Synthesis and Characterization of Bituminous Based Waterproofing Coating using Polyethylene Terephthalate and Animal Glue as Additives for Quality Enhancement

Tilahune Anteneh Ambie

A Thesis submitted to

The Department of Chemical Engineering

School of Mechanical, Chemical and Materials Engineering

Submitted in Partial Fulfillment of the Requirement for the Degree of Master's in Chemical Engineering (Specialization in Process Engineering)

Office of Graduate Studies

Adama Science and Technology University

October 2021

Adama, Ethiopia

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APPROVAL PAGE

I/we, the advisors of the thesis entitled "Synthesis and Characterization of Bituminous Based Waterproofing Coating using Polyethylene Terephthalate (PET) and Animal Glue as Additives for Quality Enhancement" and developed by Tilahun Anteneh, hereby certify that the recommendation and suggestions made by the board of examiners are appropriately incorporated into the final version of the thesis.

Major Advisor	Signature	Date
Co-advisor	Signature	Date

We, the undersigned, members of the Board of Examiners of the thesis by Tilahun Anteneh have read and evaluated the thesis entitled "Synthesis and Characterization of Bituminous Based Waterproofing Coating using Polyethylene Terephthalate (PET) and Animal Glue as Additives for Quality Enhancement" and examined the candidate during the open defense. This is, therefore, to certify that the thesis is accepted for partial fulfillment of the requirement of the degree of Master of Science in Chemical Engineering.

Chairperson	Signature	Date
Internal Examiner	Signature	Date
Dr Sintayehu Mekuria		19/11/2021
External Examiner	Signature	Date

Finally, approval and acceptance of the thesis are contingent upon submission of its final copy to the Office of Postgraduate Studies (OPGS) through the Department Graduate Council (DGC) and School Graduate Committee (SGC).

Head of Department	Signature	Date
School Dean	Signature	Date
Post graduate Dean	Signature	Date

DECLARATION

I hereby declare that this M.Sc. thesis titled "Synthesis and Characterization of Bituminous Based Waterproofing Coating using Polyethylene Terephthalate (PET) and Animal Glue as Additives for Quality Enhancement" is my authentic/original work. That is, it has not been submitted for the award of any academic degree, diploma, or certificate in any other university. All sources of materials that are used for this thesis have been duly acknowledged through citation.

Tilahun Anteneh Ambie ______________________ ______________________

Candidate Signature Date

RECOMMENDATION

I/we, the advisor(s) of this thesis, hereby certify that I/we have read the revised version of the thesis entitled “Synthesis and Characterization of Bituminous Based Waterproofing Coating using Polyethylene Terephthalate (PET) and Animal Glue as Additives for Quality Enhancement” prepared under my/our guidance by Tilahun Anteneh submitted in partial fulfillment of the requirements for the degree of Mater’s of Science in Chemical Engineering.

Therefore, I/we recommend the submission of a revised version of the thesis to the department following the applicable procedures.

Major Advisor	Signature	Date
Co-advisor	Signature	Date

ACKNOWLEDGMENT

First and foremost, I praise the almighty God for his grace to do this work, blessings, wisdom, protection, and help me throughout my life. Then, I would like to express my sincere gratitude to Dr. Mulugeta Yilma, the thesis advisor, for his unlimited support, encouragement, constructive comment, and unreserved guidance on the critical issues of the study.

Dr. Zelalem Tumsa co-advisor for sharing his academic experience, knowledge and he has been an enormous resource to me in all aspects of my academic life during my master's study. Heartfelt thanks also go to my friend for their willingness in providing and supporting me financially and their encouragement and constructive suggestion on the subject matter of the study.

I extend my deep gratitude to my best frined Sntayehu Anteneh for his willingness in providing and supporting me financially to accomplish this study. Without him I would have never been able to achieve my dream and thanks for his support, always backing me up.

I am greatly thankful to the faculty of chemical engineering department for lab fulfilments, lab assistances for their contribution in the coordination of us doing laboratory works and also great thanks to faculty of civil and materials engineering lab assistance support during characterization.

Finally, I must express my very profound gratitude to my parents for providing me with unfailing support, continuous encouragement and all my ways have been prosperous by their prayer and support.

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ABS	Acrylonitrile-Butadiene-Styrene
ASTM	American Society for Testing Materials
ASTU	Adama Science and Technology University
BTF	Bangladesh Transport Foundation
CBRI	Central building Research Institute
CIPS	Centre for Innovations in Public Systems
CR	Crumb Rubber
DSC	Differential Scanning Calorimeter
DSR	Dynamic Shear Rheometer
EVA	Ethylene-Vinyl Acetate
GDP	Gross Domestic Production
HDPE	High Density Polyethylene
HMB	Hot Mix Bitumen
ISO	International Organization for Standardization
LDPE	Low Density Polyethylene
LLDPE	Linear Low Density Polyethylene
MSW	Municipal Solid Wastes
OBC	Optimum Bitumen Content
OECD	Organizational for Economic Co-operation and Development
PAH	Polycyclic Aromatic Hydrocarbons
PC	Polycarbonate
PCDF	Polychlorinated Dibenzo Furans
PE	Polyethylene
PET	Polyethylene Terephthalate
PMB	Polymer Modified Bitumen
PP	Polypropylene
PS	Polystyrene
PVC	Polyvinyl Chloride
RH	Relative Humidity

RPE	Recycled Polyethylene
SBR	Styrene–Butadiene Rubber
SBS	Styrene–Butadiene–Styrene
SMB	Stone Mastic Building
SWM	Solid Waste Management
UN	United Nation
VOC	Volatile Organic Compounds
WMB	Warm Mix Bitumen

ABSTRACT

Now a days, in Ethiopia as a result of increasing urbanization and industrialization, there is increased plastic generation. Many types of plastics have been generated daily in Ethiopia and disposed of as waste after usage. Disposal of these wastes to the environment poses a negative impact on the environment. To overcome such a problem, minimizing the solid waste disposal by using waste plastic in bitumen modification for bituminous coating waterproofing construction pavement was an ideal solution. Globally, building construction has rapidly grown especially high demand is evident in developing countries because of the high growth of population and urbanization. Consequently, construction inputs such as waterproofing materials are in high demand. In this study, bitumen-based waterproofing material was prepared using polyethylene terephthalate and animal glue as quality enhancers. To prepare bituminous-based waterproofing material begins with the collection of plastic waste and animal glue. The waste plastic, then washed, dried, and cut with various sizes, and mixed with 60/70 grade bitumen and animal glue. Its performance was compared with bitumen and commercially available waterproofing material. In this regard, the results of laboratory tests (softening point, ductility, stability/adhesiveness, water absorption, penetration, viscosity, and FTIR) were used for characterization purposes. Consequently, the result shows that the addition of plastic wastes was observed to increase softening point, viscosity, and stability but ductility, penetration, and absorption peak were reduced as a result. The optimal performance in terms of binding property (optimum stability) was obtained at 15% PET by weight of bitumen. This can enable to recycle 15 % of waste plastic (PET) that would have been used to decrease the impact on the environment from non-biodegradable wastes and to enhance the property of bitumen for waterproofing applications. Generally, in this study, it can be concluded that the optimum selected formulation of the experiment that shows better waterproofing application was 15%, 3%, and 82% PET, animal glue, and bitumen respectively.

KEY WORDS: Polymer modified bitumen, Waterproofing material, Optimum plastic content,

CHAPTER ONE
INTRODUCTION

1.1. Background

Increasing urbanization and industrialization have contributed to increased waste plastic generation. Indiscriminate disposal of these waste plastics is a serious environmental problem. Plastics are most commonly used in the form of carrying bags, packaging material, containers, etc. Due to the accumulation of plastic wastes and as they are non- biodegradable, some of them being non-recyclable pose a serious threat to the environment. With the increasing use of plastic as packaging material, post-consumer plastic wastes became an increasingly serious environmental issue. So, there is an immediate need for adoption of environment-friendly technologies such as economic recycling, development of biodegradable plastics, conversion of plastic wastes into value-added products and fuel, use of plastic wastes for most building construction for waterproofing, recycling of (PE) bottles into fibers or bottle to bottle technologies, etc. (N.S. Kumar, 2015).

Globally, building construction has rapidly grown especially high demand is evident in developing countries because of the rapid growth of building industry, population and high volume on the building, construction of the additional building, maintenance of existing building which increases demand for quality bitumen material for waterproofing application. The modification of traditional bitumen for waterproofing always has been obtained to enhance the quality and serviceability of waterproofing materials. There is evidence of best efforts and practices that have been put in the past to improve properties of bitumen using waste polymers materials to enhance building infrastructure (M.Ahmad, et al., 2015).

It is well known to use bitumen and PET compositions to manufacture waterproofing materials, such as waterproofing membranes and waterproofing coating. The purpose of such materials is to offer protection against the elements. Because of its good weather ability and hydrophobic nature, bitumen has been used in waterproofing applications during construction (A. P. Anderson et al., 1941).

Waterproofing coating must possess key mechanical and chemical characteristics, such as pliability, resistance to cracking at low temperatures, high puncture resistance, good strength and elongation (to withstand stresses and potential movements), resistance to flow at elevated temperatures, and thermal and dimensional stability, etc. Most importantly, a waterproofing material must have minimal Susceptibility to the effects of temperature. It is also desirable that such properties be maintained even after exposure to natural elements, e.g. Sunlight, condensation, airborne contaminants, etc. so to meet these property bitumen was modified by polymer (Zanchetta et al., 2008).

In fact, according to previous studies (Z.N. Kalantar, et al., 2012) and (Y. Yildirim, 2007). The modification of bitumen with polymers or plastic wastes has resulted in building mixtures with improved waterproofing performance, including increased resistance to rutting deformation, higher stiffness at high temperatures, and reduced susceptibility to temperature variation. In some cases, a better fatigue resistance has also been found depending on the type of polymer used, which influences the rheological properties of bitumen (M. García-Morales, et al., 2006). Despite these improvements in properties, it is not common to find studies aiming at optimizing the different blends to improve properties and reduce common failure mechanisms occurring in bitumen mixtures, while reducing production costs.

The two main failure mechanisms suffered by most building coating mixtures are cracking and rutting (permanent deformation). Cracking is usually associated with brittle fracture of coating at low temperatures, while rutting is associated with the plastic or viscous behavior of coating at high temperatures. To reduce cracking, bitumen has been typically modified by the addition of elastomeric polymers; usually requiring mixing and shearing at high temperatures to uniformly disperse the polymers into the blends (Masson J, et al., 2005). In general, the elastomeric polymers added to bitumen build a physical network assisted by bitumen’s phases but do not create a chemical reaction, leaving bitumen as a continuous phase. On the other hand, thermoplastic polymers have been also added to bitumen pursuing improvements on rutting resistance at high temperatures, making use of the hardening effect of these polymers at high temperatures (Fawcett AH, et al., 1998).

Water leakage is a crucial problem for underground structures. It will shorten the life of the structures and adversely affected the service quality for users (M. Kubal, 2008). If a drainage system is applied in the underground infrastructure as an alternative to reduce water leakage, it may affect the change in the ground water table in the surrounding area. This could be a potential trigger causing geotechnical problems such as piping, land subsidence, and sinkholes (G. Wang, B. Shi, et al., 2009). Hence, controlling ground water conditions and maintaining secured waterproofing systems are essential especially in metropolitan cities where complex underground infrastructures and complex groundwater environments exist such as subways, below-grade driveways, sewers, utility tunnels, and building basements. Thus, governmental authorities have set strong design criteria and managed the construction qualities for waterproofing systems.

Factors that cause water leakage through underground concrete structures can be primarily categorized into three groups: design factors, construction factors, and maintenance factors (M. Chew, et al., 2003). However, leakage problems are primarily caused by multiple factor combinations. Therefore, water leakage should be addressed from a system perspective. An appropriate waterproofing system should be introduced at the design stage with engineering confidence.

Nonetheless, the evaluation of waterproofing systems for underground structures is rarely available, particularly for systems where frequently high hydrostatic pressures are encountered. Most of the relevant waterproofing studies are focused on components or materials such as membranes, adhesives, and waterproofing concrete rather than the system viewpoint (M. Lrisch, 2016).

Bituminous coats used in waterproofing systems of flat roofs comprise a protection layer that can be of different types and has fundamentally two functions: mechanical protection and solar radiation protection. Bitumen is a complex mixture of organic and inorganic compounds. The main organic compounds are asphaltenes and maltenes, which are responsible for the viscoelastic properties of bitumen (Gorman, W.B. and Usmani, A.M., 2000). Despite its natural viscoelastic properties, unmodified bitumen cannot be used in roofing applications because of its inherent limitations, such as brittleness at low temperatures and a tendency to flow at high temperatures. Therefore, attempts have been made to improve the properties of bitumen by combining it with natural or synthetic polymer or lattices, to obtain new materials that have high elasticity.

There are a large number of polymers being used as polymer modified bitumen, such as polyethylene terephthalate (E. Ahmadinia, et al., 2012), ethylene-vinyl acetate (U. Isacsson, et al., 1999), polyethylene (M. Garcia-Morales, et al., 2006), and high-density polyethylene (S. Hinislioglu, et al., 2004), polyvinyl chloride (Z.N. Kalantar, et al., 2012), styrene-butadiene-styrene (Ahmed trimbakwala, 2017), styrene-butadiene rubber (M. Garcia-Morales, et al., 2006), polystyrene (M. Garcia-Morales, et al., 2004), polypropylene (D. Casey, et al., 2008), and acrylonitrile-butadiene-styrene (D. Casey, et al., 2008). It has been found that not all of these polymers are very suitable for bitumen modification at high temperatures. For example, heating PVC at high temperatures can cause dangerous chloride emissions to the atmosphere, and PET has a high potential for its reuse. Moreover, it is also necessary to check whether there is a sufficient amount of polymers to be recycled in the modification of bitumen that might be available for this purpose.

So, due to the availability of raw material in the environment, PET was used for the modification of bitumen, in this study. However, the major obstacle to widespread usage of PMB in paving practice has been their tendency to phase separation at elevated temperatures because of the poor compatibility between polymer and bitumen. Nowadays, the waterproofing in Ethiopia was wearing out due to many reasons; such as climatic effects, overloading of water during the summer season, etc. before finishing the presumed service life. The application of polymer-modified bitumen for waterproofing application can minimize those problems since the polymer-modified waterproofing showed superior resistance to environmental stresses like moisture in countries where the technology has been implemented. Therefore, the main aim of this study is a synthesis of bituminous based waterproofing coating using PET waste plastic to enhance moisture resistance performance of buildings and also obtain more regid paint by adding animal glue as an additive (M.Sulyman et al., 2016).

1.2. Statement of the Problem

Many roofs throughout the world are constructed using poured concrete. These structures are usually made with reinforced concrete. They are inexpensive but require a great deal of maintenance to keep them from leaking. The root problem when using concrete as a roofing material is that ordinary concrete is a porous material. When water or humidity penetrate, the reinforcement starts to corrode, causing the concrete to crack. Increasing water also transports salts and aggressive chemicals (e.g. from acid rain) into the wall, damaging the building's substance and ruining the facade (Verma, S. S., 2008). Water leakage is a substantial threat to buildings. Water dampness flows from the top floor to the ground floor through walls. Leakage from roof top slabs results in dampness on walls, wet patches below the slab leads to staining and discoloration, water dripping, peeling off paint, fungus growth leading to unhygienic conditions, ill-health and discomfort to people living on the lower floors, reducing the life of the structure, ingress of water into the walls causes electricity faults. Due to not addressing the leakage in time, moisture and a polluted atmosphere containing sulfate, nitrate, and phosphate-based toxic chemical penetrate in building structure, resulting in corrosion of steel reinforcement in concrete, dampness on walls, roofs & floors, leakage in water tanks.

Bitumen undergoes stiffening at low temperatures, which makes it fragile in cold weather temperatures even to light impacts. At high temperatures, instead, the Viscosity of bitumen is so low that it flows spontaneously or becomes permanently deformed under minimal mechanical stress. In our study, modifiers have been added to bitumen to obtain bitumen composition having more stability of physical and mechanical properties. Like bitumen, polyethylene terephthalate is hydrophobic (water-hating) in nature. So the addition of hydrophobic polymers by wet mixing process to bitumen mix lead to improvement of strength, water repellent property of the mix. Modifiers can also increase adhesion between bitumen binder and concrete and other materials for moisture resistance, this will reduce the probability of concrete stripping (M.Sulyman et al., 2016).

Due to littering habits, inadequate waste management systems, infrastructure, plastic waste disposal is a state critical issue. Since plastics are non-biodegradable. It remains in the environment for several years and disposing of plastic wastes at a landfill is unsafe since toxic chemicals (include pesticides, petroleum products, radon, asbestos, lead, chromate copper arsenate, and creosote) leach out into the soil and under-ground water and pollute the water bodies. By this result, the local areas are affected (Schroeder, R. L., 2008).

In addition to the plastic waste disposal problem, there is a shortage of production of bitumen-based or conventional waterproofing material in Ethiopia. It is another challenge for our country which has several buildings that need to be constructed in the future as well as at the present.

Therefore, this study intends to synthesis and characterize a waterproofing material that can give protection to prevent water from entering internal and external building structures like toilets, swimming pools, water tanks, retaining walls, roofs, etc.

1.3. Objectives of the Study

1.3.1. General Objective

The general objective of this study is synthesis and characterization of bituminous based waterproofing coating using polyethylene terephthalate (PET) and animal glue as additives for quality enhancement.

1.3.2. Specific Objectives

- To produce bitumen-based waterproofing coating for concrete structure.
- To characterize the properties of unmodified bitumen and modified bitumen in terms of basic properties of waterproofing material: softening point, water absorption, ductility stability, hardness, and viscosity.
- To investigate the optimum percentage of plastic waste (PET) and animal glue to be blended with bitumen.

1.4. Scope of the Study

Generally, the scope of the study is limited to synthesis and characterization of bituminous based waterproofing material such as:

- Collection and Size reduction of PET and glue.
- Characterization of raw materials (PET and Glue).
- Modification of bitumen and studying of processing parameters, mixing ratio, reaction time, and reaction temperature.
- Production of bituminous-based waterproofing coating.
- Characterizing modified and native bitumen by using instrumental techniques like FTIR and other physical testes such as softening point, penetration, water absorption, viscosity, adhesiveness, and ductility.

- Study the possibility of using PET waste plastic, as an available waterproofing additive, to improve the performance of bitumen for waterproofing as well as to extend their service life.
- Analyzing the outcomes of waste plastic addition for waterproofing mix in wet processing.

1.5. Significance of the Study

Preparation of modified bitumen which was used as a waterproofing coating for better-performing application in terms of bond strength and water resistance to partially replace petrochemical-based waterproofing paint was a significant contribution to this study. Using cheap, locally available, environmentally friendly, and cost-effective raw materials reduce dependence on petroleum based raw materials for waterproofing application. In terms of environmental and health aspect, bitumen-based waterproofing paint reduce the absorption of water and water-based sulfate, nitrate, and carbonate and is used to improve the properties of pavement using non-biodegradable plastic waste and to look for a better way of plastic waste disposal not only in disposal but also, economically it has big significance on import substitution of non- biodegradable waste as a raw material. Therefore, this research has a higher contribution to economically, environmental, and public health.

CHAPTER TWO

LITERATURE REVIEW

2.1. Solid Waste

Waste is any material that does not have any value to the holder. This waste can be from domestic, public, commercial, or from industrial areas. According to World Bank, 1.3 billion tons of solid wastes are generate in the world. This waste is likely to increase to 2.2 billion tons per year by 2025 (World Bank, 2012).

The understanding of the society and the relationship between them and the waste management problems is critical. We have been observing several problems in the collection transportation and in the final disposal process and methods of waste.

Classification of Solid wastes can be broad, this classification is in municipal (residential and commercial), industrial, construction and demolition wastes. The municipal solid wastes (MSW) are the most non-homogeneous since they consist of the residues of nearly all materials used by humanity: Food and other organic wastes, papers, plastics, fabrics, leather, metals, glass, and other inorganic materials.

2.2. Solid Waste Management

Data on the quantities and composition of municipal solid waste is fundamental for the planning and development of waste management systems for cities.

2.2.1. Global Solid Waste Generation and Its Composition

The world generates 2.01 billion tons of municipal solid waste every year. From the total waste generated more than 33 % are not managed in an environmentally safe manner (World Bank).

The practice of managing wastes may differ between developed and developing nations, urban and rural regions and residential and industrial sectors.

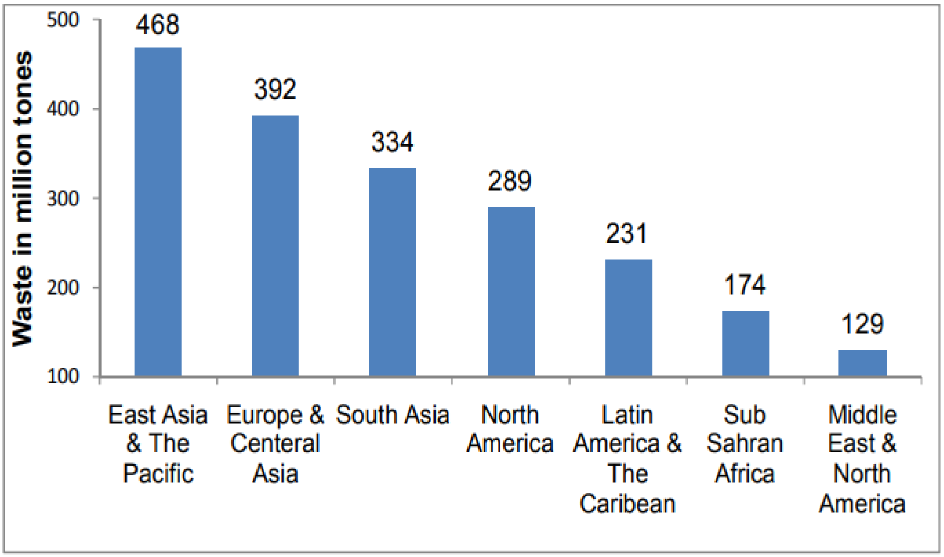


Figure 2.1: Regional annual waste generation (World Bank 'what a waste 2' report)

Waste management is all about the steps and activities required to manage wastes from the initial to the final disposal point. This process includes all the actions of collecting, transporting, disposing, and controlling of waste materials. Usually the term relates to all kinds of waste materials; whether they are formed during the production, processing or final utilization stage of raw materials or by other human activities including municipal, household and agricultural wastes as well. Waste management, is designed to minimize the negative influence of waste on the environment, health and economy of the world. The management of waste can include solid, liquid, gaseous, hazardous or organic substances, which have a harmful impact on the society.

Integrated solid waste management refers to the strategic approach to sustainable management of solid wastes covering all sources and all aspects, covering generation, segregation, transfer, sorting, treatment, recovery and disposal in an integrated manner, this process give much weight for efficient use of resource.

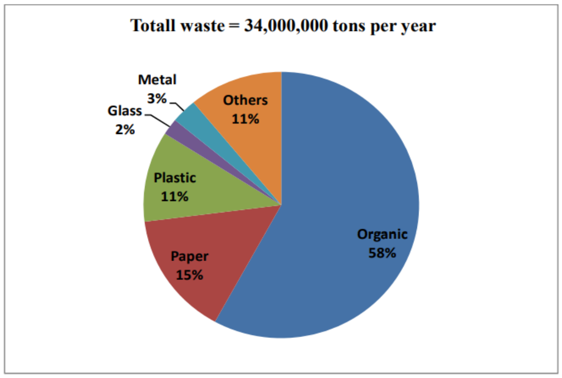


Figure 2.2: Solid waste generation of middle-income countries (Mushtaq Ahemd,1999)

This study predicts that the waste generated in these middle income countries become three folds of the base data in the coming year of 2025.

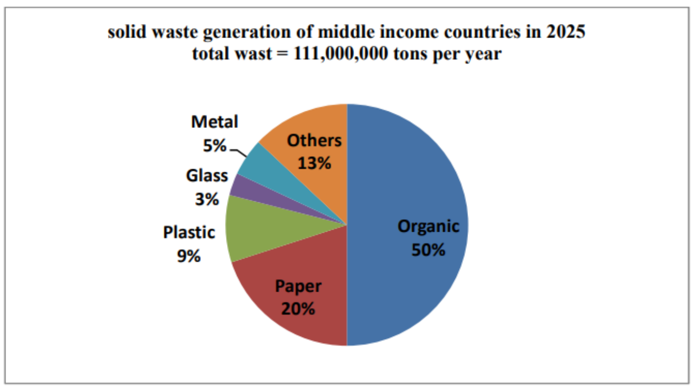


Figure 2.3: Future solid waste generation of middle-income countries (Mushtaq Ahemd, 1999)

As we can see in the above chart, the solid waste productions increased to 111,000,000 tons per year. Even though the portion of the plastic waste generated decreases from 11 % to 9 % but the amount of it is highly increased. That tells us we will have big problem coming a head of as concerning with plastic waste and its method of disposal. Therefore, we need much better way of disposing it in a way that will not have effect on our environment and in a way that will not be a challenge to human and animal health.

Waste incineration is popular in Europe, where nearly one quarter of all municipal solid waste incinerated. France has 126 waste-to-energy plants; Germany has 121 and Italy 40. (United Nations Environment Program, 2006).

2.2.2. Solid Waste Generation and Composition in Ethiopia

In our country Ethiopia, most of the regions are affected by the lack of proper waste management. Most of the cities like Bahirdar, Hawasa, Adama, Mekele, and the capital city Addis Ababa have a better waste management system than the suburb towns. Despite these cities having better solid waste management, the production of solid waste is beyond the capacity of the management system to collect and dispose it properly. As a capital city of Ethiopia, Addis Ababa has modern economic activities, social and infrastructural services relatively in a better situation than other cities of Ethiopia. Due to the population growth in the city because of natural population growth and migration from all the rural areas to the city, the existing socio-economic and infrastructural development of Addis Ababa is unable to meet the demands of the increasing population.

In the city of Oromia region Adama, waste collection executed by the City government of Adama in the formal way of waste collection. In this waste management system, the waste collected from the residential areas and transported to the dumping sites, which is a landfill area. Waste is also being disposed in huge amount in the informal way of waste management; this way of waste management is done by, people who use the waste as a source of income generation. By selecting the recyclable wastes and sell it for recyclers who are mostly located around Amede. In this place, there is one recycling market locally called “MinaleshTera”, in which scavengers sell materials collected from waste sites and some artisans made furniture from those materials (Wondafrash and Ehite, 2017).

A lot of studies and projects have undertaken on the problem of solid waste management in Ethiopia. These studies provided solutions for different aspects ranging from problem of collection to institutional management and assessment of community based projects. All contributed to the gradual improvement of the system. Even though the system of SWM is getting better and better than before, the problem caused by increasing generation of waste is still there.

The source of waste in country, Adama city are numerous, and have different percentage of contribution to the waste generated, from these sources some of them are: households, street, commercial institutes, industries, hotels and hospitals. From total generated, solid waste households’ account for 71 %, street 10 %, commercial institutions 9 %, industries 6 %, hotels 3 % and hospitals 1 % (Camilla Louise Bjerkli, 2005).

The waste generated from the residential or commercial and industrial areas have not handled in proper way. Most of the solid waste materials produced by households are disposed without adequate care. A study made by the Adama City Administration shows that, the collection coverage has been constantly increasing from 38 percent in 2000 to 40 percent, in 2001, 53% in 2002, 53.9 % in 2004 and 78 % in 2005 (AASBPDA, 2005). Improper solid waste management of collection and disposal is creating a huge health and environmental problem in the city of Adama (Dierig, 1999).

Table 2.1: Plastic generation in Ethiopia

Year	Generation volume in thousand tons
2020	308
2019	278
2018	248
2017	220
2016	195
2015	172
2014	114
2013	94
2012	81

Source; by M. Garside last edited Apr 15, 2019

Table 2.1. Shows plastic consumption in Ethiopia from 2012 up to 2019. From the data it can be concluded that plastic consumption is rapidly increasing every year. As a result, proper management of waste plastic important.

When the work of Solid waste management are carried out in the proper way of handling solid waste it will promote public health; improver hygiene; recycle materials; avoid waste; reduce waste quantities, and reduce emissions and residuals.

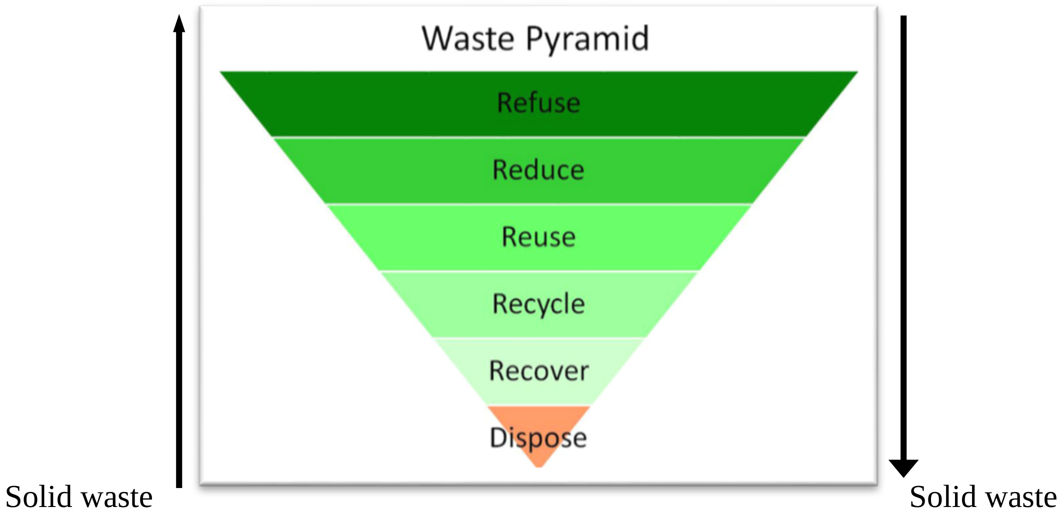


Figure 2.4: Solid waste management system(U. S environmental Protection Agency,2001)

Solid waste generation rate and composition studies are essential to the proper management of waste for a variety of reasons, including the need to:

- Estimate material recovery potential
- Identify sources of component generation
- Facilitate design of processing equipment
- Estimate physical, chemical and thermal properties of wastes, and
- (Placeholder) Maintain compliance with local state.

KAPB, (1999) Found that there were different types of diseases caused by improper handling of solid waste in the city.

Different study by UN in 2010 estimated that only 65 % of the waste generated in Ethiopia city is collected, with the rest deposited in open sites, drainage channels, and rivers (UN, 2010). The solid waste generation of a country and its gross domestic production is directly related. When the country's gross domestic production (GDP) increases the solid waste generated would be increased as well (OECD 1999).

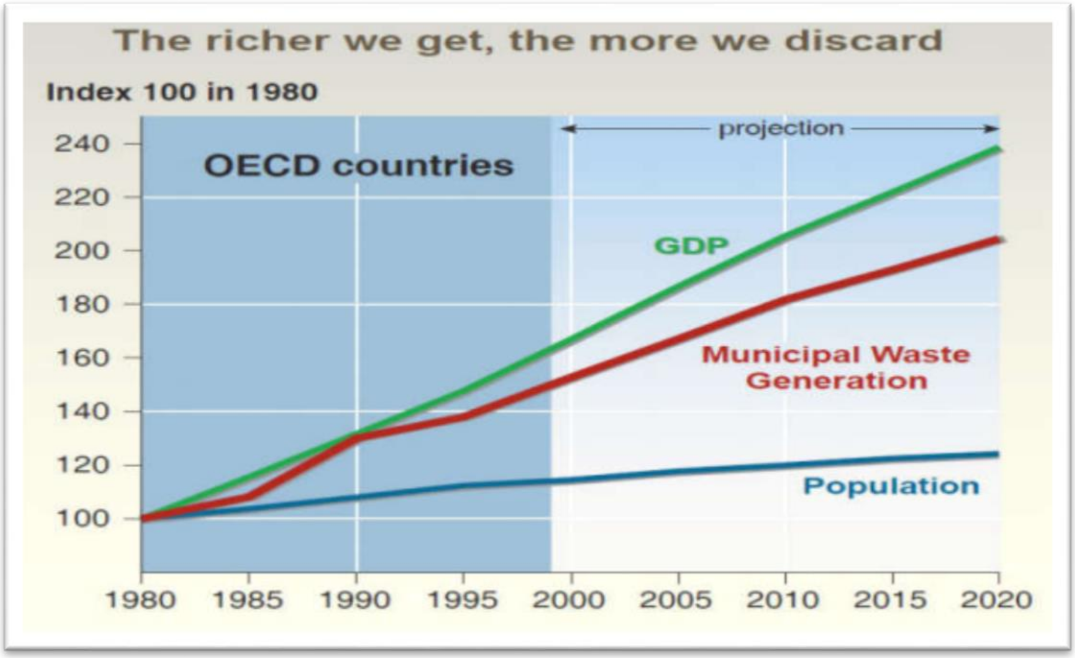


Figure 2.5: Charts that shows the relation between GDP and waste *(OECD 1999)*

2.3. Raw Materials Used For Modifiers

2.3.1. Plastic Waste

These days we accompanied with Plastic in our day to day activity. Plastics used for packaging, protecting, serving, and even disposing of all kinds of consumer goods. With the industrial revolution, mass production of goods started and plastic seemed to be a cheaper and effective raw material. Today, every vital sector of the economy starting from agriculture to packaging, automobile, building, construction, these has revolutionized by the applications of plastics.

The following are some of the benefits we can get from plastic:

- Plastic wrapping protects foods and goods, from being contaminated, plus contaminated and in that way, it saves resources.
- The lightweight packaging material saves fuel and decreases emissions during transportation.
- Plastic water supply systems and storage containers/tanks provide clean water.
- Light plastic materials (replacing metals) in cars and aircraft save fuel and decreases emissions.

- Efficient plastic insulation materials in buildings save energy and provide climate protection.
- Plastic protective clothing and safety equipment (Fireproof materials, helmets, air bags) protects form injury.
- Plastic products for medical applications are very important and contribute to improved heath (disposable syringes, blood pouches, tubing, and prosthesis).
- Solar heaters and solar panels, in parts made of plastics, provide renewable energy (Plastics Europe, 2009).

Plastic is made of a wide range of synthetic or semi-synthetic organic substances that are soft and it is capable of molded into solid objects of diverse shapes. Plastics are typically organic polymers of high molecular mass and they often contain other substances. They are usually synthetic, most commonly derived from petrochemicals and many are partially natural (LCPP 2011).

Plastics classified as thermoplastic and thermosetting materials, because of physical properties (M. Sulyman, Haponiuk, K. Formela, 2016).

Table 2.2: Example of thermoplastic and thermosetting

Thermoplastic	Thermosetting
High density polyethylene(HDPE)	Bakelite
Low density polyethylene(LDPE)	Epoxy
Polypropylene (PP)	Melamine
Polyvinylchloride (PVC)	Polyester
Polyethylene terephthalate (PET)	Polyurethane
Polystyrene (PS)	Urea-Formaldehyde alkyd
Polyvinyl Acetate (PVA)	

Source: Hossain et al., 2006

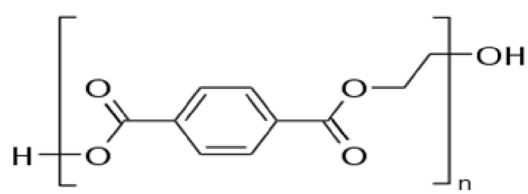
Thermoplastics:

These types of plastics become soft when it get heat and can be molded or shaped with pressure when in plastic state and, when cooled; they solidify and retain the shape or mold. Some common thermoplastics with their uses and properties are as follows: -

Polyethylene Terephthalate (PET):

PET (also abbreviated PETE) is short for polyethylene terephthalate, the chemical name for polyester. PET is a clear, strong, and lightweight plastic that is widely used for packaging foods and beverages, soft drinks, juices and water. Soft drinks and water sold in Ethiopia are bottled from PET.

PET is also popular for packaging salad dressings, peanut butter, cooking oils, toothpaste, shampoo, liquid hand soap, window cleaner, different kinds of playing balls. Special grades of PET used for carry-home food containers and prepared food trays that can warmed in the oven or microwave. The basic building blocks of PET are ethylene glycol and terephthalic acid, which combined to form a polymer chain. The resulting spaghetti-like strands of PET are extruded, quickly cooled, and cut into small pellets, the resin pellets then heated to a molten liquid that easily be molded into items of practically any shape. PET, it first synthesized in North America in the mid-1940s. Today, more than half of the world's synthetic fiber made from PET, which is polyester when used for fiber or fabric applications. When used for containers and other purposes, it is called PET or PET resin (Polyethylene terephthalate Resin Association). And the chemical structure of PET is shown below



Common properties of PET:

i. Toughness, clear, good strength, and stiffness chemical and heat resistant, good barrier properties for oxygen and carbon dioxide.
ii. It is used in packaging, soft drink, and mineral water bottles, fibers for clothing, films, food containers, transport, building and appliance industry (as it is fire resistant), etc.

High-Density Polyethylene (HDPE): Some common properties are:

i. Good process ability, excellent balance of rigidity and impact strength, excellent chemical resistance, crystalline, melting point (130 - 135 ^{0}C), and excellent water vapor barrier properties.

ii. Used for making blow molded products (various types of containers, water bottles), pipes, injection molded products (storage bins, caps, buckets, mugs), films (carrier bags), etc.

Polyvinyl Chloride (PVC): Its properties are

i. Versatility, energy-saving, adaptability to changing time and environment, durability, fire resistance.

ii. It is used in industries such as building and construction, packaging, medical, agriculture, transport. Also used for making wires and cables, furniture, footwear, domestic appliances, Films and sheets, bottles, etc.

Low-Density Polyethylene (LDPE): Characteristics of LDPE are:

i. Easy process ability, low density, semi-crystalline nature, low melting range, low softening point, good chemical resistance, excellent dielectric properties, low moisture barrier, poor abrasion, and stretch resistance.

ii. It is, used for making carrier bags, heavy-duty bags, nursery bags, small squeeze bottles. Also used in milk packaging, wire, and cable insulation, etc.

Polypropylene (PP): Properties are:

i. Low density, excellent chemical resistance, environmental stress resistance, high melting point, good process ability, dielectric properties, low cost, creep resistance.

ii. Used for making bottles, medical containers, pipes, sheets, straws, films, furniture, house wares, luggage, toys, hair dryer, fan, etc.

Polystyrene (PS): Some of the properties of polystyrene are:

i. Glassy surface, clear to opaque, rigid, hard, high clarity, affected by fats and solvents.

ii. Used for making electrical and communication equipment e.g. plugs, sockets, switch plates, coil forms, circuit boards, spacers, and housings.

Also used for making containers, toys, wall tiles, baskets, cutlery, dishes, cups, tumblers, dairy containers, etc.

Other plastics: There are many other types of plastics except these six types, often used in the engineering sector. Examples include polycarbonate (PC), nylon, and acrylonitrile butadiene styrene (ABS).

Thermosetting:

Thermosetting materials are those, once set cannot be remolded /softened by applying heat. It includes phenol, melamine, and urea-formaldehyde, unsaturated polyester, epoxy, and polyurethanes. These materials are not recyclable**.**

Table 2.3: Physical properties of some plastics

Full name	Abbreviation	Example of use
High density polyethylene	HDPE	Bottles and films
Linear low density Polyethylene	LLDPE	Film
Low density polyethylene	LPDE	Film
Polypropylene	PP	Containers, film
Polyvinylchloride	PVC	Blister packs and bottles
Polyethylene terephthalate	PET	Bottles for soft drinks, films etc.
Polystyrene	PS	Pots, thermo-Cole, trays, toys etc.

2.3.1.1. Plastic Waste Generation

The plastic bottles and plastic bags use is increasing in various purposes and their waste generation are increasing more than ever. As well, the problem of this plastic waste has grown up very rapidly. The plastic waste is not any more, just a matter of waste management. The hazards it can cause to the health of human beings and to their environment is becoming a worldwide concern.

Environmental groups estimate that between 500 billion and 1 trillion plastic bags used globally each year (CBC News, 2007).

Table 2.4: Import of plastic to Ethiopia (tons)

Type of plastics	Year			Average	shear (%)
	2009	2010	2011		
Polyethylene and related	27006.1	27006.1	27839.1	27283.8	40.58
Polypropylene and related	9270.3	13,071.0	16,955.7	13,099.0	19.48
Polyvinyl chloride and related	14,836.3	9,251.2	8,928.2	11,005.2	16.37
Ethylene-vinyl acetate and related	5484.7	5,647.7	7,990.2	6,374.2	9.48
Other polyether's	3,042.2	2,454.9	2,447.8	2,648.3	3.94
Polyethylene terephthalate	1,215.0	1,971.3	4,081.5	2,4422.6	3.60
Polyesters	828.7	1,152.7	1,143.9	1,041.7	1.55
Polymers of halogenated olefins	935.3	491.4	944.6	790.4	1.18
Alkyd resins	446.1	555.5	1,154.5	718.7	1.07
Polystyrene and related polymers	29	1,152.7	349.2	510.3	0.76
Acrylic	1011.7	156.8	292.2	487.1	0.72
Polyamides	167	980.4	130.3	425.9	0.63
Epoxide resins	343.2	12.6	887.5	414.4	0.62
Poly carbonates	5.5	0.3	16.7	7.5	0.01
Poly(methyl methacrylate)	0.6	5.9	10.7	5.8	0.01
Total	64622	63,911	73,112	67,235	100.00

Source: Ethiopian Revenues & Customs Authority, 2002

These issues are, characterized in the following points (Macur and Pudlowski, 2009).

- Plastic bags are a real hazard for the environment and especially today when they are in mass production – between four to five trillion is produced globally each year – there is no universal regulation about their disposal and their afterlife threat to the natural environment.
- If waste plastic bottles and plastics bags end up as litter in waterways they choke drainage systems, and force the flood to flow out of the system. This brought different contaminants to the land area. In addition loss of life, and losses to the economy
- Lots of rubbish with plastic bag content is floating across oceans.

Table 2.5: Waste plastic and its source

Waste plastic	Origin
High density polyethylene (HDPE)	Carry bags, bottle caps, house hold articles etc.
Low density polyethylene(LDPE)	Carry bags, sacks, milk pouches, bin lining, cosmetic and detergent bottles.
Polypropylene (PP)	Bottle caps and closures, wrappers of detergent, biscuit, vapors, packets, microwave trays for readymade meal etc.
Polyvinylchloride (PVC)	Mineral water bottles, credit cards, toys, pipes and gutters; Electrical fittings, furniture, folders and pens, medical disposables etc.
Polyethylene terephthalate (PET)	Drinking water bottles etc.,
Polystyrene (PS)	Yoghurt pots, clear egg packs, bottle caps. Foamed Polystyrene: Food trays, egg boxes, disposable cups, protective packaging etc.

Similar study done in Bahirdar shows that, the total of 24.87 tons of plastic bag waste generated annually (Ayana, 2007). This is equivalent to more than 12 million Plastic bags per year enter into the environment as the waste.

Our ambition as a developing county is to achieve a middle income ranking countries in the near future. If we can succeed in achieving our plan it will need our much effort to tackle the much increased production of solid waste in general and plastic waste in particular, that grows along with our GDP.

Ethiopia has shown an annual of 15 % increase in per capital consumption of plastic, in the past ten years. It was 0.6 kg in the year 2007 and become 2.4 kg in 2017. In the year 2020, it is estimate to be 3.2 kg per capital per year (plastering pack Ethiopia).

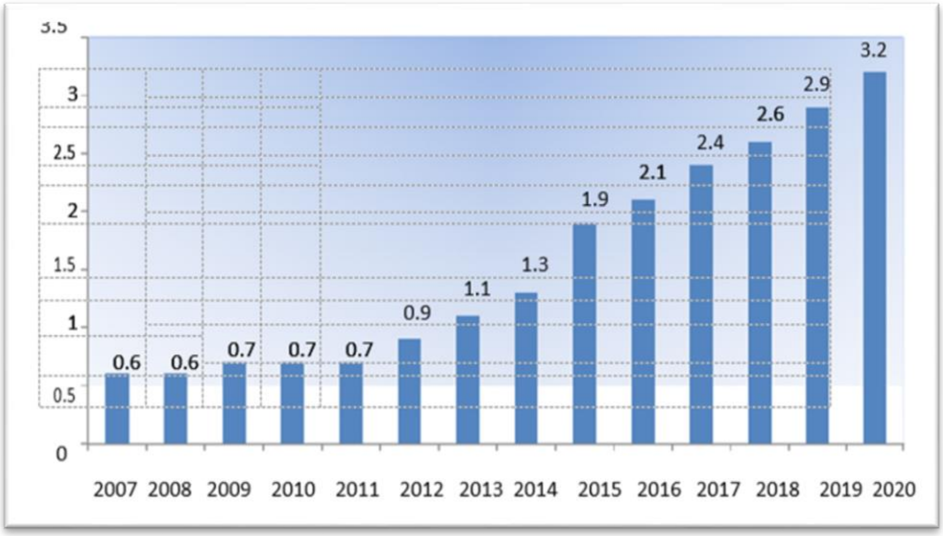


Figure 2.6: Per capital consumption of plastic in Ethiopia from 2007 to 2020 (plastprintpack Ethiopia)

The country's plastics consumption has grown by 17.5 % annually over the past ten years, from 44 KT in 2007 to 220 KT in 2017 and it estimated to be 308 kT in 2020. (Plastprintpack Ethiopia).

Plastics are cost-effective, require little energy to produce, and are lightweight and biocompatible. This makes them an ideal material for single-use disposable devices. The nature of plastics like its softness, transparency, and flexibility makes it preferable than other metal or glass products.

Durability of plastic

Plastics can last longer than most materials under any types of environmental condition. It is resistance against decomposition makes it preferable. Permanent shopping bags are durable than bags made from clothes, plastics and other natural materials.

Cost

Cost of plastic bottles, plastic bags, and any plastic made utensils are chipper in cost. These low costs of plastic products increase the demand for it. One of the factors that affect its demand is its cost. For instance, the costs of plastic bag determine the demand of the consumers for the plastic bags, as the cost of plastic bag increases the demand for the plastic bag decreases (Alexander, 2012).

Easy to use

Plastic materials are easy to handle and they are not heavy to carry them. If we take Plastic bags, they are convenient for handling and carrying goods. Moreover, they are accessible at any place and time in the shops.

2.3.1.2. Plastic Waste Collection

In these days, it is very common to see plastic bags and plastic bottles in our way to work, to school, to every corner of the town. Most of the plastic waste in domestic level waste generation is plastic bags, from the total of plastic waste generated plastic bag generated at each household accounts 92 % by weight and 89.4 % by volume. For that of packing plastic materials it take an account of 8 % by weight and 10.6 % by volume from total plastic waste (Ayana, 2007).

As a solid waste plastic wastes also collected in three different mechanisms of solid waste collection. Municipalities to collect solid waste establish these systems. These are:

Collection through municipal containers: this system of waste collection is for municipalities living near main road. Container for solid waste collection placed in an open area center to the residents so that they can put the wastes from their house to the container. When the metal containers are full, the municipal tracks take the container to land fill site.

Collection from different institutions: this kind of plastic waste and solid waste collection is done by giving access to the institutions to use the collection containers and it requires the institutes to pay for the disposal.

House-to-house collection: This plastic waste collection currently practiced in most part of the country. The residents store the waste in their compound until collectors came to take the waste. The waste collectors have small car or two-wheel pushcart that pushed by hand.

2.3.1.3. Plastic Waste Sorting

These days' plastic wastes sorted from the source where they generated. In House-to-house solid waste collection, plastic wastes and recyclable wastes are sorted alone to sell it to recycling company.

House to house collectors will not take the waste if the recyclable wastes are not sorted out.

2.3.1.4. Plastic Waste Management Options

Plastic polymers and products are extremely diverse, in terms of chemical composition, properties and applications. Several hazardous substances maybe released during the life cycle of a plastic product; and considering the large and growing global consumption of plastic products, and their long life in the environment without degradation, there must be a good way of managing it. The first and most effective method of solving problems is by trying not to create that problem. If we use Plastic the wastes we create are so difficult to manage and can create health problems we cannot reveres.

Table 2.6: List of African countries banned or put high tax on plastic use

Countries	Banned on plastic use
Benin	Benin reportedly banned plastic bags in November 2017
Botswana	Botswana introduced a levy on plastic bags that became effective in 2007. This led to many retailers charging a fee on plastic bags and consequently a reduction in plastic bag use.
Zimbabwe	Styrofoam pollution is a serious problem in Zimbabwe. The government is set to ban the ubiquitous material for use in food containers and to promote greener alternatives.
Cameroon	Cameroon outlawed disposable plastic in April 2014.There are problems considering black market activities.
Chad	There is a plastic bag ban in N'Djamena.
Eritrea	Eritrea banned plastic bags in 2005.
Ethiopia	Ethiopia has banned the production of certain types of plastic bags.
Gabon	Gabon has had a plastic bag ban since 2010.
Guinea-Bissau	Guinea-Bissau banned plastic bags in 2016, but the legislation has been poorly enforced.
Kenya	Kenya tried to ban manufacture and import of plastic bags in the year 2007 and 2011 as a way to protect the environment.
Madagascar	Madagascar introduced a plastic bag ban in 2015.

Source: Ahmedin et al., 2008

The biggest move comes from the European countries in the fight against plastic and minimizing the production of plastic waste. To reach this goal more than 30 European countries have band or put a higher tax on importers and producers.

Table 2.7: List of European countries banned or put high tax on plastic use

Countries	Band on plastic use
European Union	In November 2013, the European Commission published a proposal aiming to reduce the consumption of lightweight (thickness below 50 microns) plastic carrier bags. Under the proposal, EU member states can choose the most the most appropriate measures to discourage the use of plastic bags.
Austria	Austria has a voluntary agreement in place whereby retailers apply a charge to bags.
Belgium	Belgium has plastic bag bans in place in Wallonia and Brussels, With bans set to also be introduced to Flanders.
Bulgaria	Bulgaria has seen a significant reduction in use since applying a charge to plastic bags.
Croatia	Croatia is planning on introducing a plastic bag charge in 2019.
Denmark	In 2003, Denmark introduced a tax on retailers giving out plastic bags
Estonia	Estonia introduced a bag tax in July 2017.
Finland	Finland applies a tax to plastic bags through a voluntary agreement.
France	Following a National Assembly vote on 11 October 2014, France Banned plastic carrier bags under 50 microns starting 1 July 2016.
Georgia	Georgia has reportedly banned plastic bags, as of 2017.
Germany	Germany imposes a fee on excess packaging through its Green Dot Program, which included plastic bags. In addition, all stores in Germany that provide plastic bags must pay a recycling tax.

Source: Ahmedin et al., 2008.

The amount of plastic waste produced is increasing in Ethiopia as well as in Africa and the rest of the world, because of its harm to the environment and to human health some of the countries like France, Kenya are banning the use of plastic bag. Still most of the countries of the world are using plastic bags and other plastic products. Therefore, there must be a way to handle the waste produced.

Plastic waste handling is more difficult for countries in which are developing. Plastics are so durable that they do not decay. As a result, great amounts of discarded waste plastic products accumulate and it has become a threat to our environment. The management of plastic waste intends to decrease the environmental impact in the following order- waste minimization, reuse, recycling, energy recovery, and land filling. Waste minimization and reuse are options with limited applicability. Hence, recycling and energy recovery are alternatives to be consider. Energy recovery by incineration seems to be a suitable solution that takes advantage of the high-energy content of plastics, but presently questioned because of the possible emission of toxic compounds such as dioxins, furans (Kant and Shahidul, 2016).

2.3.1.4.1. Open Dumping

Solid waste disposal in Open dumpsite is a primitive stage of solid waste management in many parts of the world. It is one of the most poorly rendered services by municipal authorities in developing countries as the systems applied are unscientific, outdated and inefficient. Solid waste disposal sites found both within and on the outskirts of developing urban cities. With increase in the global population and the rising demand for food and other necessities, there has been a rise in amount of waste generated daily by each household. These wastes are mostly, thrown into municipal disposal sites and due to poor and ineffective management, the dumpsites turn to sources of environmental and health hazards to people living around that dumping site. These health treats comes because of the wastes contaminating the land in which we used to crop, air we breathe in and the water we drink.

2.3.1.4.2. Landfills

The Population of our country is increasing from time to time and showing impressive economic growth trend. With this population increase and economic growth, the municipal solid waste is highly increasing in the same rate the plastic waste is also increasing. The way municipal solid waste of Adama city currently managed is becoming challenging, with a big landfill laid in 33 hectares of land for the last five decades (Regassa et al., 2011).

Land filling is the easiest way of solid waste handling and disposing of waste plastic. It has considered traditionally as an easy and cheap method for disposing off all material generated by society and therefore has been and remains the dominant waste disposal option. Disposing waste plastic in landfill can elongate the decomposition of degradable materials and even cause for the ground water contamination because of leached toxic substances (Ayana, 2012).

2.3.1.4.3. Incineration

Incineration is one way of waste plastic disposal; it is burning of the waste until the plastic waste is burned-out and turns to ashes. This method of plastic disposal has many health risks to the human and animal. Incineration results in the release of carbon dioxide, a greenhouse gas, and of other air pollutants, including carcinogenic polycyclic aromatic hydrocarbons (PAHs), and dioxins (Shemwell and Levendis, 2011). Burning of plastic leads to severe health risks such as heart diseases, aggravates respiratory ailments such as asthma and emphysema and cause rashes, nausea or headaches, damages in the nervous system kidney or liver, in the reproductive and development system.

Incinerating waste to Energy has begun in our country Ethiopia probably the first African country to use waste to produce electric energy. The cost it takes to build waste to energy facility is so expensive for most developing countries and that was why we did not have one in our continent until now. These facilities established in the periphery of the capital. Expected to have a processing capacity of approximately 1400 tons of waste a day, The project came to reality with the partnership of Ethiopian Electric Power, Cambridge Industries Energy, and the China Urban Construction Design and Research Institute, to complete this project took four years to and needed around USD 3 billion (Samuel Getachew 25 August 2018).

Table 2.8: Compounds generation during incineration of plastic wastes and their harm

Name of compound	Health effects
Acetaldehyde	It damages the nervous system, causing lesions.
Acetone	Irritates the eyes, the respiratory tract.
Benz aldehyde	Irritates the eyes, skin, respiratory system, limits brain function.
Benzole	Carcinogenic, adversely affects the bone marrow, the liver, the immune system.
Formaldehyde	Serious eye damage, carcinogenic, may cause pulmonary edema.
Phosgene	Gas used in WWI. Corrosive to the eyes, skin, and respiratory organs.
Polychlorinated dib Enzo-dioxin	Carcinogenic, irritate the skin, eyes, and Respiratory System. It damages the circulatory, digestive and nervous systems, liver, bone marrow.
Polychlorinated dibenzofuran	Irritates the eyes and the respiratory system, causes Asthma
Hydrochloric acid	Corrosive to the eyes, the skin, and the respiratory tract.
Salicayl-aldehyde	Irritates the eyes, the skin, and the respiratory tract It can also affect the central nervous system.
Toluene	Irritates the eyes and the respiratory tract, can cause depression.
Xylene	Irritates the eyes, It can also affect the central nervous system. Reduces the level of consciousness and impair learning ability.
Propylene	Damages the central nervous system by lowering Consciousness.
Vinyl chloride	Carcinogenic, irritating to eyes, skin, and respiratory system.

Source: Agnes and Rajmund (2016) the Environmental impact of Plastic Waste Incineration

But incineration technology used in plastic wastes was impossible for energy production because, during the burning of plastic wastes, there were toxic chemicals are released into the environment it has harmful. Therefore incineration process was not recommended for plastic wastes.

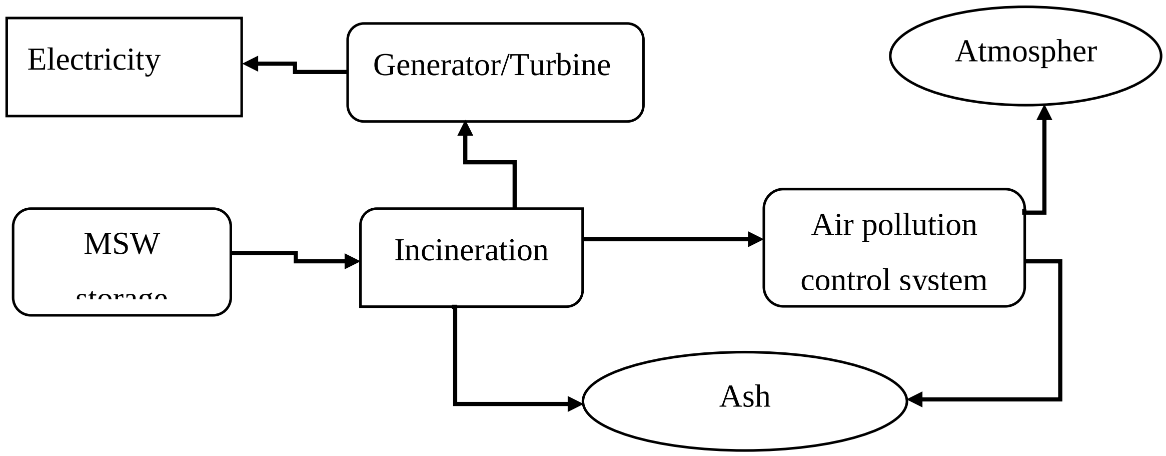


Figure 2.7: Incineration process(Mushtaq Ahemd, integrated solid waste conversion to energy)

2.3.1.4.4. Recycling

Recycling is reusing the waste material for its original function or for a different purposes. The nature of plastic is compatible with the idea of reusing because plastics can reshape, molded so that they can have real use. Some western countries like the USA send their plastic waste to other countries, which recycle and use plastic waste. Recycling or recovery of plastic in Ethiopia is performed in two ways these are formal and informal ways of reusing.

The informal plastic recovery system in Ethiopia brings several benefits to the society, from these:

- Employment opportunities to several thousands of unemployed people, which in turn reduces poverty.
- Reduces the amount of waste needed to be collected, transported, and disposed of at the landfill
- It supplies low-cost raw materials to industries, which makes the plastics factories more competitive on the market and it saves the environment from the extraction of natural resources.

In the informal plastic recovery system the collection and recovery of waste plastic performed by the workers in this system, the municipal waste management agency benefited highly from the informal way of plastic waste recovery, because the municipality is not taking any action in recovery activities.

Benefits of the informal plastic recovery recycling activity in the city are summarized as follows:

- Employment of people who would otherwise be unemployed
- Saves the city expenses for waste collection, transport, and disposal
- Reduces the number of waste materials requiring collection
- Supplies/substitutes raw materials for the industry
- Reduces the production costs of plastic products would otherwise have been lost.
- Environmentally beneficial in the form of reducing the amount of extracted raw materials, reducing the amount of waste in the landfill, and extending the life span of materials.
- Improves the health and safety conditions in the city (Camilla Louise Bjerkli, 2005).

It is possible to produce energy from waste plastic at the same time it reduces the amount of waste plastic that goes to land fill or incineration sites.

Table 2.9: Annual plastic waste consumption of recycling factors in Addis Ababa

year	Name of Companies			
	Weidong Jia Plastic Recycling Co.	Asia Chemical fiber PLC.	Great Wall Packing Material. PLC	AISAI recycled plastic manufacturing plc.
2012	40 tons	-	105 tons	-
2013	84 tons	-	170 tons	-
2014	1075 tons	175 tons	2010 ton	-
2015	1112 tons	178 tons	2030 tons	240 tons
2016	1213 tons	930 tons	2080 tons	360 tons

Source: Yohannes et al., 2017

2.3.1.5. Health Threats of Plastic Waste

There are several problems associated with plastic bag and other plastic wastes. From these Varity of issues animal death, blockage of sewage systems, deterioration of natural beauty of environment and human health problems were some of the health and environmental threats (Legesse and Diriba, 2011).

If people know how harmful burning plastic was, they would think twice before burning the waste from their house. For whatever reason our culture about wastes is to burn it, this culture has to stop. The effects of burning plastic on the environment have serious health consequences for everyone. Combustion of waste plastic could be a source of human and environmental health problems, the outcome of plastic combustion are airborne particulate emission soot and solid residue ash. Several studies have demonstrated that soot and solid residue ash possess a high potential of causing health and environmental concerns, especially Volatile organic compounds (VOCs), semi- VOCs, smoke (particulate matter), particulate bound heavy metals, polycyclic aromatic hydrocarbons (PAH's), polychlorinated dibenzo furans (PCDF's) and dioxins (Valavanidid et al., 2008). This can travel thousands of kilometers, depending on prevailing atmospheric conditions and enter our food chain. Significant amount of pollutants of environmental and health concern including carcinogens such as PAH's, nitro-PAH's and dioxins have been identified in the airborne particulate emission. These particulates are highly mutagenic (Lee et al., 1995). PAHs in the range of 8-340 ppm have observed in the soot, which is significant enough to cause cancer (Valavanidid et al., 2008).

The most dangerous health effect of burning plastic is the release of dioxin into the atmosphere. Dioxins are extremely toxic to humans and animals. They cause cancer and hormonal birth defects that passed from generation to generation. The dioxin also ends up in the soil poisoning food for humans and animals.

Other dangers of burning plastic are as follows.

- increases risk of heart disease
- aggravates respiratory ailments such as asthma and emphysema
- causes skin rashes, nausea, or headaches
- damages the nervous system
- damages the kidneys and liver
- Disrupts the reproductive, endocrinal and development systems

2.3.1.6. Benefits of Polymer/Plastic Waste for Bitumen Modification for Waterproofing

The purpose of polymer modification of bitumen is to construct durable pavement with greater stiffness and stability in Order to minimize maintenance cost. Use of polymer some time may increase cost of construction. In this case the benefit is evaluated by quality improvement of pavement. The use of RPE and CR give benefits in quality improvement and cost-effectiveness as well as environmental hazards. The benefits of PMB are assessed in three ways (Hossain, 2006).

Quality improvement of binder: Polymers in bitumen improve the following quality of bitumen:

- Polymer Increases binders viscosity that allows greater film thickness in paving mixes without excessive drain down or bleeding
- It increases the binder's qualities to better cope with cracking and dynamic deformation of the pavement internal layers.
- It improves the binder's behavior to fatigue by increasing its mechanical resistance particularly to tractive force.
- It raises the softening point of binder that helps in reducing bleeding.
- It increases elasticity and resilience at high temperatures
- It increases the cohesion of binder.
- It reduces thermal susceptibility to both low and high temperature.
- To rejuvenate aged asphalt binders.

Generally, some of the main reasons for modifying asphalt with polymers are to obtain greater resistance to flow at high temperatures, improved resistance to cracking at low temperatures, high dimensional stability over a wide temperature range, improved durability, and resistance to weathering caused by exposure to the elements and resistance to moisture.

A significant improvement in pavement is possible as-

- It increases flexibility of pavement.
- It reduces deformation in pavement.
- Improved aging and oxidation resistance due to higher binder contents, thicker binder films, and anti- oxidants in the tire rubber.
- It provides greater fatigue resistance.
- It provides greater resistance to stripping.
- It provides improved self-healing properties.
- It provides greater durability.

Environmental improvement

Use of waste plastic in building construction could lead a significant consumption of waste plastic daily generated which would be helpful in, keeping the environment clean, reducing clogging of drains causing various hazards including health hazard , reducing dumping of plastic materials wastes going into land fill etc.

2.3.1.7. Thermal Analysis of PET Waste

Thermal analysis of PET waste through differential scanning calorimeter (DSC). Thermal Study: Thermal behavior study of polymers shows that polymers get softened easily without any evolution of gas around 130-140 ^{0}C, this has been scientifically verified. At around 350 ^{0}C they get decomposed releasing gases like methane, ethane etc. and at 700 ^{0}C they undergo combustion, producing gases like CO and CO_2.

Table 2.10: Some properties of different polymers

properties	LDPE	HDPE	PP	PS	PVC	PET
Sp. Gravity	0.918-0.93	0.94-0.96	0.91-0.97	1.04-1.12	1.35-1.39	1.45-1.50
Flash point	>231	>360	400		>388	
Thermal decomposition (°C)	>270	>270-350	270-300	>300	-	-
Melting point (°C)	100-120	130-140	120-170	235-250	130-190	260

Source: BTF, 2008

Polyethylene terephthalate (PET) is linear, aromatic polyester that has an aliphatic aromatic polymer composition and thermoplastic, shows a rather hydrophobic nature due to its rigid structure, PET has the wide range of mechanical properties, relative high melting point and glass transition temperature, insensitivity to common solvents and moisture, chemical inertness (Verma, S. S., 2008). PET Characterizes tough, shatter resistant, gas permeation resistant. PET Can is recycled so that the PET can be used over and over again.

Generally, the most commonly used among them is PET which has high mechanical strength, high Young’s modulus and low elongation at break. It does not shatter on rupture and it is one of the hardest thermoplastics i.e. highly scratch resistant. Also, it exhibits low moisture and water absorbing capacity, and accordingly it has good dimensional stability. Both of these characteristics increase as the temperature rises. PET is one of the polymers that are most resistant to direct sunshine exposure. Its strength characteristics exhibit fairly small variations under the effect of UV radiation, as well as in the presence of ozone. These properties of PET make it suitable for products intended for long open air operation (A. Harper, A. Charles, 2005). So, Due to the above reasons, PET was used as a modifier for bitumen waterproofing coating.

Table 2.11: Physical properties of PET

Property	Unit	Value
Melting point	^0C	>250 – 260
Specific gravity	-	>350
Solubility in water	-	practically insoluble
Thermal conductivity	W m−1 K−1	0.15 - 0.24

Source: Mekonenn et al., 2011

Table 2.12: Toxic gas released above the deception temperature

Plastic	Toxic gases released	T (^0C)
Polyethylene Terephthalate (PET)	Light hydrocarbons (C5-C10)	>200
Polypropylene(PP)	C_2H_6	270-300
Poly vinyl Acetate (PVA)	CH_3COOH	>190
Poly vinyl chloride (PVC)	HCL	250
Polystyrene(PS)	C_6H_6	300-350
Low Density Polyethylene(LDPE)	$CH_4C_2H_6$	270-350
High Density Polyethylene(HDPE)	$CH_4C_2H_7$	270-350

Source: Centre for Innovations in Public Systems (CIPS), 2014.

2.3.2. Bitumen

Bitumen is a sticky, black and highly viscous liquid or semi-solid, in some natural deposits. It consisting essentially of hydrocarbons and their derivatives,which is soluble in trichloroethylene and is substantially nonvolatile, and softens gradually when heated. Possesses waterproofing and adhesive property, It is obtained by refinery processes from petroleum, and is also found as a natural deposit or as a component of naturally occurring asphalt, in which it is associated with mineral matte. It is the residue or by-product of fractional distillation of crude petroleum (T. W. Kennedy and J. Epps, 1985).

Bitumen Composed primarily of highly condensed polycyclic aromatic hydrocarbons, containing 95 % carbon and hydrogen 87 % carbon and 8 % hydrogen, up to 5 % sulfur, 1 % nitrogen, 1 % oxygen and 2000-ppm metals. Also bitumen is Mixture of about 300 - 2000 chemical components, with an average of around 500 - 700 (Romberg et al., 1959; Traxler, 1936; Traxler and Coombs, 1936). It is the heaviest fraction of crude oil, the one with highest boiling point (525 ºC).

Bitumen is the binding agent of the asphalt mix in the asphalt concrete mix. The quality of the bitumen always affects the strength and quality of the building. Bitumen can be different in quality.

2.3.2.1. Bitumen sources

The bitumen used in the construction industry is divided into two general categories (Mohamad Beiranvand, 2001):

1. Bitumen (mineral pitch)
2. Bitumen Produced From Distillation of Crude Oil (petroleum pitch)

2.3.2.1.1. Bitumen (natural pitch)

When volatile crude oil components is vaporized in the depths of the earth, over time and under factors such as high temperature and pressure, the black substance remains in place, which is called natural bitumen. This type of pitches is not usually pure and is a mixture of bitumen and mineral materials.

2.3.2.2.2. Petroleum Pitch

Oil pitch is obtained from the refinery of crude oil in distillation towers. In fact, what remains at the bottom of the distillation tower above 380 °C is pure oil pitch. Bitumen with different stiffness degrees for different construction applications can be obtained by setting the temperature and pressure inside the distillation towers (The Asphalt Handbook. 2nded.the asphalt institute; 1966. https://www.abebooks.com/).

2.3.2.2. Chemical Bitumen Building

Bitumen is a very complex chemical compound, composed of various hydrocarbons types, which are in colloidal form.

The chemical structure of bitumen is not fully known, and the chemical composition of the bitumen and its structure is heavily dependent on the initial crude oil from which it is derived and the processes applied for its production. Chemical compositions and crude oil structure are also very diverse. In this regard, considering the type of predominant hydrocarbons in crude oil, it can be divided into three groups of paraffin’s, asphaltenes, and naphthenes (Table 2.13).

Table 2.13: Chemical structure of different type of crude oil

Hydrocarbons	Paraffinic crude oil (%)	Naftens crude oil (%)	Asphaltenes crude oil (%)
Paraffin’s	40	12	5
Naftens	48	75	15
Aromatics	10	10	20
Asphaltenes	2	3	6

Source: Vesna Ocelic Bulatovic et al., 2013

2.3.2.3. Components of Bitumen

Bitumen consists of various hydrocarbon compounds, which according to the method of separation its compounds can be divided into different chemical groups. Bituminous components can be divided into two distinct chemical groups of asphaltenes and maltenes (petrolenes) (Robert N. H. et al, 2000). Maltenes are also classified into groups of aromatic compounds, polar aromatics (resins), and saturated aromatics (paraffin’s) (Traxler RN, 1961). These four groups are not always consistent, and there is some interference between them.

To investigate the chemical properties of bitumen, it must first be separated from each other. There are several methods for separating and identifying the quantitative and qualitative chemical bitumen composition. For this purpose, separation using the chromatographic column is the most common method. Since bitumen components have different degrees of solubility; this separation can be done using appropriate solvents with different abilities associated with chromatographic column. Each group has different physical and chemical properties and has independent and separate effects in relation to the physical and chemical properties of bitumen, which resulted from the total influences of these components, according to their quantitative ratios (Strategic Highway Research: Special Report, 2001)**.**

2.3.2.3.1. Asphaltenes

Robert N. H., (2000) defines Asphaltenes are a brittle solid substance in black to brown; in addition to carbon and hydrogen, they contain nitrogen, sulfur, and oxygen and usually have very polar compounds that contain highly aromatic complex components with high molecular weight. Asphaltenes comprise 5 to 25 % the composition of bitumen, and in terms of building, a combination of compressed aromatic rings with aliphatic lateral chains and the number of aromatic rings is 6 to 20 and even sometimes more of this.

Asphaltene rate in bitumen has many effects on rheological properties of bitumen. The higher the bitumen, the more the stiffness of the bitumen, and subsequently the degree of penetration would be less. In addition, it will result in a greater softening point and more penetration of bitumen. The H/C ratio of asphaltenes ranges from 0.98 to 1.6 (Lesueur, 2009).

2.3.2.3.2. Polar Aromatics (resins)

These compounds are usually composed of carbon and hydrogen, which also contain a small amount of oxygen, nitrogen, and sulfur. The compounds are solid and semisolid and in dark brown color. They are anticoagulants for asphaltene, and the ratio of the resin to the asphaltenes may be as high as that from the solution (sol) or gelatinous (gel) mode. The resins in bitumen have a molecular weight of 500 to 50,000. The H/C atomic ratio of 1.4 to 1.7.it is strongly adhesive, the adhesive properties of bitumen result from its resins (Mehrdad Honarmand, 1996).

2.3.2.3.3. Oil Aromatics

The aromatic oils are the least molecular weight ring compounds that contain aromatic or petroleum lateral chains and are an excellent anticoagulant for asphaltenes. The group, which consists of 40 to 60 % bitumen, is a viscous liquid in dark brown color with an average molecular weight between 300 and 2000. The aromatics have polar carbon chains and the H/C ratio of the aromatic fraction could be said to range from 1.4 to 1.6 (Javad Tanzadeh, 2001).

2.3.2.3.4. Saturated Materials (paraffin's)

Saturated compounds are composed of straight and branched chain aliphatic hydrocarbons with alkyl naphthenes and some aromatic alkyls. These compounds are often nonpolar and colorless viscose oils. The hydrogen-to-carbon molar ratio (H/C) of the saturate fraction is approximately 2 (Lesueur, 2009). The average molecular weight range has been reported to vary between 470 and 880 g/mol (Lesueur, 2009).

The components of the saturated compositions include saturated waxy and non-wax materials. Saturated compositions comprise 5 to 20 % bitumen.

2.3.2.3.5. Influence of Bitumen Components on Properties

The influence of bitumen components (i.e. the SARA fractions) on the properties of bitumen has been studied previously (Griffin and Miles, 1961; Griffinet al., 1959; McKay et al., 1978; Reerink, 1973). It was observed, by keeping the concentration of asphaltenes constant in a sample while varying the other components, that

- Increasing the aromatics content at a constant saturates-to-resins ratio has little effect on the rheology other than a marginal reduction in the shear susceptibility
- Maintaining a constant ratio of resins to aromatics and increasing the saturates content softens the bitumen
- The addition of resins hardens the bitumen and reduces the penetration index and shear susceptibility, but increases the viscosity.

It has also been shown that the rheological properties of bitumen depend strongly on the concert content (Lin et al., 1996). At a constant temperature, the viscosity of a bitumen increases as the concentration of the concert blended into the parent maltenes is increased. However, the increase in viscosity is substantially greater than would be expected if the concert were spherical, non-solvated entities. This suggests that the concert can interact with each other and/or the solvating medium. Even in a dilute toluene solution, the viscosity increase observed with increasing asphaltene concentrations corresponds to a concentration of non-solvated spheres some five times higher than the amount of concert used. Bitumen concert are believed to be stacks of plate-like sheets formed of aromatic/naphthenic ring structures. The viscosity of a solution, in particular a dilute solution, depends on the shape of the concert particles. Size is important only if the shape changes significantly as the size increases. At high temperatures, the bonds holding the concert together are broken, resulting in a change in both the size and shape of the concert or clusters. Consequently, the viscosity falls as the temperature increases. However, as a hot bitumen cools, associations between bitumen concerts occur, to produce clusters.

2.3.2.4. Grades of Bitumen Used for Pavement Purpose.

i. **Grade 30/40**: These are the thicker material having higher softening point and these are used in high temperature regions.

ii. **Grade 60/70:** These are semi viscous material having moderate softening point. It is widely used in India because of its availability & cheaper cost. It is a best suitable material in Indian roads and highways.

iii. **Grade 80/100**: This type of bitumen is thinner material & is used in tropical regions. It is having lower softening point. However, for our study, we will use 60/70 penetration grade bitumen.

2.3.2.5. Mechanical and Physical Properties of Bitumen

These two properties of bitumen are not only important during the fabrication, distribution, and density of asphalt mixtures, but these properties are also very important during servicing. Considering the mechanical and physical properties of bitumen along with its chemical properties can be one of the factors for achieving durable asphalt pavement (Mohamad Beiranvand, 2011).

2.3.2.5.1. Bitumen Behavior

Bitumen from the behavior viewpoint is a viscoelastic substance that in the environment heat and under the specified load neither the behavior of an elastic material nor the behavior of a viscous material but is a combination of these two states, which is viscoelastic. The pure bitumen behavior depends on, due to its viscoelastic nature, the temperature and loading time. In other words, the temperature and time of loading have a combined effect on bitumen behavior (Javad Tanzadeh, 1996).

In high-temperature conditions or long loading times, bitumen behaves as a viscous material (such as moving trucks on the asphalt at low speed or at a stop). Under these conditions, asphalt mix materials tolerate the load. At low temperatures or in fast loading mode (such as fast traffic motion), pure bitumen behaves like an elastic solid. In the elastic behavior resulted from the loading, the deformation is achieved, and the made change is brought back to its original state by loading. Of course, if it is more than a power or compressive resistance, it is possible to break the elastic material. Even the pure bitumen has a low elastic behavior at a low temperature, but when it is overloaded, it would be brittle and fragile, leading to the cracking. Therefore, in cold weather at low temperature, a cracking in the in asphalt pavements may occur (Mehrdad Honarmand, 1993).

In ambient conditions, between very low cold temperatures and very high warm temperatures, i.e., the average temperature of bitumen, it has the behavior of viscous fluids and the behavior of plastic solids simultaneously. Bitumen, in this case, has either viscous behavior or elastic behavior, depending on the temperature and loading time (O. Kristj and sdottir, 2006).

2.3.2.5.2. Bitumen Temperature Susceptibility

Temperature susceptibility which may be defined as how changes made in consistency or stiffness of bitumen (viscosity or degree of penetration) at different temperatures is one of the effective parameters in the behavior of bitumen that for a variety of bitumen is classified in one group (classification based on viscosity or classification based on degree of penetration) may vary. For example, the classification based on the degree of penetration, some bitumen that have the same degree of penetration at temperature of 25 °C may not be the same degree of penetration at the other temperature. Also in terms of classification based on viscosity, several asphalts may have the same viscosity at the temperature of 60 °C, but their viscosity or stiffness is not the same at higher or lower temperatures; therefore, their behavior at times of diffusion, density, and service will be different. This can affect the durability and stability of building mixtures. The greater the changes of stiffness or consistency with changes of temperature, the higher temperature susceptibility in bitumen, and the lower the change,lower temperature susceptibility in bitumen. Bitumen with temperature susceptibility will have better performance in building mixtures (Mohamad Beiranvand, 2001).

2.3.2.5.3. Bitumen Hardening

Bitumen hardening is a phenomenon that may occur under various conditions and factors in the short or long terms. The reason for this is the rapid or gradual changes in the shape and chemical compounds of bitumen due to various factors. Different processes can interfere with the chemical changes of bitumen, among which can be indicated to sublimation of light materials and escape of bitumen, oxidation, polymerization, carbonization, the absorption of bitumen oils by concerts, the chemical reaction between bitumen and mineral components of concerts, and so on (mehrdad Honarmand, 1996).

All abovementioned processes are dependent on environmental conditions, temperature, and thickness of bitumen lining on concerts in asphalt mixtures. Bitumen hardening in asphalt occurs in two stages: one is short term and fast, and the other is long term and gradual (Javad Tanzadeh, 2001). The hardening stage occurs in the short term with high speed and intensity over a short period during heating bitumen and mixing it with rocky materials at high temperatures. The second stage of hardening of the bitumen is gradually and slowly made during service. The results of the physical hardening of the bitumen reduce the degree of penetration, increase the softening point, reduce the plasticity, increase viscosity, decrease adhesion property, and increase the bitumen fragility property. The main factor in the hardening of bitumen is the changes, which occur in the chemical components of bitumen during heating the bitumen, mixing it with stone materials and at the time of service due to the abovementioned factors.

2.3.2.5.4. Bitumen Aging

The gradual changes in the physical and chemical properties of oil bitumen have been accepted as a principle. Researchers believe in this field that the most important factor of these changes is the phenomenon of aging hardening that causes the appearance of various types of damages in the asphalt. Various and different processes interfere with the gradual changes or the bitumen hardening such as oxidation, photochemical reactions, sublimation of bitumen light weight and volatile materials, polymerization, carbonization, absorption of oils in bitumen by aggregates or concrete chemical reactions between bituminous components and mineral compounds of rocky materials, and microbiological transformations. All of the processes mentioned are dependent in time, ambient temperature, heat, thickness, and membrane around concerts (Aklonis JJ, 2005).

For example, the rate of oxidation, which is the most important factor of the hardening of the materials, which it doubles with an increase 10 at 100 °C. Physical hardening is another factor of aging or usual hardening in bitumen. Physical hardening occurs when bitumen is at ambient temperature and is usually attributed to the rearrangement of bitumen molecules and slow crystallinity of waxes. Of course, physical hardening is reversible, and the initial viscosity of bitumen is obtained by heating.

Bitumen binder has the following key characteristic properties.

I. Adhesion:

Bitumen has excellent adhesive qualities provided the conditions are favorable. However, in the presence of water the adhesion does create some problems. Most of the aggregates used in road construction possess a weak negative charge on the surface. The bitumen concrete bond is because of a weak dispersion force. Water is highly polar and hence it gets strongly attached to the concrete displacing the bituminous coating (Mohamad Beiranvand, 1993).

II. Elasticity

Elasticity is the ability of a deformed material body to return to its original shape and size when the forces causing the defamation are removed. The response to relatively small stress results in a directly proportional strain as described by Robert Hooke in Hooke's law in 1660.

III. Plasticity

When temperature rose as well as when a load applied to bitumen, it will flow, but will not return to its original position when load removed. This condition referred as plastic behavior.

2.3.2.6. Drawbacks of Bitumen

- **Temperature Effect**: At high temperature bleeding of building occurs reducing performance of building.
- **Oxidation Effect:** Due to oxidation bitumen may led to cracking & crazing phenomenon.

- **Water Effect:** Due to water, bitumen strips off from the concert forming pothole on buildings being water repellent material. Reducing life of building.
- **High Cost** - Being petroleum product it costs much higher.

Table 2.14: Physical properties of Bitumen

Property	Grades of bitumen	Test method
	60/70	
Specific gravity at 25 ^{0}C	0.99	ASTM D70
Penetration at 25 ^{0}C (100g/5sec),mm	40-60	ASTM D5
Softening Point 25 ^{0}c	49-56	ASTM D36
Ductility at 25 ^{0}C,cm	60- 75	ASTM D113
Water content	0.4	ASTM D5
Flash point ^{0}C	175	ASTM D36
Viscosity@135 ℃	400±200 Cp	ASTM D12

Source: Suleiman Arafat Yero, and Mohd. Rosli Hainin, 2012

Generally, the vast majority of bitumen is used by the construction industry, as a constituent of products used in paving and roofing. Excellent waterproofing characteristics and thermoplastic behavior make it ideal for a wide range of applications. At elevated temperatures (typically between 100 and 200 ^{0}C) it acts like a viscous liquid, and can be mixed with other components and manipulated and formed as required. Once cooled, it is an inert solid that is durable and hydrophobic (repels water).

About 85 % of all the bitumen produced is used in asphalt for the construction of roads and other paved areas. Typically, asphalt will contain approximately 5 % by mass of bitumen, with the remaining 95 % consisting of a mixture of mineral aggregates and much finer materials such as limestone filler (Euro bitumen and the asphalt institute, 2011).

A further 10 % of global bitumen production is used in roofing applications, and the remaining 5 % is used mainly for sealing and insulating purposes in a variety of building materials, such as pipe coatings, carpet backing, joint sealants and paint.

Generally, raw bitumen is an interesting material which can undergo different physical states with variation in the temperature. At room temperature and below 0 ℃, asphalt is bright, rigid, and brittle. When heated above 25 ℃, asphalt begins to soften (between 60 and 80 ℃). However, the softening point depends on the nature and composition of the asphalt. At 120 ℃, asphalt behaves like a Newtonian liquid, and finally, at 200 ℃, bitumen starts decomposition, generating residues (G. Hernandez, E.M. Sanchez, 2006).

Modification of bitumen is one of the approaches to improve the bitumen performance when the asphalt produced does not meet the climatic, load and other applications structure requirement, as reported by Fitzegarald and Ki, 2000.

2.3.3. Glue

Glues have been used for thousands of year in traditional adhesive and sizing application (Hand World lingo, 2010). The earliest indication of use of glue can still be observed in the cave paintings made by our Neanderthal ancestors in Lascaux, France. Egyptian remnants unearthed in their graves show many uses of glues; perhaps the most striking are the coat and inlays in wood furniture, which was made using glue as early as 3,000 B.C. The Egyptians also use glue to produce papyrus. Greek and Roman artists used glues widely; mosaic floors and tiled walls and baths are still undamaged after thousands of years (J. Rank, 2010). The earliest known use of animal glue,for veneering, dates to the period 1500 to 2000 B.C. in ancient Egypt (Desrochers, P. 2001).

The glues used by construction makers were made from animal hides, hooves, and other parts that had been used to produce glue. The glue was ground into power or flakes. It was remixed with water and heated gently in a glue pot. This product was brown, brittle, and hard.

2.3.3.1. Type of Glue

There are many kinds of glue, some of which have been known for a long time. Liquid glue, vegetable glue, casein glue, blood albumin glue and animal glue are some of glue type (J. Rank, 2010.Glue).

2.3.3.1.1. Liquid Glue

Liquid glue are commonly made from the head, skins, bones, and swimming bladders of fish. Some liquid glue, however, are made from animal glue and from other materials. They are ready for immediate use (Glue. Retrieved on December 24/2010). Liquid animal glues can be modified with clays or calcium carbonate as fillers, and wetting and dispersing agents, plasticizers, and other modifiers as required (Hand World lingo, 2010).

2.3.3.1.2. Vegetable Glue

Vegetable glues are made from starch, usually cassava starch, and sold in powdered form. Ordinarily they required heating with water and alkali for preparation (J. Rank, 2010.Glue).

2.3.3.1.3. Casein Glue Blood Albumin Glue

Casein glues are made from casein, lime and certain other chemical ingredients. They are commonly sold in powdered form requiring only the addition of water (J. Rank, 2010.Glue).

Blood albumin glues are made from black soluble blood albumin, a product recovered from the blood of animal. These glues must be mixed just before use, since they deteriorate rapidly in standing (J. Rank, 2010.Glue).

Casein and albumen produce fair adhesives that will bond strongly too many substrates, these adhesives are brittle because they lack the built in “springs” of the helix coil of hide glue (Charles L. pearson. 2003).

2.3.3.1.4. Animal Glue

Animal glues are derivatives of proteins obtained from the simple hydrolysis of collagen, which is a principal protein constituent of animal skin; these are an impure material deeper in color with less thickening power but with greater degree of dispersive efficiency. Glue is an adhesive substance used for sticking objects or materials together or any substance applied to the surfaces of materials that binds them together and resists separation (Roberts MT, Etherington D, 1982). The term glue refers to the crude form of gelatin. Glue refers to the product found chiefly in industrial applications as an adhesive in plywood, paper board, match, abrasive, and similar industries. Gelatin refers to the product in a much purer and cleaner form found to be used in food, pharmaceutical, and photographic industries and in some specific areas of industry as an adhesive material (Allen S, Truax TR, 1922).

Adhesives occurred naturally or produced synthetically, adhesives of "animal" origin, have been found Thorndahl E., (2009) to be non-toxic, biodegradable, and environmental friendly. However, the long term storing of animal adhesives in wet state can cause darken with age and shrinks as they dry (Ebnesajjad S., 2010).

Animal glue is one of the several adhesive which exist so far. It is distinguished from other adhesives by the fact that it comes from organic compound while adhesives are chemical based. Glue is produced by persistent boiling of animal connective tissue, bones and hides in a meat packing and tanning industries. These wastes could be processed to remove collagen, the protein in the tissues. The collagen is sticky and useful for holding things together (Allen, S. W. and Truax, T. R. (1922)). The term animal glue refers broadly to all gelatin type adhesive substance used to form a surface attachment between discrete materials.

There are two major types of animal glue, hide glue and bone glue, differing in the type of raw materials used. Although process conditions may differ, both are obtained by hydrolysis of the collagen in the hide and of connective tissue or bone structure of the raw material. Both types of glue manufacturer obtain the raw material such as bone and tissues of animals from slaughter house, tanneries and meat packing companies (Cabeza, L. F., et al., 2005).

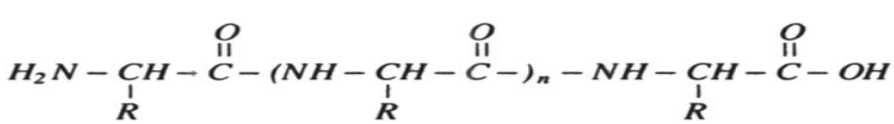
2.3.3.1.5. Chemical Structure and Properties of Animal Glues

I. Chemical Structure and Denaturation

Animal glues are natural polymers derived from mammalian or fish collagen – the major structural protein constituent of skins, connective tissue, cartilage and bones. Collagen consists of long protein molecules composed of naturally occurring amino acids that are linked in specific sequence by strong covalent bonds. Due to the spatial structure of some amino acid units and the presence of many ionisable and polar functional groups in the protein molecule, the individual chains form triple-stranded helical coils that are internally stabilized by hydrogen-bonding (Woodhead-Galloway, 1980).

Collagen itself is insoluble in cold water, and its transformation into soluble gelatin is of critical importance for the performance of the resulting glue. The transition (a process known as denaturation) is achieved by pre-treating the raw collagen with acids or bases followed by hot water extraction. During this process, the stabilizing bonds (predominantly hydrogen-bonds) are broken which causes the triple-helix formation of the collagen molecules to separate into disordered coils of single protein chains, of which gelatin is composed (Rivers and Umney, 2003). The temperature (Td) at which collagen denatures is typical for its source and is dependent on the chemical structure of the proteins. Generally, mammalian collagen has higher Td at around 40-41°C compared with that of marine species, which converts to gelatin at much lower temperatures (Holmgren, 1998). Collagen of deep, cold water fish (such as cod used for fish glue) denatures at approximately 15 °C while warm water species, which are the preferred source of isinglass produced for commercial clarification of alcoholic beverages, have a Td of up to 29 °C (Haug et al, 2004, Norlands product).

Denatured collagen in its pure form is pure gelatin. However, unless the denatured collagen is purified, the gelatin-based glue matrix gained after extraction contains many impurities, e.g. other protein degradation products, minerals and fats. Glues such as hide and bone glue, rabbit skin glue or cold-liquid fish glue contain many impurities and thus have a yellow or brown color. Bovine or porcine gelatin, available in food stores or from chemical suppliers, is the purified product. Isinglass, usually extracted directly by the end user from commercially available dried fish bladders, is naturally a very pure product. This is because fish bladders are the source containing the highest amount of collagen, which is also the least chemically linked, and thus only requires the mildest extraction procedure. Glues are Proteins composed of amino acid monomeric units covalently linked together in specific sequence through peptide bonds:



II. Gelation and Gel Strength

Gelatin in solution has the ability to form a rigid gel upon cooling, which can be repeatedly reactivated with heat. Gelation is based on the partial rearrangement of the protein solution's single random coils back into collagen-like triple helices, occurring at around 32 ºC in mammalian gelatin and at temperatures as low as around 8 ºC in cold water fish gelatin (Horman and Schlebuschm 1971, Haug et al, 2004, Badii and Howell, 2006). This renaturation only develops in sections due to natural misalignment of the single strands, and a continuous three-dimensional network structure is formed. The number of nodes that are established by hydrogen-bonds within and between the molecules determines the rigidity and elasticity of the gelatin or glue matrix, and is measured as gel strength also known as Bloom strength (Kozlov and Burdygina, 1983).

Gel strength is strongly influenced by the molecular weight of the protein molecules, but is also determined by the polymer's chemical composition (which varies with the collagen source and is also influenced during manufacture), and its concentration in solution and temperature, which affects the renaturation level (Kozlov and Burdygina, 1983, Horman and Schlebuschm 1971).

III. Molecular Weight

The molecular weight of the protein chains is one of the most important properties of gelatin-based glue as it influences many of its adhesive properties. Generally, the more vigorous the extraction process of the glue during manufacture (i.e. the more extreme the pH during pre-treatment, the longer the treatment and the higher the temperature at extraction), the more the long protein chains are broken down, which leads to increasingly lower molecular weights (Hickman et al, 2000). Mild extraction at moderate pH and low temperatures yields gelatin-based glues with long chain lengths and high molecular weight (MW) (Hull and Bangert, 1952, Haupt, 2004). As a general rule, gentle processing is appropriate for the hides of young mammals, fish skin and swim bladders because they are rich in collagen content and less stabilized by additional chemical bonds that develop in collagen with ageing. Preparation of animal glues prior to their use by conservators should also follow mild procedures (Luybavskaya, 1990, Haupt, 2004). Ideally, gelatin-based glue solutions should always be prepared fresh and not be kept heated for longer periods, as the glues will gradually degrade and lose their adhesive properties. It is generally recommended to prepare glue solutions at around 60°C, but it should be noted that heating at elevated temperatures (e.g. 80 to 90 °C) can take place without much loss of gelling power if such temperatures are limited to a few minutes only (Haupt, 2004).

IV. Stability with Ageing and Resolubility

Dry conditions cause gelatine-based glues to dry out, shrink and embrittle, due to the development of high inner stress and tensile forces within the glue matrix. In conditions of changing relative humidity (RH) low gel strength glue will deteriorate rapidly in their mechanical properties, while high gel strength glues retain their mechanical properties much better. The reason for this is because at high RH levels a continuous renaturation of the protein molecules is taking place which increases the stress in the glue matrix upon drying. Due to their more elastic molecular structure, highly renatured glues can compensate inner stresses much more successfully than low gel strength glues.

2.3.3.1.6. Uses of Glue

Animal glue currently used for book binding and directory/catalog binding, paper manufacture and converting, industrial abrasives, emulsifying agent, emulsion stabilizer, ore and metal refining, paper box manufacture, matches, gummed tape, wood working, luggage, case covering and lining, rubber compounding, textiles, glass chipping, picture frame and decorative molding composition, and leather manufacturing. Animal glue also used as gesso, a mixture of glue and whiting (Endt, W. D., and Baker, T. B., 2010).

2.3.3.1.7. Analysis of Raw Material Animal Glue

The quality of glue bought was ascertained by determining the following quality indicators of the glue: moisture content, and ash content. All results were the average of duplicate analysis.

i. Moisture Content

100 gram of the glue sample was weighed in a crucible and heated in the oven at a temperature of 60 ℃ until no form of moisture was visible. Heating was continued till no water was visible in any part of the apparatus except in the trap and the volume of water in the trap remained constant for five minutes. The sample was cooled to room temperature and weighed. The moisture content was calculated using the formula:

$$\text{Moisture content (\%)} = \frac{\text{Weight of moisture in glue}}{\text{Weight of glue before drying}} \times 100\ \% \tag{2.1}$$

ii. Determination of Ash Content

100 gram of the glue sample was weighed in a beaker. The beaker with its content was heated to 500 ℃ until the glue became very dry and the visible appearance of black spots on the glue sample. The dried glue was cooled to room temperature and weighed. The ash content of the glue was calculated using the expression:

$$\text{Ash content (\%)} = \frac{\text{Mass of dry glue sample}}{\text{Mass of original glue sample}} \times 100\ \% \tag{2.2}$$

Table 2.15: Parameters of raw material animal glue and its standard

Parameter	Raw material glue	Standard glue	Deviation
Moisture content (%)	17.88	15.00	0.1913
Ash content (%)	3.029	2.000	0.5149

Generally, the melting points of raw materials used in these thesis was describe below

Table 2.16: Melting point of raw materials

Raw materials	Melting points temperature (℃)	
	Standard	Raw material it self
60/70 grade bitumen	120	118.35
PET	240- 260	255
Animal glue	80-90	88

Generally, animal glue was used as an additive to increase the service life of waterproofing materials by increasing the amount of polymer/PET used.

2.4. Blending

The blending of polymer with bitumen is a difficult task. Compatibility is the first and main problem that we must face when we trying to modify bituminous rheology by adding polymer to it. Blending depends on the compatibility (Baker, 1998) of polymer and bitumen to each other.

Incompatible polymer cannot be blended with bitumen. Compatibility is the main considerable factor for the preparation of blend.

2.4.1. Factors Affecting Blending

The process of blending of compatible polymer with bitumen is affected by the following factors (Mohammad Abul, 2012).

Blending Mechanism: The possible problems with modified bitumen are mainly in the storage of the bitumen, mixing temperatures, and the length of time the material is held at elevated temperatures before laying. The blending of bitumen and polymer is not an easy process because two complex materials are forced together to form a two-phase system. The polymer must disperse uniformly into bitumen. Hence it is required to provide high shear force during blending. The configuration of shear blade of the stirrer of blender and the speed of the stirrer determine the shear rate. The speed of the stirrer should not be less than 800 rpm (Ibrahim, et al, 1998). However some polymer does not require high shear force such as EVA and LLDPE.

Blending Time: The duration of blending time depends on the blending temperature and applied shear rate and on the complexity of polymer system. Blending time should be kept minimum by adjusting blending temperature and applied shear rate. Too long blending time may cause the change of rheological properties of PMB.

Blending Temperature: Blending of polymer should be performed within a specified temperature range. It is an important factor. Without controlling the temperature it is not possible to prepare blend properly. The blending temperature mainly depends on the molecular weight of the polymer. Polymer of higher molecular weight requires higher blending temperature (Baker, 1998). Blending temperature of particular polymer is above its melting point. From the economic point of view and to diminish some change in asphalt or polymers, a temperature of the order of the 170-180 °C is generally satisfactory.

2.5. Process Technologies of Bitumen Modification

There are two important process technologies for the utilization of waste plastics in bitumen mix flexible pavement, namely dry process and wet process.

2.5.1. Dry Process

For the flexible pavement, hot PET (160-180 ^{0}C) is mixed with hot bitumen (100 ^{0}C) and the mix is used for building laying. The concrete is chosen on the basis of its strength, and moisture absorption capacity. The bitumen is chosen on the basis of its binding property, penetration value and viscos-elastic property. The concert, when coated with plastics, improves its quality with respect to voids, moisture absorption and soundness. The coating of plastic decreases the porosity and helps to improve the quality of the concert and its performance in the flexible pavement. It is to be noted here that concert with < 2 % porosity is only allowed by the specification. The process applies to plastic waste material only (Sandhya and Deepak, 2013).

I. Advantages of Dry Process:

- Plastic is coated over concrete - improving the surface property of concerts.
- The coating is easy & the temperature required is the same as building laying temp.
- Use of waste plastic more than 15 % is possible.
- Flexible films of all types of plastics can be used.
- Doubles the binding property of concrete.
- No new equipment is required.
- Bitumen bonding is strong than normal.
- The coated concrete show increased strength.
- Replacing bitumen to 15 % higher cost efficiency is possible.
- No degradation of building even after 5-6 yrs.' after construction.
- No evolution of any toxic gases as maximum temperature is 180 ^{0}C.

II. Disadvantages of Dry Process: The process applies to plastic waste material only.

2.5.2. Wet Process

By mixing plastic with bitumen the ability of the bitumen to withstand high-temperature increases. The plastic waste is melted and mixed with bitumen in a particular ratio. Normally, blending takes place when the temperature reaches 90 ^{0}C but when plastic is mixed, it remains stable even at 170 to 180 ^{0}C. The vigorous tests at the laboratory level proved that the bituminous PET mixes prepared using the treated bitumen binder fulfilled all the specified Marshall mix design criteria for surface course of building pavement. Another important observation was that the bituminous mixes prepared using the treated binder could withstand adverse soaking conditions underwater for a longer duration (Mohammad, 2012).

I. Advantages of Wet Process:

- This Process can be utilized for recycling of any type, size, shape of waste material (Plastics, Rubber etc.) (Anzar, 2015, Gawande, 2012).

II. Disadvantages of Wet Process:

- Time consuming- more energy for blending.
- Powerful mechanical mixer is required.
- Additional cooling is required as improper addition of bitumen may cause air pockets in building.
- Maximum % of waste plastic can be added around 20 %.

Although wet Process is time consuming- more energy for blending and Powerful mechanical mixer is required, it can be utilized for recycling of any type, size, shape of waste material (Plastics, Rubber etc.). The dry process involves the blending of waste plastic with hot PET prior to mixing with bitumen. In comparison to the wet process, this mixture type has a number of technical issues. The lack of standards and inconsistent performance have resulted in argument among practitioners and researchers in accepting the dry process for bitumen modification even though it has the potential to recycle more plastic waste compared to the wet process. But considering the limitations of this process that it is applicable to plastic waste only and hence our aim of disposing the total polymer waste for eco-friendly environment cannot be completely achieved. Wet process though it requires strong mechanical stirrer and continuous rotation, batch type production and separate chamber. If processing parameters such as heat losses, temperatures etc. are properly controlled there is reduction in the residence time which minimizes production time and thus improves productivity, hence this process is economically feasible and limitations of dry process can be overcome. As far as type of polymer waste is concerned, wet process is suitable for any type of polymeric waste (Mohammad, 2012). Depending on the above issues our project work is also focused on wet process modification of bitumen using PET waste an excellent additive. There are three wet process (Hossain, 2006). They are a) Chemical reaction process, b) Gelatin process and c) Blending process.

Chemical Reaction Process: Polymer chemically reacts with bitumen and produces blend. The process is performed at the refinery. Obtained blend from this method has higher storage stability.

Gelatin Process: Here polymers do not react with bitumen. Polymer is dispersed in to the bitumen to form a two-phase homogeneous mixer.

Blending Process: This process may be called cooking process and suitable for scrap polymer and rubber. Polymer/rubber is cooked in the bitumen in this process. This method requires a blending/cooking system. Major parts of the blending equipment are a container, a mechanical stirrer with shear blade and controlled heating facilities. Bitumen is heated in the container to make it liquid. Then the polymer in particular form (powder, shredded, pellet, latex) is added to the bitumen and stirring is continued up to completion of blending. Required blending time and temperature and speed of stirrer depend on the type of polymer used.

The drawback with these systems is that mixing uniformly is difficult and often the result is significant segregation of waste plastic.

2.6. Waterproofing

Waterproofing is protection to prevent water from entering internal and external building structures like toilets, swimming pools, water tanks, retaining walls, concrete roofs, etc. There are many different means to provide internal or external membranes in the construction industry. Internal membranes are provided via waterproofing admixtures which are added to the concrete during the mixing process. External membranes are provided using sheet membranes and liquid coatings on the concrete surface (A. P. Anderson and K. A. Wright, 2041).

Waterproofing is an essential requirement of a structure to protect itself from potential damages caused by water and other chemicals like water-born salts and sulfate, nitrates, and carbonates. (Carlisle CCW, 2013) A waterproofing system is necessary for:

- A durable structure
- Hygienic environment
- Pleasing aesthetic appearance
- Increased durability of concrete structures

- Reduce chemical attack
- Cost reduction in maintenance and Prevents growth of dangerous mold

Essential properties of waterproofing materials possess the following properties (Cheryl Roberts, 2015):

- They should minimize the absorption of water by substrate.
- They should exhibit sufficient bond strength with the substrate to resist the outward thrust caused by hydrostatic pressure.
- Puncture resistance
- Durability when expose to the environmental agents of degradation (wind, rain, temperature, and UV radiation).
- Waterproof but not vapor proof
- Flow resistance for high temperature
- Water tightness

In Ethiopia, there is no waterproofing chemical producing factory so most of the time it is imported from other country with high cost.

Table 2.17: Cost of waterproofing chemical from 2014 to 2020 years

Years	Cost of waterproofing chemicals (Birr /litter)
2014	380
2015	450
2016	650
2017	740
2018	800
2019	893
2020	980

Source: Ethiopia revenue and market analysis, 2018

2.7. Modified Bitumen in Waterproof Coating

Bituminous materials are extensively used for underground pipelines and concert protection to exclude corrosive agents, such as water, oxygen, and electrolytes, from contact with the pipe metal.

Bituminous paint is a type of bituminous coating product that provides weatherproofing and corrosion resistance to the elements. It has good adhesive properties. It is used to build a vapor-proof and protective coat by its formulation and polymerization grade. Asphalts are popular building materials widely used for paving and waterproofing and in asphalt concrete composites (Pokonova, Yu. V, 2005). The bituminous coating is also known as asphalt coating. Bituminous paint is strong, waterproof, durable, and economical. It resists manufacturing harsh chemicals and UV light. It also protects surfaces from rust by modifying them.

Since bituminous materials, like PET, are largely hydrocarbon in chemical composition, they should show little tendency to absorb water. Asphalts may contain small amounts of inorganic salts (mostly sodium chloride) derived from the original crude, which through osmotic action would cause increased water absorption. However, present-day refinery methods of treating and distilling crudes keep the salt content down to a small amount; thus the total ash content is generally less than one percent. (Mallison, 2008) has concluded from measurements on water absorption of unfilled bituminous coatings that water absorption is proportional to ash content and is negligible when the ash content is less than one percent.

The water absorption of PET (A. P. Anderson and K. A. Wright) is little due to the non-hydrocarbon constituents, the purified hydrocarbon absorbing comparatively little water itself. The inorganic salts in the PET attract water through the semipermeable hydrocarbon membrane, and since the salts do not escape, the PET absorbs water indefinitely, though slowly, when immersed in distilled water.

What makes bituminous coat highly effective as a sealant or to prevent water ingress is the fact that they're naturally insoluble in water. This makes them a particularly effective type of barrier coating (coatings that are designed to prevent corrosion by repelling the elements that could cause corrosion which in this case is water) by preventing moisture from making direct contact with the substrate. Bituminous paints also typically have strong adhesion properties with almost any material thereby increasing their versatility (Cheryl Roberts, 2015).

2.7.1. The Application of Modified Bituminous Coating

As they come in liquid form, bituminous coating can be applied just as easily as the common house coat. Depending on the shape and size of the surface, you can use typical rollers, brushes or sprayers as you see fit. It should be noted however that bituminous paints do contain solvent so VOC emissions, while not excessive, still exists so the typical safety precautions apply. Don't apply them in a tight, enclosed space unless you're wearing a mask.

The most common applications of bituminous coatings include areas that are beneath screed wet. It is an excellent protective coating and waterproofing agent, especially on surfaces such as concrete foundations.

It is not suitable for exposure to sunlight unless it is modified with a more flexible material such as polyurethane or acrylic-based polymers and other polymers.

Surface preparation is also important with bituminous paints. While they naturally have strong adhesive properties, they can be undermined by a dirty surface. When applying bituminous paints over an existing paint, it's also important to remove any loose or blistering paints beforehand. In an especially harsh environment, bituminous paints can also be applied as a top coat with an additional anti-corrosive layer used as a primer to ensure adequate protection against corrosion.

Bituminous Paints are alkaline resistant hence it is used for under water structure, weather protecting steel work, waterproofing, wood, concrete and potable water tanks.

It is also used for any exterior metal work and iron work such as fire escapes, ladders, gutters, down pipes, railings, fences and gates, etc. It is used to coat ferrous metals, non-ferrous metals and other construction materials, even in marine environments.

General, Depending on the frequency, intensity and length of time on water contact or exposure, water may penetrate into the wall and floor finishes in wet areas in the form of vapour. The accumulated water vapour may damage the moisture-sensitive materials if not blocked by waterproofing membrane/coating or if the installed waterproofing membrane is not functioning, as it should be. For most waterproofing materials the water absorption capacity is around 0.4 to 0.8 percent by weight (Bill Grayson, 2012).

2.7.2. Advantages of Using PET Modified Bitumen Coating

- Outstanding waterproof properties to ensure great protection against corrosion
- Easy to use, single component
- Elastomeric and solvent-based
- High elasticity with a permanently flexible membrane
- Excellent water-resistance after complete hardening
- Excellent adhesion to most building substrates
- Excellent resistance against Chloride and Sulphate ions
- Resistant to underground soil groundwater aggressive effect
- The membrane can be easily repaired by spot application

2.8. Results Found from different literatures

Sabina et al. (2009) evaluated the performance of waste plastic/polymer modified bituminous mix and observed that the results of marshal stability and retained stability of polythene modified bituminous mix increases 1.21 and 1.18 times higher than that of conventional mix by using 8 % and 10 % (by weight of bitumen) polythene with respect to 60/70 penetration grade of bitumen. But modified mix with 10 % polyethylene showed slightly decreased values for marshal stability than that of the mix with 8 % modifier in their results.

Bindu C.S. Beena K.S. (2010) investigates the benefits of stabilizing the stone mastic building (SMB) mixture in flexible pavement with shredded waste plastic. Conventional (without plastic) and the stabilized SMB mixtures were subjected to performance tests including marshal stability, tensile strength and compressive strength tests. Tri axial tests were also conducted with varying percentage bitumen by weight of PET (6 % to 8 %) and by varying percentage plastic by weight of mix (6 % to 12 % with an increment of 1 %). Plastic content of 10 % by weight of bitumen is recommended for the improvement of the performance of Stone Mastic building mixtures.

Gawande et al. (2012) gave an overview on waste plastic utilization in coating of building by using both wet and dry method. They said that use of modified bitumen with the addition of processed waste plastic of about 5 to10 % by weight of bitumen helps in improving the longevity and pavement performance with marginal saving in bitumen usage and according to them use of waste plastics in the manufacture of waterproofing for building and laminated roofing also help to consume large quantity of waste plastics. Thus, these processes are socially highly relevant, giving better infrastructure.

Ahmadi Nia et al. (2012) carried out an experimental research on the application of waste plastic bottles PET as an additive in stone mastic building. Wheel tracking, moisture susceptibility, resilient modulus and drain down tests were carried out in their study on the mixtures that included various percentages of waste PET as 0 %, 2 %, 4 %, 6 %, 8 % and 10 % by weight of bitumen content. Their results show that the addition of 9.5 % waste PE into the mixture has significant positive effect on the properties of SMB which could improve the mixture's resistance against permanent deformation (rutting), increase the stiffness of the mix, provide lower binder drain down and promotion of re-use and recycling of waste materials in a more environmentally and economical way.

Vargas et al. (2013) analyzed the chemically-grafted polyethylene as of bitumen modifiers. Their results show that the softening point of waterproofing increased, while the penetration degree decreased in blends prepared with grafted polyethylene and the phase distributions of micrographs from fluorescence microscopy show that non grafted polyethylene polymers were not readily miscible with bitumen. The results of rheological tests carried out in their study indicate that most of mixture blends exhibit improved performance at higher temperature with grafted polyethylene such as enhancing rutting resistance, flow activation energy and superior time–temperature dependent response as compared to the reference polyethylene blends.

Khan and Gundaliya et al. (2012) stated that the process of modification of bitumen with waste polyethylene enhances resistance to cracking, and rutting by increasing softening point, hardness and reducing stripping due to water, thereby improving the general performance of building over a long period of time. According to them, the waste polythene utilized in the mix forms coating over concrete of the mixture reduces porosity, absorption of moisture and improves binding property.

Awwad and Shbeeb (2007) indicated that the modified mixture has a higher stability and VMB percentage compared to the non-modified mixtures and thus positively influence the rutting resistance of these mixtures. According to them modifying mixture with HDPE polyethylene enhances its properties far more than the improvements realized by utilizing LDPE polyethylene.

Purity (2012) studied the behavior of bitumen mixes modified with waste polythene. He used various percentages of polythene for preparation of mixes with a selected bitumen grading as given in the IRC Code. Marshall Properties such as stability, flow value, unit weight, air voids are used to determine optimum polythene content for the given grade of bitumen (60/80) in his study. Considering these factors he observed that a more stable and durable mix for the pavements can be obtained by polymer modifications.

Reinke and Glidden (2002) tested the resistance of HMB mixtures to failure by using the DSR (dynamic shear rheometer) creep and recovery tests and reported that result shows improved resistance in case of polymer modified binders.

Karim et al. (2012) gave a potential solution to strength loss of bituminous pavement under water. They compared performance of bituminous mix under water with and without polyethylene admixture and conclude that bitumen mixes with polyethylene performed well under water and showed even better Marshall Stability than normal bituminous mix under normal condition keeping the environment safe from pollution was an added bonus.

Vasudevan (2004) utilized polythene/polypropylene Bags for integrated development of Rural and Arterial building network for socio-economic growth. He studied both dry and wet mixing process by adding polymer with respect to the weight of bitumen used. Author reported that polymer bitumen blend is a better binder compared to plain bitumen resulting higher marshal stability and decreasing the possibilities of flow.

Verma (2008) studied that plastic increases the melting point of the bitumen and makes the building flexible during winters resulting in its long life. According to author while a normal “bitumen quality” waterproofing lasts four to five years, plastic-bitumen waterproofing can last up to 10 years and it would be a boon for India’s hot and extremely humid climate, where temperatures frequently cross 50 °C and torrential rains create havoc, leaving most of the building with big potholes.

Moghaddam and Karim (2012) reported that the utilization of waste material in building pavement would be beneficial to find an alternative solution to increase the service life of building pavement and reduce environmental pollution as well. From their study it is concluded that Polyethylene (PE) reinforced mixtures possess higher stability value, flow, fatigue life in comparison with the mixtures without PE.

Sui and Chen (2011) studied application and performance of polyethylene as modifying additive in waterproofing mixture. They added polyethylene as additive to hot bitumen for some hours, and see the effect of polyethylene. They concluded that there is improvement on high temperature stability, low temperature cracking resistance and water resistance on modification and evaluate polyethylene as additive in the technical, economic and environmental aspects.

2.9. Properties of Plastic Waste Bitumen/Modified Bitumen

- Resistance to permanent deformation: The mix should not distort or be displaced when subjected to loads. The resistance to permanent deformation is more important at high temperatures.
- Fatigue resistance: the mix should not crack when subjected to repeated moisture/ice over a while
- Resistance to low-temperature cracking, this mixed property is important in cold regions.
- Durability: the mix should contain sufficient bitumen to ensure an adequate film thickness around the concrete particles. The compacted mix should not have very high air voids, which accelerates the aging process.
- Resistance to moisture-induced damage
- Skid resistance.
- Workability: the mix must be capable of being placed and compacted with reasonable effort.

The maintenance cost of the building will come down, as the building's life increased by 2 to 3 times. The durability of the building lay out with PET is, more compared with building with bitumen with the ordinary mix (Anzar, 2015).

2.10. Concretes

Concrete is a mixture of three components: water, cement, and aggregates, water acts as a bonding agent. The cement paste hardens through a chemical reaction called hydration and gains strength. The quality of the cement paste generally determines the characteristics of the concrete. The hydration between cement and water makes the concrete harden. The complete hardening of the concrete takes 28 days after casting. The strength of concrete is calculated in grades which also refer to the resistance of concrete against a certain compressive force (Daily Civil. 2017).

There are different concrete grades, for example, M10, M20, M30, and M40 but there is also the conventional grading of concrete where the strength of concrete is graded as C15, C20, and C25. The M and C terms used stand for the mix ratio in concrete which is either cubic or cylindrical in shapes. Table 1 below shows the characteristic compressive strength at 28 days and according to the strength class (Silica Fume for Sale, Microsilica Supplier in China. 2019).

Table 2.18: Different types of concrete grade and their use

Concrete grade	Mix ratio (cement, sand, and aggregate)	Compressive strengths
C15	1:2:4	15 MPa
C20	1 :1.5 :3	20 MPa
C25	1 :1: 2	25 MPa

Source: W. & Ademola Arasi, 2003

The C25 grade concrete is concrete that can withstand the compressive strength of 25MPa per square millimeter on the 28th day after casting. The C25 specimen can be a cube or cylindrical. (Adewole; K; Olabanji Ajagbe, 2015) The C25 concrete is medium strength concrete and water to cement ratio of 0.5. C25 concrete is used in all construction areas. It is a multipurpose concrete mix, usually used for the foundation of infrastructure (Concrete, B. 2019).

CHAPTER THREE

MATERIALS AND METHODS

3.1. Materials and Chemicals

3.1.1. Materials

The main materials used in this study were PET waste, animal glue, and 60/70 grade bitumen (unmodified).

3.1.2. Raw Material Preparation

A. Plastic

The waste plastic used in this research is Polyethylene terephthalate (PET) which is collected from a local company called Inova located around Bishoftu.

B. Bitumen

The bitumen used in this research is of grade 60/70. It is collected from Oromia construction Work Corporation. Grade 60/70 was chosen because it is the most used type of bitumen in our country and has a moderate softening point. The grading of the bitumen is based on, the penetration value.

C. Animal glue

The animal glue (local name misr cola) was collected in the shredded form from a shop in Adama.

3.2. Equipment used for this study

The experiment was conducted at the departments of Chemical Engineering, Materials science and Engineering, and Civil Engineering of Adama Science and Technology University.

Table 3.1: Apparatus used for Bitumen modification and tests

Equipment/Apparatus	Use of these apparatus
Ductility (H-1068)	To measure the elasticity of plain and modified bitumen
Penetrometer(UTB-0120)	To measure the strength/penetration of plain and PMB
Ring and ball apparatus(UTB-0236A)	To measure softening pointe of plain and PMB
Visco meter (Vt873)	To measure the viscosity of bitumen
Digital Balance(DS852)	To measure the weight of PE bottle waste and plain bitumen
Water bath(WB-22)	For cooling of bitumen during testing
Heating oven (DHG-9023A)	To heat bitumen, glue, and PET
Beaker(500 ml)	A container for the ring and ball apparatus during softening point test
Bag	For temporary storage of crushed plastic
Thermometer	For temperature measurement during characterization
Sieve	For separation of PET depends on their size d/c
Boalmine	To reduce the size of animal glue
mechanical mixer	To mix the modified bitumen
Peel system	To testing of its stability

3.3. Specimen Mixing of Bitumen, Animal Glue, and PET

Since the size of plastic from the company had different sizes (60 to 80 mm), it needed sieving. For this experiment particle sizes ranging from 60 mm to 36 mm were used for workability and to readily homogenize the mix.

Afterward, Bitumen was heated to the temperature of 90 ℃, which is its phase changing temperature refluxed for 30 min to remove its residual moisture. Pieces/powder PET (1 to 20 %) and animal glue were added slowly to the hot bitumen of temperature between 160 to180 ℃

(Gawande et al. 2012). The mixture was stirred (figure 3.1) with a speed of 500 to 800 rpm for about 2 hr (Kishchynskyi et al. 2016). Once the bitumen and PET were uniformly mixed, the adhesive material, animal glue (1 to 6 %) was added and mix for 1 hr. while keeping the temperature at 175 °C. The reaction is carried out under a standard atmosphere. PET-bitumen-animal-glue mixtures of different compositions were prepared and then to produce a bituminous waterproofing coat, the mixtures were cooled to reduce the force of attraction between the surfaces of molding material and for carrying out tests that shows the bitumen quality.

Finally, water absorption, softening point, adhesiveness/ stability, penetration, FTIR, ductility, and viscosity laboratory tests were conducted to understand the nature of the modified bitumen for waterproofing (waste PET, animal glue, and bitumen mix) and to find out the load-bearing capacity of the modified waterproofing material.

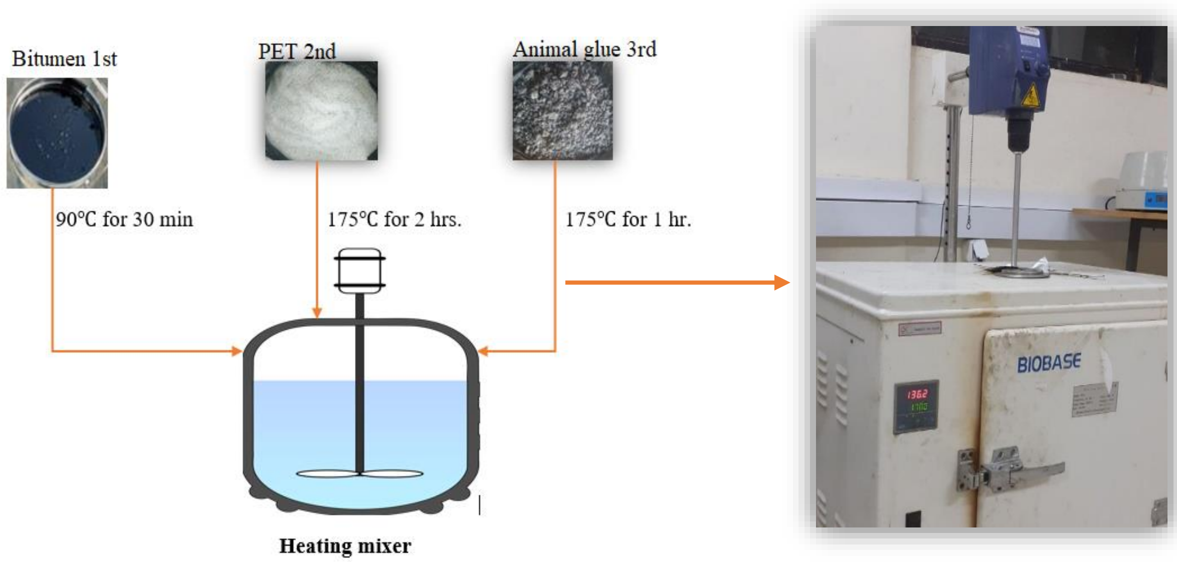


Figure 3.1: Experimental procedure of bitumen modification

3.4. Formulations of the Experiment

To investigate the synthesis and characterization of the bitumen-based waterproofing material, thirty-two experiments were conducted as shown in Table 3.2 (with animal glue) and Table 3.3 (without animal glue). Initially, 100 grams of bitumen grade (60/70) was measured.

Table 3.2: Formulation of the experiment with animal glue

Animal glue (%)	PET (%)	Mass of glue (g)	Mass of PET (g)	Mass of bitumen (g)
0	0	0	0	100
0	1	0	1	99
0	3	0	3	97
0	5	0	5	95
0	6	0	6	94
0	7	0	7	93
0	9	0	9	91
0	10	0	10	90
1	11	0.89	11	88.11
2	12	1.76	12	86.24
3	15	2.55	15	82.45
4	16	3.36	16	80.64
5	17	4.15	17	78.85
5.25	18	4.305	18	77.695
5.5	19	4.45	19	76.55
6	20	4.8	20	75.2

Table 3.3: Formulation of the experiment without animal glue

PET (%)	Mass of PET (g)	Mass of bitumen (g)
0	0	100
1	1	99
3	3	97
5	5	95
6	6	94
7	7	93
9	9	91
10	10	90
11	11	89
12	12	88
15	15	85
16	16	84
17	17	83
18	18	82
19	19	81
20	20	80

3.5. Testing Basic Property of Samples

The different percentages of polymer concentration will provide a wider range of results which helps in analyzing each type of polymer blend at a particular concentration. In this context, the experiment with modified bitumen was carried out to evaluate the performance of binder properties, Penetration/hardness test, softening point, adhesiveness, water absorption, viscosity, FTIR, and ductility.

3.5.1. Penetration Test

Penetration measures the hardness or softness of the plastic and bitumen mixture by measuring the depth in tenths of a millimeter to which a standard loaded needle will penetrate vertically in 5 seconds. A softer bitumen will have a higher penetration, while a harder bitumen will have a lower penetration.

The penetration grade of the neat bitumen with and without PET was investigated using the penetrometer following the ASTMD5-97 specification. The equipment, penetrometer consists of a needle assembly with a total weight of 100 g and a device for releasing and locking in any position.

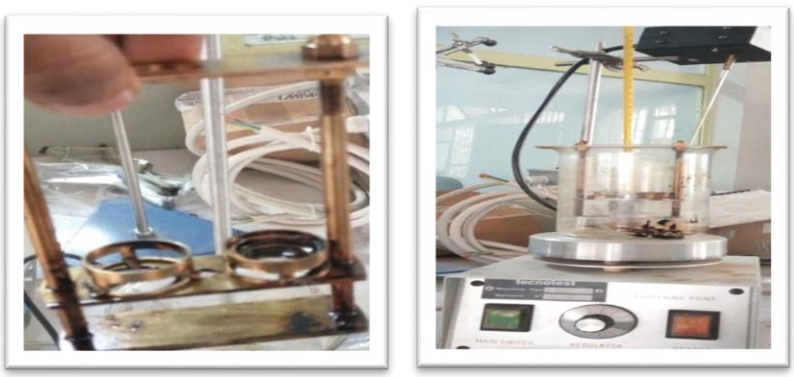
The bitumen softened to a pouring consistency stirred thoroughly to avoid the presence of any air voids in the sample and poured into containers at a depth at least 15 mm over the expected penetration. The test was conducted at a specified temperature of 25℃. In the standard test condition, a standard needle of a total load of 100 g is applied to the surface of a bitumen sample at a temperature of 25 ℃ for 5 seconds. The amount of penetration of the needle at the end of 5 seconds is measured in units of a millimeter (or penetration unit).

Figure 3.2: Penetration test or pentameter

3.5.2. Softening Point Test

Softening point denotes the temperature at which the bitumen attains a particular degree of softening under the specified condition of the test.

The test was conducted by using the Ring and Ball apparatus by ASTM D36-95 specifications. A brass ring containing a test sample of bitumen suspended in liquid like water or glycerin at a given temperature, a steel ball placed upon the bitumen sample, and the liquid medium heated at a rate of 5 ℃ per minute. Temperature is noted when the softened bitumen touches the metal plate which is at a specified distance below.



(A) (B)

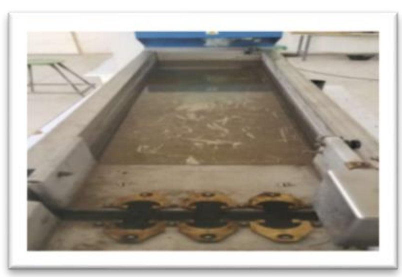
Figure 3.3: Softening point test

3.5.3. Ductility Test

This test was conducted as described in ASTM T 51. Ductility is the property of bitumen that permits it to undergo great deformation or elongation. Ductility is defined, as the distance in cm, to which a standard sample or briquette of the material will be elongated without breaking. The modified bitumen sample was heated and poured into the mold assembly placed on a plate, these samples with molds were cooled in the air and then in a water bath at 27 ℃ temperature. The excess modified bitumen was cut and the surface leveled using a hot knife, then the molds with the assembly containing sample were kept in a water bath of the ductility machine for about 90 minutes. The sides of the molds were removed, the clips were hooked on the machine and the machine was operated. The distance up to the point of breaking of the thread was considered as the ductility value, which was reported in cm. specifically, the following procedure was applied:

- The Modified bituminous material was completely melted to be tested by heating it to a temperature of 75 to 100 ℃ above the approximate softening point until it becomes thoroughly fluid. The molds were assembled on a brass plate and to prevent the material under test from sticking, thoroughly coat the surface of the plate and the interior surfaces of the sides of the molds with a mixture of equal parts of glycerin and dextrin. While filling, pour the material in a thin stream back and forth from end to end of the molds until it is more than level full. Leave it to cool at room temperature for 30 to 40 minutes and then place it in a water bath maintained at the specified temperature for 30 minutes, after which cut off the excess bitumen using a hot, straight-edged putty knife or spatula, so that the molds are just level full.
- The brass plate was placed and molds with briquette specimen in the water bath and keep it at the specified temperature for about 85 to 95 minutes. The briquette was removed from the plate; detach the side's pieces and the briquette immediately.
- The rings were attached at each end of the two clips to the pins or hooks in the testing machine, the two clips apart were pulled horizontally at a uniform speed, as specified, until the briquette ruptures. The distance was measured in cm through which the clips have pulled to produce rupture.
- While the test is being done, make sure that the water in the tank of the testing machine covers the specimen both above and below by at least 25 mm and the temperature is maintained continuously within ± 0.5 ℃ of the specified temperature.

(A)



(B)

Figure 3.4: Ductility test

3.5.4. Viscosity Test

Bitumen is a rheological, thermoplastic, and viscoelastic material. Its deformation characteristics vary not only with a load but also with the time rate of load application and temperature. It is neither elastic nor viscous in behavior. At low temperature, it exhibits elastic behavior while at high temperature it exhibits viscous behavior (X. Lu, and U. Isacsson, 2001). The neat binders lack the proper viscous-elastic balance that usually occurs due to an effective elastic network created by the molecular association. It is hypothesized that proper visco-elastic balance can be formed by creating molecular entanglement in a bitumen through the use of high molecular weight polymeric additives.

The viscosity of bitumen shows a complex response under different conditions and it influences the mixing, laying, and compaction of asphalt mixtures as well as the pavement performance (C. Binard, et al., 2004). Given these reasons viscosity measurements have been used to classify bitumen, but due to the visco-elastic nature of bitumen's the results lack uniformity as the bitumen source and molecular content might differ (Y. Edwards, and P. Redelius, 2003).

This study investigated the viscosity at production and working temperature of neat and modified bitumen. In this study the commercial additive PET was used to lower the viscosity of the binder at high temperature, making it less susceptible to high-temperature damage, and flow improver at low temperature. The additive PET is introduced to warm mix asphalt (WMA) by blending with the binder at the terminal or contractor's tank.

Viscosity Test Procedure

To measure the viscosity of bituminous coat waterproofing, the sample was heated at a minimum temperature of 60 ℃ because the sample was more or less solid at room temperature so to mix, it was viscous fluid firstly. Then, the 500 ml beaker was filled with samples up to 200 ml. Then, once the stirrer is immersed into the beaker, the stirrer starts to rotate with a speed of 60 rpm within 20 seconds after that the viscosity of the sample was recorded with a unit of centipoise (Cp) at different temperatures.

3.5.5. Water Absorption Test

This test is described in ASTM D570. Water absorption is the amount of water absorbed by a material and is used to determine the amount of water absorbed under specified conditions (J.K. Lim, 2011).

The water absorption properties of bituminous coatings have been accepted by many pipeline technologists as a measure of the pipe coating's effectiveness; low water absorption is thought to be necessary to prevent corrosion. However, a direct measurement of the water permeability of the coating should be a better criterion of its protective quality than any inference drawn from absorption (A. P. Anderson and K. A. Wright, 2001). The property of waterproofing material is marked by its ability to prevent moisture from penetrating through concrete.

For concrete pavers, the test procedure involves drying a specimen to a constant weight, weighing it, immersing it in water for a specified amount of time, and weighing it again. The increase in weight as a percentage of the original weight is expressed as its absorption of water (in percent) or the hydrophilic and hydrophobic nature of the product can be determined by ImageJ software by adding a small droplet of water to the coating sample that measures the angle between the droplet liquid and coating sample.

Water Absorption Test Procedure

Incidentally, the tests usually employed to measure water absorption have often sacrificed scientific validity to simplicity. This is particularly true of the soaking test in which cubes of bituminous materials are weighed after varying periods of immersion to determine the water absorption by a gain in weight, (A. P. Anderson and K. A.Wright, 2008).

To measure the water absorptivity of the sample, first, the mass of the sample (original mass) was measured and the sample was immersed into water containing beaker for 24 hours, followed by triplicate measurement of the mass of the sample (wet mass) within five minutes and the average value was taken. Finally, the following formula was used to calculate the percent of water absorption by the sample.

$$\text{Water Absorption in } \% = \frac{\text{Wet mass} - \text{Orginal mass}}{\text{Orginal}} \times 100\ \% \qquad (3.1)$$

In another analysis, the hydrophilic or hydrophobic nature of the bituminous coat was determined by ImageJ analysis software. This software works on the substrate coated by the sample then a small droplet of water was added on the surface of the coated substrate, finally the contact angle was recorded by measuring the angle between the substrate and the droplet. If the angle is greater than 90 degrees, it is said to be hydrophobic but the angle is less than 90 degrees, it is side to be hydrophilic.

Generally, the Water Absorption test standard ASTM D570 specifies that water absorption of strong waterproofing materials should not exceed 0.4 % to 0.8 % in critical conditions such as highly aggressive chloride or freeze-thaw exposure (Muethel, 1997).

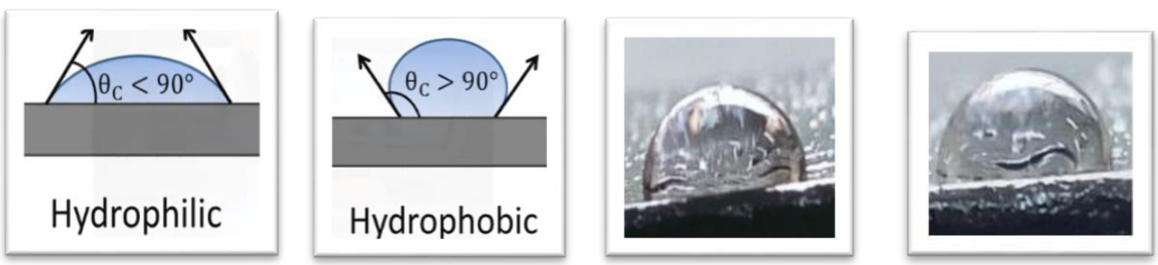


Figure 3.5: Water droplet for contact angle measurement using ImageJ software

3.5.6. Adhesiveness /Stability Test

Qualitatively, the word adhesion simply signifies the sticking together of two similar or dissimilar materials; if the materials are identical then the term "autohesion" or "cohesion" is applied, and in the case of dissimilar materials the preferred term is "heterohesion" and is related to the nature and strength of the binding forces between two materials in contact with each other. The properties of the bitumen mixture are closely related to the performance and adhesion between concrete and asphalt. Loss of adhesion that means losing its stability is caused by the breaking of adhesive bonds between the concrete surface and the bitumen binder primarily because of the coupled action of water and load (K. L. Mittal, 1976).

Since the great importance of measurement for bond strength, there have been several methods that developed recently in the coatings and adhesive industry to determine the mechanical strength of an adhesive joint depending on its substrate and application (K. Kanitpong, HU

Bahia, 2003). But for concrete substrate coating/ paint adhesion test was performed by cross-hatch cutter and tap test.

Adhesion is influenced by the properties of the concrete, such as chemical composition, surface roughness, shape, amount of cut surface, and porosity. (Khan A, Redelius P and Kringos N 2016).To improve the adhesion properties, the bitumen is modified by the addition of a variety of improving additives like PET polymers and animal glue. For a standard test of coating, a cross-hatch cutter mechanism of adhesion test was performed.

Cross hatch cutter test of adhesion

In Paint & Plating industries, the Paint adhesion test is the most common and widely used test procedure that helps to determine whether the paint or coating of the material adheres to the substrate to which they are applied or to test the adhesion strength of the coating to a substrate. This is performed using a test procedure known as the Cross Hatch test.

The cross-cut test is a method of determining the resistance of paints and coatings to separation from substrates by utilizing a tool to cut a right angle lattice pattern into the coating up to a 3mm spacing - for coating thickness of 250 µm, penetrating to the substrate (Mittal, K L 1995). The crosshatch adhesion test is conducted to ensure that the paint coating applied on a metallic substrate adheres properly assessed against ISO 2409. This test is conducted with the help of crosshatch adhesion tapes (adhesive tap ISO 2409 & ISO 8502-3 Tape, Single Roll).

Using a wet film comb

For the wet film comb analysis, Elcometer Wet Film Comb is cleaned and ensured it was undamaged. The following procedure was followed in this case:

i. The comb was holed perpendicular to the wet film and the edge of the comb was pressed into the film until it is stable on the substrate.
ii. The comb was removed from the wet film.
iii. The teeth of the comb were examined and the last tooth was located which is wetted. Read the thickness value of this tooth. The wet film thickness is between this value and the thickness value of the next dry tooth.

Cross hatch cutter test procedure

First, the metallic substrate was cleaned and the substrate with a thickness of 250 µm was coated, then a cross-hatch in finish film was cut on a substrate with a crosshatch cutter up to 3 mm space. Then the cross-hatched area was brushed. With cross-hatch tape applied to the area, a mechanically fixed pulley system was pulled off. Finally, the amount of coating removed was compared with a photographic standard to determine the coating adhesion rating or measure the mass of the sample that can be used to peel the tap from the coated surface using a fixed pulley system (Appendix XXX) and the force required to peel the tap using the formula (F = mass multiplied by gravity).

3.5.7. FTIR Analysis

The chemical variations of the bitumen's compositions can be evaluated by several techniques such as X-rays, ultraviolet fluorescence, Fourier-transform infrared spectroscopy (FTIR), etc. (Guern et al., 2010).

The FTIR is based on the absorption of infrared radiation by the analyzed material and it is the most commonly used technique to control the changes in the chemical composition of bitumen after mixing (Nivitha et al., 2016). It allows, via the detection of chemical bonds vibration characteristics, to perform the chemical function analysis of the material. For this study, FTIR tests were performed on both bitumen conditions (pure and modified).

Fourier-transform infrared (FTIR) spectroscopy (Perkin Elmer Instruments-Spectrum One, Massachusetts, USA) was applied in transmission mode to determine the functional characteristics of the Bitumen and PMBs.

This instrumental analysis was used to analyze the functional group of pure bitumen and polymer (PET) modified bitumen at different content of PET. In this analysis, only the functional group but also the absorption peak property of bitumen and polymer modified bitumen were observed.

CHAPTER FOUR

RESULTS AND DISCUSSIONS

4.1. Results

In these studies, it was noted that increasing the percentage of plastic waste highly influences the penetration, Ductility, Water absorption, Viscosity, Stability, and Softening point value of the modified bitumen.

All experimental tests were performed three times and their average result was considered for analysis.

4.1.1. Adhesiveness /Stability Test Results

The results of the adhesiveness test at different PET and Glue percentage was conducted by peel test (see the appendix xxx).

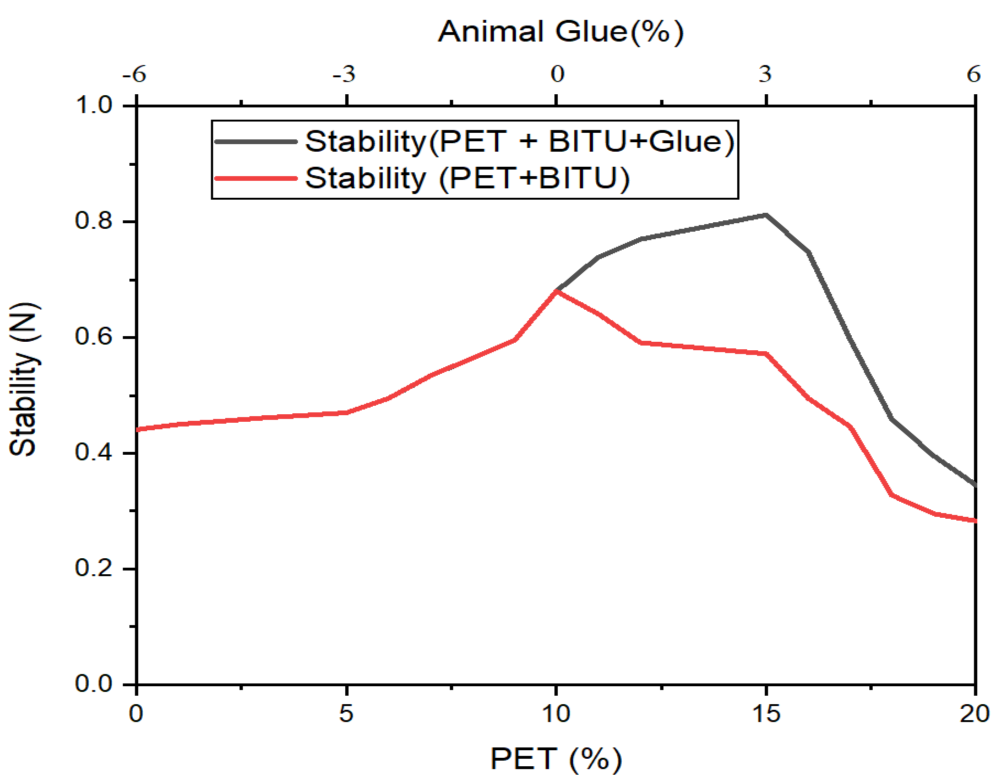


Figure 4.1: Stability results

As it can be observed from the above graph in Figure 4.1, the stability of Modified bitumen mix was increased as the waste plastic content (PET) increases till it reaches the peak at (10 %) content then it started to decline steeply at higher PET content (the red curve). The improvement of stability in PET modified bitumen mixes can be explained as a result of the better adhesion developed between modified bitumen and concrete due to intermolecular bonding, these intermolecular attractions enhance the strength of bitumen mix, which in turn help to enhance durability and stability of the mix.

Also, in figure 4.1, it can be seen that the stability was 0.45 N at (0 % PET) pure bitumen but after the addition of PET, the stability was an increase (0.75) until it riches 10 % of PET (red curve) after 10 % PET the stability started to decline due to weak bond strength between the product and the substrate. To increase the stability after 10 % PET adhesion promoter or enhancement (glue) material was required. After the addition of animal glue of 3 % (black curve), the peak for PET added in the mixture was shifted to 15 %. The reason is that the addition of glue enhanced the bond strength of the product in comparison with that of PET alone and this raised the stability of the product to a force of 0.8 N. For example, the stability of the black curve (PET +glue+ Bitumen) at 12 % of PET was around 0.75 N but the stability of the red (Bitumen + PET) curve at the same content of PET (12 %) was around 0.55 N, this shows that the addition of animal glue was important in increasing the stability by adding of 5 % PET. However, the optimum stability of commercial waterproofing material resists up to a force of 0.75 N. This result shows that PET and animal glue modified-bitumen-based waterproofing material meets adhesion requirements for the intended purpose in the construction sector. Moreover, as can be seen from the stability graph, stability showed a decline after 15 % PET and 3 % animal glue due to weak intermolecular force between the product and the substrate. This implies that adhesive material (glue) does not substitute or replace the adhesive nature of bitumen. And from this graph, the best formulation for waterproofing application was 15 %, 3 %, and 82 % of PET, Animal glue, and Bitumen respectively.

4.1.2. Penetration results

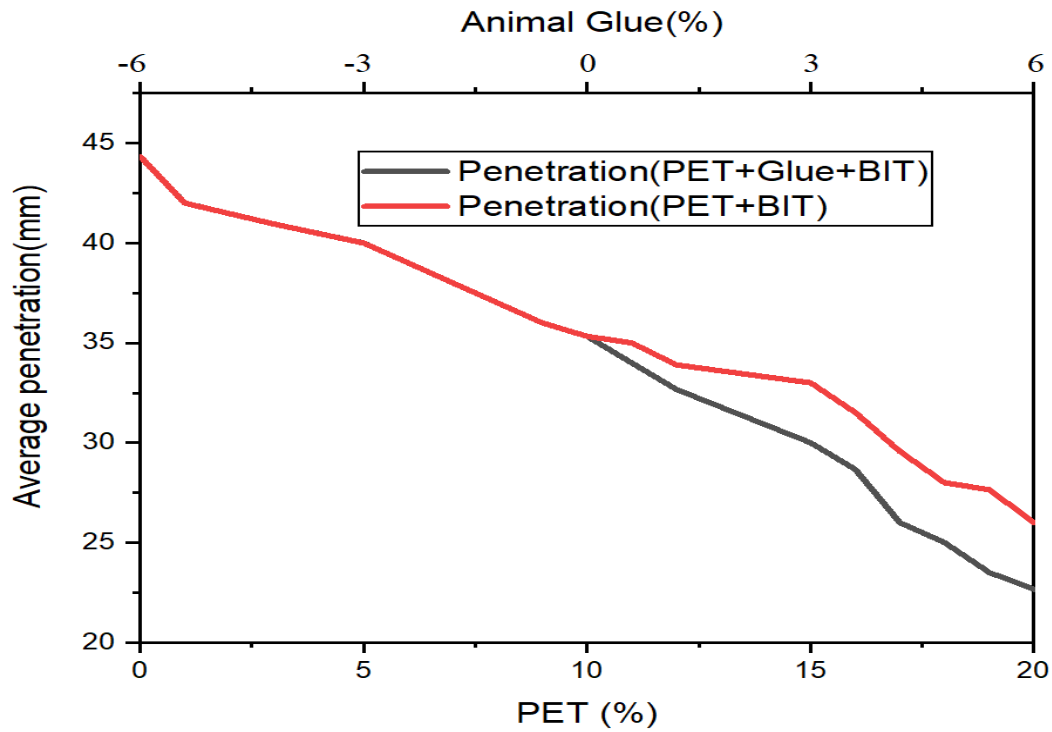


Figure 4.2: Penetration test results

As shown in Figure 4.2, the penetration values are decreasing more significantly, when 60/70 bitumen was mixed with Animal glue and PET. Thus, this significant decrease in penetration values for modified blends, indicates that there is improvement in their heat resistance characteristics (Farahani et al., 2018). In which increasing the waste plastic percentage and animal glue in the mix will decrease the penetration value by increasing the stiffness of polymer-modified bitumen-based waterproofing material. A sharp decrement in penetration values of PET-modified bitumen blends confirms the hardening effect taking place due to the change in physicochemical properties of bitumen after modification (Habib et al., 2015).

From the above graph we conclude that, after the addition of glue, the penetration decreasing rate was higher in comparison with that of PET (the black curve). For example, the penetration of the black curve (PET +Bitumen +Glue) at 20 % of PET was around 22.5 mm but the penetration of the red (BIT+PET) curve at the same content of PET (20 %) was around 26 mm, this shows that the hardness of the black curve was higher than the red one by 3.5 %.

In another word, the addition of waste plastic and glue increases the hardness of the modified bitumen. The penetration values of the blends are decreasing depending upon the percentage of glue and PET. When 6 % glue and 20 % PET by weight of bitumen are mixed, the penetration result becomes 25 mm, which is closer to a good bitumen grade 30/40 which have a penetration value range from 30 mm to 40 mm but after the addition of glue the hardness of the product was increased. This shows the better improvement in heat resistance characteristics of modified-bitumen-based material in comparison with that of PET and bitumen mix.

Therefore, considering the selected formulation for the stability test (that is 15 %, 3 %, and 82 % of PET, animal glue, and bitumen respectively), the average penetration was 31mm. This is considered to be good strength for waterproofing purposes.

4.1.3. Softening Point Test Results

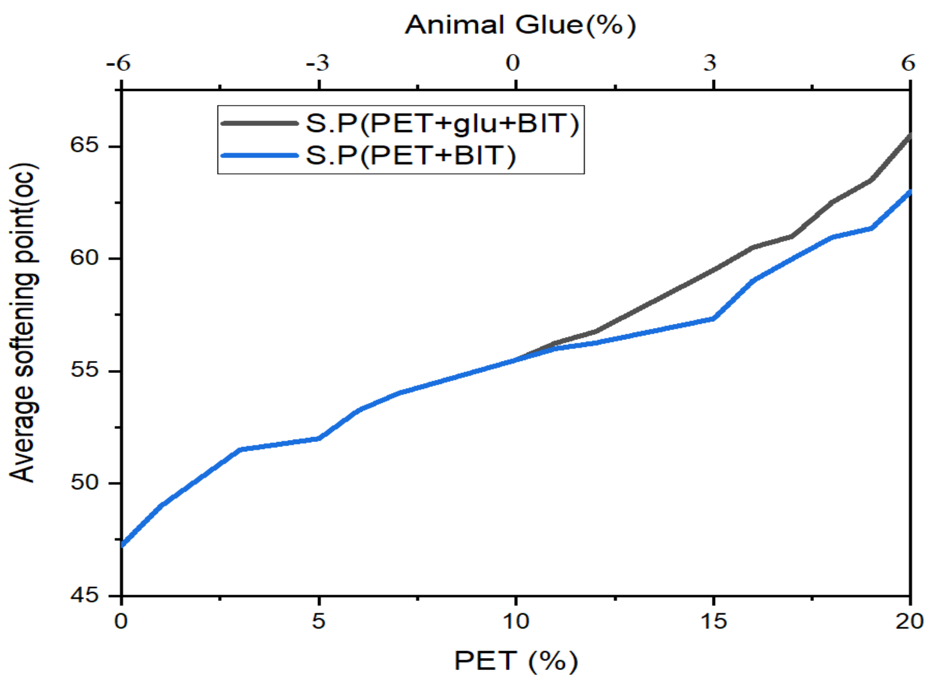


Figure 4.3: Softening point test results

Figure 4.3, shows, softening point increased by the addition of plastic waste and glue to the natural bitumen. The higher the percentage of plastic waste added, the higher was the softening point due to the glass transition temperature of polymer being higher than pure bitumen. The influence over the softening point may be due to the chemical nature of PET and glue added, hence indicating that the PET/bitumen blends have shown a significant improvement at a high in-service temperature of bitumen (Ouyang et al., 2012). However, it is widely recognized that although the softening point is a common empirical parameter used by practitioners, it does not represent clear evidence of the in-service long-term performance at high temperature and. The increase in the softening point shows that there will be lesser bleeding during summer (where the temperature is high) and suggests that the addition of PET causes a substantial resistance to deformations at both moderate temperature and high temperature (Gabriel, Feng, et al. 2017). This improvement in softening point after PET modification of bitumen is attributed to the internal structure formed by the polymer (Apia et al., 2017. As seen in the above figures 4.3, the softening point has increased compared with plain bitumen. Moreover, adding of 1% to 20 % PET and 1% to 6 % glue by weight of bitumen has increased the softening point and the maximum glue and 20 % PET by weight of bitumen have increased softening to a temperature of 65 ℃, and this makes the 60/70 grade bitumen to have a softening point of bitumen grade 30/40, which ranged from 50 ℃ to 65 ℃.

Generally, the higher softening point offers better rutting resistance at high temperatures. When the softening point is increasing there will be the reduction of susceptibility at high temperatures. This type of phenomenon shows that the resistance of the binder to the effect of heat is increased and will reduce its tendency to soften in hot weather.

From the above graph we conclude that, after the addition of glue, the softening point increasing rate was higher in comparison with that of PET (the black curve). For example, the softening point of the black curve (PET + Bitumen + Glue) at 20 % of PET was around 65.5 ℃ but the softening point of the blue (Bitumen + PET) curve at the same content of PET (20 %) was around 62.5 ℃ this shows that the softening point of the black curve was higher than the brawn one by 3 % and used in hot weather this implies that addition of glue has increased the softening temperature.

Therefore, considering the selected formulation for the stability test (that is 15 %, 3 %, and 82 % of PET, animal glue, and bitumen respectively), the average softening point was 56 ℃. This is considered to be good heat resistance for waterproofing purposes.

4.1.4. Ductility Tests Results

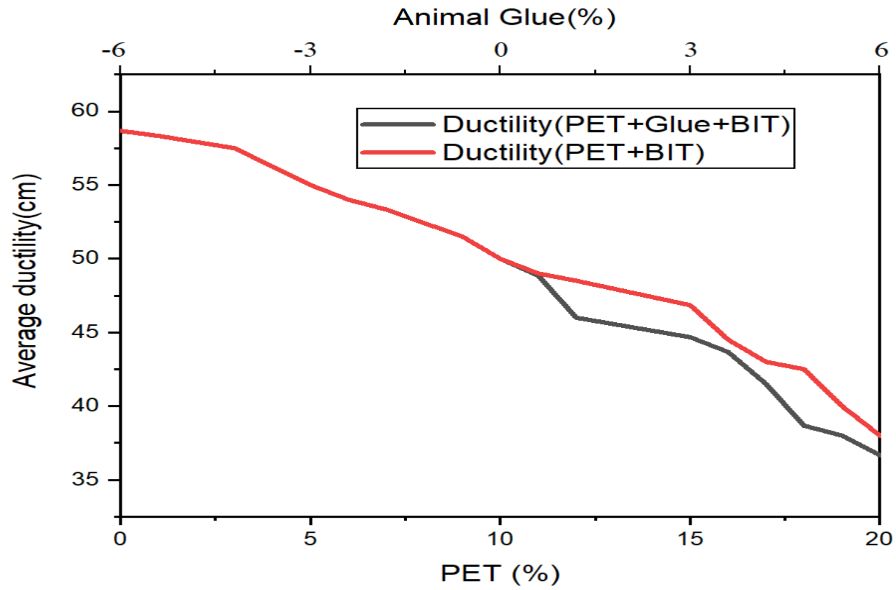


Figure 4.4: Ductility test results

As it can be seen from Figure 4.4, the ductility of the plastic waste, glue, and bitumen mix decreased because the addition of glue and plastic waste result in the interlocking of glue and plastic molecules with bitumen. A higher percentage of the modified bitumen decrease ductility due to toughness increase. Therefore, the result of the Study indicated that the ductility of modified bitumen is decreasing since the added waste plastics decrease the strength of the intermolecular force between the particles of the bitumen, making the bond between particles easily breakable. Not to decrease the ductility of the bitumen below the acceptable value (100+ cm), keep the waste plastic percentage low enough. The ductility in the presence of PET becomes 37 cm at 20 % PET and 6 % glue addition. Using more plastic waste would result in the bitumen mix (the coating concrete) being easily broken/crack.

From the above graph we conclude that, after the addition of glue, the ductility decreasing rate was higher in comparison with that of PET (the black curve). For example, the ductility of the black curve (PET + Bitumen + Glue) at 20 % of PET was around 37.5 cm but the ductility of the red (Bitumen + PET) curve at the same content of PET (20 %) was around 36 cm, this shows that the ductility of the black curve was smaller than the red one by 1.5 %. i.e. after the addition of glue, the decreasing rate of ductility was increased in comparison with PET alone with bitumen.

Therefore, considering the selected formulation for the stability test (that is 15 %, 3 %, and 82 % of PET, animal glue, and bitumen respectively), the average ductility was 44 cm. Because of polymer added, it was below the requirement of plain bitumen and can be considered to be good elasticity for waterproofing purposes.

4.1.5. Water Absorption Test Results

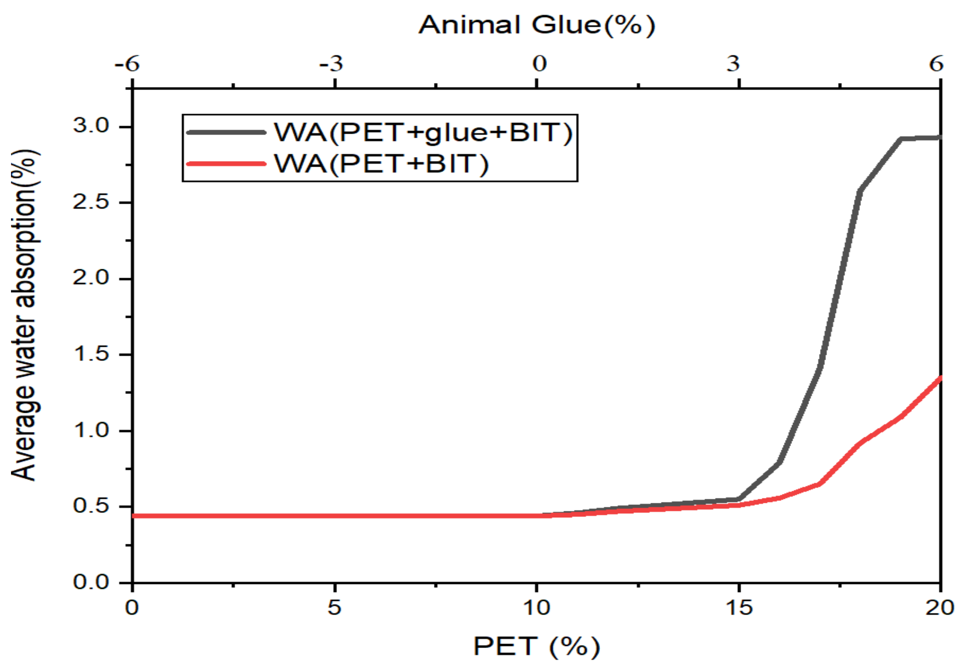


Figure 4.5: Water absorption test results

As shown in Figure 4.5, the effect of PET and animal glue on water absorption is constant until it riches 11% of PET and 1% glue, but after 11% PET and 1% glue, the water absorption increased slightly. This shows that adding up to 11% of PET and 1% of animal glues had no impact on the water absorption of modified bitumen for waterproofing. On the other hand, the water absorption of modified bitumen was increased after the addition of 11% PET and 1% glue but the rate of increase was slight until 15% PET and 3% animal glue. The red curve (PET +Bitumen) was low water absorption rate than the black (PET + Bitumen + glue) one. After the addition of animal glue, the water absorption rate was increased. This shows, glues are protein materials that absorb moisture due to their chemical characteristics, which in the presence of moisture form hydrogen bonds and results reduce glass transition temperature and strength.

This implies that the optimum content of PET and Animal glue for waterproofing application was 15 and 3 percent respectively.

From imagej software/contact angle between the liquid and sample the following results are obtained.

Table 4.1: Imagej software test results

PET (%)	0	1	3	5	6	7	9	10	11	12	15	16	17	18	19	20
Glue (%)	0	0	0	0	0	0	0	0	1	2	3	4	5	5.25	5.5	6
Contact angle(θ)	91	91	91	91	91	91	91	91	90.85	90	89	88	87.8	86	83	80

The software (Table 4.1), shows that the PET and glue content increase the samples are more hydrophobic until 16 and 4 percent PET and glue were added respectively but after 16 and 4 percent PET and glue were added the sample was more hydrophilic. This implies that the optimum percent of PET and glue that are added for waterproofing application was 16% and 4% respectively.

Generally, the contact angle between bitumen and water is close to 90^{o}, which indicates that water and bitumen are two different materials with poor compatibility and the water shows a stronger polarity than bitumen. Considering the opposite polarity of water and bitumen, those materials with favorable wettability to water show a poor wettability to bitumen. From the software, we conclude that the addition of PET and glue was a significant effect on waterproofing applications.

Therefore, considering the selected formulation for the stability test (that is 15 %, 3 %, and 82 % of PET, animal glue, and bitumen respectively), the average water absorption was 0.6%. This is considered to be good for waterproofing purposes.

4.1.6. Viscosity Test

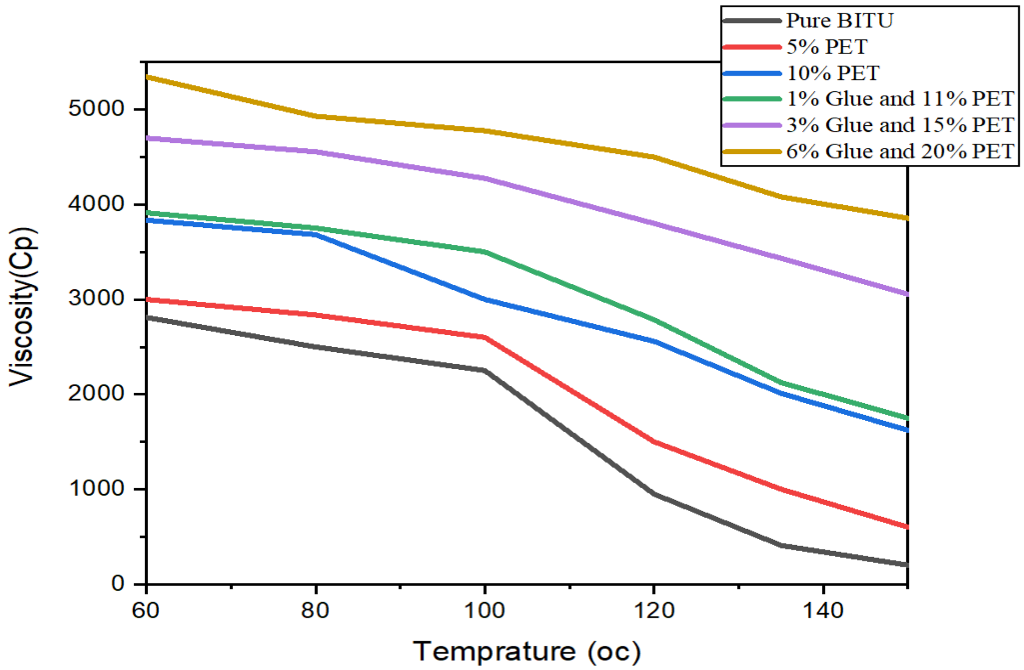


Figure 4.6: Viscosity test results

As shown in Fig. 4.6, it can be observed that the viscosity values reduce as the test temperature increases regardless of polymer content. Fig. 4.6, indicates that the base binder has the lowest viscosity values at all the chosen test temperatures as compared to the modified bitumen binders. The blend viscosity increased with the increase in polymer content at the chosen temperatures from 60 to 150 ℃, and this increase was observed in both the viscous and softening points. Commonly, a higher viscosity leads to better resistance against permanent deformation although it reduces the workability of the bitumen mix (K. Liu et al., 2018; W. Liu et al., 2018). For example and compared to virgin samples the increase in viscosity at 60 ℃ was 2810, 3000, 3835, 4700, and 5344 Cp in case of the content of PET are 0 %, 5 %, 10 %, 11%, 15 %, and 20 % respectively. The viscosity increase may be attributed to the low melting point of PET, where it is already in liquid form and may reach to rigid network at 175 °C or higher temperatures (Sango et al., 2009). At higher temperatures, the viscosity also increases but is lower than that recorded at lower temperatures. The increment in viscosity of PET-modified bitumen is also related to the higher thermal stability of PET polymer at high temperatures (Yao et al., 2016). According to Zhang et al. (Zhang et al., 2009), an increase in viscosity with the increase in modifier concentration is explained by the molecular interaction when inter-molecular and inter-particle interaction occurs in the bulk of the blend. At a temperature of 120℃ viscosity increased to 950, 1500, 2558, 3800, and 4500 Cap for the same level of addition. This indicated that the added polymer react with virgin bitumen and formed a cross-linking between asphalt and PET forming a chemical network that caused the formed PMAs to be more rigid and difficult to flow at high temperatures. For coating purposes at 135 ℃ was best.

4.1.7. FTIR Analysis

It is well-known that every organic compound has its characteristic infrared spectrum, and the chemical molecular structure of virgin bitumen and PET-modified bitumen can be obtained through the analysis of functional groups.

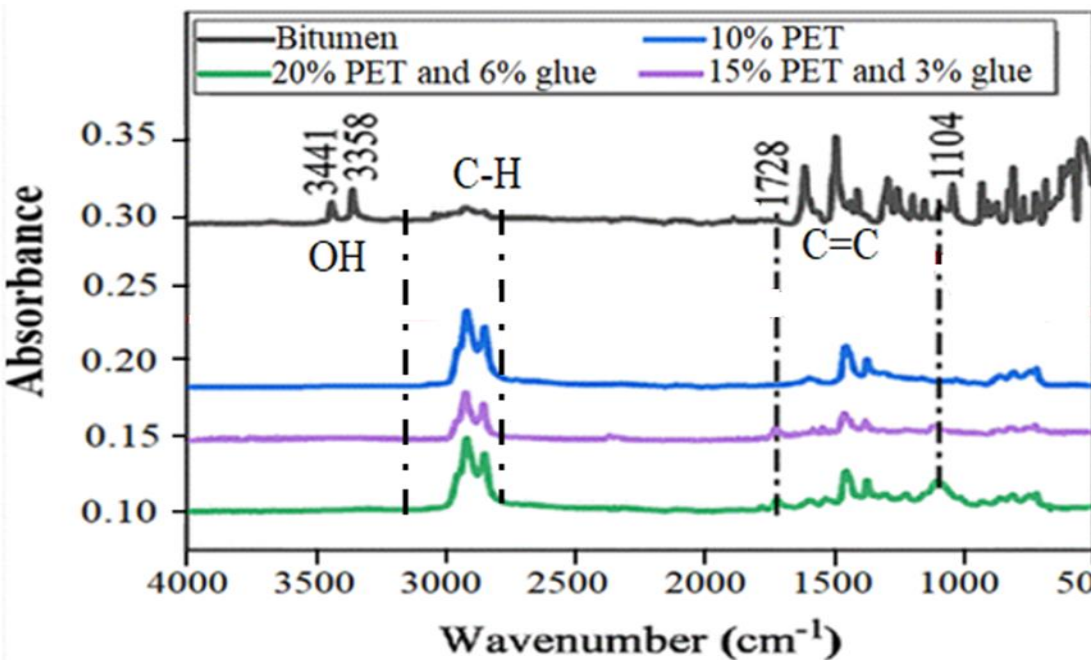


Figure 4.7: FTIR analysis of virgin and polymer modified Bitumen

As seen in Figure 4.7, it can be found that absorption peaks were generated at 3441 cm^{-1}, 2930 cm^{-1}, 2850 cm^{-1}, 1728 cm^{-1}, 1104 cm^{-1}, and others. The absorption band from 4000 to 1500 cm^{-1} was caused by the stretching vibration of OH, CH, CO, which was called the functional group region. And, except for a single bond stretching vibration, there was also vibration in the region from 1500 to 500 cm–^{1}, which was called the fingerprint region. It usually contains a large number of peaks, making it difficult to identify individual peaks. Based on the result of the characteristic absorption frequencies of organic functional groups Goo, Q.L, (2015), waves of representative functional groups are obtained.

Table 4.2: Different wave numbers with respective functional groups

Region(cm^{-1})	functional Group	Possible compounds present/absent
3700-3100	-OH	Alcohol, aldehyde, carboxylic acids
	-NH	Amides, amines
	=C-H	Alkynes
31000-3000	=C-H	Aromatic compounds
	$-CH_2$ or $–CH=CH-$	Alkenes or unsaturated rings
3000-2800	$-CH$, $-CH_2-$, $-CH_3$	Aliphatic groups
2800-2600	-CHO	Aldehydes (Fermi doublet)
2700-2400	-POH	Phosphorus compounds
	-SH	Mercaptans and thiols
	-PH	Phosphine
2400-2000	-C=N	Nitriles
	$-N=N^{+}=N$	Azides
	-C=C-	Alkynes
1870-1650	C=O	Acid halides, aldehydes, amines, amino acid, anhydrides carboxylic acid, ester, ketones, lactams, lactones.
1650-1550	C=C,C=N,NH	Unsaturated aliphatic, aromatic, unsaturated heterocyclic, amides, amines, amino acids
1550-1300	NO_2	Nitro compounds
	CH_3 and CH_2	Alkanes, alkenes, etc.
1300-1000	C-O-C and C-OH	Ethers, alcohols, sugars
	S=O, P=O, C-F	Sulpher, phosphors, and fluorine compounds
1100-800	Si-O and P-O	Organosilicon and phosphorus compounds
1000-650	=C-H	Alkenes and aromatic compounds
	-NH	Aliphatic amines
800-400	C- halogen	Halogen compounds
	Aromatic rings	Aromatic compounds

Sources: Peng Zhang et al., 2019

Hence, it can be confirmed from the infrared absorption spectrum that bitumen mainly consisted of alkanes, cycloalkanes, and aromatics and their derivatives.

Figure 4.7, shows the FTIR spectra of neat bitumen and binders with 5 %, 10 %, 15%, and 20 % of PET and 3 % and 6 % glue by weight. FTIR spectra tend to define the existing bonds as well as provide information about the molecular structure of the compounds present in the samples (Nizamuddin et al., 2015). It is observed that no new peaks were generated, and the existing absorption peaks had no significant changes. However, the intensity of the existing absorption peak changed significantly. The peak values of 3441 cm^{-1}, 2930 cm^{-1}, 2850 cm^{-1}, 2269, and 1178 cm^{-1} decreased after adding PET and glue. The absorption peaks represented the percentages of functional groups in bitumen. To evaluate the changes of peaks quantitatively, the absorbance spectra were chosen, and baseline correction was taken for FTIR spectra. The peaks are attributed to the presence of CH, OH, NH, CH_2, and CH_3 stretching vibrations (Park et al., 2010). Furthermore, it is reported that such peaks are due to NH, OH, or CH_n stretching vibrations of CH stretching vibrations of CH_2 and CH_3 hence identifying aromatic and aliphatic compounds in the blends (Chen et al., 2012). The strong peaks in the range of 3000 to 2800 cm^{-1} are typical peaks of the OH stretching vibration of alkane chains (K. Liu et al., 2018; W. Liu et al., 2018). The absorbance peaks at 1600 cm^{-1} represent the C= C aromatic stretching of the aromatic ring (Nizamuddin et al., 2015). There are few peaks observed in the range of 600 to 500 cm^{-1} for PET modified bitumen blends only suggesting that the addition of PET caused a change in absorbance peaks in this range. These peaks are contributed to C–H out-plane bending stretching vibrations (Nizamuddin et al., 2015).

As we see from figure 4.7, the peak values reduced remarkably with the addition of PET. It revealed that the percentages of hydrogen bonds, paraffin, and naphthenic and aromatic compounds decrease. Meanwhile, the molecular hydrogen of PET-modified bitumen that included 20 % PET decreased the largest; it was small compared with the neat bitumen. This indicated that the links of bitumen molecules were broken because of high-speed shearing. When the PET dosage reached 20 %, the content of paraffin was the lowest. And when the dosage was 10 %, the largest reduction happened in aromatic compounds. It can be inferred that PET adsorbed partial saturates and aromatics in the bitumen, a result of the special porous structure of the PET particle.

In addition, it can be concluded that the chemical compositions of bitumen binders changed when they were mixed with PET. The peak value of light components decreased with the increase of PET. The alkanes and aromatics declined significantly when the PET content was 10 %. However, the decline tended to be steady with increasing content. The reason was that the adsorption action was weakened when the PET exceeded the upper limit, owing to the increase in viscosity of the bitumen.

4.2. Environmental Impact of Modified Bitumen

The negative impact of Climate Change is already here. Toxic substances released by the burning of plastics, open combustion, incineration, posing a danger to the surrounding areas including vegetation and the health of individuals. Proper development of the policy to plastic waste management must be set (Centre for Innovations in Public Systems (CIPS), 2014).

There is no agreement on the time that plastic takes to degrade but it could be hundreds or thousands of years. Because of the nature of plastic's non-degradability nature, it elongates the degradation period of organic substances. The disposal of plastics in landfills is unsustainable and reduces land resources fit for other uses of higher community value. It was noted from this work that, it is possible to minimize the amount of plastic waste in our case the amount of PET that goes to landfill sites, in doing so biodegradable wastes degradation period will not be elongated as well as it is possible to save large plot of land used for landfills. The amount of PET waste left in the street, or that goes to the landfilling of solid waste Incineration plant, minimized by using PET as this thesis suggested (Shemwell and Levendis, 2011).

In this work, the temperature at which the PET was processed is 175 ℃, which is below the deception point of the plastic. Therefore, no toxic gases released into the environment are expected. And there will not be any remaining ashes of plastic like that of incineration or open burning have. Polyethylene Terephthalate (PET) releases Light hydrocarbons (C5 to C10) when burned above a temperature of 200 ^{0}C. Especially in Incineration plants, the plastic waste burned above the deception temperature of the plastic waste, and that leads to the generation of toxic gases, Due to the generation of unacceptable emissions of gases such as nitrous and sulfur oxides, dust, and dioxins, incineration is not the best mode of waste disposal.

Incineration plants use more plastic as an input to get high temperatures to make the water boil in electric energy production. More PET means more gases that are toxic and more ashes of plastic that are still destined to landfilling sites Agnes and Rajmund (2016) the Environmental impact of Plastic Waste Incineration.

The leakage of plastic into the environment is a big issue of current human beings. There is no one particular solution to deal with the pollution of plastic waste into the environment. Based on the outcome of different tests conducted in this work, and the disadvantages of current solid waste management options found in various research works, it is possible to conclude that using plastic PET in a building is a better option to minimize the health issues to humans and animal as well as to minimize environmental pollutions.

There is no proper solid waste management system in our country. Wastes are thrown into the streets, these wastes are either picked up by waste collectors or dumped there for years. In relatively developed areas of the city, scavengers collect the waste and dump it in an open area usually at a distance from a densely populated area. The existing landfills of Ethiopian cities have not been well designed. Open burning of waste on the dumpsites observed. From the wastes generated in the town, a large amount of its portion is plastic waste. Mineral water packing bottles are some of the waste plastic generated. Water bottles as a waste create a conducive environment for disease-causing vectors like that of malaria (Legesse and Diriba, 2011).

All of the issues associated with poor plastic waste management could be minimized by using plastic waste in waterproofing for construction. This process is eco-friendly and in the low-class people applicable since it serves as a source of income generation, and hence one of the best methods for easy disposal of waste plastics. On other hand due to the shortage and cost of waterproofing chemicals, it was needed to produce by using environmentally available material for moisture problems (Gawande et al. 2012).

In general, plastics have a low melting point and possess very good bonding properties. The low melting point of plastic caused the shreds to form a thin film. Higher penetration of plastic film into surface cavities due to lower viscosity gives higher bonding surface area and this gives higher strength to the mix when inter-particle gaps have been filled by the addition of bitumen. The good bonding between plastic and bitumen is also important for this good mixing and strength.

CHAPTER FIVE

CONCLUSIONS AND RECOMMENDATIONS

5.1. Conclusions

From this study, it can be concluded that by adding waste plastic to the bitumen the properties of bitumen have been optimized. Adding PET to bitumen increases its flexibility and reduces flow at high temperatures. Not only does waste plastic improve the properties of bitumen but also improves the properties of the bituminous mix. Thus, the use of waste plastic ultimately improves the performance and quality of waterproofing coating. As plastic is non-biodegradable and also harmful to the environment thus, disposal of plastic is a matter of great concern therefore use of waste plastic in waterproofing construction is an effective way of disposal of waste plastic.

Polymer-modified bitumen typically is more viscous (thicker) than unmodified binders and tends to show improved adhesive bonding to concrete particles. Thicker binder coatings usually take a longer time to become brittle, so the durability of the pavement can be improved.

The addition of PET to bitumen for waterproofing coating did have no impact on water absorption ability up to 10 % PET in comparison with virgin bitumen but above 10 % PET, the water absorption ability was increased. It is observed that by the addition of PET to the mixture, the resistance to moisture susceptibility of the mix also increases. Bitumen content with PET results in the highest adhesion strength up to an optimum of 15 %. Mixtures containing waste plastic bottles had more adhesive strength values compared to conventional waterproofing material and the adhesiveness trends initially increased by adding lower percentages of plastic bottles and decreased at a higher amount of plastic.

From the above observations, it is concluded that the use of PET in form of packets used in water bottle packaging locally results in improved engineering properties of bituminous mixes. Hence, this investigation examined not only in utilizing most beneficially, the waste non-degradable plastics, but also provides an opportunity in resulting in improved pavement material in surface courses thus making it more durable. Increasing the content of polymer/PET for bitumen modification can improve working temperature by increasing the softening point and viscosity but decreasing penetration and ductility. FTIR result shows that the addition of polymer did have no impact on the functional group in comparison to plain bitumen but the absorption peak was decreased with the addition of PET.

Bituminous coatings are effective at waterproofing and protecting various substrates, particularly metal, from the adverse effects of corrosion. Its efficient barrier protection is due mainly to its hydrophobic property, which naturally repels water and prevents moisture from contacting vulnerable substrates.

Generally, in this study, it can be concluded that the optimum selected formulation of the experiment that shows better waterproofing application was 15%, 3%, and 82% PET, animal glue, and bitumen respectively. At this formulation, the water absorption was 0.6% which is considered to be acceptable for waterproofing purposes.

5.2. Recommendations

It is recommended that future research on bitumen polymer modification pay more attention to the following points:

- The main problem in PMB was adhesion with concrete i.e. addition of polymer can improve the properties of bitumen but the adhesive strength was decrease above 15 % of PET so to increase the PET content we can add adhesion promoter chemicals like amine, sulfur, maleic anhydride, and the like for more stability.
- Instead of PET use of high molecular weight polymers such as SBS and polypropylene can be mixed with bitumen easily for better stability and also can be used not only in waterproofing coating but also used in bituminous membrane waterproofing.
- Other plastic wastes, other than PET, should also be considered in the study to see the effect of various waste plastic types such as PS, HDPE, etc. with various natures, in bitumen modification and to compare the results.

SPECIAL ACKNOLEDGMENT

This research project is funded by Adama Science and Technology University under the grant number ASTU /SM-R/140/21, Adama, Ethiopia.

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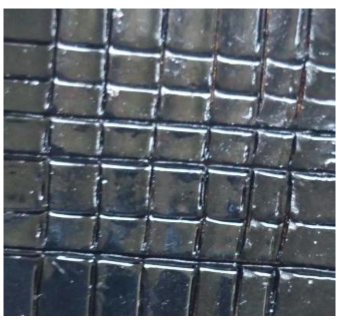
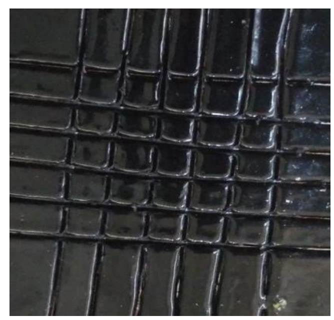
APPENDIX

Viscometer

Fixed pulley system

Tape for cross hatch cutter adhesiveness test

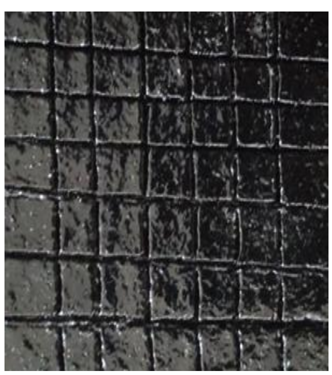




5 % PET

4 % glue and 16% PET

10% PET



12 % PET and 2 % glue

Pure Bitumen