EFFECT OF GUM ARABIC ON THE STRUCTURE-PROPERTY RELATIONSHIP IN POLY(VINYL CHLORIDE)

By

IDRIS, SANI ALHASSAN
MSc/Scie/10972/2010-2011

A Thesis submitted to the School of Postgraduate Studies, Ahmadu Bello University, Zaria,

in partial fulfillment of the requirements for the award of
Masters Degree in Physical Chemistry.

Department of Chemistry, Faculty of Science,
Ahmadu Bello University, Zaria, Nigeria.

May, 2014

DECLARATION

I declare that the work in this Thesis titled “effect of gum Arabic on the structure-property relationship in poly(vinyl chloride)” has been carried out by me in the Department of Chemistry under the supervision of Dr Paul A. P. Mamza and Prof. Adamu Uzairu. The information derived from the literature has been duly acknowledged in the text and a list of references provided. No part of this work has been presented for another degree or diploma at this or any other Institution.

Sani Idris Alhassan	Signature	Date
Name of Student		

CERTIFICATION

This Thesis titled “effect of gum Arabic on the structure-property relationship in poly(vinyl chloride)” by Sani Idris Alhassan meets the regulations governing the award of the degree of MSc Physical Chemistry of Ahmadu Bello University, and is approved for its contribution to knowledge and literary presentation.

Dr. Paul A. P. Mamza	_____	_____
Chairman, Supervisory Committee	Signature	Date
Prof. Adamu Uzairu	_____	_____
Member, Supervisory Committee	Signature	Date
Prof. Adamu Uzairu	_____	_____
Head of Department	Signature	Date
Prof. Adebayo Joshua	_____	_____
Dean, Postgraduate Studies	Signature	Date

DEDICATION

This work is dedicated to my parents

AKNOWLEDGEMENTS

I owe my success to Almighty Allah (S. W. T) for guiding me and seeing me through all my undertakings in Ahmadu Bello University, Zaria. May Allah`s Blessings and peace be among the noblest of prophets, Muhammad (S. A. W).

I wish to express my profound gratitude to my supervisor, Dr. Paul A. P. Mamza, whose efforts, advise, suggestions and constructive criticism were instrumental to the success of this work.

I am gratefully indebted to my parents, Alhaji Idris Alhassan and Hajiya Salamatu Abubakar together with my siblings, for providing me with a sound base for my moral and academic pursuits from childhood up to this stage in life.

My appreciation goes to my internal supervisors, Dr H. Abba and Dr. Abechi who went through every page of this work and made valuable suggestions and corrections.

My appreciation goes also to the entire laboratory team of the Chemistry Department, Ahmadu Bello University, Zaria, for their assistance and cooperation throughout this research. May Allah reward them abundantly, ameen.

Finally, I acknowledge the nice treatment given to me by my friends, classmates, roommates and well wishers who have contributed in one way or the other towards the success of this study. I thank you all, may God bless!

ABSTRACT

Gum Arabic exudate was collected from Acacia senegal trees around Zaria metropolis, purified in 95% ethanol and its physical and chemical modifications carried out. Physical modification of the gum involved plasticization of the gum with glycerol and ethylene glycol. The chemical method was performed by acid hydrolysis, acetolysis and acetate formation. Appearance of both modifications was observed after three days of drying. Acetic anhydride (AAN), acetolysis (ACT) and ethylene glycol (EGL) modifications became hard and solid, and were ground to powder. Glycerol (GLY) turned very sticky and acid hydrolysis (AHY) turned into a viscous liquid. From characterization of the samples, all modifications were found to be less dense than the pure gum Arabic sample (PGM). AHY sample was found to be more turbid and has the highest conductivity value followed by AAN sample. pH of all samples was found to be below 7.0, indicating acidic nature of the gums. Melting point measurements showed that all test samples have lower melting point values than the pure gum. FTIR and GC-MS spectra of the pure and chemically modified samples were studied. It was found that there were shifts and absorptions at different frequencies, indicating some degree of interaction between the gum and the modifying solvents. The gums were all mixed with PVC at different compositions and cast into films using tetrahydrofuran as solvent. The films produced were subjected to mechanical tests. The AAN sample has the highest modulus at 10, 20, 30 and 40% gum composition. For PGM, the modulus drops from 10-30% gum composition then finally increases. The ACT modification shows decrease in modulus as the percent of gum increases. Modulus of PGM drops at 20, 40, 60 and 80% gum composition. It was found that the tensile strength of the chemical modification formulations reinforced the PVC matrix at 10%/90%, 20%/80% and 30%/70% gum/PVC compositions for AAN and at 10%/90% and 20%/80% gum/PVC compositions for ACT. Though EGL showed increase at 30%/70% composition, its tensile strength is similar to that of the unmodified gum (PGM), decreasing with increasing gum concentration.

TABLE OF CONTENTS

DECLARATION ii
CERTIFICATION iii
DEDICATION iv
AKNOWLEDGEMENTS v
ABSTRACT vi
TABLE OF CONTENTS vii
LIST OF FIGURES xi
LIST OF TABLES xii
LIST OF PLATES xiii
LIST OF APPENDICES xiv
ACRONYMS xv
CHAPTER ONE 1
INTRODUCTION 1
1.1 STRUCTURE OF POLYSACCHARIDES ---- 1
1.2 STRUCTURAL MODIFICATION OF POLYSACCHARIDES ---- 1
1.2.1 Starch Acetate ---- 1
1.2.2 Hydroxylethyl ethers ---- 2
1.2.3 Acid hydrolysis ---- 2
1.2.4 Acetolysis ---- 3
1.3 PLASTICIZATION ---- 3
1.4 BRIEF HISTORY OF PVC ---- 4
1.5 PREPARATION OF VINYL CHLORIDE ---- 5
1.6 INDUSTRIAL MANUFACTURE OF PVC ---- 7
1.6.1 Suspension Polymerization Process ---- 7
1.6.2 Bulk Polymerization ---- 8
1.6.3 Emulsion Polymerization ---- 9
1.6.4 Solution Polymerization ---- 9
1.7 MECHANISM OF FORMATION ---- 10
1.7.1 Initiation ---- 10
1.7.2 Propagation ---- 11

1.7.3 Termination ---- 11
1.8 PHYSICAL PROPERTIES OF PVC ---- 12
1.9 COMPOUNDING OF PVC ---- 13
1.10 ADDITIVES FOR PVC ---- 14
1.10.1 Plasticizers ---- 14
1.10.2 Stabilizers ---- 18
1.10.3 Fillers and Reinforcements ---- 20
1.10.4 Lubricants ---- 20
1.11 PROCESSING OF PVC ---- 21
1.11.1 Extrusion ---- 21
1.11.2 Molding and Forming ---- 22
1.12 GUM ARABIC ---- 26
1.12.1 Distribution ---- 27
1.12.2 Structural Composition ---- 28
1.12.3 Chemistry of Gum arabic ---- 28
1.12.4 Physical Properties ---- 29
1.12.5 Chemical Properties ---- 31
1.12.6 Uses of Gum Arabic ---- 32
1.13 AIMS AND OBJECTVES OF THIS STUDY ---- 34
1.13.1 Aim of This Study ---- 34
1.13.2 Objectives of this Study ---- 34
CHAPTER TWO 35
REVIEW OF PAST WORKS 35
2.1 GUM ARABIC ---- 35
2.1.1 Pharmacological Properties ---- 38
2.1.2 Toxicity of Gum Arabic ---- 39
2.2 STRUCTURE AND PROPERTIES OF PVC ---- 41
2.3 EFFECT OF ADDITIVES ON THE STRUCTURE AND PROPERTIES OF PVC ---- 42
2.4 EFFECT OF PROCESSING ON THE STRUCTURE AND PROPERTIES OF PVC ---- 49
2.5 DEFECTS IN THE STRUCTURE OF PVC ---- 50
2.6 MODIFICATION OF POLY (VINYL CHLORIDE) ---- 51
2.7 DEGRADATION ---- 52

2.8 TOXICOLOGICAL CONCERNS ---- 55
2.9 PVC TESTS FOR MECHANICAL AND OTHER RELATED PROPERTIES ---- 56
CHAPTER THREE 61
MATERIALS AND METHOD 61
3.1 MATERIALS USED ---- 61
3.2 COLLECTION AND PURIFICATION ---- 61
3.3 CHARACTERIZATION ---- 61
3.3.1 Percentage Yield ---- 61
3.3.2 pH Determination ---- 62
3.3.3 Viscosity Measurement ---- 62
3.3.4 Moisture Content ---- 62
3.3.5 Ash Content ---- 62
3.3.6 Determination of Crude Protein ---- 63
3.3.7 Percentage Lipid Determination ---- 63
3.3.8 Total Carbohydrate Content ---- 64
3.3.9 Internal Energy ---- 64
3.3.10 Melting Point ---- 64
3.3.11 Density Measurement ---- 65
3.3.12 Ftir Analysis ---- 65
3.3.13 GC-MS ---- 65
3.4 GUM MODIFICATION ---- 66
3.4.1 Chemical Modification ---- 66
This was performed by acid hydrolysis, acetolysis, and acetate formation. ---- 66
3.4.2 Physical Modification ---- 67
3.5 PVC FORMULATION ---- 67
3.6 FILM CASTING ---- 67
3.7 MECHANICAL PROPERTY TESTING ---- 68
3.8 PERCENT WATER ABSORPTION ---- 68
CHAPTER FOUR 70
RESULTS AND DISCUSSION 70
4.1 PROXIMATE ANALYSIS OF PURE GUM ARABIC ---- 71
4.2 PHYSICOCHEMICAL ANALYSIS OF GUM SAMPLES ---- 72

4.3 FTIR OF ANALYSIS OF TEST SAMPLES ---------- 78
4.4 GC/MS ---------- 84
4.4.1 GC-MS of Gum Modifications---------- 84
4.5 WATER ABSORPTION---------- 90
4.6 MECHANICAL PROPERTIES---------- 90
4.6.1 Tensile strength ---------- 92
4.6.2 Elastic Modulus---------- 95
4.6.3 Percentage Elongation of the Samples ---------- 97
CHAPTER FIVE 99
CONCLUSION..... 99
RECOMMENDATION 100
REFERENCES 101
APPENDIX I 111
APPENDIX II..... 116
APPENDIX III..... 120
APPENDIX IV..... 121

LIST OF FIGURES

FIGURE **PAGE**

4.6 FTIR spectra of pure gum Arabic (PGM) …… 82

4.7 FTIR spectra of Acetolysis sample (ACT) ……..…….…… 83

4.8 FTIR spectra of acetic anhydride sample (AAN) ……...……..…… 84

4.9 FTIR spectra of acid hydrolysis sample (AHY) ……...……...……. 85

4.10 GC-MS of PGM sample ……..…….…… 93

4.11 GC-MS of ACT sample ……..……..…… 94

4.12 GC-MS of AAN sample ……...…… 95

4.13 GC-MS of AHY sample ……...…… 96

4.14 Percent water absorption of test samples at various compositions 101

4.15 Tensile strength of test samples at various compositions ...……...……. 103

4.16 Elastic modulus of test samples at varying weight of filler ...…….……...… 106

4.17 Percent elongation of test samples at varying composition of filler ...……...… 108

LIST OF TABLES

TABLE **PAGE**

1.1 Historical background of PVC……5

4.1 Proximate analysis of pure gum Arabic…….……71

4.2 Some physicochemical parameters of test samples…….……...……73

4.3 Viscosity of test samples at different concentrations……..……...79

LIST OF PLATES

Plate **page**

4.1 photographs of pure and modified gums ……...…74

LIST OF APPENDICES

AP.1.1-AP.1.4 FTIR data of test samples……...…113

AP.2.1-AP.2.4 GC-MS data of test samples …….……...…117

AP.3.1 Young moduli of test samples……..120

AP.3.2 Tensile Strength of test samples at various compositions…….…...…….....120

AP.3.3 Percent elongation of test samples at various compositions…...……121

AP.3.4 Water absorption of test samples at various compositions…….....121

AP.4.1-AP.4.26 Stress vs Strain data for test samples at various compositions……..112

ACRONYMS

AAN	Acetic Anhydride
ACT	Acetolysis
AHY	Acid Hydrolysis
AOAC	Association of Official Analytical Chemist
DMAc	Dimethyl Acetamide
DSC	Differential Scanning Calorimetry
DTA	Differential Thermal Analysis
EGL	Ethylene Glycol
EPCI	Engineering, Procurement, Construction and Installation
EVA	Ethylene Vinyl Acetate
FAO	Food and Agriculture Organization of the United Nations
FDA	Food and Drug Administration of the United States
FTIR	Fourier Transform Infra Red Spectroscopy
GLY	Glycerol
HDPE	High Density Polyethylene
ITR	Indirect Transform
LDPE	Low Density Polyethylene
MMT	Montmorillonite
PEG	Polyethylene Glycol
PET	Polyethylene Terephthalate
PG M	Pure Gum
PMMA	Poly (methyl methacrylate)
PP	Polypropylene
PVC	Poly (vinyl chloride)
RH	Rice Husk
SEM	Scanning Electron Microscopy
WAXD	Wide Angle X-Ray Diffraction
WHO	World Health Organisation

CHAPTER ONE

INTRODUCTION

Polysaccharides have been described as high molecular weight polymers formed by condensation of many monosaccharide units or their derivatives. They have also been defined as polymeric substances, the building blocks of which are monosaccharide. From the foregoing, polysaccharides could be said to be long chain carbohydrate molecules built from some monosaccharides such as glucose, rhamnose, galactose, etc. or their derivatives. Polysaccharides could be classified based on their chemical compositions. In this regard a polysaccharide which yields only one type of monosaccharide on hydrolysis is called homoglycan e.g starch, while those which yield two or more types of monosaccarides are called heteroglycan e.g. gum Arabic (Varki *et al*, 2008).

1.1 STRUCTURE OF POLYSACCHARIDES

Polysaccharides are normally isolated from their natural environments without much degredation for study. When monosaccharides come together to form polysaccharide, an anomeric hydroxyl group of one monose unit can condense with any hydroxyl group other than that of the former. The few monoses which occur as components of polysaccharides are D-glucose, D-mannose, D-fructose, D-galactose, D-xylose, L-arabinose, D-glucosamine and D-glucuronic acid.

1.2 STRUCTURAL MODIFICATION OF POLYSACCHARIDES

1.2.1 Starch Acetate

Starch acetate derivative has been reportedly prepared by the treatment of starch with acetic anhydride or vinyl acetate (Rutenberg, 1968). The products so formed are low

substituted starch esters with good hydrating capacity, flow, filming and viscosity stability. The process by which this reaction occurs is still not clear, it is however possible that the branches are being substituted by the acetate group. This would lead to smaller side chains which might enhance chain flexibility.

1.2.2 Hydroxylethyl ethers

Hydroxylethyl starch ethers are products of reaction of ethylene oxide and starch (Rutenberg, 1968). These ethers have properties similar to starch acetates including flexible film formation. The close resemblance of starch and gum Arabic makes the acetate and ether derivatives formation likely to reduce the brittleness of gum Arabic.

1.2.3 Acid hydrolysis

Acid hydrolysis of polysaccharides normally breaks polysaccharides down to their monomers, dimers and some oligosaccharides. The products of this hydrolysis are low viscous liquids. The acid hydrolysis is believed to fragment the molecules by cleaving bonds other than the (1-6) which is the most resistant to acid hydrolysis (Guthrie 1974; Bochkov, 1979).

Acid catalysed hydrolysis of O-glycosides yield corresponding alcohols and some reducing sugars via some protonated intermediates (Bochkov, 1979). This hydrolysis of monosaccharides is a slow reaction with rate constant values in the range of $10^{-4}S^{-1}$ to $10^{-6}S^{-1}$ at acid concentrations within the range of 0.01M to 0.5M HCl or H_2SO_4. The rate constant was also shown to increase with increasing acid concentration. It is therefore believed that at very high concentration, the reaction will be very fast.

1.2.4 Acetolysis

Acetolysis has been described as the treatment of polysaccharides with a mixture of acetic acid and acetic anhydride in equal weights in the presence of concentrated sulphuric acid. Products of this reaction have their (1-6) link cleaved contrary to acid hydrolysis in which the (1-6) link is very resistant (Govorchenko, 1973). This link is the least resistant to acetolysis (Guthrie, 1974). It is therefore believed that for a polysaccharide which has the (1-6) link as its branching points, the product of such acetolysed polysaccharide will be an almost linear polysaccharide.

1.3 PLASTICIZATION

Plasticization involves incorporation of plasticizer molecules into a polymer. Plasticizer molecules enter between molecules and separate the polymer molecules. Polar plasticizers, compatible with polysaccharides are attracted to polysaccharide molecules by their polar groups. The bulkiness, configuration and polarity of such plasticizers are such that arrangement of polymer molecule is affected to give room for slide chains and bulky side groups, and allow easy slippage of polymer molecules past one another.

PVC can be made softer and more flexible by the addition of plasticizers, the most widely used being phthalates. In this form, it is used in clothing and upholstery, electrical cable insulation, inflatable products and many other applications in which it would originally have replaced rubber (Titow, 1984). As an amorphous polymer, PVC resin is extensively formulated to produce an extremely large variety of compounds (Blanco, 2000). Also due to its inexpensive nature and flexibility it is used in plastic pressure pipes systems for pipelines in the water industries. The capability of PVC to perform such diverse

functions is due to its ability to incorporate various additives to suit the numerous applications (Titow, 1984).

1.4 BRIEF HISTORY OF PVC

The first mention of poly (vinyl chloride) was in 1872 by Baumann when he described formation of a white powder by the action of sunlight on vinyl chloride contained in a sealed tube. The first commercial interest in PVC was shown by the Carbide and Carbon Chemical Corporation, Du Pont and IG Farben who independently filed patents in 1928 (Brydson, 2000). At that stage it was only possible to process homopolymer in the melt state, at temperatures, where high decomposition rates occurred, whereas copolymers could be processed at lower temperatures. Effective so called external plasticization of the PVC homopolymer by incorporating plasticizers was first discovered around 1930. When compounding with dibutyl phthalate and other esters reduction in the softening point PVC occurred, this resulted in rubber-like properties at room temperature (Brydson, 2000). The historical development of PVC is highlighted below according to Titow, (1990).

Table 1.1 Historical background of PVC

Year	History
1835	Vinyl chloride monomer was first prepared by Regnault
1872	Baumann discussed the reaction of vinyl halides and acetylene in a sealed tube
1921	Plausen discovered how to polymerize PVC from dry acetylene which made PVC more than a laboratory curiosity
1928-1930	Patent disclosures of Vinyl chloride and Vinyl acrelate copolymers and polyvinyl halides. Introducing of emulsion polymerization to prepared vinyl chloride.

1930	Plasticization of PVC by phthalate ester. Introduction in non-rigid vinyl chloride plastics. Suspension polymerization of vinyl chloride in England and Germany. Technical production of chlorinated PVC polymers in Germany and USA.
1942-1943	Commercial production of PVC polymers in England.

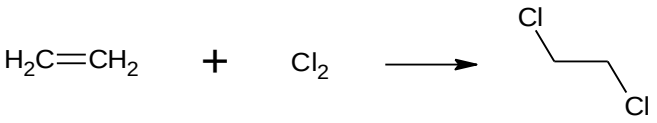
Poly(vinyl chloride) (PVC), is the third-most widely-produced plastic, after polyethylene and polypropylene. It is a vinyl polymer made of repeating vinyl groups (ethenyls) having one hydrogen replaced by chlorine. PVC is widely used in construction because it is cheap, durable and easy to assemble. PVC production is expected to exceed 40 million tons by 2016 (Martin, 2008). Generally, the more developed countries are the biggest consumers. In the United States, Canada and Japan, PVC use is about 20kg per-capita (Titow, 1984). In Africa and the Middle East, the use of PVC is about 2kg per- capita. In Eastern Europe, South America, Mexico and Asia, the average use is about 3kg per- capita, resulting in a world average of about 4kg per - capita.

1.5 PREPARATION OF VINYL CHLORIDE

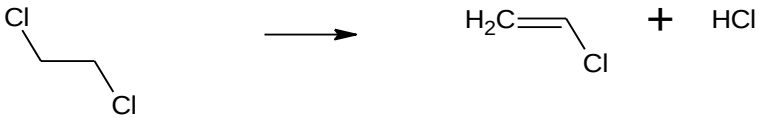
PVC is made from vinyl chloride monomer, known usually by its initials VCM through polymerization (Rossberg *et al.*, 2006; Chanda and Roy, 2006). Some monomers exist in the form of reactive gaseous chemical substances and some of these may cause health hazards when in direct contact with humans. VCM which is the raw material for PVC is a gas at ambient temperature but is usually stored in liquid form under pressure. Ethylene and chlorine are raw materials for PVC also. Upstream industries are those that provide these materials and include producers of basic petrochemicals which supply ethylene and the caustic soda industry which supplies chlorine.

By thermal cracking of naphtha or natural gas, the basic petrochemical industry manufactures ethylene and propylene etc. Naphtha is mainly supplied from the petroleum refinery industry which uses crude oil as raw material. The caustic soda industry produces caustic soda, chlorine and hydrogen via electrolysis using industrial grade salt as raw material.

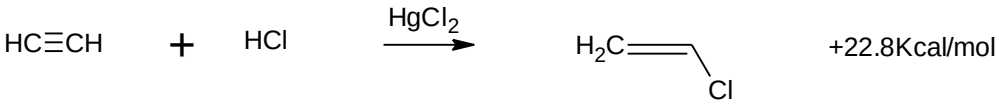
At first stage in the PVC production process ethylene and chlorine are combined to produce ethane dichloride.



When heated to 500^0C at 15-30atm, ethane dichloride (EDC) decomposes to produce vinyl chloride and hydrochloric acid.



Vinyl chloride can also be produced from acetylene and hydrogen chloride using mercuric chloride catalyst



Vinyl chloride is the building block of PVC. It is a gas with a stickly sweet odour that is easily condensed. It is very toxic (Baird and Collias, 1998).

1.6 INDUSTRIAL MANUFACTURE OF PVC

Manufacture is carried out by free radical polymerization, all the four basic polymerization processes are followed viz; suspension, emulsion, mass and solution. The degree of polymerization is controlled by variation of the polymerization temperature. The process is carried out in pressure apparatus because of the low boiling point (-13.9^{o}C) of the monomer, since radical forming agents used require polymerization temperatures of about 50^{o}C.

A total of 70-75% of all vinyl chloride is polymerized in suspension or emulsion, where yields of practically 100% are obtained with suspension and approximately 50% with emulsions. To prevent degradation or coagulation of the product, the reaction vessel is made of stainless steel or in glass-lined. Very pure water must be used in suspension polymerizates; the polymerizate is centrifuged and subsequently dried in dry tumblers. The emulsions polymerizate are worked up by either coagulation or spray-drying. In the later case, the product still contains about 5% solid impurity and therefore limited to use as paste (Hans, 1977). The solution technique is used only for specially vinyl coatings, which are generally vinyl chloride monomer copolymers and terpolymers (Reethamma, 2004).

1.6.1 Suspension Polymerization Process

In this technique, the monomer (VCM) is suspended as droplets in aqueous phase, as a result of vigorous agitation of the system (Sunmonu, 1994). The polymerization is divided into two main types, depending on the morphology of the particles that result. In bead polymerization, the polymer is soluble in its monomer and the result is a smooth, translucent bead. In powder polymerization, the polymer is not soluble in its monomer and the resultant bead will be porous and irregular (Kotoulas and Kiparissidas, 2006). In general suspension

polymerization is carried out at temperature between 60-85^{o}C under pressure of up to 250psi. Polymerization is stopped by adding an inhibitor and unreacted monomer is flashed off with vacuum. The PVC beads are then filtered in centrifuge, ashed and dried in a flash dryer. The kinetics of the polymerization within an individual bead are similar to those of typical radical polymerization (Kalfas *et al.,* 1993). The polymerization is usually carried to completion (Arshady, 1993).

1.6.2 Bulk Polymerization

The bulk polymerization system is used widely in the manufacture of a radically initiated polymerization reaction involving only the monomer, polymer and possible initiator (Sunmonu, 1994). At high conversion, however, transfer reactions that produce branched polymers can become noticeable. The gel effect can cause overheating which leads to insufficient polymerization control, degradation and possibly discoloration of the polymer.

In bulk polymerization, therefore, the polymerization is often terminated at a conversion of 40-60% and the remaining monomer is distilled off. Alternatively, the polymerization can be carried out in two stages. In the first stage, polymerization is taken up to an average conversion in large vessels e.g. in capillaries as thin layers on supports, or falling freely in thin streams. All these methods have the disadvantage that small quantities of non-converted monomer, which can have serious physiological effects, remain in the polymer (Hans, 1977). Polymerization is therefore carried out at higher temperatures like 69-76^{o}C and for 1-15 hours. There after the reaction are pumped into the second stage.

Generally, a series of large horizontal or as more modern process vertical reactants are used in the second stage. More VCM along with initiator, other ingredients and content

of the first stage reaction are charged into the reactor. Typical polymerization temperature is 55-60^{0}C and time 8 – 10 hours. It is in this stage that molecular weight can be controlled by polymerization temperature and or chain transfer agents. Bulk polymerization process is the simplest process (Saeki and Emura, 2002).

1.6.3 Emulsion Polymerization

The emulsion process is a modification of suspension polymerization in that different emulsifiers are used in slightly greater quantities. Particle size is much smaller for the dispersion resins made this way, 1-2 μm compared to 130-150 μm for the usual suspension resin. The emulsion or slurry is spray-dried because of this small particle size. Otherwise, the process is similar. Some emulsion resins are supplied as water systems or latexes. Manufacture is similar except for the drying stage (Cohan, 1975).

1.6.4 Solution Polymerization

Solution polymerization, as the name implies, refers to a system where the monomer is polymerized in a solvent. In comparison to bulk polymerization, heat control in the polymer mass is made easier by the presence of the solvent (Sunmonu, 2001). The system may be homogeneous with both the monomer and polymer soluble, or it may be heterogeneous in which case the monomer is soluble but the polymer is insoluble. The use of homogeneous solvents is exemplified by polymerizarion in butyl phthalate and in tetrahydrofuran (Krozer and Czlonkowska, 1964).

Solution process has certain advantages over bulk polymerizations. With solvent, heat transfer improves and temperature is more readily controlled. The solvent also allows more efficient agitation and consequently, the local reactions which result in overheating are eliminated. With certain heterogeneous solvent systems, it is possible to precipitate only

high molecular weight polymer, leaving low molecular weight material in solution. All these factors result in a process which produces a more uniform poly (vinyl chloride) which commands a premium price in today's market place (Koleske and Wartman, 1995).

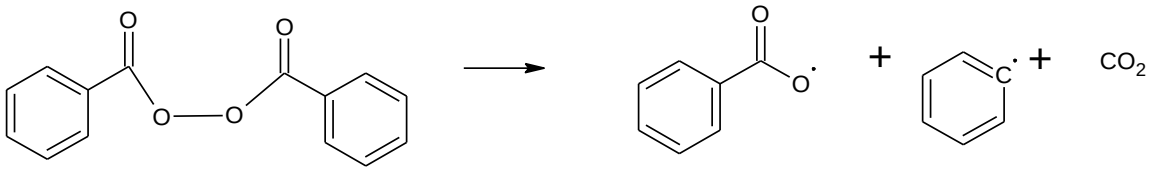
1.7 MECHANISM OF FORMATION

Vinyl chloride is a relatively un-reactive monomer, but it responds to free radical initiators of the usual type to form a high polymer. The steps involved in the polymerization are initiation, propagation, chain transfer and termination. The end result of these processes is high molecular weight poly (vinyl chloride), which is quite uniform in a chemical sense but contain a variety of molecular weight species.

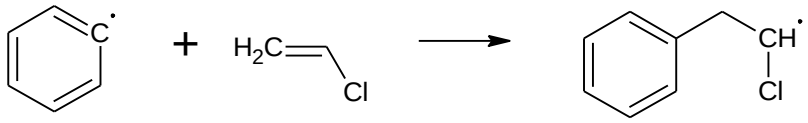
1.7.1 Initiation

There are a series of organic compounds that are readily dissociated at reasonable temperatures to produce free radicals (Nass, 1976). For the polymerization of vinyl chloride, the free radical can be generated from hydroperoxides and Azo compounds. The peroxides decompose by a first-order reaction, giving rise to two radicals, as indicated in the following equation:

Examples of peroxides used are dilauryl peroxide dicaproxyl peroide, diisopropyl peroxide and benzoyl peroxide.

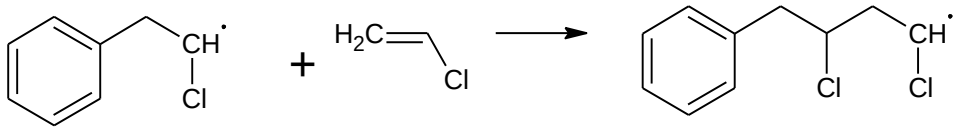


When the free radical as produced above is added to the monomer, a new free radical is produced. Phenyl radical adds on the vinyl chloride monomer in the following manner,



1.7.2 Propagation

The new free radical produced in initiation adds on to another monomer molecule to form a new free radical which further adds on another fresh monomer molecule to form another free radical and so on.

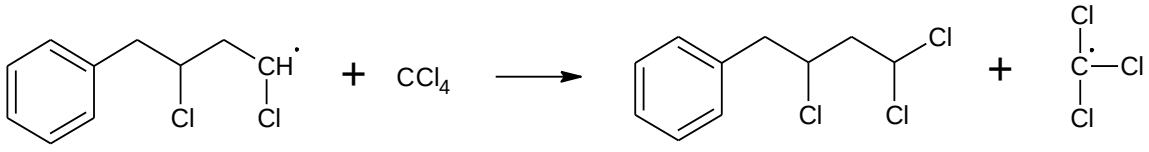


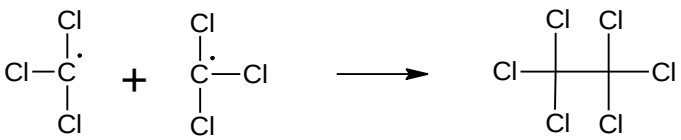
In the course of the reaction, hundreds or even thousands of monomers are added and incorporated into the polymer chain. These molecules, in principle may be added in one of two ways, “head to tail” or head to head”

Analysis revealed head to tail addition accounts for all but a few percent of the propagation reaction steps.

1.7.3 Termination

Polymerization chains are terminated by deactivating free radical, or the chain may lease growing when the free radical reacts with the solvent molecule, e.g. CCl_4





1.8 PHYSICAL PROPERTIES OF PVC

a. *Effect of plasticizer:* PVC in combination with plasticizer exhibits lower tensile strength, hardness, and modulus than the corresponding properties of the unplasticized PVC. The plasticization is usually carried out with di-2-ethylhexyl phthalate. However small amounts of the plasticizer actually imparts an increase in the value of these properties.

b. *Glass Transition Temperature:* The temperature at which an amorphous polymer changes its hard or glassy state to a soft or rubbery material is known as the glass transition temperature T_g. The T_g of unmodified commercial grade poly (vinyl chloride) is 70 – 80^oC (Simril, 1947).

c. *Melting point:* The melting point of PVC is markedly affected by polymerization temperature or by crystallinity. The crystalline melting temperature (T_m) cannot be measured by direct techniques, because polymer decomposition is too rapid at elevated temperatures even in the presence of stabilizers. To measure the melting temperature by another technique, the plasticizer (DOP) is added to the polymer at various concentrations and the stiffness modulus is measured as a function of temperature. On further increase, the crystalline network melts and there is another sharp drop modulus. The melting temperature is taken quite arbitrarily as the temperature at which the plasticized sample had stiffness modules of 10 psi.

d. *Differential Thermal Analysis:* Differential thermal analysis, DTA, is a technique that uses differences in temperature between an inert reference material and the sample under study, both being heated simultaneously at a uniform rate. The inert material changes in temperature at a constant rate while the sample investigated changes in temperature in a non-uniform manner. Also changes in heat capacity which occur at the glass transition

temperature can often be observed. The DTA technique is considered to be qualitative in nature; however, quite useful information can be obtained when it is employed.

e. *Crystalline Network in plasticized poly (vinyl Chloride):* Plasticized polymer remains tough and strong because of the presence of a non solvated, crystalline network which remains after plasticization. The development of this concept is quite interesting and important from both theoretical and an applied standpoint.

1.9 COMPOUNDING OF PVC

PVC is a polymer which consumes large number of additives during its processing. When the polymer combines with a number of carefully selected additives, it can possess a wide range of properties which enable it to be used in making different products. The myriad of PVC additives are selected on the basis of service requirements. The incorporation of these additives into PVC is generally known as compounding of PVC. Additives commonly used in the compounding process include; plasticizers, heat stabilizers, lubricants, flow promoting agents, fillers, impact modifiers, colourants and flame retardants. Rigid PVC compounds can be prepared by only using stabilizers, lubricants and flow promoters with optional additives of impact modifiers and fillers for opacity.

Additives are those materials which are physically dispersed in a polymer. The most important requirement of any additive is that it should be effective for the purpose it is designed to achieve. This effectiveness is usually enhanced by the correct procedure of incorporation of the additive molecules into the polymer matrix. Thus additives used in plastic materials are normally classified according to their specific function rather than on chemical basis (Thomas and Todd, 1971).

1.10 ADDITIVES FOR PVC

1.10.1 Plasticizers

Plasticizers are high molecular weight non volatile liquids which solvate and soften the polymer (koleske and Wartman, 1995). It is incorporated into the plastic to increase its workability and flexibility or elongation. A plasticizer may reduce the melt viscosity or lower elastic modulus of the product. Plasticized compound can be processed more easily than the rigid products because the reduced softening points make it possible to use lower temperature 140 – 160^{o}C, compared with 185 – 190^{o}C (Charles *et al.*, 2005). A plasticizer can be usually selected primarily on the basis of the cost, permanence, and low temperature brittleness requirements of the product although other properties are also of importance (Koleske and Wartman, 1995).

For a plasticizer to be effective and useful in PVC, it must contain two types of structural components, polar and non-polar. The polar portion of the molecule must be able to bind irreversibly with the PVC polymer, thus softening the PVC, while non-polar portion of the molecule allows PVC interaction to be controlled so it is not so powerful a solvent as to destroy the PVC crystallinity.

The balance between the polar and non polar portions of the molecules is critical to control its solubilizing effect; if plasticizer is too polar; it can destroy PVC crystallites, and if it is too non polar, compatibility problems may arise. Several theories have been developed to account for the observed characteristics of the plasticization process (Charles *et al.*, 2005). According to the theories plasticization at the molecular level means weakening or rupturing of selected bonds between molecules making the shaping, flexing or moulding of the material possible. For example, water is added to clay to make it possible for pottery. Also complex polymeric substances like animal horns, tortoise shell and simpler

natural resins, gums and waxes are commercialized through plasticization. Cellulose nitrate (celluloid) is the earliest resin developed by Schunbein that requires plasticizer for it processing. John and Hyatt developed camphor as plasticizer for cellulose nitrate in application involving thick objects (Nass, 1976).

The four general theories proposed to account for the effectiveness of plasticizers on certain resins are: Lubricity theory, Gel theory, free volume theory and Mechanistic theory.

i. Lubricity Theory

The Lubricity Theory states that plasticizer acts as a lubricant between polymer molecules. It is based on the assumption that rigidity arises from intermolecular friction binding the chains together in a rigid network. When the polymer is heated, these forces are weakened allowing the plasticizer molecules to be inserted between the chains. Once incorporated in to the polymer, plasticizer molecules shield the chains from each other, thus preventing the re-formation of the rigid network. Whilst attractive in its simplicity, this theory does not explain the success of some plasticizers and the failure of others (EPCI, 2010).

ii. The Gel theory

This theory considers the plasticized polymer to be neither solid nor liquid but an intermediate state, loosely held together by a three-dimensional network of weak secondary bonding forces. The bonding forces acting between plasticizer and polymer and easily overcome by applied external stresses allowing the plasticized polymer to flex, elongate or compress (Charles *et al,* 2005). While a certain concentration of plasticizer molecules will provide plasticization by this process, the remainder will act more in accordance with the

lubricity theory. Unattached plasticizer molecules will be swelling the gel and facilitating their movement thus imparting flexibity (ECPI, 2010).

iii. The Free Volume Theory

This extends the lubricity and gel theories and also allows a quantitative assessment of the plasticization process. Free volume is a measure of the internal space available in a polymer for the movement of the polymer chain, which imparts flexibility to the resin. A rigid resin such as unplasticized PVC, possesses very little free volume whereas flexible resins have relatively large amounts of free volume. Therefore, plasticizers act so as to increase the free volume of the resin and also to ensure that free volume is maintained as the resin-plasticizer mixture is cooled down after melting ((EPCI, 2010).

iv. The Mechanistic theory

In this theory, it is assumed that solvents or plasticizers of different classes are attracted to the resin macro- molecules by forces of different magnitude. This theory can be depicted as having some resemblance to Gel Theory. The mechanistic explanation of plasticization considers the interactions of the plasticizer with the PVC resin macromolecules. It assumes that the plasticizer molecules are not permanently bound to the PVC resin molecules but are free to self-associate and to associate with the polymer molecules at certain sites such as amorphous sites. As these interactions are weak, there is a dynamic exchange process whereby, as one plasticizer molecule becomes attached ata site or center, it is readily dislodged and replaced by another. Different plasticizers yield different plasticization effects because of the differences in the strengths of the plasticizer polymer and plasticizer-plasticizer interactions (Charles *et al.*, 2005).

1.10.1.1 Types Of Plasticizer

a. General purpose plasticizers (GP)

These plasticizers provide the desired flexibility to PVC along with an overall balance of optimum properties at the lowest cost. They are dialkyl phthalates range from diisoheptyl (DIHP) to diisodesyl (DIDP).

b. Performance plasticizers (PP)

These plasticizers contribute secondary performance properties desired in flexible PVC beyond the GP type, while imposing somewhat high cost. They include specific phthalates and other types of plasticizers with strong polarity. Conversely, low temperature types, such as aliphatic dibasic esters, are less solvating and have higher diffusivity, low volatility requires high molecular weight plasticizer, such as trimellites and polyesters (polymeric).

c. Specialty Plasticizers (SP)

These plasticizers provide properties beyond those typically associated with flexible PVC designed for general purpose or specialty characteristics. This exceptional characteristics are typically a function of specific chemical plasticizer families and may vary as a function of isomeric structure and/or homologous. A few phthalates meet these special requirements. Polyester plasticizers provide low volatility and low diffusivity, along with low smoke (in absence of aromaticity) under fire conditions. Epoxy plasticizers provide adjuvant thermal stability to PVC phthalate and halogenated plasticizers impose even higher cost than PP grades plasticizers.

1.10.1.2 Requisites of PVC Plasticizer

The most important requirement for a plasticizer can be summarized as:

a. *Compatibility*; for a material to act as a plasticizer it should be compatible with the polymer.

b. *Effectiveness in imparting a desirable property*; this is the parameter which expresses the amount of plasticizers required to impart a particular property to the resin.

c. *Permanence*; this defines the ability of the plasticizers to remain within the vinyl polymer and continue to be effective as a plasticizer under various exposure conditions. Thus, permanence here means ability of the plasticizer system to resist extraction or migration into an adjoining resin.

d. *Heat and light stability*; plasticizers must have good chemical stability.

1.10.2 Stabilizers

PVC degradation begins by the loss of labile chloride group as HCl and proceeds by a chain reaction generating more HCl and forming polyene sequences, giving rise to colour. The entire process depends upon many factors such as surrounding atmosphere, temperature and molecular weight of the polymer. Once dehydrochlorination of allylic chloride end group starts, new allylic groupings are formed and the reaction can proceed in zipper fashion leading to polyene structures which are largely responsible for discoloration (Baum, 1961). Stabilizers then are chemical additives that prevent, arrest, or at least minimize such changes, and so stabilize the polymer (Kauder, 1989).

At low degree of dehydrochlorination and at a reaction of 180^{o}C, there are average sequence lengths of 5-10 conjugated double bonds. The number of longer sequences decreases continually with maximum length of 25-30 conjugated double bonds. With increasing temperature and degradation, the frequency distribution shifts towards lower

sequences. At higher rate of conversion, aromatic products such as toluene are formed (straus *et al.,* 1959).

As documented in the literature, PVC stabilizers could be classified based on mode of action into the following.

1.10.2.1 Primary Stabilizers

These types of stabilizers function by reacting with allylic chlorine atoms, the intermediates in the zipper degradation chain, thereby preventing further dehydrochlorination (Scheme 3) (Fisch and Bacaloglu, 1999; Baltacioglu and Balkose, 1999; Okieimen and Sogbaike, 1995). This process should be faster than the chain propagation itself, requiring a very active nucleophile. However, the reactivity of the nucleophile should not be so high as to react with the secondary chlorine of the PVC chain, a process that rapidly exhausts the stabilizer. To be effective, the stabilizer must be associated by complex formation with the polymer chlorine atoms, which means it should have a Lewis acid character (Fisch and Bacaloglu, 1999).

1.10.2.2 Secondary Stabilizers

This type of stabilizers function by scavenging the HCl/Cl radical generated. HCl is a catalyst for the chain propagation reaction and the initiation step (Gonzalez- Ortiz *et al.*, 2005). Scavenging cannot stop the degradation process completely since it is diffusion controlled. However, HCl scavenging considerably reduces the rate of degradation and avoids the very fast process that eventually causes PVC blackening (Tamer *et al.*, 2005). Stabilization is complicated by the fact that primary stabilizers are strong Lewis acid, reacting with HCl that catalyzes the initiation and propagation of PVC degradation. To

avoid this, secondary stabilizers should be present to react with HCl to protect the primary stabilizers.

1.10.3 Fillers and Reinforcements

Fillers are particulate material, such as minerals, diatomaceous earths, and tale, which are added to polymers to reduce cost. Fibrous reinforcements, such as glass and carbon fibers, are added to polymer to increase stiffness and to some degree strength. Both types of materials tend to increase the viscosity of the polymer, especially at low shear rates, resulting in the formation of yield stress. At high shear rates, the effect is less pronounced as the viscosity approaches that of the neat resin. In addition to increase in pressure drops associated with processing these composite materials, they tend to lead wear of the screws, eventually reducing the performance of the extruder (Mascia, 1974). Fillers have been used in plastics industrially worldwide for many decades. The primary purpose for using in thermoplastic matrix is its ability to modify properties (e.g to improve strength and stiffness, scuff resistance, enhance thermal conductivity and electrical properties, dimensional stability etc. (Charles *et al*, 2005).

1.10.4 Lubricants

A lubricant is a substance that, when added in small quantities, provides a disproportionate decrease in resistance to movement of chains or segments of polymer of at least partly amorphous structure, without disproportionate change in observable properties (Grossman, 1989).

The two major classes of lubricants are designated “internal” and “external”. It is important to obtain a balance between the external and internal lubricant.

Lubricants perform several functions (Titow, 1990): reduce frictional forces between resin chains (internal), reduce frictional forces between the resin chains and the metal surface (external) and promote melt flow by reducing melt.

1.11 PROCESSING OF PVC

Resins can be softened by the application of heat processed, solidified and reheated and processed again, unlike thermosetting resin which, once solidified via the process of cross-linking, cannot be softened for reprocessing. Virgin PVC resin is rarely processed; instead, a wide variety of additives are compounded into the resin to improve processing performance and properties. These resins plus appropriate additives are then heated and shaped by flow deformation using a number of processing operations or techniques such as extrusion, injection molding, film blowing, fiber spinning, blow molding, thermoforming, compression molding etc (Mark, 1970).

1.11.1 Extrusion

Both flexible and rigid PVC can be extruded into variety of shapes including profiles, tubes and sheets, as well as wire sheeting by use of a crosshead die. The compound can be processed either from a powder blend or granulated materials. Generally, the granulated material can be handled on extrude of shorter screw length; in the case of plasticized PVC an extruder with the screw 16:1 length –to- diameter (L/D) ratio is satisfactory, whereas if powder blends are being extruded, equipment with screw of 20:1 (L/D) ratio is required for pellets and 25:1 L/D for powder single screw machines are normally used for plasticized compounds. The twin screw extruder has been developed extensively for the extrusion of rigid compounds. The temperature at which extrusion is carried out depends on the type of compounds being processed and can be determined only

by careful experimentation, to obtain the best physical properties in the finished product. The temperature of the compound as it leaves the die must be maintained at its correct value. The temperature gradient on the extruder must be adjusted so that the head temperature approximates the temperature at which the compound emerges from the break plate (Mark, 1970).

1.11.2 Molding and Forming

1.11.2.1 Injection Molding

The molding of PVC has developed rapidly with the availability of the screw type injection molding machines, prior to this, when the ram-type injection machines were standard, only plasticized PVC could be molded, and it requires special attention to prevent hold up of material with consequent degradation. Unplasticised PVC can be handled only on screw type machines, which have the advantage of being to deliver a low-viscosity homogeneous melts into the mold cavity with maximum possible pressure on the melt. The working life of rigid PVC at the temperature required for injection molding necessitates the introduction of the polymer melt into the mold in the shortest possible time once the optimum temperature had been reached, at most this should take only two cycles. This was almost impossible to achieve with a ram machine, but the reciprocating- screw injection molding machine is similar to a single-screw extruder in that a homogeneous melt is obtained by shear forces set up by the rotation of the screw. As the material accumulates at the front of the screw, the latter retracts until a present position is reached at which the volume of the accumulated molten material is sufficient to fill the mold; the screw then stops rotating and moves forwards to inject the melt into the mold. The screw then starts to rotate again and prepares the melt for the next shot.

The mold cycle can be varied over a wide range by a wide range by adjustment of the speed of rotation of the screw (20 -50rpm); and the times for the various stages of the process. The molten compound a high melt viscosity compared with the majority of moldable thermoplastics. The press during injection of rigid compounds is 12,000 to 15,000 1b/in^2, for plasticized compound it is considerably less.

1.11.2.2 Thermoforming

This is used primarily for the manufacture of packaging and disposable containers. However, it is also becoming a useful technique in the processing of engineering thermoplastics to produce parts used in the transportation industry. Polymers that are processed by this technique must have sufficient melt strength that on heating they do not sag significantly under their own weight, yet they can be deformed under pressure to take the shape of a mold. Hence, highly crystalline polymers with high melting temperature (T_m) and low molecular weight (M_w) cannot be readily thermoformed.

Thermoplastic sheet is heated usually by means of radiation but sometimes in conjunction with convection cooling to temperatures either just above T_g in the case of amorphous polymer or Tm in the case of semi crystalline polymers. The exact temperature depends on the degree of sag exhibited by the material under its own weight, which is determined by its rheological properties. The sample is then removed from the heating system and brought into position over the mold and forced to take the shape of the mold by applying pressure to the top of the sheet or by generating a vacuum on the underside of the sheet. The forming step occurs in the matter of a second. The sample is maintained in the mold until it is rigid enough to be removed from the mold without altering its shape. For example, in plug-assisted vacuum forming, the heated sheet is forced by a plug into the

mold with the remainder of the shape being produced by the application of vacuum to the underside of the sheet. However, the sheets can be forced to take on different shapes because each half of the mold can have a different shape. Furthermore, different polymers can be used for each half. The sheets must be held in the mold long enough for bonding to occur. Thermoforming can be divided into four sections: (1) sheet heating without deformation; (2) sheet stretching without significant heat transfer; (3) part cooling in the mold, and (4) post molding operations such as trimming. The time to make a part is primarily determined by step 1 and 3 because these are of the order of minutes. However, the successful functioning of the part is determined by step 2 because the distribution of wall thickness is determines in this step.

1.11.2.2 Blow Molding

Blow molding is a manufacturing process widely used to create hollow thin-wall plastic objects such as bottles, cases, containers, and bellows. A typical blow molding process begins with a heated hollow thermoplastic tube, also known as preform or parison. The plastic tube has a hole in one end, allowing compressed air to enter. It is then inflated into the closed chamber of a divided mold to conform to the shape of the mold cavity. The molded plastic will be left to cool and harden. Once released from the mold, the plastic part can be post-processed to have the holes rimmed or residues trimmed.

Not all plastics are suitable for blow molding. The most frequently used materials in blow molding are low density polyethylene (LDPE), high density polyethylene (HDPE), polypropylene (PP), poly (vinyl Chloride) (PVC), polyethylene terephthalate (PET).

The products manufactured by blow molding, although limited to hollow shaped plastics, are widely used in many industrial fields and everyday lives. The following are the products

that see a lot of blow molded parts: Automobile, Consumer, Electronics, Fuel oil tanks etc (eFunda, 2012).

1.11.2.4 Calendaring

This method is used extensively for the production of both plasticized and rigid PVC sheets: it is capable of producing high quality material at very high rates of output. It involves the use of a series of heated rolls which are fed with pre-compounding stock. As the stock passes through consecutive roll nips, a continuous sheet is formed to an appropriate thickness which can then be cooled. Both rigid and plasticized PVC are used for the production of continuous film or sheet up to approximately 1.5mm in thickness (Rossberg *et al*, 2006).

1.11.2.5 Compression Molding

This method is primarily used to process thermosetting systems and difficult to process thermoplastics, such as fiber filled systems or thermoplastic elastomers. In the case of thermoplastics, for example PVC, a preheated mass of polymer, which may be either a sheet or a pile of pellets or even powder, is placed in the mold. The temperature of the mold is set low enough to cause the polymer to solidify but not so rapidly that it will not flow. Hydraulic pressure is applied to the top or bottom plate pushing the plates together. The molds are designed to prevent the top part of the mold from touching the bottom part, which would squeeze the resin from the mold. The design of a compression molding process consists of four aspects. The first is the selection of the proper amount of material to fill the cavity when the mold valves are closed. The second is determining the minimum time required to heat the blank (empty mold cavity) to the desired processing temperature and the selection of the appropriate heating technique (radiation heating, forced convection, etc). It

is necessary to make sure that the centre reaches the desired processing temperature without the surface being held at too high of a temperature for too much time. The third is the prediction of the force required to fill the mold. Finally, the temperature mold must be determined, keeping in mind that one wants to cool the part down as rapidly as possible, but too rapid of a cooling rate will prevent the polymer from filling the mold (Charles *et al*, 2005).

Compression molding is the only way of making thick high-quality rigid sheet. A number of sheets of calendered material are pressed together to form a heavy sheet up to one inch thick. The compound used for this processing is usually based on Vinyldiene chloride. The product has excellent clarity and good impact properties. Other techniques such as injection molding are now replacing compression molding (due to improvement in molding machine that allows high pressure to be used).

1.12 GUM ARABIC

A gum, in general, is any water-soluble polysaccharide that is extractable from marine and land plants, or from microorganisms that possess the ability to contribute viscosity or gelling ability to their dispersions (Abu Baker *et al.,* 2007). The most fundamental property of a gum therefore is its water solubility and high viscosity in aqueous dispersions. For this reason, resins, latexes and other hydrophobic gums are not regarded as true gums. Among the advantages of natural gums over their synthetic counterparts are their biocompatibility, low cost, low toxicity (ecofriendliness) and relative widespread availability (Ogaji and Okafor, 2011).

Gum Arabic is obtained from tree of genus; Acacia, subfamily; Mimosodieae, family; Leguminosae (Smolinske, 1992). It is known as gum acacia, a natural gum made of

hardened sap taken from two species of the acacia tree; *Acacia senegal* and *Acacia seyal*. Gum Arabic is a pale to orange-brown solid which brakes along a glassy fracture. The best grades are whole, spheroidal-tear shaped, orange brown, with a matt surface texture. It is a nationally and internationally exported commodity, (Unanaonwi, 2011). Gum export has been the main stay of the Sudanese economy for over 400 years, (Lawal, 1998). It was used at least 4000 years ago when it was shipped as an article of commerce by Egyptian fleets. Ancient Egyptian inscriptions make frequent mention of gum Arabic called "*Kami*" which was used largely for painting as an adhesive for mineral pigments (Caius and Radha, 1939). The gum is made up of highly branched polysaccharides, and also a complex mixture of saccharides and glycoproteins, which gives it most useful property. It is perfectly edible (Smolinske, 1992). It is very soluble in water and is a neutral or slightly acidic salt of a complex polysaccharide containing Ca^{2+}, Mg^{2+} and K^{+} .

Gum Arabic is unique in that it is produced by trees only when they are in an unhealthy condition. Healthy trees have not been observed to yield gum. Most authorities believe that the formation of gum exudates is a pathological condition resulting from a microbial infection of the injured tree (Blunt, 1926). Natural factors that tend to lessen the vitality of the tree, such as poor soil, lack of moisture, and hot weather, improve gum yields, others consider the production of gum to be a normal metabolic process in the plant, with the quantity and quality produced being a function of environmental conditions (Malcom, 1936).

1.12.1 Distribution

A tree typical of Sahel climates, *Acacia senegal* is widespread in the dry regions of tropical Africa, from Senegal and Mauritania, in the west, up to Eritrea and Ethiopia in the

north-east and down to South Africa, in the south. It is primarily located in between 11^{o} and 16^{o} North latitude. Of the four renowned varieties, *senegal* is the most widespread and is found in all the regions where *Acacia senegal* trees are located, except along the West coast of central and southern Africa. Outside Africa, it is also found in Oman, Pakistan and India and has also been introduced in Egypt, Australia, Puerto Rico and the Virgin Islands (ITC, 2008).

1.12.2 Structural Composition

Gum Arabic is best described as heteropolymolecular; a polymer system containing complex polysaccharide, mostly of galactose, arabinose, rhamnose and glucoronic acid, with 2 % proteins as an integral part of its structure (Karamalla, 1998). The gum may have either a variation in monomer or a variation in the mode of linking and branching of the monomer units.

Gum Arabic is not very viscous, implying that the gum molecules are essentially globular and close- packed in shape rather than linear. Although the molecular weight reported for gum arabic have been in the 240,000 – 300,000 range, the most recent careful study of the exudates from *Acacia senegal* has shown an average molecular weight of 600,000 (Thomas, 1975).

1.12.3 Chemistry of Gum arabic

Gum Arabic is a branched-chain, complex polysaccharide, either neutral or slightly acidic, found as a mixed calcium, magnesium and potassium. The chemical composition can vary with its source, the age of the trees from which it was obtained, climatic conditions and soil environment (al-Assat *et al*, 2005).

Gum Arabic is a highly heterogenous material, but was separated into three major fractions by hydrophobic affinity chromatography (Randall et al, 1989). Most of the gum (88.4% of total), an arabinogalactin (AG), has a very low protein content (0.35%0 and molecular mass of 3.8 x 10^5 Da. The second fraction (10.4% of total), an arabinogalactan protein Complex (AGP) contained 11.8% protein and had molecular mass of 1.45 x 10^6 Da. The third fraction (1.2% of total) referred to as low molecular weight glycoprotein (GP), had a protein content of 47.3 and a molecular mass of 2.5 x 10^5 Da. The Major amino acids present in the protein of AG and AGP were hydroxyproline, serine and proline, whereas in GP, aspartic acid was the most abundant (Islam *et al.*, 1997).

Gum Arabic is primarily indigestible to both humans and animals. It is not degraded in the small intestine, but fermented in the large intestine by microorganisms to short-chain fatty acids, particularly propionic acid (phillips, 1998). Such degradation products are absorbed in the human colon and subsequently utilized energetically in metabolism (Badreldin *et al.*, 2008).

1.12.4 Physical Properties

1.12.4.1 Solubility

Gum Arabic is insoluble in oils and in most organic solvents but usually dissolves completely in hot or cold water, forming a clear, mucilaginous solution. Solutions containing up to 50% gum Arabic can be prepared and the solubility in water increases as the temperature increases. There are certain samples of gum Arabic, usually the exudates collected at the beginning of the dry season that are not completely soluble. They form stringy, mucus like fluid that separates into the phases upon standing. For low-viscosity gum

Arabic only hot ethylene glycol are effective solvents. It is also soluble in aqueous ethanol up to about 60% of alcohol (Whistler and Bemiller, 1973).

1.12.4.2 Surface tension

The addition of gum Arabic to water results in lowering of the surface tension (Banerji, 1952). Temperature has an important effect on the surface tension of a gum Arabic solution. For a 4.066% solution of purified gum Arabic at 30^{o}C, 40^{o}C and 50^{o}C, the surface tension is 61.80, 61.46 and 59.03 dynes /cm respectively. As gum Arabic concentration increases, there is slight increase in surface tension, followed by a general decrease. Addition of electrolytes and especially mineral acid gives lower surface tension.

1.12.4.3 Ageing

Age of the gum, i.e., the length of time it has remained attached to the tree after secretion may affect some of its physical properties. The colour of the gum may change from white to brown or dark-brown. The hardness may also change. Gums should be kept in dry places. Dilute gum Arabic solutions of the same temperature and concentration have the same viscosity until the appearance of bacterial growth that usually appears in 36-48 hours after the solution is prepared.

1.12.4.4 Osmotic Pressure

The osmotic pressure of boiled sodium arabate solutions is about 3% higher than that of unboiled solutions. There is a linear relationship between osmotic pressure and concentration at concentrations up to 1%. Above 1% the plot becomes a gradual curve. When sodium chloride is added, the osmotic pressure falls drastically; then the decline flattens out for concentrations above 0.2N sodium chloride. The limiting value of the

osmotic pressure at any specific gum concentration is independent of the salt concentration (Whistler and Bemiller, 1973).

1.12.5 Chemical Properties

1.12.5.1 Reactivity

Gum Arabic as the calcium, magnesium and potassium salts react with many reagents in a manner similar to that of other polysaccharide acid salts. Solutions of gum Arabic will produce precipitates or heavy gels on addition of borax, ferric chloride, basic lead acetate, mercuric nitrate, galatin, potassium silicate, sodium silicate, million's reagent and stoke's acid mercuric reagent (mantel, 1947).

In general, trivalent metal ion salts will cause precipitation gum Arabic. Dilute (1%) gum Arabic solutions can be can coagulated by the addition of Ruthenium Red (Ru_2 $(OH)_2$ $Cl_4.7NH_3.2H_20$). Hexol nitrate, or Desogen Geigy. In many application, the flocculation or thickening of gum Arabic can be prevented or retarded by the addition of soluble alkali polyphosphate ate concentration of 0.1 – 1.0% (Haller and Frankfurt, 1937).

1.12.5.2 Enzymes present

Gum Arabic contains both oxidases and peroxidases that are inactive by heating the gum solution to 80^oC or higher for one hour. The proxidase content varies but the enzyme can be inactive without affecting the viscosity by heating to 100^oC.

Diastase and pectinases have also been reported to be present in gum Arabic. The pectinases will cause precipitation of pectin when both are present in the same medium.

One of the major functional characteristics of gum Arabic is its ability to act as emulsifier for essential oils and flavours. Prolonged heating of gum Arabic solution causes

protinaceous components to precipitate out of solution, thereby influencing the gums emulsification properties (Williams, 2000).

1.12.6 Uses of Gum Arabic

1.12.6.1 Pharmaceuticals

Gum Arabic is used as an effective suspending aid and has been employed to suspend drugs and to prevent the precipitation of heavy materials from solution through the formation of colloidal suspension. It has soothing characteristics which led to its use in pharmaceutical syrup. Gum Arabic syrup is effective in masking the bitter or acid taste of medicament by its protective colloid action. Antiseptic preparations have been made with a mixture of colloidal silver bromide and gum Arabic. Silver Arabic has antiseptic properties that make it suitable as a substitute for silver nitrate and organic silver compounds in the treatment of ophthalmic infection. Gum Arabic has been used as an adhesive or binder for pharmaceutical tablets, such as aluminum acetate tablets and also as an excipient in the manufacture of pills and plasters employ. In addition many types of coatings for pill gum Arabic in the manufacture (Whistler and Bemiller, 1973).

1.12.6.2 Cosmetics

In lotions and protective creams, gum Arabic stabilizes emulsions, increases the viscosity, assists in imparting spreading properties, and adds a smooth feeling to the skin. Cosmetic pack has been made using gum Arabic as a binder. Hair fixatives based on vegetable gums have the advantage of vastly improving fixative properties without forming greasy stains on clothing. Gum Arabic mucilage's have been used in the preparation of their hair dressing (Harry, 1947).

1.12.6.3 Inks

Gum Arabic is a constituent of many special-purpose inks because of its excellent protective colloid properties. It is used to make soluble inks used by textile workers to mark cloth for cutting or sewing operations. The suspension of a pigment in a gum Arabic solution makes a satisfactory ink that can be applied with a brush or pen. Pigments such as titanium dioxide or bronze powder used for gold inks are preferably moistened first with a small amount of ethanol acetone before mixing with the gum solution. A typical white ink is made by mixing a filtered solution of 20 parts of gum Arabic in 160 parts of water with 30 parts of titanium dioxide paint pigment and O.5 part of sodium salicylate preservative (Horn and Sanko, 1953). Inks devised to imitate expensive grains by printing a pattern of wood on metal, paper stone, or inexpensive woods use gum Arabic as a suspension aid.

1.12.6.4 Medicine

Intravenous injections of gum Arabic solutions were recommended in 1933 for the treatment of nephritic edema (Osol and Farrar, 1955). A 19th century Ethiopian medical text describes a potion made from an Ethiopian species of Acacia (known as *grar*) mixed with the root of the *tacha*, then boiled, as a cure for rabies (Richard, 1990).

It has been said that gum Arabic, when used in infusion liquids, is harmful because it absorbs cations and causes an anionic unbalance. Some allergic reactions have occurred with injections of gum Arabic. The symptoms are flushing of the face, coldness of extremities, chills, nausea, vomiting and uticaria. These reactions could be controlled or prevented by administration of epinephrine (Osol and Farrar, 1955).

1.12.6.4 Foods

Gum Arabic has been used as a stabilizer in frozen products such as ice creams, and sherbets, because of its water-absorbing properties. It is widely used in the baking Industry for it viscosity and adhesive property, it is used in glazes and toppings. With the introduction of spray-dried flavours into foods, an extensive use was found for gum Arabic as a fixative for flavours (Whister and Bemiller, 1973).

The predominantly herbivorous spider *Bagheera kiplingi*, which is found in Central America and Mexico, feeds on nubs at the tips of the acacia leaves, known as Beltian bodies, which contain high concentrations of protein. These nubs are produced by the acacia as part of a symbiotic relationship with certain species of ant, which also eat them (Meehah *et al*, 2008)

1.13 AIMS AND OBJECTVES OF THIS STUDY

1.13.1 Aim of This Study

This work seeks to study the effects of locally produced additives on the structure and properties of PVC, it also intends to investigate improvement related to physical properties, while retaining, if not improving, the volume resistivity, mechanical flexibility and toughness required for a predictable industrial application.

1.13.2 Objectives of this Study

The objectives of this study are to produce and explore the use of locally derived plasticizers (gum Arabic) as an additive in the modification of PVC structure and its resultant properties. The effect of the additive in the structural arrangement will be studied and the properties of the modified PVC will be classed as a possible commercially usable material that could be utilized for end-use application.

CHAPTER TWO

REVIEW OF PAST WORKS

2.1 GUM ARABIC

Yael *et al.*, (2006) studied the overall structure of Gum Arabic by X-ray and neutron scattering at different concentrations at room temperature. They revealed that the scattering pattern is characterized by a well-defined peak. The measured data were collected for the dimensions of the incident slit-culminated beam using the indirect transformation in reciprocal space procedure (ITR) which is suited for partially ordered systems which exhibit scattering maxima (Glattter and Gruber, 1993). The position, shape and intensity of the peak depend on the concentration of the solution. As the concentration of the increases, the peak shifts to higher values of the scattering vector and broadens. This kind of scattering behavior characterizes assembles of scattering moieties with inter aggregate correlations. As the concentration increases, distance between aggregates decreases, due to crowding of the aggregates. This behavior is qualitatively different from inter particles effects, where changes in the scattering pattern result from changes in shape of the individual aggregate and are thus unaltered by the concentration. At the highest measured concentration (30%w/w), the peak becomes significantly broader, due to the onset of overlap of polymer aggregates. Interestingly, viscosity measurements show a sharp increase at about the same concentration (Whistler and BeMiller, 1973) as expected at overlap concentration of the polymer (Gennes, 1973). The high overlap concentration, unusual for linear polymers of comparable molecular weight, is in accordance with the view of the major component of

gum Arabic as a hyperbranched polymer forming an overall spheroidal shape with negligible intermolecular contact up to high concentration.

To probe the origin of the structure revealed by the scattering patterns, they investigated the scattering from aqueous solutions of arabinogalactan (AG extracted from Larch tree) at similar concentrations; the scattering patterns of these solutions differ significantly from those exhibited by gum Arabic at similar concentrations. In particular while the scattering patterns of gum Arabic solutions are dominated by a clear peak, no such peak is observed at any concentration of arabinogalactan.

The x-ray scattering pattern of gum Arabic at concentrations between (0.4% w/w) reveal a new feature that is not observed at higher concentrations; excess scattering intensity in the small "q" range ($q < 0.15nm^{-1}$), which tends to scale with scattering vector to a power nearly -1. The scattering from there dilute solutions was evaluated using the indirect transform ITP, which is suitable for isolated scattering objects with no long range order. The difference in the scattering patterns may be an indication for stiff-chain behavior in the dilute solutions (Glatter and Kratky, 1982). this phenomenon may be attributed to the protein chain of the higher molecular weight arabinogalactan protein complex, which may acquire locally a more extended conformation at low concentrations (and lower ionic strength). At low concentrations, the protein complex may locally attain an extended conformation, while at higher concentrations, the chain is more contracted.

The soil characteristics are major factors that influence the gum quality and production, particularly soil reaction (soil pH), organic carbon, nitrogen and phosphorus (Joseph *et al.*, 2010).

Properties of gum Arabic (*Acacia senegal*) were studied using variable doses of gamma radiation of 5.5, 6.5, 7.5, 8.5, 9.5, and 10.5 KGy, respectively. It was found that the highest dose of gamma radiation used achieved the best emulsification, viscosity and absorbance. The only drawback is the change of the colour of gum Arabic from white to dark red. This problem needs to be overcome for some applications (siddiq and Murwan, 2010).

Gum Arabic is a natural biopolymer with wide industrial use as a stabilizer, a thickener, an emulsifier and in additive encapsulation not only in food industry but also in textiles, ceramics, lithography, cosmetic and pharmaceutical industry (Verbeken *et al.*, 2003). Besides all the sensory and texturizing properties, GA has interesting antioxidant properties such as an efficient capacity for deactivation of excited electronic states and moderated radical scavenging capacity. There is increasing experimental evidence that associate the antioxidant function with its protein fraction, mainly by amino acid residues such as histidine, tyrosine and lysine, which are generally considered as antioxidants molecules (Marcuse, 1960, 1962; Park *et al.*, 2005).

Espinosa-Andrews *et al.*, (2010), studied chitosan-gum Arabic coacervates and quantified the amounts of polysaccharides in soluble phase and insoluble phase (coacervates). They used high pressure liquid chromatography (HPLC) technique to quantify monosaccharides produced after acidic hydrolysis in soluble phase. They also prepared Chitosan–gum Arabic coacervates at different pH and further evaluated micro-structural and rheological characteristics of the coacervates. They found that coacervates were formed due to the interaction of the functional groups of both macromolecules ($-NH_3^+$ and COO^-), using Fourier Transformation Infrared Spectroscopy (FT-IR) (Malviya *et al.*, 2010).

Osman *et al.*, (1993) fractionated GA by hydrophobic interaction chromatography to yield four fractions, all of which had a similar carbohydrate composition, but differed in their concentration of protein, amino acid composition and molecular mass distribution. All four fractions reacted with an array of anti-arabinogalactan protein monoclonal antibodies via anti-carbohydrate epitopes and were precipitated by Yariv's reagent, which indicated that all four fractions were AGPs. It was shown that at least one protein was unique to each fraction.

^{13}C NMR spectroscopy has been shown to be a powerful analytical method for the unambiguous identification of GA; samples adulterated with other gums are readily detected using this technology (Anderson *et al.,* 1991). As-Assaf *et al.,* (2005) found that analysis of GA using GPC coupled to a multi-angle laser light scattering detector, a refractive index detector and an UV detector set at 214nm provided a useful "fingerprint" for the rapid evaluation of GA for specific applications. The method was able to assess protein content and its distribution in the various gum components.

2.1.1 Pharmacological Properties

Mixtures of different types of gums (including gum Arabic) have been shown to inhibit glucose movement in vitro, and lower postprandial blood glucose and plasma insulin in human subjects when incorporated in drink containing 50g glucose (Edwards *et al.*, 1987; Torsdottir *et al.*, 1989). Injection of males containing starch showed that a decrease in the digestion rate of starch in the upper small intestine accounted for part of the effect of viscosity on glycemic response, whereas the main effect of gum was apparently to slow gastric emptying (Badreldin *et al.*, 2008).

Dental worries occur when tooth enamel is lost due to an imbalance of the demineralization and remineralization phases, and prevention can be achieved when the remineralization phase is enhanced (Aoba, 2004). Several agents have been used for that purpose including fluoride (Cheng *et al.*, 2007). Recently, it has been shown, using histopathological methods that, G.A has the ability to enhance remuneration (Onishi *et al.*, 2008), probably by supporting other remineralization activities. This supporting role was ascribed to the content of Ca^{2+}, Mg^{2+} and K^{+} salts of polysaccharides in GA, and to the effect of the gum on the metabolism of Ca^{2+} and possibly phosphate. It is also known that GA contains cyanogenetic glycosides and several different types of enzymes (such as oxidases, peroxidases and pectinases) that exhibit an antimicrobial property against certain organism such as *Prophyromonas gingivalis* and *Prevotella intermedia*.

Macrophages play an important role in the regulation of immunological process in rats. Mochida *et al.,* (1996) studied the effect of gum Arabic on macrophage activation by their ability to produce superoxide anion in vitro and found that gum Arabic suppresses macrophage activation in vitro. This confirms an earlier report that gum Arabic is capable of almost completely blocking the macrophage function (Fujiwara *et al.,* 1995). The authors inferred that such effect of gum Arabic would be considered in the therapy for chronic liver disease, as deranged function of kupffer cells and hepatic macrophages occurs in this disease and is involved in its complication such as endotoxemia.

2.1.2 Toxicity of Gum Arabic

Historically, the first case of an occupational sensitization of GA in a candy factory was reported more than seven decades ago (Badreldin *et al.*, 2008). That was followed by a number of reports causing dermatitis and asthma (Ilchyshyn and Smith, 1985). In all these

reports the offending allergen has not been identified. However, in 1998, a carbohydrate specific IgE was identified in a Chocolate confectioner with cough and dyspnea (Fotisch *et al.*, 1998). More recently, Sander *et al.*, (2006) found that sensitization to gum Arabic Carbohydrate structures occurs causing in atopic patients with pollen sensitization without obvious exposure to G.A, and that allergy to gum Arabic is mediated preferentially by Igt antibodies directed to polypeptide chains of gum Arabic.

Doi *et al.*, (2006) studied the subchronic toxicity of a new type of gum Arabic (SUPER GUM (sen), a naturally processed polysaccharide exudate from Acacia Senegal, when given to both sexes of F344 rats at dietary levels of (control), 1.25%, 2.5% and 5.0% (10 rats/sex/group). During the study, the treatment had no effect on clinical signs, survival, body weights, food and water consumption, urinalysis, opthalmology, hematology and blood biochemistry, and no gross pathological or histopathological alterations. Increased relative cecum (filled) weight, evident in box sexes of 5.0% group and females of 1.25% and 2.5% groups were considered to be a physiological adaptation. It was concluded that, at least up to a dietary level of 5% super gum (equivalent to 3117 mg/kg body weights/day for males and 3296 mg/kg body weights/day for females) caused no adverse effect. This confirms earlier reports that documented the safely of gum Arabic (Anderson, 1986). The safety of gum Arabic (5, 10, 20 or 40g in water for 4 weeks) has recently been confirmed in healthy men (Calame *et al.*, 2008).

Gum Arabic (10% in the drinking water) for either 3 or 14 days decreased urinary excretion of inorganic phosphate and increased that of calcium (Ca^{2+}) and magnesium (Mg^{2+}) and also decreased plasma concentrations of 1.25-dihydroxy vitamin D in healthy Mice (Nasir *et al*, 2007). The Magnitude of the metabolic disturbances in mice with renal

insufficiently has not been determined, but is expected to be more pronounced (Badreldin *et al.*, 2008).

2.2 STRUCTURE AND PROPERTIES OF PVC

PVC is a thermoplastic material with a linear structure and its monomers linked together in a head to fail manner (Marvel *et al.*, 1939). Tacticiy is possible in PVC due to the presence of chlorine substituent. The study of the crystalline zone indicates repeat unit distance of $5.1^{o}A^{o}$ which is consistent with syndiotactic configuration (Natta and Carradini, 1950). Later x-ray and NMR studies showed that commercial PVC is 55% syndiotactic and the rest largely atactic. However, crystallinity was found to be 5% with commercial samples. Free radical polymerization of Vinylchroride at low temperature ($-40^{o}C$) using y-radiation or polymerization using highly active initiators such as alkyl boranes favours the formation of sydiotactic structures. These are more crystalline and are different to process.

PVC is more polar than polyethylene due to the presence of C-Cl dipoles. This leads to higher extent of intermolecular interaction showing higher T_g equals to $80^{o}C$. PVC has got high dielectric constant and power factor due to the presence of dipoles. For the same reasons, the polymer is resistant to non-polar solvent. Since it is a weak proton donor, solvents of PVC are weak proton acceptors like cyclohexanone, tetrahydrofuran and 2-butanone. Suspension polymerized PVC is morphologically organized as a particle hierarchy. The largest free-flowing unit according to Terselius and Janssen 1983, and also Portingell 1982, is that the accepted nomenclature is called grain with a size of the order 100μm. The grains are composed of primary particles and agglomerates with the primary particles built up by domains (0.1 μm). The bulk and suspension polymerizations of vinyl chloride have been carried out in the presence of small known amounts of added oxygen at

54^{o}C in the presence of peroxide initiators. The Concentrations of oxygen were in the range 0-1240 ppm for 1-gal bulk polymerization systems (Garton and George, 2003). The thermal stabilities of the polymers prepared in the presence of oxygen were lower than those prepared under corresponding oxygen-free conditions. The average molecular weights of bulk polymers isolated at relatively low concentrations were reduced in the presence of oxygen, and the infrared spectra of the polymers were altered.

2.3 EFFECT OF ADDITIVES ON THE STRUCTURE AND PROPERTIES OF PVC

Virgin PVC is hard, difficult to process and extremely susceptible to rapid degradation at temperature necessary for its processing (Marvel *et al.*, 1939). The degradation of PVC during processing is brought about by the effect of heat, pressure and shear which are exerted on the material. The mechanism of PVC degradation involves dehydrochlorination, liberation of hydrogen chloride gas (HCl) to form polyene structures, which serve as points at which undesired reactions are propagated, and as points at which undesired reactors are propagated, and finally leading to deterioration of physical properties of the PVC material (Thomas and Todd, 1971). In 1926, Waldo Semon and the B.F Goodrich Company developed a method to plasticize PVC by blending it with various additives. The resultants product was more flexible and more easily processed material that soon achieved widespread commercial use. The effective so called external plasticization of the PVC homopolymer by incorporating plasticizers caused a reduction in the softening of PVC (Tester, 1973). He noticed that when PVC was compounded with butylphalate and other esters, which resulted in rubber-like properties at room temperature. It was also understood that alkaline earth metal soaps acted as heat stabilizers (Brydson, 2000). So it was realized that useful products could only be obtained if certain additives were incorporated into the

polymer matrix by process known as compounding (Thomas and Todd, 1971). However, the addition of suitable additives such as plasticizers, stabilizers, lubricants, filters and other, can transform the polymer into a soft flexible material with rubbery characteristics or into a tough rigid material. Polymer additives are important areas of innovation for polymeric materials. An additive is a material that is added to a polymer melt to enhance the processability, performance, or appearance of the polymer. The ability to modify polymer has allowed the polymer industry to produce better and stronger materials.

Effect of additives mainly plasticizers and fillers, on the mechanical properties of PVC were studied and the experimental results have shown that tensile strength decreased with increasing plasticizer content for the group of samples free of filler (Elgozali and Hassan, 2008). The trend was completely reversed in the group where the sample contained filler. They also confirmed that the elongation at break is inversely proportional to plasticizer content for the group free of filler, while it is directly proportional to plasticizer content for that containing filler. In another study by Liu and Zhang (2007), the effects of acetanilide, adipic acid and potassium hydrogen phthalate as nucleating agents on PVC crystallization were investigated by differential scanning calorimetry (DSC), wide angle x-ray diffraction (WAXD) and fourier transform infrared spectroscopy (FTIR). The experimental results indicated that all the three additives were compatible with PVC to some extent, but adipic acids compatibility with PVC was less satisfactory. They confirmed that the three additives improved PVC crystallinity and acetanilide decreased PVC glass transition temperature (T_g) and narrowed PVC melting range, while adipic acid and potassium hydrogen phthalate raised the T_g of PVC and widen its melting range. All additives did not affect PVC crystal system and all samples were in orthorhombic system. Moreover, acetanilide and adipic acid

shrinked PVC spacing and improved the crystal perfection of PVC, but potassium hydrogen phthalate swelled spacing and reduced the perfection of PVC crystal.

Labib and Williams, (1984) studied the surface properties of polyvinyl chloride containing organotin stabilizers and calcium stearate, and the surface properties of the additives themselves. They used Zeta-potential measurements to determine the charge on the surface of additive-containing polyvinyl chloride and related this to chemical reactions of the additive materials. They discovered the major chemical reactions were those involving hydrolysis of tin-ester linkages in the organotin compounds and dissociation of carboxylic acid groups. They also discovered that as a result of these reactions, the surface charge of the polymer depends strongly on the pH of the aqueous medium in contact with the surface.

Azman and Siranesswarm, studied the effects of rice husk ash (RHA) filler on processability of impact modified unplasticized polyvinyl chloride (PVC-U). They studied the processability to investigate the fusion behavior of filled impact modified PVC-U, using Brabender plasticizer with fitted mixing head. The work was carried out on the pre-prepared RHA with different loading levels. Analysis of the result showed 10parts per hundred resin RHA filled impact modified PVC-U samples had shorter fusion time and higher fusion torque compared with the other levels of filler loading. Zirconate treated samples showed longer fusion time and longer processability torque compared with the other types of coupling agents. The experimental results also related that the lower the loading of the filler, the faster the fusion during processing.

The mechanical properties of both unplasticized and plasticized PVC expose to 25% concentrated HCl/NH_3 Solutions were another set of studies investigated by Mamza and

Solomon, (2008). In their study, the stress/strain relationship before and after exposure of the samples compressed molded film, to acidic and basic media for 72 hours was investigated. The tensile testing suggested that depolymerization of PVC is enhanced in basic medium due to neutralization of liberated HC, hence resulting to decrease in its mechanical properties, while the mechanical properties of those exposed to acidic medium are appreciably reinforced due to minimal depolymerization. According to Harris (1969), the tensile properties of polymers, apart from defining the quality of production as well as their design and engineering behavior also indirectly measure other properties of the material for which corelaxation exist. For example, a plastic film of high tensile strength and elongation, in all directions, will likely have high impact strength. Tensile properties may also be used to monitor chemical or physical changes taking place in a polymer. The study of the effects of Ca/Zn stearate and organotin heat stabilizers and Zeolite, CaCO3, Celluose and Luffa flours filler, and their concentrations 2.5, 2, 10 and 20% by weight) on production of flexible PVC foams by chemical blending agent, azodicarbonamide was done by Demir *et al.*, (2008). They determined foam morphology density, compressive mechanical properties and water uptake capacities of the samples. Morphology of the sample without any filler showed that employment of CA stearate and Zn stearate stabilizers instead of organotin stabilizer increased foam formation and decreased pore sizes and regularity in pore size distribution. Foams having organotin stabilizer were more resistant to heat than the ones with Ca/Zn stearate for long heating period. Foams, including organotin-based heat stabilizer, have compact structure. It was observed that, samples containing Zeolite, $CaCO_3$, Cellulose or Luffa flour had lower pore volume but higher Young's modulus and stress values compared to unfilled samples.

Balakriahnan and Jayakrishnan, (2005) showed in their work, the animation of PVC with a concentrated aqueous solution of ethylenediamine. The animated PVC was then reacted with hexamethylene diisocyanate to incorporate the isocyanate group onto the polymer backbone. The isocyanated PVC was further reacted with polyethylene glycol (PEG), where infrared spectra analysis showed the incorporation of PEG into PVC. The thermal stability of the modified polymer was found to be lowered by the incorporation of PEG. Contact angle measurement on the surface of polymer films cast from a tetrahydrofuran solution of the polymer demonstrated that the modified polymer gave rise to a significantly hydrophilic surface compared to unmodified PVC. They still showed static platelet adhesion studies using platelet rich plasma, which showed significantly reduced adhesion on the surface of the modified PVC compared to control PVC. The study showed that bulk modification of PVC with PEG using appropriate chemistry can give rise to a polymer that possesses the anti-fouling property of PEG and such bulk modifications are less cumbersome compared to surface modifications on the finished product to impact anti-fouling properties to PVC surface. Jian and Zhen-Liang (2002), Prepared a symmetric PVC hollow fabric ultrafilteration members by phase inversion technique from 14 to 20 wt% solids including PVC and additives. They used polyvinyl pyrolidone (PVP 40, 000) Polyethylene glycol (PEG) with different molecular weights (PEG 600, PEG 800, PEG 1000) as additives and N,N-dimethylacetamide (DMAc) as a solvent. 95/5 DMAc/water and pure water were used as bore fluid to investigate the effect of gelation bath. The dope solutions, membrane structure, separation performance and mechanical properties of PVC hollow fibre membranes were studies. The structure of PVC hollow fibre membranes including external surface, internal surface and cross-section were characterized by scanning

electron microscopy (SEM) and the mechanical properties of PVC hallow fibre membranes were discussed. It was found using PVC or PEG as additives can increase the membrane porosity and enhance the permeation flux by changing the membrane morphology. Three kinds of proteins having different molecular weights were applied for the measurement of rejection. Based on the experimental results, pure water permeation fluxes of PVC/additive/DMAc hollow fibre membranes might reach 100-200 L/(m^2 h bar) while the molecular weight cut-off at PVC hollow fibre membranes will be approximately 50,000.

Chao *et al.*, (2003) prepared polyvinyl chloride)/Na+ - montmorillonite (PVC/MMT) nanocomposites with different MMT contents via melt blending. Wide-angle x-ray diffraction (WAXD) and transmission electron microscopy (TEM) were used to characterize the structures. Effects of MMT content on the mechanical properties were also studied. It was found that PVC molecular chains can intercalate into the gallery of MMT layers during melt blending process, the stiffness and toughness of the composites were improved simultaneously within 0.5 -7w% MMT content, and the transparency and mechanical properties decreased as MMT content further increased.

In another work, polyvinyl chloride/ethylene-vinyl acetate/montmorillonite (PVC/EVA/OMMT) composites were studied by melt blending method. Two kinds of montmorillonites were organically modified by trimethyloctadecyl ammonium and dimethyl bis(hydrogenated tallow) ammonium respectively. The morphology and tensile properties of the resultant composites were discussed in terms of the modifier type and OMMT content. The PVC/EVA/OMMT composites had intercalated structure which was independent of the polarity of the modifiers, while the tensile properties showed strong dependence on the

modifier type. The OMMT modified by polar modifier gave higher tensile ductile and strength of PVC/EVA/OMMT composites (Chao *et al.,* 2003).

Mazatusziha, (2006) investigated the performance of rice husk (RH) as filler for unplasticized polyvinyl chloride (PVC-U) composites. In the sample preparation, composites with different RH loadings varied from 10 to 40 ph were prepared using two-roll mill at temperature 165^{o}C before being hot pressed at temperature 185^{o}C. Tensile, flexural and izoel impact tests were conducted. Incorporation of RH fillers from 10 to 40 phr resulted in the increase of flexural modulus indicating an improvement in stiffness. The effects of acrylic impact modifier and LICA 12 coupling agent on the mechanical properties of PVC-U composite were investigated. The acrylic impact modifier was found to be effective in enhancing the impact strength at all levels of RH content. Effectiveness of the impact modifier in enhancing the impact strength decreases with increasing RH content. LICA 12 was found to be the most effective in increasing impact strength at 20phr PH loading. The processability of RH filled PVC-U composites was studied by using Brabender plasticorder. It was found that incorporation of RH resulted in decreasing the fusion time of the PVC compounds while the heat distortion temperature (HDT) increased at all RH loadings. The degradation temperature decreased with increased slightly with increasing RH content. The percentage of water absorption increased slightly with increasing RH content and treated samples exhibited lower percentage of water absorption compared to the untreated samples. The optimum composition which gave balance of properties based on stiffness and toughness of PVC-U composite were PVC-U at 10 phr of acrylic impact modifier and 20 phr of RH treated with LICA 12.

Hassan *et al.*, (2002) studied the ion selective PVC membrane electrode for the determination of methacycline hydrochloride in pharmaceutical formulation. They used methacycline-tetraphenylborate as the electroactive substance and dioctylphtalate as the plasticizing agent. They found that the potential responses of the electrode were influenced by pH of the tested solution when pH>3. Under the condition of pH 2.6, the linear response range, slope and detection limit obtained were 3.0×10^{-2} ~6.0×10^{-6}M, 52.9mv per decade and 3.4×10^{-6}M respectively.

Mamza and Nwufo, (2008) studied the swelling behavior of polystyrene (PS)/polyvinyl acetate (PVA) blends in different solvents and the effects of α-cellulose used as filler on the electrical conductivity. They found out that the variation of the type of solvent was responsible for the differences in the swelling kinetics of the blends. Their result showed that the nature of solvent control affects the degree of swelling.

2.4 EFFECT OF PROCESSING ON THE STRUCTURE AND PROPERTIES OF PVC

It is generally understood that the gelation of PVC to be the breakdown of grains and primary particles and an establishment of an entangled network locked by a network of crystallites, (Gillbert and Vyroda, 1981). At processing, gelation is accompanied by the combined action of heat, pressure and shear. It was also noticed that by heat alone, the porosity in the grain may be eliminated above a temperature of 150^{o}C as observed by Allsop, (1981), but the primary particles will not be broken down until after several minutes at a temperature of bout 220^{o}C. Compression molded PVC has been shown by small-angle x-ray scarttering (SAXS) to contain crystallites with sizes of the order of 2-4nm and a spacing of the order of 10nm (Balakrishnan and Jayakrishnan, 2005). This process

represents the major mechanism of PVC fusion even though the final state of the melt is strongly dependent on the thermomechanical history of the resin.

2.5 DEFECTS IN THE STRUCTURE OF PVC

Typical PVC molecules are b5uild up approximately 1000 vinyl chloride monomer units, joined in a predominantly head-to tail fashion. Other structural arrangements are considered defects. The types and concentrations of these defects have been summarized and the effect of preparing PVC samples under different conditions on the defect structure has been reported (Hjertberg and Strivik, 1984). Irregular structure determined in the ordinary PVC include in CH_2-CHC1-CH_2C1, 0.8-0.9/molecule, in CH_2-CH=CH_2C1, approximately 0.7/molecule. Initiator residues, approximately 0.2/molecule; total unsaturation, 1/ molecules; internal double bounds 0.1-0.2/1000 VC ; polyene sequences <5 x 10"71000VC; chloromethyl branches 4/1000 VC; 2-chloromethyl branches, «0.5/100VC; 2, 4- dichlorobutyl branches 1/1000VC; long branches, < 0.5 1000VC; tertiary chlorine, 0.5/1000VC, and head to head groups <0.7/1000 VC (Guyot, 1986).

These defects have been determined by a number of techniques. Spectroscopic studies have been used to determine the extent of branching in PVC (Cofimau 1953; Bovey *et al*, 1975) Infrared spectroscopic method are being supervised by ^{1}H and ^{13}C-NMR technique (Maddanus, 1984; Guyot, 1986).

Measurement of the hydrodynamic volume of the polymer and more recently, ^{13}C -NMR techniques have been used to determine long chain branching. Saturated chain ends can be studied by high resolution NMR spectroscopy (Darricades, 1986).

Total unsaturated in PVC can be determined by the reaction with bromine or ICI addition although ^{1}H -NMR results have been used (Hildebrand, 1982; Bossie, 1977). Un-saturation

at chain ends also has been determined by ^{1}H-NMR Internal un-saturation is determined by the cleavage of the polymer chain by low temperature ozonolysis and measurement of the average molecule weight of the resultant fragment (Petiand and Pham, 1977). Attempts to measure polyene sequences by UV and Raman spectra have given very low values suggesting. That the internal double bounds are isolated, and thus are not conjugated.

Tertiary chlorine can be estimated by ^{13}C-nmr spectroscopy, more labile tertiary and allylic chlorine atoms can be determined chemically by the exchange of chlorine by phenol or through chloride and by thiophenolysis, which is specific for allylic chlorine atoms (Robila *et al* .,1977; Biruiana *et al.,* 1997).

2.6 MODIFICATION OF POLY (VINYL CHLORIDE)

Navarro *et al.,* (2008) tested different thiol compounds for the synthesis of poly (vinyl chloride) (PVC) with halogen groups and the course of the modification reactions followed under different conditions by NMR spectroscopy and elemental analysis. From their study, it is shown that PVC can be modified without side reactions using 4-fluorothiophenol, 4-chlorothiophenol, 4-bromothiophenol, 3,4-di-fluorothiophenol, penta-fluorothiophenol and pentachlorothiophenol. The reactivities and final degrees of modification of the different nucleophiles are compared showing that, when the thiolate salt is preformed, the bromine derivative reacts quicker and higher degrees of modification are reached than with its smaller homologues. On the other hand, using the thiol compounds in combination with potassium carbonate this order is inverted and highest degrees of modification are achieved with 4-fluorothiophenol.

Aminosilane, melamine and acetic anhydride treated wood flour were added to polyvinyl chloride (PVC) and manufactured into wood-plastic composites (WPC) panels in

order to investigate the influence of modification on the resistance to basidiomycetes of the composite. The composite consisted of 50 wt% wood and 50 wt% PVC dry blend. White rot (Trametes versicolor) and brown rot (Coniophora puteana) fungi were used to inoculate the composite. All tested formulations showed high resistance to basidiomycetes under the test conditions. With regard to the modifications used, only aminosilane treated composites showed slightly decreased weight loss values compared to the untreated reference (Muller *et al.,* 2013).

2.7 DEGRADATION

The miscibility, morphology, and thermal properties of poly (vinyl chloride) blends with different concentrations of poly (methyl methacylate) (PMMA) have been studied. The interaction between the phases was studied with FTIR and by measuring the glass transition temperature (T_g) of the blends using differential scanning calorimetry. Distribution of the phases at different compositions was studied through scanning electron microscopy. The FTIR and SEM results show little interaction and gross phase separation. The thermogravimetric studies on these blends were carried out under inert atmosphere from ambient to 800^0C at different heating rates varying from 2.5 to 20^0C/min. The thermal decomposition temperatures of the first and second stage of degradation in PVC in the presence of PMMA were higher than the pure. The stabilization effect on PVC was found most significant with 10 wt% PMMA content in the PVC matrix (Ahmad *et al.,* 2008).

Wen *et al.,* (2012) studied ZnAlLa-CO_3 layered double hydroxides (LDHs) with different Zn/Al/La molar ratios as heating stabilizer in PVC resin. The synthetic materials were characterized by X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM), Brunauer-Emmett-Teller method (BET) and

particle analysis. Their results showed that the hydrotalcite-like materials had a layered structure. The ZnAlLa-CO3-LDHs as stabilizers were mixed with PVC resin. The results showed that ZnAlLa-CO3- LDHs used as single thermal stabilizers could enhance both the long-term thermal stability and initial thermal stability of PVC, and 2.4 phr (parts per hundred PVC resin) ZnAlLa-CO3-LDHs with Zn/Al/La (molar ratio)=20/8/2 had a better stabilizing effect on PVC than others. Compared with single thermal stabilizers, the composite thermal stabilizers including 0.3 phr calcium stearate ($CaSt_2$), 0.4 phr _-diketone and 2.4 phr ZnAlLa-CO3-LDHs significantly enhanced the thermal stability of PVC sample.

Thermal dehydrochlorination of PVC is complex and involves two different processes: the first process with an activation energy of about 114 kJ mol^{-1} that follows nucleation growth type kinetic model, and a second process with an activation energy of about 202 kJ mol^{-1} that follows diffusion controlled kinetic model. The first process that follows a nucleation and growth mechanism could be related with the presence of the well described labile sites in PVC where the reaction starts and follows from these nuclei into the rest of the material. The second process follows a diffusion controlled model that was supported by microscopic observation of the material that shows the formation of bubbles due to the release of the HCl during the last steps of dehydrochlorination. The kinetics of two samples with different molecular weight resulted quite similar (Pedro, 2010).

The thermal decomposition of various mixtures of acrylonitrile butadiene styrene copolymer (ABS), ABS containing brominated epoxy resin flame retardant and Sb2O3, poly(ethylene terephthalate) (PET) and poly(vinyl chloride) (PVC) has been studied by Czegeny *et al.*, (2012) in order to clarify the reactions between the components of mixed polymers. More than 40 halogen-containing molecules have been identified among the

pyrolysis products of mixed samples. Brominated and chlorinated aromatic esters were detected from the mixtures containing PET and halogen-containing polymers. A series of chlorinated, brominated and mixed chlorinated and brominated phenols and bisphenol A molecules have been identified among the pyrolysis products of polymer mixtures containing flame retarded ABS and PVC. It was established that the decomposition rate curves (DTG) of the mixtures were not simple superpositions of the individual components indicating interactions between the decomposition reactions of the polymer components. The maximal rate of thermal decomposition of both ABS and PET decreases significantly if the mixture contains brominated epoxy flame retardant and Sb_2O_3 synergist. The dehydrochlorination rate of PVC is enhanced in the presence of ABS or PET.

The thermal dehydrochlorination of model compounds for poly (vinyl chloride) was investigated theoretically. To determine the reaction paths of the thermal dehydrochlorination, geometries, structures, and energies were evaluated for reactants, products, and transition states of the proposed paths by using the density functional theory (DFT) at the B3LYP/6-31G(d) level. On the basis of the experimental observations, three possible paths of the thermal dehydrochlorination for the model compounds of PVC have been postulated. The activation energies of path (2) and path (3) are 55.1 kcal/mol and 41.5 kcal/mol at the B3LYP/6-31G (d) level, respectively (Wang *et al.*, 2009).

Stabilization of poly (vinyl chloride) and effects of acid/base on the mechanical properties of PVC was investigated by Mamza and Ikeobijiaku, (2008). The tensile testing performed suggest that depolymerization of PVC is possibly enhanced in basic medium due to possible neutralization of liberated HCl hence resulting to decrease in its mechanical

properties, while the mechanical properties of those exposed to acidic medium are appreciably reinforced due to minimum depolymerization.

Mamza and Aliyu, (2006) also studied the effect of plasticizer on the molecular weight and some mechanical properties of poly (vinyl chloride). From their study, they concluded that the plasticizer composition affects the properties of the PVC films prepared. They noticed a direct correlation between the results obtained in molecular weight determination with the mechanical properties of the PVC films.

2.8 TOXICOLOGICAL CONCERNS

PVC has brought forward a host of peculiar problems that have continually posed challenges to the ingenuity of mankind. PVC in a broad variety of ways, both good and bad, has affected the life of just about every civilized person on the face of the earth. PVC in toys, children and infant products and packaging often contain toxic additives such as phthalates, organotins, lead and cadmium to soften or stabilize the plastic. These additives are not chemically bound to the plastic and can migrate out of the product posing unnecessary toxic hazards to children and consumers (Quevauviller, 1991; Hoch, 2001). In recent years, a growing body of scientific evidence has found that toxic chemicals released by the PVC lifecycle have been found in the bodies of babies, children and adults. Babies are being born pre-polluted with potentially harmful levels of phthalates and dioxin that may possibly cause lifelong health problems (Latini *et al.*, 2003; EWG, 2005). Organotins have been measured in human blood and household dust (Kannan *et al.*, 2010). Phthalates have been found in indoor air and dust, and in human urine, blood and breast milk (CDCP, 2005). An extensive study of 2,500 individuals found metabolites of at least one phthalate in 97 percent of those tested. Phthalate levels are highest in children ages 6 to 11, and in women.

In a more recent study, certain phthalates were found to be present in 100% of girls ages 6 to 9.25. Dioxin builds up in our bodies over our lifetime and can remain there for many years. The levels of dioxin in our bodies are at or near the levels known to cause harm (USEPA, 2003). Infants can be exposed to both phthalates and dioxin in breast milk. However, despite these exposures, breast milk is still best for babies (AAP, 1999).

In the early 1970s, Dr. John Creech and Dr. Maurice Johnson were the first to clearly link and recognize the carcinogenicity of vinyl chloride monomer to humans when workers in the polyvinyl chloride section of a B.F Goodrich plant near Louisville, Kentucky, where diagnosed with liver angiosacoma also known as hemangiosarcoma, a rare disease. Since that time, studies of PVC workers in Australia, Italy, Germany and the UK have all associated cancers with exposure to vinyl chloride (Creech and Jonson, 1974).

At various times, phthalate ester plasticizers have been at center of controversy rated to possible toxicological hazards. Phosphates esters also have a history of involvement, and practically every other type of plasticizer has been suspected of causing some kind of harm to human or animal health. Vinyl heat and light stabilizers, particularly those based on lead, barium, cadium, strontium and antimony are generally materials themselves highly resistant to extraction. With respect to stabilizers, organotin salts have not escaped scrutiny and suspicion (Nass, 1976).

2.9 PVC TESTS FOR MECHANICAL AND OTHER RELATED PROPERTIES

Mechanical properties are those properties that determine the response of a body to external mechanical influences such as tensile strength, elasticity, and elongation etc. The mechanical properties of PVC films changes with the addition of plasticizers. In testing any

material, there are some obvious properties which have to be investigated and, in addition, specific properties, which are important in view of the end-use of the final product.

Generally, properties in material are classified under classes of properties which are physical, mechanical, electrical, thermal, chemical, and optical.

Physical properties include: specific gravity, hardness, porosity, (water absorption) etc. Electrical properties includes: electrical strength, flash over, volume and surface resistivity, etc. Thermal properties include: plastic yield thermal conductivity, thermal expansion, heat resistance, etc. Chemical properties includes: resistances to reagents and oils. Mechanical properties are tensile strength, modulus of elasticity, elongation, etc.() For the purpose of this research, only water absorption and mechanical properties such as listed above are considered.

Tensile Property (ASTM D638)

This is a plot of stress against strain (elongation) on graph paper. The significance of this property is the most important single indication of the strength of a material. The force necessary to pull the specimen apart is determined along with how much material stretches before breaking.

The tensile properties of polymers, apart from defining the quality of production as well as their design and engineering behavior also indirectly measure other properties of the material for which a correlation exist. For example, a plastic film of high tensile strength and elongation in all directions will likely have high impact strength. It follows that the measurement of tensile properties will correlate well with the measurement of impact strength of such material. Tensile properties may also be used to monitor the progress of chemical or physical changes taking place in a polymer.

The elastic modulus (modulus of elasticity) or tensile modulus is the ratio of stress to strain below the proportional limit of the material. It is the most useful tensile data because parts should be designed to accommodate stresses to a degree well below this.

Flexural Properties of plastics (ASTM D790)

In bending a beam is subject to both tensile and compressive stresses, since most thermoplastics do not break; In this test, even after being greatly deflected, the flexural strength cannot be calculated, instead, stress at 5% strain is calculated that is the loading in Psi necessary to stretch the other surface 5%.

Stiffness in Flexure (ASTM D 44)

This test does not distinguish plastic and elastic elements involved in the measurement and therefore, a true elastic modulus is not calculated; Instead of an apparent value is obtained and collected stiffness in flexure. It is a measure of the relative stiffness of various plastics and taken with other pertinent property data is useful in material selection.

Izod Impact (ASTM D256)

The Izod impact test indicates the energy required to break a notched specimen under standard conditions. It is calculated as lb per inch of notch and it usually calculated on the basis of a one inch specimen, although, the specimen used may be thinner in the literal direction. The Izod value is useful in comparing various types or grades of a plastic. In comparing one plastic with another, however, the Izod impact test should not be considered as a reliable indicator of overall toughness or impact strength. Some materials are notch-sensitive and derive greater concentrations of stress from the notching operation. The Izod impact test may indicate the used for avoiding sharp corners in parts made of such materials.

Tensile Impact (ASTM D18822)

This test is comparatively new having been adopted by ASTM in 1961; there is relatively little industry data available to adequately asses its accuracy and utility. However, possible advantage over the notch sensitivity factor is eliminated, and energy is used in pushing aside the broken portion of the specimen.

Rockwell Hardness (ASTM D785)

Rockwell hardness can differentiate relative hardness of different types of a given plastic but since elastic recovery is involved as well as hardness, it is not valid to compared hardness of various kinds of plastic entirely on the basis of this test.

Compressive Property of Rigid Plastics (ASTM D695)

The compressive strength of plastics is of limited design value, since plastic products (except forms) seldom fail from compressive loading alone. The compressive strength figures, however, may be useful in specification for distinguishing between different grades of a material, and also for assessing alone with other property data, the overall strength of different kinds of materials.

Deformation under Load (ASTM D621)

The test on rigid plastics indicates their ability to withstand continuous short-term compression without yielding and loosening when of a particular plastic for long creep resistance of a particular plastic for long period of time. It also a measure of the rigidity at service temperature of material, and can be used as identification for procurement

Vicat Softening Point. (ASTM D1525)

The Vicat softening temperature is a good way of comparing the heat softening characteristic of thermoplastics.

Water Absorption (ASTM D570)

Various plastics absorb varying amounts of water and the presence of absorbed water may affect plastics in different ways.

Electrical properties change most noticeable with water absorption, and this is one of the reason that polyethylene, since it absorbs almost no water, is highly favored as a dielectrics materials which absorb relatively large amount of water tend to change dimension in the process. When dimension stability is required in products made of such materials, grades with lesser tendencies to absorb water are chosen. The resistance of plastic materials to water varies significantly according to their chemical nature and if filled or reinforced.

Differential Thermal Analysis (DTA)

DTA is an instrumental technique for assessing the effects of heat on a small sample. As the temperature of the furnace containing the sample is increased in controlled manner, a thermocouple in the furnace records the response there in, whether the differential is zero (i.e. no effect other that of heating), negative (i.e. endothermic reaction taking place) or positive (i.e. exothermic reaction taking place). Thermocouple dip into the materials in the cell and the temperature (T) of the test sample and the temperature differential (DT) between this and the inert material are fed in e.m.f from to a recorder to plot AT against T (Ives, 1971).

CHAPTER THREE

MATERIALS AND METHOD

3.1 MATERIALS USED

The reagents used include: chloroform, ethanol, petroleum ether, concentrated sulphuric acid, acetic acid, acetic anhydride, glycerol and ethylene glycol were obtained from the British Drug House. The equipment used include: Brookfield's Viscometer (Brookfield Engineering Lab, Inc. Middleboro, MA, USA), pH Meter (CRISON micropH 2000, Spain), FTIR-8400S Fourier Transform Infrared Spectrophotometer and GCMS-QP2010 plus Shimadzu Japan.

3.2 COLLECTION AND PURIFICATION

The trunk of the tree *Acacia senegal* in Zaria Petropolis was incised and the gum exudates were allowed to dry and then handpicked from the trees. The dried gum was washed and dried in hot air oven at 40^0C for 48hours. The gum was then crushed to break up and then hydrated in double strength chloroform water for five days with intermittent stirring. The mucilage obtained was strained through a clean calico cloth and the gum was precipitated using 95%w/v ethanol. The precipitate gum was filtered, washed with diethyl ether then dried in hot air oven. The dried gum was pulverized and passed through sieve size No 60 (250um), (Oluyemisi et al, 2010).

3.3 CHARACTERIZATION

3.3.1 Percentage Yield

The dried and purified gum obtained was weighed and the percentage yield was expressed using weight of the crude gum as denominator.

$$percent\ yeild = \frac{wt\ of\ dry\ prified\ gum}{wt\ of\ crude\ gum}\ X\ 100$$

3.3.2 pH Determination

The pH of 1% w/v of the pure and modified gums was determined with a microprocessor based pH Meter (Model 1012, Esico, Mumbai, India). The pH meter was set to neutral at room temperature and the electrode was immersed into the solution.

3.3.3 Viscosity Measurement

2% w/v of dry gum and each gum modification were prepared and then diluted to concentrations of 1.81, 1.67, 1.54, 1.42, 1.33, 1.25, 1.17, 1.11, 1.05, and 1.0% w/v. the viscosities of the different concentrations were determined using Brookfield viscometer (Engineering Lab Inc., Middleboro, MA, USA.)

3.3.4 Moisture Content

This measures the water content of the samples. The method described by AOAC (1984) was adopted for this measurement. 2g of the gum was weighed into a pre-heated, cooled and weighed silica dish. The sample was then dried in an oven at a regulated temperature of 80^{o}C to a constant weight. The moisture was determined as percentage moisture given by

$$Moisture = \frac{wt\ of\ sample\ before\ drying - wt\ of\ sample\ after\ drying}{wt\ of\ sample\ taken}\ X\ 100$$

3.3.5 Ash Content

2g of defatted gum Arabic samples were accurately weighed into labeled crucibles, placed in a muffle furnace and ashed (incenerated) at 600^{o}C for three hours. At the end of the ashing period, the ashed sample was removed into a dessicator to cool down to room temperature and reweighed.

$$\%ash = \frac{wt\ of\ crucible\ and\ ah - wt\ of\ crucible}{wt\ of\ sample}\ X\ 100$$

3.3.6 Determination of Crude Protein

1g of the gum was weighed and introduced into the bottom of 500ml kjeldahl's flask. 20ml of concentrated sulphuric acid was added and mixed gently by swirling under tap water. 10g of NaSO4 and 1g of CuSO4 were mixed and 3g of this was introduced into the flask. Also little anti-bumping chips were added into the mixture. The mixture was boiled gently in the kjeldahl's flask in a fume cupboard until a clear green solution is obtained. The heater was turned off and the solution allowed to cool. The digest mixture was made up to the 100ml with distilled water in a 100ml volumetric flask.

10ml of 20% boric acid was measured out into 250ml beaker and four drops of indicator was added. 10ml of the digest was placed in the distillation flask. 30ml of 40% NaOH was added to the 10ml of the digest slowly from a syringe. The heating system was switched on and heating continued for 25minutes. The receiver beaker was removed and the distillate titrated with 0.1N until the end point (Amadi *et al*, 2004).

Calculation: $$\%protein = \frac{1.4 \times x \times D.F \times 100 \times 6.25}{original\ wt\ of\ sample\ (mg)}$$

i.e $\%N \times 6.25$

$$\%N = \frac{1.4 \times x \times D.F \times 100}{original\ wt\ of\ sample\ (mg)}$$

$$Dilution\ factor = \frac{100}{10}$$

3.3.7 Percentage Lipid Determination

This is done by the gravimetric method of AOAC (1984). 5g sample will be introduced into a clean, dried 500ml round bottom flask (W1) and 300ml of petroleum ether (40-60^{o}C) for the extraction will be poured into the flask fitted with soxhlet extraction unit. The round bottom flask and a condenser will then be connected to the soxhlet extractor and cold water

circulation will be put on. The heating mantle will be switched on and heating rate adjusted until the solvent reflux at a steady rate.

This process will be carried out for six hours. The solvent will be recovered and the oil dried in an oven at 70oC for one hour. The round bottom flask and oil will be left to cool and then weighed (W2). The lipid content is calculated using the relation below.

$$\%crude\ lipid\ content = \frac{W_2 - W_1}{Wt\ of\ sample}\ X\ 100$$

3.3.8 Total Carbohydrate Content

This measures the carbohydrate content and in most cases includes the fibre content of the sample. This was conveniently done by the difference method i.e.

$$Total = 100 - (\%lipid + \%moisture + \%ash + \%protein)$$

(Amadi *et al.*, 2004)

3.3.9 Internal Energy

This calculates the energy value of the sample. The energy value was calculated by the factors of 4, 9, 4 as reported by Onyeika et al, 2000. Here, the value of protein content was multiplied by 4; that of lipid by 9 and that of total carbohydrates by 4. The sum of these values was expressed in kcal/100g sample. This was the energy value of the sample.

3.3.10 Melting Point

A melting point capillary was used. A tiny sample of the gum powder was placed on a piece of weighing paper. The open end of the capillary was pushed down into the pile. A small amount of the sample then went into the open end. The closed end of the capillary was rap sharply on the bench top two or three times. A few crystals of the compound were placed in a thin walled capillary tube 10-15cm long, about 1 mm in inside diameter, and closed at one end. The capillary, which contains the sample, and a thermometer are then

suspended so they can be heated slowly and evenly. The temperature range over which the sample was observed to melt is taken as the melting point.

3.3.11 Density Measurement

Density analysis of 1%w/v of the test sample was carried out using a density bottle. The weight of the empty bottle was measured (W) and then weight of the bottle with 70ml of the test sample as W1). The difference was taken to get the actual weight of the liquid, this weight was divided by the volume to obtain the density.

3.3.12 Ftir Analysis

FTIR is commonly used for qualitative identification of various functionalities. The FTIR spectrum of the powdered gum was recorded with a Perkin Elmer RXI spectrophotometer (Connecticut, USA). The dry powder was mixed with KBr and pressed into pellets. The spectrum was obtained by scanning between 4000 and 500/cm.

3.3.13 GC-MS

GC-MS analysis was carried out on a GC clarus 500 Perkin Elmer system comprising a AOC-20i autosampler 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 1μM df, composed of 100% Dimethylpoly 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 μI was employed (split ratio of 10:1) injector temperature 250 ºC;ion-source temperature 280 ºC. The oven temperature was programmed from 110 ºC (isothermal for 2 min), with an increase of 10 ºC/min, to 200ºC, then 5ıC/min to 280ºC, ending with a 9min isothermal at 280ºC. Mass

spectra were taken at 70 eV; a scan interval of 0.5 seconds and fragments from 40 to 450 Da. Total GC running time is 36minutes.

3.4 GUM MODIFICATION

Both chemical and physical modifications were carried out on the gum Arabic.

3.4.1 Chemical Modification

This was performed by acid hydrolysis, acetolysis, and acetate formation.

1. **Acid hydrolysis**

63g of the gum powder was weighed into a beaker and diluted with 90ml distilled water to obtain 70%w/v. 20.5 g of concentrated sulphuric acid (corresponding to 10 weight percent of the dry gum Arabic in the stock) was then added to the weighed stock and held at 70^0C for four hours with continous stirring using a regulator hot plate magnetic stirrer.

2. **Acetolysis**

1:1 (weight/weight) ratio of acetic acid and acetic anhydride was thoroughly mixed in a round bottom flask. Thereafter, concentrated sulphuric acid, corresponding to 3%w/v of the mixture was added to the mixture. This mixture was known as the acetolyser.

63g of the gum was weighed in a beaker and diluted with 90ml distilled water. 20.5g of the acetolyser was then added to the stock and the temperature being held at 70^0C for four hours, after which the mixture was left to cool to ambient temperature.

3. **Acetate formation**

For this modification, 63g of the dried gum was weighed into a beaker and diluted with 90ml distilled water to obtain 70%w/v. 20.5g of acetic anhydride was then added

to the stock. The mixture was held at 70^0C for four hours after which it was left to cool to room temperature.

3.4.2 Physical Modification

The physical modification involves mixing the gum Arabic with two different compounds viz: glycerol and ethylene glycol.

1. **Glycerol**

   70 weight percent of the gum was prepared in a beaker at 70^oC. 20.5g of glycerol was thoroughly mixed with the concentrated stock and allowed to cool to room temperature.

2. **Ethylene glycol**

   Ethylene glycol (BDH) was used as received. A similar procedure to that of glycerol was employed for the plasticization of gum Arabic with ethylene glycol.

3.5 PVC FORMULATION

Different proportions of the gum Arabic and PVC by weight were weighed to give different proportion by percentage: (PVC: GA), 100%:0%, 90%:10%, 80%:20%, 70%:30%, 60%:40%, 50%:50%, 40%:60%, 30%:70%, 20%:80%, and 10%:90%. Each of these formulations was used for film casting using tetrahydrofuran, (THF) as solvent.

3.6 FILM CASTING

Each formulation was in $30cm^3$ of tetrahydrofuran. The resulting solution was stirred vigorously and allowed to stand on a water bath for 30 minutes while stirring before it was poured in to a clean dry 8.50cm Petri dishes. The dishes were kept on a flat surface in a fume cup board and allowed to stand for the solvent to evaporate. The film were removed by pouring distilled water sufficiently enough to cover the film surface and allowed to stand for

few minutes after which it was removed using spatula. Thereafter, the films were dried by blotting then between filter papers and allowed to dry in a dessicator for 48 hours before taken for mechanical property testing.

3.7 MECHANICAL PROPERTY TESTING

Honsfield tensometer testing machine was employed for this determination by the method of ASTM D-882. From the plot of stress-strain curves, the ultimate tensile strength, modulus of elasticity and elongation at break for each film was calculated.

Stress at break was evaluated using the following equation;

$$\tau_b = \frac{F}{A}$$

Where A is the cross-sectional area of the sample and F is the applied tensile force. The elongation at break was calculated using the following equation.

$$\Delta L_b = \left(\frac{L' - L_0}{L_0}\right) \text{ X } 100$$

Where, L' is the length of the sample at break and L_0 is the initial length. The modulus of elasticity was evaluated using the equation below.

$$\varepsilon = \frac{\tau_y}{(L-L_0)/L_0}$$

Where L is the length of sample at yield and τ_y is the stress at yield (Elgozali and Hassan, 2008).

3.8 PERCENT WATER ABSORPTION

This was carried out according to ASTM D570. The specimens were dried in an oven for 24hours at 50^{o}C and then placed in a dessicator to cool. Immediately upon cooling the specimens were weighed. The materials were then immersed in water at 25^{0}C for 24hours.specimens were removed, patted dry with lint free cloth and weighed.

Percentage water absorption = $\left[{(wet\ weight - dry\ weight)}/{dry\ weight} \right] \times 100$

CHAPTER FOUR

RESULTS AND DISCUSSION

Plasticizer is a compound incorporated in a polymer matrix to lower its rigidity and improve the properties of the commercial plastic product. Therefore, addition of the plasticizer often lowers the melt viscosity, glass transition temperature and the elastic modulus of the polymer. In a simplified way, properties and affects of a plasticizer can be compared with those of a solvent. A solvent (or *plasticizer*) for a given polymer may be judged by either of two separate standards, one kinetic and the other thermodynamic. A kinetically good solvent (*plasticizer*) is one that will dissolve (*in*) the polymer rapidly. In the thermodynamic sense, a good solvent (*plasticizer*) must be capable of strong interactions with the polymer. Thermodynamics dictate that a compound will be a solvent for a particular polymer when the free energy of solution, F is negative. The factors which contribute to the free energy of solution temperature, T, enthalpy, H, and entropy, S, are related by the familiar equation

$$\Delta F = \Delta H - T\Delta S$$

Because of the many degrees of local motion permitted to an amorphous polymer, its entropy of solution usually is small but positive, and the sign of ΔF depends upon the magnitude of ΔH. The enthalpy of mixing, i.e., the overall heat of mixing for two liquids is given by the Hildebrand's equation:

$$\Delta H = \phi s \phi p(\delta s - \delta p)$$

Where ϕs and ϕp are the volume fractions of the solvent and polymer, respectively and δs and δp are their respective solubility parameters. It is obvious that as (δs-δp) approaches

0, dissolution, incorporation of the plasticizer in the polymer matrix is assured by the entropy factor. One may therefore conclude that as a requirement for the solubility of polymer P in a solvent S, or *vice-versa* when the plasticizer is substituted for the solvent, δs-δp has to be small.

4.1 PROXIMATE ANALYSIS OF PURE GUM ARABIC

The table 4.1 below shows the proximate results of the gum Arabic. The moisture content of the gum was found to be 13.9% which is within the standard international specification reported in literature by (FAO, 1990). The moisture content facilitates the solubility of gum Arabic carbohydrate hydrophilic and hydrophobic proteins. The ash content determined for the gum is 3.45%, which indicates a high level of foreign matter. The ash content may be used to determine amount of insoluble matter in acid, magnesium, potassium and calcium (Mocak et al., 1998). The protein content was calculated from percentage nitrogen by means of the factor (N×6.25) as reported by Debon and Teste, (2001). The nitrogen content was 0.36 and therefore 2.25% was calculated as the protein content. These values however are slightly lower than the ones reported by Yusuf (2011). This may be due to the fact that gums vary depending on the origin and age of the tree, the exudation time, the storage time and climate and experimental errors.

Table 4.1: proximate analysis of the pure gum Arabic.

S/N	PROPERTY	VALUE
1	Moisture	13.9%
2	Ash	3.45%
3	Nitrogen	0.36%
4	Protein	2.25%

5	Crude Lipid	1%
6	Crude Fibre	7%
7	Carbohydrate	79.14%
8	Internal Energy	334.56(kcal/100g)

4.2 PHYSICOCHEMICAL ANALYSIS OF GUM SAMPLES

The samples were found to be odorless and tasteless. Their conductivity, TDS and salinity were measured using a conductivity meter. For all the test samples, AHY and ACT have the highest values with AHY going extremely high. It records 12.1‰, 20.6mS/cm and 11750mg/L for salinity, conductivity and TDS respectively. ACT follows next with 0.3‰, 685µS/cm and 335mg/L for salinity conductivity and TDS respectively. The values for all other samples are low as compared to AHY and ACT. This was due to formation of potassium, magnesium and calcium salts during their modification. The trend for salinity, conductivity and TDS for all the samples is AHY>ACT>AAH>PGM>EGL>GLY.

The texture of the gums was also observed. PGM, AAN and ACT appeared solid and were ground to powder. EGL was solid but oily due to the nature of ethylene glycol. GLY looked sticky or semi-solid. AHY was completely a dark liquid.

Table 4.2 physicochemical parameters of the pure gum as well as the gum modifications.

Parameter	ACT	AHY	EGL	AAH	GLY	PGM
Salinity(‰)	0.3	12.1	0.1	0.2	0.1	0.2
Conductivity(µS/cm)	685	20.6	308	421	261	383
TDS(mg/L)	335	11750	149.8	205	124	177.5
Turbidity	40	485	258	71	68	83
Colour	Buff	black	Ash	jasmine	Brown	White
Texture	Solid	liquid	Solid(oily)	solid	Sticky	Solid
Density	0.9944	1.0116	1.0086	1.0113	0.9951	1.0159
M.P(^{0}C)	234		242	229		245
pH	3.78	1.19	4.37	4.1	5.31	4.24

AAN



GLY



ACT



PGM



EGL



AHY



plate 4.1: photographs of the pure gum Arabic (PGM) and each gum modification, acid hydrolysis modified (AHY), Ethylene glycol modified (EGL), Glycerol modified (GLY), Acetolysing mixture modified (ACT), Acetic anhydride modified (AAN).

Turbidity is an optical characteristic of a liquid which in general terms describes the clarity of a liquid. It is always based on human observation. The trend for turbidity measurement is AHY>EGL>PGM>AAH>GLY.

pH is the measure of acidity of a sample. The pH of the pure gum and that of the modifications were quiet below 5.00, except for glycerol modified which was 5.31 at room temperature. This indicates acidic nature, because gums are generally macromolecular acids (Odeku and Fell, 2004). AHY sample is the most acidic with pH value of 1.19. This is due to the concentrated acid used in its modification. The pH value of pure gum Arabic (4.24) is in good agreement with reported pH values for gum Arabic and other *Acacia* gums by several authors. The acidity of plant gums is not unexpected since many of them are known to contain salts (Ca, Mg, K, Na and Fe) of acidic polysaccharides, the acidity of which is due to uronic acids in their structures (Abu Baker *et al.,* 2007; Ahmed *et al.,* 2009; Elnour *et al.,* 2009).

Melting point analysis of the samples was carried out but the result of AHY and EGL could not be presented due to their nature. AHY was a liquid and EGL appeared very sticky and therefore could not go down the capillary tube. The pure gum has the highest melting point. This is possibly due to the fact that the modification is believed to have led to smaller side chains which might enhance chain flexibility. The melting temperature range of 229-245 0C (all samples) suggests that the gum samples were of good thermal stability. However, high melting temperature was likely due to the heterogeneous and polydisperse nature of the unfractionated gum Arabic exudate, composition-wise (Yusuf, 2011)

Density is all about the compactness in molecular arrangement in any substance which decides how heavier or lighter any substance is. Density is the thickness in which

molecules are packed. Density measurement of the samples shows they have higher densities than water. The result indicates that the gum modifications have lower density values than the pure gum sample (PGM). This is not unexpected as the modification of the gums may have caused possible bond scission resulting in the formation of low molecular weight oligomers. Fig 4.5 below shows how densities of the various samples compare with each other.

Viscosity is a measure of the resistance of a fluid to flow. 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 macro-molecules. Viscosity of gum solutions at room temperature was found to depend on gum concentration. This relationship is also depicted in (Table 4.3). The viscosities of aqueous dispersions containing different concentrations (2 to 0.01%w/v) of pure gum Arabic and that of the modified gums were determined. The table below shows comparison between the viscosities of the gums at each concentration. When concentration was varied for each gum, the viscosities of the solutions increased with increasing concentration. Increase in viscosity with concentration is probably due to increasing number of high molecular weight polymeric chains of the gums per unit volume and increased interaction between these chains in aqueous solution or dispersion (Yusuf, 2011). At each concentration the viscosity of AHY is far below that of the other samples, this is attributed to the fact that acid hydrolysis of polysaccharides normally breaks polysaccharides down to their monomers, dimers and some oligosaccharides (Bockkov and Zaikov, 1979). The products of this hydrolysis are low viscosity liquids. The acid hydrolysis is believed to fragment the molecules by cleaving bonds other than the (1 – 6) which is the most resistant to acid hydrolysis (Guthrie, 1974).

Table 4.3: Viscosity of the test samples at different concentrations

S/N	CONC.(g/ml)	VISCOSITIES (mpas/sec)					
		PGM	EGL	GLY	ACT	AAH	AHY
1	0.01	26.4	22.8	24	23.4	33.6	13.2
2	0.0105	26.4	22.8	24.6	24	34	14.4
3	0.0111	27.6	24	24.6	24	36	14.4
4	0.0117	27.6	24	25.2	24	36	14.4
5	0.0125	28.8	24	25.2	25.2	38.4	14.4
6	0.0133	28.8	24	25.2	24	38.4	15.6
7	0.0142	30	24	25.2	24	39.6	18
8	0.0154	31.2	24.6	25.8	25.2	43.2	19.2
9	0.0167	31.2	25.2	25.8	25.2	43.8	19.2
10	0.0181	32.4	25.8	26.4	27.6	46.8	19.2
11	0.02	33.6	27.6	27.6	28.8	50.5	21.6

4.3 FTIR OF ANALYSIS OF TEST SAMPLES

FTIR spectroscopy has been proved to be a useful technique for characterization of intermolecular interactions between groups in self-polymer or different polymer molecules in blend systems. These intermolecular interactions, mainly hydrogen bonding and dipole–dipole interaction, lead to either shifts in frequency or changes in absorbance of specific functional groups (Fekete, 2005).

Fig. 4.6 is the FTIR of pure gum Arabic. The wave number 605.67cm^{-1} is a C-H bending vibration of RC=CR alkynes. 705.02cm^{-1} and 769.63cm^{-1} are the C-H out of plane vibrations of trans RCH=CHR alkenes. 1157.33cm^{-1} is typical of C-H wag of alkyl halides. The C-H rock vibration is associated with 1356cm^{-1}. The wave numbers 2727.44cm^{-1} and 2764.09cm^{-1} represent RCHOC-H functional group of aldehydes. The bands 3469.09cm^{-1} and 3553.96cm^{-1} are consequence of the presence of O-H groups. 1715cm^{-1} denote C=O stretch of carbonyls. These functional groups are present in materials like carbohydrates, starch and some other natural gums (Malik *et al.*, 2002).

For the acetolysing mixture modification, several shifts were observed as shown in Fig. 4.7. The C-H bend and C-O stretch at 605.97cm^{-1} and 1004.95cm^{-1} were shifted to 601.81cm^{-1} and 1053.17cm^{-1} respectively. N-O aromatic at 1276.92cm^{-1} was shifted to 1253.77cm^{-1}, N-H out of plane vibration was shifted from 1601.93cm^{-1} to 1630.87cm^{-1}, 1715.74cm^{-1} C=O stretch was shifted to 1734.06cm^{-1}. Isocyanides absorbing at 2153.59cm^{-1} were shifted to 2142.02cm^{-1} while the O-H stretch of alcohols was shifted from 3469.09cm^{-1} to 3471.46cm^{-1}. New bonds were formed at 1397.47cm^{-1}, 2357.09cm^{-1} and 2929cm^{-1}.

In AAN sample (Fig. 4.8), the shifts include; C-H bend in alkynes was shifted from 605.67cm^{-1} to 591.2cm^{-1}. 1004.95cm^{-1} stretch of carboxylic acid was shifted to 1052.2cm^{-1}.

N-O aromatics at 1276.92cm^{-1} and N-H out of plane at 1601.93cm^{-1} were shifted to 1253.77cm^{-1} and 1630.87cm^{-1} respectively. A shift was also seen in the absorption frequency of isocyanides from 2153.59cm^{-1} in PGM to 2145.88cm^{-1} in AAN. O-H alcohols also were shifted to 3418cm^{-1}.

The AHY modified gum Arabic shows different absorption frequencies as compared to those of ACT and AAN (as shown in Fig. 4.9). In this sample the only shift seen was from 1004.95cm^{-1} to 1053.17cm^{-1} for C-O stretch. Most of the peaks observed are for entirely new bonds. These are 1202.66cm^{-1}, 883.43cm$^{-1,}$ 2946.36cm^{-1}, 1653.05cm^{-1} and 3946.49cm$^{-1.}$

The FTIR of the modified gums revealed frequencies and peaks due to interaction between the solvents and gum Arabic matrix. The results obtained indicate the presence of several functional groups arising from the formation of new bonds and shifts in frequencies when compared to those deduced from the pure gum Arabic.

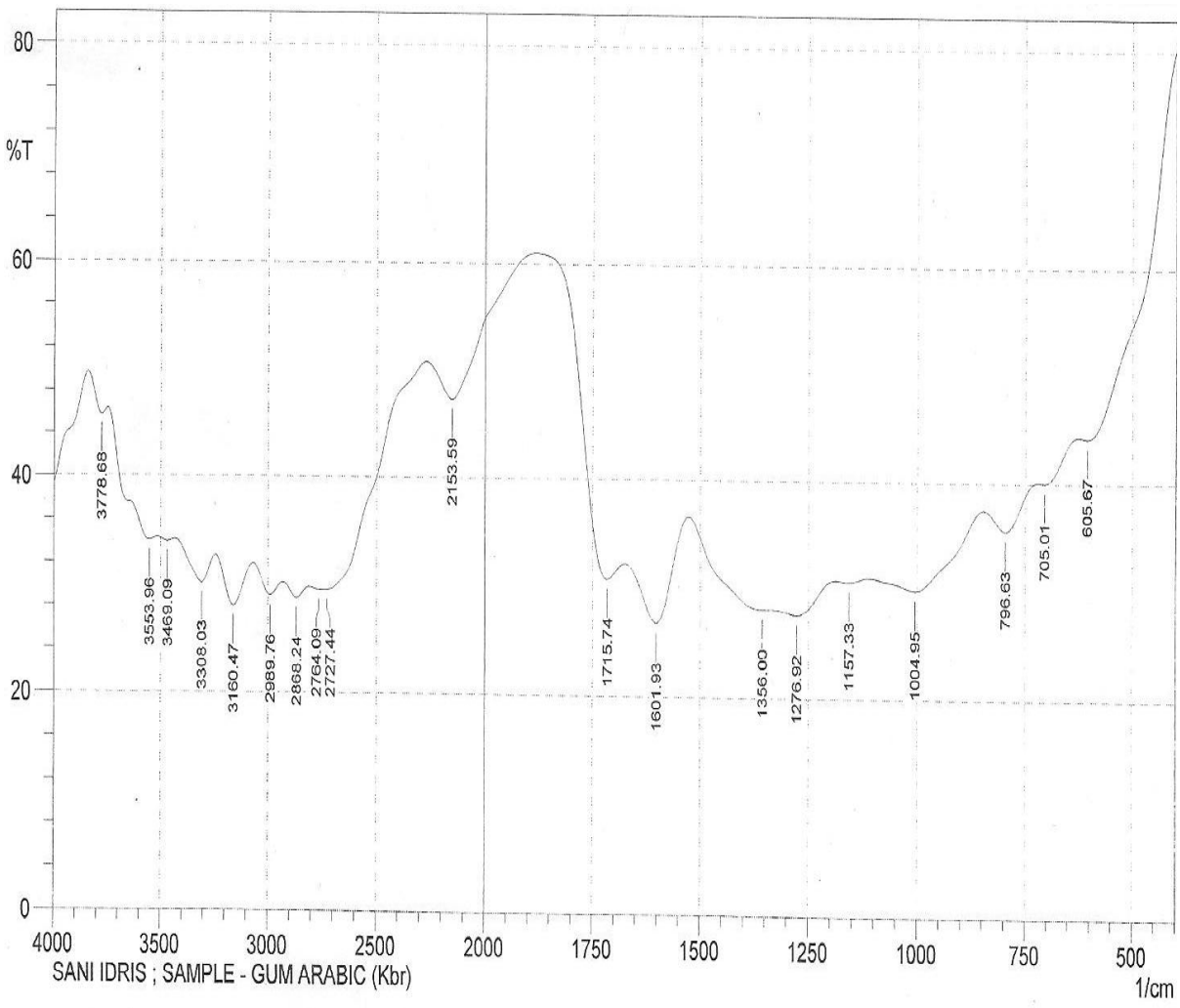


Fig 4.6: FTIR spectra of pure gum Arabic

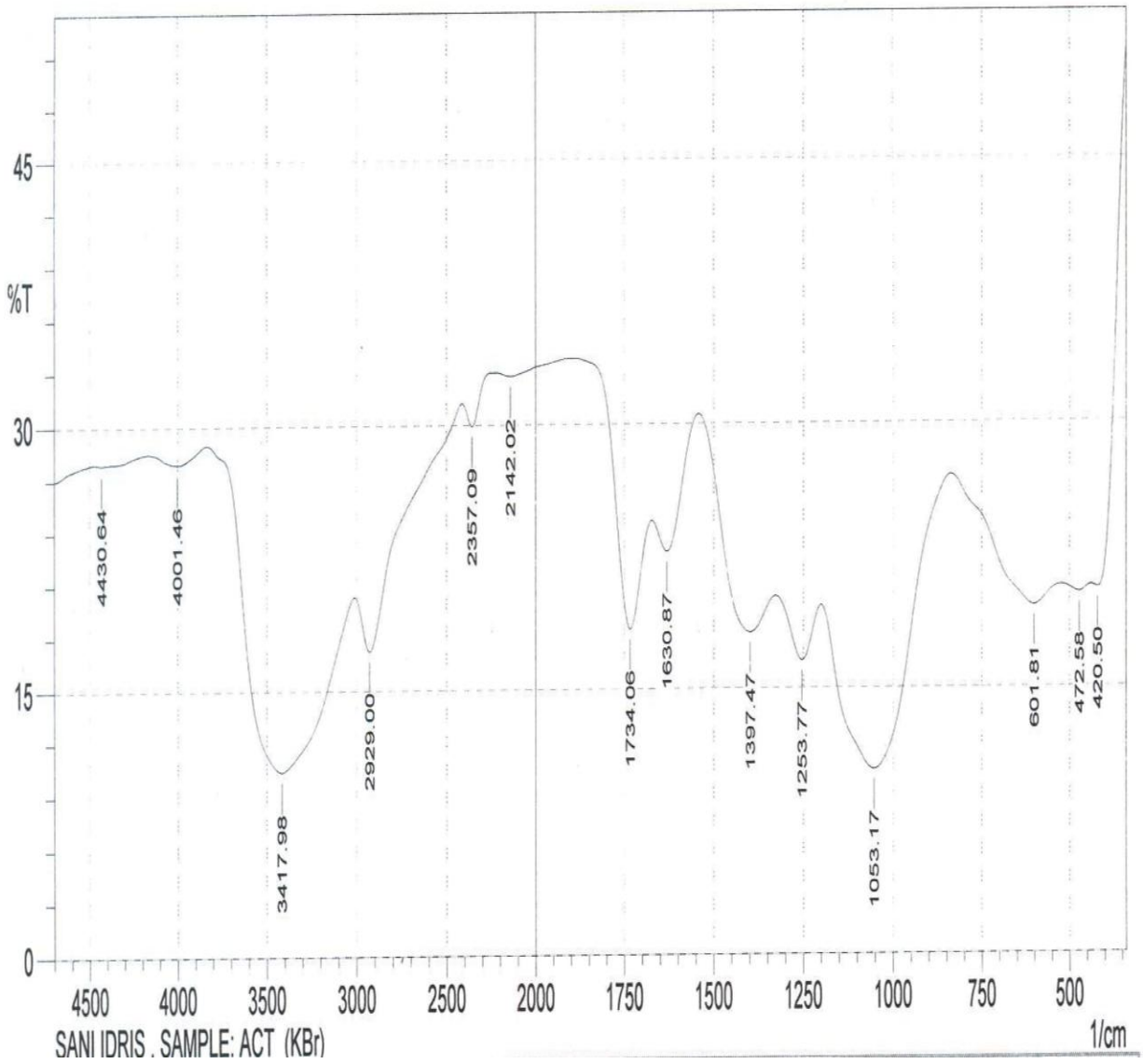


Fig 4.7: FTIR Spectra for Acetolysis gum modification (ACT)

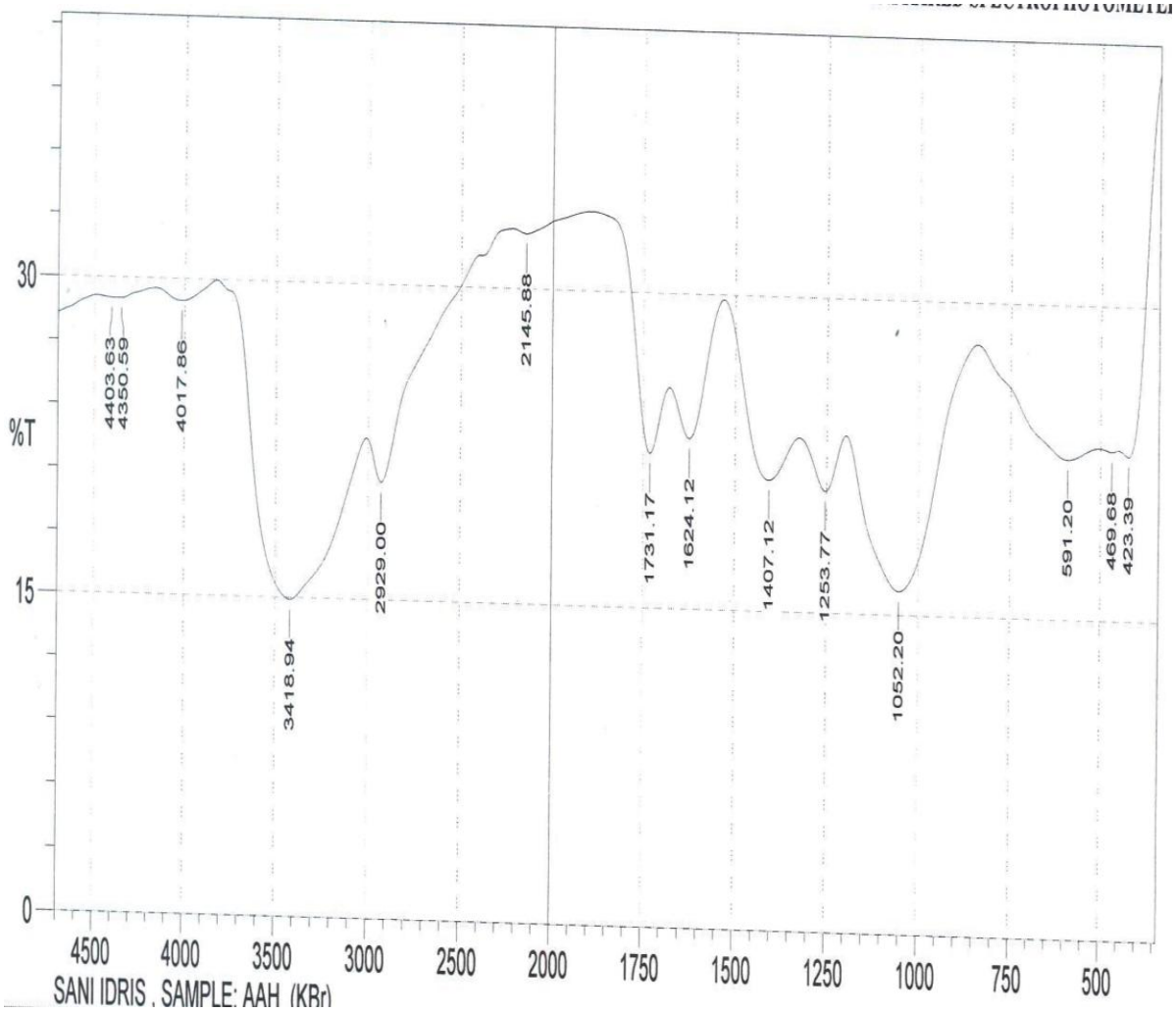


Fig 4.8: FTIR Spectra for Acetic anhydride gum Modification (AAN)

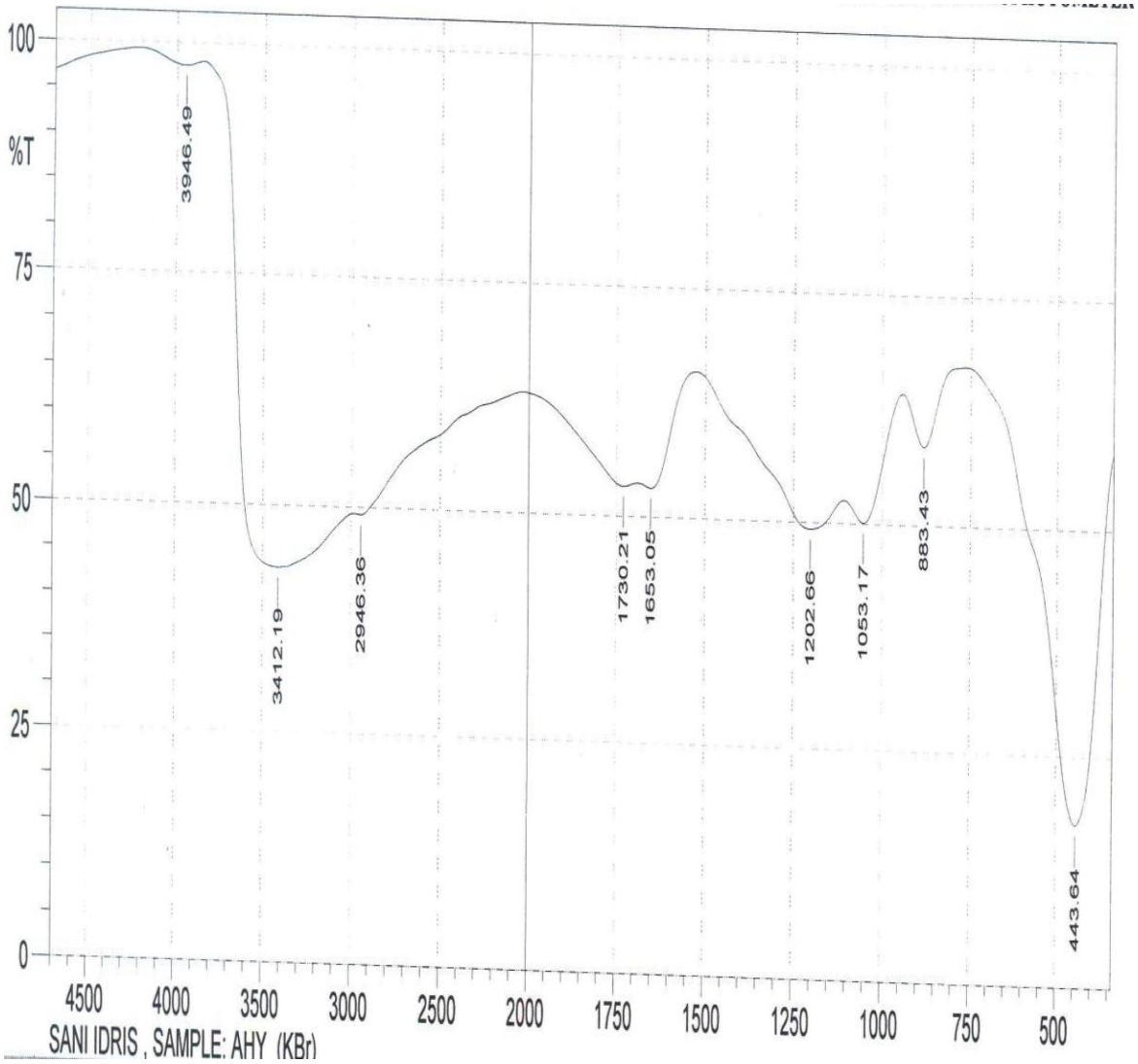


Fig 4.9: FTIR Spectra for acid hydrolysis gum modification (AHY)

4.4 GC/MS

The GC-MS spectra of PGM gum is shown in Fig. 4.10. The retention time (RT), IUPAC names of the compounds suggested by reliable spectral library, molecular weight (MW) and charge to mass ratio (m/z) are presented in Table 4.8. Since the area under a GC spectrum is proportional to concentration, area normalization of the peaks were carried out and used for estimation of percentage concentration (% C) of the respective constituent of the gums. Height normalization was also carried out and the results obtained for percentage concentration based on height normalization were comparable to those obtained from area normalization GC-MS spectra of the gum Arabic revealed 6peaks. From the results presented, it is shown that the most abundant compound is 9-octadecenoic acid which constitutes about 37.33%, then followed by 1-pentadecanecarboxylic acid with 23.77%. The least in abundance is Hydroxypropanone with 2.14%.

4.4.1 GC-MS of Gum Modifications

The GC-MS analysis of the gum modifications produced different peaks from that of the pure gum Arabic. The ACT modification showed four peaks, (Fig. 4.11). The set of compounds produced are: 2-butyn-1-ol (36.6%), 3-butyn-2-ol (28.95%), oxalic acid (21.14%) and 1,2-dimethyldiazene-1-oxide (13.31%). Acetylenic alcohol containing OH and triple bonds such as 3-butyn-2-ol and 2-butyn-1-ol are applicable in corrosion inhibition

formulation, metal complex solutions, solvent stabilizer and biodegradable chemical intermediate.

Fig. 4.12 is the GC-MS spectra of acetic anhydride. It showed only three peaks AAN. Acetyl cyanide has the highest percentage (44.46%), Ethylisopropyl methylborane (37.99%) and 1,2-dimethyldiazene-1-oxide (17.55%). 1,2-dimethyldiazene-1-oxide compound is common in both ACT and AAN GC-MS spectra

AHY has eight peaks in it GC-MS spectra, Fig 4.13. The possible compounds produced by this sample include; 2-furancarboxaldehyde (28.16%), 6-methyl-1-heptanol (26.19%), 2-flouropropene (15.53%), 5-methyl-2-furancarboxaldehyde (10.57%) and 1-(p-toluidino)-1-deoxy-beta-didopyranose (8.29%), these are the most abundant ones, all others are below 6%. Furfural being the most abundant compound is also derived from a variety of agricultural byproducts including corn, oat, wheat and saw dust. It participates in the same kind of reactions as other aldehydes and other aromatic compounds. When heated in the presence of acids, furfural irreversibly solidifies into a hard thermosetting resin.

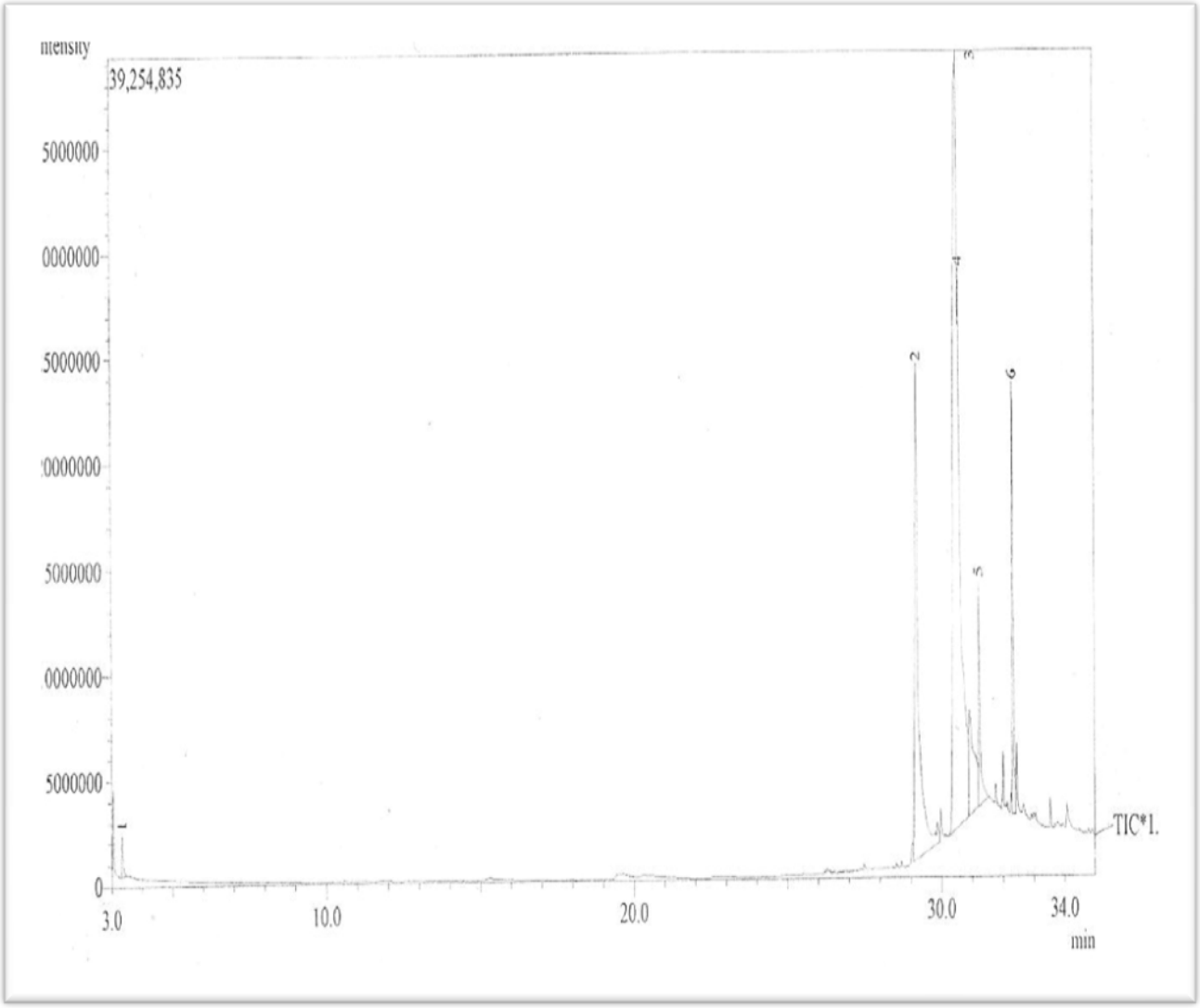


Fig 4.10: GC-MS of pure gum arabic (PGM)

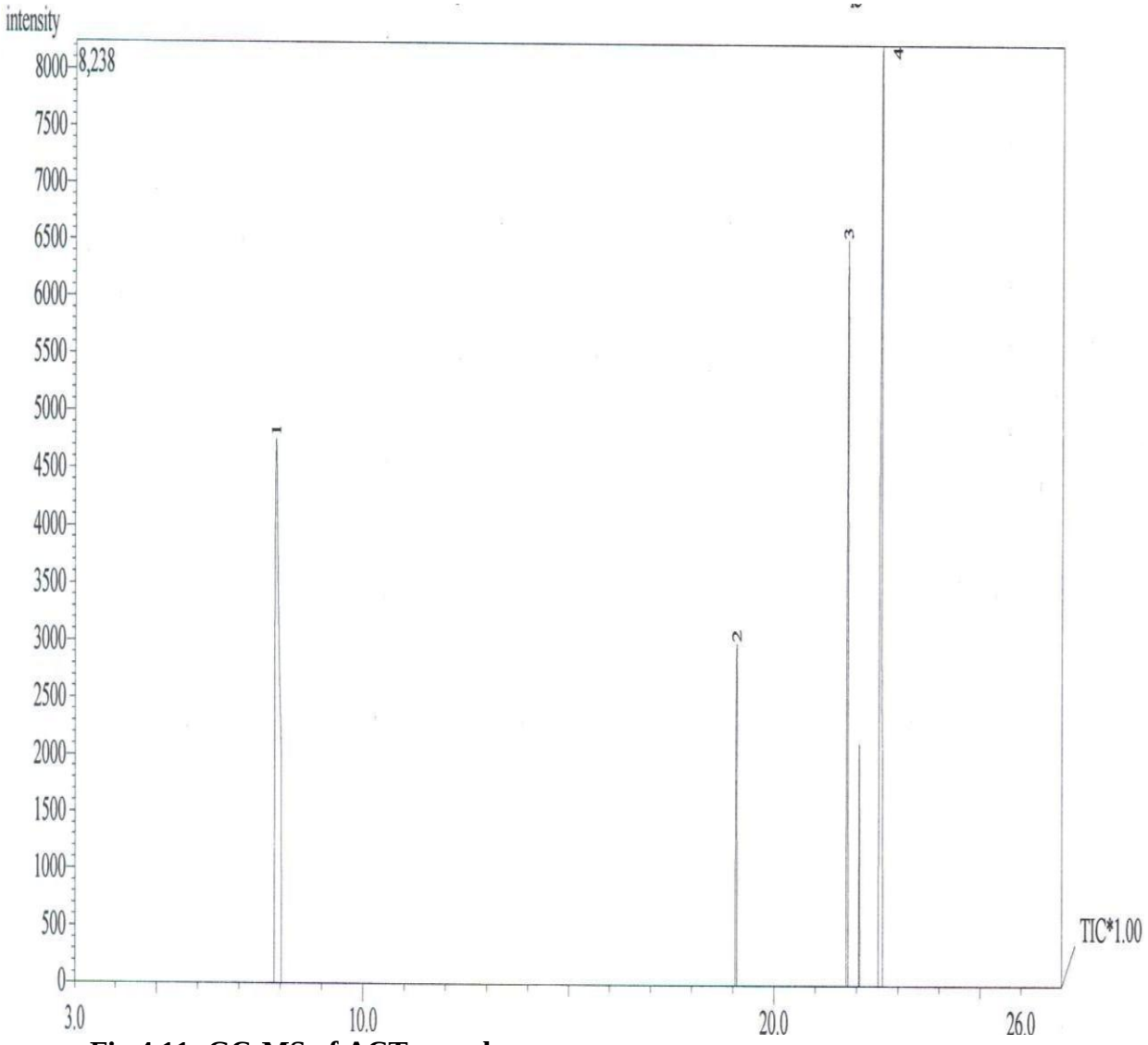


Fig 4.11: GC-MS of ACT sample

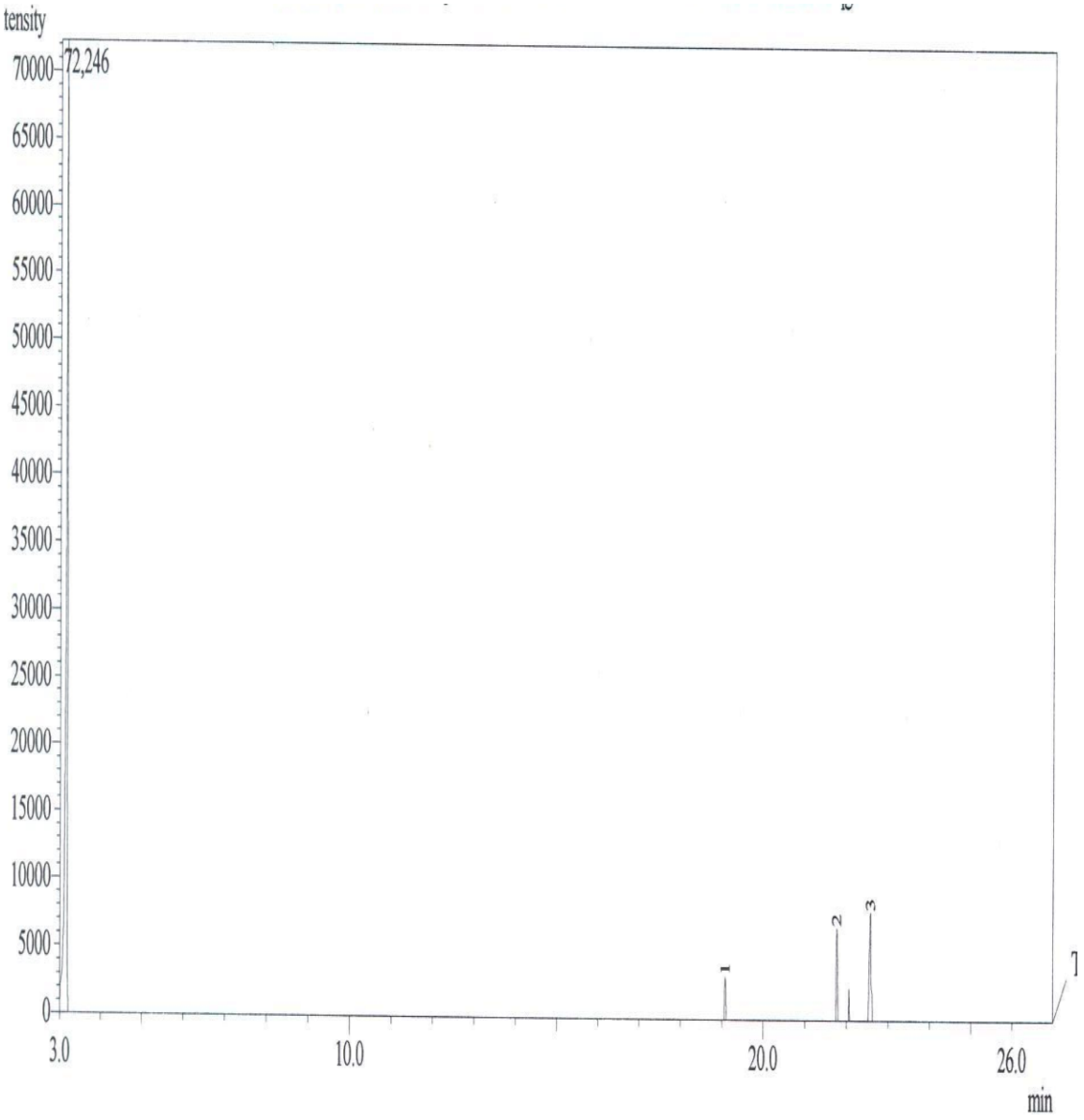


Fig 4.12: GC-MS of AAN sample

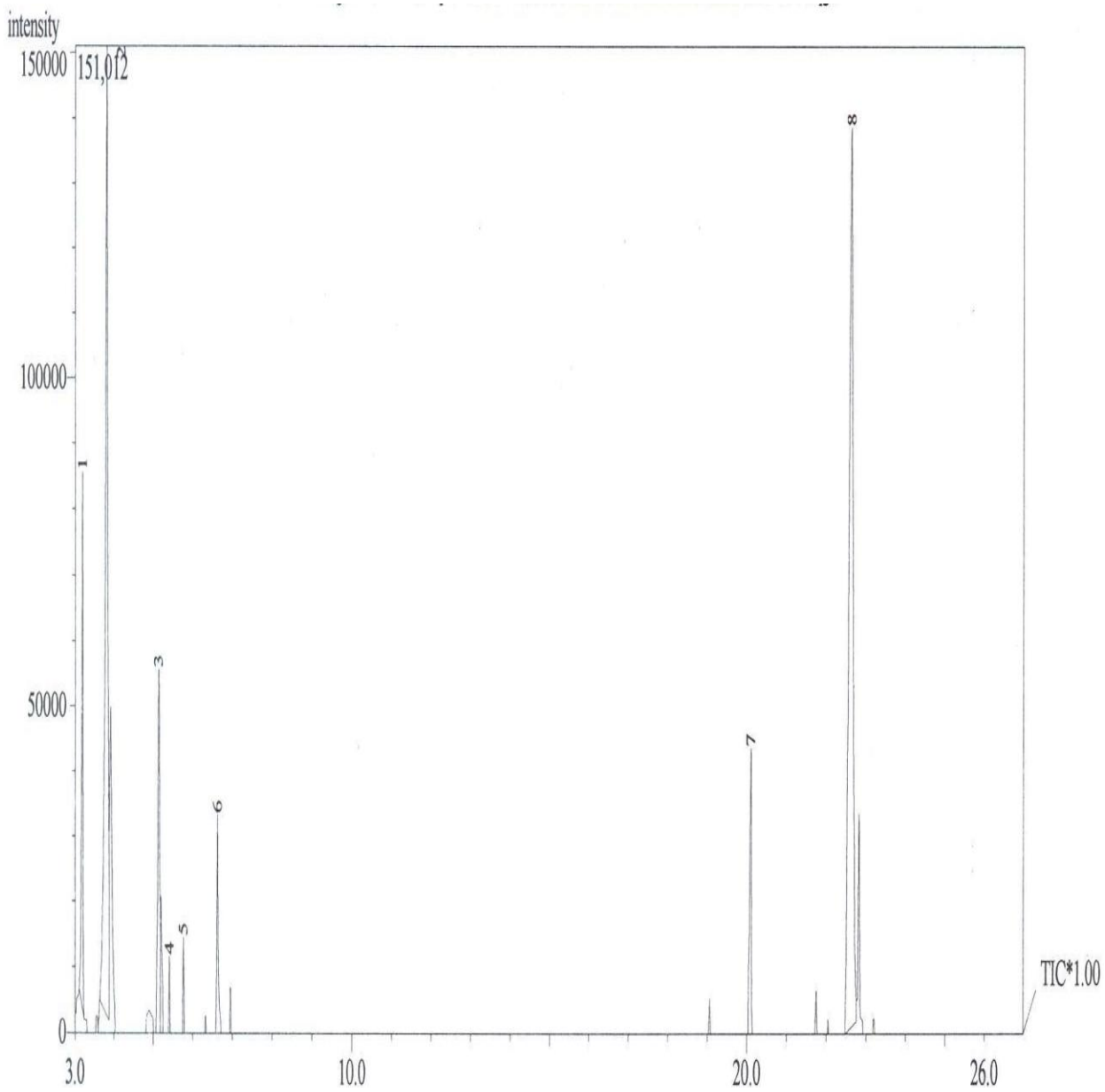


Fig 4.13: GC-MS of AHY sample

4.5 WATER ABSORPTION

The water absorption test shows that ACT modified gum absorbs water the most as shown in Fig 4.14. The next to it is EGL, followed by AAN. At 10/90, 20/80% and 30/70% (PVC/GUM) ratio, AAN samples have the lowest water absorption. However at higher compositions of gum, PGM samples showed lower absorption values than AAN. At 50/50%, ACT and PGM showed a drop in absorption. Generally, the result shows that the water absorption of the formulations increases with increasing concentration of gum sample. This behavior was expected since the water absorption of these formulations is mainly due to the presence of the gum; because the PVC matrix absorbs little water while the gum Arabic contains numerous hydroxyl groups (-OH), which are available for interaction with water molecules by hydrogen bonding. The fact that water absorption was observed, this suggests that the gum Arabic satisfactorily encapsulated the water in the PVC matrix, suggesting that no significant changes occur in the microstructure of the composite.

4.6 MECHANICAL PROPERTIES

Mechanical properties were carried out to study the tensile properties of polymer blend films and they become important as polymer technology moves from laboratory into process development. It is well known that mechanical properties might be used to assess the miscibility in polymer blends through a comparison of experimental results and predictions based on various models. Indeed, the mechanical properties of polymer blends depend on the intermolecular forces, chain stiffness, and molecular symmetry of the individual polymers used to prepare the blend (Mudigoudra *et al.*, 2012).

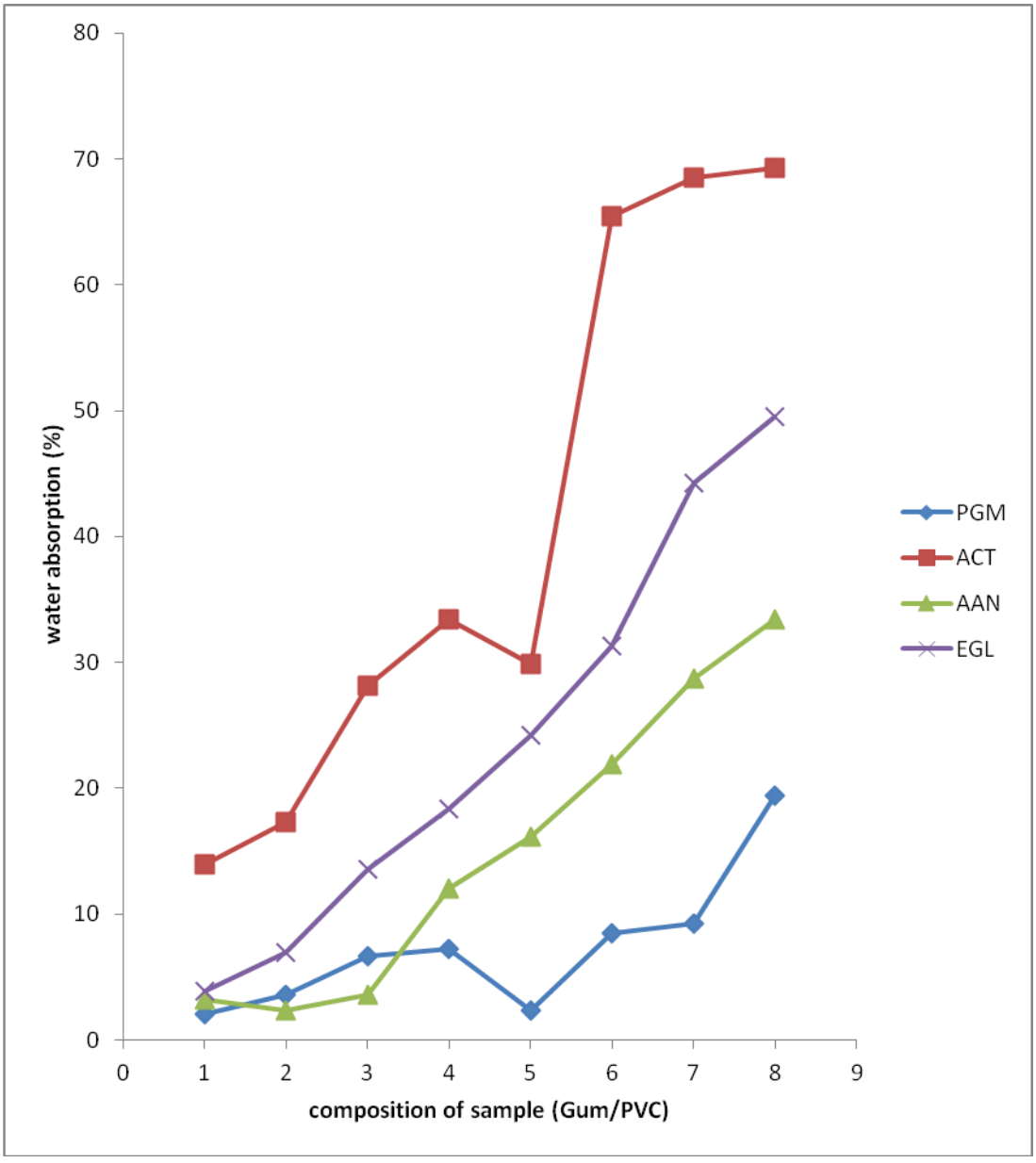


Fig 4.14: percent water absorption of test samples at various composition.

4.6.1 Tensile strength

The tensile strength of the three modified gums show different results from that of the pure gum arabic. This is revealed in fig 4.15. The tensile strength of the pure gum (PGM) records 18.8 at 90%/10% PVC/gum, it drops to 14 at 80%/20% PVC/gum and rises again to 16 at 70%/20% PVC/gum. It then continues to drop as the percentage of the gum increases tending towards zero. In EGL sample, 20.5 was recorded as the highest strength at 90%/10% PVC/gum. The value drops to 14. 2 at 80%/20% PVC/gum and increases again to 16.9 at 70%/30%. The tensile strength decreased afterwards as the percent composition of the gum increases. ACT and AAN modified materials increases with the addition of gum to the PVC matrix and increases as the amount of gum increases to a point in which the PVC can no longer support the gum. This is where the tensile properties of the formulations begin the drop, approaching zero. The results shows that there is an increase in the polymer chain length, and also cross linking of the polymer chains as the amount of modified gum increases, forming a system of interpenetrating network (IPN). This was responsible for the increase in the tensile strength as observed, whereas, PGM and EGL shows a decrease in tensile strength as the amount of the filler is increased. The plasticizer forms links with the PVC molecules and acts as a spacer between molecules of the PVC. Due to this linkage, gum Arabic has a positive effect on the mechanical properties of the polymer. It was stated that dipole interaction which occurs between polar groups of chlorine atom in PVC resin and free hydroxyl, ester, amino, etc groups in gum Arabic stand for polar group in the plasticizer. The bond forces of the polymer atoms strengthened due to the linkage established and thus free volume decreases with the addition of gum Arabic to the polymer which leads to increasing tensile strength. In the above cases, it shows that the tensile

strength of the materials increases with increase in the amount of gum Arabic; this is attributed to its polarity which increased the cohesive energy density, such that the materials tend to be held together more tightly resulting in induced mobility and flexibility.

The expected results from the chemical modifications are based on the fragmentation pattern from the gum Arabic after chemical treatment. The stress-strain curve exhibited by the gum Arabic could be linked to its relatively high molecular weight in addition to the rigid backbone. Possession of branch linkages would also add to the rigid nature of the gum. The result of this is that when cast into a film, it is very brittle and thus its main drawback in adhesion formulations. Therefore it is believed that scission of these linkages might result in low molecular weight structures which will reduce the rigidity inherent in the structure. There are two main structural linkages that are susceptible to bond scission. These are the main backbone chain of (1-3) linked D-galactopyranose units and the branching or substitution of these units at the C-6 position with various side chains.

The branch (1-6) linkages are, however, easily broken by acetolysis. The acetolysed gum Arabic was observed to exhibit lower values of tensile strength than pure gum arabic. This may be because scissions in the acetolysed system occurred at branch points. The effect is debranching which results in reduction of chain rigidity and proper re-allignment of molecules.

The result observed for the acetate derivative (AAN) of the gum Arabic also showed debranching of the chains. The effect is, however, more pronounced than the acetolysed samples, probably because of the acetate group. The re-allignment of the molecules with the polar nature of acetate group might have increased the intermolecular force of attraction, the result of which is tougher material than the untreated gum Arabic also. It is therefore

suggested that the acetate group is capable of increasing the modulus of rigidity and increase the strain at break of the gum Arabic.

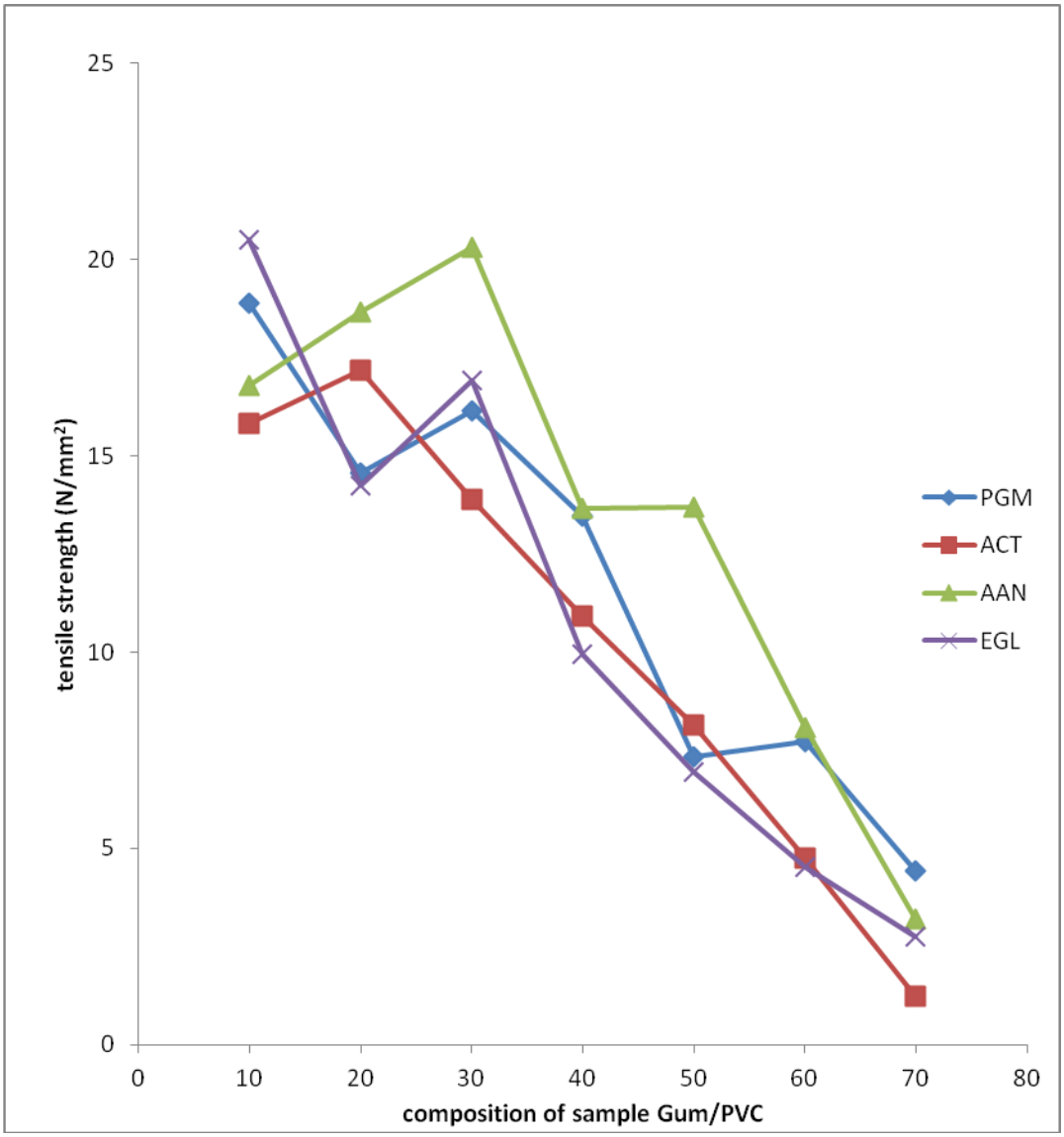


Fig 4.15: tensile strength of test samples at various compositions.

From the result also, EGL being a physically modified gum has a similarity in trend with the pure gum sample. While the chemically modified gums i.e ACT and AAN are also similar in trend. The presence of PVC is believed to increase the strength of the blend due to interlocking of the polymeric chains as well as the dipole-dipole interaction between O-H groups in the gum samples and C-Cl groups in PVC (Kim et al, 1997)

The results have shown that the structure-property typical of the unplasticized gum Arabic can be modified by the addition of plasticizing agents. The effect of the chemically modified additives was significant in the increase in values for ultimate tensile strength to a maximum value before decreasing. While the physically modified sample (EGL) does not show this property.

4.6.2 Elastic Modulus

The tensile stress data show the maximum stress supported by the plastics. The tensile stress decreased as the gum Arabic content increased. Fig 4.16 gives the elastic Young`s modulus of all the test samples. This implies that the modified gums have improved upon the pure gum Arabic. The AAN modification has the highest elastic modulus of 180.15N/m^2 at 10/90 gum/PVC and it becomes fairly constant at 30/70 and 40/60 gum/PVC composition. ACT is the next with 177N/m^2 at 10/90 gum/PVC ratio but it begins to drop as the gum concentration increases except at 30/70 gum/PVC composition where it shows a slight increase. The value for EGL records 164, still a higher value than the pure gum samples. It can be observed that the sample with the best modulus is AAN and the composition that showed good elastic behavior is 30/70 gum/PVC.

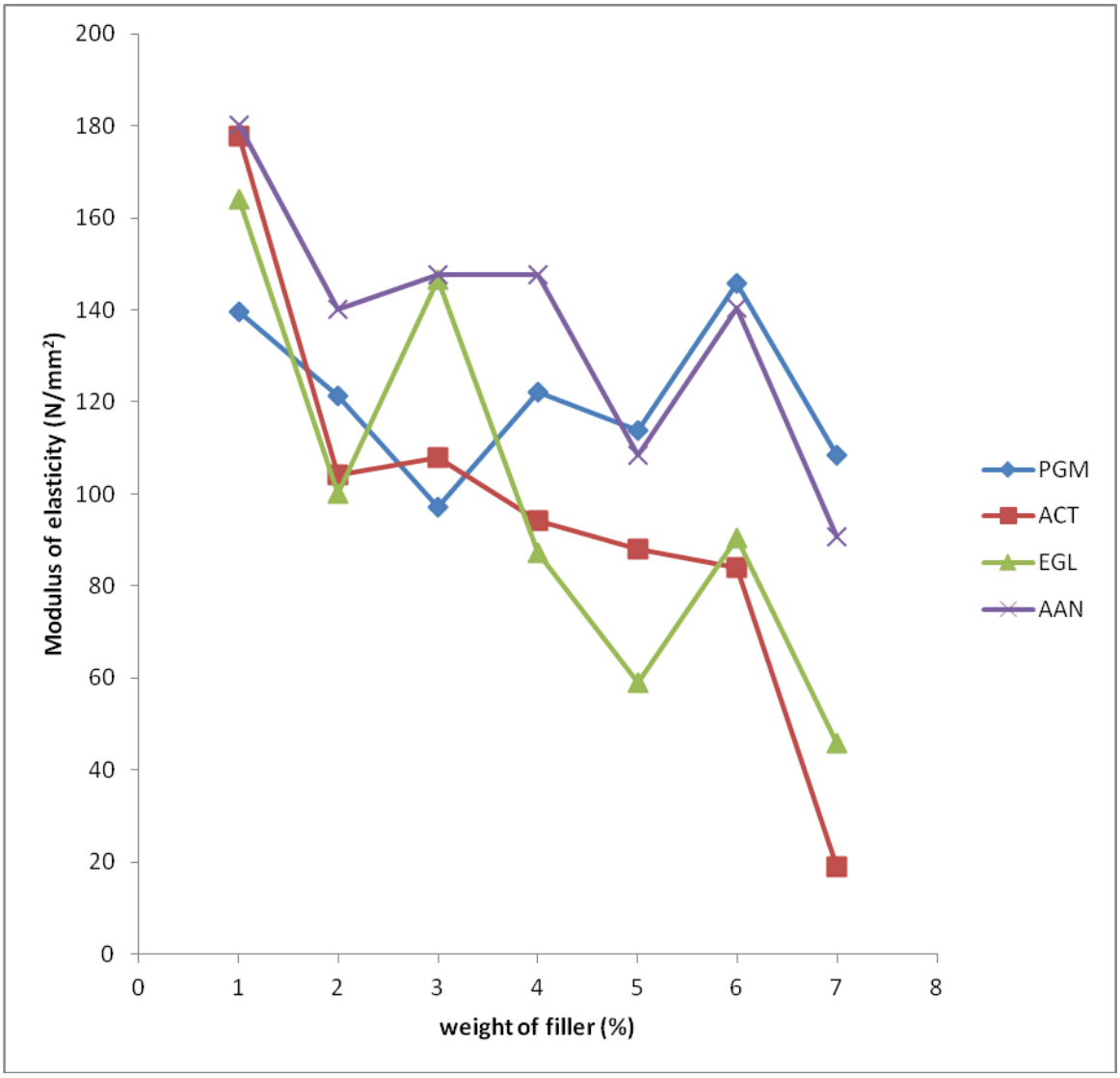


Fig 4.16: modulus of elasticity of the test samples at varying weight percent of filler

4.6.3 Percentage Elongation of the Samples

Fig. 4.17 shows comparism between pure gum sample and gum modification formulations at different compositions. At 10/90 and 20/80 gum/PVC all modified gums have higher values than the pure gum Arabic. At 30/70 however the pure gum Arabic records 17.8% while all other samples record values below that. At 50/50%, similar values of 12 and 12.3% were recorded for PGM and AAN, respectively. On comparism, the percent elongation of test sample depends on the composition, though chemically modified formulations show similarity in trend.

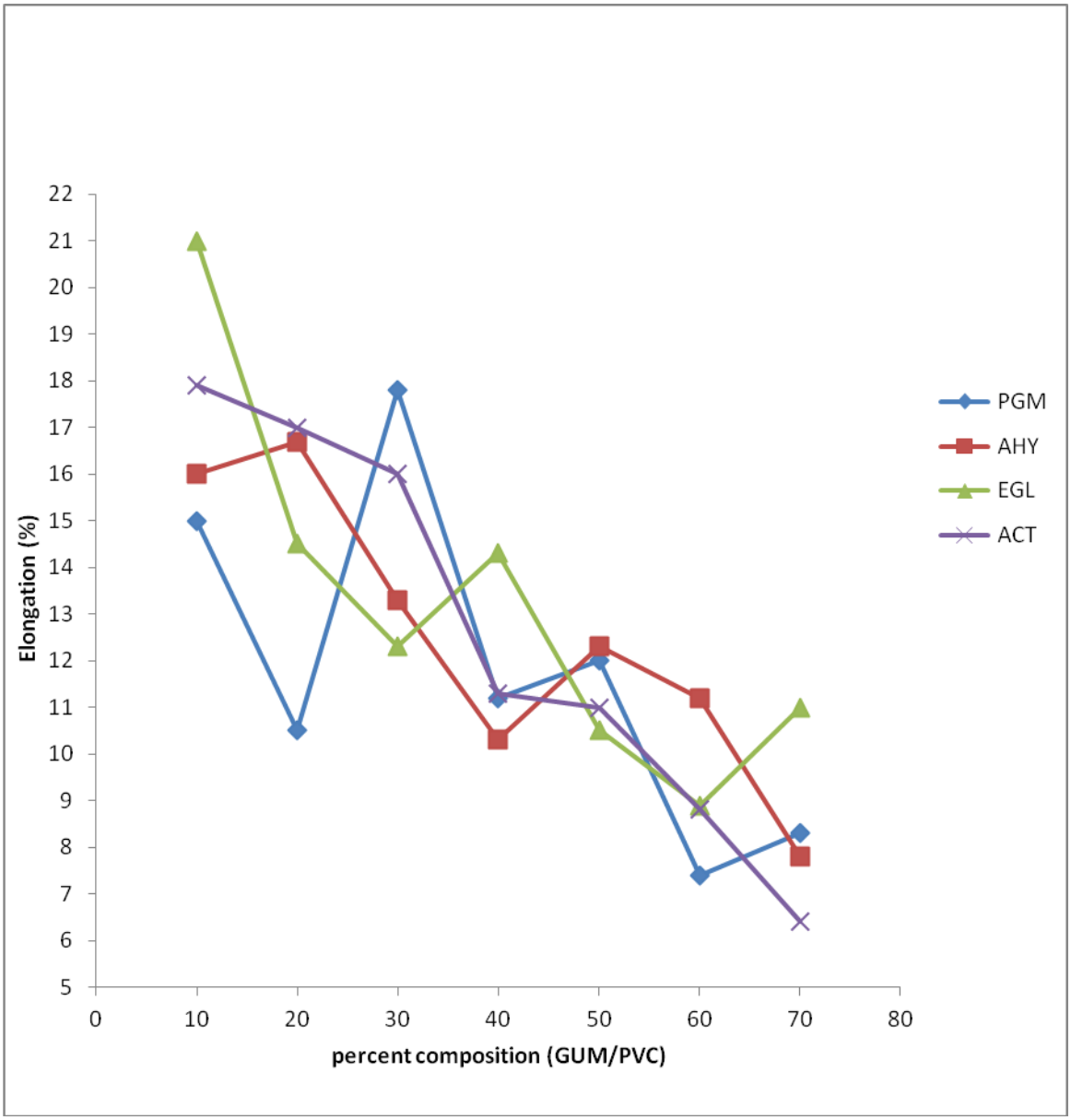


Fig 4.17: Graph of percent elongation of the test samples at varying composition.

CHAPTER FIVE

CONCLUSION

The characterization of the samples shows that the pure gum has the highest density as well as melting point. The pH measurement of the samples revealed that all the gums are acidic having pH values below 7.0. Trend in viscousity measurements at different concentrations indicate that the viscosity increases with increasing concentration of the samples, with AAN sample having highest values for all compositions. AHY samples record higher values for conductivity, salinity and TDS. FTIR and GC-MS spectra show that shifts observed in the modified gums as well as absorption at different frequencies provide evidence for the occurrence of modification of the pure gum.

Water absorption results of the samples show ACT has the highest water absorption capacity (Fig. 4.14). There are fluctuations in absorption depending on the composition of the sample, but the general trend is that absorption increases with increasing gum concentration.

The AAN sample has the highest modulus at 10, 20, 30 and 40% gum composition. For PGM the modulus drops from 10-30% gum composition then finally increases. The ACT modification shows decrease in modulus as the percent of gum increases. Modulus of PGM drops at 20, 40, 60 and 80% gum composition.

This study revealed that the tensile strength of the chemically modified formulations shows similarity in trend, while the physically modified formulation also shows similarity in trend with the pure gum formulation. ACT and AAN formulations show high strength at 10%/90%, 20%/80% and 30%/70% for AAN and 10%/90% and 20%/80% for ACT before generally decreasing. This was not the case for EGL and PGM formulation which show decrease in tensile strength as the composition of gum increases.

On comparative effectiveness, the chemical modifications showed reinforcement in the PVC matrix, while the physical modification showed plasticizing property due to decrease in tensile strength as the percentage of gum increases. The AAN sample at 30%/70% Gum/PVC composition was found to be the strongest with overall best adhesive property.

RECOMMENDATION

Natural biopolymers such as gum Arabic have shown more promising properties when used as filler/plasticizer in a PVC matrix. It is suggested that further research in reological and degredation aspect would shade more light on the compatibility of the gum not only to PVC but to other plastic polymers as well. Also another solvent apart from THF should be considered.

REFERENCES

Abdel-Ghani, S. A., Madkour, T. M., Osman, H. M. and Mohammed, R. A. (2000). Study of the Electrical Properties and Swelling Mechanism in Compressed Butyl Rubber Loaded with Carbon Black. *Egyptian Journal of Solids,* 23(2).

Ahmad, Z., Al-Awadi, N. A., and Al-Sagheer, F. (2008). Thermal Degredation Studies in Poly(vinyl chloride)/poly(methyl methacrylate) Blends. *Journal of Polymer Degredation and Stability* 93; 456-465.

Al-Assaf, S., Phillip, G. O., Williams, P. A. (2005). Studies on acacia exudates gums, part 1: the molecular weight of acacia Senegal gum exudates. *Food Hydrocolloids*. 19, 647-660.

Allsop, M. W. (1981). Development and Importance of Suspension PVC Morphology. *Pure and Applied Chemistry Journal*, volume 53(2), 449-465.

Amadi, B. A., Agomuo, E. N. and Ibegbulem, C. O. (2004). *Research Methods In Biochemistry*. Supreme Publishers, pp.105-110.

American Academy of Pediatrics, AAP, (1999). Polychlorinated biphenyls, dibenzofurans, and dibenzodioxins. In: *Handbook of Pediatric Environmental Health*. (eds. Etzel R. A and Balk S. J) AAP, Elk Grove Village, pp.215-222.

Anderson, D. M. W., Miller, J. R. A., Weiping Wang, (1999). Gum Arabic (acacia Senegal): Unambigious identification by ^{13}C-NMR Spectroscopy as adjunct to the revised JECFA specification, and the application of ^{13}C-NMR for regulatory/registratory purposes. *Food Additives and Contaminants*. 8, 405-421.

Anonymous (1984). Association of Official Analytical Chemists (AOAC) *Official Mathods of Analysis* (14th edition.). Washington D. C.

Anonymous, (1990). Food and Agricultural Organization of the United Nations (FAO). Specifications for identity and purity of certain food additives; *Food and Nutrition Paper,* 49; FAO: Rome.

Anonymous, (2002), Federal Department of Agriculture, (FDA) *Baseline survey on gum arabic*., Abuja, Nigeria, pp. 4-10.

Anonymous, (2003) United States Environmental Protection Agency (USEPA), *Exposure and human health assessment for 2,3,7,8-Tetrachlorodibenzo-p-Dioxin (TCDD) and related compounds, part III: integrated summary and risk characterization for 2,3,7,8-Tetrachlorodibenzo-p-Dioxin(TCDD) and Related Compounds.* Washington, DC.

Anonymous, (2005) Centers for Disease Control and Prevention (CDCP).. *Third national report on human exposure to environmental chemicals.* Atlanta, GA: CDC.

Aoba, T., (2004). Solubility Properties of Human tooth Mineral and Pathogenesis of Dental Caries. *Oral Diseases*. 10, 249-257.

Arshady, R. (1992). "Suspension, Emulsion, and Dispersion Polymerization: A Methodological Survey". *Colloid Polymer Science Journal* . 270: 717–732. doi:10.1007/BF00776142

ASTM D882 Test method for tensile properties of thin plastic sheeting (strip tensile) http://www.geosynthetic-institute.org (accessed on 17th February 2013)

Baird, D. G., and Collias, D. I. (1998), "*Polymer Processing*" in Encyclopeadia of Polymer Science and Technology, third edition, pp.611-643.

Balakrishnan, B. and Jayakrishnan, A. (2005), "Chemical Modification of Polyvinyl Chloride Using Poly (ethylene glycol) to Improve Blood Compatibity", *Elsevier Journal of Biomaterials*, 27(17) pp. 3495-3502.

Baltacioglu H, Balkose D. (1999). "Effect of zinc stearate and/or epoxidized soybean oil on gelation and thermal stability of PVC–DOP plastigels". *Journal of Applied Polymer Science*, 74: 2488-2498.

Biruiana E.C., Barbinta V.T., and Caraculacu A.A, (1997), *European Polymer Journal* p.13,311.

Blanco, A. (2000). Polyolefins: Mergers & Acquisitions Define the Future.*Society of Plastic Engineers*. 56(5): 41.

Bochkov A. F., and Zaikov G. E, (1979), "*Chemistry of the O-Glycosidic Bond: Formation and Cleavage*", Pergamon Press, New York.

Bossie J, (1977), *Journal of Applied Polymer Science*, pp.21, 85.

Bovey F.A., Abbas K.B., Schilling F.C.and Starnes W.H., (1975), *Macromolecules*, pp.8, 437.

Brydson J.A. (2000). *Plastics Materials.* 7th Eddition. Elsevier, Oxford, England.

Calame, W., Weseler, A. R., Viebke, C.,Flynn, C., and Siemensma, A. D., (2008), *British Journal of Nutrition*. 9, 1-7.

Chanda, M., Roy, S. K. (2006). *Plastics technology handbook*. CRC Press. p. 1–6. ISBN 978-0-8493-7039-7.

Chao, Y. W., Xiu, Y. Q., Yong, Z. H. and Yin, X. Z. (2003), "structures and Mechanical Properties of PVC/Na^+ Montmorillonite Nanocomposites", *Chinese Chemical Letters*, volume 14, No. 4, 417-418.

Charles, E. W., James, W. S., Charles, A. D., and Mark, T. B., (2005), *"PVC Handbook*", Published by Hanser Verlag, Munich, London. 95-244.

Cheng, K. K., Chalmers, I., Sheldon, T. A., (2007). Adding Floride to Water Supplies. *British Medical Journal,* 335, 699-702.

Cofimau J. D.,Ann., (1953). N.Y. Acad. Sci. pp.57, 417.

Cohan G. F (1975), "Industrial Preparation of Poly (vinyl chloride)", *Environmental Health Perspectives,* Vol. 11, p 57.

Creech and Johnson; Johnson, NM (1974), "Angiosarcoma of liver in the manufacture of polyvinyl chloride", *Journal of occupational medicine*, 16 (3): 150-1. PMID 4856325 (http://www.ncbi.nlm.nih.gov/pubmed/4856325).

Czegeny Z., Jakab E., Blazso M., Bhaskar T., and Sakata Y., (2012) " Thermal decomposition of Polymer Mixture of PVC, PET and ABS Containing Brominated Flame Retardant: Formtion of Chlorinated and Brominated Organic Compounds", *Journal of Analytical and Applied Sciences* 96, 69-77.

Darricades-Llauro M.F.and Co-workers, (1986), *J. Makromol. Sci. Chem.* pp.23, 121, 221.

Debon S. J. J and Tester R. F (2001), *Food chemistry.,* 73, 401 doi: 10.1016/S0308-8146 (00) 00312-5

Demir, H. Sipahioglu, M. Balkose, D. and Ulku,S. (2008), "Effect of Additives on Flexible PVC Foam Formation", *Journal of Material Processing Technology*, volume 195, 144-153.

Diet, nutrition and the prevention of chronic diseases, (2003) *WHO Technical Report Series* 916, Report of a Joint WHO/FAO Expert Consultation, World Health Organization, Geneva, p. 88

Doi, Y., Ichihara, T., Hagiwara, A., Imai, N., Tamano, S., Orikoshi, S., Ogasawara, K., Sasaki, Y., Nakamura, M., and Shirai., T. (2006), A ninety day oral toxicity study of a new type of processed gum arabic, from acacia tree (Acacia Senegal), exudates, in F344 rats. *Food Chem. Toxicol*.44, 560-566.

Edwards, C. A., Blackburn, N. A., Creigen, L., Davison, P., Tomlin, J., Sugden, K., Johnson, I. T., (1987), "Viscousity of food gums determined in vitro related to their hypoglycemic actions". American. *Journal of Clinical Nutrition*. 46, 72-77.

Elgozali A. and Hassan M. (2008), Effects of Additives on the Mechanical Properties of Polyvinyl Chloride. *Journal of Science and Technology*, volume 9, No. 1 pp. 1-12.

Environmental Working Group (EWG). 2005. *Body Burden – the pollution in newborns.* Washington, DC. July 14.Online: http://www.ewg.org/reports/bodyburden2/execsumm.php (21 October 2010).

Espinosa-Andrews, H., Lobato-Calleros, C., Loeza- Corte, J. M., Beristain, C. T., Rodriquez-Huezo, M. E., and Vernon- Carter, E. J., (2008) Quantification of the

Composition of Gum Arabic-chitosan coacervates by HPLC, *Revista Mexicana de Ingenieria Quimica*, 7(3): 293-298.

Fekete, E., Foldes E. and Pukanszky, B. (2005), Effect of Molecular Interaction on the Miscibility and Structure of Polymer Blends. *European Polymer Journal*, 41, 727-736.

Fisch M. H., Bacaloglu R., (1999). "Mechanism of poly(vinyl chloride) stabilization". *Plastics, Rubber and Composites*, 28(3) ,p. 119-124,1999;ISSN: 14658011.

Folkes M. J., and Hope P. S., (1993), "*Polymer blends and alloy*", London: Chapman and Hall,.

Fotisch, K., Fah, J., Wuthrich, B., Altmann, F., Haustein, D., Vieths, S. (1998), "*IgE antibodies specific for carbohydrate in patient allergic to G. A. (Acacia Senegal)".* 53, 1043-1051.

Fujiwara, K., Mochida, S., Nagoshi, S., Lijima, O., Matsuzaki, Y., Takeda, S., and Aburada, M. (1995). "Regulation of heptic macrophage by oral administration of xiao- chai-hu-tang (sho-saiko-to, TJ-9) in rats. *Journal of ethnopharmacology*, 46, 107-114.

Gilbert, M. and Vyvoda, J. C. (1981), *Polymer Science Journal*, volume 22, pp. 134, Ph. D. Thesis, University of Technology, Loughborough, UK.

Gonzalez-Ortiz L. J., Arellano M., Jasso C. F., Mendizabal E., Sanchez-Pena M. J., (2005). "Thermal stability of plasticized poly (vinyl chloride) compounds stabilized with pre-heated mixtures of calcium and/or zinc stearates". *Polymer Degradation and Stabilization* 90: 154-161.

Govorchenko, V. I., Gorbatch V. I., and Ovador Y. S., (1973). "*Carbohydrate Resources*", 29, 421

Grossman, R. F. (1989). Lubricants. In John T. Lutz, Jr. *Thermoplastic PolymerAdditives*. New York: Marcel Dekker, Inc. 281-314.

Guthrie R. D., (1974), "*Introduction to Carbohydrate Chemistry*", 4th edition, Clarendon Press, Oxford.

Guyot A., (1986), Polymer Degredation and Stability, *Pure and Applied Chemistry*, 15, 205-18.

Harris, W. D. (1969), "*Measurement of Tensile Properties of Polymers*", In W. E. Brown (Ed), Testing of Polymers, volume 4, Inter Science Publication, New York.

Hassan, Y. A., Xian, X. S. and Cheng, J. S. (2002), "Ion Selective PVC Membrane Electrode for the Determination of Methacycline hydrochloride in Pharmaceutical Formation", *Sensors Journal*, *2*(10), 424-431; doi:10.3390/s21000424

Hildebrand P, Ahrens W, Brandsetter F, and Smak P., (1982), *J. Makromol Sci. Chem.*

pp.17,1093.

Hjertberg T. and Strivik E. M., (1984), Owen ed., *Degradation and stabilization of PVC,* Elsevier Applied Science Publishers, Ltd, Banking, U.K.

Hoch, M. 2001. Organotin compounds in the environment — an overview *Applied Geochemistry, Volume 16, Issues 7-8. pp 719-743.*

Ilchyshyn, A., Smith, A. G., (1985), "Sensitivity associated with epidemic hysteria dermatologica". *Contact Dermatitis.* 13, 282-283.

International Trade Center (2008) "Gum arabic" *Market News Service Bulletin,* Quarterly Edition.

Islam, A. M., Phillips, G. O., Sljivo, M. J., Williams, P. A, (1997), "A review of recent developments on the regulatory, structural and functional aspects of gum Arabic". *Food Hydrocolloids*. 11, 493-505.

Ives G.C., Caleb Brett, Mead J.A. and Riley M.M., (1971), *Hand Book of Plastic Test Method,* London Iliiffi book, pp. 101-311.

Jian, X and Zhen-Liang, X. (2002). "Poly (vinyl chloride) Hollow Fiber Ultrafiltration Membranes Prepared from PVC/Additives/Solvents", *Journal of Membrane Science,* volume 208, 203-213.

Kalfas, G., Yuan, H., and Ray, W. (1993). "Modeling and Experimental Studies of Aqueous Suspension Polymerization Processes. 2. Experiments in Batch Reactors". *Industrial and Engineering Chemistry Research.* **32**: 1831–1838. doi:10.1021/ie00021a006

Kannan, K. et al. 2010. Organotin compounds, including butyltins and octyltins, in house dust from Albany, NewYork, USA. *Archives of Environmental Contamination and Toxicology* Volume 58, Number 4, 901-907, DOI:10.1007/s00244-010-9513-6 Online: http://www.springerlink.com/content/04233043258725u0/export-citation/ (24 October 2010).

Karamalla, K.A., N.E. Siddig and M.E. Osman, (1998). Analytical data for Acacia Senegal gum samples collected between 1993 and 1995 from Sudan. *Food Hydrocolloids*, 9: 1-6.

Kauder, O. S. (1989), Stabilizers. *Thermoplastic Polymer Additives. Theory and Practice,* Marcel Dekker 437-512.

Koleske, J. K. and Wartman, L. H. (1995), "Poly (vinyl chloride)", Gordon and Breach Science publishers.

Koning C., VanDuin M., Pagnoulle C., and Jerome R. (1998) *Prog Polymer Science* 23:707±57.

Kotoulas, Costas, and Kiparissides, Costas (2006). "A Generalized Population Balance Model for the Prediction of Particle Size Distribution in Suspension Polymerization Reactors". *Chemical Engineering Science* **61**: 332–346. doi:10.1016/j.ces.2005.07.013.

Labib, M. E. and Williams, R. (1984), The Effect of Processing Additives on the Surface Properties of Polyvinyl Chloride, *Journal of Colloids and Polymer Science*, volume 37(5), pp. 340-349.

Latini, G. et al. 2003. *In Utero* exposure to Di-(2-ethylhexyl)-phthalate and human pregnancy duration. *Environmental Health Perspectives* 111:1783-1785.

Lawal A. M., (1998), Export marketing of gum arabic. The Nigerian experience. In: Proc. of "Tech. Workshop on Gum Arabic", FDA, Abuja (Nigeria), July 1998.

Liu, Y. and Zhang, C. (2007), "The Influence of Additves on Crystallization of Polyvinyl Chloride", *Journal of Wuhan University of Technology*, Material Science, volume 22(2), 271-275.

Maddanus W.F.(1984), *Degradation and Stabilization of PVC*, Elsevier Applied Science Publishers, Ltd.

Malik, H., Gupta, N. and Sarkar, A. (2002). Anisotropic electrical conduction in gum arabic—A biopolymer. *Material Science Engineering C*. 20: 215–218

Mamza P. A. P and Aliyu A., (2011) "Effect of Plasticizer on the Molecular Weight and Some Mechanical Properties of Poly (vinyl chloride)", *International Journal of Chemical Science*. 4(2).

Mamza P. A. P and Nwofo B. T., (2006) " The Swelling Behaviour of Polystyrene (PS)/Polyvinyl acetate (PVA) Blends in Different Solvents and The Effects of α-cellulose Used as Filler on the Electrical Conductivity", *Nigerian Journal of Basic and Applied Sciences* 16(2): 161 – 165.

Mamza, P. A. P. and Solomon, C. I. (2008), "Stabilization of Polyvinyl Chloride (PVC) and Effects of Acid/Base on the Mechanical Properties of PVC", *Journal of Research in physical Science,* volume 4, No. 2. 55-105.

Marcuse, R. (1960). Antioxidative effect of amino-acids. *Nature*, Vol.186, No.4728. 886-887.

Marcuse, R. (1962). "The effect of some amino acids on the oxidation of linoleic acid and its methyl ester". *Journal of the American Oil Chemists' Society*, Vol. 39, No. 97-103.

Mark F. H. (1970) *Encyclopedia of Polymer Science and Technology*, vol. 12, Interscience Publishers, New York.

Marvel C. S., and Roy, M. F., (1939). The Structure of Vinyl Polymers, Polyvinyl Halides. *Journal of American Chemical Society* 61, 3241.

Mascia L. (1974), *The Role of Additives in Plastics*, Edward Arnold, London. pp. 1-5.

Mazatusziha, B. A. (2006), "*Mechanical Properties of Rice Husk Filled Impact Modified Unplasticized Poly(vinyl chloride) Composites*", Msc Thesis, Faculty of Chemical and Natural Resource Engineering, University of Technology Malaysia.

Meehan, C. J., Olson, E. J., and Curry, R. L. (2008) Exploitation of the Pseudomyrmex–Acacia mutualism by a predominantly vegetarian jumping spider (Bagheera kiplingi). The 93rd ESA Annual Meeting (21 August 2008)

Mocak, J., Jurasek, P., Phillips, G.O, Vargas, S.; Casadei, E. & Chikamai, B.N. (1998). The classification of natural gums. X. Chemometric characterization of exudate gums that conform to the revised specification of the gum arabic for food use, and the identification of adulterants. *Food Hydrocolloids*, Vol. 12, No. 2, 141-150.

Mochida, S., Ogata, I., Hirata, K., Ohta, Y., Yamada, S., Fujiwara, K., (1990), "Provocation of massive hepatic nacrosis by endotoxin after partial hepatectomy in rats", *Europe PubMed Central ,Gastroenterology*, 99,771-777.

Mudigoudra B. S., Masti S. P. and Chougale R. B., (2012), "investigation of Mechanical Properties of Ternary Polymer PVC/PAVc/PEG Blended Films", *Research Journal of Engineering Sciences* Vol. 1(2), 63-65.

Muller M., Gellerich A. and Militz H., (2013), "Resistance of Modified Polyvilyl chloride/Wood Flour Composites to Basidiomycetes", *European Journal Of Wood Products* DOI 10.1007/s00107-01-3-0665-8

Nasir, O. D. S., (2007), "*Physiological effects of kinases, piogliazone and G.A. on renal function* ", Doctor of Philosophy in Zoology. University of Khartoum.

Nass, L. I. (1977), Encyclopedia of PVC, (Marcel Dekker, New York), 2

Odeku, O.A. and Fell, J.T. (2004). Evaluation of Khaya gum as directly compressible matrix system for cointrolled release. *Journal of Pharmacoloy.* 56: 1365-137

Okieimen F. E., Sogbaike C. E., (1995). "Thermal dehydrochlorination of poly(vinyl chloride) in the presence of jatropha seed oil". *Journal of Applied Polymer Science*, 57: 513-518.

Onishi, T., Umemura, S., Yanagawa, M., Sasaki, Y., Ogasawara, T., Ooshima, T., (2008), "Remineralization effects of gum Arabic on caries-like enamel lesions. *Archives of Oral. Biology.* 53, 257-260.

Onyeika, E. N., Ayalogu, E. O. and Ibegbulem, C. O. (2000). Evaluation Of The Nutritional Value Of Some Crude Oil Pollution Fresh Water Fishes. *Global Journal Of Pure and Applied Sciences.* 6(2): 227-233.

Osman M. E., Menzies, A. R., Williams, P. A., Phillip, G. O. and Baldwin, T. C. (1993). The molecular characterization of the polysaccharide gum from acacia Senegal. *Carbohydrate Research*, 246, 303-318.

Park, E. Y.; Murakami, H. and Matsumura, Y. (2005). "Effects of the addition of amino acidsand peptides on lipid oxidation in a powdery model system". *Journal of Agricultural and Food Chemistry*, Vol. 53, No. 21. 8334-83417.

Pedro E. S, Anotonio P., Jose M. C., Maria J. D., and Luis A. P. (2010). Kinetic Model for Thermal Dehydrochlorination of Poly (vinyl chloride). *Elsevier Polymer Journal* 51; 3998-4007.

Petiand R. and Pham Q.T., (1977),*Makromol Chem.* pp.178,741.

Phillip, G. O., (1998), "Acacia gum (G.A.): a nutritional fibre; metabolism and caloric value. Food Addit. Contam. 15, 251-264.

Quevauviller, P. 1991. Leaching of organotin compounds from poly (vinyl chloride) (PVC) material. *Applied Organometallic Chemistry* 5(2) 125–129.

Randall, R. C., Phillips, G. O., Williams, P. A., (1989). Fractionation and characterization of gum from acacia Senegal. *Food Hydrocolloids*, 3, 65-75.

Richard Pankhurst, (1990), "*An Introduction to the Medical History of Ethiopia"* Trenton: Red Sea Press, 97.

Robila R., Buruiana E.C., and Caraculacu A.A., (1977), *European Polymer Journal* pp.13, 21.

Rossberg, M. (2006). *Chlorinated hydrocarbons*" in Ulmann`s Encyclopeadia of Indusrial chemistry, Wiley-VCH, Weinheim.

Rutenberg M. W., (1968), "*Modified Starches; Water Soluble Resins*", Reinhold Publishing Corporation, New York: Edited by Davidson R. L and Sitting M.

S. Kim, J. Klempner, K. Frisch, H. Frisch, (1997), *Journal of Applied Polymer Science*. 21, 1289.

Sander, I., Raulf-Heimsoth, M., Weimer, K., Kesphol, S., Bruning, T., Merget, R., (2006), "*Sensitization due to gum Arabic (acacia Senegal): the cause of occupational allergic asthma or cross reaction of carbohydrates*? Int. Arch. Allergy Immunol. 141, 51-56.

Stephen C. B., Christopher J. K., Carol F. E., William A., James P. H., Stephanie M., Anne-Laure L., Céline C., Christophe M., Fang Y., Kevin N., Boman G. I., William L. H., and Deborah J. C., (2009), Palmitic acid mediates hypothalamic insulin resistance by altering PKC-θ subcellular localization in rodents. *Journal of Clinical Investigation*, 119(9): 2577–2589.

Tamer K., Jale Y., Mithat Y., Mehmet S., and Micheal S. (2005). "Degradation of PVC containing mixtures in the presence of HCl fixators". *Journal of Polymers and the Environment*. 13: 365 - 379.

Tester, D. A. (1973), *"Development of PVC Technology",* Applied Science Publishers, J. H. L. Henson and A. Whelan, London.

Thomas, E. F. (1975), *"Handbook of Food Additives",* second edition, published by CRC Press, London. Volume 1, pp. 311-313.

Thomas, E. W. and Todd, J. E. (1971), Additives Ins J. D. Beadle (Ed), Plastic Forming, Macmillan Press, London. pp. 15-21.

Thongpin C., Santavitee O. and Sombatsompoo N., (2006) "*Degredation Mechanism and Mechanical Properties of PVC in PVC-PE Melt Blends: Effect of Molecular Architecture, Content and MFI of PE*". Also available online at www.interscience.wiley.com

Titow, W. V. (1990). *PVC Plastics Properties, Processing, and Applications*.: Elsevier Science Publishing CO., Inc. New York, 61-73, 294-296.

Titow, W.V. (1984), *PVC Technology*, 4th edit., Elsevier Applied Science, London.

Tobolsky, A. V. (1960). *Properties and Structure of Polymers*. Wiley. New York.

Torsdottir, I., Alpsten, M., Anderson, H., Einarsson, S. (1989), "Dietary guar gum effects on postprandal blood glucose, insulin and hydroxiproline in humans. *Journal of Nutrition*. 119, 1925-1931.

Tsuchida, E., (1994) Formation of Polyelectrolyte Complexes and Their Structure, *Journal Macromol Sci*, , 31,1-15.

Tsuchida, E., Osada, Y., and Abe, K. (1974) Formation of Polyion Complexes between Polycarboxylic Acids, *Makromol Chem*, 175: 583-592.

Unanaonwi , O. E., (2011). *"Effects of nitrogen, calcium and cation exchange capacity on gum yield in Acacia senegal under plantation and savanna woodland conditions in northern Guinea savanna, Nigeria".* iForest 4: 190-194 [online 2011-08-11] URL: http://www.sisef.it/iforest/ show.php?id=587

Utracki L. A, (1997) editor. Polymer blends handbook. Toronto: Chem-Tec Publ,.

Verbeken, D., Dierckx, S., Dewettinck, K., (2003), "Exudates Gums: Occurrence, Production and Application", *Applied Microbial Biotechnology*, 63, 10-12,

Vert, M. (1986). Polyvalent Polymeric Drug Carriers, *Ther. Drug Carr Syst*, 2: 291-327.

Vijay K. T. and Amar S. S. (2010), "Physico-chemical and Mechanical Characterization of Natural Fiber Reinforced Polymer Composites". *Iranian Polymer Journal* 11(1), 3-16. Also available online at http://journal.ippi.ac.ir

Wang X., Wang Y., Liu L., and Peng X. (2009), "Theoretical Study on the Thermal Dehydrochlorination of Model Compound for Poly (vinyl chloride)", *Journal of Molecular Structure,* 896, 34-37.

Wen R., Yang Z., Chen H., Hu Y., and Duan J., (2012) "Zn-Al-La Hydrotalcite-like Compounds as Heating Stabilizer in PVC Resin", *Journal of Rare Earths*, Vol. 30 No 9, p. 895.

Williams, P. A. (2000), "*Handbook of Hydrocolloids",* Woodhead Publishers Ltd, Cambridge, London. 155-159.

APPENDIX I

AP. 1.1: FTIR data of PGM sample

S/N	PEAK	INTENSITY	AREA	FUNCTIONAL GROUP ASSIGNMENT
1	605.67	44.2101	58.9591	C-H bend
2	705.02	40.0542	35.0379	C-H out of plane
3	769.63	35.5513	54.0166	C-H out of plane
4	1004.95	29.9274	130.0956	C-O stretch
5	1157.33	30.6632	38.4497	C-H wag
6	1276.92	27.5927	82.7976	C-O stretch
7	1356	28.0718	94.9118	C-H rock
8	1601.93	26.7422	75.5933	C=C bending
9	1715.74	30.7319	72.8561	C=O stretch
10	2153.59	47.2996	109.3269	Isocynides
11	2727.44	29.5151	191.5694	RCHOC-H stretch
12	2764.09	29.5127	33.6713	RCHOC-H stretch
13	2868.24	28.6988	64.7021	$-CH_3$
14	2989.76	28.9577	71.0448	C-H stretch
15	3160.47	27.9801	91.0552	OH dimer
16	3308.03	30.1045	93.4743	=C-H stretch
17	3469.09	33.9432	38.3168	O-H stretch
18	3553.96	34.0519	98.4620	O-H stretch
19	3778.68	45.6984	30.3044	

AP. 1.2: FTIR data of ACT

S/N	Peak	Intensity	Area	Functional Grp Assignment.
1	420.5	20.577	54.231	
2	472.58	20.322	57.702	
3	601.81	19.609	203.183	C-H stretch
4	1053.17	10.368	290.506	C-O stretch
5	1253.77	16.539	92.564	N-O
6	1397.47	18.172	142.044	C-O stretch
7	1630.87	22.785	76.959	Ar-CH=CHR
8	1734.06	18.403	127.373	C=O stretch
9	2142.02	32.737	164.355	Isocyanides
10	2357.09	29.925	86.751	Si-H
11	2929	17.321	368.2	$-CH_2-$
12	3471.98	10.414	653.785	O-H stretch
13	4001.46	27.893	183.066	
14	4430.64	27.883	168.01	

AP. 1.3: FTIR data of AHY sample

S/N	Peak (AHY)	Intensity	Area	Functional group assignment
1	443.64	17.616	159.805	-
2	883.43	58.568	35.796	C-H out of plane
3	1053.17	50.085	42.466	C-O stretch
4	1202.66	49.271	105.73	C-O stretch
5	1653.05	53.139	38.032	C=C stretch
6	1730.21	53.244	80.009	C=O stretch
7	2946.36	49.17	230.19	C-H stretch
8	3412.19	43.15	145.892	O-H stretch
9	3946.49	97.503	2.807	-

AP. 1.4: FTIR data of AAN sample

S/N	Peak	Intensity	Area	Functional group
1	423.39	22.857	61.219	
2	469.68	23.072	33.717	
3	591.2	22.65	205.45	C-Br stretch
4	1052.2	16.149	244.98	C-O stretch
5	1253.77	20.818	82.17	N-O aromatic
6	1407.12	21.27	128.654	Ar C-C stretch
7	1624.12	23.124	86.188	Ar-CH=CHR
8	1731.17	22.379	116.592	C=O stretch
9	2145.88	32.379	157.25	Isocyanides
10	2929	20.611	442.3	-CH2- stretch
11	3418.94	14.909	576.92	O-H stretch
12	4017.86	28.939	179.92	
13	4350.59	29.003	117.919	
14	4403.63	29.012	54.366	

APPENDIX II

AP. 2.1: GC-MS data of acetolysis gum modification (ACT).

Peak no.	%C	IUPAC Name	MW	MF	RT	SI	Fragmentation peaks
1	2.14	Hydroxypropanone	74	$C_3H_6O_2$	3.3	17	27(5%), 31(19%), 43(100%), 56(0%), 74(10%), 25(0%).
2	23.77	1-pentadecanecarboxylic acid	256	$C_{16}H_{32}O_2$	29.2	137	27(19%), 41(77%), 43(100%), 60(90%), 73(95%), 85(24%), 98(14%), 115(14%), 129(33%), 143(5%), 157(9%), 171(10%), 185(57%), 213(19%), 227(5%), 256(43%).
3	37.33	9-octadecenoic acid	282	$C_{18}H_{34}O_2$	30.5	173	27(10%), 41(65%), 55(100%), 69(83%), 83(67%), 97(53%), 98(36%), 112(27%), 127(14%), 151(9%), 180(7%), 222(7%), 264(37%), 282(17%).
4	5.11	n-Octadecanoic acid	284	$C_{18}H_{36}O_2$	30.6	196	27(14%), 41(70%), 43(81%), 60(100%), 73(85%), 85(24%), 98(14%), 115(11%), 129(33%), 143(5%), 171(5%), 185(12%), 199(5%), 213(5%), 241(12%), 255(10%), 284(29%).
5	10.93	Hexadecanoic acid, 1[[[(2-aminoethoxy)hydroxyphosphinyl]-1,2-ethanediyl ester	691	$C_{37}H_{74}NO_8P$	31.2	176	27(18%), 41(61%), 43(95%), 57(75%), 71(33%), 85(100), 98(66%), 112(17%), 129(19%), 140(9%), 155(7%), 239(37%), 299(7%), 313(19%).
6	20.72	9,12-octadecanoic acid	280	$C_{57}H_{104}O_6$	32.3	234	29(24%), 41(71%), 55(95%), 67(100%), 81(81%), 95(56%), 109(24%), 123(10%), 137(5%), 280 (9%).

AP. 2.2: GC-MS data of acetolysis gum modification (ACT).

Line no.	%C	IUPAC	MW	MF	RT	SI	Fragmentation peaks
1	21.14	Oxalic acid	186	$C_9H_{14}O_4$	7.9	100	26(2.3%), 27(14.28), 41(100), 44(9.3%), 57(37.2%).
2	13.31	1,2-dimethyldiazene-1-oxide	74	$C_2H_6N_2O$	19.1	100	15(4.6), 27(7%), 30(72%), 45(48.8%), 57(100%), 74(34.9%).
3	28.95	3-butyn-2-ol	70	C_4H_6O	21.8	91	12(0%), 27(23.3%), 55(100%), 69(16.3%), 70(2.3%
4	36.60	2-butyn-1-ol	70	C_4H_6O	22.6	87	13(2.3%), 27(32.6%), 39(55.8%), 42(46.5%), 69(100%), 70(9.3%)

AP.2.3: GC-MS data for acetic anhydride (AAN)

Peak no.	%C	IUPAC	MW	MF	RT	SI	Fragmentation peaks
1	17.55	1,2-dimethyldiazene-1-oxide	74	$C_2H_6N_2O$	19.1	100	15(5%), 27(7%), 30(72%), 45(49%), 57(100%), 74(35%).
2	37.99	Borane, ethylisopropyl methyl-	98	$C_6H_{15}B$	21.8	86	25(0%), 27(50%), 41(100%), 55(54%), 69(42%), 83(5%), 15(21%)
3	44.46	Acetyl cyanide	69	C_3H_3NO	22.6	90	13(2.3%), 15(21%), 40(12%), 43(100%), 69(77%), 70(5%)

AP.2.4: GC-MS data of acid hydrolysis mofication (AHY)

Peak no.	%C	IUPAC Name	MW	MF	RT	SI	Fragmentation peaks
1	15.53	2-Flouropropene	60	C_3H_3F	3.1	100	27(14%), 31(9%), 33(16%), 39(37%), 40(7%), 45(14%), 57(14%), 59(100%), 60(58%).
2	28.16	2-Furancarboxaldehyde	96	$C_5H_4O_2$	3.8	97	25(5%), 29(21%), 37(16%), 38(23%), 39(65%), 40(9%), 42(7%), 67(12%), 95(100%), 96(100%).
3	10.57	5-methyl-2-Furancarboxaldehyde	110	$C_6H_6O_2$	5.1	92	13(0%), 15(5%), 26(9%), 27(33%), 29(14%), 37(7%), 38(9%), 39(16%), 43(12%), 50(19%), 53(67%), 61(0%), 81(14%), 95(0%), 110(100%).
4	2.20	4-Hydroxybutanoic acid	104	$C_4H_8O_3$	5.4	84	31(2%), 39(16%), 40(12%), 41(47%), 42(100%), 56(33%), 73(0%), 86(49%), 103(0%).

5	2.74	2-Methyliminoperhydro-1,3-oxazine	114	$C_5H_{10}N_2O$	5.7	88	15(9%), 27(7%), 30(35%), 42(9%), 55(7%), 56(21%), 58(100), 86(2%), 114(53%).
6	6.33	Methyl 3-furancarboxylate	126	$C_6H_6O_3$	6.6	90	29(9%), 37(2%), 38(16%), 39(23%), 67(7%), 95(100%).
7	8.29	1-(p-Toluidino)-1-deoxy-beta-d-idopyranose	269	$C_{13}H_{19}NO_5$	20.0	74	33(2%), 39(12%), 42(51%), 43(56%), 60(93%), 73(100%), 91(7%), 107(5%), 118(2%), 136(2%), 149(2%)
8	26.19	6-Methyl-1-Heptanol	130	$C_8H_{18}O$	22.6	79	27(23%), 20(30%), 41(81%), 55(100%), 69(93%), 70(60%), 84(49%), 98(5%), 112(2%)

APPENDIX III

AP. 3.1 Young moduli of test samples

Composition (%)	PGM	ACT	AAN	EGL
10/90	139.6563	177.7917	180.1458	164.0363
20/80	121.3144	110.1236	140.1075	100.8687
30/70	97.1812	108.0221	147.6761	154.6206
40/60	122.2597	94.1237	147.7387	87.2582
50/50	113.747	88.0866	108.5277	90.5262
60/40	145.7784	84.0231	140.4104	58.9668
70/30	108.5525	19.1026	90.6741	37.6488

AP.3.2 Tensile strength of the test samples at various composition

Composition (%)	PGM	ACT	AAN	EGL
10/90	18.889	15.823	16.776	20.508
20/80	14.57	17.172	18.663	14.238
30/70	16.138	13.894	20.299	16.93
40/60	13.475	10.902	13.657	9.958
50/50	7.35	8.158	13.699	6.939
60/40	7.721	4.737	8.081	4.53
70/30	4.444	1.242	3.206	2.755

AP.3.3 Percent elongation of test samples at various composition

Composition (%)	PGM	ACT	AAN	EGL
10/90	15	17.9	16	21
20/80	10.5	17	16.6	14.5
30/70	17.8	16	13.3	12.3
40/60	11.2	11.3	10.3	14.3
50/50	12	11	12.3	10.5
60/40	7.4	8.8	11.2	8.9
70/30	8.3	6.4	7.8	11

AP.3.4 Water absorption of test samples at various composition

Composition (%)	PGM	ACT	AAN	EGL
10/90	2.1	14	3.2	3.9
20/80	3.6	17.3	2.4	7
30/70	6.7	28.1	3.6	13.6
40/60	7.2	33.4	12	18.4
50/50	2.4	29.9	16.2	24.2
60/40	8.5	65.4	21.9	31.3
70/30	9.3	68.5	28.7	44.3
80/20	19.4	69.3	33.4	49.5

APPENDIX IV

AP.4.1 Stress-strain data for 10/90% gum/PVC composition for PGM sample.

Area (mm^2)	Gauge length (mm)	Force (N)	Extension (mm)	Stress (N/mm^2)	Strain
6.3	24	0.0	0.0	0.0	0.0275
		18	0.66	2.857	0.0275
		33	1.08	5.238	0.045
		66	1.74	10.476	0.07
		96	2.40	15.238	0.1
		111	2.94	17.619	0.123
		119	3.60	18.889	0.15

AP.4.2 Stress-strain data for 20/80% gum/PVC composition for PGM sample.

Area (mm^2)	Gauge length (mm)	Force (N)	Extension (mm)	Stress (N/mm^2)	strain
6.795	24	0.0	0.28	0.0	0.012
		15	0.60	2.208	0.025
		36	1.08	5.322	0.045
		60	1.66	8.830	0.069
		84	2.52	12.362	0.105
		99	3.0	14.570	0.125

AP.4.3 Stress-strain data for 30/70% gum/PVC composition for PGM sample.

Area (mm^2)	Gauge length (mm)	Force (N)	Extension (mm)	Stress (N/mm^2)	Strain
7.25	24	0.0	0.0	0.0	0.00
		15	0.81	2.069	0.034
		30	1.11	4.138	0.046
		60	1.82	8.276	0.076
		87	2.62	12.000	0.109
		117	4.26	16.138	0.178

AP.4.4 Stress-strain data for 40/60% gum/PVC composition for PGM sample.

Area (mm^2)	Gauge length (mm)	Force (N)	Extension (mm)	Stress (N/mm^2)	Strain
5.64	24	0.0	0.0	0.0	0.0
		6.0	0.27	1.064	0.011
		27	0.69	4.787	0.029
		45	1.11	7.979	0.046
		66	1.74	11.702	0.073
		76	2.70	13.475	0.113

AP.4.5 Stress-strain data for 50/50% gum/PVC composition for PGM sample.

Area (mm^2)	Gauge length (mm)	Force (N)	Extension (mm)	Stress (N/mm^2)	Strain
7.755	24	0.0	0.0	0.0	0.0
		3	1.32	0.387	0.055
		15	1.5	1.934	0.063
		27	1.68	3.482	0.07
		39	1.98	5.029	0.083
		51	2.4	6.576	0.1
		57	2.76	7.350	0.115

AP.4.6 Stress-strain data for 60/40% gum/PVC composition for PGM sample.

Area (mm^2)	Gauge length (mm)	Force (N)	Extension (mm)	Stress (N/mm^2)	Strain
5.64	24	0	0	0	0
		3	0.6	0.510	0.025
		12	0.78	2.041	0.033
		21	0.99	3.571	0.041
		30	1.23	5.102	0.051
		42	1.77	7.721	0.074

AP.4.7 Stress-strain data for 70/30% Gum/PVC composition for PGM sample.

Area (mm^2)	Gauge length (mm)	Force (N)	Extension (mm)	Stress (N/mm^2)	Strain
6.75	24	0	0.9	0	0.038
		6	1.260	0.889	0.053
		21	1.500	3.111	0.063
		27	1.740	4.00	0.073
		30	1.980	4.444	0.083

ACETIC ANHYDRIDE

AP.4.8 Stress-strain data for 10/90% Gum/PVC composition for AAN sample.

Area (mm^2)	Gauge length (mm)	Force (N)	Extension (mm)	Stress (N/mm^2)	strain
4.9	24	0	0.33	0	0.0134
		18	0.72	3.674	0.031
		51	1.41	10.408	0.059
		90	2.25	18.307	0.094
		120	3.60	24.490	0.150
		141	3.84	28.776	0.160

AP.4.9 Stress-strain data for 20/80% Gum/PVC composition for AAN sample.

Area (mm^2)	Gauge length (mm)	Force (N)	Extension (mm)	Stress (N/mm^2)	Strain
5.88	24	0	0	0	0
		3	0.57	0.510	0.024
		30	1.20	5.102	0.05
		60	1.86	10.204	0.078
		102	3.24	17.350	0.135
		121.5	4.02	20.663	0.167

AP.4.10 Stress-strain data for 30/70% Gum/PVC composition for AAN sample.

Area (mm^2)	Gauge length (mm)	Force (N)	Extension (mm)	Stress (N/mm^2)	Strain
6.59	24	0	0.36	0	0.015
		15	0.75	2.276	0.031
		45	1.50	6.829	0.063
		72	2.07	10.926	0.086
		87	2.58	13.202	0.108
		114	3.18	17.299	0.133

AP.4.11 Stress-strain data for 40/60% Gum/PVC composition for AAN sample.

Area (mm^2)	Gauge length (mm)	Force (N)	Extension (mm)	Stress (N/mm^2)	Strain
6.59	24	0	0.36	0	0.015
		15	0.6	2.276	0.025
		30	0.9	4.552	0.038
		48	1.26	7.284	0.053
		69	1.74	10.470	0.073
		90	2.46	13.657	0.103

AP.4.12 Stress-strain data for 50/50% Gum/PVC composition for AAN sample.

Area (mm^2)	Gauge length (mm)	Force (N)	Extension (mm)	Stress (N/mm^2)	Strain
6.57	24	0	0	0	0
		15	0.48	2.283	0.020
		45	1.17	6.849	0.049
		60	1.65	9.132	0.069
		75	2.31	11.416	0.096
		90	2.94	13.699	0.123

AP.4.13 Stress-strain data for 60/70% Gum/PVC composition for AAN sample.

Area (mm^2)	Gauge length (mm)	Force (N)	Extension (mm)	Stress (N/mm^2)	Strain
4.45	24	0	0	0	0
		3	1.44	0.673	0.06
		12	1.68	2.694	0.07
		24	2.08	5.387	0.087
		36	2.67	8.081	0.112

AP.4.14 Stress-strain data for 70/30% Gum/PVC composition for AAN sample.

Area (mm^2)	Gauge length (mm)	Force (N)	Extension (mm)	Stress (N/mm^2)	Strain
6.55	24	3	1.2	0.053	0.045
		6	1.38	0.916	0.058
		12	1.5	1.832	0.063
		18	1.62	2.748	0.068
		21	1.86	3.206	0.078

ETHYLENE GLYCOL

AP.4.15 Stress-strain data for 10/90% Gum/PVC composition for EGL sample.

Area (mm^2)	Gauge length (mm)	Force (N)	Extension (mm)	Stress (N/mm^2)	Strain
5.9	24	0	0.24	0	0.01
		3	0.84	0.509	0.035
		30	1.56	5.085	0.065
		90	2.94	15.254	0.123
		120	3.72	20.339	0.155
		150	4.56	25.424	0.19
		180	5.22	30.508	0.218

AP.4.16 Stress-strain data for 20/80% Gum/PVC composition for EGL sample.

Area (mm^2)	Gauge length (mm)	Force (N)	Extension (mm)	Stress (N/mm^2)	Strain
4.53	24	0	0	0	0
		3	0.3	0.662	0.012
		6	0.57	1.325	0.024
		30	0.96	6.623	0.04
		54	2.10	11.921	0.088
		61.5	2.85	13.576	0.119
		64.5	3.48	14.238	0.145

AP.4.16 Stress-strain data for 30/70% Gum/PVC composition for EGL sample.

Area (mm^2)	Gauge length (mm)	Force (N)	Extension (mm)	Stress (N/mm^2)	Strain
4.43	24	0	0	0	0
		3	0.3	0.677	0.013
		6	0.42	1.354	0.018
		30	0.92	6.772	0.038
		48	1.44	10.835	0.06
		63	2.04	14.221	0.085
		75	2.94	16.930	0.123

AP.4.17 Stress-strain data for 40/60% Gum/PVC composition for EGL sample.

Area (mm^2)	Gauge length (mm)	Force (N)	Extension (mm)	Stress (N/mm^2)	Strain
7.23	24	0	0	0	0
		3	0.84	0.415	0.035
		15	1.08	2.075	0.045
		30	1.8	4.149	0.075
		51	2.4	7.054	0.1
		72	3.42	9.958	0.143

AP.4.18 Stress-strain data for 50/50% Gum/PVC composition for EGL sample.

Area (mm^2)	Gauge length (mm)	Force (N)	Extension (mm)	Stress (N/mm^2)	Strain
7.35	24	0	0	0	0
		3	0.78	0.408	0.033
		18	1.02	2.449	0.043
		33	1.5	4.449	0.063
		48	1.98	6.531	0.083
		51	2.52	6.939	0.105

AP.4.19 Stress-strain data for 60/40% Gum/PVC composition for EGL sample.

Area (mm^2)	Gauge length (mm)	Force (N)	Extension (mm)	Stress (N/mm^2)	Strain
7.28	24	3	0.48	0.412	0.020
		6	0.72	0.824	0.030
		21	1.05	2.885	0.044
		30	1.71	4.121	0.071
		33	2.13	4.532	0.089

AP.4. 20 Stress-strain data for 70/30% Gum/PVC composition for EGL sample.

Area (mm^2)	Gauge length (mm)	Force (N)	Extension (mm)	Stress (N/mm^2)	Strain
7.26	24	3	1.36	0.413	0.057
		9	1.80	1.239	0.075
		18	2.34	2.479	0.098
		20	2.64	2.755	0.11

ACETOLYSIS

AP.4.21 Stress-strain data for 10/90% Gum/PVC composition for ACT sample.

Area (mm^2)	Gauge length (mm)	Force (N)	Extension (mm)	Stress (N/mm^2)	Strain
4.53	24	0	0	0	0
		15	0.66	3.311	0.028
		42	1.29	9.271	0.054
		60	1.65	13.245	0.069
		90	2.34	19.868	0.098
		112.5	3.60	24.834	0.15
		117	4.29	25.823	0.179

AP.4.22 Stress-strain data for 30/70% Gum/PVC composition for ACT sample.

Area (mm^2)	Gauge length (mm)	Force (N)	Extension (mm)	Stress (N/mm^2)	Strain
6.04	24	0	0	0	0
		12	0.72	1.987	0.031
		30	1.08	4.967	0.045
		60	1.80	9.934	0.075
		84	2.58	13.907	0.108
		96	3.84	15.894	0.16

AP.4.23 Stress-strain data for 40/60% Gum/PVC composition for ACT sample.

Area (mm^2)	Gauge length (mm)	Force (N)	Extension (mm)	Stress (N/mm^2)	Strain
7.43	24	0	0	0	0
		18	0.54	2.423	0.023
		42	1.02	5.653	0.043
		60	1.56	8.075	0.065
		75	2.10	10.094	0.088
		81	2.7	10.902	0.113

AP.4.24 Stress-strain data for 50/50% Gum/PVC composition for ACT sample.

Area (mm^2)	Gauge length (mm)	Force (N)	Extension (mm)	Stress (N/mm^2)	Strain
8.09	24	0	0	0	0
		3	0.48	0.371	0.02
		30	1.14	3.708	0.048
		48	1.74	5.933	0.073
		60	2.16	7.417	0.09
		66	2.64	8.158	0.11

AP.4.25 Stress-strain data for 60/40% Gum/PVC composition for ACT sample.

Area (mm^2)	Gauge length (mm)	Force (N)	Extension (mm)	Stress (N/mm^2)	Strain
7.6	24	0	0	0	0
		3	0.9	0.395	0.038
		15	1.26	1.974	0.053
		27	1.71	3.553	0.071
		33	2.04	4.342	0.085
		36	2.1	4.737	0.088

AP.4.26 Stress-strain data for 70/30% Gum/PVC composition for ACT sample.

Area (mm^2)	Gauge length (mm)	Force (N)	Extension (mm)	Stress (N/mm^2)	Strain
6.04	24	0	0	0	0
		3	0.6	0.497	0.025
		7.5	1.53	1.242	0.064