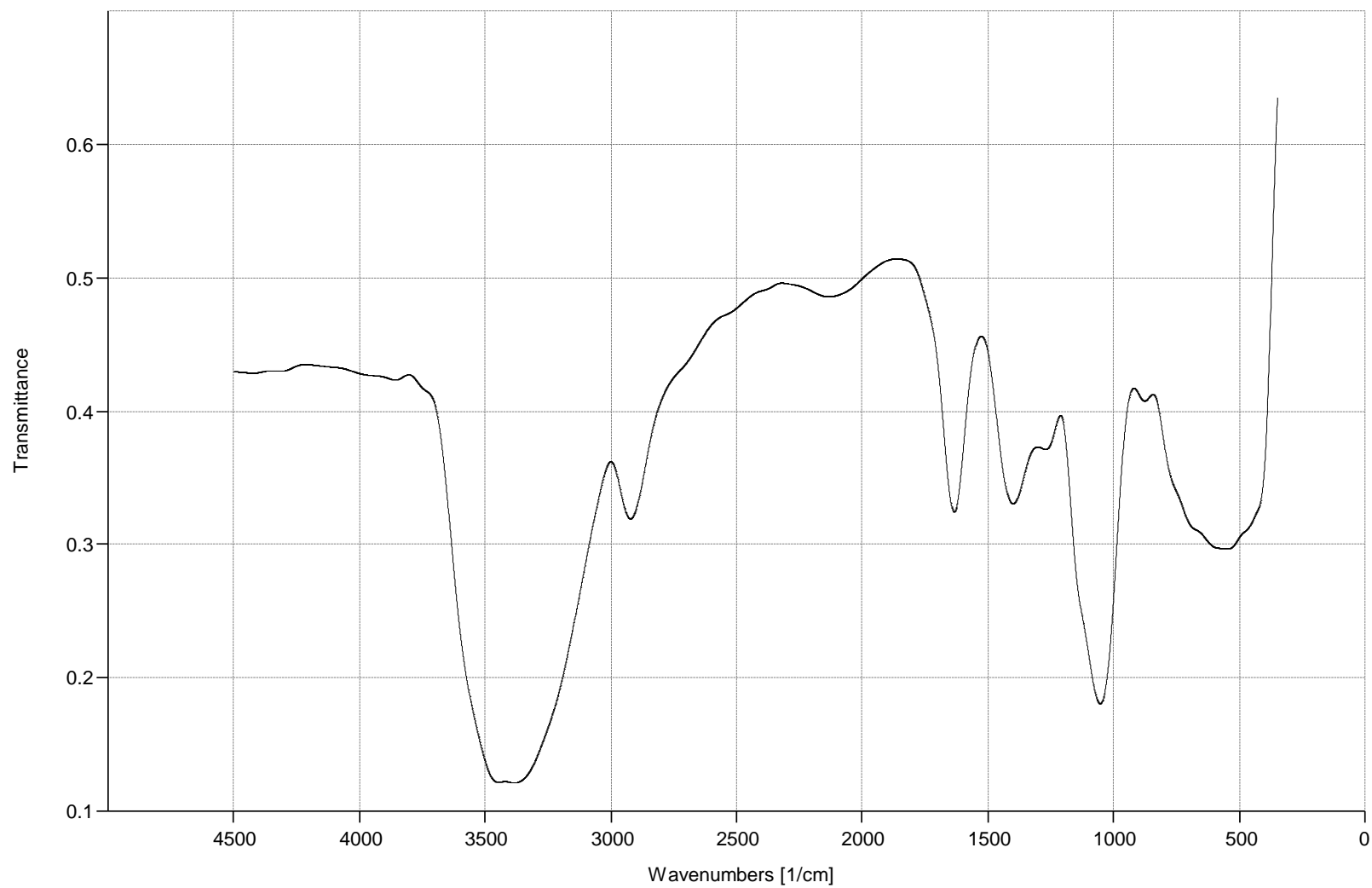


Fig. 4.42: FTIR spectrum of the blend (AO:AS) 80:20

Table 4.14: Frequencies and peaks of IR absorption by (AO:AS) 80:20 gum

Peak	Intensity	Area	Assignments/Functional Groups
415.67	30.5386	51.1787	C-C bending
1053.17	21.7391	190.5627	C-O stretch
1257.63	32.3488	45.4585	C-H wag
1411.94	29.6587	112.3713	C-H bend
1633.76	29.1341	147.2666	C=C stretch
2927.08	27.7154	313.4564	C-H aliphatic stretch
3400.62	17.0493	505.3967	O-H stretch
3869.33	37.3823	160.702	Asymmetric O-H stretching

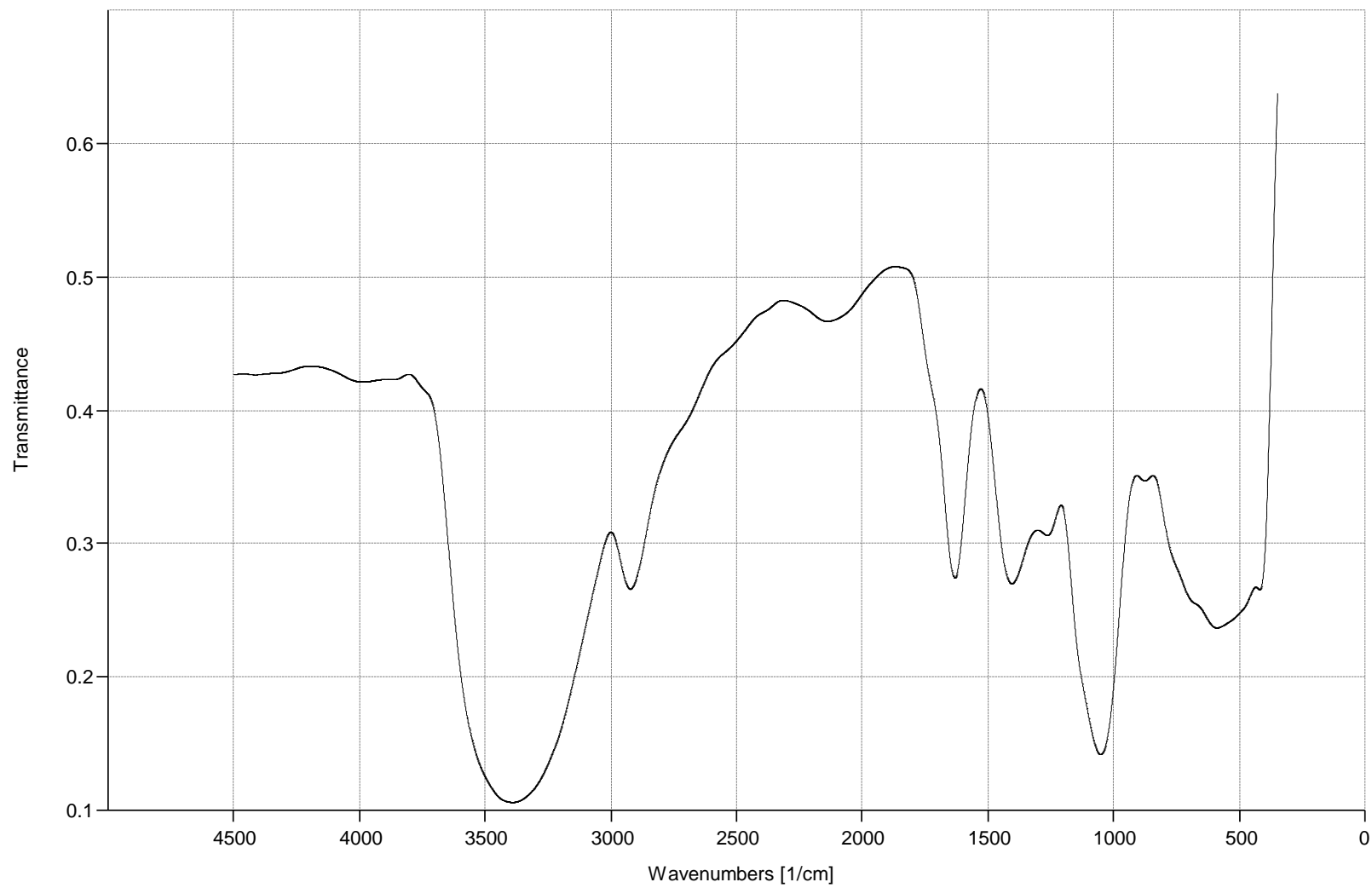


Fig. 4.43: FTIR spectrum of the blend (AO:AS) 60:40 gum

Table 4.15: Frequencies and peaks of IR absorption by (AO:AS) 60:40 gum

Peak	Intensity	Area	Assignments/Functional Groups
418.57	24.4542	40.3518	C-C bending
878.6	30.53656	30.702	=CH out of plane
1054.13	14.1816	207.4885	C-O stretch
1263.42	26.6594	51.7568	C-H wag
1408.08	23.4601	130.6395	C-H bend
1633.76	23.7817	166.0186	C=C stretch
2383.13	38.186	54.6091	C=O Asymmetric stretching CO <sub>2</sub>
2925.15	22.652	306.0876	C-H aliphatic stretch
3405.44	10.7176	610.1579	O-H stretch
3874.16	33.5721	62.3005	Asymmetric O-H stretching

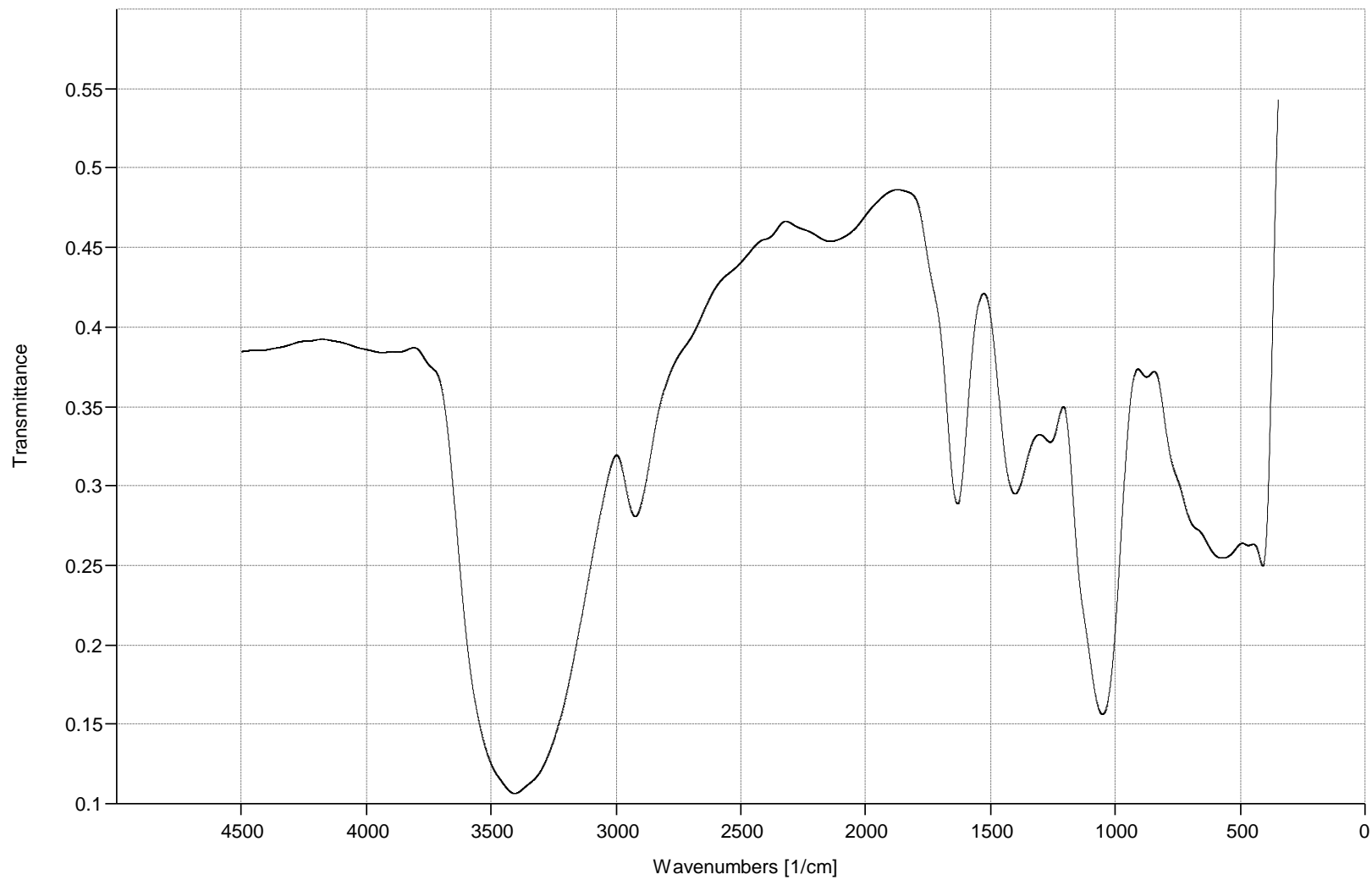


Fig. 4.44: FTIR spectrum of the blend (AO:AS) 50:50 gum

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Table 4.16: Frequencies and peaks of IR absorption by (AO:AS) 50:50 gum

Peak	Intensity	Area	Assignments/Functional Groups
411.82	24.9741	51.1227	C-C bending
877.64	36.862	27.4387	=CH out of plane
1054.13	15.6435	185.7729	C-O stretch
1263.42	32.7689	44.9877	C-H wag
1404.22	29.5088	105.538	C-H bend
1634.73	28.8866	136.8063	C=C stretch
2926.11	28.0868	278.6494	C-H aliphatic stretch
3409.3	10.6629	578.9569	O-H stretch
3878.98	38.4484	29.1462	Asymmetric O-H stretching

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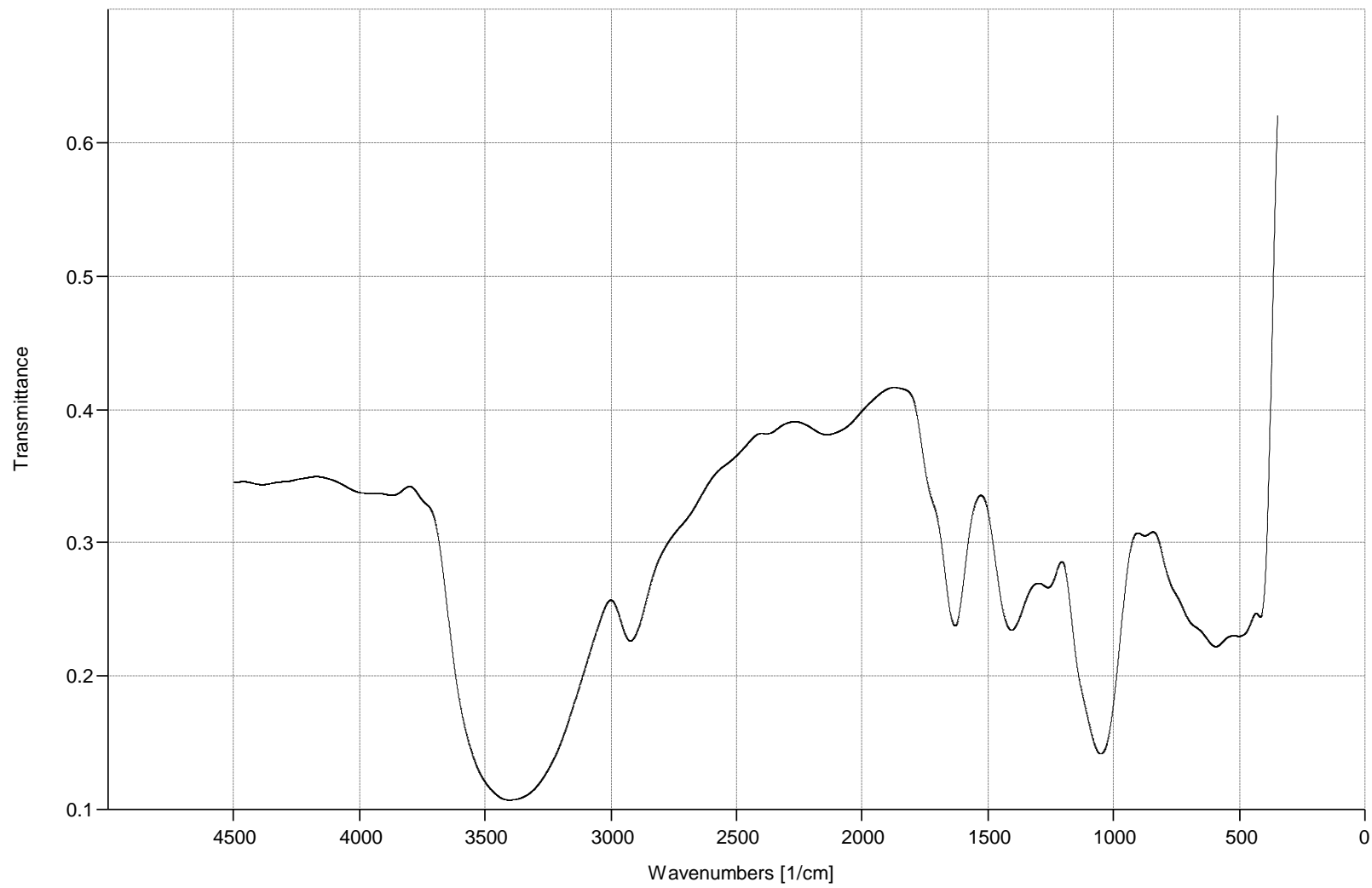


Fig. 4.45: FTIR spectrum of the blend (AO:AS) 40:60 gum

Table 4.17: Frequencies and peaks of IR absorption by (AO:AS) 40:60 gum

Peak	Intensity	Area	Assignments/Functional Groups
421.46	26.5555	38.9368	C-C bending
878.6	34.7155	29.069	=CH out of plane
1054.13	14.201	197.5053	C-O stretch
1266.31	30.6264	46.235	C-H wag
1406.15	26.9956	113.3192	C-H bend
1632.8	27.4489	136.3899	C=C stretch
2924.18	26.6011	281.9715	C-H aliphatic stretch
3392.9	10.6106	576.539	O-H stretch
3876.08	42.3019	30.1581	Asymmetric O-H stretching

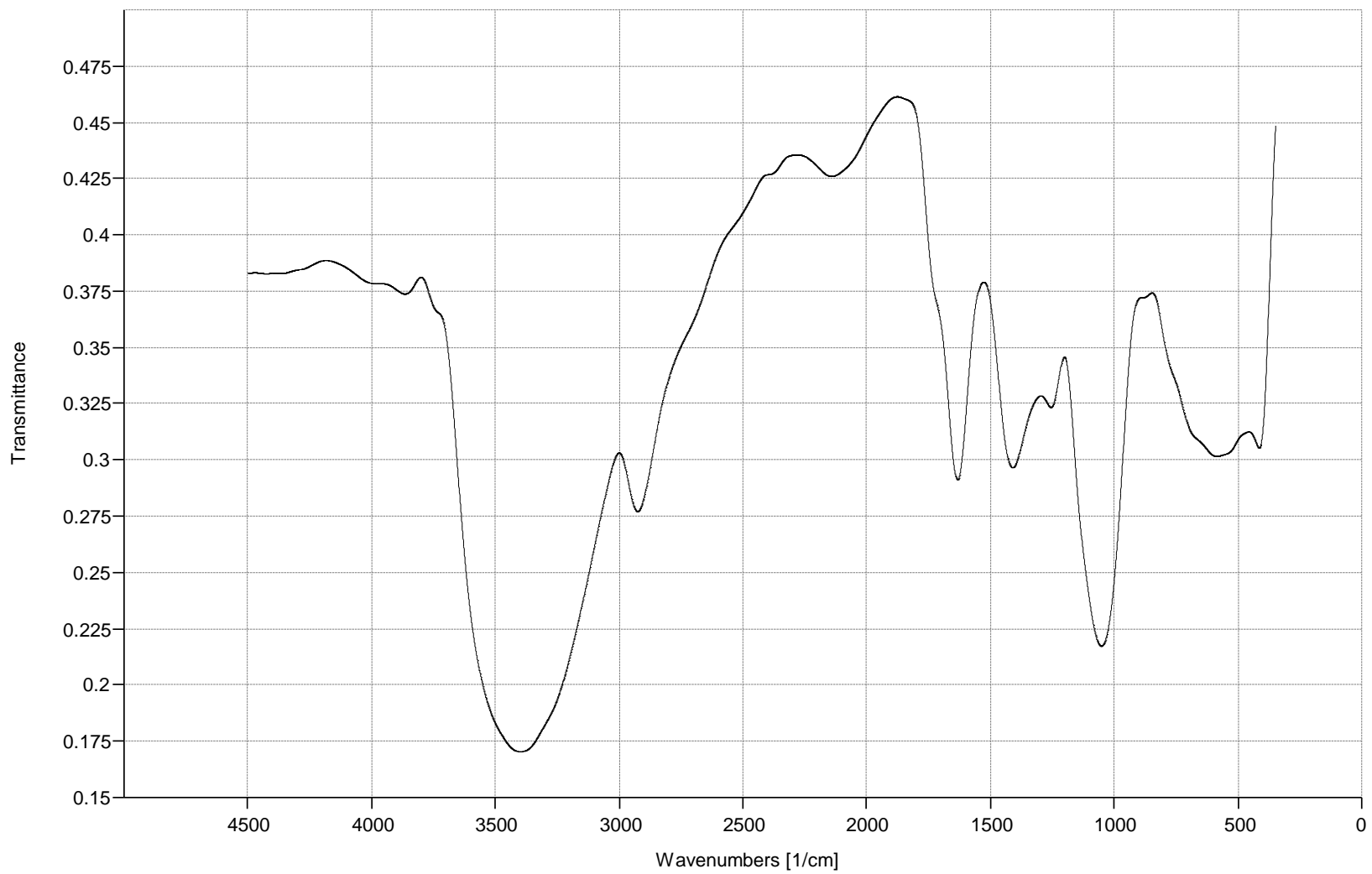


Fig. 4.46: FTIR spectrum of the blend (AO:AS) 20:80 gum

Table 4.18: Frequencies and peaks of IR absorption by (AO:AS) 20:80 gum

Peak	Intensity	Area	Assignments/Functional Groups
877.64	40.9094	27.1294	=CH out of plane
1055.1	18.1001	165.1805	C-O stretch
1276.92	37.1548	37.0062	C-H wag
1402.3	33.0787	95.6923	C-H bend
1635.69	32.6426	129.5543	C=C stretch
2924.18	31.9787	252.3399	C-H aliphatic stretch
3385.18	12.1532	295.8472	O-H dimer
3446.91	12.1828	236.4313	O-H stretch
3862.58	42.3611	149.4282	Asymmetric O-H stretching

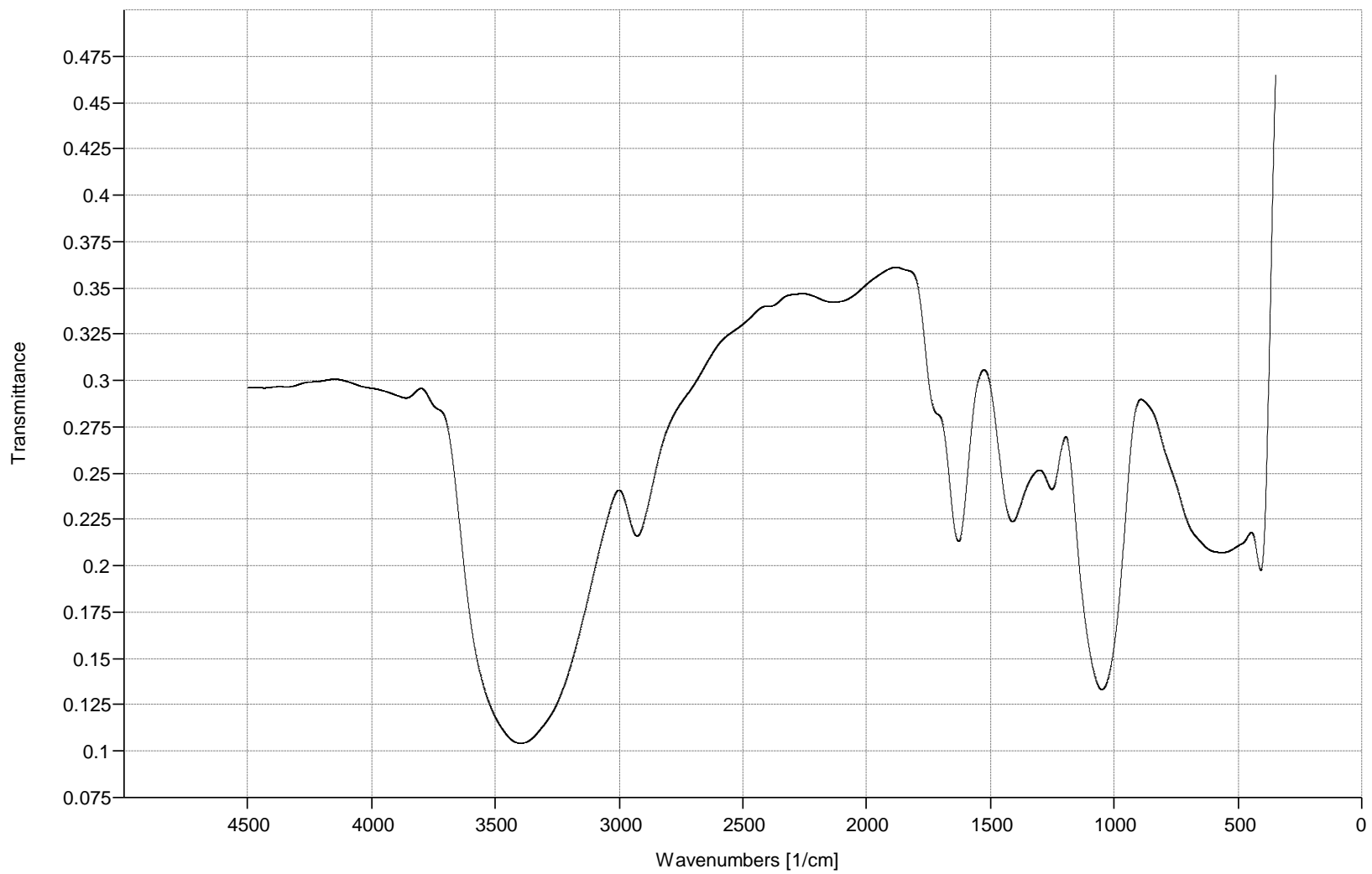


Fig. 4.47: FTIR spectrum of the blend (AS:KS) 80:20 gum

Table 4.19: Frequencies and peaks of IR absorption by (AS:KS) 80:20 gum

Peak	Intensity	Area	Assignments/Functional Groups
409.89	18.768	58.785	C-C bending
1052.2	13.338	218.404	C-O stretch
1256.77	24.149	63.101	C-H wag
1412.9	22.4	134.068	C-H bend
1639.87	21.34	189.707	C=C stretch
2399.53	34.016	67.451	C=O Asymmetric stretching CO <sub>2</sub>
2929.97	21.624	323.51	C-H aliphatic stretch
3400.62	10.443	629.047	O-H stretch
3863.55	29.072	184.311	Asymmetric O-H stretching

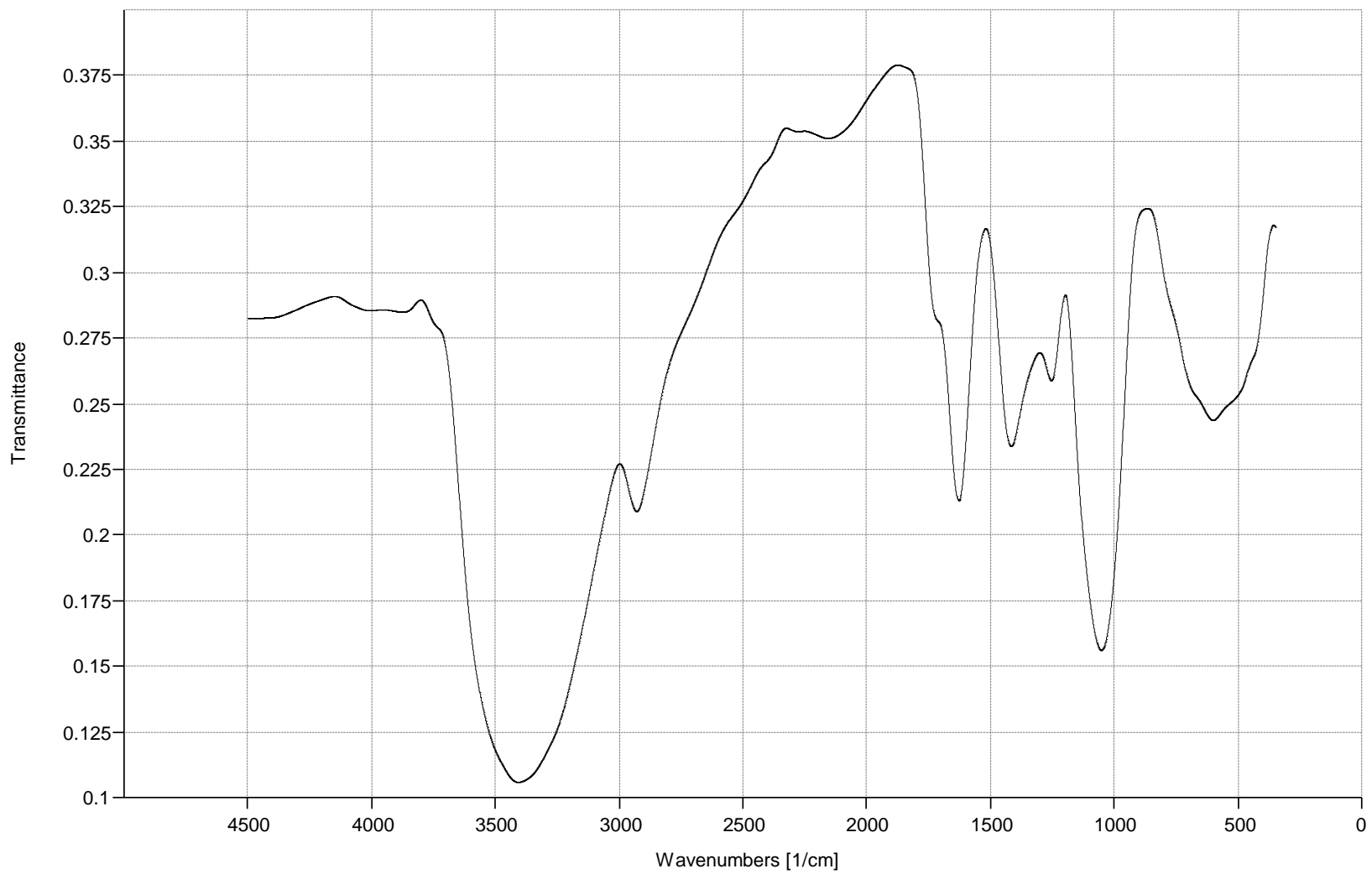


Fig. 4.48: FTIR spectrum of the blend (AS:KS) 60:40 gum

Table 4.20: Frequencies and peaks of IR absorption by (AS:KS) 60:40 gum

Peak	Intensity	Area	Assignments/Functional Groups
1053.17	15.626	212.8181	C-O stretch
1258.59	26.0097	59.8507	C-H wag
1416.76	23.4241	124.7028	C-H bend
1628.94	21.4537	186.8013	C=C stretch
2930.93	20.9544	387.9829	C-H aliphatic stretch
3407.37	10.5917	638.3243	O-H stretch
3878.01	28.4898	81.7853	Asymmetric O-H stretching

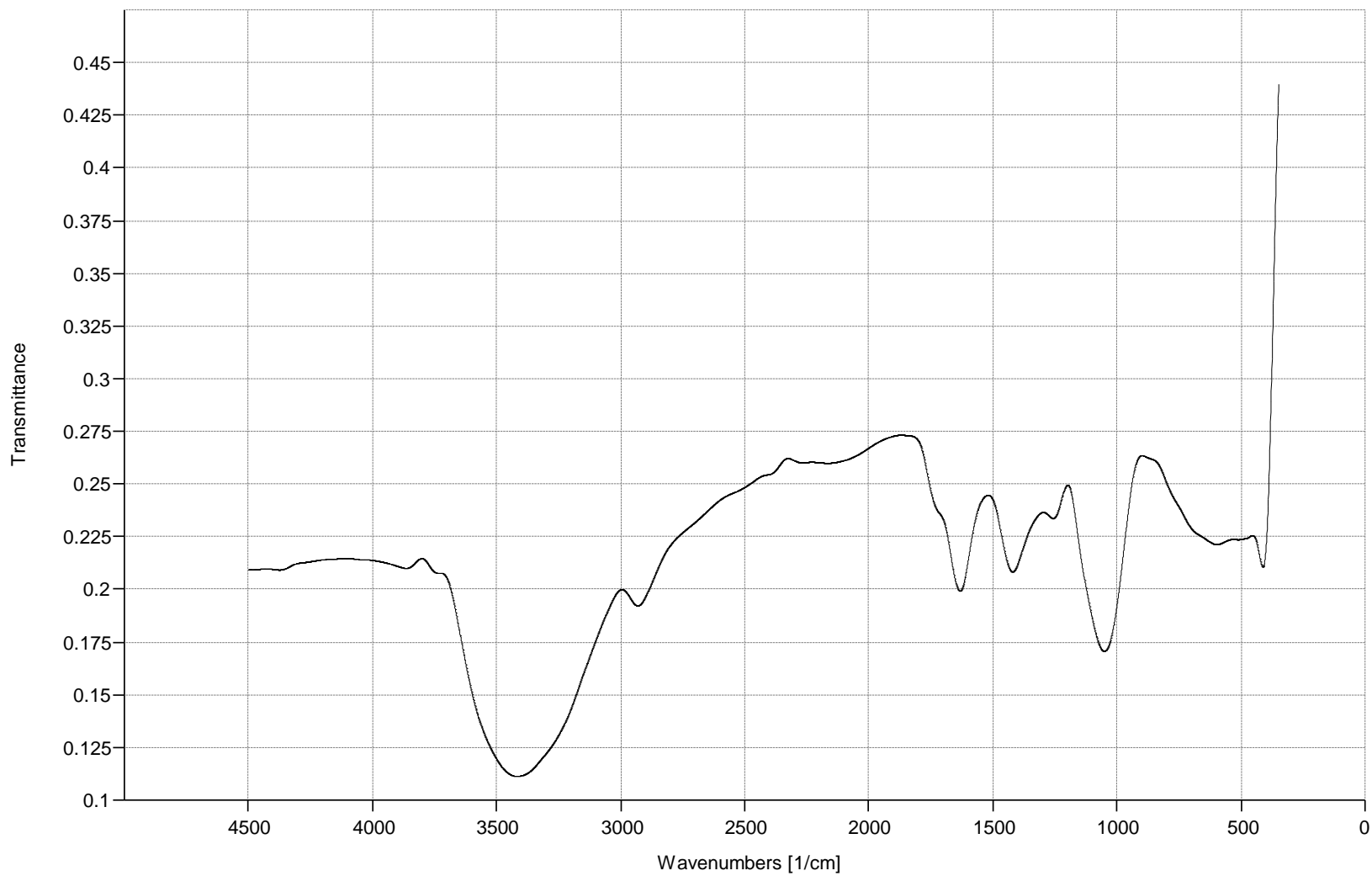


Fig. 4.49: FTIR spectrum of the blend (AS:KS) 50:50 gum

Table 4.21: Frequencies and peaks of IR absorption by (AS:KS) 50:50 gum

Peak	Intensity	Area	Assignments/Functional Groups
412.78	21.072	62.596	C-C bending
1053.17	17.069	203.354	C-O stretch
1259.56	23.374	60.013	C-H wag
1422.55	20.837	143.427	C-H bend
1634.73	19.932	217.867	C=C stretch
2933.83	19.223	426.003	C-H aliphatic stretch
3419.9	11.143	611.773	O-H stretch
3737.2	20.784	49.595	Asymmetric O-H stretching

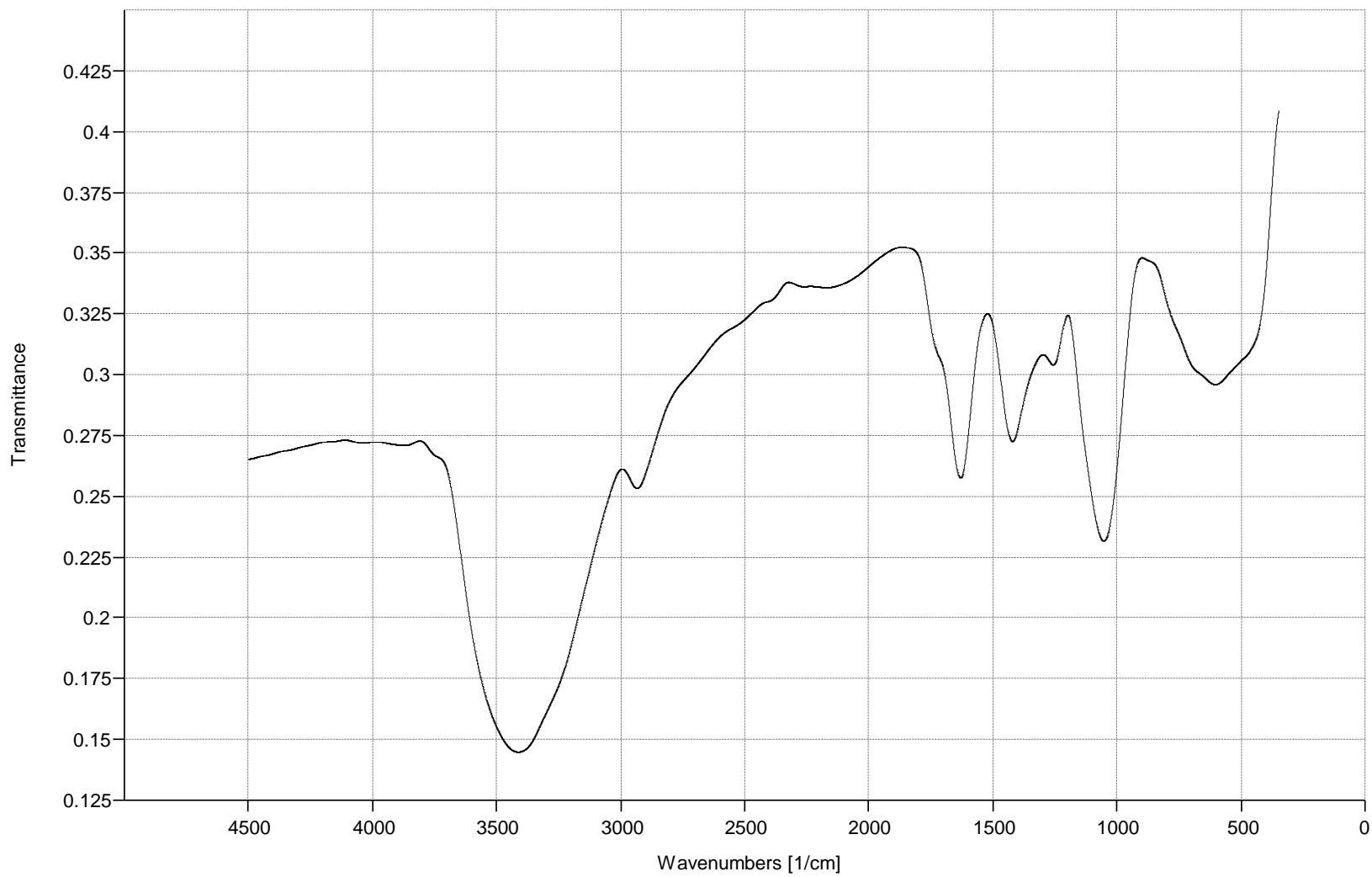


Fig. 4.50: FTIR spectrum of the blend (AS:KS) 40:60 gum

Table 4.22: Frequencies and peaks of IR absorption by (AS:KS) 40:60 gum

Peak	Intensity	Area	Assignments/Functional Groups
1055.1	23.179	167.601	C-O stretch
1262.45	30.465	50.947	C-H wag
1422.55	27.315	117.321	C-H bend
1631.83	25.855	172.811	C=C stretch
2936.72	25.364	351.331	C-H aliphatic stretch
3415.08	14.489	577.334	O-H stretch
3878.01	27.104	97.689	Asymmetric O-H stretching

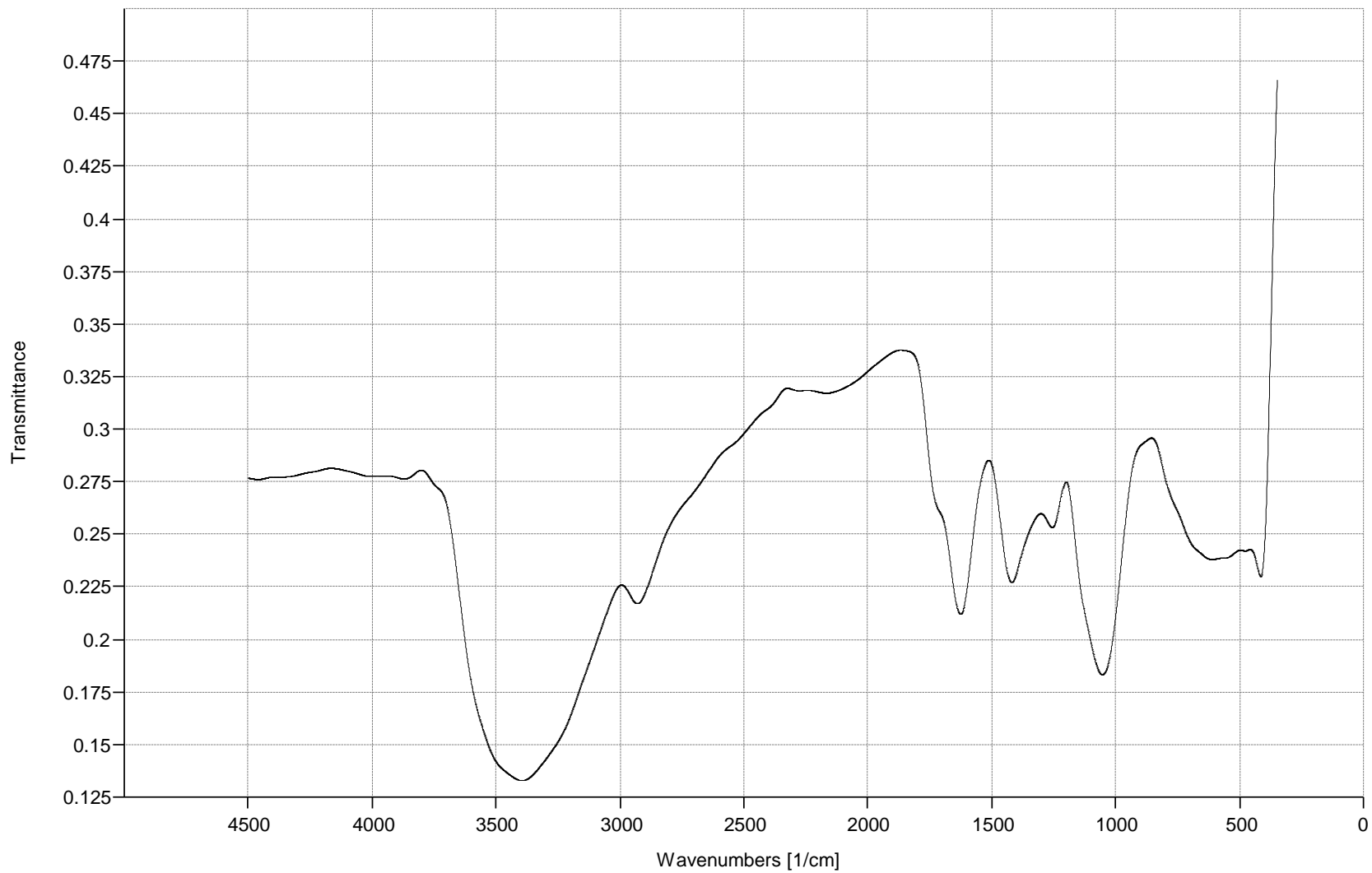


Fig. 4.51: FTIR spectrum of the blend (AS:KS) 20:80 gum

Table 4.23: Frequencies and peaks of IR absorption by (AS:KS) 20:80 gum

Peak	Intensity	Area	Assignments/Functional Groups
416.64	23	60.408	C-C bending
1056.06	18.328	215.993	C-O stretch
1258.58	25.33	59.177	C-H wag
1421.58	22.718	126.013	C-H bend
1627.97	21.203	201.043	C=C stretch
2932.86	21.708	379.505	C-H aliphatic stretch
3397.72	13.299	602.813	O-H stretch
3875.12	27.64	79.41	Asymmetric O-H stretching

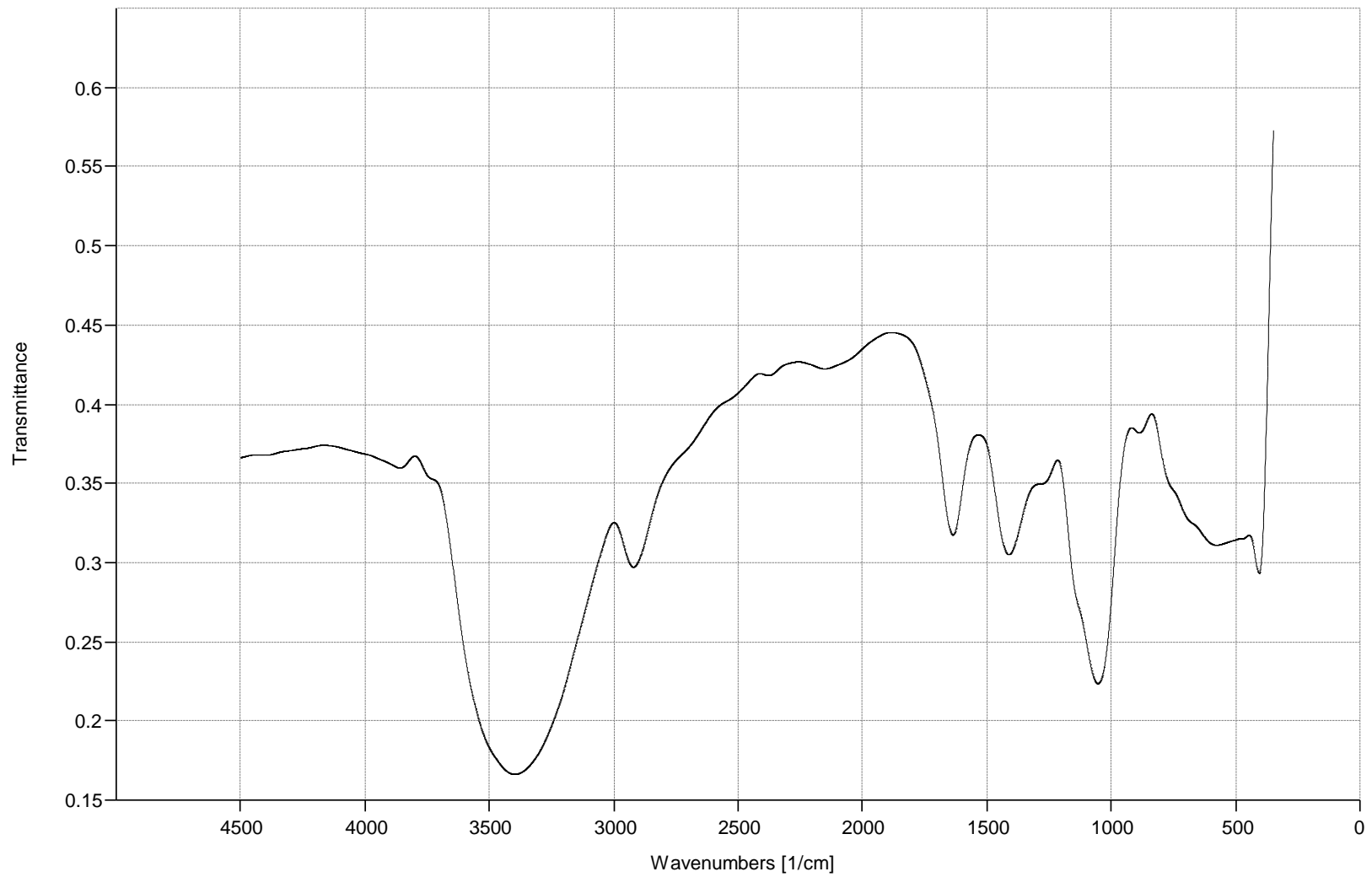


Fig. 4.52: FTIR spectrum of the blend (AO:KS) 80:20 gum

Table 4.24: Frequencies and peaks of IR absorption by (AO:KS) 80:20 gum

Peak	Intensity	Area	Assignments/Functional Groups
406.99	29.3386	44.1848	C-C bending
889.21	38.1999	33.4822	=CH out of plane
1056.06	22.3712	159.4313	C-O stretch
1413.87	30.5079	148.3311	C-H bend
1638.58	31.7581	142.5717	C=C stretch
2380.24	41.6206	57.3793	C=O Asymmetric stretching CO <sub>2</sub>
2923.22	29.7243	257.1742	C-H aliphatic stretch
3399.65	16.6438	501.0995	O-H stretch
3861.62	35.9894	158.8628	Asymmetric O-H stretching

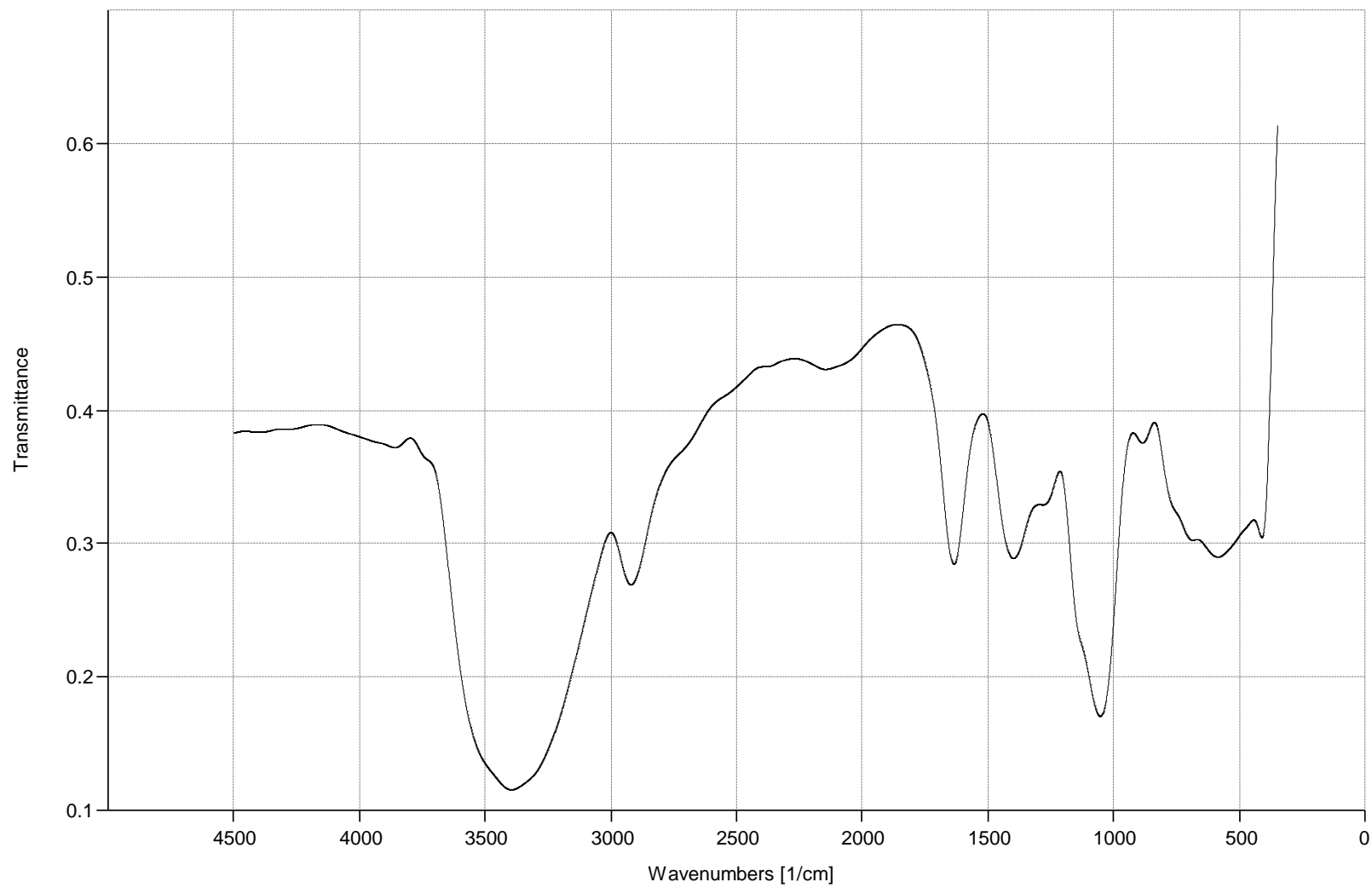


Fig. 4.53: FTIR spectrum of the blend (AO:KS) 60:40 gum

Table 4.25: Frequencies and peaks of IR absorption by (AO:KS) 60:40 gum

Peak	Intensity	Area	Assignments/Functional Groups
411.82	30.4733	41.109	C-C bending
887.28	37.5496	35.1445	=CH out of plane
1055.1	17.0682	174.4468	C-O stretch
1284.63	32.9141	38.6651	C-H wag
1400.37	28.8835	108.8893	C-H bend
1636.65	28.4813	141.6488	C=C stretch
2922.25	26.9202	312.676	C-H aliphatic stretch
3397.72	11.5603	566.474	O-H stretch
3860.65	37.2157	154.7617	Asymmetric O-H stretching

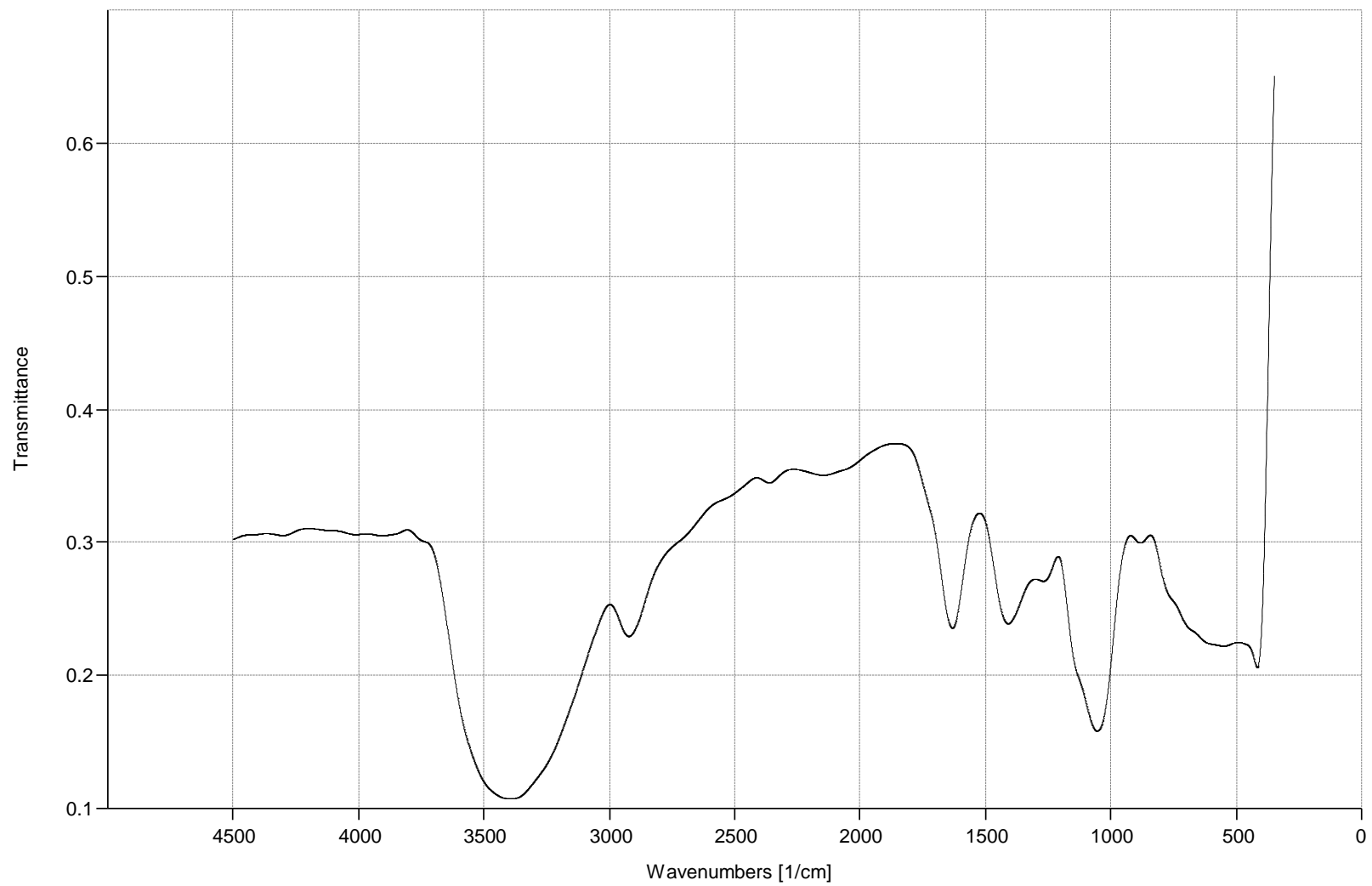


Fig. 4.54: FTIR spectrum of the blend (AO:KS) 50:50 gum

Table 4.26: Frequencies and peaks of IR absorption by (AO:KS) 50:50 gum

Peak	Intensity	Area	Assignments/Functional Groups
417.6	20.6078	80.043	C-C bending
884.39	29.9603	40.5821	=CH out of plane
1057.03	15.8319	191.8199	C-O stretch
1272.1	27.0917	50.0963	C-H wag
1411.94	23.8949	127.2774	C-H bend
1633.76	23.571	169.8053	C=C stretch
2364.81	34.4829	66.4966	C=O Asymmetric stretching CO <sub>2</sub>
2924.18	22.9476	310.3547	C-H aliphatic stretch
3395.79	10.7486	618.9796	O-H stretch
3908.88	30.5135	82.7506	Asymmetric O-H stretching

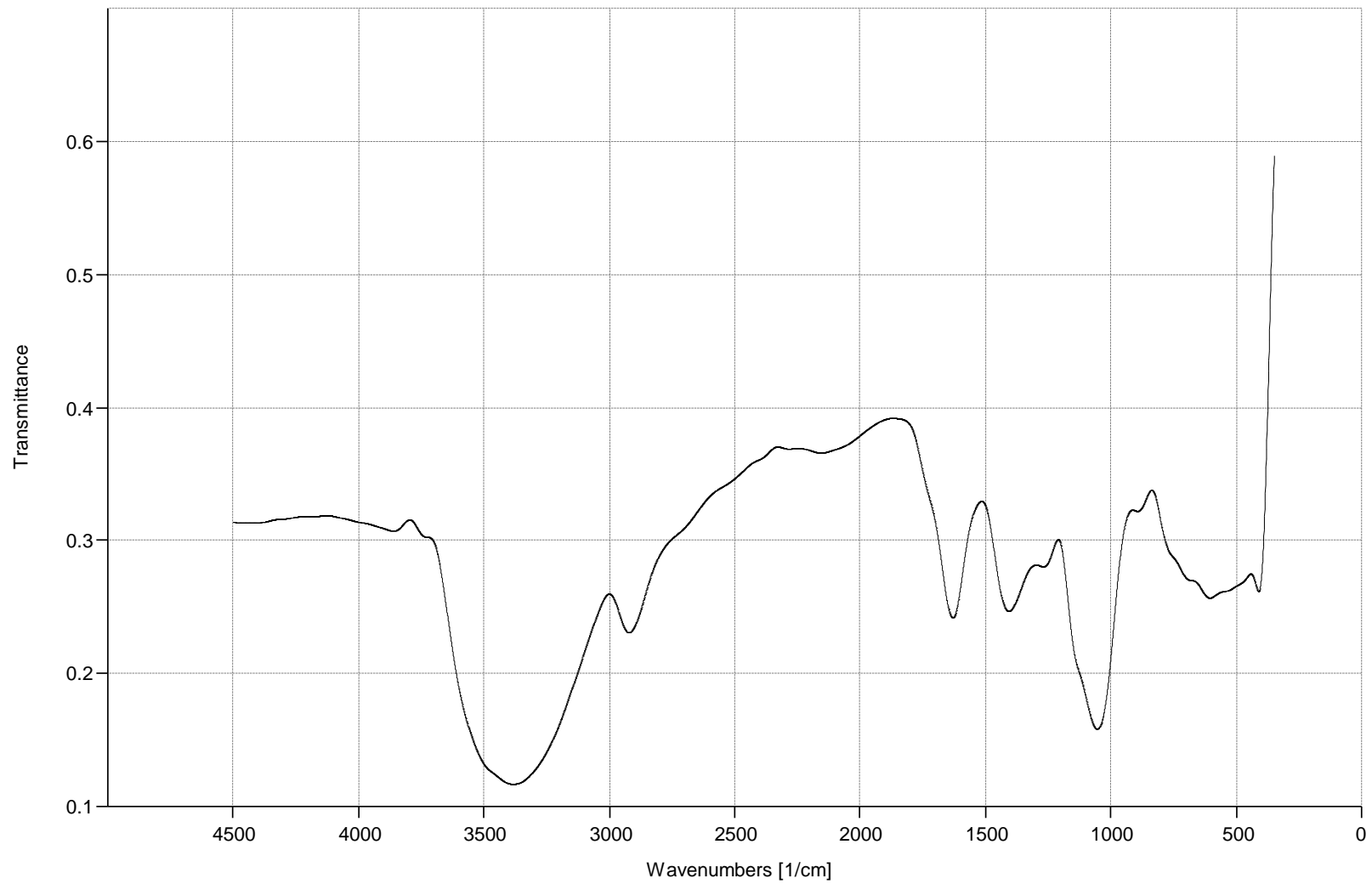


Fig. 4.55: FTIR spectrum of the blend (AO:KS) 40:60 gum

Table 4.27: Frequencies and peaks of IR absorption by (AO:KS) 40:60 gum

Peak	Intensity	Area	Assignments/Functional Groups
411.82	26.1753	44.7828	C-C bending
895	32.2033	36.4765	=CH out of plane
1056.06	15.8348	192.7462	C-O stretch
1271.13	28.0311	47.1254	C-H wag
1409.05	24.6784	121.536	C-H in plane bending (CH <sub>3</sub> )
1631.83	24.1946	174.8024	C=C stretch
2923.22	23.0694	344.1531	C-H aliphatic stretch
3385.18	11.6802	592.8059	O-H stretch
3861.62	30.7208	166.3921	Asymmetric O-H stretching

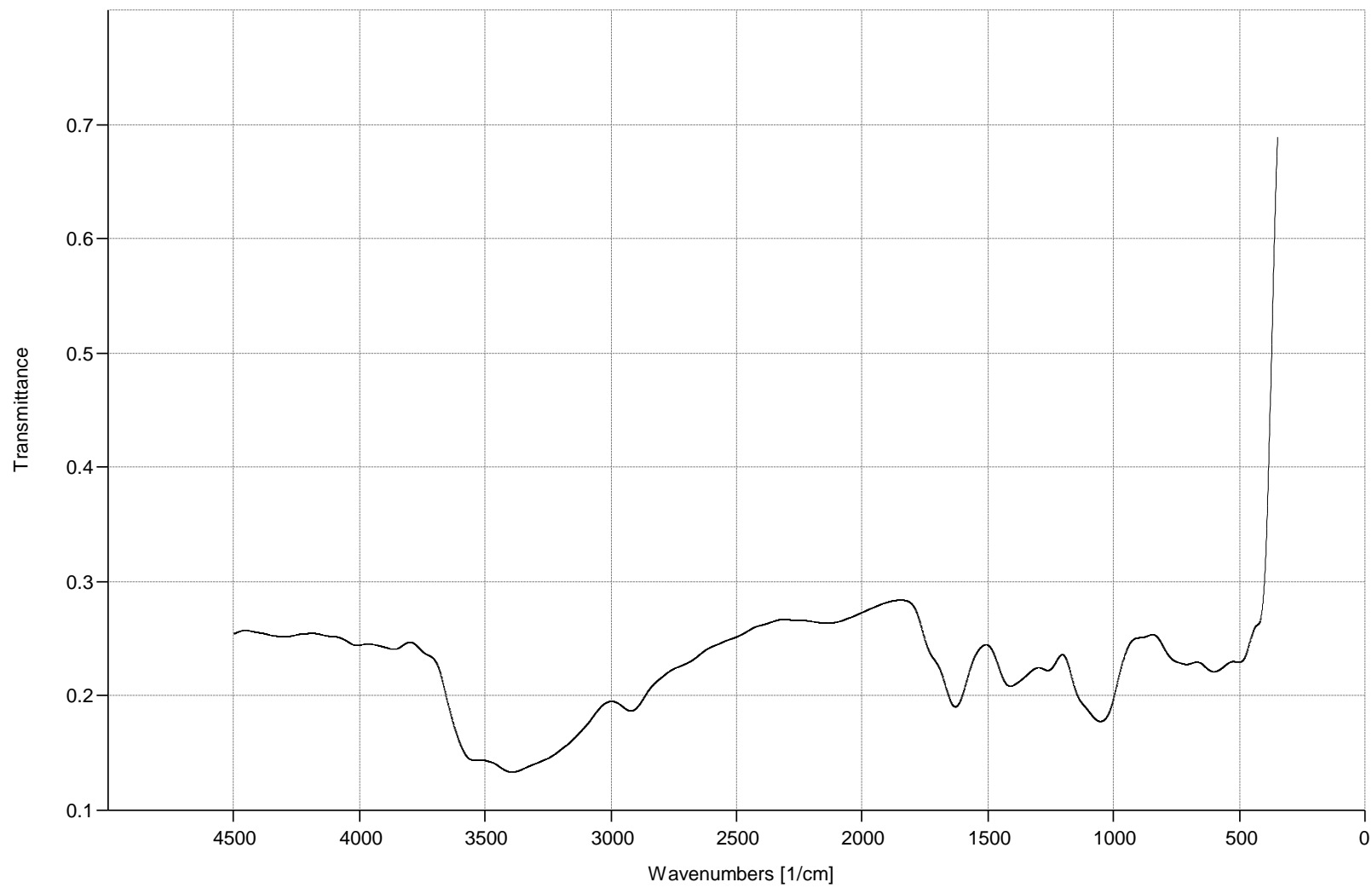


Fig. 4.56: FTIR spectrum of the blend (AO:KS) 20:80 gum

Table 4.28: Frequencies and peaks of IR absorption by (AO:KS) 20:80 gum

Peak	Intensity	Area	Assignments/Functional Groups
508.26	22.967	91.61	C-C bending
715.61	22.901	110.099	=CH out of plane
1054.13	17.799	239.454	C-O stretch
1268.24	22.292	60.276	C-H wag
1411.94	20.881	136.491	C-H bend
1631.83	19.134	210.314	C=C stretch
2923.22	18.725	436.834	C-H aliphatic stretch
3394.83	13.382	424.558	O-H stretch
3541.42	14.394	199.69	O-H stretch
3868.37	24.124	100.523	Asymmetric O-H stretching

#### 4.11 GC-MS Study

Spectra obtained from gas chromatography mass spectrophotometer (GCMS) of the blends AO:KS, AS:AO, and AS:KS gums are shown in Figs. 4.60 to 4.62.

Fig. 4.60 shows the GC-MS spectrum of AO:KS blend, the IUPAC names. The GC-MS spectrum of the blend displayed 9 significant peaks. Since area under the chromatogram is proportional to concentration, area normalization was carried out and percentage concentrations of the respective chemical constituents were evaluated. The results obtained shows that the most abundant component of the blending of *Anacardium occidentale* and *Khaya senegalensis* (AO:KS) is ricinoleic acid (39.31%), followed by oleic acid (20.93%). The least abundant constituent was found to be octadecanoic acid (3.41%). Other constituents of the gum included 9-Octadecanoic acid (9.74%), methyl,cis,cis-9,12-octadecadienoate (6.49%), 13-hexyloxacyclotridec-10-en-2-one (5.13%), methyl hexadecanoate (5.42%), Ricinoleic acid methyl ester (5.16%) and 1-pentadecanecarboxylic acid (4.41%).

In Fig. 4.61 Analysis of GC-MS spectrum of AS:AO gum blend shows the presence of C<sub>19</sub> and C<sub>18</sub> streams of carboxylic acid namely, 9-octadecanoic acid (22.11%) and 6-octadecanoic acid (55.76%). These compounds were resolved at retention time ranging from 27.463 and 28.049 min but eluting out at line 3 and 4 respectively were found to have to be the most abundant constituents of the blend AS:AO. In line 1, methylhexadecanoate (3.97%) was found to be the least abundant; it was eluted at a retention time of 25.717 min. Other constituent of this blend includes 1-pentadecane carboxylic acid (10.78%) and 9,12-octadecadienoic acid (7.38%) eluted out at line 2 and 5 respectively. Corresponding retention time for these acids was 26.258 and 30.683 minutes.

Line 3 of the GC-MS of AS:KS gum in Fig. 4.62, revealed the presence of 30.67 % of methyl(16E)-16-octadecanoate (retention time = 27.465 min) which is the second most abundant constituent of the blend AS:KS. The most abundant compound eluted out was found to be oleic acid (47.90 %) with retention time 28.051 minutes. various streams of carboxylic acids were identified. These included 5.91 % hexadecanoic acid, 9.30 % 1-pentadecane carboxylic acid and 6.21 % steric acid.

The molar mass and chemical formulas of these compounds were presented below each spectrum as well as the resolution of each line in the spectra of the blends AS:KS, AO:KS and AS:AO gum which revealed the occurrence of several fragmentation peak for each fraction.

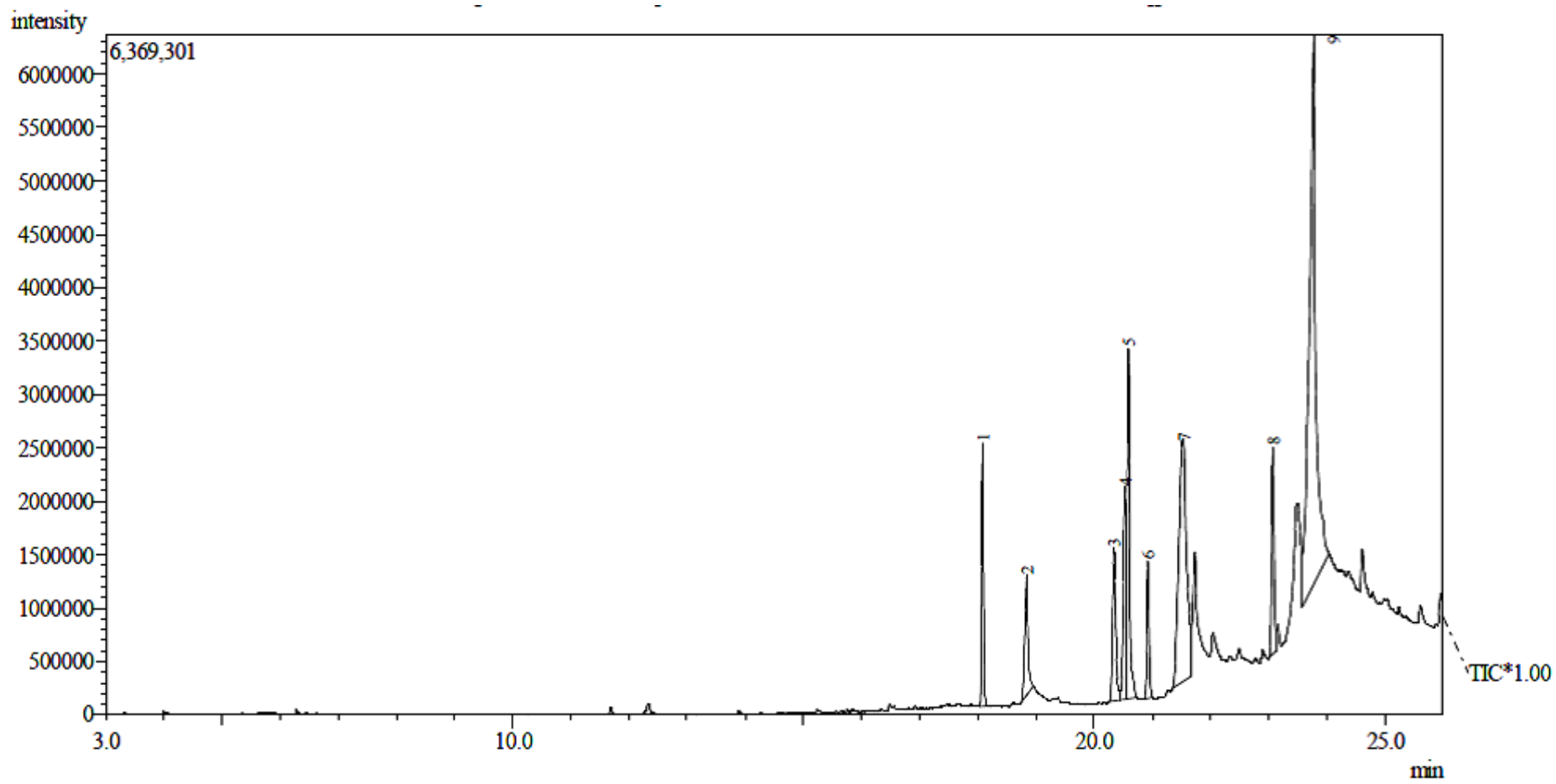
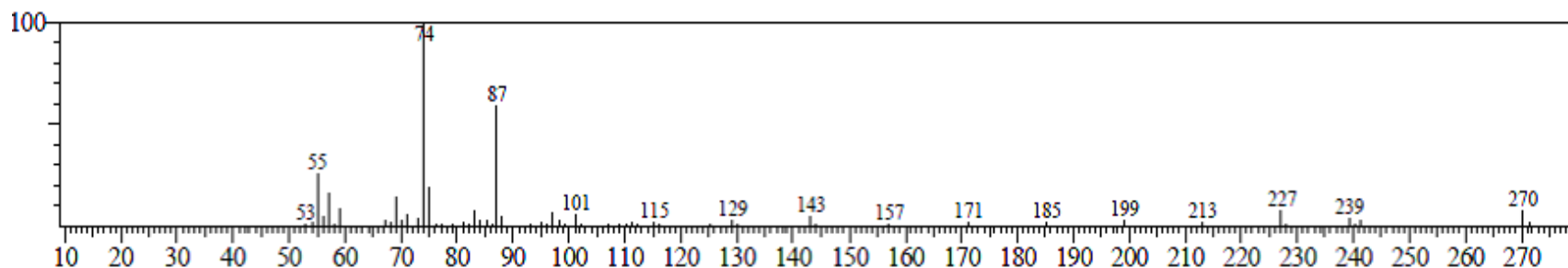


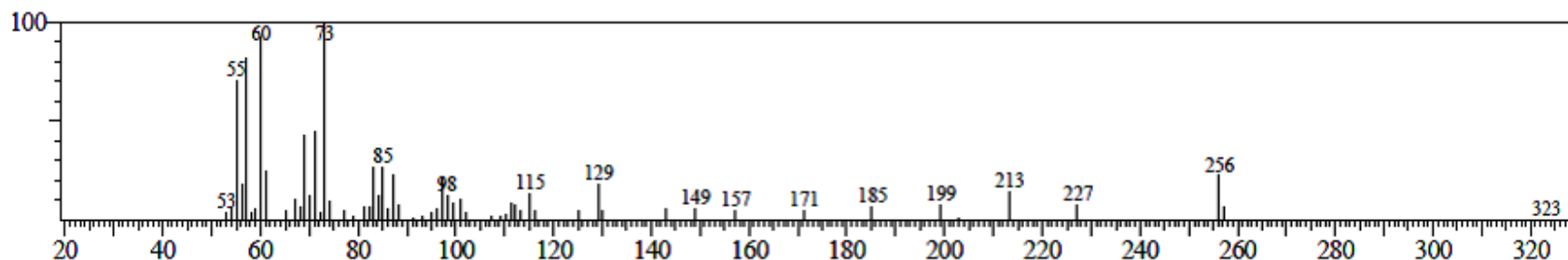
Fig. 4.57: GCMS Spectrum of the blend AO:KS (50:50) gum

CHARACTERISTICS SUGGESTED COMPOUNDS IDENTIFIED FROM GC-MS OF THE GUM BLEND AO:KS

Line No	Iupac Name	Molecular Formular	Molar Mass (g/mol)	Retention Time	Mass Peak	Area %
1	Methyl hexadecanoate	C <sub>17</sub> H <sub>34</sub> O <sub>2</sub>	270	18.083	66	5.42



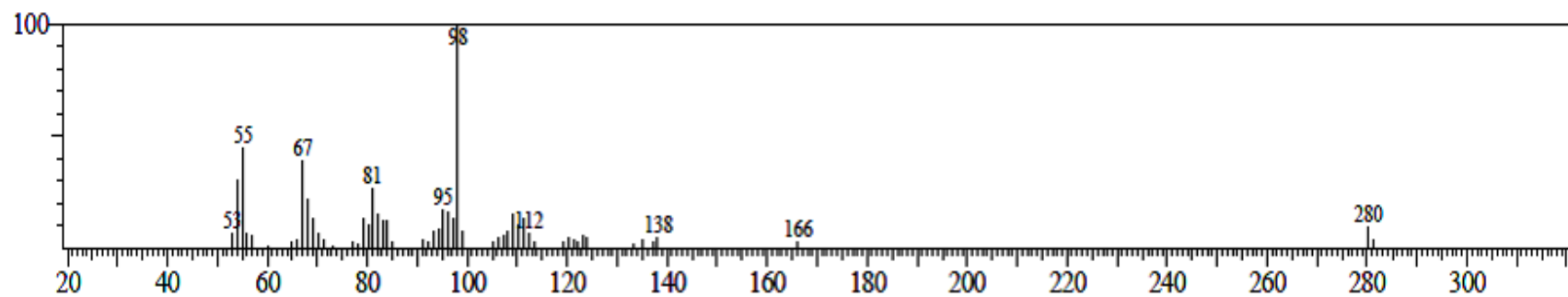
2	1-pentadecenecarboxylic	C <sub>16</sub> H <sub>32</sub> O <sub>2</sub>	256	18.838	60	4.41
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3	13-hexyloxacyclotridec-10-en-2-one	$C_{18}H_{32}O_2$	280	20.344	54	5.13
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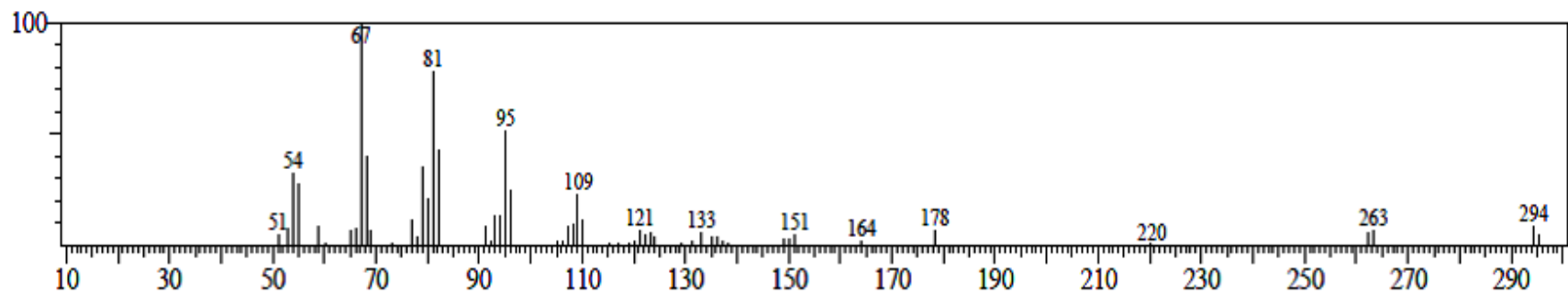
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4	Methyl cis, cis-9, 12-octadecadienate	$C_{19}H_{34}O_2$	294	20.532	57	6.49
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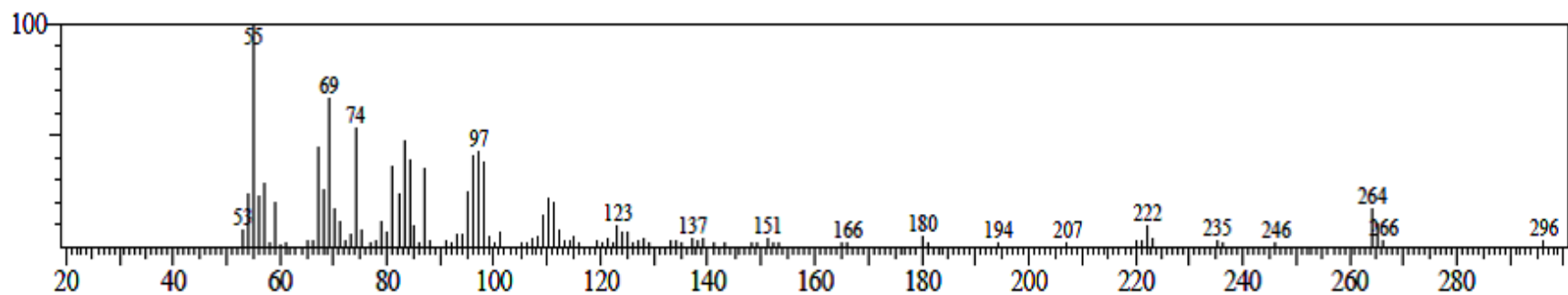
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5	9-octadecanoic acid	$C_{19}H_{36}O_2$	296	20.592	97	9.74
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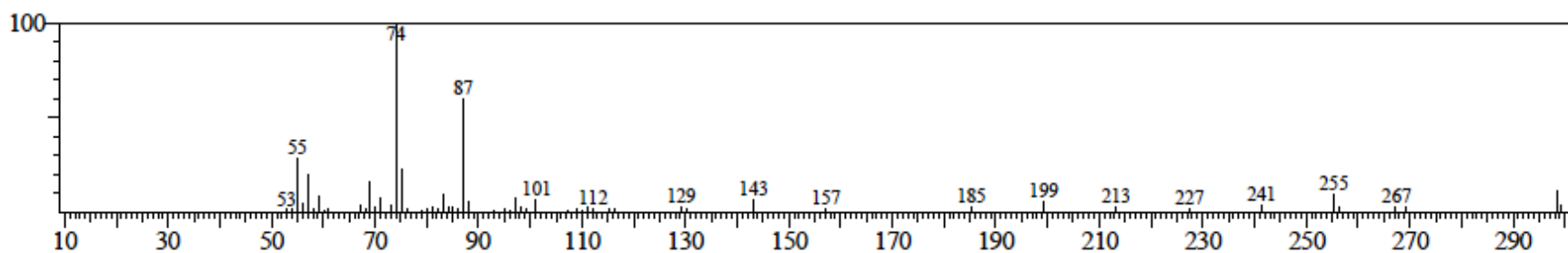
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6	Octadecanoic acid	$C_{19}H_{38}O_2$	298	20.926	59	3.41
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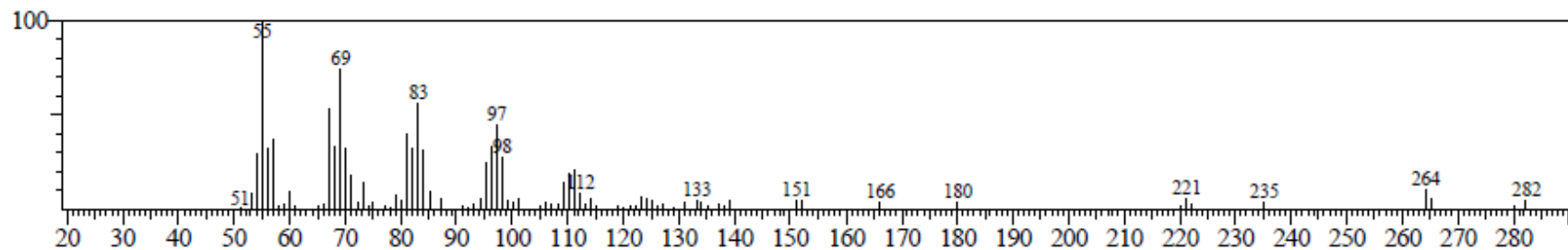
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7	Oleic acid	$C_{18}H_{34}O_2$	282	21.515	83	20.93
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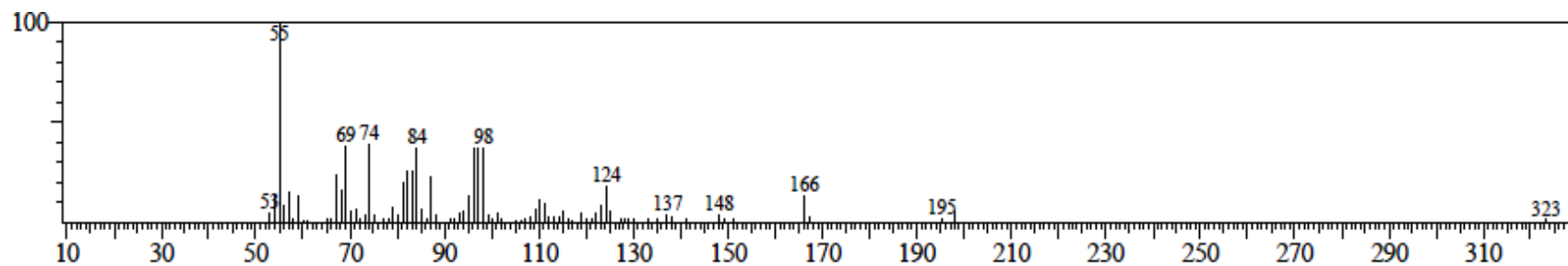
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8	Ricinoleic acid methyl ester	$C_{19}H_{36}O_3$	323	23.074	82	5.16
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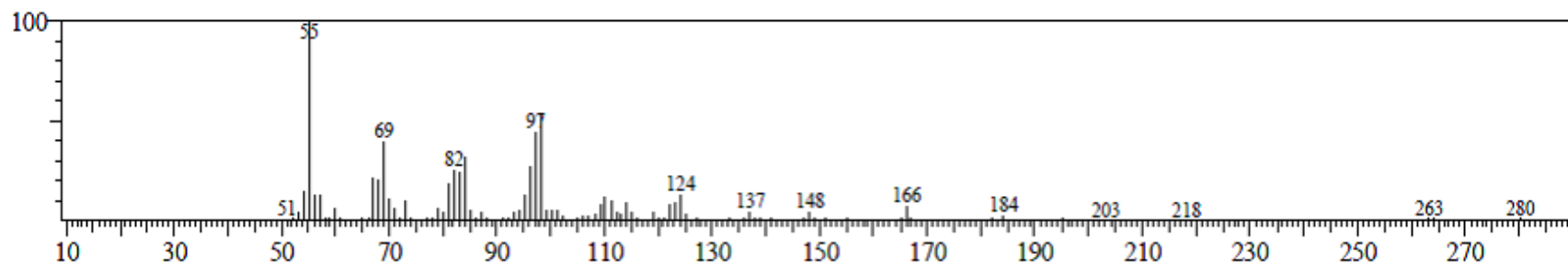
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9	Ricinoleic acid	$C_{18}H_{34}O_3$	298	23.774	100	39.31
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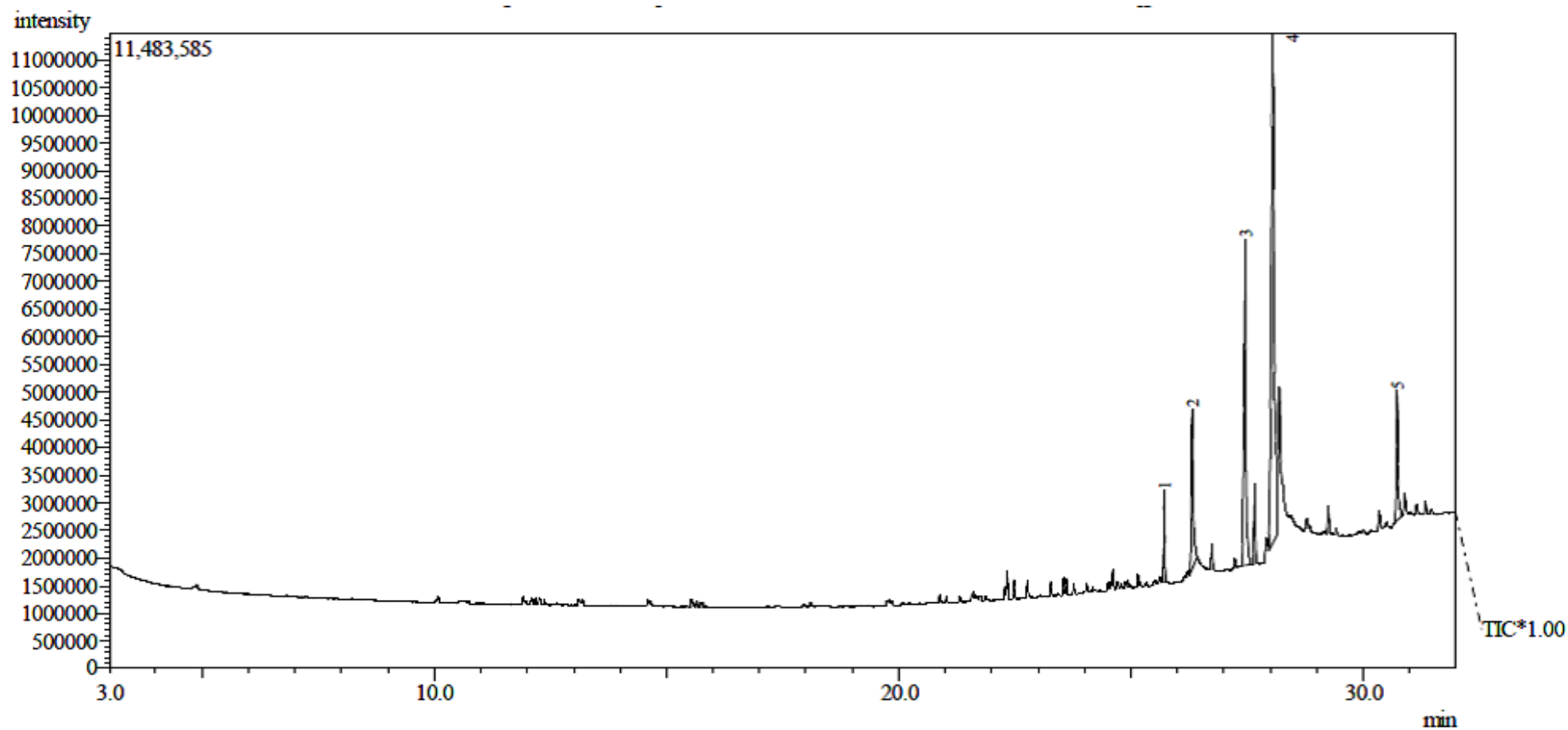
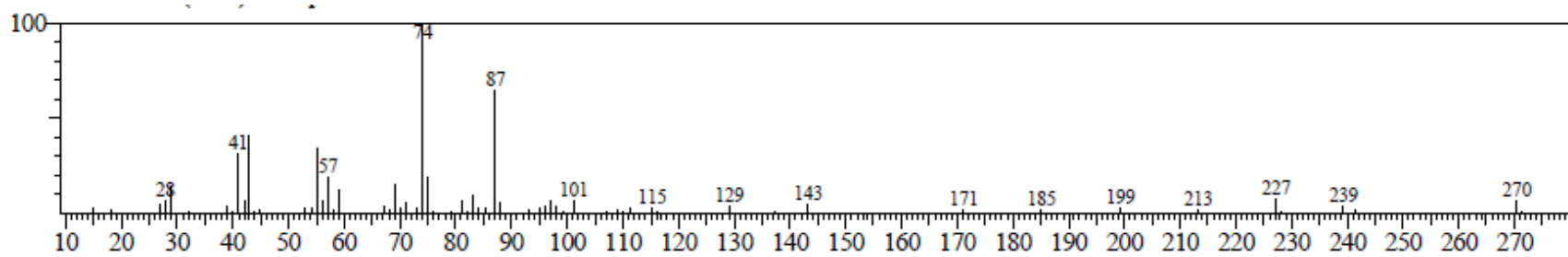


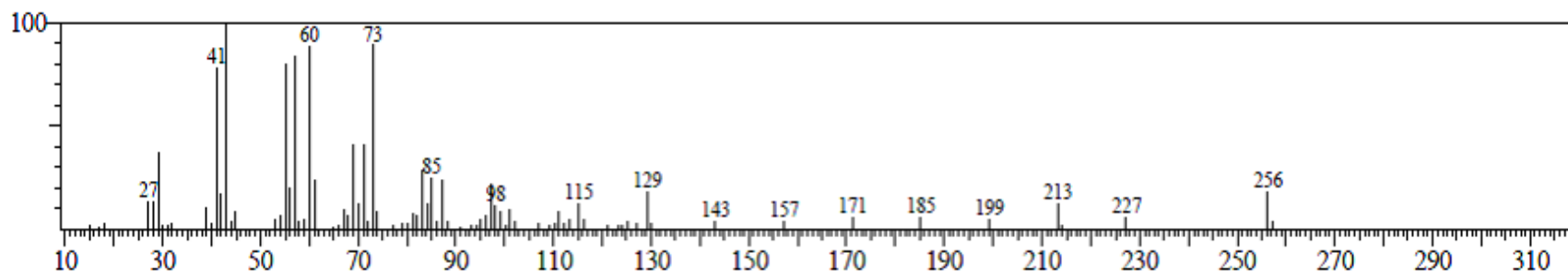
Fig. 4.58: GCMS Spectrum of the blend AS:AO (50:50) gum

CHRACTERISTIC SUGGESTED COMPOUNDS IDENTIFIED FROM GC-MS OF THE GUM BLEND AO:AS

Line No	Iupac Name	Molecular Formular	Molar Mass (g/mol)	Retention Time	Mass Peak	% Conc
1	Methyl hexadecnoate	C <sub>17</sub> H <sub>34</sub> O <sub>2</sub>	270	25.717	67	3.97



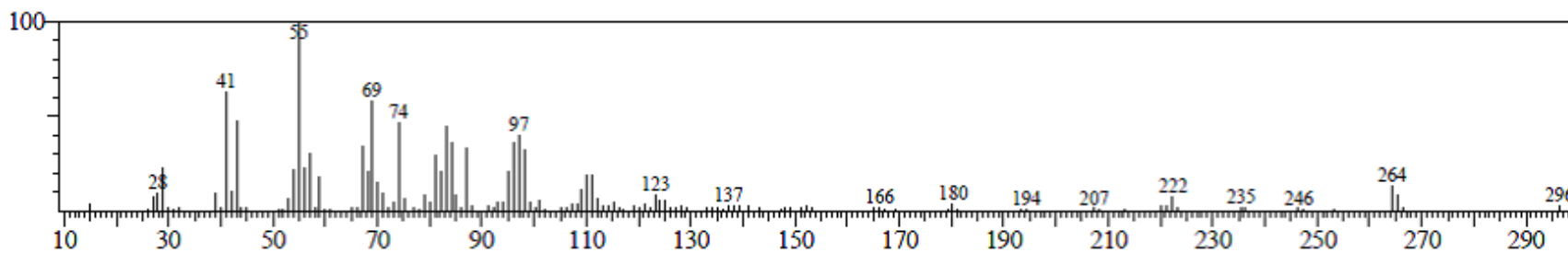
2	1-pentadecane carboxylic acid	C <sub>16</sub> H <sub>32</sub> O <sub>2</sub>	256	26.316	83	10.78
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3	9-octadecenoic acid	$C_{19}H_{36}O_2$	296	27.463	125	22.11
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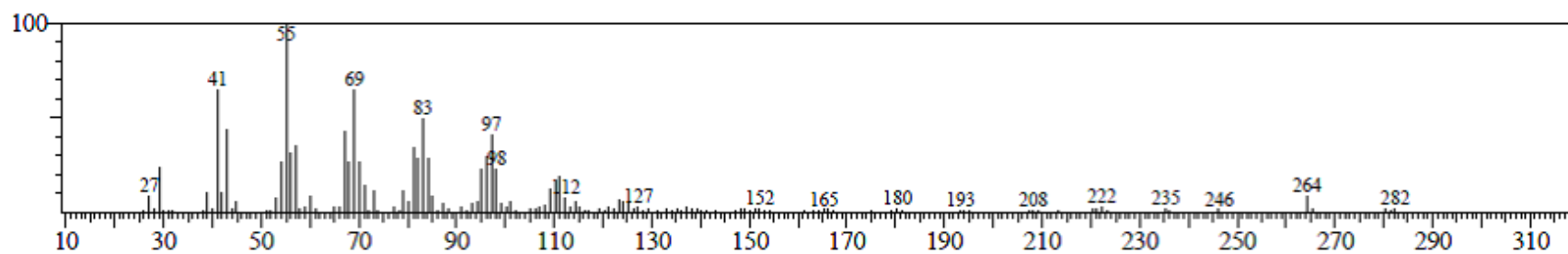
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4	6-octadecenoic acid	$C_{18}H_{34}O_2$	282	28.049	133	55.76
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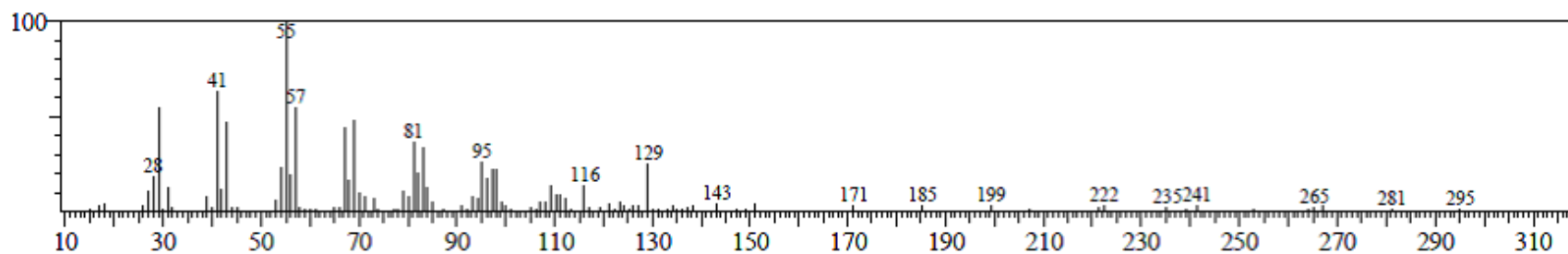
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5	9,12-Octadecadienoic acid	$C_{19}H_{34}O_2$	295	30.732	106	7.38
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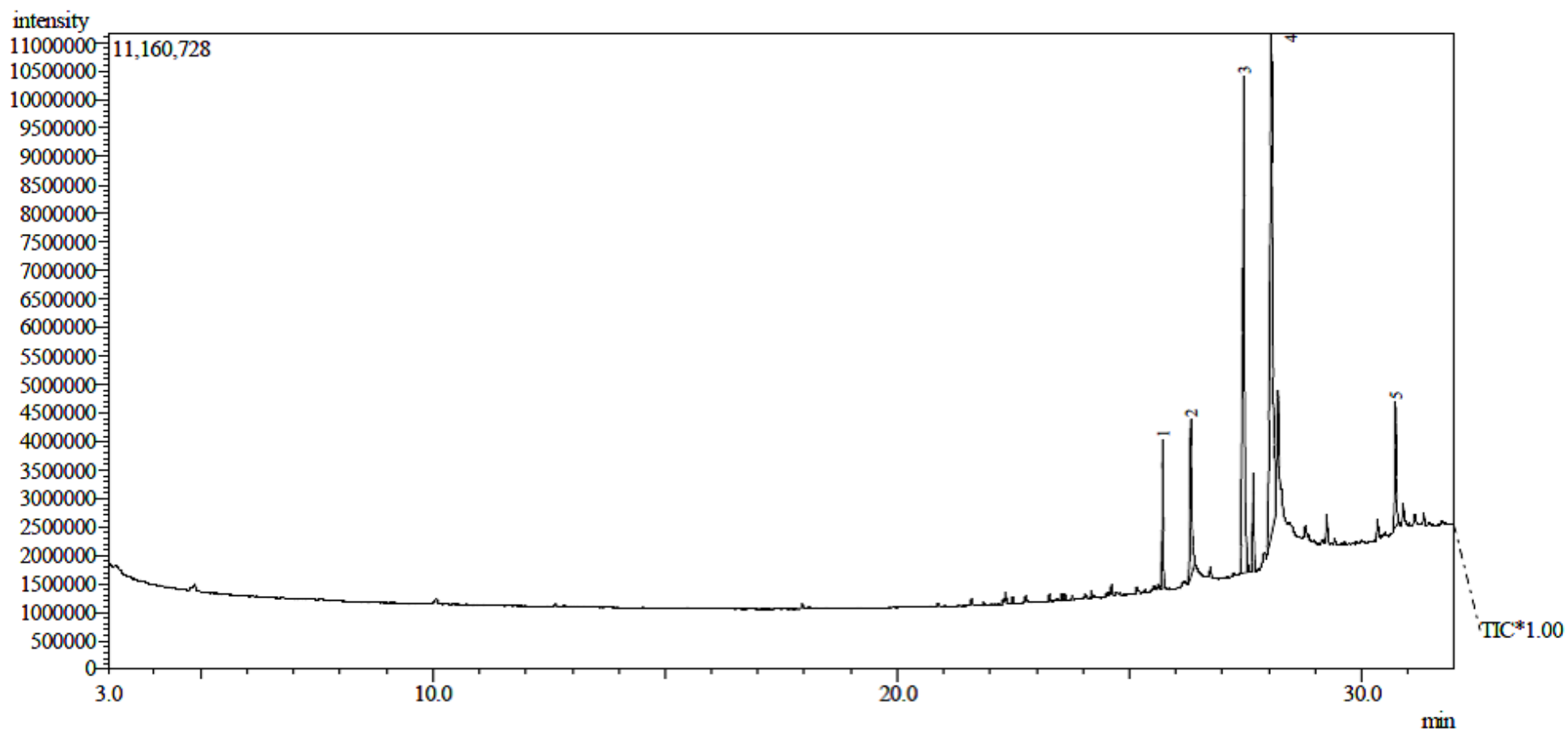
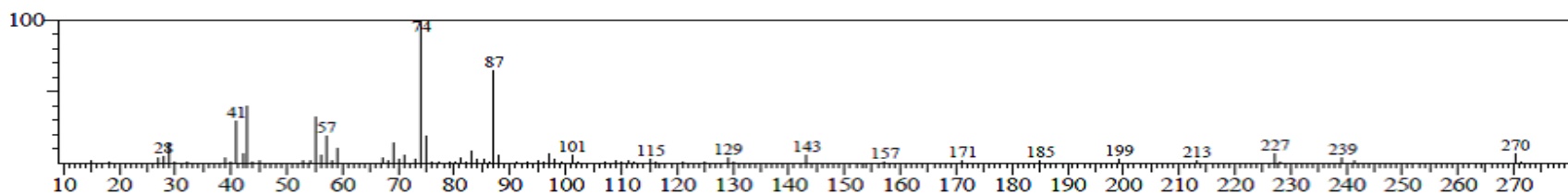


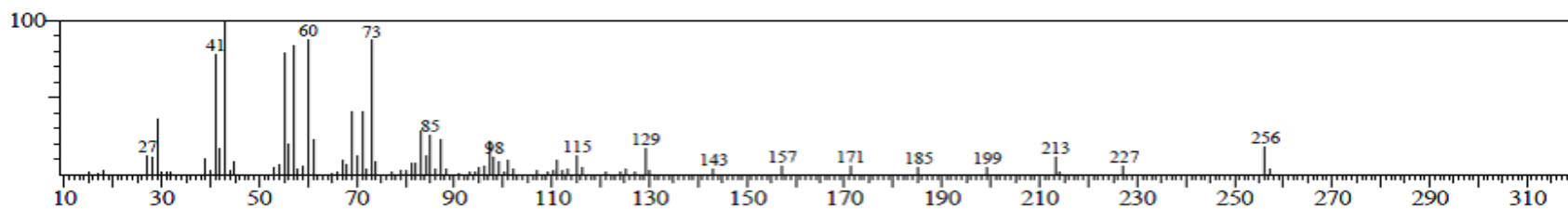
Fig. 4.59: GCMS ANALYSIS OF THE SAMPLE AS:KS

Characteristics Suggested Compounds Identified From GC-MS Of The Gum Blend AS: KS

Line No	Iupac Name	Molecular Formular	Molar Mass (g/mol)	Retention Time	Mass Peak	Area%
1	Hexadecanoic acid	C <sub>17</sub> H <sub>34</sub> O <sub>2</sub>	270	25.716	76	5.91



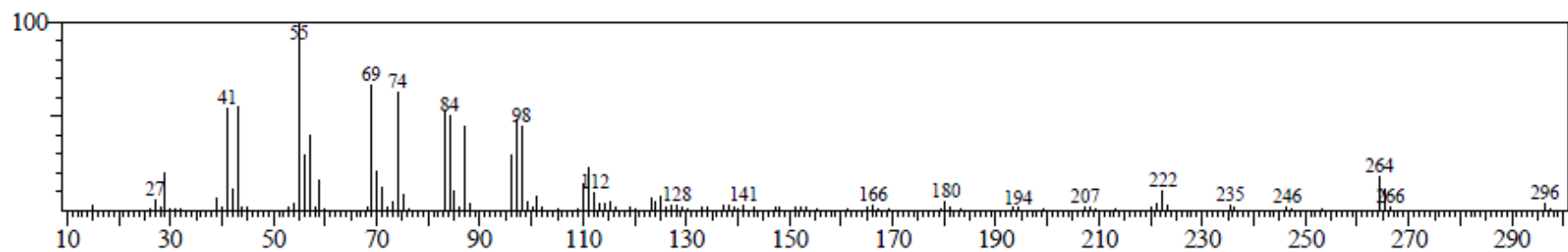
2	1-pentadecane carboxylic	C <sub>19</sub> H <sub>32</sub> O <sub>2</sub>	256	26.316	81	9.30
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3	Methyl(16E)-16-octadecanoate	$C_{19}H_{36}O_2$	296	27.465	110	30.67
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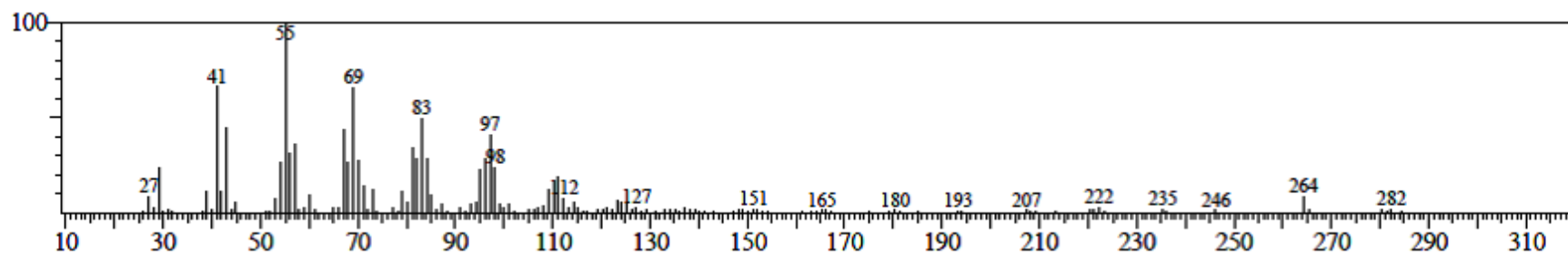
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4	Oleic acid	$C_{18}H_{34}O_2$	282	28.051	134	47.90
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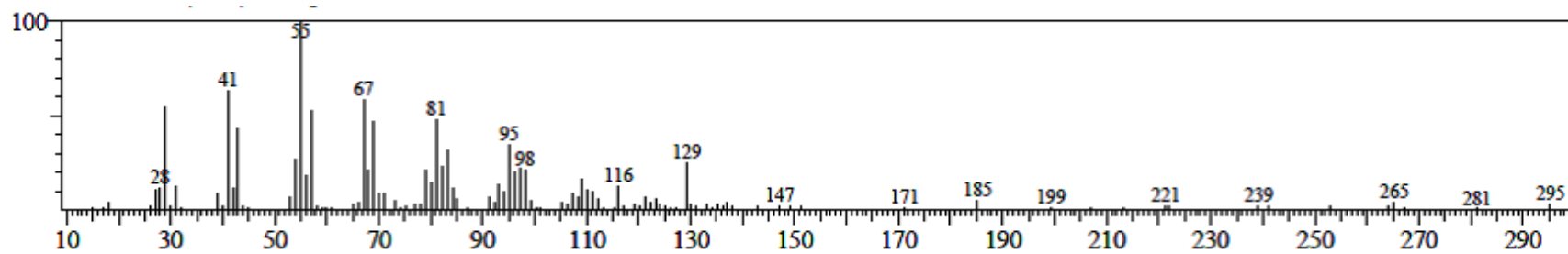
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5	Stearic acid	$C_{19}H_{38}O_2$	298	30.730	106	6.21
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## CHAPTER FIVE

### 5.0 CONCLUSIONS AND RECOMMENDATIONS

#### 5.1 CONCLUSIONS

From the findings of the present study, the following conclusions and recommendations are made:

Physiochemical analysis of the blends AS:AO, AS:KS and AO:KS revealed that the gums are acidic and soluble in water hence hydrophilic, but are insoluble in any organic solvent except for AS:KS (20:80) which is slightly soluble in ethanol. It was discovered that not only can the properties of some of the gums such as *Khaya senegalensis* and cashew gum be improved; even the colour and clarity of the gums were improved when blended with gums with lighter shades.

The mean concentration of these blends when correlated with a standard gum Arabic (AS), was found to have high concentration of Mg, K and Fe, although they are below WHO permissible limits for food gums, These gums can serve as important source of electrolyte in the body.

Rheological modeling revealed that the viscosities of the gums vary with temperature, concentration of gum and concentration of electrolyte. All the gums with exception of AO and the blends AS:AO (50:50), (40:60), (20:80), AO:KS; (50:50), (40:60) were found to have random coil conformation.

The blend AS:AO (20:80) has the least amount of activation energy required for the gum to flow when exposed to heat, while Ks and the blend AO:KS (80:20) require a larger activation energy.

The intrinsic viscosity were found to increase in the AS:AO, AS:KS blends when AS and KS gums were added to the blends respectively and the interaction parameter  $\alpha$  for all AS:AO blend

is negative hence repulsion interaction, while all AS:KS all the blends with exception of 50:50 and 80:20 indicates attraction in within the blends in an aqueous solution.

The slope for the master curve for most of the blends were found to be more than 1.3 which is close to the finding from Morris *et al.*, 1981, who determined the slope for several food gums in dilute dispersion to be around 1.4 hence most of these blends can be used as food thickeners and binders in pharmaceutical industries since its edible.

## 5.2 RECOMMENDATION

In recommendation, it is advised that the blend AS:KS (20:80) could be used in place of AS gum used as food thickener and excipients in pharmaceutical industries since it was found to have intrinsic viscosity value higher than that of gum arabic (AS).

Investigations into the antimicrobial and toxicological tests on the blends is recommended since the gums appear to possess properties closely related to gums used in pharmaceutical, food and other industries.

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APPENDIX 1

Rheological Studies of Pure Gums And Their Blends

Reduced Viscosity

$$\eta_{red} = \frac{\eta_{sp}}{c}$$

REDUCED VISCOSITY

AS	0.579	0.600	0.664	0.328	0.362
AO	0.072	0.062	0.060	0.057	0.111
KS	0.462	0.526	0.249	0.249	0.158
AS:AO (80:20)	0.421	0.520	0.671	0.396	0.430
AS:AO (60:40)	0.394	0.170	0.173	0.158	0.226
AS:AO (50:50)	0.376	0.136	0.158	0.204	0.362
AS:AO (40:60)	0.118	0.124	0.143	0.170	0.226
AS:AO (20:80)	0.090	0.102	0.121	0.158	0.294
AS:KS (80:20)	0.457	0.498	0.256	0.215	0.294
AS:KS (60:40)	0.466	0.532	0.664	0.283	0.317
AS:KS (50:50)	0.475	0.464	0.241	0.294	0.430
AS:KS (40:60)	0.516	0.469	0.241	0.181	0.113
AS:KS (20:80)	0.566	0.492	0.173	0.158	0.204
AO:KS (80:20)	0.412	0.204	0.219	0.238	0.158
AO:KS (60:40)	0.362	0.119	0.113	0.113	0.113
AO:KS (50:50)	0.172	0.192	0.166	0.170	0.249
AO:KS (40:60)	0.371	0.204	0.196	0.215	0.362
AO:KS (20:80)	0.403	0.447	0.226	0.283	0.407

RELATIVE VISCOSITY

$$\text{Relative viscosity: } \eta_{rel} = \frac{\eta_{solution}}{\eta_{solvent}}$$

$$\eta_r = \frac{\eta}{\eta_0}$$

Effect of Concentration on Viscosity at 30°C

	1g	0.8g	0.6g	0.4g	0.2g
AS	1.579	1.480	1.398	1.131	1.072
AO	1.072	1.050	1.036	1.023	1.022
KS	1.462	1.421	1.149	1.100	1.032
AS:AO (80:20)	1.421	1.416	1.403	1.158	1.086
AS:AO (60:40)	1.394	1.136	1.104	1.063	1.045
AS:AO (50:50)	1.376	1.109	1.095	1.081	1.072
AS:AO (40:60)	1.118	1.100	1.086	1.068	1.045
AS:AO (20:80)	1.090	1.081	1.072	1.063	1.059
AS:KS (80:20)	1.457	1.398	1.154	1.086	1.059
AS:KS (60:40)	1.466	1.425	1.398	1.113	1.063
AS:KS (50:50)	1.475	1.371	1.145	1.118	1.086
AS:KS (40:60)	1.516	1.376	1.145	1.072	1.023
AS:KS (20:80)	1.566	1.394	1.104	1.063	1.041
AO:KS (80:20)	1.412	1.163	1.131	1.095	1.032
AO:KS (60:40)	1.362	1.095	1.068	1.045	1.023
AO:KS (50:50)	1.172	1.154	1.100	1.068	1.050
AO:KS (40:60)	1.371	1.163	1.118	1.086	1.072
AO:KS (20:80)	1.403	1.357	1.136	1.113	1.081

Effect of Temperature on Viscosity

	$\eta_{rel}$ Concentration) at 30°C, 1g	$\eta_{rel}$ at 40°C, 1g	$\eta_{rel}$ at 50°C, 1g	$\eta_{rel}$ at 60°C, 1g	$\eta_{rel}$ at 70°C, 1g	$\eta_{rel}$ at 80°C, 1g	$\eta_{rel}$ at 90°C, 1g
AS	1.579	1.548	1.529	1.466	1.416	1.396	1.187
AO	1.072	1.036	1.000	0.964	0.941	0.935	0.729
KS	1.462	1.407	1.140	1.100	1.100	0.991	0.977
AS:AO (80:20)	1.421	1.385	1.145	1.122	1.109	1.115	1.112
AS:AO (60:40)	1.394	1.362	1.127	1.086	1.077	1.060	1.070
AS:AO (50:50)	1.376	1.172	1.131	1.113	1.072	1.041	1.047
AS:AO (40:60)	1.118	1.109	1.086	1.068	1.045	1.032	1.033
AS:AO (20:80)	1.090	1.072	1.054	1.032	1.018	1.014	1.019
AS:KS (80:20)	1.457	1.407	1.362	1.140	1.127	1.111	1.112
AS:KS (60:40)	1.466	1.425	1.385	1.149	1.122	1.120	1.117
AS:KS (50:50)	1.475	1.443	1.412	1.167	1.109	1.129	1.131
AS:KS (40:60)	1.516	1.471	1.430	1.376	1.122	1.143	1.150
AS:KS (20:80)	1.566	1.516	1.480	1.430	1.158	1.180	1.182
AO:KS (80:20)	1.412	1.122	1.018	0.991	0.973	0.982	0.986
AO:KS (60:40)	1.362	1.081	1.068	1.045	1.027	1.037	1.033
AO:KS (50:50)	1.172	1.095	1.059	1.036	0.995	1.000	1.009
AO:KS (40:60)	1.371	1.158	1.140	1.090	1.054	1.046	1.051
AO:KS (20:80)	1.403	1.357	1.118	1.077	1.041	1.041	1.033

Effect of Concentration on Viscosity

Specific Viscosity

$$\text{Specific viscosity: } \eta_{sp} = \eta_{rel} - 1$$

	$\Gamma_{sp}$ @30C, 1g	$\Gamma_{sp}$ at 30°C, 0.8g	$\Gamma_{sp}$ at30°C, 0.6g	$\Gamma_{sp}$ at30°C, 0.4g	$\Gamma_{sp}$ at30°C, 0.2g
AS	0.579	0.480	0.398	0.131	0.072
AO	0.072	0.050	0.036	0.023	0.022
KS	0.462	0.421	0.149	0.100	0.072
A:AO (80:20)	0.421	0.416	0.403	0.158	0.086
AS:AO (60:40)	0.394	0.136	0.104	0.063	0.045
AS:AO (50:50)	0.376	0.109	0.095	0.081	0.072
AS:AO (40:60)	0.118	0.100	0.086	0.068	0.045
AS:AO (20:80)	0.090	0.081	0.072	0.063	0.059
AS:KS (80:20)	0.457	0.398	0.154	0.086	0.059
AS:KS (60:40)	0.466	0.425	0.398	0.113	0.063
AS:KS (50:50)	0.475	0.371	0.145	0.118	0.086
AS:KS (40:60)	0.516	0.376	0.145	0.072	0.023
AS:KS (20:80)	0.566	0.394	0.104	0.063	0.041
AO:KS (80:20)	0.412	0.163	0.131	0.095	0.032
AO:KS (60:40)	0.362	0.095	0.068	0.045	0.023
AO:KS (50:50)	0.172	0.154	0.100	0.068	0.050
AO:KS (40:60)	0.371	0.163	0.118	0.086	0.072
AO:KS (20:80)	0.403	0.357	0.136	0.113	0.081

EFFECT OF TEMPERATURE ON SPECIFIC VISCOSITY

	$\Gamma_{sp}$ at 30°C, 1g	$\Gamma_{sp}$ at 40°C, 1g	$\Gamma_{sp}$ at 50°C, 1g	$\Gamma_{sp}$ at 60°C, 1g	$\Gamma_{sp}$ at 70°C, 1g	$\Gamma_{sp}$ at 80°C, 1g	$\Gamma_{sp}$ at 90°C, 1g
AS	0.579	0.548	0.529	0.466	0.416	0.396	0.187
AO	0.072	0.036	0.000	-0.036	-0.059	-0.065	-0.271
KS	0.462	0.407	0.140	0.100	0.100	-0.009	-0.023
AS:AO (80:20)	0.421	0.385	0.145	0.122	0.109	0.115	0.112
AS:AO (60:40)	0.394	0.362	0.127	0.086	0.077	0.060	0.070
AS:AO (50:50)	0.376	0.172	0.131	0.113	0.072	0.041	0.047
AS:AO (40:60)	0.118	0.109	0.086	0.068	0.045	0.032	0.033
AS:AO (20:80)	0.090	0.072	0.054	0.032	0.018	0.014	0.019
AS:KS (80:20)	0.457	0.407	0.362	0.140	0.127	0.111	0.112
AS:KS (60:40)	0.466	0.425	0.385	0.149	0.122	0.120	0.117
AS:KS (50:50)	0.475	0.443	0.412	0.167	0.109	0.129	0.131
AS:KS (40:60)	0.516	0.471	0.430	0.376	0.122	0.143	0.150
AS:KS (20:80)	0.566	0.516	0.480	0.430	0.158	0.180	0.182
AO:KS (80:20)	0.412	0.122	0.018	-0.009	-0.027	-0.018	-0.014
AO:KS (60:40)	0.362	0.081	0.068	0.045	0.027	0.037	0.033

AO:KS (50:50)	0.172	0.095	0.059	0.036	-0.005	0.000	0.009
AO:KS (40:60)	0.371	0.158	0.140	0.090	0.054	0.046	0.051
AO:KS (20:80)	0.403	0.357	0.118	0.077	0.041	0.041	0.033

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## APPENDIX 6

### Effect of Varying Salt Concentration on the Viscosity of Polymer and their Blends

#### Effect of Potassium Chloride (KCl) at 28°C

	$\Gamma_{sp}$ at 28°C, 0.2KCl	$\Gamma_{sp}$ at 28°C, 0.4KCl	$\Gamma_{sp}$ at 28°C, 0.6KCl	$\Gamma_{sp}$ at 28°C, 0.8KCl	$\Gamma_{sp}$ at 28°C, 1.0KCl
AS	0.367	0.376	0.380	0.385	0.394
AO	0.054	0.059	0.072	0.086	0.095
KS	0.371	0.380	0.398	0.416	0.439
AS:AO (80:20)	0.172	0.163	0.149	0.136	0.122
AS:AO (60:40)	0.149	0.140	0.131	0.122	0.113
AS:AO (50:50)	0.072	0.109	0.122	0.100	0.385
AS:AO (40:60)	0.059	0.077	0.090	0.095	0.109
AS:AO (20:80)	0.081	0.090	1.005	0.104	0.113
AS:KS (80:20)	0.140	0.145	0.145	0.140	0.145
AS:KS (60:40)	0.095	0.113	0.131	0.154	0.167
AS:KS (50:50)	0.122	0.357	0.371	0.380	0.385
AS:KS (40:60)	0.362	0.380	0.407	0.425	0.439
AS:KS (20:80)	0.439	0.448	0.457	0.475	0.484
AO:KS (80:20)	0.086	0.095	0.109	0.122	0.136
AO:KS (60:40)	0.095	0.104	0.127	0.131	0.145
AO:KS (50:50)	0.371	0.357	0.167	0.140	0.113
AO:KS (40:60)	0.416	0.412	0.394	0.385	0.376
AO:KS (20:80)	0.425	0.412	0.403	0.394	0.385

APPENDIX 7

Effect of Potassium Chloride (KBr)

	$\Gamma_{\text{sp}}$ at 28°C, 0.2KBr	$\Gamma_{\text{sp}}$ at 28°C, 0.4KBr	$\Gamma_{\text{sp}}$ at 28°C, 0.6KBr	$\Gamma_{\text{sp}}$ at 28°C, 0.8KBr	$\Gamma_{\text{sp}}$ at 28°C, 1.0KBr
AS	0.416	0.407	0.389	0.376	0.357
AO	0.009	0.027	0.036	0.041	0.041
KS	0.466	0.448	0.443	0.430	0.416
AS:AO (80:20)	0.109	0.100	0.086	0.077	0.068
AS:AO (60:40)	0.113	0.109	0.100	0.090	0.081
AS:AO (50:50)	0.127	0.118	0.109	0.095	0.086
AS:AO (40:60)	0.131	0.122	0.113	0.100	0.095
AS:AO (20:80)	0.154	0.145	0.131	0.118	0.104
AS:KS (80:20)	0.163	0.154	0.145	0.131	0.118
AS:KS (60:40)	0.421	0.403	0.394	0.385	0.371
AS:KS (50:50)	0.385	0.380	0.376	0.367	0.357
AS:KS (40:60)	0.416	0.407	0.403	0.398	0.389
AS:KS (20:80)	0.457	0.448	0.443	0.434	0.425
AO:KS (80:20)	0.059	0.050	0.041	0.000	0.032
AO:KS (60:40)	0.081	0.072	0.063	0.054	0.041
AO:KS (50:50)	0.095	0.086	0.077	0.072	0.063
AO:KS (40:60)	0.145	0.131	0.127	0.118	0.109
AO:KS (20:80)	0.172	0.167	0.149	0.140	0.127

## APPENDIX 8

### Effect of Potassium Chloride (AlCl<sub>3</sub>)

	Γ <sub>βp</sub> at 28°C, 0.2AlCl <sub>3</sub>	Γ <sub>βp</sub> at 28°C, 0.4AlCl <sub>3</sub>	Γ <sub>βp</sub> at 28°C, 0.6 AlCl <sub>3</sub>	Γ <sub>βp</sub> at 28°C, 0.8 AlCl <sub>3</sub>	Γ <sub>βp</sub> at 28°C, 1.0AlCl <sub>3</sub>
AS	0.367	0.385	0.403	0.421	0.439
AO	0.041	0.054	0.068	0.072	0.081
KS	0.538	0.561	0.579	0.602	0.620
AS:AO (80:20)	0.136	0.145	0.158	0.163	0.172
AS:AO (60:40)	0.131	0.136	0.145	0.154	0.163
AS:AO (50:50)	0.118	0.127	0.136	0.145	0.149
AS:AO (40:60)	0.109	0.118	0.127	0.140	0.145
AS:AO (20:80)	0.095	0.104	0.118	0.127	0.131
AS:KS (80:20)	0.367	0.376	0.389	0.398	0.407
AS:KS (60:40)	0.385	0.394	0.403	0.412	0.425
AS:KS (50:50)	0.398	0.403	0.421	0.434	0.443
AS:KS (40:60)	0.412	0.421	0.430	0.439	0.457
AS:KS (20:80)	0.430	0.439	0.452	0.466	0.475
AO:KS (80:20)	0.145	0.131	0.122	0.113	0.104
AO:KS (60:40)	0.131	0.118	0.109	0.104	0.090
AO:KS (50:50)	0.154	0.158	0.167	0.357	0.371
AO:KS (40:60)	0.167	0.172	0.371	0.385	0.389
AO:KS (20:80)	0.357	0.367	0.380	0.389	0.398

APPENDIX 9

RHEOLOGICAL MODELS

HUGGINS

$$\frac{\eta_{sp}}{c} = [\eta] + k^l[\eta]^2 c$$

	$\Gamma_{sp}/C$ (CONCENTRATION) at 30°C, 1g	$\Gamma_{sp}/C$ at 30°C, 0.8g	$\Gamma_{sp}/C$ at 30°C, 0.6g	$\Gamma_{sp}/C$ at 30°C, 0.4g	$\Gamma_{sp}/C$ at 30°C, 0.2g
AS	0.362	0.328	0.664	0.600	0.579
AO	0.111	0.057	0.060	0.062	0.072
KS	0.158	0.249	0.249	0.526	0.462
AS:AO (80:20)	0.430	0.396	0.671	0.520	0.421
AS:AO (60:40)	0.226	0.158	0.173	0.170	0.394
AS:AO (50:50)	0.362	0.204	0.158	0.136	0.376
AS:AO (40:60)	0.226	0.170	0.143	0.124	0.118
AS:AO (20:80)	0.294	0.158	0.121	0.102	0.090
AS:KS (80:20)	0.294	0.215	0.256	0.498	0.457
AS:KS (60:40)	0.317	0.283	0.664	0.532	0.466
AS:KS (50:50)	0.430	0.294	0.241	0.464	0.475
AS:KS (40:60)	0.113	0.181	0.241	0.469	0.516
AS:KS (20:80)	0.204	0.158	0.173	0.492	0.566
AO:KS (80:20)	0.158	0.238	0.219	0.204	0.412
AO:KS (60:40)	0.113	0.113	0.113	0.119	0.362
AO:KS (50:50)	0.249	0.170	0.166	0.192	0.172
AO:KS (40:60)	0.362	0.215	0.196	0.204	0.371
AO:KS (20:80)	0.407	0.283	0.226	0.447	0.403

## APPENDIX 10

Kraemer

$$\frac{\ln \eta_r}{c} = [\eta] + k^L [\eta]^2 c$$

	ln $\Gamma$ <sub>rel</sub> /C (CONCENTRATION) at 30°C, 1g	ln $\Gamma$ <sub>rel</sub> /C at 30°C, 0.8g	ln $\Gamma$ <sub>rel</sub> /C at 30°C, 0.6g	ln $\Gamma$ <sub>rel</sub> /C at 30°C, 0.4g	ln $\Gamma$ <sub>rel</sub> /C at 30°C, 0.2g
AS	0.349	0.308	0.559	0.490	0.457
AO	0.110	0.056	0.059	0.061	0.070
KS	0.156	0.237	0.232	0.439	0.379
AS:AO (80:20)	0.412	0.368	0.564	0.435	0.351
AS:AO (60:40)	0.221	0.154	0.165	0.159	0.332
AS:AO (50:50)	0.349	0.196	0.151	0.129	0.319
AS:AO (40:60)	0.221	0.164	0.137	0.119	0.111
AS:AO (20:80)	0.286	0.154	0.116	0.098	0.087
AS:KS (80:20)	0.286	0.206	0.239	0.419	0.376
AS:KS (60:40)	0.307	0.268	0.559	0.443	0.383
AS:KS (50:50)	0.412	0.278	0.225	0.394	0.389
AS:KS (40:60)	0.112	0.175	0.225	0.399	0.416
AS:KS (20:80)	0.200	0.154	0.165	0.415	0.448
AO:KS (80:20)	0.156	0.227	0.205	0.189	0.345
AO:KS (60:40)	0.112	0.111	0.109	0.113	0.309
AO:KS (50:50)	0.243	0.164	0.158	0.179	0.159
AO:KS (40:60)	0.349	0.206	0.185	0.189	0.316
AO:KS (20:80)	0.392	0.268	0.212	0.382	0.338

## APPENDIX 11

The intrinsic viscosity calculated from the slope of Tanglertpaibul and Rao plot which has the best fit for the parameters fit into a model are given below

	Intrinsic Viscosity $\eta$ (dl/g)	R <sup>2</sup>
AS	68.1	0.951
AO	6.3	0.915
KS	59	0.912
AS:AO (80:20)	46.3	0.823
AS:AO (60:40)	38.4	0.738
AS:AO (50:50)	31.6	0.605
AS:AO (40:60)	8.8	0.992
AS:AO (20:80)	4	0.987
AS:KS (80:20)	55.4	0.905
AS:KS (60:40)	55.8	0.869
AS:KS (50:50)	51.5	0.885
AS:KS (40:60)	64.4	0.934
AS:KS (20:80)	69	0.87
AO:KS (80:20)	41.4	0.809
AO:KS (60:40)	36.4	0.689
AO:KS (50:50)	16.5	0.968
AO:KS (40:60)	33.7	0.764
AO:KS (20:80)	44.3	0.874

## APPENDIX 12

### Determination of Molecular Conformation and Polymer Interaction

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The power-law equation

$$\eta_{sp} = aC^b$$


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It's used to estimate the exponent b from the slope of double logarithmic plot of  $\eta_{sp}$  against concentration and provides an indication of the conformation of polysaccharides (Lai *et al.*, 2000)

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	b <sub>law</sub> values	R <sup>2</sup>
AS	1.392	0.95
AO	0.730	0.828
KS	1.715	0.969
AS:AO (80:20)	1.094	0.918
AS:AO (60:40)	1.182	0.816
AS:AO (50:50)	0.776	0.55
AS:AO (40:60)	0.584	0.998
AS:AO (20:80)	0.266	0.918
AS:KS (80:20)	1.356	0.9
AS:KS (60:40)	1.376	0.916
AS:KS (50:50)	1.072	0.836
AS:KS (40:60)	1.979	0.984
AS:KS (20:80)	1.673	0.86
AO:KS (80:20)	1.414	0.936
AO:KS (60:40)	1.482	0.838
AO:KS (50:50)	0.809	0.95
AO:KS (40:60)	0.889	0.765
AO:KS (20:80)	1.028	0.836

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APPENDIX 13

	$b_H$ (Huggins parameter)	$R^2$	K(Huggins Parameter)
AS	7.65	0.9514	0.0016
AO	12.17	0.9125	0.3066
KS	0.24	0.9156	0.0001
AS:AO (80:20)	1.86	0.8235	0.0009
AS:AO (60:40)	8.24	0.7382	0.0056
AS:AO (50:50)	4.34	0.6055	0.0043
AS:AO (40:60)	3.03	0.9928	0.0391
AS:AO (20:80)	4.89	0.987	0.3056
AS:KS (80:20)	10.18	0.9059	0.0033
AS:KS (60:40)	4.21	0.8697	0.0014
AS:KS (50:50)	7.06	0.8855	0.0027
AS:KS (40:60)	16.06	0.9347	0.0039
AS:KS (20:80)	18.05	0.8704	0.0038
AO:KS (80:20)	8.19	0.8095	0.0048
AO:KS (60:40)	10	0.6896	0.0075
AO:KS (50:50)	0.95	0.969	0.0035
AO:KS (40:60)	4.03	0.7643	0.0035
AO:KS (20:80)	4.8	0.8741	0.0024

The Huggins parameter from the Huggins equation for polymer-polymer solvent solution is given as  $b_H$

#### APPENDIX 14

##### Determination of polymer interaction

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Blends	bm1	$\alpha$
AS:AO (80:20)	8.470435	-6.61044
AS:AO (60:40)	9.332653	-1.09265
AS:AO (50:50)	9.77943	-5.43943
AS:AO (40:60)	10.23665	-7.20665
AS:AO (20:80)	11.18244	-6.29244
AS:KS (80:20)	5.339197	4.840803
AS:KS (60:40)	3.442796	0.767204
AS:KS (50:50)	2.649995	4.410005
AS:KS (40:60)	1.960796	14.0992
AS:KS (20:80)	0.893197	17.1568
AO:KS (80:20)	8.345291	-0.15529
AO:KS (60:40)	5.239937	4.760063
AO:KS (50:50)	3.957017	-3.00702
AO:KS (40:60)	2.853937	1.176063
AO:KS (20:80)	1.187291	3.612709

Thermodynamic parameter determination using Arrhenius-frenkel and frenkel-eyring model

$\ln \eta$	30	40	50	60	70	80	90
AS	0.456909	0.436648	0.424883	0.382581	0.34804	0.333835	0.171358
AO	0.069897	0.035559	0	-0.03687	-0.06062	-0.06669	-0.31612
KS	0.37949	0.34163	0.131266	0.094899	0.094899	-0.00926	-0.02364
AS:AO (80:20)	0.35123	0.325422	0.135227	0.115266	0.103096	0.10904	0.106295
AS:AO (60:40)	0.331937	0.308948	0.11929	0.082476	0.074108	0.058182	0.067746
AS:AO (50:50)	0.318865	0.158665	0.123298	0.107169	0.069897	0.040638	0.04567
AS:AO (40:60)	0.111226	0.103096	0.082476	0.065669	0.044255	0.031749	0.032187
AS:AO (20:80)	0.086634	0.069897	0.052876	0.031183	0.017938	0.01373	0.018519
AS:KS (80:20)	0.376389	0.34163	0.308948	0.131266	0.11929	0.1049	0.106295
AS:KS (60:40)	0.382581	0.35441	0.325422	0.139172	0.115266	0.113164	0.110488
AS:KS (50:50)	0.388735	0.367028	0.34484	0.154797	0.103096	0.121361	0.122962
AS:KS (40:60)	0.415968	0.385662	0.35758	0.318865	0.115266	0.133531	0.139356
AS:KS (20:80)	0.448276	0.415968	0.391797	0.35758	0.147015	0.16528	0.167413
AO:KS (80:20)	0.34484	0.115266	0.017938	-0.00909	-0.02752	-0.01861	-0.01412
AO:KS (60:40)	0.308948	0.078301	0.065669	0.044255	0.026787	0.036203	0.032187
AO:KS (50:50)	0.158665	0.090775	0.057158	0.035559	-0.00454	0	0.009302
AO:KS (40:60)	0.31557	0.147015	0.131266	0.086634	0.052876	0.045053	0.050124
AO:KS (20:80)	0.33841	0.30562	0.111226	0.074108	0.039917	0.040638	0.032187